Development of novel carbon thin film electrodes for electrochemical analysis of trace heavy metals in aqueous solutions

Wang, Zhaomeng

2012

Wang, Z. (2012). Development of novel carbon thin film electrodes for electrochemical analysis of trace heavy metals in aqueous solutions. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/52236>

<https://doi.org/10.32657/10356/52236>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DEVELOPMENT OF NOVEL CARBON THIN FILM
ELECTRODES FOR ELECTROCHEMICAL ANALYSIS
OF TRACE HEAVY METALS IN AQUEOUS SOLUTIONS**

WANG ZHAOMENG

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2012

**DEVELOPMENT OF NOVEL CARBON THIN FILM ELECTRODES FOR ELECTROCHEMICAL
ANALYSIS OF TRACE HEAVY METALS IN AQUEOUS SOLUTIONS**

2012

**DEVELOPMENT OF NOVEL CARBON THIN FILM
ELECTRODES FOR ELECTROCHEMICAL ANALYSIS
OF TRACE HEAVY METALS IN AQUEOUS SOLUTIONS**

WANG ZHAOMENG

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2012

Abstract

Contamination and mismanagement of water resources have released toxic metals such as mercury (Hg), lead (Pb), cadmium (Cd) and copper (Cu), etc. into the environment. The presence of these toxic metals in aquatic ecosystems affects directly or indirectly biota and human being. Hence, fast detection and determination of trace toxic heavy metals in aqueous solutions are necessary to reduce fatal cases due to misconsumption of polluted water. Anodic stripping voltammetry (ASV) has been widely used for detection of heavy metals in solutions due to its remarkably low detection limit (ng/L), capability of simultaneous determination of multi-elements, low operating power and relatively low cost. The stripping step of ASV can be pulse, squarewave, linear or staircase. Square-wave anodic stripping voltammetry (SWASV) has been recognized as a powerful technique for detection of trace heavy metals in various aqueous solutions, because of its unique accumulation/preconcentration of analyte species contained in the solutions.

In the past, glassy carbon electrode (GCE) has been widely used in electroanalytical applications because of its robust and smooth surface nature, as well as a large potential window. However, its electroanalytical performance frequently suffers from gradual loss of surface activity. In order to improve reproducibility, stability and sensitivity, a bismuth (Bi) thin film was coated on a GC substrate whose surface was modified with a porous thin layer of polyaniline (PANI) via multipulse potentiostatic electropolymerization to form a novel type of Bi/PANI/GCE in this study. The new electrodes were successfully used to simultaneously detect Cd^{2+} and

Pb²⁺ ions with reference to SWASV signals. The experimental results depicted that the environmentally-friendly Bi/PANI/GCEs had the ability to rapidly monitor trace heavy metals even in the presence of surface-active species in the solutions.

The electroanalytical performance of GCEs coated with PANI-multiwalled carbon nanotube (MWCNT) nanocomposite coatings (PANI-MWCNT/GCE) was investigated by detecting the Pb²⁺ ions in a 0.1 M acetate buffer solution using SWASV. It was found that the PANI-MWCNT/GCEs had a better performance than the bare GCEs. Different solvents were attempted for better dispersion of MWCNTs in the PANI matrices for more sensitive stripping signals. The surface morphology and structure of the PANI-MWCNT/GCEs were examined using field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM) and Raman spectroscopy, showing that the conductive PANI matrices worked as both a conductor to electrically connect the individual MWCNTs, and a binder to mechanically join the MWCNTs.

Recently, graphene-based electrochemical sensors have also been developed to trace toxic heavy metals in aqueous solutions. Graphene possesses various unique properties with its atomic carbon layers of nanometer thicknesses, high electrical conductivity, fast transfer of electrons and alleviation of the fouling effect of surfactants. Graphene-based electrochemical sensors can be modified with nafion to improve their sensitivity in tracing heavy metals, thus greatly enhancing stripping current signals. There are several viable deposition techniques for fabrication of doped-graphene based electrode materials, such as chemical vapour deposition

(CVD), physical vapour deposition (PVD) and spin coating, which are usually followed by high temperature treatment.

In this work, few-layer graphene ultrathin films were synthesized via a novel solid-state carbon diffusion method by rapid thermal processing (RTP) of nickel/amorphous carbon (Ni/a-C) bilayers or Ni-C mixed layers, which were all sputtering-coated on silicon (Si) substrates with or without a silicon dioxide (SiO_2) layer.

For the Ni/a-C bilayer coated samples, the samples were heated at 1000 °C for 3 min to allow the C atoms from the a-C layers to diffuse into the top Ni layers to form C rich surface layers. Upon rapid cooling, the saturated C atoms in the C rich surfaces of the Ni layers precipitated and formed the ultrathin graphene films on the top of the remaining Ni/a-C layers. The formation of the ultrathin graphene films was confirmed by Raman spectroscopy, HR-TEM, electron diffraction, FE-SEM, X-ray photoelectron spectroscopy (XPS), and electrical impedance measurement by a 4-point probe. The formation mechanism of the graphene films was investigated with respect to Ni/a-C bilayer thickness and substrate surface condition (with or without a SiO_2 layer). It was found that SiO_2 nanowires arose on the thermally treated Ni/a-C bilayer coated Si substrates without a SiO_2 layer, which may be due to the reactions between the thermally diffused Si atoms from the Si substrates and the residual oxygen in the RTP chamber, with the Ni layers as a catalyst. The key factors that prevent the formation of the SiO_2 nanowires were discussed.

The synthesized ultrathin graphene films were used as the working electrodes for simultaneous detection of trace Pb^{2+} and Cd^{2+} ions (as low as 7 nM) in acetate buffer solutions (pH 5.3) using SWASV. The effects of substrate surface condition, Ni layer thickness, and preconcentration potential and time on the structure and electrochemical properties of the graphene electrodes were systematically investigated. Compared to conventional diamond-like carbon (DLC) electrodes, the graphene electrodes developed in this study had better repeatability, higher sensitivity and higher resistance to passivation caused by surface active species in the solutions. The interference between the Cd^{2+} and Pb^{2+} stripping peaks was also investigated. With further modifications by using PANI porous layer and/or Bi nanoparticles, the graphene electrodes showed good repeatability, ultrahigh sensitivity (as low as 0.33 nM) and good resistance to passivation during the simultaneous detection of trace Pb^{2+} and Cd^{2+} ions.

For the Ni-C mixed layer coated samples, the graphene thin films were synthesized using the same thermal processing method. During heating, the C atoms dissolved into the Ni lattices. However, during rapid cooling, the solubility of C atoms in Ni was sharply reduced, leading to the precipitation of excess C atoms and the formation of graphene thin films on the outer surfaces of the Ni-C layers. Raman spectroscopy and XPS were used to characterize the structure and composition of both the as-deposited and the thermally treated Ni-C coated samples with respect to the C content of the Ni-C thin films. The graphene thin film electrodes were used as the working electrodes in the simultaneous detection of trace Pb^{2+} , Cd^{2+} and Cu^{2+} ions in

acetate buffer solutions modified with bismuth (Bi). The Bi-modified graphene electrodes showed the significantly enhanced electroanalytical performance. The electroanalytical performance of the graphene electrodes was also investigated with respect to the Si substrate surface conditions (with or without a SiO₂ layer).

Keywords: Graphene; Glassy carbon; Carbon nanotube; Magnetron sputtering; Solid-state carbon diffusion; Nickel-amorphous carbon bilayer; Nickel-carbon mixed layer; Polyaniline; Bismuth; Aqueous solution; Trace Pb(II), Cd(II) and Cu(II); Square wave anodic stripping voltammetry.

Acknowledgements

I would like to express my sincere appreciation and gratitude to my supervisor, Prof. Liu Erjia, for his invaluable advice and encouragement throughout the duration of this project. He has not only provided enthusiasm and support, but also imparted his personal wisdom that will last forever. Without his help, the project would be impossible to accomplish and the attainment would be much compromised.

My sincere thanks would be extended to Dr. Khun Nay Win and Dr. Yang Guocheng, for their valuable discussions in this research and their guidance in the experiment work. I would like to show my special thanks to the technicians in Materials Lab 1, School of MAE, NTU, for their technical assistance and support.

Thanks also go to Nanyang Technological University, Singapore for providing me a Ph.D. scholarship for this research. The financial support from the Environment & Water Industry Development Council (EWI), Singapore is gratefully acknowledged.

Last but not least, I would like to thank my friends and many others who have in one way or another contributed to the completion of the work.

List of Publications

Journals:

1. **Zhaomeng Wang**, Hongwei Guo, Erjia Liu, Guocheng Yang, Nay Win Khun, “Bismuth/Polyaniline/Glassy Carbon Electrodes Prepared with Different Protocols for Stripping Voltammetric Determination of Trace Cd and Pb in Solutions Having Surfactants”. *Electroanalysis*. 22(2) (2010): 209-215.
2. **Zhaomeng Wang**, Erjia Liu, Donghao Gu, Yongsheng Wang, “Glassy carbon electrode coated with polyaniline-functionalized carbon nanotubes for detection of trace lead in acetate solution”. *Thin Solid Films*. 519(15) (2011): 5280-5284.
3. **Zhaomeng Wang**, Erjia Liu, Xing Zhao, “Glassy carbon electrode modified by conductive polyaniline coating for determination of trace lead and cadmium ions in acetate buffer solution”. *Thin Solid Films*. 519(15) (2011):5285-5289.
4. Yongsheng Wang, Ming Jen Tan, **Zhaomeng Wang**, Jianjun Pang, Anders W.E. Jarfors, “In vitro corrosion behaviors of $Mg_{67}Zn_{28}Ca_5$ alloy: From amorphous to crystalline”. *Materials Chemistry and Physics*. 134(2-3) (2012):1079-1087.
5. **Zhaomeng Wang**, Erjia Liu, “Graphene ultrathin film electrode for detection of lead ions in acetate buffer solution”. *Talanta* 103 (2013):47-55.
6. **Zhaomeng Wang**, Erjia Liu, Pui Mun Lee, “Graphene thin film electrodes synthesized by thermally treating co-sputtered nickel-carbon mixed layers for detection of trace lead, cadmium and copper ions in acetate buffer solutions”. *Thin Solid Films* (Accepted. Ref. No.: TSF-D-12-02069R2).
7. **Zhaomeng Wang**, Erjia Liu, “Graphene ultrathin film electrodes modified with bismuth nanoparticles and polyaniline porous layers for simultaneous detection of lead and cadmium ions in acetate buffer solutions”. *Thin Solid Films* (Accepted. Ref. No.: TSF-D-12-02068R2).

8. **Zhaomeng Wang**, Erjia Liu, “Synthesis of graphene through nickel catalyzed solid-state carbon diffusion”. *Scientific Reports* (Under Review, Ref. No.: SREP-13-01101).

Patent

Erjia Liu, Wenguang Ma, Guocheng Yang, Aiping Liu, Nay Win Khun, **Zhaomeng Wang**, “Microelectrode array sensor for detection of heavy metals in aqueous solutions”, Singapore Patent Application No.: 201004224-0. Intellectual Property Office of Singapore (09/07/2010) (filed).

Conferences

1. (Oral) **Zhaomeng Wang**, Erjia Liu, “Applications of PANI Modified Glassy Carbon Electrodes in Anodic Stripping Determination of Heavy Metals”, Symposium F, *International Conference on Materials for Advanced Technologies 2009 (ICMAT 2009)*, Singapore, 28 June-3 July 2009.
2. (Oral) **Zhaomeng Wang**, Erjia Liu, Donghao Gu, Yongsheng Wang, “Polyaniline-carbon nanotube coating modified glassy carbon electrodes for detection of trace lead in acetate solution”, Symposium OPF 4974, *The 5th International Conference on Technological Advanced of Thin Films & Coatings (Thin Films 2010)*, Harbin (China), 11-14 July, 2010.
3. (Poster) **Zhaomeng Wang**, Erjia Liu, “The polyaniline modified glassy carbon electrodes to determination of trace lead and cadmium ions”, Symposium OPF 4982, *The 5th International Conference on Technological Advanced of Thin Films & Coatings (Thin Films 2010)*, Harbin (China), 11-14 July, 2010.
4. (Oral) E. Liu, Hongwei Guo, **Zhaomeng Wang**, Guocheng Yang and Nay Win Khun, “Bismuth/polyaniline/glassy carbon electrodes for detection of trace cadmium and lead”, Symposium 03 (Electroanalysis and Electrochemical Sensors), *60th Annual Meeting of the International Society of Electrochemistry*, Beijing (China), 16-21 Aug 2009.
5. (Oral) **Zhaomeng Wang**, Erjia Liu "Graphene thin film synthesized via solid

carbon diffusion by thermally treating the co-sputtering deposited nickel-carbon mixed layer and its application for detection of heavy metal ions in acetate buffer solution", *Symposium of Electrochemistry of Thin Films, 6th International Conference on Technological Advances of Thin Films and Coatings (ThinFilms2012)*, Singapore, 14-17 Jul 2012.

6. (Poster) **Zhaomeng Wang**, Erjia Liu "Bismuth and polyaniline modified graphene thin film synthesized via solid carbon diffusion method for simultaneous detection of heavy metal ions in acetate buffer solution", *Symposium of Electrochemistry of Thin Films, 6th International Conference on Technological Advances of Thin Films and Coatings (ThinFilms2012)*, Singapore, 14-17 Jul 2012.

Project Involved

Environment & Water Industry Development Council (EWI): "Nitrogenated diamondlike carbon-platinum nanocomposite thin film microelectrodes for detection of trace metals in water or biofluid", Proj. No.: 0601-IRIS-035-00 (2007-2010).

Table of Contents

Abstract	i
List of Publications	vii
Table of Contents	x
List of Tables	xiv
List of Figures	xv
Nomenclatures	xx
Chapter 1: Introduction	1
1.1 Background.....	1
1.1.1 Carbon Electrode Materials.....	1
1.1.2 Electrode Modification.....	3
1.2 Challenges	5
1.3 Objective.....	6
1.4 Scope	7
1.5 Novelty	8
1.6 Organization of Thesis.....	10
Chapter 2: Literature Review	11
2.1 Electrochemistry	11
2.2 Electrochemical Analysis	12
2.3 Configuration of Three-electrode Electrochemical Cell.....	13
2.3.1 Working Electrode.....	13
2.3.1.1 Potential Window	15
2.3.1.2 Hydrogen and Oxygen Evolution Overpotentials [76].....	18
2.3.2 Reference Electrode	20
2.3.3 Counter Electrode.....	22
2.3.4 Electrolyte	23
2.4 Techniques for Electrochemical Analysis.....	23
2.4.1 Cyclic Voltammetry.....	25
2.4.2 Anodic Stripping Voltammetry	29
2.4.3 Square Wave Anodic Stripping Voltammetry.....	33
2.5 Working Electrode Materials.....	36
2.5.1 Platinum	37
2.5.2 Mercury	38
2.5.3 Diamond-like Carbon.....	39
2.5.4 Glassy Carbon	40
2.6 Modification of Working Electrodes	41
2.6.1 Electrode Passivation	41
2.6.2 Modification of Electrodes with Conductive Polymers	42
2.6.2.1 Background of Conductive Polymers.....	42
2.6.2.2 Aniline.....	45
2.6.2.3 Polyaniline.....	46
2.6.2.4 Applications of PANI	51

2.6.3	Modification of Electrodes with Bismuth	51
2.7	Graphene.....	52
2.7.1	Fabrication Methods of Graphene.....	54
2.7.1.1	Mechanical Exfoliation of Bulk Graphite	55
2.7.1.2	Chemical Exfoliation of Graphite	55
2.7.1.3	Thermal Decomposition of Silicon Carbide.....	57
2.7.1.4	Chemical Vapor Deposition.....	58
2.7.1.5	Solid-state Carbon Diffusion.....	59
2.7.2	Methods to Characterize Graphene	60
2.7.3	Application of Graphene as Sensors	61
2.7.4	Limitations of Previous Research	62
Chapter 3:	Experimental Details	63
3.1	Materials	63
3.2	Preparation of Thin Films and Working Electrodes.....	64
3.2.1	GCE.....	65
3.2.2	MWCNT-PANI Modified GCE.....	65
3.2.3	Graphene Thin Film Electrode	66
3.2.4	Modification of Electrodes with PANI or Bismuth	68
3.3	Characterization.....	69
3.4	Electrochemical Measurements and Applications	70
Chapter 4:	Polyaniline and Bismuth Modified Glassy Carbon Electrodes	73
4.1	Introduction	73
4.2	PANI Modified GCEs.....	74
4.2.1	PANI Layer Deposition via CV Method	74
4.2.2	Effect of PANI Layer Thickness on Stripping Peak Current.....	77
4.2.2.1	Effect of Aniline Concentration on SWASV Response.....	77
4.2.2.2	Effect of PANI Deposition Time on SWASV Response.....	79
4.2.2.3	Effect of Solution pH	80
4.2.3	Reaction Reversibility of PANI Modified Electrodes	81
4.2.4	Calibration Curves of PANI/GCEs.....	82
4.3	Bi Modified PANI Electrodes.....	84
4.3.1	Effect of Bi ³⁺ Concentration.....	85
4.3.2	Effects of Preconcentration Potential and Time	86
4.3.3	Calibration Curves of Bi/PANI/GCEs.....	88
4.3.4	Stability Analysis of Bi/PANI/GCEs.....	89
4.4	PANI-Functionalized MWCNTs Modified GCEs	92
4.4.1	Comparison of GCEs Modified with PANI and MWCNTs by Various Methods with Respect to SWASV Response	92
4.4.2	Confirmation of Successful Modification of MWCNTs and PANI.....	96
4.5	Summary.....	99
Chapter 5:	Graphene Thin Films Synthesized via Solid-state Carbon Diffusion.....	101
5.1	Introduction	101
5.2	Graphene Thin Films Synthesized via Solid-state Carbon Diffusion by Thermally Treating Sputtering Deposited Nickel/Amorphous Carbon Bilayers	102

5.2.1	Structure of Graphene Films	102
5.2.2	Atomic Contents of Elements in Thin Films Before and After Rapid Thermal Processing	107
5.2.3	Mechanism of Formation of Graphene Films	111
5.2.4	Effects of Ni Layer Thickness and Si Substrate Surface Condition	113
5.2.5	Mechanism of the Formation of SiO ₂ Compounds and/or Nanowires during RTP and Their Effects	122
5.2.6	Formation and Prevention of Formation of SiO ₂ Compounds	123
5.2.7	Effect of SiO ₂ Compounds	125
5.2.8	Effect of a-C Layer Thickness	128
5.2.9	Number of Graphene Layers	131
5.3	Graphene Thin Films Synthesized via Solid-State Carbon Diffusion From Co-sputtering Deposited Nickel-carbon Mixed Layers	133
5.3.1	Formation Mechanism of Graphene Thin Films	133
5.3.2	Effect of Si Substrate Surface Condition	133
5.3.3	Effect of Ni-C Mixed Layer Thickness	135
5.4	Further Discussions on Metal-catalyzed Graphene Fabrication	137
5.5	Summary	141
Chapter 6:	Electrochemical Analysis by Using Graphene Thin Film Electrodes	142
6.1	Introduction	142
6.2	Electrochemical Analysis by Using Graphene Thin Film Electrodes Synthesized via Thermally Treating Sputtering Deposited Ni/a-C Bilayers	143
6.2.1	Bare Graphene Thin Film Electrodes without Modification	143
6.2.1.1	Electrochemical Characteristics of Graphene Electrodes	143
6.2.1.2	Comparison of Graphene Electrodes with Other Electrodes	148
6.2.1.3	Effects of Preconcentration Potential and Time	149
6.2.1.4	Effect of Ni Layer Thickness on SWASV Response	152
6.2.1.5	Calibration Curves Measured by Graphene Electrodes	154
6.2.1.6	Stability Analysis of Graphene Electrodes	158
6.2.1.7	Comparison of Electrochemical Performances of Graphene Electrodes Fabricated using Different Methods	162
6.2.2	Polyaniline and Bismuth Modified Graphene Thin Film Electrodes	164
6.2.2.1	Effect of Bi Modification	164
6.2.2.2	Effect of PANI Modification	166
6.2.2.3	Calibration Curves Measured by Bi/PANI/Graphene Electrodes ..	173
6.3	Electrochemical Analysis by Using Bi Modified Graphene Thin Film Electrodes Synthesized via Thermally Treating Ni-C Mixed Layers	177
6.3.1	Effect of Si Substrate Surface Condition	177
6.3.2	Effect of Bi ³⁺ Concentration	178
6.3.3	Effects of Preconcentration Potential and Time	180
6.3.4	Calibration Curves Measured by the Bi/Graphene Electrodes	183
6.4	Summary	185
Chapter 7:	Conclusions and Contributions	187
7.1	Conclusions	187

7.2 Contributions	189
References.....	191
Appendix 1: Standard Redox Potentials of Some Common Heavy Metals at 25 °C.....	200
Appendix 2: Binary Phase Diagram of Ni-C	201
Appendix 3: Nernst Equation and Its Limitations.....	202

List of Tables

Table 2-1 Standard potentials of various reference electrodes [77]	22
Table 2-2 Comparison between ASV and CSV	30
Table 3-1 HAc-NaAc buffer solutions	64
Table 3-2 Summary of all kinds of electrodes used in this study	64
Table 4-1 Description of main oxidation peaks of PANI coated on GCEs via CV method [67, 69, 123, 124]	76
Table 4-2 Comparison of GCEs and PANI/GCEs	84
Table 4-3 Normalized stripping current, I_p/I_{pmax} , for 25 nM Cd^{2+} and 25 nM Pb^{2+} ions vs. surfactant concentrations measured using Bi/GCEs and Bi/PANI/GCEs.	90
Table 4-4 Fabrication procedures of different coatings containing MWCNT-COOH and/or PANI	93
Table 5-1 C atomic content with respect to C sputtering power	135
Table 5-2 Comparison of two groups of graphene fabrication techniques	138
Table 5-3 Comparisons of graphene fabrication techniques via thermal processing	140
Table 7-1 Comparison of GCEs and PANI/GCEs	189

List of Figures

Fig. 2-1 Schematic diagrams of typical 3-electrode electrochemical cells	13
Fig. 2-2 Schematic layout of three electrodes: working electrode (WE), reference electrode (RE) and counter electrode (CE).....	14
Fig. 2-3 Cyclic voltammogram measured with a boron doped diamond electrode in 1 M KCl [75].....	16
Fig. 2-4 Current-potential curves showing the factors that control the potential window [72]	16
Fig. 2-5 Stability diagram of water [72].....	18
Fig. 2-6 Potential ranges vs. Saturated calomel electrode (SCE) for Hg, C and Pt electrodes in various electrolytes [72].....	20
Fig. 2-7 Schematic diagram of Ag/AgCl reference electrode [77].....	22
Fig. 2-8 Applied potential wave front in cyclic voltammetry	26
Fig. 2-9 A typical cyclic voltammogram measured with a glassy carbon electrode in a solution containing 0.1 M KCl and 5 mM $K_3Fe(CN)_6$ [72]	27
Fig. 2-10 Scan rate influence on CV in a solution containing 0.2 M Na_2SO_4 and 1 mM $K_4Fe(CN)_6$ [72]	28
Fig. 2-11 Periodic table with some elements highlighted, which ionic species can be determined using ASV or CSV [72].....	31
Fig. 2-12 Stripping voltammogram of Cd, Pb, Cu and Hg [81].....	32
Fig. 2-13 Square wave potential wave front [72].....	34
Fig. 2-14 Structure of amorphous carbon [84].....	39
Fig. 2-15 Ternary phase diagram of bonding in amorphous carbon-hydrogen compounds [85].	40
Fig. 2-16 Energy band gap for metal, semiconductor and insulator.....	43
Fig. 2-17 Repeat units of several pristine forms of conductive polymers [95]	44
Fig. 2-18 Chemical structure of aniline monomer [100].....	45
Fig. 2-19 Molecular structure of PANI [100].....	48
Fig. 2-20 Synthesis and redox chemistry of PANI [100]	49
Fig. 2-21 Emeraldine form of PANI [100]	50
Fig. 2-22 Graphene is an atomic-scale honeycomb lattice made of carbon atoms [6].....	53
Fig. 2-23 Image of graphene in a transmission electron microscope [6]	53
Fig. 2-24 Graphene: the parent of all graphitic forms [6]	54
Fig. 2-25 Deposition of chemically derived graphene films [23]	56
Fig. 2-26 Photograph of graphene in transmitted light [112]......	61
Fig. 4-1 In-situ cyclic voltammograms of a PANI coating measured during its deposition up to 40 cycles with a scan rate of 50 mV/s from -0.2 to 0.9 V.	75
Fig. 4-2 SEM micrographs of PANI coatings on Si substrate deposited by CV method for (a) 25, (b) 30 and (c) 35 cycles.	77
Fig. 4-3 Stripping voltammograms measured using different PANI/GCEs fabricated with increasing aniline concentration. The inset shows effect of aniline concentration on peak	

currents of 3 μM Pb^{2+} and 3 μM Cd^{2+} . The supporting electrolyte is 0.1 M acetate buffer solution (pH 5.3). The peak heights at -0.72 and -0.46 V refer to Cd^{2+} and Pb^{2+} in the solutions, respectively.	78
Fig. 4-4 Effect of PANI deposition time.	80
Fig. 4-5 Voltammograms measured with PANI/GCE in solutions containing 3 μM Pb^{2+} and 3 μM Cd^{2+} at different pH values. The inset shows the effect of pH value on stripping peak current.....	81
Fig. 4-6 Surface activity tests for PANI/GCEs and GCEs. The PANI/GCEs were fabricated using 7.3 μM aniline and CV deposited for 30 cycles. The inset shows the measuring method of peak currents.	82
Fig. 4-7 Stripping voltammograms for (a) PANI/GCE and (b) GCE with increasing Pb^{2+} and Cd^{2+} concentrations. All tests were conducted in 0.1 M acetate buffer solutions of pH 5.3.	83
Fig. 4-8 Stripping peak currents and calibration curves of PANI/GCEs and GCEs for Cd^{2+} and Pb^{2+} determination. The inset shows calibration curves of the two electrodes for detection of Cd^{2+} ions with an enlarged view. All tests were conducted in 0.1 M acetate buffer solutions of pH 5.3.	83
Fig. 4-9 Effect of Bi^{3+} concentration on stripping peak currents of 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line).	86
Fig. 4-10 Effect of preconcentration potential on stripping peak currents of 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) tested by Bi/PANI/GCEs in supporting electrolytes of 20 mM H_2SO_4 and 30 mM KCl containing 1.25 μM Bi^{3+}	87
Fig. 4-11 Effect of preconcentration time on stripping peak currents of 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) tested by Bi/PANI/GCEs in supporting electrolytes of 20 mM H_2SO_4 and 30 mM KCl containing 1.25 μM Bi^{3+}	88
Fig. 4-12 Stripping voltammograms of Cd^{2+} and Pb^{2+} of concentrations of 25, 50, 75, 100, 125 and 150 nM from bottom to top, respectively, which were measured using Bi/PANI/GCE. The insets show the respective calibration curves.	89
Fig. 4-13 Stability performance of Bi/PANI/GCE in a solution containing 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) in the presence of 8 mg/L of Triton X-100	91
Fig. 4-14 Stripping voltammograms measured using different coated electrodes for determination of Pb^{2+} (1.5 μM) in 0.1 M acetate buffer solution.....	94
Fig. 4-15 Stability performance of (a) MWCNT-COOH and (b) MWCNT-PANI coated electrodes in terms of anodic stripping peak current of Pb^{2+} (1.5 μM) in 0.1 M acetate buffer solution with respect to number of tests.	95
Fig. 4-16 Stripping voltammograms of different electrodes modified in (a) ethanol solution containing MWCNT-COOH and PANI, (b) ethanol only and (c) sulfuric acid solution containing MWCNT-COOH and PANI.....	96
Fig. 4-17 FE-SEM micrographs of (a) MWCNT-COOH coating, (b) MWCNT-PANI coating, and (c) same coating as (b) viewed with a higher magnification. (d) shows a TEM image of same coating as (b).	97
Fig. 4-18 Raman spectra of (a) MWCNT-COOH, (b) PANI and (c) MWCNT-PANI coatings.	98
Fig. 4-19 Cyclic voltammogram of MWCNT-PANI coated electrode.....	99

Fig. 5-1 (I) Raman spectra of (a and b) an a-C single film deposited on a Si substrate before and after thermal processing at about 1000 °C, respectively, (c and d) Ni/a-C bilayers deposited on Si and SiO ₂ /Si substrates, respectively, before thermal processing, and (e and f) Ni/a-C bilayers deposited on Si and SiO ₂ /Si substrates, respectively, after thermal processing at about 1000 °C. (II) An enlarged view of the spectra shown in (c and d).	103
Fig. 5-2 (a and b) HR-TEM images showing (a) the lattice structure of a graphene film formed by thermal processing of a Ni/a-C/SiO ₂ /Si sample and (b) an enlarged view of the marked rectangular area in (a) overlaid with a model of graphene planar lattice structure, and (c) an electron diffraction pattern of the graphene film.	106
Fig. 5-3 FE-SEM cross-section views of as-deposited Ni:60/C:40/Si (a) and Ni:60/C:40/SiO ₂ /Si (b), and thermally treated Ni:60/C:40/Si (c) and Ni:60/C:40/SiO ₂ /Si (d).	108
Fig. 5-4 Contents of C, O, Si and Ni of the cross sections of thermally treated samples: (a) Ni:60/C:40/Si and (b) Ni:60/C:40/SiO ₂ /Si, all measured with EDX.	110
Fig. 5-5 A model for formation of a graphene film via solid carbon diffusion during RTP of a Ni/a-C bilayer coated on a SiO ₂ /Si substrate.	112
Fig. 5-6 Raman spectra of (a) Ni:0/C:40/SiO ₂ /Si and (b) Ni:20/C:40/SiO ₂ /Si before and after thermal treatment.	115
Fig. 5-7 Raman peak ratios of thermally treated samples: (a) Ni:t1/C:40/SiO ₂ /Si and (b) Ni:t1/C:40/Si with respect to Ni sputtering time.	117
Fig. 5-8 Raman spectra of thermally treated Ni:20/C:40 deposited on (a) SiO ₂ /Si and (b) Si substrates.	117
Fig. 5-9 Electrical resistivities of thermally treated Ni:t1/C:40 deposited on (a) SiO ₂ /Si and (b) Si substrates, with respect to Ni sputtering time. The inset in (a) shows a magnified view of the resistivities in the range of 20-80 min.	118
Fig. 5-10 FE-SEM micrographs showing surface morphologies of thermally treated Ni:t1/C:40/SiO ₂ /Si and Ni:t1/C:40/Si samples with respect to Ni sputtering time (t1) for 0 min (a & b), 10 min (c & d), 20 min (e & f), 40 min (g & h), and 60 min (i & j), respectively.	121
Fig. 5-11 A model for formation of SiO ₂ compounds (or even nanowires) during the growth of graphene film via solid carbon diffusion during RTP of a Ni/a-C bilayer coated on a Si substrate.	122
Fig. 5-12 FE-SEM micrographs of thermally treated Ni:60/C:0 deposited on (a) Si and (b) SiO ₂ /Si substrates.	123
Fig. 5-13 XRD spectra of thermally treated Ni:20/C:40/Si and Ni:20/C:40/SiO ₂ /Si.	125
Fig. 5-14 FE-SEM micrographs of thermally treated Ni/a-C bilayers deposited on (a) Si and (b) SiO ₂ /Si substrates, respectively.	126
Fig. 5-15 Raman I_D/I_G and I_{2D}/I_G ratios of thermally treated Ni:20/C:t2 deposited on SiO ₂ /Si and Si substrates.	128
Fig. 5-16 Raman peak positions of thermally treated Ni:60/C:t2 deposited on SiO ₂ /Si and Si substrates with respect to C sputtering time: (a) D, (b) G and (c) 2D peaks.	130
Fig. 5-17 A model for fabrication of graphene with thermal processing of a Ni-C mixed layer co-sputtering deposited on Si substrate.	133
Fig. 5-18 Raman spectra of thermally treated Ni-C mixed layers (C of 3.5 at.%) deposited on	

Si substrates without and with a SiO ₂ coating.....	135
Fig. 5-19 Raman spectra of thermally treated Ni-C/Si samples with C atomic contents (in the as-deposited Ni-C mixed layers) of about (a) 0.7 at.%, (b) 1.8 at.%, (c) 3.5 at.%, (d) 4.9 at.%, (e) 6.1 at.%, and (f) 9.8 at.%.....	137
Fig. 6-1 Potentiodynamic polarization curves of (a) as-deposited Ni/a-C/Si, (b) as-deposited a-C _{single} and (c) thermally treated Ni/a-C/Si electrodes.....	144
Fig. 6-2 CV surface activity curves of (a) thermally treated Ni/a-C/Si and (b) as-deposited a-C _{single} electrodes. (c) EIS curves of thermally treated Ni/a-C/Si and as-deposited a-C _{single} electrodes.	146
Fig. 6-3 A cyclic voltammogram showing the potential window of thermally treated Ni/a-C/Si in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO ₃	147
Fig. 6-4 Stripping voltammograms of Pb ²⁺ ions of 1 μM in 0.1 M acetate buffer solutions measured using (a) as-deposited a-C _{single} , (b) thermally treated Ni/a-C/Si, and (c) thermally treated Ni/a-C/SiO ₂ /Si electrodes. The inset shows an enlarged view of (a).148	
Fig. 6-5 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb ²⁺ (1 μM) measured by thermally treated Ni/a-C/Si electrodes with respect to preconcentration potentials.	151
Fig. 6-6 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb ²⁺ (1 μM) measured by thermally treated Ni/a-C/Si electrodes with respect to preconcentration time.	152
Fig. 6-7 Anodic stripping peak currents measured using thermally treated Ni/a-C/Si electrodes with respect to (a) Pb ²⁺ concentration with varying Ni sputtering time and (b) Ni sputtering time with a fixed Pb ²⁺ concentration of 1.5 μM.....	154
Fig. 6-8 (a) Stripping voltammograms and (b) calibration results with respect to Pb ²⁺ concentrations measured using thermally treated Ni/a-C/Si electrodes with Ni sputtering time fixed at 30 min. (c) Stripping voltammograms of 30 and 100 nM Pb ²⁺ and (d) anodic stripping peak currents with respect to Pb ²⁺ concentrations measured using thermally treated Ni/a-C/Si electrodes with Ni sputtering time fixed at 30 min with UPD method.....	157
Fig. 6-9 Long-term repeatability of a thermally treated Ni/a-C/Si electrode tested for 46 cycles in an acetate solution containing 1 μM Pb ²⁺	159
Fig. 6-10 (a) Stripping voltammograms of 500 nM Pb ²⁺ without and mixed with 100 nM Cd ²⁺ and (b) influence of Cd ²⁺ concentration on stripping peak current of Pb ²⁺ (500 nM), with all the data measured by using thermally treated Ni/a-C/Si electrodes.....	160
Fig. 6-11 (a) Influence of SDS concentration on I_p/I_{pmax} ratio of Pb ²⁺ (1 μM) and (b) stability performance tested in an acetate solution containing 1 μM Pb ²⁺ and 8 mg/L SDS, with all the data measured using thermally treated Ni/a-C/Si electrodes.....	162
Fig. 6-12 Stripping voltammograms with respect to 1 μM Pb ²⁺ measured using three graphene electrodes fabricated by three kinds of methods.....	163
Fig. 6-13 (a) Anodic stripping peak currents of Cd ²⁺ and Pb ²⁺ with respect to Bi ³⁺ concentrations and (b) anodic voltammograms with 1.25 μM Bi ³⁺ dissolved in electrolyte, measured by a graphene electrode in 0.1 M acetate buffer solutions (pH 5.3) containing 1.2 μM Cd ²⁺ and 0.5 μM Pb ²⁺	165
Fig. 6-14 Cyclic voltammograms recorded during PANI deposition on a graphene electrode	

for 30 cycles in a 0.25 M H ₂ SO ₄ electrolyte containing 7.3 μ M aniline with a scan rate of 50 mV/s and a potential range of -0.2 to 0.9 V.	166
Fig. 6-15 Tafel plots measured by graphene electrodes without/with PANI modification in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO ₃	167
Fig. 6-16 SWASV I_p/I_{pmax} ratios of Pb ²⁺ measured by Bi/graphene and Bi/PANI/graphene electrodes with respect to SDS concentrations in 0.1 M acetate buffer solutions (pH 5.3) containing 1 μ M Pb ²⁺ and 1.25 μ M Bi ³⁺	168
Fig. 6-17 Stripping peak currents of Pb ²⁺ measured for 32 cycles with a Bi/PANI/graphene electrode in a 0.1 M acetate buffer solution (pH 5.3) containing 1 μ M Pb ²⁺ and 1.25 μ M Bi ³⁺	169
Fig. 6-18 FE-SEM micrographs of (a) graphene, (b) PANI/graphene, (c) Bi/graphene and (d) Bi/PANI/graphene electrodes.	170
Fig. 6-19 FTIR spectra of (a) graphene and (b) PANI/graphene electrodes.	171
Fig. 6-20 Stripping voltammograms of Pb ²⁺ (1 μ M) measured by graphene, PANI/graphene, Bi/graphene and Bi/PANI/graphene electrodes in a 0.1 M acetate buffer solution (pH 5.3) containing 1 μ M Pb ²⁺	172
Fig. 6-21 (a) Stripping voltammograms measured with respect to increased Pb ²⁺ from 0.1 to 1.1 μ M, (b) and (c) relationships between Pb ²⁺ peak currents and Pb ²⁺ concentrations in the ranges of (b) 0.33 nM ~ 1.1 μ M and (c) 0.33 ~ 5 nM, and (d) stripping voltammograms of 0, 4 and 120 nM Pb ²⁺ , measured using PANI/graphene electrodes without and with 1.25 μ M of Bi ³⁺ ions in 0.1 M acetate buffer solutions (pH 5.3).	175
Fig. 6-22 Stripping voltammograms of Pb ²⁺ (0.1 μ M) measured by thermally treated Ni-C mixed layers (C of 3.5 at.% in the as-deposited mixed layers) deposited on Si substrates without or with a SiO ₂ coating.	178
Fig. 6-23 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb ²⁺ (1 μ M) measured by a Bi/graphene electrode with respect to Bi ³⁺ concentrations.	180
Fig. 6-24 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb ²⁺ (1 μ M) measured by a Bi/graphene electrode with respect to preconcentration potentials.	181
Fig. 6-25 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb ²⁺ (1 μ M) measured by a Bi/graphene electrode with respect to preconcentration time.	182
Fig. 6-26 (a) Stripping voltammograms of Cd ²⁺ , Cu ²⁺ and Pb ²⁺ , and (b-c) anodic stripping peak currents with respect to concentrations of (b) Cd ²⁺ and Cu ²⁺ , and (c) Pb ²⁺ , all measured with a Bi/graphene electrode.	184

Nomenclatures

a-C: amorphous carbon

a-C_{single}: sample with only a single a-C layer deposited on Si substrate

AFM: atomic force microscopy

ASV: anodic stripping voltammetry

Bi: bismuth

Bi/GCE or **Bi/PANI/GCE:** GCE or PANI/GCE modified with Bi via SWASV test

Bi/graphene or **Bi/PANI/graphene electrode:** graphene or PANI/graphene electrode modified with Bi via SWASV test

CNT: carbon nanotube

CSV: cathodic stripping voltammetry

CV: cyclic voltammetry

CVD: chemical vapor deposition

DI water: deionized water

DLC: diamond like carbon

EDX: Energy Dispersive X-ray spectroscopy

EIS: Electrochemical impedance spectroscopy

FE-SEM: field-emission scanning electron microscopy

GCE: glass carbon electrode

Graphene electrode: working electrode formed by thermally treating Ni/a-C/Si

HAc: CH₃COOH

HOPG: highly ordered pyrolytic graphite

HR-TEM: high resolution transmission electron microscopy

MWCNT: multiwalled carbon nanotube

MWCNT-COOH: carbon nanotube carboxylate

MWCNT-PANI: PANI modified MWCNT-COOH

NaAc: CH_3COONa

Ni: nickel

Ni/a-C: nickel/amorphous carbon bilayer

Ni-C: nickel-carbon mixed layer

Ni_{single}: sample with only a single Ni layer deposited on Si substrate

PANI: polyaniline

PANI/graphene electrode: graphene electrode modified with PANI layer

RTP: rapid thermal processing

SDS: sodium dodecyl sulfate

SiC: silicon carbide

SiO₂/Si substrate: thermally oxidized Si substrate

SWASV: square wave anodic stripping voltammetry

TEM: transmission electron microscopy

Thermally treated Ni/a-C/Si or thermally treated Ni/a-C/SiO₂/Si electrode:

thermally treated Ni:20/C:40 bilayer coated Si or SiO₂/Si sample used as electrode

Thermally treated Ni:t1/C:t2/SiO₂/Si or thermally treated Ni:t1/C:t2/Si: thermally treated Ni/a-C bilayer coated SiO₂/Si or Si samples, where t1 and t2 are related to Ni and a-C deposition durations (min), respectively.

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

Chapter 1: Introduction

1.1 Background

The presence of toxic heavy metals such as mercury (Hg), lead (Pb), cadmium (Cd) and copper (Cu), etc. in aquatic ecosystems affects directly or indirectly biota and human being, resulting in an ever-increasing demand for the determination of heavy metal contaminants in the ecosystems [1, 2]. Square-wave anodic stripping voltammetry (SWASV) has been widely recognized as a powerful technique for detection of trace heavy metals in various aqueous solutions at low cost [3, 4], because it couples unique accumulation/preconcentration of analyte species contained in the solutions [5]. SWASV is based on a preconcentration by electrodeposition of metallic ions from a sample solution onto a working electrode surface, followed by anodic stripping of the analyte from the electrode surface into the sample solution [4].

1.1.1 Carbon Electrode Materials

Carbon is a unique and intriguing material with a diversity of technological applications. With a $1s^2 2s^2 2p^2$ electronic ground state configuration, carbon naturally exists in many allotropic forms such as graphite, diamond, bucky ball (C₆₀) and so on.

In the past, glassy carbon electrode (GCE) has been widely used in electroanalytical applications because of its robust and smooth surface nature, as well as a large potential window. However, its electroanalytical performance frequently

suffers from gradual loss of surface activity.

Recently, graphene, a single atomic sheet of graphite packed into a dense honeycomb crystal structure, has attracted great interest, as a functioning material for electronics, sensing, and energy applications [6-9] owing to its unique electrical [10-12], optical [13], mechanical [14] properties, extraordinary electronic transport properties, large surface area, and high electrocatalytic activities [15], since experimentally produced in 2004 [16].

However, one of critical challenges in synthesis of graphene is to produce a large surface area of it. There are generally four types of fabrication methods, namely, mechanical cleavage of highly ordered pyrolytic graphite (HOPG), chemical exfoliation of graphite (deposition of a dispersed graphene oxide (GO), followed by an oxygen reduction process) [17, 18], thermal decomposition of SiC [19], and chemical vapor deposition (CVD) of C using a hydrocarbon compound (e.g. methane) on a substrate surface with a transition metal film as a catalyst (e.g., nickel (Ni)) [20]. However, these methods have their own limitations. The mechanical cleavage HOPG usually produces a limited surface area of graphene [16, 21, 22]. Graphene produced with thermal decomposition of SiC exhibits a poor uniformity and its thickness greatly depends on the crystallographic orientation of the SiC surfaces [22]. The most popular fabrication method of graphene the reduction of graphene oxide (GO) which was prepared by a modified Hummers' method [23]. However, because of the van der Waals and π - π stacking interactions among individual graphene sheet interactions, the as-reduced graphene sheets from GO (prepared by a modified

Hummers' method [23]) tend to form irreversible agglomerates and even restack to form graphite when graphene dispersion solutions are dried [24-26]. Using CVD, a precise control of number of graphene atomic layers is difficult due to the sensitivity of such growth to various process parameters, e.g. heating period and flowing gas composition, and a precise control of number of graphene atomic layers is difficult. In addition, some by-products, e.g. carbon nanotubes (CNTs) and amorphous carbon (a-C) are usually produced together with graphene films.

Development of some biosensors based on graphene has been reported [27-31] and their advantages are obvious in various fields, e.g. large detection area, unique sensing mechanism, and ease of functionalization [32]. However, chemical binders (e.g. teflon) have been usually used to mix with graphene films or powders to form a kind of graphene paste with a thickness of μm scale. Such graphene paste could reduce its electrical conductivity and surface activity due to the effect of the binder.

1.1.2 Electrode Modification

The metal nanoparticles, such as bismuth (Bi) [5, 33] and tin [34, 35], can modify electrodes to enhance the sensitivities of the electrodes by forming alloys with target metals. It was reported that Bi modified electrodes are less susceptible to oxygen background interferences than Hg ones [36]. Recently, Bi modified electrodes have become an attractive new subject of electroanalytical investigations as they could be a potential replacement for Hg and Hg film electrodes [36-40]. Several types of Bi modified electrodes showed excellent advantages over Hg film electrodes when

applied to detect trace heavy metals using stripping voltammetry [36, 38, 41-46].

One of main problems associated with various electrodes is the interferences that arise from various surface-active substances that are adsorbed onto the electrode surfaces and cause passivation of the electrodes [38, 47, 48]. The passivation that is caused by various surface active species (e.g. sodium dodecyl sulfate (SDS)) in the electrolyte is one of the major problems faced by the electrochemical electrodes, especially carbon (e.g. glassy carbon, diamond like carbon, carbon nanotube, graphene) electrodes. Natural environmental samples, in which trace heavy metals need to be analyzed, usually contain some kinds of surface-active substances [49, 50]. The surface active species in the electrolyte can be easily adsorbed onto the electrode surfaces and cause the reduction of the surface activities of the electrodes, resulting in lower sensitivities and worse repeatability [38]. The adsorption of surfactants onto electrode surfaces may affect both deposition and stripping steps, leading to weaker or broader peaks and shifts in peak potentials. These effects depend upon specific surfactants and target metals, and reflect the interfacial properties of electrodes [38, 39, 51]. To alleviate such interferences, efforts have been made by means of various surface manipulations on electrodes, such as adsorbed and self-assembled monomolecular layers of ligands on gold electrodes [52-54], composite electrodes prepared by mixing ligands with carbon paste [55, 56], polymer film modified electrodes [39, 47, 48, 50, 57-59], and so on. The principle of these approaches is that modified films work like a membrane that can mechanically prevent surface-active substances from reaching electrode surfaces by hindering their diffusion through the

films, while metal cations with smaller sizes can relatively easily diffuse through the films and eventually reach the electrode surfaces [47].

To eliminate the passivation effect, electrode surfaces can be modified with polymers, e.g. amine [60], cysteamine [61] and nafion [62-65], but, one of the main disadvantages is the poor electrical conductivity of these polymers. Thus, electrically conductive polymers, such as polyaniline (PANI) [66, 67] and polypyrrole (PPy) [68], are preferred to modify electrodes.

1.2 Challenges

The surface active species in the solutions can poison the sensors and cause the passivation of the electrodes, which can reduce the sensitivity of the electrodes. The elimination of the passivation effects on the electrodes is one of the core problems in the electrochemical analysis studies.

The formation of graphene ultrathin films via this solid-state carbon diffusion method has only been confirmed with Raman [69] and XRD [70] measurements so far. The presence of the graphene film via this solid-state carbon diffusion method still needs to be confirmed systemically.

Though the studies of the effects of thermal processing temperature and a-C layer thickness on the formation and structure of graphene films have been reported [69, 70], the effects of catalyst (e.g., Ni) layer thickness and substrate surface condition (e.g., Si substrate without or with a thermally oxidized SiO₂ layer) have not been reported. In the previous reports [69, 70], only the Si substrate with a thermally oxidized SiO₂ layer was used and seldom present the reasons. In this thesis, the Si

substrate without a thermally oxidized SiO₂ layer will also be used, and the advantages/disadvantages and possible products and application fields should be investigated.

During the fabrication of graphene ultrathin films via solid-state carbon diffusion method, only the Ni/a-C bilayers were used in the previous studies [69, 70]. Can the Ni and C atoms in other forms (e.g., the Ni and C mixed layer fabricated via co-sputtering deposition) be used for the graphene fabrication via this method? What are the critical requirements for the formation of graphene via thermal treating?

Usually, the chemical binders (e.g., teflon) have been usually used to mix with graphene films or powders to form a kind of graphene paste with a thickness of μm scale [27-31]. Such graphene paste could reduce its electrical conductivity and surface activity due to the effect of the binder. Thus fabrication of a new type of graphene electrode whose graphene film can fully cover and strongly attach to the substrate with good electrical conductivity is necessary.

1.3 Objective

This project aims to develop GCEs and graphene ultrathin film electrodes with PANI and/or Bi modifications, and to study their structural characteristics and performance in electrochemical analysis with the following objectives:

- To optimize the fabrication parameters of ultrathin graphene films via rapid thermal treating Ni/a-C bilayers or Ni-C mixed layers;

- To investigate the effects of Si substrate surface condition (with or without SiO₂ layer) and Ni/a-C bilayer thickness on the graphene structure and electroanalytical performance, and to study the formation mechanism of SiO₂ compounds (nanowires) formed in the graphene films fabricated on the Si substrates without a SiO₂ layer, and explore the ways to prevent the formation of such SiO₂ compounds;
- To study the critical aspects for the fabrication of graphene films via thermal treating;
- To optimize the deposition conditions of PANI coatings and Bi modification on GCEs and graphene ultrathin film electrodes;
- To simultaneously detect trace heavy metals in aqueous solutions using the graphene ultrathin film electrodes.

1.4 Scope

- PANI coatings will be electrochemically deposited onto GCEs via cyclic voltammetric (CV) method. The PANI/GCEs will be used for electrochemical analysis by detecting Cd²⁺ and Pb²⁺ ions with SWASV. The pH value of electrolytic solutions and SWASV parameters (like preconcentration time and potential) will be optimized and compared with GCEs;
- Bismuth will be used to further modify the above PANI/GCEs for detection of trace heavy metals;

- Graphene ultrathin films will be fabricated via a solid-state carbon diffusion method by rapid thermal processing of Ni/a-C bilayers or Ni-C mixed layers, and the formation of graphene will be confirmed via various analytical methods;
- The effects of Si substrate surface condition (with or without a SiO₂ layer) and Ni/a-C bilayer thickness on the graphene film structure will be studied;
- The application of graphene ultrathin film fabricated via this solid-state carbon method has not been reported previously. In this manuscript, the graphene films are used as electrodes for electrochemical simultaneous detection of heavy metal ions.
- The effects of Ni/a-C bilayer thicknesses and substrate surface conditions (e.g., Si substrate without or with a thermally oxidized SiO₂ layer) on the performances during electrochemical analysis of heavy metals will be discussed.
- Usually during the SWASV tests, various metal ion concentrations in the electrolyte affect each other. In this manuscript, the interferences of those metal ion concentrations on the SWASV performances will be discussed.
- The electrodes were usually modified with other materials for different purposes. In this project the graphene electrodes will be modified with PANI (conductive polymer) coatings and the Bi nanoparticles, in order to enhance the electrodes' sensitivities and stabilities, and also to eliminate the passivation effects.

1.5 Novelty

- This thesis describes a novel approach to metal-catalyzed fabrication of graphene based on solid-state carbon diffusion via rapid thermal processing. Though

the formation of graphene is similar to a CVD method, the carbon source used in this fabrication process is an embedded solid carbon material (e.g., carbon in a Ni/a-C bilayer or Ni-C mixed layer produced by magnetron sputtering deposition) rather than a hydrocarbon gas.

- The effects of Ni and a-C layer thicknesses on the graphene surface structure and electroanalytical performance were studied.
- Besides the Ni/a-C bilayer, a new C source that is a Ni-C mixed layer was introduced for the fabrication of graphene via solid-state carbon diffusion method.
- The Si substrates with or without a thermally oxidized SiO₂ layer were used for graphene fabrication, and the advantages/disadvantages and possible applications were investigated. The by-products (e.g., SiO₂ nanowires) formed on the Si substrates without a thermally oxidized SiO₂ layer were confirmed, and the measures to prevent such by-products were discussed.
- Based on the various graphene fabrication methods (e.g., CVD, solid-state carbon diffusion), the mechanism of the metal-catalyzed formation of graphene was summarized, and the critical aspects for its fabrication were investigated.
- The graphene ultrathin films were successfully used as working electrodes for the simultaneous sensitive detection of trace heavy metal ions in acetate buffer solutions. An under-potential deposition technique was introduced for ultra-low metal concentration detection.

- With the modification of the graphene electrodes using a PANI coating, the electrodes can have better repeatability and higher resistance to the passivation caused by surface active species that could poison the electrodes.

1.6 Organization of Thesis

The thesis has seven chapters. Chapter 1 overviews the challenges, novelty, objective and scope of the project. Chapter 2 summarizes the state-of-the-art background of electrochemistry and techniques of electrochemical analysis, and the basic knowledge of GCE and graphene, and the electrode modifications with polyaniline (PANI) and bismuth (Bi). Chapter 3 details the methodologies used for this research and experiment procedures. The results are discussed and analyzed systematically in Chapters 4-6. Based on the analyses of the results, the conclusions are drawn in Chapter 7.

Chapter 2: Literature Review

2.1 Electrochemistry

Electrochemistry is a branch of chemistry that deals with the relationship between electricity and chemical reactions. It deals with the study of charge transfer processes at the electrode/solution interface, either in equilibrium at the interface, or under partial or total kinetic control. Most of the charge transfer processes are transfer of electrons, which can cause the change of oxidation state of a molecule or ion. This electron transfer is also known as oxidation-reduction (redox) reactions, which occurs between the working electrode and the electrolyte. Oxidation is a process whereby an atom or ion loses an electron to give another atom or ion. In contrast, reduction is a process whereby an atom or ion gains an electron from another atom or ion. This can be represented in the simplest case of oxidized species, *ox*, and reduced species, *red*, both soluble in solution, by $ox + ne^- \leftrightarrow red$, where *ox* receives *n* electrons in order to be reduced into *red*. Electrochemistry provides insight into diverse topics such as the construction of batteries, the spontaneity of reactions, electroplating and the corrosions of metals [71].

This redox process takes place in a compartment known as electrolytic cell. In the chemical electrolysis setup, it consists of a solution filled with ionic conductors (electrolyte), two/three electrodes and an electrochemical work station, which can offer an external applied potential and record/analysis the output signal. All electrodes have to be conductive or semi-conductive in order to run chemical electrolysis process.

The electrolytic cell consisting of two electrodes is not much useful in electrochemical analysis, because it is not easy to control the working electrode's potential which controls the redox reaction to occur.

2.2 Electrochemical Analysis

The presence of toxic heavy metals such as mercury (Hg), lead (Pb), cadmium (Cd) and copper (Cu), etc. in aquatic ecosystems affects directly or indirectly biota and human being, resulting in an ever-increasing demand for the determination of heavy metal contaminants in the ecosystems [1, 2].

Electrochemical analysis is the science of carrying out analytical chemistry by electrochemistry [72]. Electrochemical analysis quantifies via concentration analysis of the analyte species during redox.

Electrochemical analysis has a wide range of applications, for either the biological, clinical and environmental field. An example is bio-electrochemical analysis which has been used for biosensors in detecting biological compounds. However, one of the most important applications for electrochemical analysis is the use as sensors. There are many types of sensors available, such as potentiometric (ion selective) sensors, surface-modified voltammetric electrode sensors, pH sensors, hyphenated technique sensors and voltammetric sensors which is the focus of this thesis [73].

2.3 Configuration of Three-electrode Electrochemical Cell

As for electrochemical analysis, it measures the current from the applied potential and it requires three electrodes connection along with the potentiostat instrument. The three electrodes named working electrode, reference electrode and counter electrode. Fig. 2-1a shows a typical three electrodes electrochemical cell set-up, which can be used for rod-shaped working electrode. Fig. 2-1b shows another electrolytic cell, which can be used for the plate-shaped working electrode, like silicon wafer.

Fig. 2-1 Schematic diagrams of typical 3-electrode electrochemical cells

2.3.1 Working Electrode

Working electrode, also known as indicator electrode, is a semi-conductive or conductive electrode that allows the potential to flow through into the solution to conduct a current flow. It works as a platform for the redox reactions of interest to occur. It can work as anodic or cathodic, depending on the oxidation or reduction of the reaction on the electrode. It serves as a transducer that responds to the excitation

signal and the concentration of the substance of interest in the electrolyte solution.

In voltammetry measurement, the working electrode is usually used in conjunction with a reference electrode and a counter electrode to form a three electrodes system. The potential of the working electrode is measured with respect to the reference electrode and the current with respect to the counter electrode, as shown in Fig. 2-2. The resulting potential is corrected for the difference between the standard potential of the reference electrode (e.g., calomel, Ag/AgCl) and the potential of the working electrode.

Fig. 2-2 Schematic layout of three electrodes: working electrode (WE), reference electrode (RE) and counter electrode (CE).

From Faraday's laws of electrolysis, it is seen that the current flow through the working electrode indicates that chemical reaction has occurred. Some information of Faraday's laws of electrolysis are shown below:

Faraday's 1st Law of Electrolysis - The mass of a substance altered at an electrode during electrolysis is directly proportional to the quantity of electricity

transferred at that electrode. Quantity of electricity refers to the quantity of electrical charge, typically measured in coulomb.

Faraday's 2nd Law of Electrolysis - For a given quantity of electricity (electric charge), the mass of an elemental material altered at an electrode is directly proportional to the element's equivalent weight. The equivalent weight of a substance is its molar mass divided by an integer that depends on the reaction undergone by the material.

2.3.1.1 Potential Window

Usually it is also desired that the electrode material is inert in the region of potential in which the electroanalytical determination is carried out. In aqueous solution, usually, because the ions except H^+ and OH^- are to be detected, so it requires that the potential position of expected ions redox should within the overpotentials range between hydrogen and oxygen evolution, and this range is called electrochemical potential window. The wider the potential window the more kinds of elements in solution can be detected by electrochemical analysis. CV scan was performed in order to measure the potential windows of the electrodes. Hupert et al. [74] reported cyclic voltammograms obtained at diamond electrode in 1 M KCl shown in Fig. 2-3.

Fig. 2-3 Cyclic voltammogram measured with a boron doped diamond electrode in 1 M KCl [75]

The useful potential ranges of electrode materials are determined by the effects as listed in Fig. 2-4.

Fig. 2-4 Current-potential curves showing the factors that control the potential window [72]

All those effects together decide the positions of the potential window. Take Fig. 2-4 as an example, for the right/left part, the factor (1)/(5) whose current greatly rises/drops firstly as the potential increases/decreases is the most important factor to

decide the positive/negative range of the potential window.

Different water solutions and solvents have varying effects on the working potential range of the electrodes. The pH values of the solution can greatly affect the hydrogen and oxygenation evolution. Higher pH can shift the potential window to negative, and vice versa. This can be explained using Nernst equation (Appendix 3) easily, as shown below:

$$pH = -\lg[H^+] \Rightarrow [H^+] = 10^{-pH} \quad (2-1)$$

For hydrogen evolution $2H^+ + 2e^- \rightarrow H_2(g)$, at 25 °C and unit H_2 partial pressure

$$E = E_{H^+/H_2}^0 + \frac{0.0591}{n} \log\left(\frac{[H^+]^2}{P_{H_2}}\right) = 0 + \frac{0.0591}{2} \log\left(\frac{(10^{-pH})^2}{1}\right) = -0.0591 pH \quad (2-2)$$

For oxidation of water $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$, at 25 °C and unit H_2 partial pressure

$$E = E_{O_2/H_2O}^0 + \frac{0.0591}{n} \log\left(\frac{P_{O_2} \cdot [H^+]^4}{P_{H_2O}}\right) = 1.229 + \frac{0.0591}{4} \log\left(\frac{1 \times (10^{-pH})^4}{1}\right) \quad (2-3)$$

$$= 1.229 - 0.0591 pH$$

These two equations can be used to theoretically calculate the thermodynamically stable region of water, as shown in Fig. 2-5.

Fig. 2-5 Stability diagram of water [72]

2.3.1.2 Hydrogen and Oxygen Evolution Overpotentials [76]

The theoretical potential of the hydrogen and oxygen evolution can be calculated using the Nernst Equation (Appendix 3). But actually, the hydrogen evolution potential is lower and the oxygen evolution potential is higher than their theoretical values. These potential shifts are called hydrogen or oxygen evolution overpotential, respectively [76]. The overpotential is caused by the electrode polarization, which occurs when the electron flow speed is higher than the electron reaction speed: on anode, the electrons are flown away, but the reaction is too slow to recruit the electrons, thus the anodic potential shifts positive (anodic polarization); on cathode, the electrons are transferred to the electrode surface, but the reaction is too slow to consume these excessive electrons, so the cathodic potential shifts negative (cathodic polarization). The electrode polarization can be the combination of two effects: concentration polarization and activation polarization.

- Concentration polarization: because of the reaction consumptions, the solute near the working electrode surface got a relatively lower concentration than the bulk solution, and the diffusion is not fast enough to offset this concentration difference. The Nernst equation (Appendix 3) uses the bulk solution concentration that is higher than the real concentration, and this can give inaccurate potential.

- Activation polarization: because all the electrodes can not react as fast as ideal electrode, so a more positive/negative potential is needed than the theoretical value for the oxidation/reduction to occur. This shifted potential is called activation overpotential. This effect influences greatly during gas evolution. The activation overpotential η and current density i have a relationship defined by Tafel equation: $\eta = a + b \cdot \lg i$, where a and b are Tafel coefficients, and the electrode material has small influence on b but big influence on a . Thus, a is used as the criterion of the electrode activation overpotential. Theoretically, the oxygen evolution $\text{O}_2/\text{H}_2\text{O}$ occurs at 1.23 V. But due to overpotential, the real potential of oxygen evolution is 1.36 V. This is mainly caused by the activation overpotential.

The common working electrodes are mercury, gold, platinum and glass carbon electrode (GCE). Some of these common electrode working ranges is represented in Fig. 2-6 with respect to different pH values of the solution. From Fig. 2-6, as discussed previously, for the same electrode (with the same Tafel coefficient a), different water solutions and solvents have varying effects on the working potential range of the electrode. Higher pH can shift the potential window to a negative value, and vice versa.

Fig. 2-6 Potential ranges vs. Saturated calomel electrode (SCE) for Hg, C and Pt electrodes in various electrolytes [72]

While with the same pH of the solution, Fig. 2-6 shows that due to the small hydrogen evolution overpotential, the hydrogen evolution on the Pt electrode is quite easy; while on Hg the hydrogen evolution overpotential is high and the hydrogen evolution is not easy. So platinum (also gold and glassy carbon) electrodes are suitable for electrochemical determination of organic molecules or some metals with positive standard potential (e.g., Au) by anodic scanning, in which the limit of the range for water oxidation is considerably high, as shown in Fig. 2-6; while the mercury electrodes are appropriate for electrochemical determination of most of the metals with negative standard potential (e.g., Pb, Cd, Cu) by cathodic scanning, where the potential for the hydrogen discharge is large.

2.3.2 Reference Electrode

Reference electrode is an electrode used as a potential standard that is

independent of the electrolyte or the reactions on electrodes. It plays the role of measuring the potential difference and controlling the working electrode's potential.

In the electrochemical cell set up, the reference electrode is in conjunction with the working electrode and counter electrode. Reference electrode keeps the cell equilibrium by potential control, where there should be little or no current flow. The reference electrode is usually placed near to the working electrode and its position should not interfere with mass transfer of electrolyte species.

A good reference electrode should also be relatively stable and constant during the experiment. Its potential is maintained with respect to the Standard hydrogen electrode, which is a standard reference used to determine the other electrodes' potential. Standard hydrogen electrode is not recommended for laboratory practices because it is too fragile for handling.

Due to easier availability, Ag/AgCl is chosen as the reference electrode eventually. The interior consists of high purity Ag wire which is then coated with silver chloride or chloridized in HCl or KCl, as shown in Fig. 2-7. This wire is then bathed in KCl or NaCl saturated solution and contact with the external electrolyte can be made via a junction (e.g., porous glass). The redox reaction is:

$$AgCl + e^- \leftrightarrow Ag + Cl^-.$$

Fig. 2-7 Schematic diagram of Ag/AgCl reference electrode [77]

Table 2-1 shows some common reference electrode potentials at 25 °C, with standard hydrogen electrode as a reference point.

Table 2-1 Standard potentials of various reference electrodes [77]

Reference electrode	Electrode potential (mV) at 25 °C
Standard hydrogen electrode	0
Saturated calomel electrode	+ 245
Ag/AgCl, 1 M KCl	+ 236
Ag/AgCl, 4 M KCl	+ 200
Ag/AgCl, saturated KCl	+199

2.3.3 Counter Electrode

A counter electrode which can also be known as auxiliary electrode is different from the working electrode as its potential and current are not important and not measured. Thus counter electrode is made of inert material such as platinum wire (or plate) or graphite so as not to interfere with any redox activity of interest. The presence of counter electrode is to facilitate current flow through the cell and also to

ensure that no current flows towards the reference electrode to interfere the potential of reference electrode. This requires the surface area of counter electrode should be at least 10 times bigger than that of working electrode.

2.3.4 Electrolyte

Electrolyte should contain basic ions between electrodes and the cell to allow for control and/or measurements of the electrode potential [72]. Electrolyte basically also contains the sample species or ions needed for investigation. The basic ions are used as a salt bridge to facilitate current flow through the cell and to compensate the losses of electrons during the redox reaction, so the concentrations of these basic ions should be bigger than that of the target ions or species.

2.4 Techniques for Electrochemical Analysis

Electrochemical analysis is the science of carrying out analytical chemistry by electrochemistry [72]. There are basically four types of electrochemical analysis depending on which aspects of the cell are controlled and which are measured: conductimetric, potentiometric, amperometric and voltammetric [77]. Conductimetric is the measurement of solution resistance to determine concentration of charge. However, this method is not commonly used in water quality applications [77]. In potentiometry (the difference in electrode potentials is measured), with a selected reference electrode, at high impedance, the potential of the working electrode can be determined at zero current [77]. Next, in amperometry, current through the working

electrode is measured when a fixed potential is applied. The magnitude of current is proportional to the concentration of the electrolyte [77]. However, this method tends to be more expensive and measurements are sensitive to contaminants. Finally, voltammetry (the cell's current is measured while actively altering the cell's potential) is when the potential of an electrode is varied while at the same time the corresponding current induced is measured and recorded to obtain a voltammograms. Thus by measuring either the voltage or current, qualitative and quantitative analysis of the redox species can take place. There are two types, polarographic and stripping. The latter is the focus method for electrochemical analysis of metal ions for this research and details will be further discussed.

Advantages of voltammetry, in particular stripping voltammetry, are mostly quantitative as qualitative analysis tends to lack specificity [77]. These include simultaneous detection of different species that react at different applied potential which helps to save time, very low detection limits between 10^{-1} to 10^{-11} M range, which increases its sensitivity, wide range of applications and its insensitivity to convection which means the electrochemistry process is not affected by the decomposition or deposition of the cell electrodes.

Voltammetric sensors are of particular importance for environmental analysis, in particular in the field of water quality and waste monitoring treatment. In countries such as India (Chennai), metal tracing is crucial for determining the pollution level along its coastal areas for a better monitoring of the ecosystem [78]. Under US's Safe Water Drinking Act (SWDA), there is a maximum tolerance level for contaminants in

water. Contaminants can thus be grouped into inorganic and organic. Examples of inorganic ones are fluoride, barium, silver, cadmium, lead and copper. Lead and cadmium are generally found from corrosion of pipes that are used for the distribution of water to households. Organic chemicals include pesticides, herbicides, etc.

2.4.1 Cyclic Voltammetry

In the voltammetric techniques, one commonly used analysis technique is the cyclic voltammetry (CV), which is a type of potentiodynamic electrochemical measurement. CV is a technique devoted to the theoretical study of the behavior of redox couples. It is used to study the redox potential and behaviour of the substance of interest.

As shown in Fig. 2-8, CV applies a triangular shaped ramping scan potential versus time between the working electrode and reference electrode, and at the same time the current is recorded and plotted vs. the corresponding potential as shown in Fig. 2-9 for analysis. The potential range (Low E to High E) has to be adjusted to a suitable range for the redox activity to exist.

Fig. 2-8 Applied potential wave front in cyclic voltammetry

In CV of reversible reactions with this kind of applied triangular shaped scanning at the working electrode, those with fast electrode kinetics relative to the time-scale of the sweep, the redox couples in the solution are exposed to oxidation and afterwards to a reduction, or vice versa. This means that the product of the initial oxidation or reduction on the first (forward) scan is then reduced or oxidized, respectively, on reversing the scan direction. The reversible redox system can be repeated several times in this kind of experiment.

The current begins to rise as potentials are reached where electrode reaction can occur. This creates a concentration gradient which sucks in more electroactive species until depletion effects set in and the current begins to fall again. In a CV experiment, as a range of potentials is applied to the system, the corresponding current response is measured and plotted as a peak-shaped curve, as shown in Fig. 2-9, which is tested using glassy carbon electrode in 0.1 M KCl and 5 mM $K_3Fe(CN)_6$ solution with scan rate of 50 mV/s, scanned from -0.2 to 0.8 V.

The cyclic voltammogram consists of a closed curve, with a reversible redox couples showing both the cathodic and the anodic peaks, on the cathode curves and anodic curves respectively. Because different metals or species have different redox potentials, which can be theoretically calculated using Nernst equation (Appendix 3), so the peak potentials (peak positions) on cyclic voltammogram can be used to identify the category of the target species.

Fig. 2-9 A typical cyclic voltammogram measured with a glassy carbon electrode in a solution containing 0.1 M KCl and 5 mM $K_3Fe(CN)_6$ [72]

Some important results from the cyclic voltammograms are cathodic peak potential E_{pc} , anodic peak potential E_{pa} , cathodic peak current i_{pc} and anodic peak current, i_{pa} . The measurement methods of these parameters are also shown in Fig. 2-9. The characteristic of the peaks in the cyclic voltammogram is highly depended on the rate of electron transfer, mass transports, concentration of the electrolyte, temperature of the electrolyte and the electro-active species reaction between the working

electrode and the electrolyte. The influence of scan rate of CV to the peak responses is shown in Fig. 2-10, indicating that as the scan rate reduces both the redox peak currents and background currents reduce.

Fig. 2-10 Scan rate influence on CV in a solution containing 0.2 M Na_2SO_4 and 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$ [72]

If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of oxidized species and reduced species are maintained at the values required by the Nernst equation. For a reversible electrode reaction, anodic and cathodic peak currents are approximately equal in absolute value, with the measuring methods shown in Fig. 2-9, but opposite in sign. The reversibility indicates a very high electron transfer rate, and the magnitude of the current greatly depends on the mass transports of the electro-active species.

In contrast, the presence of only one peak would define that it is an irreversible (or quasi-reversible) process, either oxidation or reduction, since re-reduction or

re-oxidation, respectively, cannot to occur. In this case the peak potential varies with the sweep rate: higher sweep rates will shift an oxidation to more positive potentials and a reduction to more negative potentials. The irreversibility or quasi-reversibility means the electron transfer rate is low, in which case even though there are electro-active species on the electrode surface the reaction is difficult to completely occur. The majority of redox couples fall between the two extremes and exhibit quasi-reversible behavior. This means that the reverse peak appears but is smaller than the forward peak.

This CV technique is commonly used as a tool for fundamental and diagnostic studies of electrochemical processes under various conditions, since it provides a fast and simple method for initial characterization of a redox-active system. In addition to providing an estimate of the redox potential, it can also provide information about the rate of electron transfer between the electrode and the analyte, and the stability of the analyte in the electrolyzed oxidation states. However, the limitation of this technique is its poor sensitivity. As a result, it is not reliable for badly defined electrode surface and not suitable for routine quantitative analysis [79].

2.4.2 Anodic Stripping Voltammetry

Pollutants in water include a wide spectrum of chemicals, pathogens, and physical chemistry or sensory changes due to the contamination, over-use and mismanagement of water resources [77]. Many of the chemical substances are toxic. The presence of toxic metals such as mercury, lead and copper in the environment has

been a source of worry to environmentalists, government agencies and health practitioners because these metals in the aquatic ecosystem have far-reaching implications directly to the biota and indirectly to human being. The tracing and determination of these poisonous metals in solutions are of major importance in electrochemical analysis.

There are two types of stripping method used for electrochemical analysis: anodic stripping voltammetry (ASV) and cathodic stripping voltammetry (CSV, also known as adsorptive stripping voltammetry). Both methods are at potential control, resulting in a peak current height that is proportional to the concentration of the accumulated species and hence the bulk concentration [73]. The difference between ASV and CSV are tabulated in Table 2-2, and their applications in Fig. 2-11. ASV has been widely used for detection of heavy metals in various samples because of its remarkable low detection limits [80].

Table 2-2 Comparison between ASV and CSV

	Preconcentration process	Stripping process
ASV	Reduction reaction	Oxidation reaction
CSV	Oxidation reaction	Reduction reaction

under potential control with a constant increase rate of scanning potential, leading to an oxidation reaction of the preconcentrated particles on the working electrode surface. The potential control of stripping step can be linear, staircase, squarewave, or pulse. These are widely used for the investigation of electrode processes. When the potential is scanned to a specific value at which the previously reduced species begins to be oxidized and gives off electrons which are measured as a current response. Voltammogram is current-potential profile as shown in Fig. 2-12 that is obtained by measurement of this current response as a function of applied stripping potential. The last step is a cleaning step, in which the potential is held at a more oxidizing potential than the analyte of interest for a period of time in order to fully remove it from the electrode, to be prepared for next test. Thus this potential sweep method consists of scanning a chosen region of potential and measuring the current response arising from the electron transfer and associated reactions that occur.

Fig. 2-12 Stripping voltammogram of Cd, Pb, Cu and Hg [81]

In the voltammograms the category of the target species can be identified by the

peak potentials (peak positions in the current-potential profiles) at which the species begin to be oxidized. Similar as the peaks in cyclic voltammograms, Nernst equation (Appendix 3) can be used to theoretically calculate these peak potentials. The height (and area) of the current peak is proportional to the concentration of the corresponding target species in the bulk solution. Naturally, they can also give quantitative information, since the currents obtained are directly proportional to concentration.

Although electrochemical stripping voltammetry measurement is a simple, quick and cheap way of tracing metals, their sensitivity changes with electrode properties (electrical conductivity, surface roughness, surface cleanliness), operation parameters (scan rate, deposition potential, deposition time, methods) and environmental parameters (current flow, pH value of solution, temperature, metal concentration, metals solubility).

2.4.3 Square Wave Anodic Stripping Voltammetry

Square Wave Anodic Stripping Voltammetry (SWASV) is one of the most common ASV techniques for heavy metal tracing analysis, and has been widely recognized as a powerful technique for detection of trace heavy metals in various aqueous solutions at low cost [3, 4], because it couples unique accumulation/preconcentration of analyte species contained in the solutions [5]. This technique represents a further development of differential pulse anodic stripping voltammetry, which is another common technique of ASV. SWASV is based on a

preconcentration by electrodeposition of metallic ions from a sample solution onto a working electrode surface, followed by anodic stripping of the analyte from the electrode surface into the sample solution [4].

During SWASV stripping step, the controlled potential is scanned through the defined range, but an additional square wave is applied, as shown in Fig. 2-13, where WP is wave period; WA is wave amplitude; WI is wave increase; SE is starting potential; EE is ending potential; t_0 is starting time; t_f is ending time; n is wave number; 1 and 2 stands for the forward and reverse pulse, respectively within the same wave period; i_{1n} and i_{2n} are the average currents of the forward and reverse pulse of wave n , respectively.

Fig. 2-13 Square wave potential wave front [72]

The recorded current i_n is the difference between the average currents in the forward i_{1n} and reverse pulse i_{2n} within each wave period. The calculations are shown below, with E_{1n} and E_{2n} is applied potential of forward and reverse pulse, respectively of wave n ; i_{Fn} is Faradic current at wave n ; i_n is recorded current of wave n ; i_{bn} is

background current at wave n .

$$t = t_f - t_0 = n \times WP; \quad (2-4)$$

$$E_{1n} = n \times WI + WA; \quad E_{2n} = n \times WI - WA; \quad i_{1n} = i_{Fn} + i_{bn}; \quad i_{2n} = -i_{Fn} + i_{bn}; \quad (2-5)$$

$$i_n = i_{1n} - i_{2n} = 2 \times i_{Fn}. \quad (2-6)$$

Thus for the recorded current i_n , the background current i_{bn} can be eliminated, leaving only the doubled Faradic current i_{Fn} . Detection limit using square wave voltammetry ranges from 5-50 $\mu\text{g/L}$ [79]. The sensitivity of this technique can be increased by increasing either the amplitude of the square wave or the frequency. The limits of the enhancement are strictly related to the kinetics aspects of the redox system. It must not be slower than the velocity of the scanning of potential. Reasonable amplitudes are in the range of 5-25 mV. Larger amplitudes yield a larger response, but Faradic peaks will get broader and potential resolution will be lost at very large amplitude. The scan rate is proportional to the frequency. A proper choice of frequency is of the utmost importance. On each step, it is superimposed on a high frequency square wave in the range of 20-100 Hz. Similar to short pulse duration's in pulse voltammetry, the influence of capacitive current is larger at higher frequencies [72].

Square wave voltammetry has several advantages. Among these are its excellent sensitivity and the rejection of background currents. The interference due to capacitive current are lowered to minimum because the current is sampled just at the end of the half waves, when the current of the double electrical layer is the least. In addition, the advantage of this technique over others is the increase number of

samples, enabling higher scan speeds while retaining a good resolution on the potential axis.

2.5 Working Electrode Materials

Electrochemical stripping is recognized as a powerful tool for the detection of trace heavy metals. Proper choice of the working electrode is crucial for the success of the stripping operation. A number of experimental design factors have to be considered if it is decided to perform an analytical with electrochemical detection. These design factors depend on the technique employed, the electrode material and the electrode and cell configuration [43].

The reliability and repeatability of experiments can be aided by assuring a constant flux of electroactive species to the electrode. This is done by using controlled convective flow over the electrode or by creating a sufficient high concentration gradient. The additional advantage of this approach is that, because of the greater mass transport, sensitivity is increased and detection limits are lowered.

Detection limits can also be affected by other electrode reactions which can occur in the same potential range. The most prevalent of these is the reduction of oxygen, since its solubility in solutions open to the atmosphere is up to 10^{-4} M. Oxygen must be removed from the solution by passage of an inert gas, prepurified nitrogen or argon, through the solution to diminish the oxygen partial pressure to a very low value.

Electrode surface cleanliness is an important parameter influencing the

responsiveness of all electrodes. In a very general way, adsorbed contaminants can either block specific surface sites, thus inhibiting surface sensitive redox reactions or increase the electron-tunneling distance for redox analytes, thereby lowering the probability of tunneling (i.e., the rate of electron transfer). This phenomenon is called electrode poisoning, which has been one of the main limitations to the widespread use of electrochemical analysis by non-experts. The electrode poisoning can be diminished by electrode modifications using porous polymer films, which will be discussed later.

2.5.1 Platinum

Platinum (Pt) possesses high resistance to chemical attack, excellent high-temperature characteristics, and stable electrical properties. All these properties have been exploited for industrial applications. Platinum does not oxidize in air at any temperature, but can be corroded by cyanides, halogens, sulfur, and caustic alkalis. This metal is insoluble in hydrochloric and nitric acid, but does dissolve in the mixture known as aqua regia (forming chloroplatinic acid). Pt dissolution is more severe in phosphoric acid than in perchloric acid.

Novel metals like Pt and Au have been commonly used for microelectrodes. However, in aqueous solutions, detection of analyses is often not possible at negative potentials using such electrodes due to the high background currents produced by hydrogen evolution reactions on Pt. Metal electrodes are limited in terms of sensitivity by surface oxidation and reduction [82]. Mercury electrodes can eliminate

this problem of Faradic currents to detect the trace elements in aqueous solution by anodic stripping voltammetric.

2.5.2 Mercury

Mercury (Hg) was the first metal to be used extensively, in the form of the dropping mercury electrode because of its cyclic operation – continual drop growth, release and renewal – avoiding many of the problems of electrode poisoning in complex matrix; however, mercury's useful potential range is limited by its oxidation which means that, essentially, only reductions can be investigated. There are some metallic ions that cannot be determined at mercury (for example, Au, Ag and Hg). Although solid electrode materials were developed in order to permit oxidation reactions, there were no electrode materials being as good as mercury for studying reduction owing to its extended negative limits. Mercury electrode is not as safe as other electrodes, and many governments have already placed severe restrictions on the use of mercury [83]. There are a number of safety actions to be taken into consideration, from preparation of the experiment, end of the experiment, end of the working day to maintenance and disposal. Any mishandling of the mercury electrode will cause toxicity to human as well as experimental result deviation. Instead, mercury-coated carbon-based electrodes such as graphite and glassy carbon have been used extensively. But these electrodes are not mechanically stable and require the mercury drop electrode to be replenished, resulting in the generation of hazardous waste.

2.5.3 Diamond-like Carbon

Diamond like carbon (DLC) is a metastable form of amorphous carbon (Fig. 2-14) containing a significant fraction of sp^3 bonds. The structure of DLC modeled by Robertson [84] is a random network of covalently bonded carbon atoms in the different hybridizations, with a substantial degree of medium range order on the 1 nm scale. DLC has some extreme properties similar to diamond, such as hardness, elastic modulus and chemical inertness, but these are achieved in an isotropic disordered thin film with no grain boundaries.

Fig. 2-14 Structure of amorphous carbon [84]

DLC is a name attributed to a variety of amorphous carbon materials with carbon atoms bonded in mainly a mixture of sp^3 and sp^2 hybridizations, some containing up to about 50 at% hydrogen (a-C:H), other containing less than 1 % hydrogen (a-C). The bond types have a considerable influence on the material properties of amorphous carbon films. If the sp^2 type is predominant the film will be softer, and if the sp^3 type is predominant the film will be harder.

The attractive features of diamond include wide electrochemical potential window in aqueous media, very low capacitance, and extremely high electrochemically stability.

The compositions of the various forms of amorphous C-H compounds on a ternary phase diagram are displayed in Fig. 2-15, as first used by Jacob [85]. There are many a-Cs with disordered graphitic ordering such as glassy carbon and evaporated a-Cs which lie in the lower left corner. sp^2 -carbon is a versatile material that has a wide range of applications in electrochemistry. Because of its reasonable electrical conductivity and good corrosion resistance towards many electrolytes, carbon has found widespread acceptance in electrodes [86].

Fig. 2-15 Ternary phase diagram of bonding in amorphous carbon-hydrogen compounds [85].

2.5.4 Glassy Carbon

Sp^2 -carbon, such as glassy carbon (GC), has been widely used for electrochemical analysis in aqueous media, as it exhibits a relatively wide electrochemical potential window. GC has a number of properties, including having robust and smooth surfaces, high conductivity, impermeability, and unreactivity, which makes it an excellent electrode material. However, this glassy carbon electrode

(GCE) has serious limitations, including high background currents, deactivation via fouling and gradual loss of surface activity. This is due to the irreversible absorption of product formed in the electrochemical oxidation reaction. It is an inherent property of glassy carbon to undergo deactivation upon exposure to the laboratory environment or working solution, which is due to factors such as oxidation and adsorption of contaminants and reaction products. The porous nature of the electrode may also complicate the voltammetric response, since redox sites which lie in deep pores will be subject to greater uncompensated solution resistance than sites close to the outer surface of the electrode [87].

2.6 Modification of Working Electrodes

Various electrodes, such as Hg, DLC, GC, and graphene electrodes, are usually further modified with some polymers, metal nanoparticles or ceramics, depending on applications.

2.6.1 Electrode Passivation

One of main problems associated with various bare (not modified) electrodes is the interferences that arise from various surface-active substances that are adsorbed onto the electrode surfaces and cause passivation of the electrodes [38, 47, 48]. Natural environmental samples, in which trace heavy metals need to be analyzed, usually contain some kinds of surface-active substances [49, 50]. The adsorption of the surfactants onto electrode surfaces may affect both deposition and stripping steps,

leading to weaker or broader peaks and shifts in peak potentials. These effects depend upon specific surfactants and target metals, and reflect the interfacial properties of these bare electrodes [38, 39, 51]. To alleviate such interferences, efforts have been made by means of various electrode surface manipulations, such as adsorbed and self-assembled monomolecular layers of ligands on gold electrodes [52-54], composite electrodes prepared by mixing ligands with carbon paste [55, 56, 88, 89], polymer film modified electrodes [57-59, 90, 91], and so on. The principle of these approaches is that modified films work like a membrane that can mechanically prevent surface-active substances from reaching electrode surfaces by hindering their diffusion through the films, while metal cations with smaller sizes can relatively easily diffuse through the films and eventually reach the electrode surfaces [47].

Usually, to eliminate the passivation effect, electrode surfaces can be modified with polymers, e.g., amine [60], cysteamine [61] and nafion [62-65], but one of the main disadvantages is the poor electrical conductivity of these polymers. Thus, electrically conductive polymers, such as polyaniline (PANI) [66, 67] and polypyrrole [68], are preferred to modify electrodes.

2.6.2 Modification of Electrodes with Conductive Polymers

2.6.2.1 Background of Conductive Polymers

Conductive polymers are a new class of materials which exhibit highly reversible redox behavior, and it shows the unusual combination of electrical conductivity

properties of metals and plastic properties of polymers which can be formed into thin, mechanically strong, flexible and compact films [92]. One key property distinguishing classical polymers from metals is their lower electrical conductivity.

Fig. 2-16 shows the energy band structure for different materials, illustrating the conductivity for each material. For a material to be conducting, there must be a supply of mobile charge carriers: free electrons or 'holes' [93]. In addition, there must be an easy, high mobility path for them to follow through the materials [94].

In traditional polymers such as polyethylenes, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material.

Fig. 2-16 Energy band gap for metal, semiconductor and insulator

The situation is completely different in conductive polymers, a key property of which is the presence of conjugated double bonds along the backbone of the polymers. The common electronic feature of pristine (undoped) conducting polymers is the conjugated system, which is formed by the overlap of carbon p_z orbitals and

alternating carbon-carbon bond lengths (indicates the alternating single and double bonds) along the backbone of the polymers. In some systems, notably PANI, nitrogen, p_z orbitals and C_6 rings also are part of the conjugation path.

Fig. 2-17 shows the chemical repeat units of the pristine forms of several families of conducting polymers - that is, *trans*- and *cis*-polyacetylene (CH)_x; polythiophene (PT); polypyrrole (PPy); and the leuco-emeraldine-base (LEB), emeraldine-base (EB), and pernigraniline-base (PNB) forms of polyaniline (PANI).

Fig. 2-17 Repeat units of several pristine forms of conductive polymers [95]

The biggest advantage of conductive polymers compared with non-organic semiconductors is that conductive polymers can combine the mechanical properties (flexibility, toughness, malleability, elasticity, etc.) of plastics with high electrical conductivities. Their properties can be fine-tuned using the exquisite methods of organic synthesis.

Research in electro active polymers, particularly in aromatic conducting polymers, has received considerable attention worldwide in the past few years

because of their potential applications in the fields of microelectronics, optics and optoelectronics [96]. Among the various conducting polymers, PANI has become the most attractive because of its facile preparation, high conductivity, and good environmental stability [43]. Despite being known for over 150 years, research on PANI really took off in the 1980s after the birth of conducting polymers [97]. It was originally known as aniline black, obtainable by polymerization of the monomer aniline. Being environmentally stable in its conducting form, low cost of synthesis, excellent physical and chemical properties, PANI has been widely recognized as an important conducting polymer.

2.6.2.2 Aniline

Aniline can be known as phenylamine or aminobenzene and has a chemical formula of $C_6H_5NH_2$. It consists of a phenyl group attached to an amino group [98, 99]. Fig. 2-18 illustrates the chemical structure of aniline.

Fig. 2-18 Chemical structure of aniline monomer [100]

Physical properties of aniline:

Appearance colorless liquid;
Molar mass 93.13 g mol^{-1} ;
Density 1.0217 g/ml ;
Melting point $-6.3 \text{ }^{\circ}\text{C}$;
Boiling point $184.13 \text{ }^{\circ}\text{C}$;
Solubility in water 3.6 g/100 mL at $20 \text{ }^{\circ}\text{C}$.

There are several forms of aniline that can be derived by heating or other alternative applications, such forms are polyaniline, monomethyl aniline, dimethyl aniline and aniline hydro-chloride. Chemically, aniline is a weak base. Aromatic amines such as aniline are, in general, much weaker bases than aliphatic amines. Aniline reacts with strong acids to form anilinium (or phenylammonium) ion ($\text{C}_6\text{H}_5\text{-NH}_3^+$) which can form into a conductive compound - Polyaniline, or reacts with acyl halides to form amides.

2.6.2.3 Polyaniline

Known for more than 150 years, PANI is the oldest and potentially the most useful conducting polymers of the semi-flexible rod polymer family. It is derived from monomer aniline and has a molecular formula of $[(\text{C}_{12}\text{H}_{10}\text{N}_2)_y \cdot (\text{C}_{12}\text{H}_8\text{N}_2)_{(1-y)}]_n$. It is a highly porous structure that contains electrostatic redox sites which can be oxidized and reduced.

Polymerization of Aniline

There are a number of techniques to fabricate PANI, for instance electrochemical, chemical, photo-chemical and enzyme-catalyzed. Anodic oxidation of aniline on an inert metallic electrode is the most often used method in synthesis of

polyaniline. This method is commonly used since electrochemical methods offer some advantages over traditional chemical methods. The resulting product is free from oxidant contamination, as distinct from the chemical synthesis and do not necessarily need to be extracted from the initial monomer/solvent/oxidant mixture. Better control of synthesis parameters, such as monomer concentration, temperature and deposition voltage. This method provides the possibility of coupling with physical spectroscopic techniques such visible IR, Raman and ellipsometry, for *in situ* characterization.

The anodic oxidation of aniline is generally affected on an inert electrode material, such as carbon or semiconductors [101]. One such common technique is electrochemical technique by CV. In the CV, PANI undergoes a reversible redox process continuously from oxidation to reduction, and vice versa.

At the beginning of polymerization, the oligomers are formed and undergo oxidation process. Gradually, the oligomers' radical cation couple with the aniline's and results in the propagation of the chain. When the PANI is doped, it causes the PANI to be self catalyzed due to the presence of amine group in the PANI chains, which reactivates the aromatic ring by performing electron donating or electron accepting. So the efficient polymerization of aniline is achieved only in an acidic medium, where aniline exists as an anilinium cation. A variety of inorganic and organic acids of different concentration have been used in the syntheses of PANI. The resulting PANI, protonated with various acids, differs in solubility, conductivity and stability.

Polymerized from the aniline monomer, polyaniline can be found in one of three idealized oxidation states: leucoemeraldine - white/clear; emeraldine - green or blue; pernigraniline - blue/violet, as shown in Fig. 2-19.

Fig. 2-19 Molecular structure of PANI [100]

Leucoemeraldine ($y = 1$) is a white/clear polymer with benzenoid structure (fully reduced form), in which all the nitrogen atoms are amine; Pernigraniline ($y = 0$) is a blue/violet polymer with quinoid structure (fully oxidized form), in which all the nitrogen atoms are imine. Both Leucoemeraldine and pernigraniline are poor conductors. The only state that is conductive after doping is emeraldine (neutral oxidized form). It has a neutral, doped state with an approximately equal proportion of reduced and oxidized repeating units ($y = 0.5$), which gives a green/blue polymer. But without doping, the emeraldine base state PANI is also not conductive. Doping emeraldine base (EB) with acid (dopant) results to a conductive emeraldine salt (ES). This product is called Panipol. Among the three states, emeraldine is the best form of PANI which has a high stability at room temperature and high conductivity when doped [100]. Fig. 2-20 shows the protonation and redox reactions between the various forms of polyaniline.

Fig. 2-20 Synthesis and redox chemistry of PANI [100]

Doping and Conductivity

Fig. 2-21 illustrates the chemical structure, synthesis, reversible acid/base doping/dedoping and redox chemistry of PANI. In natural condition, PANI in emeraldine base (EB) exists as insulator. In the emeraldine oxidation state, polyaniline becomes electrically conducting when doped with an acid. The doping level can be tuned simply by controlling the pH of the dopant acid solution. In acid with low $\text{pH} < 4$, it exists as semi-conductor. The conductivity of polyaniline increases reversibly with doping from the undoped insulating base form ($\sigma \leq 10^{-10}$ S/cm) to the fully doped, conducting salt form ($\sigma \geq 1$ S/cm).

Besides the concentration and pH of the acid, the conductivity can also be affected by the temperature and humidity. Conductivity can also be controlled either chemically or electrochemically by changing the oxidation state.

The electrical conductivity of PANI based compositions can be closely controlled over a wide range. For neat PANI compositions, conductivity levels as high as 100 S/cm can be achieved. The full range of conductivity levels from less than 10^{-10} to 10^{-1} S/cm (melt processing) and 10 S/cm (solution processing), can be achieved for polymer blends containing PANI compositions. An important advantage is that the classical high percolation threshold for the onset of electrical conductivity observed in globular carbon black filled plastics does not exist.

2.6.2.4 Applications of PANI

The advantages of PANI are redox reversibility, light-weight, flexible, environmental stability, electrical conductivity and easy to fabricate into desired shapes as it can process in molten and solution states. Besides, it provides a good protection against discharges of static electricity [106]. PANI can have a high conductivity due to H^+ doping. This property makes PANI attractive in many applications such as electronic, electrochemical and photo-electrochemical devices, light emitting devices, nonlinear optical devices, smart windows, rechargeable batteries, capacitors, diodes, transistors, corrosion inhibitors and, of course, sensors [106].

Usually, for electrochemical analysis, the graphene electrodes are modified with polymers, e.g., amine [60], cysteamine [61] and nafion [62-65], to form the polymer-graphene composites which are used as sensors for the detection of heavy metal ions. But one of the main disadvantages is the poor conductivity of the polymers used, thus the electrically conductive polymers, such as polyaniline (PANI) [66, 67] or polypyrrole [68], are preferred as active materials to modify the electrodes.

2.6.3 Modification of Electrodes with Bismuth

Recently, bismuth-film (Bi-film) electrodes have become an attractive new subject of electroanalytical investigations as they could be a potential replacement for mercury and mercury film electrodes [36-40, 107, 108]. It was reported that Bi-film electrodes are less susceptible to oxygen background interferences than Hg ones [36].

Several types of bismuth electrodes showed excellent advantages over mercury film electrodes when applied to detect trace heavy metals using stripping voltammetry [36, 38, 41-46, 109]. The benefits of bismuth film electrodes include simple preparation, high sensitivity, obvious signal, excellent resolution, and low toxicity [43]. Furthermore, bismuth film electrodes can be further modified by coverage with polymeric layers, such as the use of Nafion-coated bismuth film electrode, which could minimize the interferences from surface-active materials and is very attractive for practical stripping applications [43].

2.7 Graphene

Recently, graphene, a single atomic sheet of graphite packed into a dense honeycomb crystal structure, has attracted great interest, as a functioning material for electronics, sensing, and energy applications [6-9] owing to its unique electrical [10-12], optical [13], and mechanical [14] properties, extraordinary electronic transport properties, large surface area, and high electrocatalytic activities [15], since it was experimentally produced in 2004 [16]. Graphene is a flat monolayer of sp^2 -bonded carbon atoms bonded into a two-dimensional hexagonal network (honeycomb crystal lattice) [6] as shown in Fig. 2-22. Carbon atoms connected by strong covalent ‘in-plane’ σ - σ bonds. The C-C bond length in graphene is about 0.142 nm as shown in Fig. 2-23.

Fig. 2-22 Graphene is an atomic-scale honeycomb lattice made of carbon atoms [6]

Fig. 2-23 Image of graphene in a transmission electron microscope [6]

A graphene sheet is thermodynamically unstable with respect to other fullerene structures if its size is less than about 20 nm. If unsupported, the nanosized flat graphene have a tendency to scroll and buckle, to its lower energy state [110]. Graphene is the least stable structure until about 6000 atoms and becomes the most stable one (as within graphite) only for sizes larger than 24,000 carbon atoms. As shown in Fig. 2-24, graphene can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite [6]. Graphite is stacked layers of graphene sheets (separated by 0.3 nm) by weak Van der Waals forces.

Fig. 2-24 Graphene: the parent of all graphitic forms [6]

Four different types of graphenes can be defined: single-layer graphene, bilayer graphene, few-layer graphene (number of layers ≤ 10) and multilayer graphene (number of layers > 10) [111]. Ideally graphene is a single-layer material, but graphene samples with two or more layers are being investigated with equal interest [111].

Recently, graphene has attracted great interest, as a functioning material for electronics, sensing, and energy applications [6-9] owing to its incredible electrical [10-12], optical [13], and mechanical [14] properties. However, one of critical challenges in synthesis of graphene is to produce a large surface area of it.

2.7.1 Fabrication Methods of Graphene

There are generally four types of fabrication methods for single and multi-layer graphene, namely, mechanical cleavage of highly ordered pyrolytic graphite (HOPG), chemical exfoliation of graphite (deposition of a dispersed graphene oxide, followed by an oxygen reduction process) [17, 18], thermal decomposition of SiC [19], and

chemical vapor deposition (CVD) of C using a hydrocarbon compound (e.g., methane) on a substrate surface with a transition metal film as a catalyst (e.g., nickel (Ni)) [20].

2.7.1.1 Mechanical Exfoliation of Bulk Graphite

In 2004, the British researchers obtained graphene by mechanical exfoliation of graphite. They used Scotch tape to repeatedly split graphite crystals into increasingly thinner pieces. Single (or few)-layer graphene has been generally prepared by micromechanical cleavage. But mechanical exfoliation of bulk graphite always resulted in limited surface area of graphene [16, 21, 22], thus not suitable for large scale synthesis of single-layer graphene or of few-layer graphene.

2.7.1.2 Chemical Exfoliation of Graphite

The chemical exfoliation of graphite usually involves 3 steps: Step 1: Graphene Oxide suspensions by oxidizing graphite using a Hummers method: the graphite powders was dispersed and separated in a ultrasonic bathes in a mixture of sulfuric acid H_2SO_4 , sodium nitrate NaNO_3 , and potassium permanganate KMnO_4 , to get a solution contain graphene oxide pieces. Being hydrophilic, graphene oxide disperses readily in water, breaking up into macroscopic flakes, mostly one layer thick. In theory, chemical reduction of these flakes would yield a suspension of graphene

flakes. Step 2: Deposition of Chemically derived graphene Films. The concentration, volume, and spreading time for achieving uniform deposition for 300 mm chemically derived graphene thin film via modified spin coating method was 0.4 mg/mL, 60 mL, and 30 min, respectively. As shown in Fig. 2-25, the wafers were dipped into 50 wt % potassium hydroxide (KOH) solution for 15 min to enhance the hydrophilicity of the surface. After casting the graphene oxide solution onto center of the substrates, time was allowed prior to rotation. When rotation started, nitrogen gas was blown at center region of the substrates to accelerate the vaporization of the solvent to get uniform and continuous deposited films. The thickness of the resulting reduced graphene oxide film can be tuned by changing the spin coating parameters. When all the solvent was vaporized, chemically derived graphene films were deposited on the substrates. Step 3: Chemical reduction of graphene oxide sheets. Researchers have developed a method of placing graphene oxide paper in a solution of pure hydrazine (a chemical compound of nitrogen and hydrogen), which reduces the graphene oxide paper into single-layer graphene. In addition, mass production of graphene from chemical reduction of graphene oxide provides an inexpensive source for large-scale applications.

Fig. 2-25 Deposition of chemically derived graphene films [23]

For chemical exfoliation of graphite, because of the van der Waals and π - π stacking interactions among individual graphene sheet interactions, the as-reduced graphene sheets from graphene oxide (prepared by a modified Hummers' method [23]) tend to form irreversible agglomerates and even restack to form graphite when graphene dispersion solutions are dried [24-26].

2.7.1.3 Thermal Decomposition of Silicon Carbide

Epitaxial growth of graphene by thermal decomposition of silicon carbide (SiC) is well known that ultrathin graphitic films grow on (0001) face of a 6H-SiC wafer crystals when the silicon carbide is heated to high temperatures (>1100 °C) for 1~20 min under ultrahigh vacuum conditions. The Si atoms volatilized, and the remaining carbon atoms reorganized to generate graphene layers. It is also possible to grow these films at more moderate vacuum conditions using ovens with controlled background gas (e.g., an argon atmosphere of 1 bar). The face of the silicon carbide used for graphene creation (the silicon-terminated or carbon-terminated) highly influences the thickness, mobility and carrier density of the graphene. Specifically they grow on the 0001 (silicon-terminated) and 0001 (carbon-terminated) faces of 4H-SiC and 6H-SiC. Growth on the silicon-terminated face is slow and terminates after relatively short times at high temperatures. The growth on the carbon-terminated face apparently does not self-limit so that relatively thick layers (~ 5 up to 100 layers) can be achieved. Thus this process produces a sample size that is dependent upon the size of the SiC

substrate used, and the graphene exhibited poor uniformity and contained a multitude of domains whose thickness greatly depends on the crystallographic orientation of the SiC surfaces [22].

2.7.1.4 Chemical Vapor Deposition

Chemical vapor deposition (CVD) of hydrocarbons on the surfaces of single crystals of metals (e.g., Ni, Ru, Ir, Cu) uses the atomic structure of a metal substrate to seed the growth of the graphene (epitaxial growth). The CVD approach to producing graphene relies on dissolving carbon into the nickel substrate, and then forcing it to precipitate out by cooling the nickel, which is a dissolution-precipitation type. The thickness and crystalline ordering of the precipitated carbon is controlled by the cooling rate and by the atomic concentration of carbon dissolved in the nickel. This concentration is in turn controlled by the type and concentration of the carbonaceous gas, and the thickness of the nickel layer. Graphene grown on Ru doesn't typically yield a sample with a uniform thickness of graphene layers, and bonding between the bottom graphene layer and the substrate may affect the properties of the carbon layers. Graphene grown on Ir on the other hand is very weakly bonded, uniform in thickness, and can be made highly ordered. Like on many other substrates, graphene on iridium is slightly rippled. Due to the long-range order of these ripples generation of mini-gaps in the electronic band-structure (Dirac cone) becomes visible. High-quality sheets of few-layer graphene exceeding 1 cm^2 (0.2 sq in) in area have been

synthesized via chemical vapor deposition on thin Ni films. An improvement of this technique has been found in copper foil where the growth automatically stops after a single graphene layer, and arbitrarily large graphene films can be created. Using CVD, a precise control of number of graphene atomic layers is difficult due to the sensitivity of such growth to various process parameters, e.g., heating period and flowing gas composition. In addition, some by-products, e.g., carbon nanotubes (CNTs) and amorphous carbon (a-C) layers are usually produced together with graphene films. Also, the strong bonding between graphene and corresponding substrate not only significantly alters the transport properties of graphene, but also complicates the separation of graphene from substrate surface. Graphene grown on metal film is limited by metal's small grain size, which causes the presence of multilayers at the grain boundaries, and is also limited by the high solubility of carbon.

2.7.1.5 Solid-state Carbon Diffusion

A new approach of metal-catalyzed fabrication of graphene based on solid-state carbon diffusion via a rapid thermal processing at a high temperature was recently reported [69, 70], which is similar to a CVD method but the C source used with this approach is an existing solid C layer rather than a hydrocarbon compound [69, 70]). During the thermal processing, the C atoms first dissolve into a top Ni layer by diffusion during heating at a high temperature (800-1100 °C), and then are expelled

from the Ni layer during cooling due to a sharp fall of the solubility of C in the Ni layer. The presence of graphene fabricated via solid-state carbon diffusion using a-C as the C source can be confirmed with Raman [69] and XRD [70] measurements. Compared to the CVD method, this method could have a better control of graphene film thickness due to a fixed, finite C supply and may be less sensitive to fabrication parameters. Also the agglomerates effects [24-26] that usually occur for the film by chemical exfoliation of graphite can be eliminated for the graphene films fabricated by this method. In this project, the solid-state carbon diffusion method will be used to fabricate the graphene ultrathin films.

2.7.2 Methods to Characterize Graphene

Graphene can be characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), X-ray diffraction (XRD), and Raman spectroscopy:

- AFM directly gives the number of layers.
- STM and TEM images are useful in determining the morphology and structure of graphene.
- Raman spectroscopy has emerged to be an important tool for the characterization of graphene samples.

Single-layer graphene placed on a silicon wafer with a 300 nm thick layer of SiO₂, becomes visible in an optical microscope. The key for the success probably was

the use of high throughput visual recognition of graphene on a proper chosen substrate, which provides a small but noticeable optical contrast.

This one atom thick crystal can be seen with the naked eye because it absorbs approximately 2.3% of white light as shown in Fig. 2-26 [112].

Fig. 2-26 Photograph of graphene in transmitted light [112].

2.7.3 Application of Graphene as Sensors

Graphene has been the subject of intense research since it was first isolated in free-standing form in 2004, because of its thermodynamic stability, extremely high charge-carrier mobilities, and mechanical stiffness, the last of which distinguishes it from monoatomic metallic films. Graphene is an excellent candidate for electrodes due to its low resistivity, high mechanical strength, and high thermal and chemical stability. Comparing to one-dimensional carbon nanotubes, as electrode, graphene is expected to excel carbon nanotubes because it offers large detection area, biocompatibility, and exceptional and unique electronic properties such as ultrahigh mobility and ambipolar field-effect.

Development of some biosensors based on graphene has been reported [27-31] and their advantages are obvious in various fields, e.g., large detection area, unique

sensing mechanism, and ease of functionalization [32]. However, chemical binders (e.g., teflon) have been usually used to mix with graphene films or powders to form a kind of graphene paste with a thickness of μm scale. Such graphene paste could reduce its electrical conductivity and surface activity due to the effect of the binder.

2.7.4 Limitations of Previous Research

Though the studies of the effects of thermal processing temperature and a-C layer thickness on the formation and structure of graphene films have been reported [69, 70], the effects of catalyst (e.g., Ni) layer thickness and substrate surface condition (e.g., Si substrate without or with a thermally oxidized SiO_2 layer) on the formation and structure of graphene films have not been reported. In this research, graphene thin films were fabricated via solid-state carbon diffusion using a sputtering deposited a-C layer as the C source and a sputtering deposited Ni layer as the catalyst (i.e., a Ni/a-C bilayer stack) on Si and thermally oxidized Si (SiO_2/Si) substrates. The effects of Ni/a-C bilayer thickness and Si substrate surface condition on the formation of SiO_2 nanowires on the graphene film were then studied.

Chapter 3: Experimental Details

3.1 Materials

All the chemicals used were of analytical reagent grade and stored at RT.

For Electrode Modification:

Aniline monomers (Fluka) were freshly distilled under reduced pressure and stored at low temperature under a nitrogen atmosphere.

PANI (emeraldine base, MW ca. 5000) was supplied by Aldrich.

MWCNTs provided by Aldrich had inner diameters of 2-6 nm, outer diameters of 10-15 nm, and lengths of 0.1-10 μm .

Stock solutions of $\text{Bi}(\text{NO}_3)_3$ (Sigma), $\text{Fe}(\text{NO}_3)_3$ (Sigma) and H_2SO_4 (Sigma) were diluted using DI water to a concentration of 1 mM, 0.25 M and 0.25 M, respectively, all of which were stored at RT.

For Graphene Fabrication:

A pure graphite target (99.999% C) and a pure Ni target (99.99% Ni) were supplied by PLASMATERIALS and MATERION, respectively.

For Electrode Characterization:

Stock solutions of Potassium Ferricyanide Trihydrate ($\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) (Resource) and Potassium Ferrocyanide Trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) (Resource)

were diluted using DI water to a concentration of 5 mM each, while Potassium Chloride (KCl) (Riedel-de Haën) was distilled to 0.1 M.

For Electrochemical Analysis:

CH₃COOH (HAc) (Fluka) and CH₃COONa (NaAc) (Fluka) were used for the preparation of a 0.1 M acetate buffer solutions. Different volume fractions of the HAc and NaAc solutions will result in different pH values of the mixtures, with details shown in Table 3-1.

Table 3-1 HAc-NaAc buffer solutions

0.1 M HAc (mL)	32	16	8	4	2	1	1	1	1	1	1
0.1 M NaAc (mL)	1	1	1	1	1	1	2	4	8	16	32
pH	3.19	3.5	3.8	4.1	4.4	4.7	5.0	5.3	5.6	5.9	6.22

Stock solutions of Pb(NO₃)₂ (Sigma), Cu(NO₃)₂ (Sigma) and Cd(NO₃)₂ (Sigma) were diluted using deionized (DI) water to a concentration of 1 mM each and stored at room temperature (RT ~ 22 °C). All the chemicals used were of analytical reagent grade.

3.2 Preparation of Thin Films and Working Electrodes

The electrodes used in this thesis are tabulated in Table 3-2. The details of the fabrication of those electrodes will be discussed in the following parts of this section.

Table 3-2 Summary of all kinds of electrodes used in this study

	GCE	DLC (a-C_{single})	Graphene
--	------------	-----------------------------------	-----------------

PANI	PANI/GCE		PANI/Graphene
Bi	Bi/GCE		Bi/Grpahene
Bi and PANI	Bi/PANI/GCE		Bi/PANI/Graphene
PANI and MWCNTs	MWCNT-PANI		

3.2.1 GCE

A glassy carbon electrode (GCE) surface was polished thoroughly with 0.3 μm $\alpha\text{-Al}_2\text{O}_3$ powder slurry on a soft cloth and then sonicated in ethanol and doubly distilled water for 3 min each to remove alumina particles and other possible contaminants.

3.2.2 MWCNT-PANI Modified GCE

The fabrication of MWCNT-PANI modified GCEs was performed as follows. Firstly carboxylation of MWCNTs was conducted using a common method [113] by sonicating the MWCNTs (0.5 g) in a mixed solution (150 mL) of concentrated H_2SO_4 and HNO_3 (3:1, V/V) for 4 hours. 500 mL of DI water was added into this mixed solution and then the solution was cooled to RT. The suspension was filtered through a membrane filter (0.25 micron pore size), and the MWCNTs remaining on the filter were washed with a 0.05 M NaOH solution followed by rinsing with DI water to pH 7.0, and then filtered again. Finally, the functionalized MWCNTs were dried in an

oven at 110 °C. Such prepared carbon nanotube carboxylate was confirmed to be MWCNT-COOH.

The prepared MWCNT-COOH (10 mg) was then mixed with PANI (10 mg) and sonicated in 150 mL of H₂SO₄ (0.25 M) for 2 h to form PANI modified MWCNTs (MWCNT-PANI). Next, thoroughly polished GCEs using a 0.3 µm α-Al₂O₃ powder slurry on a soft cloth were sonicated in DI water for 3 min to remove possible contaminants. The cleaned GCEs were dipped into the previously mixed H₂SO₄ solution containing MWCNT-PANI for 15 min, and then dipped into the clean H₂SO₄ solution (0.25 M) to remove the loosely attached species and also to dope the PANI to make it electrically conductive.

3.2.3 Graphene Thin Film Electrode

P-Si (111) wafers (boron doped, resistivity: 0.01-0.02 ohm-cm, thickness: ~525 µm) without and with a thermally oxidized SiO₂ layer of about 300 nm in thickness, designated as Si and SiO₂/Si substrates, respectively, were cut into square pieces of about 1.2 cm × 1.2 cm. Before being transferred into the deposition chamber, they were cleaned with acetone, ethanol and DI water ultrasonic baths successively, and finally dried with compressed air. During the sputtering processes, an Ar gas flow rate of 10 sccm and a deposition pressure of 5 mTorr in the deposition chamber were maintained. Before film depositions, the substrate surfaces were further cleaned using Ar plasma with a RF power of 50 W for 10 min in the deposition chamber. The

sputtering parameters for the deposition of Ni/a-C bilayers and Ni-C mixed layers are described as follows.

For sputtering deposition of Ni/a-C bilayers: The a-C layers of about 50 nm in thickness were deposited on the Si or SiO₂/Si substrates via DC magnetron sputtering deposition using a pure graphite target ($\geq 99.99\%$ C) as the C source with a DC sputtering power of 200 W applied for 40 min (a deposition rate of about 1.2 nm/min). A Ni layer of about 100 nm thick was deposited on the top of the a-C layers also via DC magnetron sputtering process. The DC sputtering power applied to the Ni target ($\geq 99.99\%$ Ni) and time for the deposition of the Ni layers were respectively 50 W and 30 min (a deposition rate of about 2.9 nm/min). For comparison, the samples with only a single a-C layer (200 nm thick, designed as a-C_{single}) and a single Ni layer (100 nm thick, designated as Ni_{single}) were also prepared. The sputtering deposition rates for the both a-C and Ni were estimated by measuring the layer thicknesses of some samples prepared under similar deposition conditions using FE-SEM (JEOL JSM-7600F).

For co-sputtering deposition of Ni-C mixed layers: The Ni-C mixed layers with varying C contents were deposited on the substrates via DC magnetron co-sputtering deposition, with a DC power of 50 W applied to the Ni target and varying DC powers ranging from 25 to 200 W applied to the graphite target. The duration of the co-sputtering deposition of the Ni-C films was maintained at 90 min.

The deposited samples were then left to cool in the vacuum chamber for 1 hour to prevent any thermal shock to the Ni-C thin films [111].

The coated samples were post thermally treated at 1000 °C via rapid thermal processing (RTP) with both heating and cooling rates of 20 °C/s, a dwell time of 3 min, and a continuous Ar gas flow of 200 sccm to prevent the oxidation.

All the parameters for the a-C and Ni deposition and thermal processing were optimized in order to get the optimum electrochemical performance.

The thermally treated Ni/a-C bilayer coated samples were designated as thermally treated Ni:t1/C:t2/SiO₂/Si or Ni:t1/C:t2/Si, depending on the substrate surface conditions, where t1 and t2 were related to the respective Ni and a-C deposition durations (min). For example, Ni:20/C:40/SiO₂/Si means a sample with a thermally oxidized Si substrate being covered firstly with an a-C layer, and then a Ni layer on the top, which were sputtering deposited for 40 min (at 200 W) and 20 min (at 50 W), respectively.

3.2.4 Modification of Electrodes with PANI or Bismuth

With 7.3 µM aniline dissolved in a 0.25 M H₂SO₄ electrolyte, the PANI film was electrochemically coated on the working electrode surface via a CV method, with a scan rate of 50 mV/s and a potential range of -0.2 to 0.9 V for 30 cycles, with continuous stirring. The parameters for the PANI layer deposition were previously optimized with respect to the best performance of the electrode in detection of Pb²⁺ via SWASV [5]. With PANI modification, the graphene electrode and GCE were designated as PANI/graphene electrode and PANI/GCE, respectively.

During SWASV tests, with Bi^{3+} dissolved in the electrolyte, the graphene and PANI/graphene electrodes, or GCE and PANI/GCE were designated as Bi/graphene and Bi/PANI/graphene electrodes, or Bi/GCE and Bi/PANI/GCE, respectively.

3.3 Characterization

The bonding structures of the Ni/a-C bilayer or Ni-C mixed layer coated samples before and after thermal processing were characterized by Raman spectroscopy (RENISHAW 1000, He-Ne laser of 633 nm wavelength) with the *Raman* peaks fitted using a Gaussian function.

The electrical conductivities of the samples were measured by a four-point probe (Pro4-440N) with all the sample thicknesses assumed to be 525 μm that was the thickness of the Si wafer substrates.

The surface morphology of the samples was measured using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F).

The crystal structure of the graphene films formed on the thermally treated Ni/a-C bilayer coated SiO_2/Si substrates was characterized with X-Ray Diffraction (XRD, Empyrean, PANalytical), high resolution transmission electron microscopy (HR-TEM, JEOL 2010) and electron diffraction. For a TEM measurement, the Ni layer of a sample was etched away in a 0.25 M $\text{Fe}(\text{NO}_3)_3$ solution from the edges towards the center of the sample, leaving a thin jasper-colored flocculent C film floating in the solution, and this C film was then transferred onto a copper grid and was ready for the measurement.

X-ray photoelectron spectroscopy (XPS) and Energy Dispersive X-ray Detector (EDX) were used to analyze the elemental contents of the both as-deposited and thermally treated samples.

The PANI layers were also characterized by Fourier transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet 6700, IR mode).

3.4 Electrochemical Measurements and Applications

All electrochemical experiments were performed using an electrochemical workstation (CHI 660C) having a conventional three-electrode cell configuration comprising a sample of 7.5 mm in diameter as the working electrode, a platinum mesh as the counter electrode and an Ag/AgCl (saturated KCl) as the reference electrode. A magnetic stirrer (Heidolph MR3001K) was used to stir (400 rpm) the testing solutions. The electrolyte contained the basic ions for conductivity, and the target ions or species for analysis. All the electrochemical experiments were carried out under a nitrogen environment at room temperature.

The thermally treated Ni:20/C:40 bilayer coated Si and SiO₂/Si samples, which were used as electrodes for electrochemical detection of trace heavy metals, were designated as thermally treated Ni/a-C/Si and thermally treated Ni/a-C/SiO₂/Si electrodes, respectively. The as-deposited a-C_{single}/Si samples were designated as a-C_{single} electrodes.

In a SWASV measurement, an electrode was dipped into a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO₃ and predetermined concentrations of Pb²⁺

and Cd^{2+} that were the target metals to be investigated. A preconcentration potential of -1 V was first applied to the working electrode for 180 s (preconcentration time) for the deposition of target metals, with continuous stirring (400 rpm) by a magnetic stirrer (Heidolph MR3001K). Next, a quiet time of 30 s was taken to stabilize the solution. Finally, the anodic stripping was performed from -1.1 to 0.2 V with a frequency of 50 Hz, increment of 5 mV/s, amplitude of 50 mV and sensitivity of 0.1 mA/V, with voltammograms recorded for analysis. For repetitive measurements, the electrode surfaces were recleaned after each test at 0.2 V for 180 s with continuous magnetic stirring (400 rpm) to remove the residual metals for the preparation of next experiment.

The corrosion performance of the electrodes was evaluated via a Tefel Plot method in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO_3 with a potential applied from -0.8 to 0.4 V, a scan rate of 1 mV/s, and a sensitivity of 0.1 mA/V.

The reaction reversibility and surface activity of the electrodes were tested via a conventional CV method with the electrodes scanned from -0.2 to 0.9 V in a solution containing 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl with a scan rate of 50 mV/s and a sensitivity of 0.1 mA/V.

The potential window of the electrodes was tested via CV with the electrodes scanned from -1.5 to 1.6 V in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO_3 with a scan rate of 100 mV/s and a sensitivity of 1 mA/V.

Electrochemical impedance spectroscopic (EIS) measurements were carried out in a solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl with an amplitude of 0.01 V, potential of 0.24 V and frequencies in the range of 5×10^{-3} to 10^5 Hz.

Chapter 4: Polyaniline and Bismuth Modified Glassy Carbon Electrodes

4.1 Introduction

Recently, bismuth-film (Bi-film) electrodes have become an attractive new subject of electroanalytical investigations as they could be a potential replacement for mercury and mercury film electrodes. One of main problems associated with Bi-film electrodes is the interferences that arise from various surface-active substances that are adsorbed onto the electrode surfaces and cause passivation of the electrodes. Modified electrodes based on incorporation of conducting polymer (CP) films have received considerable attention for detection of trace heavy metals due to their superior electrical conductivities, good adhesive strengths and suitable structural characteristics. Recently, many efforts have been focused on the development of new superior nanocomposite materials based on CNT fillers for particular applications [114], such as polymer-CNT and metals-CNT [115-120], hydroxyapatite-CNT [120], MWCNT and M1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC)-CNT and N-Hydroxysuccinimide (NHS)-CNT [121].

In this study, polyaniline/glassy carbon electrodes (PANI/GCEs) and Bi/PANI/GCEs were prepared by electrodeposition, and a novel multiwall carbon nanotube (MWCNT)-PANI nanocomposite coating was prepared onto GCEs through an easy and effective one-step sonication synthesis. The modified electrodes were employed for stripping voltammetric analysis of trace amounts of Cd^{2+} and Pb^{2+} ions in an acetate buffer solution.

4.2 PANI Modified GCEs

Polyaniline (PANI) coatings were electrodeposited on the surfaces of glassy carbon electrodes (GCEs) to form new electrodes, i.e., PANI/GCEs. It was found that with increasing deposition time, the PANI coatings became more compact while the charge transfer resistance of the coatings became higher. The PANI/GCEs were used to detect Cd^{2+} and Pb^{2+} ions contained in a 0.1 M acetate buffer solution using SWASV. It was found that the PANI/GCE had a highest anodic stripping peak current in a solution of pH 5.3. The study of the cleaning performance of the PANI/GCEs indicated that there were less remaining metals on the surfaces of the PANI/GCEs compared to the bare GCEs after cleaning at a potential of 0.4 V, which was probably due to that the PANI coatings could effectively prevent the deposition of the metals into the surface defects of the GCEs. The PANI coatings could also reduce the passivation effect of the GCEs, thus improving the repeatability of the electrodes.

4.2.1 PANI Layer Deposition via CV Method

Usually there are two ways to increase the amount of PANI coating during polymerization: higher aniline concentration in solution and longer deposition time. In this chapter, the polymerization time was increased by increasing the scan cycles during the electro-deposition. The PANI was deposited onto the GCE surface in the electrolytic solution of 0.25 M H_2SO_4 containing 7.3 mM aniline monomers using the CV method as shown in Fig. 4-1 [67]. There are three main oxidation peaks on the

cyclic voltammograms, and the detailed description of these oxidation peaks are listed in Table 4-1. The oxidation peaks at about 0.235 V are related to the transformation of the deposited PANI coatings from leucoemeraldine form (fully reduced state) to emeraldine salt (neutral state). The small oxidation peaks at about 0.4 V, which are not obvious, but can be identified with reference to the corresponding reduction peaks at around 0.37 V, are due to the branched structure [122] of the PANI layers [67]. The oxidation peaks at about 0.513 V refer to the state transformation from emeraldine to pernigraniline (fully oxidized state) [67, 123]. The oxidation peaks at about 0.706 V are related to the polymerization reaction of aniline [67, 69]. The peak currents of the two main oxidation peaks at about 0.235 and 0.513 V are related to the amounts of PANI deposited on the GCE surfaces [67, 69].

Fig. 4-1 In-situ cyclic voltammograms of a PANI coating measured during its deposition up to 40 cycles with a scan rate of 50 mV/s from -0.2 to 0.9 V.

For the peaks at potentials higher than 0.8 V, besides the reasons of oxygen evolution and PANI degradation that are all familiar, the reason may also be due to the aniline polymerization, because the PANI coating can be deposited if the CV scan range is slightly below 0.8 V.

Table 4-1 Description of main oxidation peaks of PANI coated on GCEs via CV method [67, 69, 123, 124]

Peak Position (V)	Reason	Appearance
0.235	Oxidation state transformation from leucoemeraldine (fully reduced) state to emeraldine (neutral) state of PANI.	From nearly transparent to dark green.
0.513	Due to the branched structures of PANI.	No color change.
0.706	Oxidation state transformation from emeraldine (neutral) state to pernigraniline (fully oxidized) state.	From dark green to dark blue.
>0.8	Due to aniline polymerization, PANI degradation or oxygen evolution.	

As the number of scan cycles increases, the two main peaks increase in height, which indicates that the thicker PANI coatings have been formed. Because the PANI oxidation peaks are higher than 0.1 V as shown in Fig. 4-1, the PANI coatings are ‘electro-inactive’ within the potential range from -1.4 to 0.1 V (vs. Ag/AgCl), and thus they are neither oxidizable nor reducible and hence have no interferences with the redox reactions of the metal ions in the solutions [67, 106]. Thus, the PANI coatings can be used to modify the GCEs for the application of anodic stripping voltammetric determination of trace heavy metals.

The PANI coatings have a porous and branched structure that can increase the specific surface area. From the SEM micrographs shown in Fig. 4-2, the PANI coatings appear to be denser with the increased number of deposition cycles. The coating deposited with 25 cycles is thin and nonuniform due to a relatively short deposition time. As the number of scan cycles increases to 30 and 35, the coatings get thicker and more uniform.

Fig. 4-2 SEM micrographs of PANI coatings on Si substrate deposited by CV method for (a) 25, (b) 30 and (c) 35 cycles.

4.2.2 Effect of PANI Layer Thickness on Stripping Peak Current

Usually there are two ways to increase the amount of PANI coating during polymerization: a higher aniline monomer concentration in a solution and a longer polymerization time. In this work, polymerization time was increased by increasing the number of scan cycles during the CV deposition.

4.2.2.1 Effect of Aniline Concentration on SWASV Response

Fig. 4-3 shows the influence of aniline concentrations during PANI deposition to anodic stripping responses, indicating that as aniline concentration increases from

7.30 to 18.25 mM the peak currents of Pb^{2+} and Cd^{2+} both drop, which may be due to the reduction of the surface porosity and increase of surface charge transfer resistance. Compared with the bare GCE without aniline, the PANI/GCE fabricated with aniline of 7.3 mM has a slightly smaller Pb^{2+} peak but a much higher Cd^{2+} peak than those of the GCE.

Fig. 4-3 Stripping voltammograms measured using different PANI/GCEs fabricated with increasing aniline concentration. The inset shows effect of aniline concentration on peak currents of $3 \mu\text{M}$ Pb^{2+} and $3 \mu\text{M}$ Cd^{2+} . The supporting electrolyte is 0.1 M acetate buffer solution (pH 5.3). The peak heights at -0.72 and -0.46 V refer to Cd^{2+} and Pb^{2+} in the solutions, respectively.

With the higher aniline concentration during PANI deposition, the morphology of PANI coatings has a bigger charge transfer resistance as previously discussed by the author [67], which indicates a weaker surface activity. This is why as aniline concentration increases, the stripping currents reduce. Usually a too low aniline concentration is also not preferred; otherwise there are not enough aniline monomers

to form the complete layer with high porosity. So with a balance aniline of 7.3 mM is preferred due to the highest stripping peaks and high enough specific surface area.

4.2.2.2 Effect of PANI Deposition Time on SWASV Response

In this work, for the PANI films fabricated by the multipulse potentiostatic method, the thickness effect with respect to deposition time is illustrated in Fig. 4-4 [5] that shows the stripping responses to 25 nM Cd^{2+} and 25 nM Pb^{2+} , together with the Bi plating (1.25 μM). Below a certain PANI layer thickness, the stripping peak currents of the both metal ions increase when the PANI deposition time is increased. However, when the PANI layer is beyond a critical thickness, the stripping responses to Cd^{2+} and Pb^{2+} become weaker and slower with a further increase of the PANI deposition time. This is in agreement with Ref. [43] that reported that the stripping peak intensity would first increase and then weaken as the aniline concentration was increased. The reason might be a competition between two effects, i.e., enhancing effect due to the porous structure of the PANI layers that can offer a bigger surface area to enhance the accumulation of the metals and suppressing effect due to the thicker PANI films that could reduce the conductivity of the films. To compromise between the two effects, a deposition time of about 160 s is selected. From Fig. 4-4, it can be expected that the Bi/PANI/GCEs with the PANI deposition of 160 s can achieve a higher current response than the Bi/GCEs that have no PANI deposition.

Fig. 4-4 Effect of PANI deposition time.

4.2.2.3 Effect of Solution pH

The simultaneous anodic stripping voltammetric determination of Pb^{2+} and Cd^{2+} ions using the PANI/GCEs in the 0.1 M acetate buffer solutions containing Pb^{2+} and Cd^{2+} of 3 μM each with respect to the pH values of the solutions is illustrated in Fig. 4-5 [67]. The stripping peak currents of the both metals increase as the pH increases from 3.5 to 5.3. However, when the pH is higher than 5.3, the both peak currents drop. When the pH reduces from 5.3 to 3.5, the PANI coatings have increased conductivities due to higher concentrated H^+ doping at lower pH values, which may tend to increase the peak currents. However, the PANI coatings more positively charged can repulse the metal ions that are also positively charged due to higher concentrated H^+ doping at lower pH values. In addition, the hydrogen evolution at a lower pH can be much easier, which can reduce the electrode surface activities. Because of these two effects, the peak currents of the PANI/GCEs drop with the

decrease of pH from 5.3 to 3.5. The following discussion will be based on the results measured from the solutions of pH 5.3 that favors higher stripping responses.

Fig. 4-5 Voltammograms measured with PANI/GCE in solutions containing $3 \mu M$ Pb^{2+} and $3 \mu M$ Cd^{2+} at different pH values. The inset shows the effect of pH value on stripping peak current.

4.2.3 Reaction Reversibility of PANI Modified Electrodes

For ideal reversible electrodes, the shifted ratio $I_{pc} / I_{pa} = 1$, where I_{pc} and I_{pa} are reduction and oxidation peaks respectively, with the measuring method shown in the inset of Fig. 4-6. Usually the electrodes are not reversible, which offer a shifted ratio bigger than 1. Based on Fig. 4-6, we can calculate that:

$$\text{For GCE, } I_{pc} / I_{pa} = 40.45 \mu A / 31.76 \mu A \approx 1.27 ; \quad (4-1)$$

$$\text{For PANI/GCE, } I_{pc} / I_{pa} = 38.20 \mu A / 33.67 \mu A \approx 1.13. \quad (4-2)$$

Thus after the PANI modification, the electrode has a smaller shift ratio which is much near 1, indicating a better reversibility compared with bare GCE.

Fig. 4-6 Surface activity tests for PANI/GCEs and GCEs. The PANI/GCEs were fabricated using 7.3 μM aniline and CV deposited for 30 cycles. The inset shows the measuring method of peak currents.

4.2.4 Calibration Curves of PANI/GCEs

For each electrode, the SWASV experiments are performed with increasing both the Pb^{2+} and Cd^{2+} concentrations simultaneously from 100 to 333 nM with an increment of 33.3 nM, with the results shown in Fig. 4-7. For the both GCEs and PANI/GCEs, the stripping peak currents referring to both Pb^{2+} and Cd^{2+} are recorded and four calibration curves are drawn, respectively, as shown in Fig. 4-8, from which it is observed that the both types of electrodes have near linear calibration curves, indicating that the PANI/GCEs perform well with increased Pb^{2+} and Cd^{2+} concentrations. A disadvantage is that the PANI/GCEs have lower stripping peak currents than the GCEs for the both Pb^{2+} and Cd^{2+} ions as shown in Fig. 4-8.

Fig. 4-7 Stripping voltammograms for (a) PANI/GCE and (b) GCE with increasing Pb^{2+} and Cd^{2+} concentrations. All tests were conducted in 0.1 M acetate buffer solutions of pH 5.3.

Fig. 4-8 Stripping peak currents and calibration curves of PANI/GCEs and GCEs for Cd^{2+} and Pb^{2+} determination. The inset shows calibration curves of the two electrodes for detection of Cd^{2+} ions with an enlarged view. All tests were conducted in 0.1 M acetate buffer solutions of pH 5.3.

The calibration formula is $I = A + B \times C$, where I is the peak current in μA , C is the target metal concentration in μM , B ($\mu\text{A}/\mu\text{M}$) is the slope of calibration curve

implying the sensitivity of the electrode. The formulas of the calibration curves in Fig. 4-8 are listed below, with R standing for the correlation coefficient of the calibration curves:

$$\text{GCE for Pb}^{2+}: I = -3.588 + 31.898C, R=0.996; \quad (4-3)$$

$$\text{GCE for Cd}^{2+}: I = -0.198 + 1.942C, R=0.997; \quad (4-4)$$

$$\text{PANI/GCE for Pb}^{2+}: I = -2.238 + 19.448C, R=0.996; \quad (4-5)$$

$$\text{PANI/GCE for Cd}^{2+}: I = -0.165 + 1.418C, R=0.986. \quad (4-6)$$

The results determined from Fig. 4-8 are tabulated in Table 4-2, which shows that the PANI/GCEs have advantages for Pb^{2+} ion detection over the GCEs due to the lower detection limit and higher correlation coefficient of the PANI/GCEs. Nevertheless, the GCEs can perform better for Cd^{2+} detection. The detection limit was the smallest concentration in the peak current-concentration profile that fits the linearly calibration curve. Below the detection limit, the increase of the current is not linearly related to the metal concentrations.

Table 4-2 Comparison of GCEs and PANI/GCEs

	Detection limit (nM)		Sensitivity ($\mu\text{A}/\mu\text{M}$)		R	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
GCE	133.3	133.3	31.90	1.94	0.996	0.997
PANI/GCE	100	133.3	19.45	1.42	0.996	0.986

4.3 Bi Modified PANI Electrodes

To improve reproducibility, stability and sensitivity, a bismuth (Bi) thin film was coated on a glassy carbon (GC) substrate whose surface was modified with a porous thin layer of polyaniline (PANI) via multipulse potentiostatic electropolymerization to

form a new Bi/PANI/GC electrode (Bi/PANI/GCE). The new electrode was used successfully for simultaneous detection and determination of Cd^{2+} and Pb^{2+} ions, and various parameters were studied with reference to SWASV signals. The experimental results depicted that the environment-friendly Bi/PANI/GCEs had the ability to rapidly monitor trace heavy metals even in the presence of surface-active compounds.

4.3.1 Effect of Bi^{3+} Concentration

The amount of deposited Bi can be controlled by varying the Bi^{3+} concentration in the bulk solutions. The effect of the Bi^{3+} concentration ranging from 25 nM to 10 μM on the stripping responses to 25 nM Cd^{2+} and 25 nM Pb^{2+} is investigated using the Bi/PANI/GCEs (Fig. 4-9 [5]). The stripping peak currents for the two metal ions increase with increased Bi^{3+} concentration when the Bi^{3+} concentration is lower than 250 nM. However, the Pb^{2+} stripping peak currents almost stabilize with further increased Bi^{3+} concentration when the Bi^{3+} concentration is higher than 250 nM, while the Cd^{2+} peak currents achieve a maximum at 1.25 μM Bi^{3+} and then turn to decrease at higher Bi^{3+} concentrations. Previous results reported in Ref. [36, 43] demonstrated that a Bi^{3+} -to-target metal ion concentration ratio larger than 4 would be good enough to obtain high quality data from different electrodes. Thus, a Bi^{3+} concentration of 1.25 μM will be used in the following sections of this chapter. For the Bi/PANI/GCEs used in a solution having a Bi^{3+} concentration of 1.25 μM as shown in Fig. 4-9, the peak currents are higher than those measured from the PANI/GCEs in a solution having no Bi^{3+} .

Fig. 4-9 Effect of Bi³⁺ concentration on stripping peak currents of 25 nM Cd²⁺ (solid line) and 25 nM Pb²⁺ (dash line).

From the above discussion, it can be concluded that a major merit of the Bi/PANI/GCEs is their higher current responses to the both Pb²⁺ and Cd²⁺ ions than other three types of electrodes.

4.3.2 Effects of Preconcentration Potential and Time

The influence of preconcentration potential varied in the range of -1.4 and -0.9 V on the current responses to 25 nM Cd²⁺ and 25 nM Pb²⁺ is shown in Fig. 4-10 [5]. The stripping peak currents of both Cd²⁺ and Pb²⁺ rapidly increase when the preconcentration potential decreases from -0.9 to -1.3 V due to more complete reductions of Cd²⁺ and Pb²⁺ to their neutral forms, but the peak currents drop when the preconcentration potential becomes more negative than -1.3 V due to hydrogen evolutions that can reduce the surface activities of the electrodes. Therefore, a

preconcentration potential of about -1.3 V is considered optimal for the determination of Cd^{2+} and Pb^{2+} .

Fig. 4-10 Effect of preconcentration potential on stripping peak currents of 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) tested by Bi/PANI/GCEs in supporting electrolytes of 20 mM H_2SO_4 and 30 mM KCl containing $1.25 \mu\text{M Bi}^{3+}$.

The effect of preconcentration time on the stripping peak currents of both 25 nM Cd^{2+} and 25 nM Pb^{2+} is illustrated in Fig. 4-11 where the stripping peak currents of the both metals increase with increasing preconcentration time till about 320 s beyond which the curve slopes are slightly lower which may be due to the electrode saturation with the Cd and Pb in the reduced states. An accumulation time of 120 s is used to avoid the saturation of the electrodes for higher target metal concentrations.

Fig. 4-11 Effect of pre-concentration time on stripping peak currents of 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) tested by Bi/PANI/GCEs in supporting electrolytes of 20 mM H_2SO_4 and 30 mM KCl containing 1.25 $\mu M Bi^{3+}$

4.3.3 Calibration Curves of Bi/PANI/GCEs

Fig. 4-12 shows the SWASVs measured from the Bi/PANI/GCEs for the detection of Cd^{2+} and Pb^{2+} with the concentrations varying from 25 to 150 nM each in the solutions having mixed electrolytes of 20 mM H_2SO_4 and 30 mM KCl [5]. With the deposition time of 160 s, the calibration curves for the Cd^{2+} and Pb^{2+} are linear in the range of 25–150 nM and can be represented by equations 4-7 and 4-8, respectively,

$$I(\mu A) = 0.2679 [Cd^{2+}](nM^{-1}) - 0.3022 \quad (4-7)$$

and

$$I(\mu A) = 0.2682 [Pb^{2+}](nM^{-1}) - 4.4147 \quad (4-8)$$

The regression coefficients of Eqs 1 and 2 are 0.9989 and 0.9996, respectively, and the relative standard deviations from 10 measurements of 25 nM Cd^{2+} and 25 nM Pb^{2+} by using the same Bi/PANI/GCE are about 5.95% and 3.31%, respectively.

Therefore, the detection limits of Cd^{2+} and Pb^{2+} are about 1.1 nM and 16.5 nM, respectively.

Fig. 4-12 Stripping voltammograms of Cd^{2+} and Pb^{2+} of concentrations of 25, 50, 75, 100, 125 and 150 nM from bottom to top, respectively, which were measured using Bi/PANI/GCE. The insets show the respective calibration curves.

4.3.4 Stability Analysis of Bi/PANI/GCEs

Bi-film electrodes are particularly prone to interferences from surfactants that can be adsorbed onto and foul the electrode surfaces [125], and the effect of typical surfactants on Bi-film electrodes has also been reported [47]. In this study, the effects of different types of surfactants on the repeatability and stability of the Bi/PANI/GCEs are evaluated and compared with those on the Bi/GCEs that are a type of Bi-film electrodes. Table 4-3 presents the stripping currents normalized with the maximum stripping current, i.e., $I_p/I_{p\text{max}}$, measured with respect to different concentrations of the three surfactants dissolved in the electrolytic solutions

containing 25 nM Cd^{2+} and 25 nM Pb^{2+} ions using the two types of electrodes [5]. Obviously, for the both kinds of electrodes in the same electrolytic solutions (with same type and same concentration of surfactants), the Cd stripping peak currents are more sensitive to the type of surfactants than the Pb stripping peak currents. For the both electrodes, the cationic surfactant, cetyltrimethylammonium bromide (CTAB), gives the least decreases in stripping currents, the Triton X-100 induces moderate decreases in stripping currents, and the sodium dodecyl sulfate (SDS) induces the most significant drops in stripping currents. Compared to the Bi/GCEs, it is clear that the Bi/PANI/GCEs are much more tolerant to the presence of the surface-active compounds for the detection of both Pb and Cd. The resistance of the Bi/PANI/GCEs to the surfactants is attributed to the presence of the PANI layer that has formed an effective barrier to prevent the macromolecules from transporting to the electrode surfaces [47], which is another major advantage of the Bi/PANI/GCEs over the Bi/GCEs. Ref. [47] reported that a Nafion-coated Bi-film electrode (NCBFE) was used to detect target metals Cd^{2+} , Pb^{2+} and Zn^{2+} in a solution containing Triton X-100 and the results indicated that the NCBFE was much more tolerant to the presence of nonionic surface-active compounds than Bi-film electrode. The merit of a porous polymeric film was that it formed an effective barrier to prevent the macromolecules from moving to the electrode surface [47].

Table 4-3 Normalized stripping current, $I_p/I_{p\max}$, for 25 nM Cd^{2+} and 25 nM Pb^{2+} ions vs. surfactant concentrations measured using Bi/GCEs and Bi/PANI/GCEs.

Metal	Electrode	Surfactant	
-------	-----------	------------	--

ion		Triton X-100 (μM)			SDS (μM)			CTAB (μM)			
		3	8	13	3	8	13	3	8	13	
Cd^{2+}	Bi/GCE	60	49	38	40	32	25	80	72	60	$I_p/I_{p\max}$ (%)
	Bi/PANI/GCE	79	50	39	70	42	33	92	89	80	
Pb^{2+}	Bi/GCE	65	52	35	45	30	26	88	82	72	
	Bi/PANI/GCE	83	54	40	71	48	34	97	92	87	

The short-term stability of the Bi/PANI/GEs is tested for eight SWASV cycles in a solution containing 25 nM Cd^{2+} and 25 nM Pb^{2+} in the presence of 8 mg/L of Triton X-100 with the experimental results shown in Fig. 4-13 [5].

Fig. 4-13 Stability performance of Bi/PANI/GCE in a solution containing 25 nM Cd^{2+} (solid line) and 25 nM Pb^{2+} (dash line) in the presence of 8 mg/L of Triton X-100

The relative standard deviations from the 8 measurements of Cd^{2+} and Pb^{2+} are about 1.3% and 1.1%, respectively. Thus, the stability of the Bi/PANI/GCEs is satisfactory. For the Bi/GCEs, the stripping peak currents exhibit a decreasing trend due to the accumulating fouling on the electrode surfaces. The mechanical robustness of the Bi/PANI/GCEs is good, especially compared with the Bi/GCEs. A single PANI membrane can be used for a few hours without apparent deterioration of the current

signals. In addition, the PANI coatings also provide a good protection to the Bi-films from mechanical damage.

4.4 PANI-Functionalized MWCNTs Modified GCEs

The performance of GCEs coated with polyaniline-multiwalled carbon nanotube (MWCNT-PANI) nanocomposite coatings was investigated in detecting Pb^{2+} ions in a 0.1 M acetate buffer solution using SWASV [66]. It was found that the MWCNT-PANI coated electrodes had a better performance than the bare GCEs. Different solvents were used to get a better dispersion of MWCNTs in the PANI matrix for higher stripping signals. The surface morphology and structure of the coated electrodes were examined using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and micro Raman spectroscopy, showing that the conductive PANI matrix worked as both a conductor to electrically connect the individual MWCNTs, and a binder to mechanically join the MWCNTs.

4.4.1 Comparison of GCEs Modified with PANI and MWCNTs by Various

Methods with Respect to SWASV Response

Fig. 4-14 illustrates the anodic stripping voltammograms of Pb^{2+} (1.5 μM) in the 0.1 M acetate buffer solution measured using 5 different electrodes with the details summarized in Table 4-4 [66].

Table 4-4 Fabrication procedures of different coatings containing MWCNT-COOH and/or PANI.

Electrode No.	<i>Ea</i>	<i>Eb</i>	<i>Ec</i>	<i>Ed</i>	<i>Ee</i>
Electrode name	GCE	PANI	MWCNT-COOH	MWCNT-PANI	Dry-MWCNT-PANI
Solvent		Sulfuric acid (0.25 M)			
Solute		PANI (0.06 mg/mL)	MWCNT-COOH (0.06 mg/mL)	PANI (0.06 mg/mL) and MWCNT-COOH (0.06 mg/mL)	PANI (0.06 mg/mL) and MWCNT-COOH (0.06 mg/mL)
Coating procedure	N/A	A bare GCE was dipped into a mixed solution for 15 min to adsorb the species onto the electrode surface, and then the coated electrode was dipped into sulfuric acid (0.25 M) for another 15 min to remove loose species.			20 mL of mixed solution was dropped onto electrode surface, and then the coated surface was dried.

From Fig. 4-14 it can be seen that, the electrode coated with PANI has a slightly higher peak than the bare GCE, which is due to the porous conductive PANI coating [67, 122] that can give a larger surface area exposed to the solution. With a layer of MWCNT-COOH, the electrode has an obviously stronger current response than that of the bare GCE and PANI coated electrode, which is due to the significant increases of the surface activity and conductivity of the MWCNTs, indicating the advantages of the incorporation of the MWCNTs. The electrode coated with the MWCNT-PANI has the highest stripping peak current, because of the larger exposed surface area of PANI and the higher surface activity of MWCNT.

Fig. 4-14 Stripping voltammograms measured using different coated electrodes for determination of Pb^{2+} (1.5 μM) in 0.1 M acetate buffer solution.

For the electrode modified by the Dry-MWCNT-PANI coating, the coating is fabricated by drying the mixture solution on the bare GCE, instead of by absorption (MWCNT-PANI coated electrode). From Fig. 4-14, the electrode coated with the MWCNT-PANI by drying the mixture solution has a much weaker peak current but a higher background current than the one coated with the MWCNT-PANI, possibly due to the thicker and denser MWCNT-PANI composite coating on the electrode fabricated by drying the mixture solution. Thus, the following measurements are preformed using the MWCNT-PANI modified electrodes.

As shown in Fig. 4-15, the MWCNT-COOH electrode (line a) has a trend of decreasing as the number of stripping tests increases. This is mainly due to two factors as follows. When the testing time is prolonged, the surface active compounds in the electrolyte can degrade the surface activity of the bare CNTs, causing the

passivation of the electrode. Another reason is that the CNTs may be exfoliated from the substrate surface because of the stirring of the solution. With the incorporation of PANI, the MWCNT-PANI electrode (line b) has a better repeatability, because the porous PANI matrix can block the bulk surface active compounds from reaching the electrode surface and thus eliminates the passivation of the electrode [5]. In addition, the PANI matrix can act as a binder which can firmly attach the MWCNTs onto the electrode surface.

Fig. 4-15 Stability performance of (a) MWCNT-COOH and (b) MWCNT-PANI coated electrodes in terms of anodic stripping peak current of Pb^{2+} ($1.5 \mu\text{M}$) in 0.1 M acetate buffer solution with respect to number of tests.

In this study, a 0.25 M sulfuric acid solution was used as the solvent to dissolve or disperse the PANI and MWCNT-COOH. Some other solvents, such as DI water, ethanol, acetone, acetic acid, iso-propanol, toluene and hexane, were also used for the dispersion of CNTs and PANI. It is found that the PANI has a very small solubility in DI water and hexane, a small solubility (possibly dispersed well with at least 30 min) in sulfuric acid and toluene, and can be dissolved well in ethanol, acetone, acetic acid and iso-propanol. For comparison, one more electrode was fabricated using a similar procedure to that for the one coated with the MWCNT-PANI, but with the MWCNTs and PANI being dissolved in ethanol instead of sulfuric acid solution. Fig. 4-16 shows

the voltammograms of Pb^{2+} ions measured using the electrodes fabricated in different solvents. The electrode treated in the ethanol having the MWCNT-PANI for 15 min has a higher peak current (curve a) than the one treated in the pure ethanol for the same duration (curve b), showing the advantage of the MWCNT-PANI composite coating. The electrode treated in the sulfuric acid solution containing PANI and MWCNT-COOH (MWCNT-PANI, line c) has a highest peak current (curve c). Fig. 3 implies that the use of ethanol can cause the passivation of the electrode surface, thus reducing the surface activity of the electrode used, which may be attributed to the ethanol attached to either bare electrode or MWCNT or both surfaces to form a monolayer blocking the further reactions.

Fig. 4-16 Stripping voltammograms of different electrodes modified in (a) ethanol solution containing MWCNT-COOH and PANI, (b) ethanol only and (c) sulfuric acid solution containing MWCNT-COOH and PANI.

4.4.2 Confirmation of Successful Modification of MWCNTs and PANI

The FE-SEM micrographs in Fig. 4-17 show the surface morphology of the MWCNT-COOH and MWCNT-PANI coated electrodes. For the electrode coated with the MWCNT-PANI, uniformly distributed, entangled MWCNT and PANI

networks can be observed from Fig. 4-17b and c. The conductive PANI matrix works as a binder to firmly hold the MWCNTs and also as a channel for the transport of the charges between the MWCNTs in the coating. The TEM image of the MWCNT-PANI coated electrode (Fig. 4-17d) shows that the outer surfaces of the individual MWCNTs (light color cores) have been fully covered by the PANI molecules (dark color shells).

Fig. 4-17 FE-SEM micrographs of (a) MWCNT-COOH coating, (b) MWCNT-PANI coating, and (c) same coating as (b) viewed with a higher magnification. (d) shows a TEM image of same coating as (b).

The presence of PANI in the MWCNT-PANI coating is confirmed by the Raman spectra shown in Fig. 4-18. The two main peaks at about 1333.3 and 1584.8 cm^{-1} in Fig. 4-18a are attributed to the graphitic structure of the MWCNTs. For the PANI,

there are more peaks as shown in Fig. 4-18b, and the two main peaks at about 1163 cm^{-1} and 1468 cm^{-1} are assigned to ‘in-plane C-H bonding’ and ‘>C=N- stretching’, respectively. All of the above four main peaks appear in the Raman spectrum of the MWCNT-PANI coated electrode (Fig. 4-18c), showing the presence of the both MWCNTs and PANI that are mixed together.

Fig. 4-18 Raman spectra of (a) MWCNT-COOH, (b) PANI and (c) MWCNT-PANI coatings.

A further cyclic voltammetric test using the MWCNT-PANI coated electrode is shown in Fig. 4-19, where the three pairs of peak currents are corresponding to the oxidation transformations of the PANI, which has validated the presence of PANI in the nanocomposite coating.

Fig. 4-19 Cyclic voltammogram of MWCNT-PANI coated electrode.

4.5 Summary

PANI coatings and Bi nanoparticles were electrodeposited on glassy carbon electrodes to form the PANI/GCE and Bi/PANI/GCE electrodes. It was found that the PANI coatings reduced the passivation of the electrodes, which was attributed to their branched structures [67, 122] that could block the surface active molecules from reaching the electrode surfaces. The parameters for the fabrication of the Bi/PANI/GCEs and the determination of the two trace heavy metals, i.e., Cd and Pb, were optimized and the influences of several surfactants on the stripping behaviors of the Bi/GCEs and Bi/PANI/GCEs were investigated. The results showed that the porous PANI interlayers could offer a high specific electrode surface area, diminish accumulating fouling on the electrode surface as caused by the surfactants. Thus, the developed Bi/PANI/GCE configuration provides an excellent platform for electrochemical analysis and has a good potential for the development of other chemical sensors or biosensors in the presence of surfactants.

Novel MWCNT-PANI nanocomposite coatings offered a possibility to produce three-dimensional nanostructured films that combined the conductivity of PANI with the large surface area and good conductivity of CNTs. The MWCNT-PANI coated GCE electrodes had good performance in the anodic stripping analysis of trace Pb in a 0.1 M acetate buffer solution. It was also found that sulfuric acid was a better solvent compared to some common organic solvents, e.g., ethanol and acetone, for the dispersion of the MWCNTs in the PANI matrix. The uniform distribution of the MWCNTs in the PANI matrix was confirmed with FE-SEM, TEM, Raman spectroscopy and electrochemical analysis.

Chapter 5: Graphene Thin Films Synthesized via Solid-state Carbon Diffusion

5.1 Introduction

Fabricated via solid-state carbon diffusion by thermally treating the Ni/a-C bilayer, the formation of graphene was previously confirmed only by Raman [69] and XRD [70] measurements, and only the studies on the effects of thermal processing temperature and a-C layer thickness on the formation and structure of graphene films have been reported [69, 70], without any possible applications mentioned. Before this report, the effects of catalyst (e.g., Ni) layer thickness and substrate surface condition (e.g., Si substrate without or with a thermally oxidized SiO₂ layer) on the formation and structure of graphene films have not been reported.

In this chapter, the presence of graphene fabricated via solid-state carbon diffusion using a sputtering deposited a-C layer as the C source and a sputtering deposited Ni layer as the catalyst (i.e., a Ni/a-C bilayer stack) on Si and thermally oxidized Si (SiO₂/Si) substrates was systematically evaluated using many methods. In addition, the effects of the thicknesses of Ni and a-C layers and substrate surface condition (e.g., Si substrate without or with a thermally oxidized SiO₂ layer) on the formation and structure of graphene films were studied.

Besides the Ni/a-C bilayers, the graphene thin films were also synthesized by thermally treating Ni and C (Ni-C) mixed layers which were co-sputtering deposited on Si substrates without or with a SiO₂ layer. During the high temperature heating, the C atoms dissolved into the Ni atom seas. However, during the rapid cooling, the

solubility of C atoms in Ni was sharply reduced, leading to the precipitation of excess C atoms and the formation of graphene thin films on the outer surfaces of the Ni-C layers. Raman spectroscopy was used to characterize the structure of the graphene films with respect to the C atomic contents in the Ni-C mixed layers. The Si substrate surface conditions (with or without a SiO₂ layer) were also investigated with respect to the Raman spectra.

5.2 Graphene Thin Films Synthesized via Solid-state Carbon Diffusion by Thermally Treating Sputtering Deposited Nickel/Amorphous Carbon Bilayers

5.2.1 Structure of Graphene Films

The as-deposited a-C layer of about 200 nm thickness shows a broad Raman band with overlapped D and G peaks as shown in Fig. 5-1a, indicating a relatively high sp³ content in the a-C layer [126]. Sullivan et al. showed that due to the shorter bond length of sp², the formation of sp² sites with their σ planes aligned in the plane of compression could relieve the biaxial compressive stress [127]. Therefore, the transformation of sp³ to sp² can relieve biaxial compressive stresses [128-130]. The thermal processing of the a-C layer promotes the formation of sp² bonds due to graphitization, as evidenced by the split of the D and G peaks and the shifts of the D and G peak positions to higher wave numbers (Fig. 5-1b).

Fig. 5-1 (I) Raman spectra of (a and b) an a-C single film deposited on a Si substrate before and after thermal processing at about 1000 °C, respectively, (c and d) Ni/a-C bilayers deposited on Si and SiO₂/Si substrates, respectively, before thermal processing, and (e and f) Ni/a-C bilayers deposited on Si and SiO₂/Si substrates, respectively, after thermal processing at about 1000 °C. (II) An enlarged view of the spectra shown in (c and d).

Compared to the a-C coated sample (Fig. 5-1a), the as-deposited Ni/a-C bilayers coated on the Si and SiO₂/Si substrates (Fig. 5-1c and d) show much weaker overlapped D and G peaks (as shown in Fig. 5-1 II), which is due to the surface

coverage by the Ni top layer. The thermally treated Ni/a-C bilayers deposited on Si and SiO₂/Si (Fig. 5-1e & f) substrates depict split D and G peaks that are much stronger compared to the as-deposited ones (Fig. 5-1c & d), indicating the dissolution of the C atoms from the a-C underlayer into and the nucleation and growth of a new C layer upon the Ni top layer via C diffusion. The low I_D/I_G ratios (0.128 for thermally treated Ni/a-C/SiO₂/Si and 0.588 for thermally treated Ni/a-C/Si) and relatively strong 2D peaks as shown in Fig. 5-1e and f indicate that the formed new C layers are graphene ultrathin films. The mechanism for the formation of graphene, which will be discussed later, is quite different from that of the in-situ conversion of sp³ to sp² by thermally treating the solely a-C coated sample. The I_D/I_G ratio in Fig. 5-1e is relatively higher than that in Fig. 5-1f, which is in agreement with the literature [131] and will also be discussed later.

A smaller full width at half maximum (FWHM) of a G peak is an indication of a higher degree of graphitic ordering in the a-C film [132, 133]. As shown in Fig. 5-1, the FWHMs of the G peaks for the thermally treated Ni/a-C/SiO₂/Si (f) and Ni/a-C/Si (e) are about 23.82 and 29.67 cm⁻¹, respectively, which are much smaller than those of the a-C single layer film coated samples before (246.17 cm⁻¹, Fig. 5-1a) and after (143.67 cm⁻¹, Fig. 5-1b) thermal processing, indicating a higher degree of graphitic ordering in the thermally treated Ni/a-C bilayers.

Because of the remarkably high electron mobility at RT, the electrical conductivity along the in-plane direction of graphene is high [134]. After thermal processing, the resistivity of the Ni/a-C/SiO₂/Si sample reduces from about 3.389 to

0.196 $\Omega\cdot\text{cm}$ measured by 4-point probe. The great drop of the resistivity of the sample after thermal processing is attributed to the formations of sp^2 bonding and graphitic ring-like sp^2 clusters. The sp^2 rich graphitic ordered clusters can form a conduction path for electrons.

The lattice structure of the graphene film formed on the thermally treated Ni/a-C/SiO₂/Si sample studied using HR-TEM is shown in Fig. 5-2a, which indicates that the film has a planar shape, instead of a shape of cylinder (e.g., carbon nanotube) or sphere (e.g., fullerene). Fig. 5-2b is an enlarged view of the rectangle area marked in Fig. 5-2a and clearly illustrates a honeycomb crystal lattice of the graphene film. The graphene structure is well fitted with a model of graphene planar lattice structure as shown in Fig. 5-2b, in which each dark hole represents a hole of the benzene ring as surrounded by the C atoms in light color. The centre distance between each two dark holes in the TEM image is about 0.235 nm, indicating a side length of about 0.136 nm of a benzene ring, which is very close to the theoretical value of the C-C bond length in graphene (0.142 nm). The electron diffraction pattern of the thermally treated Ni/a-C/SiO₂/Si sample is shown in Fig. 5-2c, in which a hexagonal pattern of seven dots with one in the center of the hexagon indicates the crystal structure of the newly formed graphene film, which well matches with the graphene structure as reported in the literature [17, 111, 135]. The lattice structures and electron diffraction patterns are similar for the thermally treated Ni/a-C bilayers deposited on the Si substrates both with and without SiO₂ layers.

Fig. 5-2 (a and b) HR-TEM images showing (a) the lattice structure of a graphene film formed by thermal processing of a Ni/a-C/SiO₂/Si sample and (b) an enlarged view of the marked rectangular area in (a) overlaid with a model of graphene planar lattice structure, and (c) an electron diffraction pattern of the graphene film.

The Raman spectra, electrical resistivity results, electron diffraction patterns and TEM images have all confirmed the formation of graphene films from the thermally treated Ni/a-C bilayers.

5.2.2 Atomic Contents of Elements in Thin Films Before and After Rapid

Thermal Processing

Fig. 5-3a & b show the cross-section views of the as-deposited Ni:60/C:40 bilayers on the Si and SiO₂/Si substrates, respectively. Fig. 5-3c is a cross-section view of the thermally treated Ni:60/C:40/Si, showing that the a-C and Ni layers after thermal processing were mixed with each other, forming a new layer of about 347.8 nm in thickness (region ii), which is much thicker than the as-deposited Ni/a-C bilayer ($46+186 = 232$ nm) (Fig. 5-3a), indicating that the Ni and a-C mixed layer is expanded after thermal processing. There is another layer (region i) of about 64.7 nm in thickness, which could distort the graphene structures and will be discussed later. The thermally treated Ni:60/C:40/SiO₂/Si (Fig. 5-3d) shows that the a-C and Ni layers are also mixed with each other and form a new layer of about 157 nm in thickness (region iv) that is much thinner than the as-deposited Ni/a-C bilayer ($52+165 = 217$ nm, Fig. 5-3b), indicating that part of the a-C layer is oxidized and evaporated in the form of CO and CO₂ during thermal processing, which will be further discussed later. The thicker mixed Ni/a-C layer (region ii) of the thermally treated Ni:60/C:40/Si is mainly induced by the Si from the Si substrate and residue oxygen in the RTP chamber during thermal treatment. While for the Ni/a-C bilayer deposited on the

SiO₂/Si substrate with a SiO₂ layer of about 300 nm thick as shown in Fig. 5-3b & d, the SiO₂ layer is chemically and thermally stable and dense, and does not release any Si atoms into Ni [136], the diffusion of Si atoms from the Si substrate is blocked, so the layer in region iv of Fig. 5-3d is thinner. This can be further confirmed with EDX and XPS measurements later. Another fact is that Fig. 5-3d does not clearly show a newly formed film similar to that in the region i in Fig. 5-3c. For both Fig. 5-3c & d, the graphene films formed are very thin and obviously difficult to measure by FE-SEM.

Fig. 5-3 FE-SEM cross-section views of as-deposited Ni:60/C:40/Si (a) and Ni:60/C:40/SiO₂/Si (b), and thermally treated Ni:60/C:40/Si (c) and Ni:60/C:40/SiO₂/Si (d).

Fig. 5-4a shows the atomic contents of C, O, Si and Ni with respect to the depth of the thermally treated Ni:60/C:40/Si from its top surface with reference to Fig. 5-3c. At the depth near the interface of regions ii and iii the C content is low after thermal processing, indicating that almost the whole as-deposited a-C layer at this interface was dissolved into the Ni layer through diffusion during heating at 1000 °C. The C atomic percentage increases from region iii to i indicating that the C atoms that previously dissolved in the Ni layer during heating are expelled towards the outer surface during cooling, and finally precipitate on the outer surface of the Ni layer to form a graphene layer. The O atoms from the residual O₂ in the RTP chamber can diffuse through the Ni/a-C bilayer during heating and finally reach the Si substrate, so the O content progressively reduces from region i to iii as shown in Fig. 5-4a. The Si content progressively reduces from region iii to i, indicating that during heating the Si atoms have diffused from the Si substrate towards the outer surface of the sample, and part of those Si atoms can react with the diffused O atoms.

(a)

Fig. 5-4 Contents of C, O, Si and Ni of the cross sections of thermally treated samples: (a) Ni:60/C:40/Si and (b) Ni:60/C:40/SiO₂/Si, all measured with EDX.

Fig. 5-4b illustrates the atomic contents of C, O, Si and Ni with respect to the depth of the thermally treated Ni:60/C:40/SiO₂/Si from its top surface with reference to Fig. 5-3d. In region iv that is a Ni layer, the C atomic percentage increases towards the outer surface of the sample, indicating that during cooling the C atoms previously dissolved in the Ni layer have been expelled towards the outer surface of the coating. The Si atomic percentage in region iv of Fig. 5-4b is much lower than that in region ii of Fig. 5-4a, indicating that the Si diffusion from the SiO₂/Si substrate has been efficiently blocked by the chemically and thermally stable SiO₂ dense layer [136]. The O atomic percentage in region iv is lower and its trend is quite different from that in regions i and ii in Fig. 5-4a, which increases towards the outer surface, because that for the layers coated on the SiO₂/Si substrate, the diffused O atoms from the RTP chamber mainly react with the C atoms and then exhaust in a gas form (CO or CO₂), while for the layers coated on the Si substrate the O atoms can also react with the

thermally diffused Si atoms from the Si substrate with Ni as the catalyst to form the SiO₂ compounds, in which the O atoms can be detected by EDX. The Ni atomic percentage in region iv of Fig. 5-4b is comparable with that in region ii of Fig. 5-4a. For the thermally treated Ni:60/C:40/SiO₂/Si, almost no Si atoms have diffused into the Ni layer (region iv) during thermal processing, and at the same time part of the sputtered a-C layer has been burnt away, thus leading to a thinner film thickness as shown in Fig. 5-3d, compared with the as-deposited sample.

The above assumption can be further proved by the XPS results that after thermal processing, the surface of Ni:60/C:40/Si has atomic contents of about 68.1, 14.7, 17.1 and 0.2 at.% for C, O, Si and Ni, respectively, while those for the thermally treated Ni:60/C:40/SiO₂/Si are about 97.5, 0, 0, 2.5 at.%, respectively. Thus, the high Si and O atomic contents in the Si based samples indicate the diffusion of Si and O atoms during heating, so region i in Fig. 5-3c is possibly a mixture of graphene, SiC and SiO₂.

5.2.3 Mechanism of Formation of Graphene Films

From Fig. 5-3 and Fig. 5-4, the fabrication mechanism of a graphene film can be summarized as two major steps as schematically shown in Fig. 5-5: (i) the C atoms from the a-C layer diffuse into the top Ni layer during heating to form a highly concentrated or saturated Ni-C solid solution based on a binary phase diagram of Ni-C (Appendix 2); and (ii) during rapid cooling the solubility of C in the Ni layer abruptly drops and the excess amount of dissolved C atoms precipitate firstly at the Ni

grain boundaries, and then the precipitation extends to cover the entire outer surface of the Ni layer.

Fig. 5-5 A model for formation of a graphene film via solid carbon diffusion during RTP of a Ni/a-C bilayer coated on a SiO₂/Si substrate.

It was reported that the C atoms surrounding a Ni cluster upon thermal processing preferably develops in a ring shape [133], which the Ni cluster plays a role of catalyst to promote the formation of more six-ring graphite-like sp^2 ordering in step ii. Thus the C precipitates will form in the form of graphene due to the influence of the Ni lattices. This mechanism is similar to the one for the graphene fabrication by means of a common CVD method, except that the C source is usually a hydrocarbon compound in a CVD process. The generated graphene layers can be either skimmed or allowed to freeze for removal afterwards for other applications (e.g., optical or electrical devices).

Based on the above discussion, it can be expected that with longer C sputter deposition duration, it would be difficult for the whole as-deposited a-C layer to completely dissolve into the Ni top layer at 1000 °C within 3 min. It means that with other parameters and conditions fixed, there should exist a specific C sputtering duration t_0 (resulting in a specific a-C layer thickness), below which the fabricated graphene film thickness can increase with increased C sputtering duration, and

beyond which the graphene film thickness will not be significantly affected by the C sputtering duration.

5.2.4 Effects of Ni Layer Thickness and Si Substrate Surface Condition

Fig. 5-6 shows the Raman spectra of the Ni:0/C:40/SiO₂/Si and Ni:20/C:40/SiO₂/Si samples, both before and after thermal processing. The as-deposited Ni:0/C:40/SiO₂/Si without a Ni layer shows the overlapped D and G peaks (Fig. 5-6a), which is an indication of the a-C layer. The thermally processed Ni:0/C:40/SiO₂/Si shows a slight split of the D and G peaks, indicating an increase of the sp² concentration due to thermal graphitization, while its high I_D/I_G ratio is due to a high concentration of sp² defects (or structural disorder that breaks the translational symmetry, e.g., graphite edges, impurities, cracks, dislocations or vacancies), indicating that the sp² bonds are mainly in the form of randomly ordered graphite species in which the σ planes of the sp² bonding are randomly packed. With a thin Ni layer on the top of the a-C layer, the as-deposited Ni:20/C:40/SiO₂/Si (Fig. 5-6b) shows a much weaker overlap of D and G peaks, which may be due to the coverage of the top Ni layer that can prevent the laser beam from reaching the a-C underlayer. After thermal processing, the sample Ni:20/C:40/SiO₂/Si shows the obviously separated and higher D (at about 1345.4 cm⁻¹) and G (at about 1586.4 cm⁻¹) peaks, indicating that the C atoms from the a-C layer have diffused through the Ni layer during heating and precipitated on the surface of the Ni layer during cooling. A low I_D/I_G ratio (about 0.148) of the thermally treated Ni:20/C:40/SiO₂/Si as shown in Fig.

5-6b implies that a thin layer of graphite material, most likely in the form of graphene is formed, instead of randomly packed graphite species containing a lot of defects as observed from the thermally treated Ni:0/C:40/SiO₂/Si (Fig. 5-6a). The 2D peak at about 2672.9 cm⁻¹ is closely related to the well-ordered stacking of atomic layers of the graphene film, and a high I_{2D}/I_G ratio indicates a graphene ultra thin film with a few atomic layers. In Fig. 5-6, that only the thermally treated Ni:20/C:40/SiO₂/Si has an obvious 2D peak means that the orderly stacked graphene films can only be formed on the surfaces of the thermally treated Ni:20/C:40/SiO₂/Si samples, instead of the samples without a Ni layer. Thus the Ni layer in the sample Ni:20/C:40/SiO₂/Si plays a role as a catalyst that promotes the nucleation and growth of the graphene layer on its surface.

Fig. 5-6 Raman spectra of (a) Ni:0/C:40/SiO₂/Si and (b) Ni:20/C:40/SiO₂/Si before and after thermal treatment.

Fig. 5-7 shows the I_D/I_G and I_{2D}/I_G Raman peak ratios of the thermally treated Ni:t1/C:40 bilayers deposited on the both SiO₂/Si and Si substrates, with respect to varied Ni sputtering durations (t1). Deposited on both kinds of substrates, the I_D/I_G and I_{2D}/I_G ratios show similar trends with increasing Ni sputtering durations, and the thermally treated Ni:0/C:40 shows the highest I_D/I_G and the lowest I_{2D}/I_G ratios, indicating that the samples without a Ni layer have no graphene film formed. The lowest I_D/I_G ratio appears at a Ni deposition time of 20 min (about 0.15 and 0.55 for the Ni/a-C bilayer deposited on the SiO₂/Si and Si substrates, respectively, with their spectra shown in Fig. 5-8), implying an excellent graphene film with the lowest defect concentration. The highest I_{2D}/I_G ratio also corresponds to a Ni deposition time of 20 min (1.13 and 0.72 for the Ni/a-C bilayers deposited on the SiO₂/Si and Si substrates, respectively, with their spectra shown in Fig. 5-8), indicating a graphene film with a few atomic layers. With Ni deposition time longer than 20 min, the I_D/I_G ratios

increase and the I_{2D}/I_G ratios reduce, due to that more carbon atoms can dissolve in the thicker Ni layers during heating, leading to thicker graphene films formed during cooling as well.

Comparing between Fig. 5-7a & b, the thermally treated samples based on the SiO_2/Si substrates always have relatively lower I_D/I_G and higher I_{2D}/I_G ratios than the similar Ni/a-C bilayers deposited on the Si substrates, indicating that the SiO_2/Si substrates are more suitable for the fabrication of graphene films used for electrical and optical devices.

(a)

(b)

Fig. 5-7 Raman peak ratios of thermally treated samples: (a) Ni:t1/C:40/SiO₂/Si and (b) Ni:t1/C:40/Si with respect to Ni sputtering time.

Fig. 5-8 Raman spectra of thermally treated Ni:20/C:40 deposited on (a) SiO₂/Si and (b) Si substrates.

Fig. 5-9 shows the electrical resistivities of the thermally treated Ni:t1/C:40/Si and Ni:t1/C:40/SiO₂/Si with respect to Ni deposition duration, which are measured by 4-point probes. The electrical resistivity of the samples decreases with increasing Ni

deposition time for all the thermally treated samples. Nevertheless, the electrical resistivities of the SiO_2/Si substrate based samples are consistently higher than the Si substrate based samples, due to the insulating SiO_2 layers that can block the electrical current transferring through the Si substrates.

(a)

(b)

Fig. 5-9 Electrical resistivities of thermally treated Ni:t1/C:40 deposited on (a) SiO_2/Si and (b) Si substrates, with respect to Ni sputtering time. The inset in (a) shows a magnified view of the resistivities in the range of 20-80 min.

Fig. 5-10 shows the FE-SEM micrographs of the thermally treated bilayers (Ni:t1/C:40) deposited on both the SiO₂/Si and Si substrates with increasing Ni layer deposition duration (t1). The thermally treated Ni:0/C:40 without a Ni layer deposited on the both substrates show the surfaces containing randomly distributed holes with different sizes and shapes (Fig. 5-10a & b), which is possibly due to the shrinkage of the a-C layers during rapid cooling. The thermally treated Ni:10/C:40/SiO₂/Si (Fig. 5-10c) and Ni:20/C:40/SiO₂/Si (Fig. 5-10e) show partially transparent milky films covering the a-C layers. For the thermally treated Ni:10/C:40/SiO₂/Si (Fig. 5-10c), the Ni layer is very thin and does not completely cover the entire a-C layer due to the shrinkage of the Ni layer after thermal processing. For the thermally treated Ni:40/C:40/SiO₂/Si (Fig. 5-10g) and Ni:60/C:40/SiO₂/Si (Fig. 5-10i), the Ni layers are relatively thick and almost all the C atoms can be dissolved into the Ni layers, leading to smoother surfaces than that of the Ni:20/C:40/SiO₂/Si (Fig. 5-10e).

Fig. 5-10 FE-SEM micrographs showing surface morphologies of thermally treated Ni:t1/C:40/SiO₂/Si and Ni:t1/C:40/Si samples with respect to Ni sputtering time (t1) for 0 min (a & b), 10 min (c & d), 20 min (e & f), 40 min (g & h), and 60 min (i & j), respectively.

The morphology of the generated graphene films greatly depends on the surface condition of the Si substrates used. The graphene films formed on the Si substrate based samples are always much rougher compared to the one formed on the SiO₂/Si substrate based sample shown in Fig. 5-10. A possible reason is that the Si atoms in the Si substrate without a SiO₂ layer may diffuse into the a-C and Ni layers when the temperature is higher than 450 °C [137] and form some compounds, e.g., silicon carbide, SiO₂ compounds as shown in Fig. 5-11, resulting in the formation of graphene edges, cracks, dislocations or vacancies. The detailed discussion of SiO₂ compounds will be shown below.

Fig. 5-11 A model for formation of SiO₂ compounds (or even nanowires) during the growth of graphene film via solid carbon diffusion during RTP of a Ni/a-C bilayer coated on a Si substrate.

5.2.5 Mechanism of the Formation of SiO₂ Compounds and/or Nanowires

during RTP and Their Effects

It is found that some SiO₂ nanowires arise on the thermally treated Ni:10/C:40/Si sample as shown in Fig. 5-10d. However, no SiO₂ nanowires can be found on the thermally treated Ni:0/C:40 deposited on the both SiO₂/Si and Si substrates (Fig. 5-10a & b). On the other hand, a number of SiO₂ nanowires are observed on the thermally treated Ni:60/C:0/Si as shown in Fig. 5-12a. Thus, the Ni layers (instead of the a-C layers) have promoted the growth of the SiO₂ nanowires on the Si substrate based samples. A possible explanation is that the residual oxygen in the RTP chamber can diffuse through the Ni and a-C layers during heating to react with the Si atoms from the Si substrates with the Ni layers as a catalyst as evidenced by the EDX results shown in Fig. 5-4a. It was reported that Ga [138], Pd/Au [139] and SnO₂ [140] are popular catalysts for the growth of SiO₂ nanowires via CVD with Si substrates used as a Si source. Similarly in this work, the Ni layers have played a role of a catalyst in the formation of the SiO₂ nanowires. The above explanation can be validated by the

FE-SEM micrograph shown in Fig. 5-12b where no nanowires are found on the thermally treated Ni:60/C:0/SiO₂/Si that has a similar Ni/a-C bilayer to that deposited on a Si substrate as shown in Fig. 5-12a. This is because the SiO₂/Si substrate has a chemically and thermally stable and dense interface (a SiO₂ layer) that can effectively isolate the O and Si atoms from reactions [136].

Fig. 5-12 FE-SEM micrographs of thermally treated Ni:60/C:0 deposited on (a) Si and (b) SiO₂/Si substrates.

5.2.6 Formation and Prevention of Formation of SiO₂ Compounds

Compared to thermally treated Ni:10/C:40/Si (Fig. 5-10d), fewer nanowires (locations not shown) are generated on thermally treated sample Ni:20/C:40/Si, while for thermally treated Ni:40/C:40/Si and Ni:60/C:40/Si there are totally no nanowires as shown in Fig. 5-10 (h & j). This indicates that for a sample deposited on the Si substrates, a thick Ni layer can also work like the SiO₂ layer to insulate the diffused Si and O atoms from reacting with each other. Similarly, a thicker a-C layer can also work as insulator to protect the Si substrate, which can be proven by the samples Ni:60/C:0/Si (with nanowires grown, Fig. 5-12a) and Ni:60/C:40/Si (no nanowires

grown, Fig. 5-10 j). Thus for the samples deposited on Si substrates, a thick a-C and/or Ni layer can greatly eliminate the formation of SiO₂ nanowires, but there are still some SiO₂ nanosized compounds generated and doped in the graphene film (not in nanowires shape), leading to rougher surfaces (as confirmed in Fig. 5-10) and higher concentrations of sp² defects as has been confirmed by the higher I_D/I_G ratios as shown in Fig. 5-7, than the ones deposited on the SiO₂/Si substrates. By the way, the fact that Si and O atomic contents in region (i) in Fig. 5-4a are higher than the region (iv) in Fig. 5-4b, also proves the formation of SiO₂ compounds in region (i) which is mixed with the generated C layer. This also explains why with a longer Ni deposition time (20~60 min), the surfaces of the thermally treated Ni/a-C deposited on Si substrates become smoother as shown in Fig. 5-10 (f, h and j).

The formation of those SiO₂ compounds can be further confirmed with low-angle XRD studies.

Fig. 5-13 shows the XRD spectra of the thermally treated Ni:20/C:40/Si and Ni:20/C:40/SiO₂/Si. The peaks located at about 26.3 ° of the both curves are due to graphite (002), indicating the successful fabrication of the multilayer or few-layers of graphene. The small peaks located at around 41.3 ° and 73.56 ° in the spectrum of the thermally treated Ni:20/C:40/Si are attributed to the formation of SiO₂ (200) and SiC (027) compounds, respectively. The SiO₂ layer on the substrate for the sample Ni:20/C:40/SiO₂/Si can effectively depress the thermal diffusion of the Si atoms from

the Si substrate, without the formation of SiO_2 or SiC compounds, which is consistent with the previous discussion.

Fig. 5-13 XRD spectra of thermally treated Ni:20/C:40/Si and Ni:20/C:40/SiO₂/Si.

5.2.7 Effect of SiO_2 Compounds

The SiO_2 compounds formed on the Si substrate based samples during thermal processing can serve as defects in the graphene films, which promote the segmentation of the graphene films with a rougher film surface as confirmed by atomic force microscopy (AFM) measurements (figures not shown) and FE-SEM micrograph (Fig. 5-14a), leading to higher I_D/I_G Raman peak ratios (Fig. 5-7). Before thermal processing, the root-mean-square surface roughnesses (R_q) of the both samples are about 2.8 nm that is comparable with that reported in the literature [141]. After thermal processing, the R_q of the Ni/a-C bilayer deposited on the SiO_2/Si

substrate is about 16.1 nm that is smaller than that of the similar bilayer grown on the Si substrate based samples (~ 54.2 nm). In addition, Cancado *et al.* [142] have reported that the in-plane crystallite size, L_a (nm), of nanographite can be determined by Raman spectroscopy using the equation $L_a = (2.4 \times 10^{-10}) \lambda_l^4 (I_D / I_G)^{-1}$, where λ_l is the laser wavelength in nanometer and I_D/I_G is the intensity ratio of the D and G peaks. With $\lambda_l = 633$ nm and I_D/I_G ratios of about 0.588 for the Ni/a-C/Si and 0.128 for the Ni/a-C/SiO₂/Si from Fig. 5-1e and f, L_a is about 65.5 nm and 301 nm for the thermally treated Ni/a-C bilayers deposited on the Si and SiO₂/Si substrates, respectively. L_a for the graphene formed on the SiO₂/Si substrate based sample can also be estimated from FE-SEM image (Fig. 5-14b), which is about 300 nm and much bigger than those (usually smaller than 50 nm) fabricated by other commonly used methods [143]. Both the surface roughness measurement and the grain size calculation indicate that the graphene films formed on the Si substrate based samples are rougher segmented compared to those formed on the SiO₂/Si substrate based samples.

Fig. 5-14 FE-SEM micrographs of thermally treated Ni/a-C bilayers deposited on (a)

Si and (b) SiO₂/Si substrates, respectively.

The electrical conductivity measurements by 4-point probe show that the electrical resistivity of the Ni/a-C/Si sample slightly increases from about 4.2 mΩ-cm before thermal processing to about 4.9 mΩ-cm after thermal processing, while the electrical resistivity of the Ni/a-C/SiO₂/Si greatly reduces from about 3389.5 mΩ-cm before thermal processing to about 195.6 mΩ-cm after thermal processing, indicating that less conductive compounds (e.g., SiO₂ compounds) have formed only on the thermally treated Si substrate based samples.

Thus as a short summary, the formation of SiO₂ compounds on the Si based samples is due to the thermal diffusion of Si from the Si substrate and the O atoms from the residual O₂ in chamber, which react with each other, under catalytic effect of Ni. The generated SiO₂ compounds can lead to higher graphene structure defects, rougher surfaces, smaller graphene grain size and lower electrical conductivities, which are not preferred. Without any protection methods, the high amount of SiO₂ compounds will form in a nanowire shape. With a protection of Ni and/or a-C thin layer, only few SiO₂ compounds formed doped in the graphene film instead of a nanowire shape. With the protection of a SiO₂ layer coated on the Si substrate before the Ni and a-C sputtering (a SiO₂/Si substrate), the formation of SiO₂ compounds can be absolutely eliminated.

5.2.8 Effect of a-C Layer Thickness

The influence of the a-C layer thickness on the Raman peak ratio is also investigated. As shown in Fig. 5-15, with the Ni sputtered for 20 min the I_D/I_G Raman peak ratios of the Ni:20/C:t2 bilayers deposited on the SiO₂/Si and Si substrates have the lowest values at a C sputtering duration of 40 min. Because the Ni layer sputtered for 20 min is very thin (~ 60 nm), it is difficult for the entire sputtered a-C layer to completely dissolve into the Ni layer during heating. Thus with a C sputtering time longer than 40 min, the remaining a-C layers after thermal processing can contribute to higher I_D/I_G ratios. However, a graphene film formed with a thinner sputtered a-C layer corresponding to a shorter C sputtering time may not be able to fully cover the Ni layer, leading to more edge defects and a higher I_D/I_G ratio.

Fig. 5-15 Raman I_D/I_G and I_{2D}/I_G ratios of thermally treated Ni:20/C:t2 deposited on SiO₂/Si and Si substrates.

Fig. 5-16 shows the Raman peak positions of the Ni:60/C:t2 bilayers deposited on the SiO₂/Si and Si substrates with respect to C sputtering time. The D peak at around 1350 cm⁻¹ is mainly due to the breathing mode of sp² sites existing only in

aromatic rings (e.g., graphitic ordering) but not in chains, via double-resonance that requires defects to be activated [144]. However, sp^3 bonding, e.g., inside diamond, usually shows a single Raman active mode (a zone centre mode of T_{2g} symmetry) at about 1332 cm^{-1} that is just slightly lower than and usually mixed up with the D peak. The samples based on the Si substrates have greater D peak red-shifts towards the diamond reference line as shown in Fig. 5-16a, indicating a higher concentration of sp^3 bonds compared to the samples based on the SiO_2/Si substrates. Thus, the fractions of the sputtered a-C layers grown on the Si substrates used to form the graphene films are lower. The G peak at around 1580 cm^{-1} is due to both in-plane breathing and stretching modes of any pairs of sp^2 sites in either C=C chains (e.g., ethylene) or aromatic rings (at a higher wavenumber) [144]. The G peaks are at similar positions for all the samples as shown in Fig. 5-16b, while the G peak positions for the SiO_2/Si substrate based samples are more stable. The intensity, shape and position of a 2D Raman peak of a graphene film are dependent on the number of C atomic layers in the graphene film [145]. For a single layer graphene, its 2D band at about 2670.7 cm^{-1} can be sharp and symmetric. The 2D band of a multilayer graphene becomes broader and blue-shifted. All the samples prepared on the SiO_2/Si substrates with respect to C sputtering time have stable 2D peak positions at around 2670 cm^{-1} . However, all the samples prepared on the Si substrates show lower 2D peak positions ($\sim 2664\text{ cm}^{-1}$) as shown in Fig. 5-16c, and the 2D peak positions illustrate greater red-shifts corresponding to shorter C sputtering time. Compared to highly oriented pyrolytic graphite (HOPG) [111], all the thermally treated samples used in this study

depict higher G peak positions (about 7 cm^{-1} higher) and lower 2D peak positions (about $17\sim 27\text{ cm}^{-1}$ lower), indicating that the fabricated graphene films are composed of only a few C atomic layers, which are not multilayer graphene [131, 146].

(a)

(b)

(c)

Fig. 5-16 Raman peak positions of thermally treated Ni:60/C:t2 deposited on SiO₂/Si and Si substrates with respect to C sputtering time: (a) D, (b) G and (c) 2D peaks.

5.2.9 Number of Graphene Layers

Graphene films with different structures including multilayer graphene, few-layer graphene, bilayer graphene and single-layer graphene could be formed. The number of atomic layers in a graphene film depends on the thicknesses of a-C and Ni layers, heating temperature and duration, cooling rate and environment. A thicker a-C layer can supply more C atoms, and a higher anneal temperature can accelerate the C diffusion and increase the C content in the Ni layer, both of which can possibly result in a higher number of atomic layers in the graphene film. However, a thin Ni layer can only dissolve and store limited C atoms during heating, which limits the number of graphene atomic layers.

As seen from the TEM image shown in Fig. 5-2a, the graphene film should have a few-layer graphene structure. Usually for a single-layer graphene, the C atoms are arranged in the benzene-ring shaped grids in white color with the holes in dark color separated by the grids and the grids are corresponding to the actual arrangement of the C atoms as shown in Fig. 5-2b. However, for a graphene film of at least 2 atomic layers with the offset in the Bernal (AB) stacking, the grids are in dark color with bright dots separated by the grids, and each bright dot appears where two C atoms from the neighboring layers of graphene (with the Bernal (AB) stacking) align in the projection. Fig. 5-2b shows a thin edge of the graphene film zoomed from Fig. 5-2a, where the film shows the bright grids, indicating a single-layer graphene structure. However, the major portion of the graphene film except the edges (Fig. 5-2a) shows a few-layer graphene structure having dark grids and bright dots. The electron

diffraction pattern shown in Fig. 5-2c is measured from a few-layer graphene, instead of a single layer graphene.

In a Raman measurement, a small shift in G peak as a function of number of atomic layers in a graphene has been reported in the literature [147]. Usually, more graphene layers lead to a red-shift of G peak position, according to the equation: $\omega_G(\text{cm}^{-1}) = 1580.7 + 8.14 / n$, where ω_G is the G peak position and n is the mean number of graphene layers [146]. For the thermally treated Ni/a-C bilayers deposited on the Si and SiO₂/Si substrates, ω_G is 1586.72 cm⁻¹ and 1583.36 cm⁻¹, respectively, as shown in Fig. 5-1e and f, and n is estimated to be about 1.35 and 3.06, respectively, which are consistent with the TEM measurement as shown in Fig. 5-2. In addition, the I_{2D}/I_G ratios, approximately equal to 0.69 and 1.13 for the respective samples based on the Si and SiO₂/Si substrates, indicate the graphene films of less than 10 atomic layers. According to the FWHM analysis from Fig. 5-1, the 2D peaks for the thermally treated Ni/a-C/SiO₂/Si (f) and Ni/a-C/Si (e) exhibit a symmetric single Lorentzian line shape with the FWHMs of about 47 and 57.9 cm⁻¹, respectively, both of which are slightly larger than that (about 36.5 cm⁻¹) for the single-layer graphene [135], confirming that the few-layer graphene films have been formed.

From the above TEM and Raman results, the fabricated films were few-layer graphene (number of graphene layers < 10) instead of multi-layer graphene (number of graphene layers > 10) [111].

5.3 Graphene Thin Films Synthesized via Solid-State Carbon Diffusion

From Co-sputtering Deposited Nickel-carbon Mixed Layers

5.3.1 Formation Mechanism of Graphene Thin Films

The process of graphene films used in this study is similar to the synthesis process of graphene films via metal-catalyzed crystallization of a-C through thermal annealing [78], where a Ni/a-C bilayer (Fig. 5-5) deposited on a SiO₂/Si substrate was thermally treated at 1000 °C [78]. As schematically shown in Fig. 5-17, during heating at 1000 °C for 3 min, the C atoms can be dissolved into Ni lattices, while during cooling the C solubility in the Ni lattices sharply reduces and the excess C atoms precipitate on the surface of the Ni-C layer to form a graphene film. This is because at the temperature far below melting point, the surface diffusion is more favourable than lattice (bulk), grain boundary and dislocation diffusivities [148].

Fig. 5-17 A model for fabrication of graphene with thermal processing of a Ni-C mixed layer co-sputtering deposited on Si substrate.

5.3.2 Effect of Si Substrate Surface Condition

Fig. 5-18 shows the Raman spectra of the thermally treated Ni-C mixed layer deposited on both Si and SiO₂/Si substrates, in which the G band is located at about 1600 cm⁻¹ and the D band is located at around 1350 cm⁻¹. The G peak is corresponded

to an E_{2g} mode of graphite and is related to the vibration of sp^2 -bonded carbon atoms [149] while the D peak is due to optical phonons around K associated with breathing mode of sp^2 rings and requires a defect to be activated via double-resonance [150]. The D and G peak intensity ratio, I_D/I_G , indicates the quantity of defects in a graphitic material [151, 152]. The I_D/I_G ratios are about 1.83 and 0.29 for the Si and SiO₂/Si based samples, respectively. The smaller I_D/I_G ratio of the SiO₂/Si based sample indicates that its graphene film has fewer defects than the one formed on the Si substrate. Thus, the graphene film formed on the SiO₂/Si substrate has better electrical or optical properties. The higher I_D/I_G ratio of the Si based sample can be explained by the reactions between the Si atoms diffused out from the substrate and the residual oxygen in the RTP chamber during the thermal processing with the Ni in the Ni-C layer as a catalyst [138-140], which produce gaseous products and SiO₂ species that are trapped underneath the graphene layer and distort the film structure [153], thus leading to more sp^2 defects [154]. However, for electrochemical analysis, a graphene film with more surface active sites (edge defects and sp^2 defects) where the local surfaces are relatively rougher (higher surface aspect ratios) is more favourable. The 2D bands of the Raman spectra in Fig. 5-18 confirm the formation of the graphene films, which are located at around 2658.5 cm⁻¹ and 2675.5 cm⁻¹ for the Si and SiO₂/Si based samples, respectively. According to the double resonance theory [144], there should not be a shift in 2D peak position unless an environmental effect does exist. Hence, the shift of the 2D band observed in Fig. 5-18 may be caused by the different surface conditions of the Si and SiO₂/Si substrates. The I_{2D}/I_G ratio can be related to

the number of graphene sheets grown [151]. The I_{2D}/I_G for the graphene formed on the Si substrate (~ 0.67) is bigger than that of the graphene formed on the SiO_2/Si substrate (0.45), which means that the graphene film formed on the Si substrate has a smaller number of graphene sheets.

Fig. 5-18 Raman spectra of thermally treated Ni-C mixed layers (C of 3.5 at.%) deposited on Si substrates without and with a SiO_2 coating.

5.3.3 Effect of Ni-C Mixed Layer Thickness

The C atomic contents in the as-deposited Ni-C mixed layers with respect to C sputtering powers ranging from 25 to 200 W are summarized in Table 5-1. With a fixed Ni sputtering power of 50 W, the C atomic content is almost linearly proportional to the C sputtering power.

Table 5-1 C atomic content with respect to C sputtering power.

DC sputtering power on C target (W)	DC sputtering power on Ni target (W)	C atomic content in as-deposited Ni-C layer (at.%)
25	50	0.7

50		1.8
75		3.5
100		4.9
150		6.1
200		9.8

Fig. 5-19 shows the Raman spectra of the graphene films formed from the Ni-C layers of different C contents. With 0.7 at.% C (Fig. 5-19a) and 1.8 at.% C (Fig. 5-19b), D, G and 2D Raman peaks are hardly resolved, which may be due to the insufficient C for precipitation during cooling. The C atoms can also be depleted by the oxidization with the residual oxygen in the RTP chamber. However, with C contents higher than 3.5 at.%, the 2D peaks gradually diminish (Fig. 5-19d-f) compared with that in Fig. 5-19c, indicating the increasing numbers of graphene sheets, which means that higher C contents in the Ni-C layers can promote the saturation of C in the Ni lattices during heating and then the precipitation of C on the outer surface of the Ni-C layer in the form of graphene during cooling. However, if the number of graphene sheets is too large, the electronic band structure tends to approach that of graphite [145]. Therefore, I_{2D} decreases as the number of graphene sheets increases. With 3.5 at.% C (Fig. 5-19c), the 2D peak is the strongest, and the D and G peaks are less overlapping, indicating the optimal graphene film structure. Thus, the following discussion will be related to the results measured using the graphene electrodes formed from the Ni-C layers having 3.5 at.% C.

Fig. 5-19 Raman spectra of thermally treated Ni-C/Si samples with C atomic contents (in the as-deposited Ni-C mixed layers) of about (a) 0.7 at.%, (b) 1.8 at.%, (c) 3.5 at.%, (d) 4.9 at.%, (e) 6.1 at.%, and (f) 9.8 at.%.

5.4 Further Discussions on Metal-catalyzed Graphene Fabrication

The four types of commonly used fabrication methods for single and multi-layer graphene can be divided into two groups: Group 1: Graphene separation from multilayered graphene or graphite, e.g., mechanical cleavage of highly ordered pyrolytic graphite (HOPG), or chemical exfoliation of graphite (deposition of a dispersed graphene oxide, followed by an oxygen reduction process) [17, 18]. Group 2: Graphene fabricated by reorganization of carbon free atoms, e.g., thermal decomposition of SiC [19, 155], chemical vapor deposition (CVD) [20], and solid-state carbon diffusion as discussed in this thesis. For group 1, the graphene sheets already exist in the raw materials (e.g. HOPG or MLG), but just stacked with thousands of graphene layers, and/or mixed with other carbon forms (e.g. amorphous carbon in graphite), and the fabrication is just to separate or peel a single atomic layer

of such graphene sheet off its stack. For group 2, the carbon atoms do not exist in the form of graphene sheet in the raw materials, but in the form of hydrocarbon compounds [69, 70], SiC or amorphous carbon. The comparison of these two groups is summarized in Table 5-2.

Table 5-2 Comparison of two groups of graphene fabrication techniques

	Group 1		Group 2		
	Mechanical cleavage	Chemical exfoliation	Thermal decomposition of SiC	CVD	Solid-state carbon diffusion
Thermal Processing Required?	No	No	Yes	Yes	Yes
Time Taken	A few hours	One day	Half day	Two days	One day
Easy handling?	Practice Required	Practice Required	Yes	No	Yes
Wafer Sized scale Fabrication?	No	Yes	No	Yes	Yes
Vulnerable to contamination?	Yes	Yes	No	No	No

For the fabrication methods in group 2, the requirements are summarized as below:

(a) Carbon source. The carbon atoms can be from the hydrocarbon compounds, SiC or amorphous carbon.

(b) Crystal lattice structure with small lattice mismatch with graphene. Usually the appropriate transition metal catalytic grains like Ni, Cu, Pt, Ru and Fe are suitable.

(c) High Temperature. Usually heating at a high temperature is used. At high temperature, the catalytic atoms (e.g., Ni, Cu) can form their lattice grains who has

small lattice mismatch with graphene (about 1.1% for Ni [156]), and the carbon atoms can decompose and dissolved in those lattice grains. Usually, at higher temperature, the solubility of the carbon atoms in the catalytic solution is higher or even saturated. For the method of thermal decomposition of SiC, the situation is different. During heating, the Si atoms in the outer surface of SiC will sublimation at high vacuum pressure, leaving only the C atoms on the outer surface [19, 155]. Those C atoms will be the carbon source for the graphene, while the remaining lattice structure of SiC grains serves like the catalytic lattice structures as previously discussed [19, 155].

(d) Cooling process. During cooling, the solubility of C in the catalytic grain abruptly drops and the excess amount of dissolved C atoms epitaxial precipitate firstly at the catalytic grain boundaries, and then the precipitation extends to cover the entire outer layer surface. The size of graphene domains was consistent with these dimensions of the flat grain surfaces, strongly suggesting epitaxial growth on the microcrystallites [156]. For a metal catalytic with a higher carbon solubility difference at high and low temperatures as mentioned above, more carbon atoms can be expelled out from its metal-carbon alloy during cooling, thus more graphene layers can be generated, with high graphene defects and sometimes mixed with amorphous carbons, which is usually not preferred for electrical or optical applications. But those graphene defects can lead to better performances in electrochemical applications.

(e) Surrounding protection gas environment during thermal processing (e.g., H₂ and/or Ar). During heating, the residual oxygen in the ambient can oxide the carbon atoms and the protection gases like Ar gas mixed with H₂ are recommended.

The above 5 points can be summarized in Table 5-3 as shown below.

Table 5-3 Comparisons of graphene fabrication techniques via thermal processing

	Thermal decomposition of SiC	CVD	Solid-state carbon diffusion
Carbon Source	Internal carbon source	External carbon source	Internal carbon source
With catalytic metals?	No	Yes	Yes
Lattice structure for epitaxial growth	Si lattice	Transition metal lattice	Transition metal lattice
Surrounding gas	Ar and/or H ₂	Hydrocarbon mixed with Ar and/or H ₂	Ar and/or H ₂
During heating	Si atoms sublimation	Hydrocarbon decomposition and C atoms dissolve in catalytic metals	C atoms dissolve and diffuse in catalytic metals
During cooling	C atoms precipitate to form graphene films		
Overall conductivity with substrate	Poor, due to the absence of catalytic layer	Good	Good

The fabrication methods like CVD, solid-state carbon diffusion method by thermal treating of Ni/a-C bilayers or Ni-C mixed layers as mentioned in this thesis can well fit the above discussions. The above 5 points are suggested to be the guidance for the exploration of the new metal-catalyzed graphene fabrication methods in future.

The advantages or disadvantages of the fabricated graphene films via different methods depend on its applications. For example, for electrical and optical applications, a graphene film with less graphene defects and detachable from the substrate is better. In this case, the methods like mechanical cleavage of highly

ordered pyrolytic graphite, or chemical exfoliation of graphite are preferred. For applications require large scale of graphene at low cost, the method of chemical exfoliation of graphite (deposition of a dispersed graphene oxide, followed by an oxygen reduction process) is advised. For electrochemical applications, the graphene films with high defect contents and good electrical connections with substrate are the key considerations, and the method of CVD and solid state carbon diffusion using the Si substrates instead of SiO₂/Si as substrate are suggested.

5.5 Summary

In this chapter, Ni/a-C bilayer thin films and Ni-C mixed layers were deposited on Si and SiO₂/Si substrates by DC magnetron sputtering deposition followed by rapid thermal processing to produce graphene ultrathin films using a solid-state carbon diffusion method. The formation of graphene films was confirmed with various methods. The influence of the Si substrate surface condition (i.e., without or with a SiO₂ layer) on the formation of the graphene films was comparatively studied and the results showed that the SiO₂ layers on the Si substrate surfaces effectively prevented from the formation of SiO₂ compounds in the graphene films.

Chapter 6: Electrochemical Analysis by Using Graphene Thin Film Electrodes

6.1 Introduction

It was reported that graphene films fabricated using mechanical cleavage and chemical exfoliation of graphite methods need to be transferred to other substrates [145], leading to possible contamination and oxidization of the graphene films at the interface, resulting in a poor electrical connection with the substrates. Compared to those methods, the graphene films fabricated via solid-state carbon diffusion of the thermally treated Ni/a-C bilayer or Ni-C mixed layer coated samples offer a good adhesion of the graphene films to the substrates with a much better electrical connection that is preferred for electrochemical analysis.

In this work, graphene films fabricated via thermally treating Ni/a-C bilayers and Ni-C mixed layers were used as working electrodes for simultaneous detection of trace heavy metal ions (Cu^{2+} , Pb^{2+} and Cd^{2+}) in acetate buffer solutions (pH 5.3) with SWASV. The Si substrate surface conditions (with or without a SiO_2 layer) were investigated with respect to the graphene electrodes' electroanalytical performance. The graphene electrodes modified with PANI porous layers and Bi nanoparticles showed excellent repeatability, ultrahigh sensitivity (~ 0.33 nM) and good resistance to passivation caused by surface active species adsorbed on the electrode surfaces.

6.2 Electrochemical Analysis by Using Graphene Thin Film Electrodes Synthesized via Thermally Treating Sputtering Deposited Ni/a-C Bilayers

6.2.1 Bare Graphene Thin Film Electrodes without Modification

6.2.1.1 Electrochemical Characteristics of Graphene Electrodes

Fig. 6-1 shows the corrosion test results of the as-deposited and thermally treated Ni/a-C/Si, as well as the as-deposited a-C_{single}. It appears that the as-deposited Ni/a-C bilayer has the smallest corrosion potential (about -0.59 V) and the highest polarization current (about 73.8 nA) among the three electrodes (Fig. 6-1a), because of the top Ni layer. However, the thermally treated Ni/a-C bilayer film has the highest corrosion potential at around -0.07 V (Fig. 6-1c) and the lowest polarization current (about 7.66 nA) than both the as-deposited Ni/a-C bilayer film (about -0.59 V and 73.8 nA, Fig. 6-1a) and the a-C_{single} (about -0.31 V and 16.2 nA, Fig. 6-1b), indicating that the thermally formed graphene film can fully cover and protect the sample surface from electrochemical corrosion, and thus make the transfer of a graphene film to a substrate surface for electrochemical analysis unnecessary.

Fig. 6-1 Potentiodynamic polarization curves of (a) as-deposited Ni/a-C/Si, (b) as-deposited a-C_{single} and (c) thermally treated Ni/a-C/Si electrodes.

Fig. 6-2a depicts a steady cyclic voltammogram measured using a thermally treated Ni/a-C/Si sample, from which the well-defined oxidation and reduction peaks due to the $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox couple are observed. The electroactive surface area can be calculated according to the Randles-Sevcik equation: $I_p = 2.69 \times 10^5 A C D^{1/2} n^{3/2} \nu^{1/2}$, where I_p is the maximum current (A), A is the electroactive surface area (cm^2), C corresponds to the bulk concentration of the redox probe (mol/cm^3), D is the diffusion coefficient of the ion in solution (cm^2/s), n is the number of electrons participating in the redox reaction, and ν is the scan rate of the potential perturbation (V/s). In this work, $n = 1$, $C = 5 \times 10^{-6} \text{ mol cm}^{-3}$, $\nu = 0.05 \text{ V/s}$, and $D = 6.70 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. I_p of the anodic peak measured from Fig. 6-2a is about $1.03 \times 10^{-3} \text{ A}$. Thus, the electroactive surface area of this electrode is estimated to be about 1.32 cm^2 , which is much larger than the exposed circular area of the electrode (about 0.442 cm^2 with a diameter of 0.75 cm). An obviously high surface aspect ratio ($1.32/0.442=2.99$) indicates that this graphene based electrode has a good

electrochemical reacting ability. For an ideally reversible electrode, the ratio $I_{pc}/I_{pa} = 1$, where I_{pc} and I_{pa} are the reduction and oxidation peaks, respectively. For a non-reversible electrode, the I_{pc}/I_{pa} ratio shifts away from unity. As illustrated in Fig. 6-2a, I_{pc} and I_{pa} approximately equal 1101.5 and 1029.8 μA , respectively, resulting in an I_{pc}/I_{pa} ratio of about 1.07 that indicates a good reversibility of the electrode. For comparison as shown in Fig. 6-2b, the as-deposited a-C_{single} electrode (a-C film of about 200 nm thick) has much smaller electroactive surface area (about 0.05 cm²) and surface aspect ratio (0.05/0.442 $\approx$ 0.113), and a similar I_{pc}/I_{pa} ratio (40.6 μA /38.7 μA $\approx$ 1.05). The obviously bigger electroactive surface area and surface aspect ratio of the thermally treated Ni/a-C/Si indicates a much better electrochemical sensitivity than the as-deposited a-C_{single} electrode.

(a)

(b)

(c)

Fig. 6-2 CV surface activity curves of (a) thermally treated Ni/a-C/Si and (b) as-deposited a-C_{single} electrodes. (c) EIS curves of thermally treated Ni/a-C/Si and as-deposited a-C_{single} electrodes.

EIS is a powerful tool to characterize the interfacial properties of surface-modified electrodes. In the Nyquist plots shown in Fig. 6-2c the linear sections characteristic of lower frequency kinetic control zone are attributable to diffusion-limited electron transfer, and the squeezed semicircle portions observed in the high frequency kinetic control zones correspond to a charge-transfer-limited

process. Charge transfer resistance R_{ct} (Ω) that equals the squeezed semicircle diameter at high frequencies on a Nyquist plot controls the interfacial electron transfer rate of the redox probe between the solution and the electrode surface. From Fig. 6-2c, R_{ct} of the thermally treated Ni/a-C/Si is about 36.9 Ω , which is much smaller than that of the as-deposited a-C_{single} electrode ($\sim 436.4 \Omega$), indicating that for the thermally treated Ni/a-C/Si, the resistance of electron transfer at the electrolyte-electrode interface is much smaller, and during the electrochemical reactions the electrons transferred to or from the interface can be more easily delivered.

The potential window of the thermally treated Ni/a-C/Si electrode is about 2.5 V (-1.25 V to 1.25 V) as shown in Fig. 6-3, indicating that this electrode can be used for the electrochemical detection of a wide range of heavy metal ions.

Fig. 6-3 A cyclic voltammogram showing the potential window of thermally treated Ni/a-C/Si in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO₃.

6.2.1.2 Comparison of Graphene Electrodes with Other Electrodes

Fig. 6-4 compares the SWASV responses of the as-deposited a-C_{single}, and thermally treated Ni/a-C/Si and Ni/a-C/SiO₂/Si electrodes to 1 μM Pb²⁺ dissolved in the 0.1 M acetate buffer solutions (pH 5.3). a-C_{single} has been reported to be a commonly used electrode that has stable performance and high sensitivity comparable with glassy carbon electrode (GCE) [66, 67]. From Fig. 6-4a, a quite low stripping peak current of Pb²⁺ (~ 2.42 μA) indicates that the detection limit of Pb²⁺ by the a-C_{single} electrode is around 1 μM . Compared to the a-C_{single} electrode, the thermally treated Ni/a-C/Si electrode (Fig. 6-4b) has a much higher Pb²⁺ stripping peak current of about 289 μA due to the excellent surface activity and enhanced specific surface area of the graphene film.

Fig. 6-4 Stripping voltammograms of Pb²⁺ ions of 1 μM in 0.1 M acetate buffer solutions measured using (a) as-deposited a-C_{single}, (b) thermally treated Ni/a-C/Si, and (c) thermally treated Ni/a-C/SiO₂/Si electrodes. The inset shows an enlarged view of (a).

The thermally treated Ni/a-C/SiO₂/Si electrode (Fig. 6-4c) has a lower Pb²⁺ peak current than the thermally treated Ni/a-C/Si electrode (Fig. 6-4b), possibly because of the poor conductivity of the SiO₂/Si substrates. From the 4-point probe measurements, the electric resistivity of the thermally treated Ni/a-C/Si electrode is about 4.9 mΩ·cm, while that of the thermally treated Ni/a-C/SiO₂/Si electrode is about 195.6 mΩ·cm. For the thermally treated Ni/a-C/SiO₂/Si electrode, the electrons generated or required during the electrochemical reactions on the electrode surface are difficult to pass through the SiO₂ layer on the Si substrate, making this electrode look like a capacitor, which explains why the thermally treated Ni/a-C/SiO₂/Si electrode has a much higher background current than the Si substrate based electrodes. Another possible reason is that the graphene film fabricated by the thermal treatment of the Ni/a-C/Si is much rougher than the similar film formed on the SiO₂/Si substrate as discussed previously. A higher density of edge defects offers more electrochemically active sites on the film surface and also the rough surface offers a higher specific surface area, both of which lead to a higher sensitivity for electrochemical analysis. Thus, the thermally treated Ni/a-C/Si electrodes are chosen for the following electrochemical analysis.

6.2.1.3 Effects of Preconcentration Potential and Time

With the Pb²⁺ concentration maintained at 1 μM, the preconcentration potential and time are optimized. When the preconcentration potential is varied in the range from -0.6 to -1.2 V as shown in Fig. 6-5a & b, the Pb²⁺ stripping response is higher at

more negative potentials, at which more Pb^{2+} can be reduced to their neutral states ($\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0$), almost all of which can be oxidized during the following anodic stripping process ($\text{Pb}^0 \rightarrow \text{Pb}^{2+} + 2\text{e}^-$), leading to higher stripping peak currents. However, if the preconcentration potential is too low, the hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$) can occur, from which the H_2 bubbles generated could adsorb on and block the electrode surface. That is the reason why the anodic stripping peak currents are almost constant with the preconcentration potential lower than -1.1 V as shown in Fig. 6-5b. The hydrogen evolution can be delayed with a higher pH value of the electrolyte, which can shift the potential window to a more negative range, but a higher pH value than 5.3, when other parameters maintained constant, can lead to a lower stripping peak current [5], which is not preferred. Thus, -1 V is an optimized preconcentration potential at pH 5.3.

(a)

Fig. 6-5 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb²⁺ (1 μM) measured by thermally treated Ni/a-C/Si electrodes with respect to preconcentration potentials.

With the increase of preconcentration time from 0 to 270 s, more Pb²⁺ can be reduced and deposited onto the electrode surface during the deposition process ($\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0$), and almost all of them can be oxidized during the following anodic stripping process ($\text{Pb}^0 \rightarrow \text{Pb}^{2+} + 2\text{e}^-$), leading to higher anodic stripping peak currents as shown in Fig. 6-6a & b. However, if a too long preconcentration time is used, the electrode surface could be saturated with the Pb deposits in the case of a high Pb²⁺ concentration in the solution. Thus, 180 s at -1 V is an optimized preconcentration time.

(a)

(b)

Fig. 6-6 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb^{2+} ($1 \mu\text{M}$) measured by thermally treated Ni/a-C/Si electrodes with respect to preconcentration time.

6.2.1.4 Effect of Ni Layer Thickness on SWASV Response

The effect of the Ni layer thickness is studied with respect to the performance of the graphene film electrodes in the detection of Pb^{2+} . Fig. 6-7a shows that the anodic stripping peak currents almost linearly increase with increasing Pb^{2+} concentration

from 1 to 1.7 μM for all the thermally treated Ni/a-C/Si electrodes with respect to Ni sputtering time from 0 to 80 min (a deposition rate of about 2.9 nm/min), of which the a-C layers are about 50 nm. Compared to all other electrodes, the thermally treated a-C/Si electrode without a Ni layer has the smallest SWASV peak currents at all the Pb^{2+} concentrations from 1 to 1.7 μM . A possible reason is that the a-C layer after thermal processing is too thin, which may be damaged during the SWASV tests. With the Ni sputtering time increased from 0 to 80 min, the Pb^{2+} stripping peak currents first increase and then reduce, with their maximum values at about 30 min for the Ni sputtering time corresponding to a Ni layer thickness of about 100 nm as seen in Fig. 6-7b. With the Ni deposition time lower than 30 min the Ni layers are some what too thin and they may shrink after thermal processing, so the electrode surfaces can not be fully covered by the graphene films that grow only on the Ni surfaces, leading to the lower anodic stripping peak currents. On the other hand, with the Ni sputtering time longer than 30 min, the Ni layers are some what too thick so that after thermal processing almost all the C atoms are dissolved in the Ni layers and the precipitated C atoms on the Ni surfaces are insufficient to form continuous graphene films. Thus, for a a-C layer of 50 nm in thickness, an optimal Ni deposition time is about 30 min corresponding to about 100 nm thick Ni layer, which is used for the following discussion.

(a)

(b)

Fig. 6-7 Anodic stripping peak currents measured using thermally treated Ni/a-C/Si electrodes with respect to (a) Pb^{2+} concentration with varying Ni sputtering time and (b) Ni sputtering time with a fixed Pb^{2+} concentration of 1.5 μM.

6.2.1.5 Calibration Curves Measured by Graphene Electrodes

Fig. 6-8a shows the stripping voltammograms measured with the thermally treated Ni/a-C/Si electrode for the detection of Pb^{2+} ions with concentrations ranging from 0 to 1200 nM in the acetate buffer solutions. The Pb^{2+} anodic stripping peak

currents increase in proportion to the Pb^{2+} concentrations and the anodic stripping peaks are sharp. As shown in Fig. 6-8b, the calibration curve of the Pb^{2+} peak current with respect to Pb^{2+} concentration in the range of 7-1200 nM Pb^{2+} is almost linear, which can be represented by the following equation determined by the regression of Pb^{2+} stripping peak currents on Pb^{2+} concentrations:

$$I = 0.36 + 0.49[\text{Pb}^{2+}] \quad (6-1)$$

where I is the peak current in μA , and $[\text{Pb}^{2+}]$ is the Pb^{2+} concentration in nM in the 0.1 M acetate buffer solution (pH 5.3). The regression coefficient of the above equation is about 0.997, indicating a good linear relationship between Pb^{2+} anodic stripping peak currents and Pb^{2+} concentrations. The Pb^{2+} detection limit of this graphene electrode is about 7 nM which is much lower than that of the as-deposited a- C_{single} electrode (about 1 μM , Fig. 6-4a). The high regression coefficient and low detection limit indicate the excellent performance of the thermally treated Ni/a-C/Si electrode in electrochemical analysis.

(b)

(c)

(d)

Fig. 6-8 (a) Stripping voltammograms and (b) calibration results with respect to Pb^{2+} concentrations measured using thermally treated Ni/a-C/Si electrodes with Ni sputtering time fixed at 30 min. (c) Stripping voltammograms of 30 and 100 nM Pb^{2+} and (d) anodic stripping peak currents with respect to Pb^{2+} concentrations measured using thermally treated Ni/a-C/Si electrodes with Ni sputtering time fixed at 30 min with UPD method.

With the Pb^{2+} concentrations lower than 46 nM, a single anodic stripping peak is located at around -0.51 V, while with the Pb^{2+} concentrations higher than 46 nM, the second anodic stripping peak appears at around -0.64 V that is overlapped with the first one as shown in Fig. 6-8c. The peak at -0.51 V is due to a phenomenon so called under-potential deposition (UPD), wherein a Pb^0 monolayer is deposited on the electrode surface of a different material. With a higher Pb^{2+} concentration, a multilayer of Pb^0 can be deposited on the pre-deposited Pb^0 monolayer, and this phenomenon is called bulk deposition (BD). For the BD, the anodic stripping peak potential is mainly controlled by the Nernst potential and increases with a higher Pb^{2+} concentration as shown in Fig. 6-8a & c. For the UPD, due to the strong bonding

between the monolayer and the electrode surface, the anodic stripping peak potential is slightly higher than the reversible Nernst potential as shown in Fig. 6-8c.

The UPD has been reported [157] and used for surface modifications with metal catalysts. As shown in Fig. 6-8d, the anodic stripping peak currents measured with the UPD method almost linearly increase with increasing Pb^{2+} concentrations. Thus, the UPD method can also be used for the electrochemical detection of metal ions at nM level.

6.2.1.6 Stability Analysis of Graphene Electrodes

Usually for repeated test cycles, the SWASV peak currents of an electrode increase, because after each cycle of test there are always some residual solid Pb in reduced state on the electrode surface, which can contribute to the anodic stripping currents of the following cycles. The ionization of the residual Pb^0 after a test cycle by electrochemical oxidation ($\text{Pb}^0 \rightarrow \text{Pb}^{2+} + 2\text{e}^+$) requires a positive potential of about 0.2 V (vs. Ag/AgCl) to be applied to the working electrode for about 180 s before next cycle. The long-term repeatability of an optimized graphene electrode is about 46 test cycles in an acetate solution containing 1 μM Pb^{2+} as shown in Fig. 6-9, in which the anodic stripping peak currents keep almost constant with a standard deviation of about 6.2, indicating a good repeatability. Thus this graphene electrode fabricated by this method will be a excellent platform for further modifications with various polymers or metal nano-particles.

Fig. 6-9 Long-term repeatability of a thermally treated Ni/a-C/Si electrode tested for 46 cycles in an acetate solution containing 1 μM Pb^{2+} .

The interference of Cd^{2+} (100 nM) in the electrolyte on the anodic stripping peak currents of Pb^{2+} (500 nM) is studied as shown in Fig. 6-10a, in which a peak locates at about -0.875 V is attributed to Cd^{2+} . As shown in Fig. 6-10b, the detection limit of Cd^{2+} is as low as 20 nM. With increased Cd^{2+} concentrations from 20 to 1200 nM, the anodic stripping peak currents of Pb^{2+} (500 nM) slightly reduce, which may be due to the saturation of the reduced heavy metals (Pb^0 and Cd^0) on the electrode surface with higher Cd^{2+} concentrations.

(a)

(b)

Fig. 6-10 (a) Stripping voltammograms of 500 nM Pb^{2+} without and mixed with 100 nM Cd^{2+} and (b) influence of Cd^{2+} concentration on stripping peak current of Pb^{2+} (500 nM), with all the data measured by using thermally treated Ni/a-C/Si electrodes.

Surface-active compounds (e.g., sodium dodecyl sulfate (SDS)) can be adsorbed onto electrode surfaces, causing the passivation of the electrodes and lowering the sensitivities of the electrodes [38]. Fig. 6-11a shows the anodic stripping currents normalized with the maximum stripping current, i.e., I_p/I_{pmax} , measured by an optimized graphene electrode with respect to different concentrations of the SDS

dissolved in the electrolytic solutions. The anodic stripping peak currents of 1 μM Pb^{2+} reduce with higher SDS concentrations until 6 mg/L, after which the anodic stripping peak currents are almost constant. For comparison, the $I_p/I_{p_{\max}}$ ratios of polyaniline and bismuth modified glassy carbon electrodes have been reported to be about 71 % and 48 % [5], which are much lower than those measured by the graphene electrode (about 83 % and 67 % with 3 and 8 mg/L SDS added in the electrolyte, respectively). Thus, the graphene electrodes used in this study are much more tolerant to the presence of the surface-active compounds for the detection of Pb^{2+} ions. The short-term stability of an optimized graphene electrode is about 11 test cycles in a solution containing 1 μM Pb^{2+} in the presence of 8 mg/L SDS, with almost constant anodic stripping peak currents measured as shown in Fig. 6-11b.

(a)

Fig. 6-11 (a) Influence of SDS concentration on I_p/I_{pmax} ratio of Pb^{2+} ($1 \mu M$) and (b) stability performance tested in an acetate solution containing $1 \mu M Pb^{2+}$ and $8 mg/L$ SDS, with all the data measured using thermally treated Ni/a-C/Si electrodes.

6.2.1.7 Comparison of Electrochemical Performances of Graphene Electrodes

Fabricated using Different Methods

Three types of graphene electrodes were fabricated via (1) solid-state carbon diffusion (thermally treated Ni/a-C/Si sample), (2) CVD [145] and (3) chemical exfoliation of graphite [158], which are the most commonly used methods. For the graphene electrode fabricated via CVD [145] and chemical exfoliation of graphite [158], the fabrication methods can be found in their reference papers, but with a Si substrate used instead of the SiO_2/Si substrate for better electrical conductivities. As shown in Fig. 6-12, the graphene electrode fabricated via the solid-state carbon diffusion method has a higher anodic stripping peak than the one fabricated using the CVD method. One of the possible explanations is that by the CVD method, the outer carbon atoms that are thermally decomposed from the hydrocarbon gas can be

blocked by this generated graphene layer from dissolving into and diffusing inside the Ni layer. Thus the formation of graphene is self-terminated by the previously formed graphene layer, resulting in a thinner graphene films. But for a solid-state carbon diffusion method, the carbon atom supply is inside the sample and their diffusion can not be blocked by the formation of the graphene film, resulting in a rougher graphene film with higher defects contents. As has mentioned, a higher density of edge defects offers more electrochemically active sites on the film surface and also the rough surface offers a higher specific surface area, both of which lead to a higher sensitivity for electrochemical analysis.

Fig. 6-12 Stripping voltammograms with respect to 1 μM Pb^{2+} measured using three graphene electrodes fabricated by three kinds of methods

From Fig. 6-12, the graphene electrode fabricated using the chemical exfoliation of graphite has the lowest anodic stripping peak. One of the possible explanations is that during the chemical exfoliation, the electrochemical properties of the generated graphene sheets should be poisoned by the chemicals used (e.g., strong acids and

oxidants). Another possible explanation is the poor electrical connection between the graphene film and the substrate used. The electrical conductivity within a single graphene fragment (single crystal) is perfect, but for a big graphene sheet containing thousands of graphene fragments, its electrical conductivity is mainly depends on the connections between the overlapped graphene fragments. For the other two methods used, the Ni layer can serve as the electrical conductor to connect all the graphene sheets in the film, resulting in a much smaller electrical resistivity (about 4.9 mΩ-cm) compared with the one fabricated by chemical exfoliation method (about 1.44×10^7 Ω-cm).

6.2.2 Polyaniline and Bismuth Modified Graphene Thin Film Electrodes

6.2.2.1 Effect of Bi Modification

As shown in Fig. 6-13a, the SWASV peak currents measured by a graphene electrode for simultaneous detection of Cd^{2+} and Pb^{2+} ions increase with higher Bi^{3+} concentrations, indicating that the electrode sensitivity is obviously improved by introducing the Bi^{3+} ions into the electrolyte. It was reported that for a too high Bi^{3+} concentration, the electrode surface could be saturated with the Bi based alloys, which was not preferred [5]. Thus, in the following discussion, an optimized Bi^{3+} concentration of about 1.25 μM is used according to the previous studies [5]. As shown in Fig. 6-13b, the voltammogram measured with the graphene electrode in the electrolyte without Bi^{3+} shows only 2 peaks located at about -0.83 V for Cd^{2+} and

about -0.62 V for Pb^{2+} . When 1.25 μM of Bi^{3+} ions is added in the electrolyte, both the Pb^{2+} and Cd^{2+} stripping peaks in the voltammogram are significantly enhanced compared to those measured in the electrolyte without Bi^{3+} , with an additional stripping peak observed at around -0.1 V for Bi^{3+} .

(a)

(b)

Fig. 6-13 (a) Anodic stripping peak currents of Cd^{2+} and Pb^{2+} with respect to Bi^{3+} concentrations and (b) anodic voltammograms with 1.25 μM Bi^{3+} dissolved in electrolyte, measured by a graphene electrode in 0.1 M acetate buffer solutions (pH 5.3) containing 1.2 μM Cd^{2+} and 0.5 μM Pb^{2+} .

6.2.2.2 Effect of PANI Modification

As previously discussed in Fig. 4-1 [67], the successful deposition of the PANI layers on the graphene electrodes can be confirmed with the three pairs of peaks in the cyclic voltammograms as shown in Fig. 6-14 as labeled as 1, 2 and 3, whose means were tabulated in Table 4-1.

Fig. 6-14 Cyclic voltammograms recorded during PANI deposition on a graphene electrode for 30 cycles in a 0.25 M H_2SO_4 electrolyte containing 7.3 μM aniline with a scan rate of 50 mV/s and a potential range of -0.2 to 0.9 V.

It was reported that the corrosion protection of metal surfaces can be achieved by modification with a PANI coating [159, 160]. From the Tefel plots shown in Fig. 6-15, the corrosion current measured by the PANI/graphene electrode (about 54.6 nA) is much smaller than that of the bare graphene electrode without a PANI layer (about 202.1 nA), while the corrosion potential of the PANI/graphene electrode (about -0.055 V) is higher than that of the bare graphene electrode (about -0.101 V), which indicates a better corrosion resistance of the PANI/graphene electrode.

Fig. 6-15 Tafel plots measured by graphene electrodes without/with PANI modification in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO_3 .

Fig. 6-16 shows the SWASV peak currents measured using the Bi/graphene and Bi/PANI/graphene electrodes with respect to SDS concentrations dissolved in the 0.1 M acetate buffer solutions (pH 5.3) containing $1 \mu\text{M Pb}^{2+}$ and $1.25 \mu\text{M Bi}^{3+}$, which are normalized with the maximum stripping peak current measured in the electrolyte without SDS, i.e., $I_P/I_{P_{max}}$. With increasing SDS concentration from 0 to 8 mg/L, the $I_P/I_{P_{max}}$ ratios reduce for the both electrodes, indicating the occurrence of the passivation of the electrodes. The Bi/PANI/graphene electrode has consistently higher $I_P/I_{P_{max}}$ ratios than the Bi/graphene electrode, implying that the electrode modified with the PANI layer is more tolerant to the surface-active compounds (SDS), which can be explained with the branch-structured [122] PANI molecules that can prevent the surface active species from reaching the electrode surface [5, 67, 122]. For comparison, the $I_P/I_{P_{max}}$ ratios of glassy carbon electrodes modified with PANI and Bi are about 71 % and 48 % [5] measured in electrolyte solutions containing 3 and 8

mg/L SDS, respectively, which are much lower than those (about 88.3 % and 59.2 %, respectively) measured with the Bi/PANI/graphene electrode in the similar solutions used in this study, indicating that the graphene film electrode has better passivation resistance than commonly used glassy carbon electrodes.

Fig. 6-16 SWASV I_p/I_{pmax} ratios of Pb^{2+} measured by Bi/graphene and Bi/PANI/graphene electrodes with respect to SDS concentrations in 0.1 M acetate buffer solutions (pH 5.3) containing 1 μM Pb^{2+} and 1.25 μM Bi^{3+} .

The repeatability of the Bi/PANI/graphene electrode was tested for 32 cycles in a 0.1 M acetate buffer solution (pH 5.3) containing 1 μM Pb^{2+} and 1.25 μM Bi^{3+} with the SWASV peak currents recorded as depicted in Fig. 6-17. The peak currents greatly increase for the first 3 tests, after which the peak currents stabilize and maintain almost constant with further increased test cycles, indicating a good repeatability of the PANI modified electrode with reduced passivation.

Fig. 6-17 Stripping peak currents of Pb^{2+} measured for 32 cycles with a Bi/PANI/graphene electrode in a 0.1 M acetate buffer solution (pH 5.3) containing 1 μM Pb^{2+} and 1.25 μM Bi^{3+} .

The FE-SEM image of the bare graphene electrode shown in Fig. 6-18a shows that the graphene film has a rough surface, which is due to the thermal expansion and shrinkage of the sample caused by the thermal processing. The PANI coated graphene electrode (Fig. 6-18b) has a similar surface morphology as the bare graphene electrode (Fig. 6-18a), which may be due to that the PANI layer is too thin to be viewed with SEM. The FTIR spectra was used to confirm the formation of the PANI films on the graphene electrodes and will be shown later. The FE-SEM image of the Bi/graphene electrode surface shows a lot of nanosized bright dots (about 3 nm diameter) as seen in Fig. 6-18c, which are attributed to the as-deposited Bi nanoparticles. With the modifications by both PANI and Bi, the Bi nanoparticles on the Bi/PANI/graphene electrode surface (Fig. 6-18d) are slightly bigger (about 10 nm diameter) than those on the Bi/graphene electrode surface (Fig. 6-18c). A possible

reason is the adsorption and preconcentration effects of a porous PANI coating on metal ions (e.g., Hg^{2+} , Cu^{2+} , Pb^{2+} , In^{2+} , Cd^{2+} , Co^{2+} and Ni^{2+}) [161, 162], which leads to a relatively higher Bi^{3+} concentration around the electrode surface, and thus, the larger as-deposited Bi nanoparticles on the Bi/PANI/graphene electrode surface as shown in Fig. 6-18d.

Fig. 6-18 FE-SEM micrographs of (a) graphene, (b) PANI/graphene, (c) Bi/graphene and (d) Bi/PANI/graphene electrodes.

Fig. 6-19 shows the FTIR spectra of the graphene and PANI/graphene electrodes. Compared to the graphene electrode (Fig. 6-19a), the PANI/graphene

electrode depicts two main absorption bands of PANI (Fig. 6-19b), which locate at about 1585 and 1497 cm^{-1} corresponding to the stretching mode of C=C double bonds in the quinonoid and benzene rings, respectively [163]. The peak at about 1302 cm^{-1} is typical of a standard PANI base and assigned to the C-N stretching in the neighborhood of the aromatic rings [164]. The diketone rings have a characteristic vibration peak at about 1152 cm^{-1} , indicating that the generated PANI is in a form of emeraldine base (EB) that is a neutral state [151, 165]. The absorption band at about 1445 cm^{-1} is attributed to the *o*-coupled aniline [166]. The above confirms the successful formation of the PANI layer on the graphene electrode.

Fig. 6-19 FTIR spectra of (a) graphene and (b) PANI/graphene electrodes.

The stripping voltammograms of Pb^{2+} (1 μM) measured with the graphene electrodes without/with PANI and/or Bi modifications are compared in Fig. 6-20. The bare graphene electrode has a stripping peak current of about 380.2 μA , which is

relatively small. The PANI/graphene electrode has a slightly higher response compared to the bare graphene electrode, which may be due to the higher specific surface area of the branch-structured PANI layer [67]. With 1.25 μM Bi^{3+} introduced in the electrolyte, the Bi/graphene electrode has a greatly increased SWASV peak than the PANI/graphene and bare graphene electrodes, which is due to the in-situ deposited Bi-Pb alloys that can promote the reduction of Pb^{2+} to form Pb^0 . The Bi/PANI/graphene electrode has the highest anodic stripping peaks among the four, due to the higher specific surface area [5] and the preconcentration effect of the branch structured porous PANI layer on the deposition of the metal ions [161, 162], combined with the enhancement effect of the Bi based nanoparticles.

Fig. 6-20 Stripping voltammograms of Pb^{2+} (1 μM) measured by graphene, PANI/graphene, Bi/graphene and Bi/PANI/graphene electrodes in a 0.1 M acetate buffer solution (pH 5.3) containing 1 μM Pb^{2+} .

6.2.2.3 Calibration Curves Measured by Bi/PANI/Graphene Electrodes

As shown in Fig. 6-21a, the voltammogram measured with the PANI/graphene electrode in the solution without Bi^{3+} and Pb^{2+} is smooth and has no obvious stripping peak. With $1.25 \mu\text{M}$ of Bi^{3+} ions added in the electrolyte, an obvious Bi^{3+} stripping peak current (about $112.9 \mu\text{A}$) is observed at around -0.08 V . With the Pb^{2+} ions added to the electrolyte, the stripping peak current of Bi^{3+} (about $91.9 \mu\text{A}$), which is deposited together with Pb^{2+} to form the Bi-Pb alloys on the PANI/graphene electrode surface, is slightly smaller compared to the one measured in the electrolyte having no Pb^{2+} . As shown in Fig. 6-21a, with Pb^{2+} concentrations increased from 0.1 to $1.1 \mu\text{M}$, the stripping peak currents of Pb^{2+} almost linearly increase, and their respective peak positions shift from about -0.65 to -0.59 V . The shift of the stripping peak positions toward less negative potentials at higher target metal concentrations can be explained by the Nernst potential.

(a)

(b)

(c)

(d)

Fig. 6-21 (a) Stripping voltammograms measured with respect to increased Pb^{2+} from 0.1 to 1.1 μM , (b) and (c) relationships between Pb^{2+} peak currents and Pb^{2+} concentrations in the ranges of (b) 0.33 nM $\sim$ 1.1 μM and (c) 0.33 $\sim$ 5 nM, and (d) stripping voltammograms of 0, 4 and 120 nM Pb^{2+} , measured using PANI/graphene electrodes without and with 1.25 μM of Bi^{3+} ions in 0.1 M acetate buffer solutions (pH 5.3).

The anodic stripping peak currents of Pb^{2+} with increased concentrations from 0.33 nM to 1.1 μM are recorded with the corresponding calibration curve shown in Fig. 6-21b. The Pb^{2+} peak currents are almost linearly proportional to the Pb^{2+} concentrations in the range of 0.1~1.1 μM Pb^{2+} , which can be represented by the following equation:

$$I(\mu\text{A}) = -45.05 + 490.12[\text{Pb}^{2+}](\mu\text{M}) \quad (6-2)$$

where I is the peak current in μA and $[\text{Pb}^{2+}]$ is the Pb^{2+} concentration in μM in the 0.1 M acetate buffer solution (pH 5.3). The regression coefficient of the above equation is about 0.995, indicating a good linear relationship between Pb^{2+} anodic stripping peak currents and Pb^{2+} concentrations.

The range for the ultralow Pb^{2+} concentrations (0.33~5 nM) in Fig. 6-21b is magnified in Fig. 6-21c, from which a near linear relationship between the stripping peak currents and the Pb^{2+} concentrations is also observed, which can be described by the following equation:

$$I(\mu\text{A}) = 0.42 + 0.67[\text{Pb}^{2+}](\text{nM}) \quad (6-3)$$

where I is the peak current in μA and $[\text{Pb}^{2+}]$ is the Pb^{2+} concentration in nM. The regression coefficient of the equation is about 0.996.

The detection limit of Pb^{2+} by the Bi/PANI/graphene electrodes is about 0.33 nM which is much lower than that of the bare graphene electrode (about 7 nM, Fig. 6-8b). The high regression coefficient and low detection limit indicate the excellent performance of the Bi/PANI/graphene electrodes.

The SWASV peak currents of Pb^{2+} with respect to ultralow Pb^{2+} concentrations can be measured with an under-potential deposition (UPD) condition [157], which is related to a phenomenon wherein a metal monolayer is deposited onto the electrode surface of a foreign material. With a higher metal ion concentration and a sufficient deposition duration a multilayer metal can be deposited onto the pre-deposited monolayer, which is called bulk deposition (BD) [157]. As reported in the literature [157], UPD is usually used for the surface modification with metal catalysts. In this study, UPD is successfully employed for anodic stripping voltammetry. As shown in Fig. 6-21d, the voltammogram has no stripping peak if no Pb^{2+} ions are added in the electrolyte solution. With the electrolyte containing 4 nM Pb^{2+} , a single Pb^{2+} peak is observed at around -0.58 V in the voltammogram, which is due to the UPD condition,

while with a higher Pb^{2+} concentration (120 nM) in the electrolyte, two peaks can be found at around -0.645 V (BD) and around -0.55 V (UPD) in the voltammogram. This is because for the electrochemical detection of trace heavy metals by means of SWASV, the anodic stripping peak positions of BD are mainly controlled by the Nernst potential and would increase with higher Pb^{2+} concentrations as confirmed by Fig. 6-21a. Due to the strong bonding between metal deposits and electrode surface, the potentials corresponding to the anodic stripping peaks of UPD are more positive than those of BD.

6.3 Electrochemical Analysis by Using Bi Modified Graphene Thin Film

Electrodes Synthesized via Thermally Treating Ni-C Mixed Layers

6.3.1 Effect of Si Substrate Surface Condition

It can be seen from Fig. 6-22 that the background current of the Stripping voltammogram of Pb^{2+} (0.1 μM) measured by the graphene electrode formed on the SiO_2/Si substrate is very high with a broad and weak peak, which may be due to the poor conductivity of the SiO_2 layer of the SiO_2/Si substrate. On the other hand, the anodic stripping peak of Pb^{2+} measured by the graphene electrode coated on the Si substrate, which is positioned at around -0.615 V, is stronger and sharper (full width at half maximum (FWHM) of about 0.073 V), indicating that it is a much more effective electrode. The excellent performance of the Si substrate based graphene electrode can also be explained by the higher sp^2 defects that offer more surface active sites for the electrochemical reactions to take place. Therefore, the following

discussion will be focused on the results measured with only the Si substrate-based graphene electrodes.

Fig. 6-22 Stripping voltammograms of Pb²⁺ (0.1 μM) measured by thermally treated Ni-C mixed layers (C of 3.5 at.% in the as-deposited mixed layers) deposited on Si substrates without or with a SiO₂ coating.

6.3.2 Effect of Bi³⁺ Concentration

The Bi³⁺ ions dissolved in the electrolyte can enhance the anodic stripping peak currents of the heavy metals as shown in Fig. 6-23, where the anodic stripping peak currents of the Pb²⁺ ions measured with a Bi/graphene electrode are almost linearly proportional to the Bi³⁺ concentrations. In Fig. 6-23a, the FWHMs and peak positions are all similar with respect to the Bi³⁺ concentrations ranging from 0 to 2.5 μM . According to a previous study [38], Bi³⁺ can also be reduced ($\text{Bi}^{3+} + 3\text{e}^- \rightarrow \text{Bi}^0$) and deposited, together with target metals, on the electrode surface during preconcentration. Thus, those reduced metals can form binary- or multi-component alloys that have a strong adsorptive ability to facilitate the reduction of those target

metal ions. Usually, with the addition of Bi in electrochemical analysis, there is a peak at about -0.1 V in the stripping voltammograms, which is attributed to Bi^{3+} . The Bi^{3+} peak position may overlap with some target metals (e.g., Cu^{2+}) [112], hence, making the detection of such target metals difficult. Nevertheless, the Bi^{3+} stripping peaks shown in Fig. 6-23a have very small amplitudes, which may not fully prevent the electrode from measuring the target metals that have overlapping stripping peaks with Bi at around -0.1 V.

(a)

Fig. 6-23 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb^{2+} ($1 \mu\text{M}$) measured by a Bi/graphene electrode with respect to Bi^{3+} concentrations.

6.3.3 Effects of Preconcentration Potential and Time

Fig. 6-24 shows the anodic stripping peak currents of Pb^{2+} ($1 \mu\text{M}$) measured by a Bi/graphene electrode with respect to the preconcentration potentials with the stripping potential of Pb^{2+} located at around -0.615 V . With relatively high preconcentration potentials ($> -0.7 \text{ V}$), it is difficult for Pb^{2+} to be reduced and deposited on the electrode surface, and thus the anodic stripping currents are near zero (Fig. 6-24b). However, with preconcentration potentials lower than -0.7 V , more Pb^{2+} ions can be reduced to their neutral states ($\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0$), leading to greatly increased anodic stripping peak currents. As shown in Fig. 6-24a, the FWHMs increase from about 0.061 V to 0.079 V with a decreasing preconcentration potentials from -0.8 to -1.2 V , which are still quite small. However, to avoid the hydrogen evolutions ($\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$) that usually occur at a low potential and can reduce the

surface activities of the electrodes, the following analyses will be concentrated on the results measured with the optimized preconcentration potential of -1 V.

(a)

(b)

Fig. 6-24 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb^{2+} ($1 \mu\text{M}$) measured by a Bi/graphene electrode with respect to preconcentration potentials.

Similarly, the preconcentration time is also optimized as shown in Fig. 6-25, where the anodic stripping peak currents are almost linearly proportional to the preconcentration time. This is because with a longer deposition time, more metal ions

can be reduced and deposited on the electrode surface. Then, during the anodic stripping period, those deposited metals are oxidized ($\text{Pb}^0 \rightarrow \text{Pb}^{2+} + 2e^-$), resulting in higher anodic stripping currents. On the other hand, to avoid the oversaturation of the target metals on the electrode surfaces, the preconcentration time is optimized as 180 s.

Fig. 6-25 (a) Stripping voltammograms and (b) anodic stripping peak currents of Pb^{2+} ($1 \mu\text{M}$) measured by a Bi/graphene electrode with respect to preconcentration time.

6.3.4 Calibration Curves Measured by the Bi/Graphene Electrodes

Fig. 6-26a shows the voltammograms for the simultaneous detection of Pb^{2+} (1-1.7 μM), Cd^{2+} (0-0.7 μM) and Cu^{2+} (0-0.7 μM), which are measured with a step increment of 0.1 μM . The Bi/graphene electrode is most sensitive to Pb^{2+} followed by Cu^{2+} and then Cd^{2+} . When the concentration of Cu^{2+} is 0, there is only a small peak located at about -0.05 V, which is attributed to the Bi^{3+} peak. In Fig. 6-26b, both the Cu^{2+} and Cd^{2+} stripping peak currents are almost linearly proportional to their concentrations in the solutions, which can be expressed as:

$$I = 0.29 + 23.5C_{\text{Cd}^{2+}} \quad (6-4)$$

and
$$I = 22.12 + 196.68C_{\text{Cu}^{2+}} \quad (6-5)$$

where I is the anodic stripping peak current in μA , and $C_{\text{Cd}^{2+}}$ and $C_{\text{Cu}^{2+}}$ are the concentrations of Cd^{2+} and Cu^{2+} in μM , respectively. The regression coefficients (R) of the above two equations are 0.936 and 0.998, respectively, indicating the good matches of the above two calibration equations with the experimental results.

(b)

(c)

Fig. 6-26 (a) Stripping voltammograms of Cd^{2+} , Cu^{2+} and Pb^{2+} , and (b-c) anodic stripping peak currents with respect to concentrations of (b) Cd^{2+} and Cu^{2+} , and (c) Pb^{2+} , all measured with a Bi/graphene electrode.

The anodic stripping peak currents of Pb^{2+} also increase with the increasing Pb^{2+} concentrations in the range of 1-1.7 μM as shown in Fig. 6-26c, but not linearly. A possible reason is because of the relatively higher concentrations of Pb^{2+} compared to the concentrations of Cd^{2+} and Cu^{2+} . Hence, the electrode surface can be easily saturated by the deposited Pb^0 , which makes the electrode surface turn to a Pb

covered surface. Therefore, it is deduced that a too long preconcentration time should be avoided for a relatively high target metal concentration in a solution.

6.4 Summary

In this chapter, graphene ultrathin film electrodes fabricated via solid-state carbon diffusion by thermally treating the Ni/a-C bilayers or Ni-C mixed layers were used as electrodes for electrochemical detection of Cu^{2+} , Pb^{2+} and Cd^{2+} ions in acetate buffer solutions without or with modification of conductive PANI porous layers and Bi nanoparticles.

The graphene films fabricated on the Si substrates without a SiO_2 layer were more suitable for electrochemical analysis. The Ni layer thickness and preconcentration potential and time were optimized for the electrochemical analysis. The optimized graphene electrodes showed excellent performance in terms of repeatability, stability and sensitivity (e.g., a detection limit of about 7 nM Pb^{2+}). The graphene electrodes showed a high resistance to surface passivation caused by surface active compounds (e.g., SDS). The graphene electrodes also performed well in the simultaneous detection of Pb^{2+} and Cd^{2+} ions. The interference of Cd^{2+} on the Pb^{2+} anodic stripping peak currents was also investigated.

During the electrochemical detection of Pb^{2+} and Cd^{2+} ions in acetate buffer solutions using the conductive PANI porous layers and Bi nanoparticles modified graphene electrodes, it was observed that the Bi nanoparticles could significantly enhance the sensitivity of the graphene electrodes, while the PANI porous layers

could efficiently suppress the passivation of the electrodes. The anodic stripping peak currents measured with the Bi/PANI/graphene electrodes showed an excellent linear proportionality to the Pb^{2+} concentrations. With the UPD condition, the Bi/PANI/graphene electrodes showed an ultralow detection limit of about 0.33 nM Pb^{2+} .

Chapter 7: Conclusions and Contributions

7.1 Conclusions

PANI coatings and Bi particles were electrodeposited on glassy carbon electrodes to form the PANI/GCE and Bi/PANI/GCE electrodes. The porous PANI interlayers could offer a high specific electrode surface area, diminish accumulating fouling on the electrode surface as caused by the surfactants. Novel MWCNT-PANI nanocomposite coatings offered a possibility to produce three-dimensional nanostructured films that combined the conductivity of PANI with the large surface area and good conductivity of CNTs.

Ni/a-C bilayer thin films were deposited on Si and SiO₂/Si substrates by DC magnetron sputtering deposition followed by rapid thermal processing to produce graphene ultrathin films using a solid-state carbon diffusion method. The formation of graphene films was confirmed with various methods, e.g., FE-SEM, Raman, TEM, XRD, AFM and 4-point probes. The influence of the Si substrate surface condition on the formation of the graphene films was comparatively studied and the results showed that the graphene films fabricated on the Si substrates with a SiO₂ layer had smoother surfaces and less structural defects, and were more suitable for the electrical or optical applications; while the graphene films fabricated on the Si substrates without a SiO₂ layer were rougher with more structural defects, and more suitable for electrochemical analysis. The possible reason was that the SiO₂ layers on the Si substrate surfaces effectively prevented the formation of SiO₂ compounds (or even nanowires), which

could disorder the graphene film structure. Based on the Raman results, the Ni layer thickness was optimized to be about 100 nm. For a thinner (or thicker) Ni layer than 100 nm, not enough (or too much) carbon could dissolve into the thicker Ni layers during heating, leading to the formation of incomplete single-layer graphene films (or thicker graphene films) after rapid cooling.

With graphene films used as working electrode, the Ni layer thickness and preconcentration potential and time were optimized for the electrochemical analysis. The optimized graphene electrodes showed an excellent performance in terms of repeatability, stability and sensitivity (e.g., a detection limit of about 7 nM Pb^{2+}).

The graphene electrodes were further modified with both conductive PANI porous layers and Bi nanoparticles to form Bi/PANI/graphene electrodes. It was observed that the Bi nanoparticles could significantly enhance the sensitivity of the graphene electrodes, while the PANI porous layers could efficiently suppress the passivation of the electrodes. With the UPD condition, the Bi/PANI/graphene electrodes showed an ultralow detection limit of about 0.33 nM Pb^{2+} . The interferences between the multi trace heavy metals (e.g., Cd^{2+} and Pb^{2+}) were also studied.

The graphene thin films were also synthesized using the co-sputtering deposited Ni-C mixed layers. The formation of graphene was confirmed by Raman spectra, and the Si substrate surface conditions (without or with a SiO_2 layer) were investigated. The addition of Bi^{3+} in the electrolyte could greatly enhance the anodic stripping peak currents of the target metal ions. The Bi modified graphene electrodes formed on the

Si substrates were successfully used in the simultaneous detection of the Pb^{2+} , Cd^{2+} and Cu^{2+} ions in the acetate buffer solutions.

The electrochemical analytical performance of the electrodes used in this thesis is summarized in Table 7-1. It can be concluded that PANI and/or Bi modifications can greatly reduce the detection limits and increase the sensitivities of the GCE and graphene electrodes. The graphene electrodes have much better performance than the GCE electrodes. The Bi/PANI/graphene electrodes have even higher detection sensitivities and even lower detection limits.

Table 7-1 Comparison of GCEs and PANI/GCEs

	Detection limit (nM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	<i>R</i>
GCE	133.3	31.90	0.996
PANI/GCE	100	19.45	0.996
Bi/PANI/GCE	16.5	268.2	0.9996
Graphene	7	490	0.997
Bi/PANI/graphene by BD method	0.33	490.12	0.995
Bi/PANI/graphene by UPD method		670	0.996

7.2 Contributions

The PANI and MWCNT-PANI nanocomposite coatings on the GCE electrodes were optimized and studied.

The graphene ultrathin films were fabricated via a novel solid-state carbon diffusion method by thermally treating the sputtering deposited Ni/a-C bilayer thin films. The formation of graphene films was systematically confirmed with various methods. The influence of the Si substrate surface condition on the formation of the

graphene films was comparatively studied and the results showed that the graphene films formed on the SiO₂/Si substrates had less structural disorder, while the graphene films formed on the Si substrates showed a much better performance in electrochemical analysis of trace heavy metals in acetate buffer solutions. The SiO₂ compounds or even nanowires were found on the Si based samples. The effect, reason and possible elimination of the formation of such SiO₂ compounds were discussed. The as-deposited Ni and a-C layer thicknesses were optimized for the fabricated graphene film structure and electroanalytical performance. The graphene electrodes were further modified with both conductive PANI porous layers and Bi nanoparticles to form Bi/PANI/graphene electrodes. It was observed that the Bi nanoparticles could significantly enhance the sensitivity of the graphene electrodes, while the PANI porous layer could efficiently suppress the passivation of the electrodes.

The Ni-C mixed layers coated on Si or SiO₂/Si substrates by co-sputtering were also introduced for the fabrication of graphene film electrodes that were further modified with Bi and had an excellent performance in the simultaneous detection of the Pb²⁺, Cd²⁺ and Cu²⁺ ions.

References

1. Aualiitia, T.U. and W.F. Pickering, *ANODIC-STRIPPING VOLTAMMETRIC STUDY OF THE LABILITY OF CD, PB, CU IONS SORBED ON HUMIC-ACID PARTICLES*. Water Research, 1986. **20**(11): p. 1397-1406.
2. Heitzmann, M., et al., *Voltammetric sensing of trace metals at a poly(pyrrole-malonic acid) film modified carbon electrode*. Electroanalysis, 2005. **17**(21): p. 1970-1976.
3. Achterberg, E.P. and C. Braungardt, *Stripping voltammetry for the determination of trace metal speciation and in-situ measurements of trace metal distributions in marine waters*. Analytica Chimica Acta, 1999. **400**: p. 381-397.
4. Jia, J.B., et al., *Properties of poly(sodium 4-styrenesulfonate)-ionic liquid composite film and its application in the determination of trace metals combined with bismuth film electrode*. Electroanalysis, 2008. **20**(5): p. 542-549.
5. Wang, Z.M., et al., *Bismuth/Polyaniline/Glassy Carbon Electrodes Prepared with Different Protocols for Stripping Voltammetric Determination of Trace Cd and Pb in Solutions Having Surfactants*. Electroanalysis, 2010. **22**(2): p. 209-215.
6. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nature Materials, 2007. **6**(3): p. 183-191.
7. Wang, X., L.J. Zhi, and K. Mullen, *Transparent, conductive graphene electrodes for dye-sensitized solar cells*. Nano Letters, 2008. **8**(1): p. 323-327.
8. Geim, A.K. and P. Kim, *Carbon wonderland*. Scientific American, 2008. **298**(4): p. 90-97.
9. Lin, Y.M., et al., *Operation of Graphene Transistors at Gigahertz Frequencies*. Nano Letters, 2009. **9**(1): p. 422-426.
10. Morozov, S.V., et al., *Giant intrinsic carrier mobilities in graphene and its bilayer*. Physical Review Letters, 2008. **100**(1).
11. Chen, J.H., et al., *Intrinsic and extrinsic performance limits of graphene devices on SiO₂*. Nature Nanotechnology, 2008. **3**(4): p. 206-209.
12. Wang, X.R., et al., *Room-temperature all-semiconducting sub-10-nm graphene nanoribbon field-effect transistors*. Physical Review Letters, 2008. **100**(20).
13. Nair, R.R., et al., *Fine structure constant defines visual transparency of graphene*. Science, 2008. **320**(5881): p. 1308-1308.
14. Lee, C., et al., *Measurement of the elastic properties and intrinsic strength of monolayer graphene*. Science, 2008. **321**(5887): p. 385-388.
15. Hatchett, D.W. and M. Josowicz, *Composites of Intrinsically Conducting Polymers as Sensing Nanomaterials*. Chemical Reviews, 2008. **108**(2): p. 746-769.
16. Novoselov, K.S., et al., *Electric field effect in atomically thin carbon films*. Science, 2004. **306**(5696): p. 666-669.
17. Stankovich, S., et al., *Graphene-based composite materials*. Nature, 2006. **442**(7100): p. 282-286.
18. Novoselov, K.S., et al., *Two-dimensional gas of massless Dirac fermions in graphene*. Nature, 2005. **438**(7065): p. 197-200.
19. Rutter, G.M., et al., *Scattering and interference in epitaxial graphene*. Science, 2007. **317**(5835): p. 219-222.
20. Dato, A., et al., *Substrate-free gas-phase synthesis of graphene sheets*. Nano Letters, 2008.

- 8(7): p. 2012-2016.
21. Zhang, Y.B., et al., *Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices*. Applied Physics Letters, 2005. **86**(7).
 22. Liu, F. and Y. Zhang, *Substrate-free synthesis of large area, continuous multi-layer graphene film*. Carbon, 2010. **48**(9): p. 2394-2400.
 23. Hummers, W.S. and R.E. Offeman, *Preparation of Graphitic Oxide*. Journal of the American Chemical Society, 1958. **80**(6): p. 1339-1339.
 24. Williams, G., B. Seger, and P.V. Kamat, *TiO₂-Graphene Nanocomposites. UV-Assisted Photocatalytic Reduction of Graphene Oxide*. Acs Nano, 2008. **2**(7): p. 1487-1491.
 25. Xu, C., X. Wang, and J. Zhu, *Graphene-Metal Particle Nanocomposites*. The Journal of Physical Chemistry C, 2008. **112**(50): p. 19841-19845.
 26. Liu, J., et al., *Toward a Universal "Adhesive Nanosheet" for the Assembly of Multiple Nanoparticles Based on a Protein-Induced Reduction/Decoration of Graphene Oxide*. Journal of the American Chemical Society, 2010. **132**(21): p. 7279-7281.
 27. Mohanty, N. and V. Berry, *Graphene-Based Single-Bacterium Resolution Biodevice and DNA Transistor: Interfacing Graphene Derivatives with Nanoscale and Microscale Biocomponents*. Nano Letters, 2008. **8**(12): p. 4469-4476.
 28. Lu, C.H., et al., *A Graphene Platform for Sensing Biomolecules*. Angewandte Chemie-International Edition, 2009. **48**(26): p. 4785-4787.
 29. Ohno, Y., et al., *Electrolyte-Gated Graphene Field-Effect Transistors for Detecting pH Protein Adsorption*. Nano Letters, 2009. **9**(9): p. 3318-3322.
 30. Dong, X.C., et al., *Electrical Detection of DNA Hybridization with Single-Base Specificity Using Transistors Based on CVD-Grown Graphene Sheets*. Advanced Materials, 2010. **22**(14): p. 1649-+.
 31. He, S.J., et al., *A Graphene Nanoprobe for Rapid, Sensitive, and Multicolor Fluorescent DNA Analysis*. Advanced Functional Materials, 2010. **20**(3): p. 453-459.
 32. Huang, Y.X., et al., *Nanoelectronic biosensors based on CVD grown graphene*. Nanoscale, 2010. **2**(8): p. 1485-1488.
 33. Li, J., et al., *High-sensitivity determination of lead and cadmium based on the Nafion-graphene composite film*. Analytica Chimica Acta, 2009. **649**(2): p. 196-201.
 34. Tian, Y.Q., N.B. Li, and H.Q. Luo, *Simultaneous Determination of Trace Zinc(II) and Cadmium(II) by Differential Pulse Anodic Stripping Voltammetry Using a MWCNTs-NaDBS Modified Stannum Film Electrode*. Electroanalysis, 2009. **21**(23): p. 2584-2589.
 35. Zhu, W.W., N. Bing, and H.Q. Luo, *Simultaneous determination of chromium(III) and cadmium(II) by differential pulse anodic stripping voltammetry on a stannum film electrode*. Talanta, 2007. **72**(5): p. 1733-1737.
 36. Wang, J., et al., *Bismuth-coated carbon electrodes for anodic stripping voltammetry*. Analytical Chemistry, 2000. **72**(14): p. 3218-3222.
 37. Hocevar, S.B., et al., *A study on operational parameters for advanced use of bismuth film electrode in anodic stripping voltammetry*. Electroanalysis, 2002. **14**(24): p. 1707-1712.
 38. Wang, J., *Stripping analysis at bismuth electrodes: A review*. Electroanalysis, 2005. **17**(15-16): p. 1341-1346.
 39. Kokkinos, C. and A. Economou, *Stripping analysis at bismuth-based electrodes*. Current Analytical Chemistry, 2008. **4**(3): p. 183-190.

40. Bobrowski, A. and J. Zarebski, *Catalytic adsorptive stripping voltammetry at film electrodes*. Current Analytical Chemistry, 2008. **4**(3): p. 191-201.
41. Malakhova, N.A., N.Y. Stojko, and K.Z. Brainina, *Novel approach to bismuth modifying procedure for voltammetric thick film carbon containing electrodes*. Electrochemistry Communications, 2007. **9**(2): p. 221-227.
42. Wang, J., U.A. Kirgoz, and J.M. Lu, *Stripping voltammetry with the electrode material acting as a 'built-in' internal standard*. Electrochemistry Communications, 2001. **3**(12): p. 703-706.
43. Zhu, W.W., N.B. Li, and H.Q. Luo, *Anodic stripping voltammetry determination of Pb(II) and Cd(II) at a bismuth/poly(aniline) film electrode*. Analytical Letters, 2006. **39**(11): p. 2273-2284.
44. Wang, J., et al., *Bismuth-coated screen-printed electrodes for stripping voltammetric measurements of trace lead*. Electroanalysis, 2001. **13**(1): p. 13-16.
45. Hutton, E.A., et al., *Bismuth film electrode for simultaneous adsorptive stripping analysis of trace cobalt and nickel using constant current chronopotentiometric and voltammetric protocol*. Electrochemistry Communications, 2003. **5**(9): p. 765-769.
46. Lin, L., et al., *Catalytic adsorptive stripping determination of trace chromium(VI) at the bismuth film electrode*. Talanta, 2005. **65**(1): p. 144-148.
47. Kefala, G., A. Economou, and A. Voulgaropoulos, *A study of Nafion-coated bismuth-film electrodes for the determination of trace metals by anodic stripping voltammetry*. Analyst, 2004. **129**(11): p. 1082-1090.
48. Adraoui, I., M.E. Rhazi, and A. Amine, *Fibrinogen-coated bismuth film electrodes for voltammetric analysis of lead and cadmium using the batch injection analysis*. Analytical Letters, 2007. **40**(2): p. 349-367.
49. Gouveia-Caridade, C., R. Pauliukaite, and C.M.A. Brett, *Influence of Nafion coatings and surfactant on the stripping voltammetry of heavy metals at bismuth-film modified carbon film electrodes*. Electroanalysis, 2006. **18**(9): p. 854-861.
50. Daniele, S., M.A. Baldo, and C. Bragato, *Recent developments in stripping analysis on microelectrodes*. Current Analytical Chemistry, 2008. **4**(3): p. 215-228.
51. Economou, A., *Bismuth-film electrodes: recent developments and potentialities for electroanalysis*. Trac-Trends in Analytical Chemistry, 2005. **24**(4): p. 334-340.
52. Yang, W.R., et al., *Exploring the use of the tripeptide Gly-Gly-His as a selective recognition element for the fabrication of electrochemical copper sensors*. Analyst, 2003. **128**(6): p. 712-718.
53. Turyan, I. and D. Mandler, *SELF-ASSEMBLED MONOLAYERS IN ELECTROANALYTICAL CHEMISTRY - APPLICATION OF OMEGA-MERCAPTOCARBOXYLIC ACID MONOLAYERS FOR ELECTROCHEMICAL DETERMINATION OF ULTRALOW LEVELS OF CADMIUM(II)*. Analytical Chemistry, 1994. **66**(1): p. 58-63.
54. Steinberg, S. and I. Rubinstein, *ION-SELECTIVE MONOLAYER MEMBRANES BASED UPON SELF-ASSEMBLING TETRADENTATE LIGAND MONOLAYERS ON GOLD ELECTRODES .3. APPLICATION AS SELECTIVE ION SENSORS*. Langmuir, 1992. **8**(4): p. 1183-1187.
55. Baldwin, R.P., J.K. Christensen, and L. Kryger, *VOLTAMMETRIC DETERMINATION OF TRACES OF NICKEL(II) AT A CHEMICALLY MODIFIED ELECTRODE BASED ON DIMETHYLGlyOXIME-CONTAINING CARBON PASTE*. Analytical Chemistry, 1986. **58**(8):

- p. 1790-1798.
56. Etienne, M., J. Bessiere, and A. Walcarius, *Voltammetric detection of copper(II) at a carbon paste electrode containing an organically modified silica*. Sensors and Actuators B-Chemical, 2001. **76**(1-3): p. 531-538.
 57. Guadalupe, A.R. and H.D. Abruna, *ELECTROANALYSIS WITH CHEMICALLY MODIFIED ELECTRODES*. Analytical Chemistry, 1985. **57**(1): p. 142-149.
 58. Turyan, I., M. Atiya, and D. Mandler, *Comparing different approaches for assembling selective electrodes for heavy metals*. Electroanalysis, 2001. **13**(8-9): p. 653-659.
 59. Yang, W.R., J.J. Gooding, and D.B. Hibbert, *Redox voltammetry of sub-parts per billion levels of Cu²⁺ at polyaspartate-modified gold electrodes*. Analyst, 2001. **126**(9): p. 1573-1577.
 60. Wang, B., et al., *Chemical amination of graphene oxides and their extraordinary properties in the detection of lead ions*. Nanoscale, 2011. **3**(12): p. 5059-5066.
 61. Zhou, H., et al., *Sensitive and selective voltammetric measurement of Hg(2+) by rational covalent functionalization of graphene oxide with cysteamine*. Analyst, 2012. **137**(2): p. 305-308.
 62. Li, J. and E. Wu, *Adsorption of hydrogen on porous materials of activated carbon and zeolite NaX crossover critical temperature*. The Journal of Supercritical Fluids, 2009. **49**(2): p. 196-202.
 63. Willemse, C.M., et al., *Metallo-Graphene Nanocomposite Electrocatalytic Platform for the Determination of Toxic Metal Ions*. Sensors, 2011. **11**(4): p. 3970-3987.
 64. Li, J., et al., *Nafion-graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium*. Electrochemistry Communications, 2009. **11**(5): p. 1085-1088.
 65. Li, J., et al., *Nafion-graphene nanocomposite film as enhanced sensing platform for ultrasensitive determination of cadmium*. Electrochemistry Communications, 2009. **11**(5): p. 1085-1088.
 66. Wang, Z.M., et al., *Glassy carbon electrode coated with polyaniline-functionalized carbon nanotubes for detection of trace lead in acetate solution*. Thin Solid Films, 2011. **519**(15): p. 5280-5284.
 67. Wang, Z.M., E.J. Liu, and X. Zhao, *Glassy carbon electrode modified by conductive polyaniline coating for determination of trace lead and cadmium ions in acetate buffer solution*. Thin Solid Films, 2011. **519**(15): p. 5285-5289.
 68. Adraoui, I., et al., *Lead Determination by Anodic Stripping Voltammetry Using a p-Phenylenediamine Modified Carbon Paste Electrode*. Electroanalysis, 2005. **17**(8): p. 685-693.
 69. Zheng, M., et al., *Metal-catalyzed crystallization of amorphous carbon to graphene*. Applied Physics Letters, 2010. **96**(6).
 70. Saenger, K.L., et al., *In situ x-ray diffraction study of graphitic carbon formed during heating and cooling of amorphous-C/Ni bilayers*. Applied Physics Letters, 2010. **96**(15).
 71. Brown, T.L., *Chemistry : the central science*. 11th ed ed[2008], c2009: Pearson Prentice Hall. 147-172.
 72. Settle, F.A., *Handbook of Instrumental Techniques for Analytical Chemistry*1997: Prentice Hall PTR. 57-121.
 73. Brett, C.M.A., *Electroanalysis*1998: Oxford University Press. 88-115.

74. Hupert, M., et al., *Conductive diamond thin-films in electrochemistry*. Diamond and Related Materials, 2003. **12**(10-11): p. 1940-1949.
75. Khun, N.W. and E. Liu, *Effect of Platinum and Ruthenium Incorporation on Voltammetric Behavior of Nitrogen Doped Diamond-Like Carbon Thin Films*. Electroanalysis, 2009. **21**(23): p. 2590-2596.
76. Raven, P.H.R.F.E., Susan E. Eichhorn, *Biology of Plants*. 7 ed 2005, New York: W.H. Freeman and Company Publishers. 115-127.
77. Minear, R.A., *Water analysis*. Vol. 1. 1982-1984: Academic Press. 361.
78. Pacyna, E.G., et al., *Global anthropogenic mercury emission inventory for 2000*. Atmospheric Environment, 2006. **40**(22): p. 4048-4063.
79. Protti, P., *AMEL Electrochemistry*. Introduction to Modern Voltammetric and Polarographic Analysis Techniques 2001. 37.
80. Wang, J., *Stripping Analysis* 1985: Deerfield Beach. 119.
81. Zhang, Z., et al., *Synthesis and Electrochemical Sensing Toward Heavy Metals of Bunch-like Bismuth Nanostructures*. Nanoscale Research Letters, 2010. **5**(2): p. 398-402.
82. Bonet, F., et al., *Electrochemical reduction of noble metal species in ethylene glycol at platinum and glassy carbon rotating disk electrodes*. Solid State Ionics, 1999. **126**(3-4): p. 337-348.
83. Agra-Gutierrez, C., et al., *Anodic stripping voltammetry of copper at insonated glassy carbon-based electrodes: application to the determination of copper in beer*. Analyst, 1999. **124**(7): p. 1053-1057.
84. Robertson, J., *AMORPHOUS-CARBON*. Advances in Physics, 1986. **35**(4): p. 317-374.
85. Jacob, W. and W. Moller, *ON THE STRUCTURE OF THIN HYDROCARBON FILMS*. Applied Physics Letters, 1993. **63**(13): p. 1771-1773.
86. Wang, J., et al., *Glassy carbon paste electrodes*. Electrochemistry Communications, 2001. **3**(4): p. 203-208.
87. Marsh, J.H. and S.W. Orchard, *VOLTAMMETRIC STUDIES OF GLASSY-CARBON ELECTRODES ACTIVATED IN AIR AND STEAM*. Carbon, 1992. **30**(6): p. 895-901.
88. Santos, L.M. and R.P. Baldwin, *ELECTROCATALYTIC RESPONSE OF COBALT PHTHALOCYANINE CHEMICALLY MODIFIED ELECTRODES TOWARD OXALIC-ACID AND ALPHA-KETO ACIDS*. Analytical Chemistry, 1986. **58**(4): p. 848-852.
89. Ye, J.N., R.P. Baldwin, and K. Ravichandran, *INDIRECT ELECTROCHEMICAL DETECTION IN LIQUID-CHROMATOGRAPHY*. Analytical Chemistry, 1986. **58**(11): p. 2337-2340.
90. Wier, L.M., A.R. Guadalupe, and H.D. Abruna, *MULTIPLE-USE POLYMER-MODIFIED ELECTRODES FOR ELECTROANALYSIS OF METAL-IONS IN SOLUTION*. Analytical Chemistry, 1985. **57**(9): p. 2009-2011.
91. Turyan, I., et al., *On-line analysis of mercury by sequential injection stripping analysis (SISA) using a chemically modified electrode*. Electroanalysis, 2001. **13**(1): p. 79-82.
92. Kumara, D. and R.C. Sharma, *European Polymer Journal*. Advances in Conductive Polymers, 1998. **34**(8): p. 1053-1060.
93. Callister, D.W., *Material Science and Engineering: An Introduction*. 6th ed 2003, New York: John Wiley & Sons. 848.
94. Calvert, P., *Electrically Conducting Polymers*. Nature, 1980. **284**(5753): p. 213-215.

95. Du, C., et al., *Morphological behaviour of osteoblasts on diamond-like carbon coating and amorphous C-N film in organ culture*. Biomaterials, 1998. **19**(7-9): p. 651-658.
96. Hussain, A.M.P. and A. Kumar, *Electrochemical Synthesis and Characterization of Chloride Doped Polyaniline*. Bulletin of Materials Science, 2003. **26**(3): p. 329-334.
97. Li, D., J.X. Huang, and R.B. Kaner, *Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications*. Accounts of Chemical Research, 2009. **42**(1): p. 135-145.
98. Inzelt, G., *Simultaneous chronoamperometric and quartz crystal microbalance studies of redox transformations of polyaniline films*. Electrochimica Acta, 2000. **45**(22-23): p. 3865-3876.
99. Inzelt, G., et al., *Electron and proton conducting polymers: recent developments and prospects*. Electrochimica Acta, 2000. **45**(15-16): p. 2403-2421.
100. Dam, M.E.R., et al., *COMPARATIVE-STUDY OF POLYMER-COATED MERCURY FILM ELECTRODES FOR VOLTAMMETRIC ANALYSIS OF LEAD AND CADMIUM IN THE PRESENCE OF SURFACTANTS*. Electroanalysis, 1995. **7**(1): p. 70-78.
101. Genies, E.M., et al., *Polyaniline - A Historical Survey*. Synthetic Metals, 1990. **36**(2): p. 139-182.
102. Sazou, D. and C. Georgolios, *Formation of conducting polyaniline coatings on iron surfaces by electropolymerization of aniline in aqueous solutions*. Journal of Electroanalytical Chemistry, 1997. **429**(1-2): p. 81-93.
103. de Barros, R.A. and W.M. de Azevedo, *Polyaniline/silver nanocomposite preparation under extreme or non-classical conditions*. Synthetic Metals, 2008. **158**(21-24): p. 922-926.
104. Zhang, L., C. Zhang, and J. Lian, *Electrochemical synthesis of polyaniline nano-networks on p-aminobenzene sulfonic acid functionalized glassy carbon electrode: Its use for the simultaneous determination of ascorbic acid and uric acid*. Biosensors and Bioelectronics, 2008. **24**(4): p. 690-695.
105. Cruz-Silva, R., et al., *Electrochemical polymerization of an aniline-terminated self-assembled monolayer on indium tin oxide electrodes and its effect on polyaniline electrodeposition*. Thin Solid Films, 2008. **516**(15): p. 4793-4802.
106. Zarbin, A.J.G., M.A. De Paoli, and O.L. Alves, *Nanocomposites Glass Conductive Polymers*. Synthetic Metals, 1999. **99**(3): p. 227-235.
107. Economou, A., *Electrochemical Stripping Analysis*. Current Analytical Chemistry, 2008. **4**(3): p. 168-169.
108. Hocevar, S.B., et al., *Potentiometric stripping analysis at bismuth-film electrode*. Electroanalysis, 2002. **14**(2): p. 112-115.
109. Lin, L., et al., *Adsorptive stripping voltammetric measurements of trace uranium at the bismuth film electrode*. Analytica Chimica Acta, 2005. **535**(1-2): p. 9-13.
110. Shenderova, O.A., V.V. Zhirnov, and D.W. Brenner, *Carbon Nanostructures*. Critical Reviews in Solid State and Materials Sciences, 2002. **27**(3-4): p. 227-356.
111. Rao, C.N.R., et al., *Graphene: The New Two-Dimensional Nanomaterial*. Angewandte Chemie-International Edition, 2009. **48**(42): p. 7752-7777.
112. Kuzmenko, A.B., et al., *Universal Optical Conductance of Graphite*. Physical Review Letters, 2008. **100**(11): p. 117401.
113. Kim, D.K., K.W. Oh, and S.H. Kim, *Synthesis of Polyaniline/Multiwall Carbon Nanotube Composite via Inverse Emulsion Polymerization*. Journal of Polymer Science Part B-Polymer

- Physics, 2008. **46**(20): p. 2255-2266.
114. Chen, G.Z., et al., *Carbon nanotube and polypyrrole composites: Coating and doping*. Advanced Materials, 2000. **12**(7): p. 522-526.
 115. Tu, W.W., J.P. Lei, and H.X. Ju, *Noncovalent nanoassembly of porphyrin on single-walled carbon nanotubes for electrocatalytic reduction of nitric oxide and oxygen*. Electrochemistry Communications, 2008. **10**(5): p. 766-769.
 116. Du, P., et al., *Single-walled carbon nanotubes functionalized with poly(nile blue A) and their application to dehydrogenase-based biosensors*. Electrochimica Acta, 2007. **53**(4): p. 1811-1823.
 117. Gao, X.H., et al., *Carbon nanotubes/poly(1,2-diaminobenzene) nanoporous composite film electrode prepared by multipulse potentiostatic electropolymerisation and its application to determination of trace heavy metal ions*. Electroanalysis, 2006. **18**(5): p. 485-492.
 118. Zhu, L.D., et al., *Amperometric glucose biosensors based on integration of glucose oxidase onto Prussian blue/carbon nanotubes nanocomposite electrodes*. Electroanalysis, 2006. **18**(18): p. 1842-1846.
 119. Liu, G.D., et al., *Ultrasensitive voltammetric detection of trace heavy metal ions using carbon nanotube nanoelectrode array*. Analyst, 2005. **130**(7): p. 1098-1101.
 120. Pan, D.W., et al., *Fabrication and Characterization of Carbon Nanotube-Hydroxyapatite Nanocomposite: Application to Anodic Stripping Voltammetric Determination of Cadmium*. Electroanalysis, 2009. **21**(8): p. 944-952.
 121. Morton, J., et al., *Detection of Trace Heavy Metal Ions Using Carbon Nanotube-Modified Electrodes*. Electroanalysis, 2009. **21**(14): p. 1597-1603.
 122. Goyer, R.A., *LEAD TOXICITY - CURRENT CONCERNS*. Environmental Health Perspectives, 1993. **100**: p. 177-187.
 123. Wang, Z. and E. Liu, *Graphene ultrathin film electrode for detection of lead ions in acetate buffer solution*. Talanta, 2013. **103**(0): p. 47-55.
 124. Shim, Y.B., M.S. Won, and S.M. Park, *ELECTROCHEMISTRY OF CONDUCTIVE POLYMERS-VIII - INSITU SPECTROELECTROCHEMICAL STUDIES OF POLYANILINE GROWTH MECHANISMS*. Journal of the Electrochemical Society, 1990. **137**(2): p. 538-544.
 125. Wang, J., et al., *Effect of surface-active compounds on the stripping voltammetric response of bismuth film electrodes*. Electroanalysis, 2001. **13**(14): p. 1153-1156.
 126. Robertson, J., *Diamond-like amorphous carbon*. Materials Science & Engineering R-Reports, 2002. **37**(4-6): p. 129-281.
 127. Sullivan, J.P., T. Friedmann, and A. Baca, *Stress relaxation and thermal evolution of film properties in amorphous carbon*. Journal of Electronic Materials, 1997. **26**(9): p. 1021-1029.
 128. McCulloch, D.G., et al., *Mechanisms for the behavior of carbon films during annealing*. Physical Review B, 2004. **70**(8).
 129. Ferrari, A.C., et al., *Stress reduction and bond stability during thermal annealing of tetrahedral amorphous carbon*. Journal of Applied Physics, 1999. **85**(10): p. 7191-7197.
 130. Kalish, R., et al., *Thermal stability and relaxation in diamond-like-carbon. A Raman study of films with different sp(3) fractions (ta-C to a-C)*. Applied Physics Letters, 1999. **74**(20): p. 2936-2938.
 131. Kang, H.C., et al., *Epitaxial graphene field-effect transistors on silicon substrates*. Solid-State Electronics, 2010. **54**(9): p. 1010-1014.

132. Prawer, S., et al., *Systematic variation of the Raman spectra of DLC films as a function of $sp(2):sp(3)$ composition*. Diamond and Related Materials, 1996. **5**(3-5): p. 433-438.
133. Abrasonis, G., et al., *Growth regimes and metal enhanced 6-fold ring clustering of carbon in carbon-nickel composite thin films*. Carbon, 2007. **45**(15): p. 2995-3006.
134. Tan, C.W.T.C.W., et al., *Microstructure and through-film electrical characteristics of vertically aligned amorphous carbon films*. Diamond and Related Materials, 2011. **20**(3): p. 290-293.
135. Dai, B.Y., et al., *Rational design of a binary metal alloy for chemical vapour deposition growth of uniform single-layer graphene*. Nature Communications, 2011. **2**.
136. Hofrichter, J., et al., *Synthesis of Graphene on Silicon Dioxide by a Solid Carbon Source*. Nano Letters, 2010. **10**(1): p. 36-42.
137. Takeuchi, H., et al., *Thermal budget limits of quarter-micrometer foundry CMOS for post-processing MEMS devices*. Ieee Transactions on Electron Devices, 2005. **52**(9): p. 2081-2086.
138. Pan, Z.W., et al., *Molten gallium as a catalyst for the large-scale growth of highly aligned silica nanowires*. Journal of the American Chemical Society, 2002. **124**(8): p. 1817-1822.
139. Elechiguerra, J.L., J.A. Manriquez, and M.J. Yacaman, *Growth of amorphous SiO₂ nanowires on Si using a Pd/Au thin film as a catalyst*. Applied Physics a-Materials Science & Processing, 2004. **79**(3): p. 461-467.
140. Xiao, Z.D., et al., *High-density, aligned SiO₂ nanowire arrays: Microscopic imaging of the unique growth style and their ultraviolet light emission properties*. Journal of Physical Chemistry B, 2006. **110**(32): p. 15724-15728.
141. Lin, Y.H., et al., *Structure and characterization of the multilayered Ti-DLC films by FCVA*. Diamond and Related Materials, 2010. **19**(7-9): p. 1034-1039.
142. Cancado, L.G., et al., *General equation for the determination of the crystallite size L_a of nanographite by Raman spectroscopy*. Applied Physics Letters, 2006. **88**(16).
143. Subrahmanyam, K.S., et al., *A study of graphenes prepared by different methods: characterization, properties and solubilization*. Journal of Materials Chemistry, 2008. **18**(13): p. 1517-1523.
144. Mazzamuto, F., et al., *Edge shape effect on vibrational modes in graphene nanoribbons: A numerical study*. Journal of Applied Physics, 2011. **109**(6).
145. Lee, Y., et al., *Wafer-Scale Synthesis and Transfer of Graphene Films*. Nano Letters, 2010. **10**(2): p. 490-493.
146. Das, A., B. Chakraborty, and A.K. Sood, *Raman spectroscopy of graphene on different substrates and influence of defects*. Bulletin of Materials Science, 2008. **31**(3): p. 579-584.
147. Gupta, A., et al., *Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films*. Nano Letters, 2006. **6**(12): p. 2667-2673.
148. Li, J., et al., *High-sensitivity determination of lead and cadmium based on the Nafion-graphene composite film*. Analytica Chimica Acta, 2009. **649**(2): p. 196-201.
149. Hojati-Talemi, P. and G.P. Simon, *Preparation of graphene nanowalls by a simple microwave-based method*. Carbon, 2010. **48**(14): p. 3993-4000.
150. Mazzamuto, F.M.F., et al., *Edge shape effect on vibrational modes in graphene nanoribbons: A numerical study*. Journal of Applied Physics, 2011. **109**(6).
151. Sedenkova, I., et al., *Conformational transition in polyaniline films - Spectroscopic*

- conductivity studies of ageing. *Polymer Degradation and Stability*, 2008. **93**(2): p. 428-435.
152. Beams, R., L.G. Cancado, and L. Novotny, *Low Temperature Raman Study of the Electron Coherence Length near Graphene Edges*. *Nano Letters*, 2011. **11**(3): p. 1177-1181.
 153. Stolyarova, E., et al., *Observation of graphene bubbles and effective mass transport under graphene films*. *Nano letters*, 2008. **9**(1): p. 332-337.
 154. Hu, S., et al., *Electrochemical detection of rutin with a carbon ionic liquid electrode modified by Nafion, graphene oxide and ionic liquid composite*. *Microchimica Acta*, 2012. **178**(1-2): p. 211-219.
 155. Choi, J., H. Lee, and S. Kim, *Atomic-Scale Investigation of Epitaxial Graphene Grown on 6H-SiC(0001) Using Scanning Tunneling Microscopy and Spectroscopy*. *Journal of Physical Chemistry C*, 2010. **114**(31): p. 13344-13348.
 156. Nandamuri, G., S. Roumimov, and R. Solanki, *Remote plasma assisted growth of graphene films*. *Applied Physics Letters*, 2010. **96**(15).
 157. Herrero, E., L.J. Buller, and H.D. Abruna, *Underpotential deposition at single crystal surfaces of Au, Pt, Ag and other materials*. *Chemical Reviews*, 2001. **101**(7): p. 1897-1930.
 158. Yamaguchi, H., et al., *Highly Uniform 300 mm Wafer-Scale Deposition of Single and Multilayered Chemically Derived Graphene Thin Films*. *Acs Nano*, 2010. **4**(1): p. 524-528.
 159. Ahmad, N. and A.G. MacDiarmid, *Inhibition of corrosion of steels with the exploitation of conducting polymers*. *Synthetic Metals*, 1996. **78**(2): p. 103-110.
 160. Fahlman, M., S. Jasty, and A.J. Epstein, *Corrosion protection of iron/steel by emeraldine base polyaniline: An X-ray photoelectron spectroscopy study*. *Synthetic Metals*, 1997. **85**(1-3): p. 1323-1326.
 161. Krishna, M.V.B., et al., *Preconcentration and speciation of inorganic and methyl mercury in waters using polyaniline and gold trap-CVAAS*. *Talanta*, 2005. **68**(2): p. 329-335.
 162. Endo, N., et al., *Adsorption of trace metal ions in aqueous solution onto polyaniline poly(vinylalcohol) composite colloid*. *Transactions of the Materials Research Society of Japan*, Vol 31, No 2, ed. S. Somiya and M. Doyama. Vol. 31. 2006, Amsterdam: Elsevier Science Bv. 337-340.
 163. Trchova, M. and J. Stejskal, *Polyaniline: The infrared spectroscopy of conducting polymer nanotubes (IUPAC Technical Report)*. *Pure and Applied Chemistry*, 2011. **83**(10): p. 1803-1817.
 164. Kang, E.T., K.G. Neoh, and K.L. Tan, *Polyaniline: A polymer with many interesting intrinsic redox states*. *Progress in Polymer Science*, 1998. **23**(2): p. 277-324.
 165. Surwade, S.R., et al., *Oligoaniline intermediates in the aniline-peroxydisulfate system*. *Synthetic Metals*, 2009. **159**(5-6): p. 445-455.
 166. Stejskal, J., et al., *The genesis of polyaniline nanotubes*. *Polymer*, 2006. **47**(25): p. 8253-8262.

Appendix 1: Standard Redox Potentials of Some Common Heavy Metals at 25 °C

Standard Reduction Potentials at 298K, 1M, 1atm

	HALF-REACTION	E° (V)
↑ strong oxidizing agents	$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+2.87
	$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.07
	$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
	$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.77
	$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$	+1.70
	$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
	$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
	$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
	$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.36
	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
	$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.23
	$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.23
	$\text{Br}_2(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	+1.07
	$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.96
	$2 \text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
	$\text{Hg}_2^{2+} + 2 \text{e}^- \rightarrow 2 \text{Hg}(\text{l})$	+0.85
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
	$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
	$\text{MnO}_4^-(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 3 \text{e}^- \rightarrow \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$	+0.59
↓ strong reducing agents	$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.53
	$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.40
	$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
	$\text{AgCl}(\text{s}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
	$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{SO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.20
	$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightarrow \text{Cu}^+(\text{aq})$	+0.15
	$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
	$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
	$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
	$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
	$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
	$\text{Co}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
	$\text{PbSO}_4(\text{s}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
	$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
	$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
	$\text{Cr}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
	$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.83
	$\text{Mn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.18
	$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
	$\text{Be}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Be}(\text{s})$	-1.85
	$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
	$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
	$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
	$\text{Sr}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
	$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
	$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.93
	$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05

Appendix 2: Binary Phase Diagram of Ni-C

Appendix 3: Nernst Equation and Its Limitations

Nernst Equation

In electrochemistry, the Nernst equation as shown in Eq.A3-1 is an equation which can be used (in conjunction with other information) to determine the equilibrium reduction potential of a half-cell. It can also be used to determine the total voltage (electromotive force) for a full electrochemical cell. It is named after the German physical chemist who first formulated it, Walther Nernst.

$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{a_{red}}{a_{ox}} \right) = E^0 + \frac{RT}{nF} \ln \left(\frac{a_{ox}}{a_{red}} \right) \quad (\text{A3-1})$$

where:

- E^0 is the standard redox potential, as shown in Appendix 1;
- R is the universal gas constant: $R = 8.314472 \text{ JK}^{-1}\text{mol}^{-1}$;
- T is the absolute temperature, with unit of K;
- n is the number of electrons transferred in the cell reaction;
- $F = 9.64853399 \times 10^4 \text{ Cmol}^{-1}$ is the Faraday constant, the number of coulombs per mole of electrons;
- a is the chemical activity for the relevant species. $a_X = \gamma_X \bullet C_X$, where γ_X is the activity coefficient of species X , and C_X is the concentration of X . Since activity coefficients tend to unity at low concentrations, activities in the Nernst equation are frequently replaced by simple concentrations;
- ox and red stand for oxidizer and reducer, respectively: $ox + ne^- \leftrightarrow red$.

At room temperature ($T = 298.15 \text{ K}$),

$$\frac{RT}{F} \ln 10 \approx 0.059 \quad (\text{A3-2})$$

$$\text{So } E = E^0 - \frac{0.0591}{n} \log \left(\frac{[red]}{[ox]} \right) = E^0 + \frac{0.0591}{n} \log \left(\frac{[ox]}{[red]} \right) \quad (\text{A3-3})$$

For example for the dissolution of metallic copper in the cell with concentrations

$[H^+] = 0.01 \text{ M}$ and $[Cu^{2+}] = 0.1 \text{ M}$:

Half cell anode reaction equation:

receiving electrons;

$$\begin{aligned} E_{anode} &= E_{H_2/H^+}^0 + \frac{0.0591}{n} \log \left(\frac{[H^+]^2}{P_{H_2}} \right) = 0 + \frac{0.0591}{2} \log \left(\frac{[H^+]^2}{1} \right) \\ &= \frac{0.0591}{2} \log \left(\frac{0.01^2}{1} \right) = -0.1182 \text{ (V)} \end{aligned} \quad (\text{A3-5})$$

Half cell cathode reaction equation:

releasing electrons;

$$\begin{aligned} E_{cathode} &= E_{Cu^{2+}/Cu}^0 + \frac{0.0591}{n} \log \left(\frac{[Cu^{2+}]}{a_{Cu}} \right) = 0.337 + \frac{0.0591}{2} \log \left(\frac{[Cu^{2+}]}{1} \right) \\ &= 0.337 + \frac{0.0591}{2} \log \left(\frac{0.1}{1} \right) = 0.337 - 0.0296 = 0.307 \text{ (V)} \end{aligned} \quad (\text{A3-7})$$

$$\Rightarrow E = E_{cathode} - E_{anode} = 0.307 - (-0.1182) = 0.426 \text{ (V)}. \quad (\text{A3-8})$$

Or, in another method using the full cell equation:

$$\begin{aligned} \Rightarrow E &= E_{cathode} - E_{anode} \\ &= \left\{ E_{Cu^{2+}/Cu}^0 + \frac{0.0591}{n} \log \left(\frac{[Cu^{2+}]}{a_{Cu}} \right) \right\} - \left\{ E_{H_2/H^+}^0 + \frac{0.0591}{n} \log \left(\frac{[H^+]^2}{P_{H_2}} \right) \right\} \\ &= \{ E_{Cu^{2+}/Cu}^0 - E_{H_2/H^+}^0 \} + \frac{0.0591}{n} \left\{ \log \left(\frac{[Cu^{2+}]}{a_{Cu}} \right) - \log \left(\frac{[H^+]^2}{P_{H_2}} \right) \right\} \\ &= (E_{Cu^{2+}/Cu}^0 - E_{H_2/H^+}^0) + \frac{0.0591}{n} \log \left(\frac{[Cu^{2+}] \times P_{H_2}}{a_{Cu} \times [H^+]^2} \right) \\ &= (0.337 - 0) + \frac{0.0591}{2} \log \left(\frac{0.1 \times 1}{1 \times 0.01^2} \right) = 0.337 + 0.0887 = 0.426 \text{ (V)} \end{aligned} \quad (\text{A3-10})$$

Limitations of Nernst Equation

In dilute solutions, the Nernst equation can be expressed directly in terms of concentrations (since activity coefficients are close to unity). But at higher concentrations, the true activities of the ions must be used. This complicates the use of the Nernst equation, since estimation of non-ideal activities of ions generally requires experimental measurements.

The Nernst equation also only applies when there is no net current flow through the electrode. The activity of ions at the electrode surface changes when there is current flow, and there are additional overpotential and resistive loss terms which contribute to the measured potential.

At very low concentrations of the potential determining ions, the potential predicted by Nernst equation approaches towards $\pm\infty$. This is physically meaningless because, under such conditions, the exchange current density becomes very low, and then other effects tend to take control of the electrochemical behavior of the system.