Electrodeposition of conducting coating on insulator substrate

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NANYANG
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**ELECTRODEPOSITION OF CONDUCTING COATING ON
INSULATOR SUBSTRATE**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

ELECTRODEPOSITION OF CONDUCTING COATING ON INSULATOR SUBSTRATE

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2016

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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Abstract

Electrochemical deposition is widely employed for active or functional coatings on conductive substrates. The need of conductive substrate restricts the use of electrodeposition on insulator surfaces with the exception of electroless deposition which is generally used for deposition of metals and lacks in-situ control. The emergence of deformable and wearable electronics device has prompted the search for coating methods on foldable and flexible surfaces which may not be conductive, in order to meet the rising demand of the modern wearable electronic devices requirements.

Under specific non-equilibrium conditions, space charge dominated electrodeposition has been earlier reported on insulators, with prior 2 nm thick discontinuous gold coating. In this work, we employ pulse electrodeposition (short alternating pulse current or potential) to provide high electric field in proximity configuration to enable the space charge dominated mechanism for electrodeposition on insulator (EDI) without metal precoating. A continuous nanofibrous polyaniline film was successfully coated onto insulating cellulose paper, glass, polyester and PET. This approach does not require the use of buffer or catalyst and it possesses potential for possible large scale fabrication. The samples were characterized using Scanning Electron Microscopy, Raman Spectroscopy and Fourier transform infrared spectroscopy.

To demonstrate the vast potential of this EDI method, the polyaniline coated on insulator substrates using EDI were fabricated into functional gas sensors that exhibit quick response to low concentration of NO₂ (5 ppm).

Abstract

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Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Figure Captions	ix
Abbreviations	xi
Chapter 1 Introduction	1
1.1 Hypothesis (science)/Problem Statement (engineering)	1
1.2 Objectives and Scope	3
1.3 Dissertation Overview	3
1.4 Findings and Outcomes/Originality	4
References	4
Chapter 2 Literature Review	5
2.1 Overview	5
2.1.1 Electrochemical Deposition	5
2.1.2 Polyaniline	9
2.1.3 Gas Sensor	11
References	12
Chapter 3 Experimental Methodology (typically 20 – 30 pages)	13

3.1	Rationale for selection of Methods/Materials/Simulations, etc	13
3.2	Synthesis.....	14
3.2.1	Nanocellulose.....	14
3.2.2	Electrodeposition	14
3.2.3	Electrodeposition	15
3.3	Characterization	15
3.4	Device fabrication	16
	References.....	17
Chapter 4	Electrodeposition on Insulator.....	19
4.1	Introduction	19
4.2	Experimental Methods	20
4.2.1	Electrodeposition	21
4.2.2	Fourier Transform Infrared (FTIR) Spectroscopy	21
4.2.3	Raman spectroscopy	21
4.3	EDI of Polyaniline on Insulator	21
4.3.1	EDI on various Insulator	21
4.3.2	Fourier Transform Infrared (FTIR) Spectroscopy	23
4.3.3	Raman spectroscopy	24
4.3.4	Scanning Electron microscopy	25
4.4	EDI Gold on Insulator	27
4.3.1	EDS of Gold.....	28
	References.....	28

Chapter 5	Applications of Electrodeposition on Insulators	29
5.1	Introduction	29
5.2	Experimental Methods	30
4.2.1	Fabrication of Gas sensor Device	30
5.3	Gas sensing of Polyaniline	31
5.3	Gas sensing of Polyaniline	33
Chapter 6	Other Applications	35
6.1	Introduction	35
6.2	Experimental Methods	36
4.2.1	Modified EDI	36
6.3	EDI Polyaniline	36
References		37
Chapter 7	Discussion and Future Work	38
7.1	General Discussion	39
7.1.1	Sub Discussion 1	39
References		41

Figure Captions

- Figure 1.1** Classification of electrochemical deposition
- Figure 2.1** Thin Electrochemical setup for electrodeposition on insulator
- Figure 2.2** (a) electrodeposition on insulator with buffer layer (b) electrodeposition on insulator without buffer layer
- Figure 2.3** Thin electrochemical setup for -4°C electrodeposition
- Figure 2.4** Oxidization states and doped states of polyaniline
- Figure 2.5** (a) Polyaniline electrodeposited via pulse electrodeposition (b) Polyaniline electrodeposited via cyclic voltammetry
- Figure 2.6** List of hazardous gas and the acceptable concentration levels
- Figure 2.7** Chemical and biological sensor applications of polyaniline nanofibres
- Figure 3.1** Setup of working electrode for EDI
- Figure 3.2** Schematic diagram of Gas sensor Device
- Figure 3.3** Schematic diagram of Gas sensor testing
- Figure 4.1** (a) Polyaniline/glass (b) Polyaniline/PET (c) Polyaniline/Nanocellulose (d) Polyaniline/Polyester
- Figure 4.2** Raman spectroscopy of polyaniline

Figure 4.3 FTIR Spectra of polyaniline

Figure 4.4 (a) Polyaniline electrodeposited on insulator substrate in 0.1 mol H₂SO₄ (b) Polyaniline electrodeposited on insulator substrate in 0.2 mol H₂SO₄ (c,d) Polyaniline electrodeposited on insulator substrate in 1 mol H₂SO₄

Figure 4.5 FESEM of electrodeposition of polyaniline on surface of polyester substrate (a) Polyaniline electrodeposited on polyester substrate (61x magnification), (b) Polyaniline electrodeposited on polyester substrate (8410x magnification), (c) Polyaniline electrodeposited on polyester substrate (3550x magnification), (d) Polyaniline electrodeposited on polyester substrate (12220x magnification)

Figure 4.6 FESEM of electrodeposition of Gold on polyester substrates (a) gold electrodeposited on polyester substrate (131x magnification) (b) gold electrodeposited on polyester substrate (1330x magnification) (c) gold electrodeposited on polyester substrate (12,080x) (d) gold electrodeposited on polyester substrate (25,270x)

Figure 4.7 FESEM EDX of EDI gold.

Figure 5.1 (a) Gas Sensor device fabricated from polyaniline/nanocellulose (b) Gas Sensor device polyaniline/glass(c) IV graph of gas sensor device (d) FESEM image of polyaniline/glass

Figure 5.2 (a) Response of Polyaniline/Glass to 5 ppm NO₂ (b) Response of polyaniline/NC to 5 ppm NO₂ (c) Response of polyaniline/polyester to 5 ppm NO₂.

Figure 5.3 a) FESEM of electrodeposition of polyaniline on glass substrate using stainless steel mesh as the conductive component of working electrode (b) Optical

microscope image of electrodeposition of polyaniline on glass substrate using stainless steel mesh as the conductive component of working electrode

Abbreviations

DI	De ionized
ECD	Electrodeposition
EDI	Electrodeposition on Insulator
EDS	Energy Dispersive X-ray Spectroscopy
ELD	Electroless Deposition
E_{polym}	Polymerization Potential
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
NC	Nanocellulose
PANI	Polyaniline
PC	Polycarbonate
PED	Pulse Electrodeposition
PET	Polyethylene Terephthalate
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TCE	Transparent Conducting Electrodes
T_{on}	Time on (Deposition Duration)
T_{off}	Time off (Rest Duration)

Abbreviations

Chapter 1

Introduction

This chapter starts off with the hypothesis of this work and fundamentals of electrodeposition. This is followed by the scope and objectives of this work including the summary of subsequent chapters.

1.1 Hypothesis/Problem Statement

Electrochemical deposition has been developed for decades for the ever increasing types of applications in electronic market ranging from micro/nanoelectronics, optics and sensors. Particularly in the semiconductor industries, the fabrication of semiconductor chips evolved over the decades with the incremental amount of transistor within a single chip resulting in drastic decrement of transistor size. This creates challenges for on chip-wiring and therefore electrodeposition of copper is employed as current state of the art technology used in copper metallization of damascene layers [1].

The main driving force for utilization of electrochemical deposition is that it is cheap, convenient, and the coated surface properties can be premeditated by practitioners and in addition, multilayers of nanoscale films can be fabricated, allowing productions of new materials [2, 3].

Electrochemical deposition can generally be classified into electrodeposition and electroless deposition. Electroless depositions employ the spontaneous (autocatalytic, without power supply) redox reactions to deposit metal on conductive or insulator substrates. During electroless deposition, substrates were immersed in solution containing metal ions and with the aid of reductant such as sodium hypophosphite, the metal ions can be reduced into metal particles and deposited on the substrate. Electroless deposition only requires single electrode which both cathodic and anodic reaction occurs on the same electrolyte and electrode interface.

However, it is hard to control the deposition condition in-situ in contrast to electrodeposition in which the current or voltage can be applied to control the deposition in-situ. Electrodeposition can be conducted in 2 or 3 electrodes electrochemical cell consisting of working, counter or reference electrode. During electrodeposition external power supply provides electrons for reduction of metal ions and deposition on working electrode. In contrast to electroless deposition, cathodic reaction occurs on the working electrode while anodic reaction occurs on the counter electrode in the case of electrodeposition of metal. Electrodeposition utilizes external power supply for redox reactions for depositions of metals which therefore restricting its application to conductive substrates [4].

Figure 1: Classification of electrochemical deposition

Apart from deposition of metals, electrodeposition also establishes impeccable means for synthesis of conducting polymers also known as electrochemical polymerization (electropolymerization). In electropolymerization, positive potential is applied near the oxidation potential of monomer (E_{polym}) allowing polymer film to progressively grown on substrate surface [5].

Although electrodeposition on insulators without prior metallization will realize numerous potential application, to date not much research had been reported.

1. Direct electrodeposition on insulator substrate can be achieved without any pretreatment
2. Electrodeposition on insulator will result in the fromation of dendritic structures due to non uniform electric field distribution.

1.2 Objectives and Scope

The objective of this project is to achieve electrodeposition of conductive polyaniline on insulator substrates using a modified deposition condition with space charge mechanism. Gas sensor device will be subsequently fabricated to demonstrate the functionality of the electrodeposited layer on insulator. Measurements of its sensing response and gas detection limit of the devices are conducted.

1.3 Dissertation Overview

Chapter 1 illustrates the rationale of developing electrodeposition on insulators and includes background information of electrodeposition and challenges and limitation of such deposition method.

Chapter 2 provides a literature review of the current progress of electrodeposition on insulators substrate, including the problem faced in electrodeposition on insulator without premetallization and thermal manipulation. This chapter also includes literature review about polyaniline electrochemical properties and the synthesis method.

Chapter 3 provides a comprehensive description of experimental procedures for the fabrication of gas sensor electrodes and devices. Types of equipment and testing parameters will also be included.

Chapter 4 consists of the first part of results and discussion that describes the finding of EDI of polyaniline and gold on different insulator substrates and characterizations of polyaniline coating.

Chapter 5 consists of characterization of polyaniline based gas sensor fabricated from electrodeposited polyaniline on insulator substrates

Chapter 6 summarizes the works on electrodeposition of conductive coating on insulators and the application of the deposited layers.

Chapter 7 provides recommendation and possible further research directions that could benefit this field or generate interest for future development of this field.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Develop electrodeposition on insulator methods directly without deposition of prior conductive layer. Electrodeposition of metal and conducting polymer on insulators were demonstrated in this thesis.
2. Realizing functional polyaniline based gas sensor device on various insulator substrates based on electrodeposition on insulator

References:

- [1] W. Schwarzacher, "Electrodeposition: a technology for the future," *Interface*, vol. 15, pp. 32-35, 2006.
- [2] M. P. M. Schlesinger, *Fundamentals of Electrochemical Deposition* United states of America: John Wiley & Sons, 2006.
- [3] M. Paunovic, M. Schlesinger, and D. D. Snyder, "Fundamental Considerations," in *Modern Electroplating*, ed: John Wiley & Sons, Inc., 2010, pp. 1-32.
- [4] M. Schlesinger, "Electroless and Electrodeposition of Silver," in *Modern Electroplating*, ed: John Wiley & Sons, Inc., 2010, pp. 131-138.
- [5] M. A. Vorotyntsev, V. A. Zinovyeva, and D. V. Konev, "Mechanisms of Electropolymerization and Redox Activity: Fundamental Aspects," in *Electropolymerization*, ed: Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 27-50

Chapter 2

Literature Review

The literature review will be divided into three parts, namely electrochemical deposition on insulator, characteristics of polyaniline and properties of gas sensor. The different synthesis methodology and progress will be discussed in this section.

2.1 Electrochemical deposition

Electrochemical deposition on insulator had been developed a century ago mainly for more artistic relevance purpose. However, more practical applications had begun to emerge in this century. Most methods of deposition required the presence of conductive layers on the insulator substrate in order for electrodeposition to occur. Methods such as graphiting, bronzing and dip coating in metallic solution were reported to be used as surface treatment prior to electrodeposition [2, 4, 6].

Subsequently, since the introduction of electroless plating, many chemical-bath electrolyte compositions and substrates such as polyimide were introduced for metallization of polymer. Detail steps of electroless deposition can be generalized into 5 steps, mainly cleaning, surface modification, sensitization, catalyzing and activating with rinsing in between each step. Electroless deposition of Nickel had been well-studied and commonly used in the industry for improving corrosion and hardness resistance of metallic parts. Due to the long duration of each step and poor adhesion of film and lack in situ control during deposition compared to electrodeposition, several other alternative methods had been created for conventional electrodeposition on insulator [4].

2.1.1 Electrodeposition with prior metallization

One of the main criteria for electrodeposition is that the electrodes need to be conductive in order to receive electrochemical potential from external source which triggers redox reactions to occur on the surface of the substrate. Chazalviel reported electrodeposition as a consequence of the formation of space charge on the growing front of electrodeposits [7]. Space charge is generated due to depletion of anions around the cathodes. This condition can be satisfied with dilute electrolyte, thin electrochemical setup and high electric field. Subsequently, electrodeposition of copper on insulator was reported with the aid of 2 nm of non-continuous and non-conductive gold buffer layers prior to electrodeposition. [8] In addition, 100 nm thick conductive gold coating (gold edge) is coated at the edge of insulator

substrates for electrodeposition to initiate. The cathode and anode were made of wires in contact with the glass slides, at which electrodeposition will start at the cathode and deposit towards the anode and in the process electrodeposition will occur on insulative glass slide.

Figure 1: Thin Electrochemical setup for insulator electrodeposition [8]

However, the disadvantages of this method of electrodeposition are the reliance of buffer layer (a layer of 5 nm thick gold nanoparticles sputtered before electrodeposition) and sputtered 100 nm gold layer at the edge, requiring prior metallization before electrodeposition and the electrodeposits were nanoaggregates only suitable to serve as a seeding layer [8]. No resistance measurement value was reported likely due to the difficulty to form a continuous layer. The effects of buffer layer used in the electrodeposited on insulator was studied and reported subsequently [9]. It is noted that the buffer layer is not a crucial for such electrodeposition but the presence of buffer will greatly improve the uniformity of the electrodeposited layer as shown on figure 2.

Figure 2: (a) electrodeposition on insulator with buffer layer (b) electrodeposition on insulator without buffer layer [9]

Subsequently to eliminate the reliance on buffer layer, a new approach to electrodeposition on insulator was reported. With similar thin electrochemical cell setup and dilute electrolyte but replacing the buffer layer and gold edge with freezing temperature applied during electrodeposition. However, the setback of this setup is that only electrolyte freeze with a single ice nuclei can be used for electrodeposition. This cause a series of repetitive freezing and thawing until single ice nuclei is formed which might be time consuming and not energy efficient. The freezing of electrolytes leaves an ultrathin layer of high concentrated electrolyte on the surface for electrodeposition. The ultrathin layer electrolyte is found to be an important factor for formation of smoother and straighter deposits [10].

2.1.2 Electrodeposition with repetitive thermal manipulation

Figure 3: Thin electrochemical setup for -4°C electrodeposition [10]

Figure 3 shows the electrochemical setup for electrodeposition in -4°C , in the setup 2 glass slides (1&2) are separated by cathode and anode (3&4) wires and placed on top of a Peltier element which controls the temperature of the whole setup. The setup was cooled to -4°C , allowing the electrolyte to freeze partially while electrode still in contact with liquid

electrolyte. The electrolyte will be thawed and freeze until only single or few ice nuclei was formed [10-12].

Usage of buffer layer or freezing electrolyte are condition that might complicate the progress of electrodeposition on insulator into real applications. However, both studies have explained key understanding for electrodeposition on insulators. Firstly, buffer layer shows that the contact of insulator with electrical conductor is crucial for achieving uniform coating. Secondly, ultrathin electrolyte and low temperature will improve electrodeposition coating and higher concentration of electrolyte might work with ultrathin electrolyte. Lastly, no attempts on electrodeposition of continuous conducting polymer layer on insulators were reported.

2.2 Polyaniline

Polyaniline is one of the oldest known conducting polymers which were known as polyaniline black previously before the discovery of its conductivity. Conducting polymer conducts electricity by its conjugated bonds system in the polymeric backbone created by oxidation of the monomer and the polymeric chain [13]. The subsequent doping in acidic medium allows protonation of polyaniline backbone which creates polaron responsible for the electrical conducting properties. Polyaniline consists of 3 distinguishable oxidation states namely, leucoemeraldine, emeraldine and pernigraniline which in leucoemeraldine state polyaniline are fully reduced and pernigraniline fully oxidized. However, polyaniline can only conduct electricity in one of its oxidation state, emeraldine salt, in this state polyaniline is half oxidized and doped in acidic medium [14].

2.2.1 Oxidation states of polyaniline

Figure 4: Oxidation states and doped states of polyaniline

Upon doping, the oxidation state is known as salt while undoped states are known as base. The conducting properties and its tunable conductivities allows polyaniline to be used for various applications including gas sensors, supercapacitors, anti-statics, electrochromics, transparent display, corrosion inhibitors and even electromagnetic interference shielding. Apart from its functionality, facile synthesis methods of polyaniline such as chemical polymerization using oxidant such as ammonium persulfate or electrodeposition were widely used.

2.2.2 Synthesis of polyaniline

Chemical synthesis of nanofibrous polyaniline was also explored with interfacial polymerization where polymerization of polyaniline occurs on the interface of two immiscible liquids.

Alternatively, electrodeposition of polyaniline can be employed to polymerization and directly deposited on ideal conductive substrate. During electrodeposition, anodic oxidation of aniline monomers occurs on inert conductive electrodes with an applied potential or current. Electrodeposition of polyaniline nanofibres can achieve by using pulse galvanostatic electrodeposition. By switching current between deposition current and zero current, polarization between the electrode and electrolyte interface occurs. The duration of deposition and zero current are known as T_{on} and T_{off} respectively [15].

Figure 5: (a) Polyaniline electrodeposited via pulse electrodeposition (b) Polyaniline electrodeposited via cyclic voltammetry [16]

2.3 Gas Sensor

The atmospheric gases that engulf our world encompass different chemical species both essential and hazardous to life forms. While vital gas are required to maintain at adequate levels and hazardous gases such as combustibles hydrocarbon gases, toxic gases, volatile organic compounds and other pollutants are required to keep below certain levels governed by standards. Many of such hazard gas are products of industrial activity and monitoring systems are therefore in demands for both professional and non-professional usage [17, 18].

Figure 6: List of hazardous gas and the acceptable concentration levels [17]

The common materials used for fabrication of gas sensors are metal oxides and conducting polymers. The setback for semiconducting metal oxides gas sensor is the need for high service temperature to enhance sensitivity. Therefore, conducting polymers were studied for its shorter response time, tunable conductivity and low cost [19, 20].

Polyaniline has garnered interest of gas sensor due to its faster response, superior sensitivity and better reversibility over other conducting polymer such as polypyrrole. As mentioned previously, polyaniline resistance varies greatly when emeraldine salt is reduced or oxidized. Therefore a wide range of oxidizing and reducing gas can be detected with sensors fabricated from polyaniline nanofibres [19, 21].

Sensing Material	Diameter (nm)	Analyte	Detection Limit (LOD)	Response Time
Polyaniline/ In_2O_3	90	H_2 , NO_2 , CO	~ 2 ppm	~ 30 s
Polyaniline	30–50	H_2	0.06%	~ 100 s
Polyaniline	60–80	nitrite	5×10^{-6} M	~ 5 s
Polyaniline/Au nanoparticles	30–50	glucose	5×10^{-7} M	~ 5 s
Polyaniline/CSA	~100	H_2	<1%	-
Polyaniline	40–80	NH_3 , HCl, EtOH	~0.5 ppm	~100 s
Polyaniline/Au nanoparticles	80	H_2S , CH_3SH	~1 ppm	~20 s
Polyaniline	30–40	CO	~1 ppm	~100 s
Polyaniline	335	NH_3	0.5 ppm	~75 s
Polyaniline	30–120	HCl, NH_3 , N_2H_4 , CHCl_3 , CH_3OH	100 ppm	2~200 s
SWCNT/Polyaniline	15	NO_2 , H_2S	500 ppb	~10 min
Graphene/Polyaniline	25–50	H_2	-	~1 min
Polyaniline/Au nanoparticles	250–320	H_2S	0.1 ppb	<2 min
polyaniline	100	humidity	-	~1 min
Polyaniline/PVB/PEO	100	humidity	-	~50 s
Polyaniline	-	microRNA	5 fM	30–60 min
polyaniline	~200	<i>Bacillus cereus</i>	~10 CFU/mL	-

Figure 7: Chemical and biological sensor applications of polyaniline nanofibres [20-22]

Reference

- [2] M. P. M. Schlesinger, *Fundamentals of Electrochemical Deposition* United states of America: John Wiley & Sons, 2006.
- [3] M. Paunovic, M. Schlesinger, and D. D. Snyder, "Fundamental Considerations," in *Modern Electroplating*, ed: John Wiley & Sons, Inc., 2010, pp. 1-32.
- [4] M. Schlesinger, "Electroless and Electrodeposition of Silver," in *Modern Electroplating*, ed: John Wiley & Sons, Inc., 2010, pp. 131-138.
- [5] M. A. Vorotyntsev, V. A. Zinovyeva, and D. V. Konev, "Mechanisms of Electropolymerization and Redox Activity: Fundamental Aspects," in *Electropolymerization*, ed: Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 27-50.

- [6] M. Stern and A. L. Geary, "Electrochemical Polarization: I. A Theoretical Analysis of the Shape of Polarization Curves," *Journal of The Electrochemical Society*, vol. 104, pp. 56-63, January 1, 1957 1957.
- [7] J. N. Chazalviel, "Electrochemical aspects of the generation of ramified metallic electrodeposits," *Physical Review A*, vol. 42, pp. 7355-7367, 12/01/ 1990.
- [8] V. Fleury, W. A. Watters, L. Allam, and T. Devers, "Rapid electroplating of insulators," *Nature*, vol. 416, pp. 716-719, 04/18/print 2002.
- [9] P. Andreazza, C. Andreazza-Vignolle, I. Kante, T. Devers, A. Levesque, and L. Allam, "Buffer layer effect in nanostructured tin electrodeposition on insulating and conducting substrates," *Progress in Solid State Chemistry*, vol. 33, pp. 299-308, // 2005.
- [10] Y.-Y. Weng, B. Zhang, S.-J. Fu, M. Wang, R.-W. Peng, G.-B. Ma, *et al.*, "Self-templating growth of copper nanopearl-chain arrays in electrodeposition," *Physical Review E*, vol. 81, p. 051607, 05/25/ 2010.
- [11] B. Zhang, Y.-Y. Weng, X.-P. Huang, M. Wang, R.-W. Peng, N.-B. Ming, *et al.*, "Creating In-Plane Metallic-Nanowire Arrays by Corner-Mediated Electrodeposition," *Advanced Materials*, vol. 21, pp. 3576-3580, 2009.
- [12] S. Zhong, Y. Wang, M. Wang, M.-Z. Zhang, X.-B. Yin, R.-W. Peng, *et al.*, "Formation of nanostructured copper filaments in electrochemical deposition," *Physical Review E*, vol. 67, p. 061601, 06/16/ 2003.
- [13] G. A. Snook, P. Kao, and A. S. Best, "Conducting-polymer-based supercapacitor devices and electrodes," *Journal of Power Sources*, vol. 196, pp. 1-12, 2011.
- [14] S. Stafström, J. L. Brédas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang, *et al.*, "Polaron lattice in highly conducting polyaniline: Theoretical and optical studies," *Physical Review Letters*, vol. 59, pp. 1464-1467, 09/28/ 1987.
- [15] M. S. Chandrasekar and M. Pushpavanam, "Pulse and pulse reverse plating—Conceptual, advantages and applications," *Electrochimica Acta*, vol. 53, pp. 3313-3322, 3/10/ 2008.
- [16] H. H. Zhou, S. Q. Jiao, J. H. Chen, W. Z. Wei, and Y. F. Kuang, "Effects of conductive polyaniline (PANI) preparation and platinum electrodeposition on

- electroactivity of methanol oxidation," *Journal of Applied Electrochemistry*, vol. 34, pp. 455-459, 2004/04/01 2004.
- [17] N. Yamazoe, "Toward innovations of gas sensor technology," *Sensors and Actuators B: Chemical*, vol. 108, pp. 2-14, 7/22/ 2005.
- [18] K. A. Mirica, J. G. Weis, J. M. Schnorr, B. Esser, and T. M. Swager, "Mechanical Drawing of Gas Sensors on Paper," *Angewandte Chemie International Edition*, vol. 51, pp. 10740-10745, 2012.
- [19] K. Potje-Kamloth, "Gas Sensing with Conducting Polymers," in *Electropolymerization*, ed: Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 153-171.
- [20] E. Song and J.-W. Choi, "Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing," *Nanomaterials*, vol. 3, pp. 498-523, 2013.
- [21] J. Qi, X. Xu, X. Liu, and K. T. Lau, "Fabrication of textile based conductometric polyaniline gas sensor," *Sensors and Actuators B: Chemical*, vol. 202, pp. 732-740, 10/31/ 2014.
- [22] X. B. Yan, Z. J. Han, Y. Yang, and B. K. Tay, "NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization," *Sensors and Actuators B: Chemical*, vol. 123, pp. 107-113, 4/10/ 2007.

Chapter 3

Experimental Methodology

In this chapter, the rationale of selecting experimental method studied in this thesis were discussed. The fundamentals and classifications of electrochemical deposition that leads to its strength and limitations will be discussed in this chapter without neglecting the existing and potential applications of electrochemical deposition. In addition, the experimental conditions of electrodepositions and testing were also described.

3.1 Rationale for selecting EDI

Electrodeposition has been widely studied for decades and eventually employed in the semiconductor industry for manufacturing. At the same time, electrodeposition has also been used for development and research of novel materials such as graphene, Molybdenum sulfide and many other materials.

Industries favor electrodeposition as it is a cheap, fast, robust and scalable deposition method favorable for practical application. Electrodeposition is cheaper as it does not require ultra-high vacuum during deposition and it is not a line of sight process. Therefore, it can even form conformal coating on complex shapes. On the other hand, the growth of electrodeposits can also be optimized and controlled down to its morphology, crystallographic orientation and even the chirality.

Electrodeposition belongs to bottom-up process, as the electrodeposit film were assembled and grown from the precursor in the electrolyte triggered by the applied potential.

However, the prospect of electrodeposition has been limited by the reliance on conductive substrate in order for the electrical potential to flow through the electrochemical cell. The rationale for working on EDI is to minimize the limitation of electrodeposition and increase the applications of electrodeposition.

3.2 Synthesis

3.2.1 Synthesis of Nanocellulose

Nanocellulose (NC) was purchased at concentration of 3 wt% in water. Nanocellulose fibre slurry was fabricated using ultramass collider that separates nanofibres from natural plant cellulose by creating large shear zone [23].

NC substrates were made with 0.5 g of NC added to 100 mL of Deionized (DI) water and stirred for 3 hour to ensure proper dispersion of NC. Subsequently, the solution was filtrated through polycarbonate membrane with 0.02 μm pore size via vacuum filtration and dried in oven before peeling out the NC film.

3.2.2 Electrodeposition of Polyaniline

For electrodeposition on insulator, the working electrode was modified with the inclusion of both conducting stainless steel and an insulator substrate.

Figure 8: Setup of working electrode for insulator electrodeposition

3.2.2.1 Electrodeposition of polyaniline on insulator

Polyaniline was synthesized by pulse electrodeposition of stainless steel and insulator substrate in H_2SO_4 electrolyte. The electrolyte solution contains 0.91ml of aniline monomer in 100mL of 1 M H_2SO_4 . Monomer was stirred for one hour in room temperature and insulator substrate was presoaked in electrolyte prior to electrodeposition. The working electrode consists of stainless steel and NC confined by two pieces of glass slides to simulate a thin electrochemical cell. Pulse electrodeposition of polyaniline was conducted with galvanic cycle performed from 0 A to 0.02 A in a Potentiostat/Galvanostat (Solatron cell test system 1470E) with three electrode cell setup. The cell comprises of stainless steel and NC film as working electrode, silver-silver chloride (Ag/AgCl in 3M NaCl) electrode as reference electrode and 20 mm by 10 mm Pt sheet as counter electrode.

3.2.2.1 Electrodeposition of Gold on insulator

Gold coating was synthesized by pulse electrodeposition of stainless and insulator substrate in H_2SO_4 electrolyte. The electrolyte solution contains 0.5 mM of HAuCl_4 in 100 mL of 0.5 M H_2SO_4 . Electrolyte was stirred for one hour in room temperature and insulator substrate was presoaked in electrolyte prior to electrodeposition.

3.3 Material characterization

The morphology of polyaniline and gold films were studied under field emission scanning electron microscope (FESEM, JEOL-6340 &). Resistivity measurements were carried out using 4 point probe (Advanced Instrument Technology, CMT-SR2000N). Oxidation states of polyaniline were determined by Raman spectroscopy (Witec confocal Raman microscopy with laser wavelength of 488 nm).

3.4 Gas sensing device fabrication and testing

The performances of the sensors were evaluated by monitoring the response in the presence of NO_2 gas. Gold electrodes were sputtered onto polyaniline films through a shadow mask at 20 mA for 2 minutes as shown in figure 9. A constant voltage 0.1 V was supplied by Keithley 4200 semiconductor while current were constantly monitored as shown in figure 10, under the presence of 5 ppm of NO_2 gas at the flow rate of 50 cc/min at an interval of 50 s exposure time and 50 s recovery time. The response time was measured based on the total time required for sensor to achieve 90 % change in resistance during adsorption and similarly for recovery time during desorption.

Figure 9: Schematic diagram of Gas sensor Device

Figure 10: Schematic diagram of Gas sensor testing

- [23] "Nature's polymer," *Chemistry & Industry*, vol. 76, pp. 28-31, 2012.
- [2] M. P. M. Schlesinger, *Fundamentals of Electrochemical Deposition* United states of America: John Wiley & Sons, 2006.

Chapter 4

Electrodeposition on insulator

The strategies adopted to realize electrodeposition of polyaniline and gold on various insulators substrates will be discussed in this chapter. Polyaniline were electrodeposited directly on glass, Nanocellulose, polyester and PET substrates to demonstrate potential applications for foldable, wearable and flexible devices. Further characterization were conducted to observe the morphology of electrodeposits and oxidation states of polyaniline samples. The oxidation state of electrodeposit polyaniline were suitable for fabrication of gas sensor device.

4.1 Introduction

A simple electrochemical cell setup was proposed for the electrodeposition of insulators. The aim of this setup is to eliminate the reliance of non-continuous buffer gold coating on insulator substrate and the stringent sub-ambient temperature of electrochemical cell. The modification will reduce process variations and improve industrial relevance. In addition, this proposed cell setup also aims to fabricate actual conductive electrodeposits coating which can be materialized into practical applications and eventually alter the morphology of the resultant deposits.

In most literatures, electrodeposition on insulator employs a typical non-continuous buffer gold layer as the activation sites for heterogeneous nucleation or sub ambient temperature to improve the uniformity of electrodeposits [8-12]. In this proposed setup, the role of gold buffer layer was replaced by aligning the insulator substrate surfaces in proximity with a piece of stainless steel at which electrodeposition was allowed to occur on the interface. In this setup, the entire surface of insulator was placed in proximity with a discrete electrical conductors without the need of sputtered or precoated conductive layer on insulators.

Alternatively, cycles of freezing and thawing of electrolyte were reported to improve electrodeposition on insulator which occurred due to a localized increment in electrolyte concentration in contradiction to Chazaviel model [7]. However, it should be noted that freezing the electrolyte increases the concentration of electrode because of the electrolyte volume reduction. In our proposed setup, the insulator and conductive working electrode were held together leaving only very thin film of electrolyte in between.

4.2 Experimental Methods

4.2.1 Electrodeposition of polyaniline on insulator substrate

Polyaniline was successfully coated on insulator substrate via pulse electrodeposition in room temperature and without any buffer layer. Pulse electrodepositions were conducted with 15,000 cycles of galvanic cycle deposition for duration of 150 seconds at 20 mA.

4.2.2 Electrodeposition of gold on insulator substrate

Gold was electrodeposited on polyester via EDI in 1 M H_2SO_4 and HAuCl_4 salts in room temperature without any buffer layer. The electrodeposition condition were pulse potential at -0.7 V for 1 hour at the frequency of 50 Hz.

4.3 Electrodeposition on insulator

4.3.1 Electrodeposition of polyaniline on insulator

Figure 11(a) Polyaniline deposited on glass (b) Polyaniline deposited on PET (c) Polyaniline deposited on Nanocellulose (d) (i) Polyaniline deposited on Polyester (ii) Bare Polyester

Polyaniline was successfully coated on insulator substrate via pulse electrodeposition in room temperature and without any buffer layer. Pulse electrodepositions were conducted with 15,000 cycles of galvanic cycle deposition for duration of 150 seconds at 20 mA. Polyaniline was then electrodeposited on other insulator substrates like glass, polyester and polyethylene terephthalate (PET) substrate as shown in Figure 11. The ability to deposit on various insulator substrates such as flexible PET, foldable cellulose, wearable polyester and rigid glass illustrate the potential of wide range applications.

Sheet resistance of the polyaniline samples were measured with 4 point probe and the resistances were given between 300-1000 Ω /sq. A large variation in sheet resistance was a direct consequence of the acid molarity, morphological changes and the insulator substrate material.

4.3.2 Raman Spectroscopy of Polyaniline electrodeposits on insulator

Figure 12: Raman spectroscopy of Polyaniline

Raman spectrum for electrodeposited polyaniline on glass is presented in figure 12 for the evaluation of the oxidation state of the electrodeposited polyaniline on insulator. Four peaks can be observed in the spectrum namely 1213 cm^{-1} , 1332 cm^{-1} , 1537 cm^{-1} and 1635 cm^{-1} . Peak from 1213 cm^{-1} represents C-N stretching vibration of C-C in quinone and peak from 1332 cm^{-1} suggests the presence of stretching vibration of CN^+ in polaron. Whereas, peak from 1635 cm^{-1} was contributed by stretching mode in the phenyl rings and peak from 1537 cm^{-1} was contributed by C=C stretching vibration of C-C in quinone.

Peak at 1332 cm^{-1} suggests the presence of polaron which confirms that polyaniline is in protonated emeraldine salt state as shown in figure 4 [24].

4.3.3 FTIR Spectroscopy of Polyaniline

Figure 13: FTIR Spectra of polyaniline on glass

The FTIR spectrum of electrodeposited polyaniline on glass is presented in Figure 13. Absorption peak from 1151 cm^{-1} suggested the presence of C-H bending vibrations and peak from 1501 cm^{-1} was contributed by the presence of C=N stretching of aromatic compounds. While C=C stretching or aromatic nuclei were represented by peak from 1635 cm^{-1} , C-H stretching was represented by peak from 2931 cm^{-1} and N-H stretching was represented by peak around 3400 cm^{-1} . Peaks observed in this spectrum were commonly reported in electrodeposited polyaniline [25].

4.3.4 FESEM of Polyaniline/Nanocellulose

Figure14: (a) Polyaniline electrodeposited on nanocellulose substrate in 0.1 M H₂SO₄ (b) Polyaniline electrodeposited on nanocellulose substrate in 0.2 M H₂SO₄ (c,d) polyaniline electrodeposited on nanocellulose substrate in 1 M H₂SO₄

Polyaniline was observed under FESEM for morphological studies and the images were represented by figure 14. Polyaniline was observed to form uniform coating of nanoaggregates smaller than 50 nm on nanocellulose when electrodeposited in 0.1 M H₂SO₄ which were similar to morphology reported in literature [8, 9].

Morphology of Polyaniline was observed to change when concentration of H₂SO₄ electrolyte increases. Polyaniline nanoaggregates are flattened when the electrolyte concentration increases to 0.2 M and further increment of electrolyte to 1 M results in the formation Polyaniline nanofibres with diameter around 100 nm. Polyaniline was known to form nanofibres in higher electrolyte concentration via pulse electrodeposition while the electrodeposition on insulators typically favors dilute electrolyte (up to 0.1 mol/L) as an important criterion for deposition occur [7, 8]. In our results, the formation of nanofibres

can occur on the insulator at higher electrolyte concentration (at 1 mol/L) in this modified setup. The possible deposition mechanism is that the growing electrodeposits get in contact with the insulator substrates and initiated electrodeposition on insulator surface. At the same time, the resistance also shown improvement as the morphology of polyaniline changes from nanoaggregates (figure 12b: 300 K Ω /sq) to nanofibres (figure 12c, d: 1 K Ω /sq).

4.3.5 FESEM Polyaniline/Polyester

Figure15: FESEM of electrodeposition of polyaniline on surface of polyester substrate (a) Polyaniline electrodeposited on polyester substrate (61x magnification), (b) Polyaniline electrodeposited on polyester substrate (8410x magnification), (c) Polyaniline electrodeposited on polyester substrate (3550x magnification), (d) Polyaniline electrodeposited on polyester substrate (12220x magnification)

Polyaniline was electrodeposited on polyester in 1M H_2SO_4 and it was observed in FESEM for morphological study. When electrodeposition of polyaniline was conducted on insulative polyester substrate as shown in Figure 13a-d, polyaniline electrodeposits were observed to deposit along the polyester fibre. This aspect of electrodeposition on fibrous insulator substrate was not found to be reported previously. Some nanofibre of polyaniline was observed on the surface of the fabric as shown in Figure 13d. Electrodeposition on insulative fibrous substrate shows promising potential as a possible approach for fabrication of free standing and wearable devices.

4.4 EDI Gold on insulator

Figure 16: FESEM of electrodeposition of Gold on polyester substrates (a) gold electrodeposited on polyester substrate (131x magnification) (b) gold electrodeposited on polyester substrate (1330x magnification) (c) gold electrodeposited on polyester substrate (12,080x) (d) gold electrodeposited on polyester substrate (25,270x)

Gold was electrodeposited on polyester via EDI in 1 M H_2SO_4 at -0.7 V for 1 hour at the frequency of 50 Hz. Apart from polyaniline, gold was also electrodeposited to demonstrate the possibility of electrodepositing metallic material on insulator via EDI. Gold nanoparticles and vertical nanorods were observed to be deposited on polyester substrates from FESEM images presented in figure 18a-d. Resistance of the gold coating was measured to be around 300 k Ω /sq.

Figure17: FESEM EDX of EDI gold on Glass

FESEM EDX was performed on samples with Gold electrodeposited on glass via EDI in 1 M H_2SO_4 at -0.7 V for 1 hour at the frequency of 50 Hz. The EDX spectrum verified the presence of gold in the electrodeposit on gold/glass sample.

The vertical gold nanorods are desirable morphology for applications such as energy storage, gas sensing and even amphiphobic coating. The gold coating can be incorporated into the gas sensor device by electrodepositing polyaniline as a core shell engulfing over the vertical nanorods in order to increase surface area of sensing material. As the response time of gas sensors shorten when the surface area of sensing material increases.

Reference

- [7] J. N. Chazalviel, "Electrochemical aspects of the generation of ramified metallic electrodeposits," *Physical Review A*, vol. 42, pp. 7355-7367, 12/01/ 1990.

- [8] V. Fleury, W. A. Watters, L. Allam, and T. Devers, "Rapid electroplating of insulators," *Nature*, vol. 416, pp. 716-719, 04/18/print 2002.
- [9] P. Andreazza, C. Andreazza-Vignolle, I. Kante, T. Devers, A. Levesque, and L. Allam, "Buffer layer effect in nanostructured tin electrodeposition on insulating and conducting substrates," *Progress in Solid State Chemistry*, vol. 33, pp. 299-308, // 2005.
- [10] Y.-Y. Weng, B. Zhang, S.-J. Fu, M. Wang, R.-W. Peng, G.-B. Ma, *et al.*, "Self-templating growth of copper nanoparticle-chain arrays in electrodeposition," *Physical Review E*, vol. 81, p. 051607, 05/25/ 2010.
- [11] B. Zhang, Y.-Y. Weng, X.-P. Huang, M. Wang, R.-W. Peng, N.-B. Ming, *et al.*, "Creating In-Plane Metallic-Nanowire Arrays by Corner-Mediated Electrodeposition," *Advanced Materials*, vol. 21, pp. 3576-3580, 2009.
- [12] S. Zhong, Y. Wang, M. Wang, M.-Z. Zhang, X.-B. Yin, R.-W. Peng, *et al.*, "Formation of nanostructured copper filaments in electrochemical deposition," *Physical Review E*, vol. 67, p. 061601, 06/16/ 2003.
- [24] V. P. J. Vivekanandan, A. Mahudewaran and P. S. Vijayanand, "Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods," *Scholars research library*, 2011.

Chapter 5

Application of Electrodeposition on insulators

The motivation of developing electrodeposition on insulators is to overcome the limitation of electrodeposition and increase the potential applications of such deposition methods. Some of the potential applications of EDI will be discussed in this chapter. In particular, fabrication of polyaniline samples on glass, NC and polyester into functional gas sensor devices and evaluate its performance.

5.2 Experimental methods

To demonstrate one of the potential applications of EDI, polyaniline deposited on glass, nanocellulose and polyester via EDI were fabricated into gas sensor devices. Polyaniline coating was deposited on the insulator substrates in 1 M H_2SO_4 electrolyte for 200 seconds at a frequency of 100 Hz and current densities of 20 mA in room temperature. Gold electrodes were then sputtered onto the polyaniline surface as illustrated in figure 9. The aim is to develop and demonstrate the polyaniline electrodeposited via EDI as functional gas sensor.

The performances of the sensors were evaluated by monitoring the response in the presence of NO_2 gas. Gold electrodes were sputtered onto polyaniline films through a shadow mask at 20 mA for 2 minutes as shown in figure 9. A constant voltage 0.1 V was supplied by Keithley 4200 semiconductor while current were constantly monitored as shown in figure 10, under the presence of 5 ppm of NO_2 gas at the flow rate of 50 cc/min at an interval of 50 s exposure time and 50 s recovery time. The response time was measured based on the total time required for sensor to achieve 90 % change in resistance during adsorption and similarly for recovery time during desorption.

5.3.1 Gas sensor device

Figure 18: (a) Gas Sensor device fabricated from polyaniline/nanocellulose (b) Gas Sensor device polyaniline/glass (c) IV graph of gas sensor device (d) FESEM image of polyaniline/glass

The gas sensor devices were successfully fabricated as shown in figure 18a,b. Devices were observed under optical microscope to ensure that there is no contact between the gold electrodes and optical microscope measurement confirms that electrodes were 100 μm apart. The IV graph represented in figure 18c suggests that the two-terminal resistor device is stable, demonstrating stable resistance across electrode of 1 kΩ between -0.1 V to +0.1 V potential.

5.3.2 Gas sensing response

Figure 19: (a) Response of Polyaniline/Glass to 5 ppm NO_2 (b) Response of Polyaniline/Nanocellulose to 5 ppm NO_2 (c) Response of Polyaniline /polyester to 5 ppm NO_2

We have successfully fabricated the electrodeposited film into functional gas sensor for detection of gaseous NO_2 in room temperature. The testing was conducted in enclosed chamber with NO_2 exposure time of 50 s (gas on) follow by 50 s of N_2 gas purging (gas off).

Figure 19a-c shows the resistance change of polyaniline on different insulator substrates when exposed to 5 ppm of NO_2 gas. Upon exposure of NO_2 gas, the resistance of

polyaniline increases instantly and recovers when the NO₂ gas valve was turned off, the behavior of emeraldine salt polyaniline is consistent with literature. During the exposure of the oxidizing NO₂ gas, protonated polyaniline in emeraldine salt state will be slightly oxidized and results in an incremental resistance [22]. All the sample shows fast response to 5 ppm NO₂ gas in comparison to literature show in Table 1 [26-30], the response time of polyaniline/glass, polyaniline/ nanocellulose and polyaniline/ polyester gas sensor are 10 s, 15 s and 27 s. The response time for polyaniline /polyester sample (27 s) is noticeably longer than polyaniline/glass (10 s) and polyaniline/NC (15 s) samples possibly due to morphological differences as observed in FESEM figure 14 & 15. In comparison the nanorods observed in polyaniline/glass and polyaniline/NC samples have larger surface area, therefore it enhances diffusion of gas [21, 31] and promotes the rate of oxidation of emeraldine salt which results in faster response time.

Table 1: Response time of polyaniline gas sensor to NO₂ gas

Material	Synthesis method	Detection concentration	Response time	Reference
Polyaniline + HCl	Interfacial polymerization	10 ppm	104s	[25]
Polyaniline + EB	Langmuir Blodgett	20 ppm	10s	[27]
Polyaniline + HCl/SnO ₂	Self assembly	1 ppm	80s	[28]
Polyaniline+ HCl	Potentiostatic	20 ppm	840 s	[29]
Polyaniline H ₂ O	Electrospinning	1 ppm	240 s	[30]
Polyaniline + HCl	Cyclic Voltammetry	20 ppm	1140 s	[29]
Polyaniline + H ₂ SO ₄	EDI	5 ppm	10, 15, 27 s	This work

The polyaniline /glass and polyaniline /nc gas sensor devices were able to retain sensing capabilities for 10 cycles while polyaniline /polyester gas sensor devices were able to sustain 4 cycles. This is possibly due to swelling from moisture absorbed from the surrounding.

Reference

- [25] X. Yan, Z. Han, Y. Yang, and B. Tay, "NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization," *Sensors and Actuators B: Chemical*, vol. 123, pp. 107-113, 2007.
- [26] D. Xie, Y. Jiang, W. Pan, D. Li, Z. Wu, and Y. Li, "Fabrication and characterization of polyaniline-based gas sensor by ultra-thin film technology," *Sensors and Actuators B: Chemical*, vol. 81, pp. 158-164, 2002.
- [27] D. Sutar, N. Padma, D. Aswal, S. Deshpande, S. Gupta, and J. Yakhmi, "Preparation of nanofibrous polyaniline films and their application as ammonia gas sensor," *Sensors and Actuators B: Chemical*, vol. 128, pp. 286-292, 2007.
- [28] J.-S. Do and W.-B. Chang, "Amperometric nitrogen dioxide gas sensor based on PAN/Au/Nafion® prepared by constant current and cyclic voltammetry methods," *Sensors and Actuators B: Chemical*, vol. 101, pp. 97-106, 2004.
- [29] A. Bishop-Haynes and P. Gouma, "Electrospun polyaniline composites for NO₂ detection," *Materials and manufacturing processes*, vol. 22, pp. 764-767, 2007.
- [30] S. Virji, J. Huang, R. B. Kaner, and B. H. Weiller, "Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms," *Nano Letters*, vol. 4, pp. 491-496, 2004/03/01 2004.

Chapter 6

Other potential Application of Electrodeposition on insulators

Apart from gas sensing application, the potential of EDI can be massive as the established industrial applications of electrodeposition favors well controlled microstructures of electrodeposits. Uniform electrodeposits film will be discussed in comparison with nanorods electrodeposits mentioned in previous chapters. With control over the microstructures, EDI can be employed for other potential applications that do not favor nanorods morphologies.

6.2 Experimental methods

6.2.1 Electrodeposition of polyaniline on insulator

Polyaniline was successfully coated on insulator substrate via pulse electrodeposition in room temperature and without any buffer layer. Pulse electrodepositions were conducted with 15,000 cycles of galvanic cycle deposition for duration of 150 seconds at 20 mA. However, to achieve a uniform coating of polyaniline, instead of stainless steel sheets, stainless steel mesh were used instead to initiate electrodeposition on insulators.

6.3 Uniform EDI Polyaniline film

Figure 20: (a) FESEM of electrodeposition of polyaniline on glass substrate using stainless steel mesh as the conductive component of working electrode (b) Optical microscope image of electrodeposition of polyaniline on glass substrate using stainless steel mesh as the conductive component of working electrode.

During EDI, the area of electrodeposit on insulator substrates typically correspond to the area of the stainless steel confined within the working electrode. This suggests possibility that this electrodeposition exhibits a line of sight deposition in contrary to conventional electrodeposition [32]. To evaluate our hypothesis, we replaced stainless steel sheet with stainless steel mesh, consisting of 100 μm opening. The resultant electrodeposit films observed under both optical microscope and SEM can be found in figure 20. The conformal uniform film and the features of the mesh were not transferred onto the insulator substrates.

This experiment suggests that the growth of electrodeposit on insulators is not considered line of sight deposition and indicate the spreading of the electrolyte through diffusion has led to the uniform coverage despite the use of a patterned conductive mesh in the working electrode.

The morphology of polyaniline can therefore alters from nanofibrous or conformal coating on glass substrates by changing the conductive component from stainless steel sheets to stainless steel mesh via EDI.

Reference

- [31] J. A. Switzer, "Atomic Layer Electrodeposition," *Science*, vol. 338, pp. 1300-1301, December 7, 2012 2012.

Chapter 7

Discussion and Future work

In this chapter, works presented in this thesis will be treaded together and presented from a broader perspective as a general discussion that checks the achieved data with the objectives set in this thesis. The discussion also includes the potential issues that requires more future efforts and other potential future development work that can help to increase the potential usage of EDI.

Electrodeposition of metal (gold) and electropolymerization (polyaniline) on insulator substrates were demonstrated via EDI setup at room temperature without any prior sputtering on substrates. Vertical gold nanorods were found to be deposited onto polyester substrates. Nanofibrous polyaniline formation was also deposited on flexible, transparent and foldable insulator substrates. Further characterization was conducted on Polyaniline samples by Raman spectroscopy to affirm the oxidation state electrodeposits to be the protonated emeraldine salt.

Polyaniline based samples deposited via EDI were fabricated into functional gas sensor device and shown fast response to NO₂. This result confirms that fabrication of flexible, wearable and rigid gas sensors is a potential application of EDI.

It is essential to compare EDI with the other electrochemical deposition method, as electroless deposition is known to be able to deposit on insulator substrates. However, similar to electrodeposition, it requires an electron source in order for reduction of metals coating to occur. This electron source for electroless deposition on insulator depends on dipping or coating substrates with metallic particles or metal salt before initiating the electroless deposition, which is not essential in our EDI technique. Furthermore, we have demonstrated the deposition of conducting polymer using EDI onto insulative substrates which can function as gas sensor.

In summary the works on EDI of polyaniline and EDI of gold demonstrated the feasibility of electrodeposition on various insulator substrates and demonstrated the fabrication of functional gas sensors, one of the many possible applications that could be developed from this modified electrodeposition (EDI). This is a pioneering approach in electrodeposition on insulator directly without prior metallization treatment in ambient temperature. We are certain that this work will contribute significantly to advancement in electrodeposition on insulators and development of functional devices for other applications.

Electrodeposition on insulator (EDI) removes the restriction of electrodeposition by allowing electrodeposition on insulator substrates. Since the mechanism of such electrodeposition requires the growing electrodeposits to “invade” with insulator substrates

[8] which requires electrodeposit to be in contact with the substrates. Promoting vertical aligned growth of electrodeposit will promote better contact between the electrodeposits and insulator substrate. This can be possibly achieved by inducing magnetic field during electrodeposition to modify the morphology of electrodeposits [33, 34].

The potential of EDI can be vast if it can demonstrate deposition of variety class of materials to cater for wider applications. In relation to poor cyclic stability as the biggest drawback of our polyaniline based gas sensor mentioned in chapter 5, carboneous material such as graphene can be adopted into current systems to improve cyclic stability of gas sensor devices. Such combinations of material can exhibit properties for several other applications such as supercapacitors, electrochromic, memory devices, etc.

Massive attention had been garnered on 2D materials [35] such as graphene [36], phosphorene [37] and 2d compounds such as Mxenes [38]. EDI will be a suitable platform for deposition of such materials on insulator material for applications such as transparent conductors for graphene. Apart from deposition, fabrication of 2d compounds might translate into reality if electrocodeposition of different types of 2D materials is conducted with precise control over its thickness and even distribution during nucleation [32, 39].

3D printing has been popularized for its ability to fabricate complicated devices and prototypes through automation rapidly but lacks the ability to control microstructures[40, 41]. Electrodeposition 3D printer allows 3D printing of metals with microstructures[41], while EDI can also achieve microstructure however without imposing restriction on substrates selection. The incorporation of EDI on 3D printing can enhance the versatility of 3D printer without losing microstructure controls.

Reference

1. Schwarzacher, W., *Electrodeposition: a technology for the future*. Interface, 2006. **15**(1): p. 32-35.
2. Schlesinger, M.P.M., *Fundamentals of Electrochemical Deposition* 2006, United states of America: John Wiley & Sons.
3. Paunovic, M., M. Schlesinger, and D.D. Snyder, *Fundamental Considerations*, in *Modern Electroplating*. 2010, John Wiley & Sons, Inc. p. 1-32.
4. Schlesinger, M., *Electroless and Electrodeposition of Silver*, in *Modern Electroplating*. 2010, John Wiley & Sons, Inc. p. 131-138.
5. Vorotyntsev, M.A., V.A. Zinovyeva, and D.V. Konev, *Mechanisms of Electropolymerization and Redox Activity: Fundamental Aspects*, in *Electropolymerization*. 2010, Wiley-VCH Verlag GmbH & Co. KGaA. p. 27-50.
6. Stern, M. and A.L. Geary, *Electrochemical Polarization: I. A Theoretical Analysis of the Shape of Polarization Curves*. Journal of The Electrochemical Society, 1957. **104**(1): p. 56-63.
7. Chazalviel, J.N., *Electrochemical aspects of the generation of ramified metallic electrodeposits*. Physical Review A, 1990. **42**(12): p. 7355-7367.
8. Fleury, V., et al., *Rapid electroplating of insulators*. Nature, 2002. **416**(6882): p. 716-719.
9. Andreazza, P., et al., *Buffer layer effect in nanostructured tin electrodeposition on insulating and conducting substrates*. Progress in Solid State Chemistry, 2005. **33**(2-4): p. 299-308.
10. Weng, Y.-Y., et al., *Self-templating growth of copper nanopearl-chain arrays in electrodeposition*. Physical Review E, 2010. **81**(5): p. 051607.
11. Zhang, B., et al., *Creating In-Plane Metallic-Nanowire Arrays by Corner-Mediatea Electrodeposition*. Advanced Materials, 2009. **21**(35): p. 3576-3580.
12. Zhong, S., et al., *Formation of nanostructured copper filaments in electrochemical deposition*. Physical Review E, 2003. **67**(6): p. 061601.
13. Snook, G.A., P. Kao, and A.S. Best, *Conducting-polymer-based supercapacitor devices and electrodes*. Journal of Power Sources, 2011. **196**(1): p. 1-12.

14. Stafström, S., et al., *Polaron lattice in highly conducting polyaniline: Theoretical and optical studies*. Physical Review Letters, 1987. **59**(13): p. 1464-1467.
15. Chandrasekar, M.S. and M. Pushpavanam, *Pulse and pulse reverse plating—Conceptual, advantages and applications*. Electrochimica Acta, 2008. **53**(8): p. 3313-3322.
16. Zhou, H.H., et al., *Effects of conductive polyaniline (PANI) preparation and platinum electrodeposition on electroactivity of methanol oxidation*. Journal of Applied Electrochemistry, 2004. **34**(4): p. 455-459.
17. Yamazoe, N., *Toward innovations of gas sensor technology*. Sensors and Actuators B: Chemical, 2005. **108**(1–2): p. 2-14.
18. Mirica, K.A., et al., *Mechanical Drawing of Gas Sensors on Paper*. Angewandte Chemie International Edition, 2012. **51**(43): p. 10740-10745.
19. Potje-Kamloth, K., *Gas Sensing with Conducting Polymers*, in *Electropolymerization*. 2010, Wiley-VCH Verlag GmbH & Co. KGaA. p. 153-171.
20. Song, E. and J.-W. Choi, *Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing*. Nanomaterials, 2013. **3**(3): p. 498-523.
21. Qi, J., et al., *Fabrication of textile based conductometric polyaniline gas sensor*. Sensors and Actuators B: Chemical, 2014. **202**(0): p. 732-740.
22. Yan, X.B., et al., *NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization*. Sensors and Actuators B: Chemical, 2007. **123**(1): p. 107-113.
23. *Nature's polymer*. Chemistry & Industry, 2012. **76**(7): p. 28-31.
24. Do Nascimento, G.M. and M. Temperini, *Studies on the resonance Raman spectra of polyaniline obtained with near-IR excitation*. Journal of Raman Spectroscopy, 2008. **39**(7): p. 772-778.
25. J. Vivekanandan, V.P., A. Mahudewaran and P. S. Vijayanand, *Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods*. Scholars research library, 2011.
26. Yan, X., et al., *NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization*. Sensors and Actuators B: Chemical, 2007. **123**(1): p. 107-113.

27. Xie, D., et al., *Fabrication and characterization of polyaniline-based gas sensor by ultra-thin film technology*. Sensors and Actuators B: Chemical, 2002. **81**(2): p. 158-164.
28. Sutar, D., et al., *Preparation of nanofibrous polyaniline films and their application as ammonia gas sensor*. Sensors and Actuators B: Chemical, 2007. **128**(1): p. 286-292.
29. Do, J.-S. and W.-B. Chang, *Amperometric nitrogen dioxide gas sensor based on PAN/Au/Nafion® prepared by constant current and cyclic voltammetry methods*. Sensors and Actuators B: Chemical, 2004. **101**(1): p. 97-106.
30. Bishop-Haynes, A. and P. Gouma, *Electrospun polyaniline composites for NO₂ detection*. Materials and manufacturing processes, 2007. **22**(6): p. 764-767.
31. Virji, S., et al., *Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms*. Nano Letters, 2004. **4**(3): p. 491-496.
32. Switzer, J.A., *Atomic Layer Electrodeposition*. Science, 2012. **338**(6112): p. 1300-1301.
33. Devos, O., et al., *Magnetic field effects on nickel electrodeposition*. Journal of The Electrochemical Society, 1998. **145**(2): p. 401-405.
34. Gorobets, O.Y., et al., *Nickel electrodeposition under influence of constant homogeneous and high-gradient magnetic field*. The Journal of Physical Chemistry C, 2008. **112**(9): p. 3373-3375.
35. Hamm, J.M. and O. Hess, *Two Two-Dimensional Materials Are Better than One*. Science, 2013. **340**(6138): p. 1298-1299.
36. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nat Mater, 2007. **6**(3): p. 183-191.
37. Favron, A., et al., *Photooxidation and quantum confinement effects in exfoliated black phosphorus*. Nat Mater, 2015. **14**(8): p. 826-832.
38. Xu, C., et al., *Large-area high-quality 2D ultrathin Mo₂C superconducting crystals*. Nat Mater, 2015. **14**(11): p. 1135-1141.
39. Thiemig, D., R. Lange, and A. Bund, *Influence of pulse plating parameters on the electrocodeposition of matrix metal nanocomposites*. Electrochimica Acta, 2007. **52**(25): p. 7362-7371.

40. Hu, J. and M.-F. Yu, *Meniscus-Confined Three-Dimensional Electrodeposition for Direct Writing of Wire Bonds*. Science, 2010. **329**(5989): p. 313-316.
41. Ladd, C., et al., *3D printing of free standing liquid metal microstructures*. Advanced Materials, 2013. **25**(36): p. 5081-5085

APPENDIX

Candidate reply to Examiners

The candidate would like to thank the examiners for the valuable comments and questions. The questions have contributed in improving the quality of this thesis.

Examiner 1's Comment

Electrochemical deposition is usually conducted to deposit coatings on conductive substrates, which has been a restriction for this method to deposit films on insulating surfaces. However, the recent emergence of deformable and wearable electronic devices sometimes require deposition methods than allow coating of functional materials nonconductive substrates. Therefore, the candidate's master research study is timely and is of both scientific and technological significance. The candidate developed a space charge dominated electrodeposition method that can be used to deposit coatings on insulator without metal pre-coating, which is called pulse electrodeposition (short alternating pulse current or potential) with high electric fields in proximity configurations. With this method, the candidate realized continuous deposition of nanofibrous polyaniline film on various insulating substrates, including cellulose papers, glasses, polyester and PET. Furthermore, the approach has no requirement to use buffer or catalyst, so that it has a high potential for large scale production and thus practical applications. In addition, the polyaniline coatings on insulating substrates have been demonstrated for gas sensor applications, with promising sensitive performances to low concentration of NO₂ (5 ppm). The report is well organized and the results are clearly presented and convincingly explained. Therefore, the candidate is recommended to pass the master examination.

Questions: What is the working principle of the sensors? How about selectivity of the sensors?

Candidate's reply:

The 3 main oxidation states of polyaniline are Leucoemeraldine, Emeraldine and Pernigraniline. Leucoemeraldine is the fully reduced state and Emeraldine is the partially oxidized state and Pernigraniline is the fully oxidized state. Polyaniline is the most conductive when it is protonated Emeraldine, also known as Emeraldine salt. Emeraldine Salt and Emeraldine Base (non protonated) are usually used for gas sensor applications [31, 42].

For Emeraldine base, upon exposure to NO_2 , the gas will be absorbed and act as electron acceptor creating CN^+ polarons in polyaniline. This results in a decrease in resistance of polyaniline coating and eventually when the NO_2 gas desorbs, the resistance of polyaniline recovers [30]. However, for Emeraldine salt, upon exposure to NO_2 , the gas will be absorbed and oxidized the conducting Emeraldine salt, resulting in an increase resistance. The resistance recovers when NO_2 gas desorbs [31, 43, 44].

The chemiresistive gas sensor reported in this thesis comprises of the active gas sensing layer made up of Emeraldine salt polyaniline layer that was connected with two gold electrodes as contacts. Polyaniline was deposited on the insulator substrate via EDI and it behaves like a resistor. During testing, a constant potential is applied to the sample and upon exposure to NO_2 gas, the resistance of Polyaniline increases and results in a drop in current level. The resistance of Polyaniline increases upon exposure to NO_2 and recovers when NO_2 desorbs.

Figure 2: (a) Oxidations states of polyaniline (b) Protonation of Emeraldine [43].

Polyaniline had been reported to demonstrate detection of a broad range of gases such as NH_3 , NO_2 , CO_2 and CO [45]. However, the response time varies for different gas analyte along with different method of protonation. In this thesis, devices were only tested with NO_2 gas. Device do not show any response to N_2 gas prior to the exposure to NO_2 gas.

Examiner 2

Electrochemical depositions have been widely used for active coatings on conductive substrates. For insulators, electrochemical depositions are lack of in-situ control and normally need metal precoating and the quality of deposition layers are very low. In this work, the author put a stainless steel sheet near the insulator surface and employ pose electrodeposition. This new method doesn't require metal precoating. Continuous nano fibrous polyaniline films were successfully coated onto insulating cellulose paper, glass, and polyester. These films were fabricated into functional gas sensors, which show quick response to low concentration of NO₂ gas. The thesis is well written in general. Some comments and suggestions are listed below.

- 1) In page 47 of the pdf file, the author assigned four Raman peaks. Any references?
- 2) In page 49 of the pdf file, what is the scale bar in figure 14a? Can some scale bar be used in figure 14 for easy comparison?
- 3) In page 57 of the pdf file, there is a fluctuation of IV graph around 0V in figure 18c. Why?
- 4) In page 58 of the pdf file, the author discussed the polyaniline gas sensors. Can the author provide the relation between resistance change and NO₂ concentration? What's the detection limit for this new polyaniline gas sensor?
- 5) In page 62 of the pdf file, the author claimed that the stainless steel mesh can have better uniform coating of polyaniline than stain less steel sheets. Why?
- 6) The author should pay attention to the format of this thesis, such as
 - a) In page 11 of the pdf file, "(typically 20-30 pages)" should be deleted.
 - b) In page 12 of the pdf file, both the titles of section 3.2.2 and section 3.2.3 are electrodeposition
 - c) In page 13 of the pdf file, 4.2.1 in chapter 5 should be 5.2.1; 4.2.1 in chapter 6 should be 6.2.1, ...
 - d) Different fonts are used from the bottom of page 27 to the top of page 29, page 31, ...
 - e) The reference is messy.

Candidate's reply

- 1) The references have been added
- 2) The Scale bar have been added
- 3) The IV graph shown in figure 18c was tested on Polyaniline/NC device. The fluctuation around 0V could be due to the moisture content in nanocellulose substrates as it has hygroscopic properties [46]. New polyaniline/NC samples were fabricated and kept in low humidity environment with desiccant before conducting IV graph measurement. In the new IV graph obtained, no noise or fluctuation was observed as shown below. The figure has been updated in the revised thesis.

Figure A.1: IV graph of gas sensor device kept in low humidity environment

- 4) The polyaniline gas sensor is in Emeraldine salt, upon exposure to NO_2 , the gas will be absorbed and oxidizes the conducting Emeraldine salt resulting in an increase resistance. The resistance recovers when NO_2 gas desorbs. When the concentration of NO_2 introduced to the gas sensor is above the detection limit, the resistance changes over time. As the concentration of NO_2 decreases, the

change in resistances reduces and below detection limit, no significant change in resistance will be observed.

The measurable detection limit for this new gas sensor is 1.25 ppm of NO₂.

- 5) Electrodeposits deposited via EDI conducted with stainless sheets were observed to form nanorods morphology. However when EDI was conducted with stainless steel mesh, the morphology of the polyaniline was observed to be uniform film. This difference in morphology could be attributed to the uniform distribution of effective electrical field in the stainless steel mesh.
- 6)
 - a. Additional text had been deleted
 - b. The content page had been edited
 - c. The content page had been edited
 - d. The font had been corrected
 - e. Reference had been rearranged with EndNote

Reference

1. Schwarzacher, W., *Electrodeposition: a technology for the future*. Interface, 2006. **15**(1): p. 32-35.
2. Schlesinger, M.P.M., *Fundamentals of Electrochemical Deposition* 2006, United states of America: John Wiley & Sons.
3. Paunovic, M., M. Schlesinger, and D.D. Snyder, *Fundamental Considerations*, in *Modern Electroplating*. 2010, John Wiley & Sons, Inc. p. 1-32.
4. Schlesinger, M., *Electroless and Electrodeposition of Silver*, in *Modern Electroplating*. 2010, John Wiley & Sons, Inc. p. 131-138.
5. Vorotyntsev, M.A., V.A. Zinovyeva, and D.V. Konev, *Mechanisms of Electropolymerization and Redox Activity: Fundamental Aspects*, in *Electropolymerization*. 2010, Wiley-VCH Verlag GmbH & Co. KGaA. p. 27-50.
6. Stern, M. and A.L. Geary, *Electrochemical Polarization: I. A Theoretical Analysis of the Shape of Polarization Curves*. Journal of The Electrochemical Society, 1957. **104**(1): p. 56-63.

7. Chazalviel, J.N., *Electrochemical aspects of the generation of ramified metallic electrodeposits*. Physical Review A, 1990. **42**(12): p. 7355-7367.
8. Fleury, V., et al., *Rapid electroplating of insulators*. Nature, 2002. **416**(6882): p. 716-719.
9. Andreazza, P., et al., *Buffer layer effect in nanostructured tin electrodeposition on insulating and conducting substrates*. Progress in Solid State Chemistry, 2005. **33**(2–4): p. 299-308.
10. Weng, Y.-Y., et al., *Self-templating growth of copper nanopearl-chain arrays in electrodeposition*. Physical Review E, 2010. **81**(5): p. 051607.
11. Zhang, B., et al., *Creating In-Plane Metallic-Nanowire Arrays by Corner-Mediated Electrodeposition*. Advanced Materials, 2009. **21**(35): p. 3576-3580.
12. Zhong, S., et al., *Formation of nanostructured copper filaments in electrochemical deposition*. Physical Review E, 2003. **67**(6): p. 061601.
13. Snook, G.A., P. Kao, and A.S. Best, *Conducting-polymer-based supercapacitor devices and electrodes*. Journal of Power Sources, 2011. **196**(1): p. 1-12.
14. Stafström, S., et al., *Polaron lattice in highly conducting polyaniline: Theoretical and optical studies*. Physical Review Letters, 1987. **59**(13): p. 1464-1467.
15. Chandrasekar, M.S. and M. Pushpavanam, *Pulse and pulse reverse plating—Conceptual, advantages and applications*. Electrochimica Acta, 2008. **53**(8): p. 3313-3322.
16. Zhou, H.H., et al., *Effects of conductive polyaniline (PANI) preparation and platinum electrodeposition on electroactivity of methanol oxidation*. Journal of Applied Electrochemistry, 2004. **34**(4): p. 455-459.
17. Yamazoe, N., *Toward innovations of gas sensor technology*. Sensors and Actuators B: Chemical, 2005. **108**(1–2): p. 2-14.
18. Mirica, K.A., et al., *Mechanical Drawing of Gas Sensors on Paper*. Angewandte Chemie International Edition, 2012. **51**(43): p. 10740-10745.
19. Potje-Kamloth, K., *Gas Sensing with Conducting Polymers*, in *Electropolymerization*. 2010, Wiley-VCH Verlag GmbH & Co. KGaA. p. 153-171.
20. Song, E. and J.-W. Choi, *Conducting Polyaniline Nanowire and Its Applications in Chemiresistive Sensing*. Nanomaterials, 2013. **3**(3): p. 498-523.

21. Qi, J., et al., *Fabrication of textile based conductometric polyaniline gas sensor*. Sensors and Actuators B: Chemical, 2014. **202**(0): p. 732-740.
22. Yan, X.B., et al., *NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization*. Sensors and Actuators B: Chemical, 2007. **123**(1): p. 107-113.
23. *Nature's polymer*. Chemistry & Industry, 2012. **76**(7): p. 28-31.
24. Do Nascimento, G.M. and M. Temperini, *Studies on the resonance Raman spectra of polyaniline obtained with near-IR excitation*. Journal of Raman Spectroscopy, 2008. **39**(7): p. 772-778.
25. J. Vivekanandan, V.P., A. Mahudswaran and P. S. Vijayanand, *Synthesis, characterization and conductivity study of polyaniline prepared by chemical oxidative and electrochemical methods*. Scholars research library, 2011.
26. Yan, X., et al., *NO₂ gas sensing with polyaniline nanofibers synthesized by a facile aqueous/organic interfacial polymerization*. Sensors and Actuators B: Chemical, 2007. **123**(1): p. 107-113.
27. Xie, D., et al., *Fabrication and characterization of polyaniline-based gas sensor by ultra-thin film technology*. Sensors and Actuators B: Chemical, 2002. **81**(2): p. 158-164.
28. Sutar, D., et al., *Preparation of nanofibrous polyaniline films and their application as ammonia gas sensor*. Sensors and Actuators B: Chemical, 2007. **128**(1): p. 286-292.
29. Do, J.-S. and W.-B. Chang, *Amperometric nitrogen dioxide gas sensor based on PAN/Au/Nafion® prepared by constant current and cyclic voltammetry methods*. Sensors and Actuators B: Chemical, 2004. **101**(1): p. 97-106.
30. Bishop-Haynes, A. and P. Gouma, *Electrospun polyaniline composites for NO₂ detection*. Materials and manufacturing processes, 2007. **22**(6): p. 764-767.
31. Virji, S., et al., *Polyaniline Nanofiber Gas Sensors: Examination of Response Mechanisms*. Nano Letters, 2004. **4**(3): p. 491-496.
32. Switzer, J.A., *Atomic Layer Electrodeposition*. Science, 2012. **338**(6112): p. 1300-1301.

33. Devos, O., et al., *Magnetic field effects on nickel electrodeposition*. Journal of The Electrochemical Society, 1998. **145**(2): p. 401-405.
34. Gorobets, O.Y., et al., *Nickel electrodeposition under influence of constant homogeneous and high-gradient magnetic field*. The Journal of Physical Chemistry C, 2008. **112**(9): p. 3373-3375.
35. Hamm, J.M. and O. Hess, *Two Two-Dimensional Materials Are Better than One*. Science, 2013. **340**(6138): p. 1298-1299.
36. Geim, A.K. and K.S. Novoselov, *The rise of graphene*. Nat Mater, 2007. **6**(3): p. 183-191.
37. Favron, A., et al., *Photooxidation and quantum confinement effects in exfoliated black phosphorus*. Nat Mater, 2015. **14**(8): p. 826-832.
38. Xu, C., et al., *Large-area high-quality 2D ultrathin Mo₂C superconducting crystals*. Nat Mater, 2015. **14**(11): p. 1135-1141.
39. Thiemig, D., R. Lange, and A. Bund, *Influence of pulse plating parameters on the electrocodeposition of matrix metal nanocomposites*. Electrochimica Acta, 2007. **52**(25): p. 7362-7371.
40. Hu, J. and M.-F. Yu, *Meniscus-Confined Three-Dimensional Electrodeposition for Direct Writing of Wire Bonds*. Science, 2010. **329**(5989): p. 313-316.
41. Ladd, C., et al., *3D printing of free standing liquid metal microstructures*. Advanced Materials, 2013. **25**(36): p. 5081-5085.
42. Fratoddi, I., et al., *Chemiresistive polyaniline-based gas sensors: A mini review*. Sensors and Actuators B: Chemical, 2015. **220**: p. 534-548.
43. Haynes, A. and P.-I. Gouma, *Polyaniline-Based Environmental Gas Sensors*, in *Sensors for Environment, Health and Security*, M.-I. Baraton, Editor. 2009, Springer Netherlands. p. 451-459.
44. Sarfraz, J., et al., *Printed hydrogen sulfide gas sensor on paper substrate based on polyaniline composite*. Thin Solid Films, 2013. **534**: p. 621-628.
45. Bai, H. and G. Shi, *Gas sensors based on conducting polymers*. Sensors, 2007. **7**(3): p. 267-307.
46. Kang, W., et al., *Foldable Electrochromics Enabled by Nanopaper Transfer Method*. Advanced Functional Materials, 2015. **25**(27): p. 4203-4210.