Synthesis and characterization of reduced graphene oxide-based composites

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**SYNTHESIS AND CHARACTERIZATION OF REDUCED
GRAPHENE OXIDE-BASED COMPOSITES**

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ABSTRACT

Graphene, a new class of two-dimensional crystalline material, has shown remarkable electronic, mechanical and thermal properties and great importance in the fundamental research and practical applications. Therefore, graphene is desirable for preparation of composites by mixing it with various metal or semiconductor nanostructures. In order to obtain graphene-based composites with well control of the composite morphology and properties, several methods have been designed and conducted.

First, graphene oxide (GO) and reduced graphene oxide (rGO) have been prepared by a modified Hummers method and the hydrazine reduction process, respectively. Through various characterization techniques, their structures and properties have been investigated. The conductive rGO films are fabricated by reduction of spin-coated GO films. By varying the solution volume in the spin-coating process, the film thickness can be adjusted and hence the film transmittance and sheet resistance can be controlled.

Second, Cu/rGO nanostructured composites have been synthesized through the electrochemical deposition method. The chronoamperometry has been applied to study the Cu nucleation modes on rGO. This work shows that the Cu nucleation, morphology and density on rGO films can be altered by changing the deposition conditions, such as deposition potential, electrolyte concentration and pH.

Third, ZnO/rGO composites have also been obtained through the electrochemical method. The morphology of ZnO is dependent on the thickness of rGO film and the deposition potential. The thicker rGO film and higher deposition potential is beneficial for the growth of crystalline ZnO nanorods. Moreover, a hybrid solar cell using ZnO nanorods deposited on annealed rGO film has been fabricated as a conceptual application, producing a power conversion efficiency of 0.31%.

Fourth, the Cu₂O/rGO composites obtained by the electrochemical deposition have been explored as well. By changing the pH value of electrolyte, Cu₂O with different morphologies and semiconducting behaviors can be deposited on rGO. In order to improve the n-type conducting behavior of Cu₂O, chlorine has been electrochemically doped into the Cu₂O/rGO composites. The amount of chlorine precursor (CuCl₂) in the electrolyte has two-sided effects on the doping of Cl-Cu₂O/rGO composites as it determines donor concentration and simultaneously affects the surface coverage of Cu₂O crystals on the rGO electrode.

Finally, solution processing approach has been chosen for the synthesis of bifunctional Fe₃O₄-Pt/rGO composite. The as-synthesized composite possesses the magnetic property of Fe₃O₄ nanoparticles and the catalytic property of Pt nanoparticles. By varying the amount of iron and platinum precursors, the nanoparticle density on rGO sheets can be adjusted. In addition, the Fe₃O₄-Pt/rGO composite can catalyze the reduction of methylene blue and be recycled within 1 min by applying an external magnetic field for at least 16 times.

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CHAPTER 1

INTRODUCTION

1.1 Background

Graphene, a newly discovered two-dimensional (2D) crystalline material, is a single layer of carbon atoms closely packed in form of a honeycomb lattice [1]. The “star-material” demonstrates exceptional electronic properties and shows great importance in the research field of carbon nanostructures. Novoselov and Geim [2] reported the remarkable ambipolar electric field effect of graphene with extremely high charge carrier mobility (up to $10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) at room temperature. Besides, graphene exhibits a great breaking strength of 42 N/m with a corresponding Young’s modulus of 1.0 TPa [3] and a superior room-temperature thermal conductivity of $\sim 5000 \text{ Wm}^{-1}\text{K}^{-1}$ [4]. Single-layer graphene also demonstrates an extraordinary large surface area of $2630 \text{ m}^2/\text{g}$ [5]. With these fascinating properties, graphene has been incorporated into various composite materials for a wide range of applications.

Before the discovery of graphene, carbon nanotubes (CNTs), one-dimensional (1D) carbon materials, are favorable for the fabrication of various composites due to their excellent electrical conductivity, high mechanical strength and large surface area [6]. However, with the emergence of graphene, CNTs are being replaced in many composite fabrications because they have three major problems: poor solubility, difficult manipulation and high production cost [7, 8]. In contrast, although graphene and CNTs have the nearly identical chemical makeup, graphene can easily form stable aqueous dispersion and be produced in a large-scale with low cost through the chemical

conversion from graphite [9]. Moreover, graphene has shown comparable or even better mechanical, electrical and electrochemical properties than CNTs [7, 10-12].

In recent studies, graphene-based composites have been extensively reported and can be categorized into three classes. The first class is the graphene-polymer composites. Graphene could enhance the electrical conductivity, mechanical strength and thermal conductivity of polymer composites, such as polystyrene [13], polyaniline [11], silicone [14]. In addition, Ramanathan reported functionalized graphene sheets (FGS) rendered poly(methyl methacrylate), poly(acrylonitrile) and poly(acrylic acid) better mechanical and thermal properties compared to unmodified single-walled carbon nanotubes [7]. This was due to the more intimate interactions between FGS and the polymers resulted from the special wrinkled sheet morphology of FGS and functional groups present on them [7].

The second class of graphene-based composites is graphene-metal nanoparticle (NP) composites. Graphene with extremely large surface area has been used as a promising template to support different metal NPs, such as Au [15-17], Ag [18, 19], Pt [16, 20], and Pd [16, 21]. Such composites have great potentials for surface enhanced Raman scattering [19], electrochemical sensing [20] and various catalytic reactions [21].

The third class of graphene-based composites is graphene-semiconductor NP composites. Semiconductor NPs, like TiO₂ [22], SnO₂ [23, 24] and CdS [25], can be anchored onto the graphene sheets, showing superior performances in lithium ion batteries [23], electrochemical supercapacitors [24] and solar cell applications [25].

In summary, graphene with unique physical and chemical properties is desirable for composite fabrications. It is important to explore graphene-based composites further by developing different strategies for the composite synthesis and/or designing different

combinations of graphene and interesting materials. But the premise is that the structure and properties of graphene are well understood.

1.2 Literature Review

1.2.1 Methods to produce graphene

Graphene is composed of a single layer of sp^2 -hybridized carbon atoms bound into a 2D honeycomb lattice [1]. It is a basic building unit to form various carbon nanostructures, such as 0D fullerenes, 1D nanotubes, and 3D graphite (Figure 1-1) [1].

Figure1-1. 2D graphene is a basic building unit for 0D fullerenes, 1D nanotubes and 3D graphite [1].

Efforts to produce graphene started from 1859 by Brodie [26], and till now four different methods have been widely used to obtain graphene. They are micromechanical exfoliation of graphite (also named as the ‘Scotch tape’ method) [2], chemical vapor

deposition (CVD) or epitaxial growth [27, 28], chemical reduction of graphene oxide (GO) [9, 29] and bottom-up synthesis from organic precursors [30, 31]. Table 1-1 summarizes the advantages and disadvantages of each method [32, 33].

Table 1-1. Advantages and disadvantages of four different methods to produce graphene.

Method	Advantages	Disadvantages
Micromechanical exfoliation of graphite	Able to acquire high quality graphene	Low throughput, low yield
CVD or epitaxial growth	Able to obtain high quality and large area graphene	Require stringent growth conditions and careful control for uniform growth of graphene
Chemical reduction of GO	Low cost, possible for high-volume production	Produce poor quality graphene with extensive modification of graphene
Bottom up synthesis from organic precursors	Size controllable synthesis of graphene	Difficult to yield large graphene with narrow size distribution and almost impossible to avoid side reactions

1.2.2 Introduction to graphene oxide (GO)

In our study, the chemical reduction of GO has been applied to synthesize graphene (also referred as reduced graphene oxide, rGO). GO, the precursor of rGO, is usually prepared by the Hummers and Offeman's method [34]. This method involves the treatment of the graphite with the strong acid of sulfuric acid and the strong oxidizer of potassium permanganate. As-obtained GO is similar in structure to graphene but has a decoration of abundant oxygen functional groups. The most accepted structural model of

GO is the Lerf-Klinowski model [35]. This model describes that GO has a layered structure with major components of epoxy and hydroxyl groups on the basal planes as well as minor components of carbonyl and carboxyl groups at the edges. Afterwards, Gao et al. proved five- and six-membered-ring lactols were present on the periphery of GO and added them into the structural model (Figure 1-2) [36].

Figure 1-2. Structural model of graphene oxide [36].

GO is hydrophilic due to the presence of oxygen functionalities on its layered structure and water molecules intercalated between the layers [37]. It can be easily exfoliated to form a stable colloidal suspension in water [32, 38] or some organic solvents [32, 39] through the ultrasonic treatment. The surface charge measurement shows the zeta potential of GO is about -40 mV in water at a concentration of 0.05 mg/mL at pH = 7 [9]. The negative charge on GO could be attributed to the ionization of carboxyl and hydroxyl groups on its surface.

1.2.3 Methods to produce stable dispersion of reduced graphene oxide (rGO)

Subsequently, graphene (or rGO) can be produced upon chemical reduction of GO. The commonly used reducing agents are hydrazine [9, 29], dimethylhydrazine [13], hydroquinone [40], NaOH and KOH [41]. In addition to chemical reduction, rGO can be

achieved through thermal reduction via high temperature deoxygenating process [42, 43], hydrothermal dehydration of GO using supercritical water as the reducing agent [44], and electrochemical reduction [45]. Most of the oxygen functional groups can be removed and the electrical conducting property of the conjugated graphitic network can be re-established after reduction of GO. Hence rGO becomes conductive and hydrophobic, and then aggregation is often observed during the process of reducing GO.

However, it is necessary to produce homogeneous rGO dispersion in bulk quantity for further device fabrications. The most simple method without the addition of any surfactant is to reduce GO in an alkaline solution ($\text{pH} = 10$ by adding ammonia) using hydrazine [9]. The reported optimal weight ratio of hydrazine to GO for the reduction is 7:10 [9]. Under the abovementioned conditions, stable, pure and conducting rGO aqueous solution can be obtained.

Figure 1-3. (A) Chemical structure of PEG-OPE [49]. (B) Two-step synthesis of PEG-OPE-functionalized rGO sheets [49].

The homogeneous rGO dispersion can also be achieved through noncovalent functionalization of rGO with some polymers or organic molecules. For example, stable rGO dispersion in water can be obtained by adding an amphiphilic polymer of poly(sodium-4 styrene sulfonate) [46], conducting polymer of sulfonated polyaniline [47] or a pyrene derivative of 1-pyrenebutyrate [48] during reduction with hydrazine. Moreover, our group reported the hydrazine reduction of GO in the presence of an amphiphilic conjugated polymer of PEG-OPE (Figure 1-3) [49]. As-obtained rGO had a strong π - π interaction with PEG-OPE and could be dispersed well in various organic solvents and water.

Besides, covalent functionalization of rGO, which often involves the reactions between functional molecules and oxygenated groups on GO or rGO, can reinforce the bonding between rGO and other functionalized material in the composite and produce homogeneous rGO dispersion. Si et al. reported the sulfonation of GO with aryl diazonium salt of sulfanilic acid, which introduced negatively charged $-\text{SO}_3^-$ groups on GO to stabilize rGO in water upon hydrazine reduction [50]. Lomeda et al. functionalized surfactant (sodium dodecylbenzenesulfonate, SDBS) protected rGO through aryl diazonium treatment (Figure 1-4) [51]. This method was developed from that for functionalization of CNTs. The resulted rGO can be dispersible in N,N' -dimethylformamide (DMF), N,N' -dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) [51]. Niyogi et al. demonstrated that rGO soluble in tetrahydrofuran (THF), CCl_4 and 1,2-dichloroethane could be achieved through reactions between octadecylamine (ODA) and carboxylic acid groups on oxidized graphite [52].

Figure 1-4. Schematic illustration of diazonium functionalization of SDBS-wrapped hydrazine reduced GO [51].

1.2.4 Methods to produce graphene–metal/metal oxide composites

Generally the graphene-metal/metal oxide composites can be obtained through two approaches. One way is to anchor the metal nanoparticles (NPs) or metal oxide nanostructures through the reduction of metal/metal oxide precursors onto the functionalized graphene sheets.

Muszynski et al. acquired graphene-Au NP composite through chemical reduction of AuCl_4^- ions in the suspension of ODA functionalized graphene (graphene-ODA) by NaBH_4 (Figure 1-5A) [53]. However, it was uncertain about the reason for stabilization of the Au NPs. Our group demonstrated the attachment of Au nanodots onto octadecyl thiol (ODT) functionalized reduced graphene oxide (rGO) through photochemical reduction of HAuCl_4 (Figure 1-5B) [54]. Due to the patterned self-assembly of ODT molecules on rGO, Au nanodots were self-assembled on rGO through the Au-S bonding. However, Au NPs were hardly formed onto the graphene surface without any oxygen functionalities, which served as reactive sites for the NPs nucleation and growth [55].

Figure 1-5. Schematic illustration of rGO-Au NP composite preparation through (A) chemical reduction of AuCl₄⁻ ions in the rGO-ODA suspension [53], (B) photochemical reduction of HAuCl₄ onto ODT functionalized rGO [54].

Similarly, graphene-TiO₂ composite can be achieved through in situ crystallization of TiO₂ precursors onto sodium dodecyl sulfate (SDS) functionalized graphene sheets [56]. With the help of SDS, graphene can be dispersed well in the water and hence TiO₂ precursors can be uniformly nucleated on the graphene through the hydrophilic head groups of SDS [56]. The used low temperature process could produce graphene-based composites with rodlike rutile TiO₂ or spherical aggregated anatase TiO₂ with the addition of sodium sulfate (Figure 1-6) [56].

Figure 1-6. Schematic illustration of graphene-TiO₂ composite preparation based on SDS mediated stabilized graphene [56].

Figure 1-7. Schematic illustration of the ethylene glycol reduction approach to synthesize graphene-metal NP composites. (1) Oxidation of graphite to obtain GO. (2) Exfoliation of GO. (3) Attachment of metal NPs on GO. (4) Reduction of GO in the presence of metal NPs [16].

The other way to fabricate graphene-metal/metal oxide composite is to reduce graphene oxide (GO) and metal/metal oxide precursors in one reaction pot. For example, reduction of GO by ethylene glycol in the presence of metal NPs (Figure 1-7) [16], like

Au, Pt and Pd is a general method to acquire graphene-metal NP composites. Metal NPs in the synthesis process are not only beneficial for the catalytic reduction of GO but also important for the prevention of graphene aggregation during the chemical reduction [16]. Another simple approach to obtain graphene-metal composite is to reduce GO and metal salts simultaneously in water using hydrazine or in toluene using oleylamine with the assistance of microwave irradiation [57]. Similarly, Fe_3O_4 NPs can be anchored onto the graphene template through the simultaneous solvothermal reduction of GO and FeCl_3 in diethylene glycol with addition of NaOH [58].

1.2.5 Solar cells constructed with graphene or graphene oxide (GO)

Over the last decade the demand for a transparent and conductive layer for fabrication of electronic devices shows a continuous increase. Two dominant materials used for such layer are indium tin oxide (ITO) and fluorine tin oxide (FTO). Although ITO exhibits better performance than FTO, it has several key drawbacks which limit its applications: 1) ITO is a ceramic material, and it is brittle and easily cracks or fractures at low strains of 2-3%, which leads to degraded conductivity when microcracks propagate [59]; 2) ITO is unstable in acidic or basic environment [60]; 3) ITO has a high index of refraction (~ 2) which results in significant reflection when coated on lower index substrates [61]; 4) indium is limited on earth and hence expensive for industrial applications [60, 61]; 5) deposition of ITO is inefficient and costly using vacuum based techniques [61]; 6) ITO is susceptible to ion diffusion into the polymer layers in organic solar cells [62]; 7) ITO shows poor transparency in the near infrared region which limits the solar energy absorption of optoelectronic devices [60, 62].

Therefore, an economical material with higher stability, better transparency and excellent conductivity is highly desired for solar cell fabrications. Recently, graphene with superior electronic, optical and mechanical properties is proposed to be a promising substitute for ITO. Major advantages to use graphene as transparent electrodes include: 1) the capability to fabricate graphene film electrodes with ultra-high surface smoothness; 2) the high transparency of ultrathin graphene films in visible and near-infrared regions; 3) the great thermal and chemical stability as well as the excellent biocompatibility of graphene films; 4) the outstanding flexibility and stretchability of graphene films for flexible electronic device fabrications; 5) the low cost to produce graphene films [61, 62].

1.2.5.1 Methods to fabricate graphene films

Many techniques have been developed to fabricate transparent and conductive graphene films, including dry processing and solvent-assisted techniques. A superior film fabrication method is featured with uniform coating with controllable thickness, high reproducibility, yield and throughput. Chemical vapor deposition (CVD) is a typical dry processing technique and able to produce 3 nm thick graphene films of remarkable quality with a low sheet resistance of 700 Ω/sq and a high optical transmittance of 90% (Figure 1-8) [63]. The graphene films grown by ambient pressure CVD on polycrystalline Ni can be transferred to other substrates for different applications [63].

Figure 1-8. (A) Optical image of CVD-grown graphene film transferred to a glass substrate (graphene film can be identified by referring to the broken edge at the bottom). (B) Optical transmittance of the 3 nm graphene film on glass [63].

Solvent-assisted techniques to obtain graphene films include vacuum filtration [9, 64, 65], dip coating [60], spray deposition [66], Langmuir-Blodgett technique [67], spin coating [68], etc. Graphene or reduced graphene oxide (rGO) films can be prepared using either stable rGO suspension directly [65, 67] or GO suspension to acquire GO films, followed by thermal or chemical reduction [9, 60, 64, 66, 68]. Figure 1-9 exhibits the optical images and transmittance spectra of a 9 nm thick GO film spin coated on the quartz substrate and reduced GO films with increasing thicknesses [68]. It is clearly observed that the highly transparent GO film (leftmost in Figure 1-9A) becomes much darker after reduction by 1100 °C annealing (see the third film with a similar thickness of 8 nm from the left in Figure 1-9A). Figure 1-9C suggests the high temperature (1100 °C) annealing is more effective for GO reduction than the combination of hydrazine and 400 °C annealing and hence produces rGO films with lower sheet resistances. As-

produced rGO films show sheet resistances of 100-1000 Ω/sq with $\sim 80\%$ optical transmittance to 550 nm light, approaching those grown by CVD method [63].

Figure 1-9. (A) Optical images of a 9 nm thick GO film (leftmost) spin coated on the quartz substrate and reduced GO films by 1100 $^{\circ}\text{C}$ annealing with increasing thicknesses, (B) Transmittance spectra of films in (A), (C) Plot of sheet resistance vs. optical transmittance at 550 nm for films reduced by either combination of hydrazine treatment at 40 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$ annealing or 1100 $^{\circ}\text{C}$ annealing [68].

1.2.5.2 Use of graphene as transparent electrodes in solar cells

It is a common practice to apply graphene films for window electrodes in solar cells [60, 69-72]. A dye-sensitized solar cell has been constructed using the dip-coated graphene (or rGO) film on quartz as a transparent anode, a compact blocking TiO_2 layer for electron transport, a spiro-OMeTAD layer for hole transport and Au as cathode (Figure 1-10) [60].

Figure 1-10. (A) Illustration of the dye-sensitized solar cell with a rGO electrode, four layers from top to bottom are rGO, TiO₂, dye-sensitized heterojunction, and Au, respectively. (B) Energy level diagram of the device in (A) [60].

Table 1-2. Summary of I-V characteristics of rGO-device and FTO-device [60].

Device	Photocurrent density (J_{sc}) [mA/cm ²]	Open-circuit voltage (V_{oc}) [V]	Filling factor (FF)	Power conversion efficiency (PCE) [%]
rGO-device	1.01	0.7	0.36	0.26
FTO-device	3.02	0.76	0.36	0.84

The current-voltage (I-V) characteristics of the as-constructed device (rGO-device) and the same device except that FTO is used to replace the rGO electrode (FTO-device) are summarized in Table 1-2. In comparison with FTO-device, rGO-device shows a poorer performance with lower J_{sc} and PCE due to the higher resistance and relatively lower light transmittance of rGO electrode and the electronic interfacial change. However, there is room for efficiency enhancement of rGO-based devices via using large-size (micrometer-scale) rGO sheets or by improving the quality of rGO films through thermal

treatment of rGO, other synthesis approaches (e.g. bottom-up approach) or more appropriate engineering procedures.

Wang et al. also fabricated an organic solar cell using CVD-grown graphene films with sheet resistances of 1350-210 Ω/sq and corresponding transmittances of 91%-72% as the transparent anodes [69]. The as-fabricated solar cell was composed of a graphene anode, a poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) buffer layer, a poly (3-hexyl)thiophene (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) composite active layer as well as a cathode containing thermal evaporated LiF and Al (Figure 1-11) [69].

Figure 1-11. (A) Illustration of the organic solar cell structure using graphene transferred onto the glass as the anode. (B) Energy level diagram of the device in (A) [69].

The graphene-based solar cell shows a poor performance with a low PCE of 0.21% resulted from a nonuniform coating of PEDOT:PSS on the hydrophobic graphene. To improve the cell efficiency, the hydrophilicity of graphene can be improved by UV/ozone treatment. As a result, the cell efficiency increases to 0.74% but the FF decreases because

the conductivity of graphene deteriorates after the UV/ozone treatment. Another approach to enhance the cell performance through noncovalent functionalization of graphene with pyrene acid succidymidyl ester (PBASE) could improve the surface wettability of graphene without compromising its conductivity. Meanwhile, work function of PBASE-modified graphene is slightly higher than the original graphene, which produces a higher open circuit voltage and provides a better hole collection. Table 1-3 summarizes the I-V characteristics of the organic solar cells based on graphene, graphene treated by UV, graphene modified with PBASE and an additional structurally identical device using ITO as the anode for comparison.

Table 1-3. Summary of I-V characteristics of various organic solar cells [69].

Solar cell	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%]
graphene	2.39	0.32	27	0.21
graphene treated by UV	5.56	0.55	24.3	0.74
graphene modified with PBASE	6.05	0.55	51.3	1.71
ITO	9.03	0.56	61.1	3.10

Although the rGO-based solar cells show poorer performance than those FTO or ITO based cells, rGO electrodes show better chemical and mechanical stability than ITO electrodes. Zhao et al. demonstrated the PANI-rGO devices were very stable in acidic electrolytes after 300 cycles with larger optical contrast and shorter switching time than PANI-ITO devices [73]. Tung et al. showed the conductance of rGO-CNTs hybrid spin

coated on poly(ethylene terephthalate) (PET) was nearly unchanged after bending at 60° for more than 10 times while the ITO film on PET exhibited a 3 orders of magnitude increase in resistance [74].

1.2.5.3 Use of graphene as an electron-acceptor material in solar cells

Figure 1-12. (A) PL spectra of P3OT and P3OT/graphene. (B) Illustration of the organic solar cell structure using graphene as an electron-acceptor material. (C) Energy level diagram of the device in (A) [76].

By functionalization of GO with phenyl isocyanate, which helps GO dispersed in the organic solvents [75], the obtained graphene could strongly interact with conjugated polymers and be readily used in organic solar cells. Upon introduction of graphene, photoluminescence (PL) of poly(3-octylthiophene) (P3OT) is dramatically reduced, indicating the strong electronic interactions between P3OT and graphene (Figure 1-12A) [76]. The obvious PL quenching of P3OT by graphene also suggests that graphene could be used as a novel electron-accepting material in the solar cells. The solar cell is fabricated using PEDOT-PSS modified ITO as the transparent electrode, spin coated

P3OT/graphene composite as the active layer as well as the vacuum-deposited LiF and Al as the cathode (Figure 1-12B) [76].

The P3OT/graphene based solar cells with different graphene content, 0, 1, 5, and 15 wt% have been fabricated. The device with 5 wt% graphene produces the best efficiency of 0.32% with the highest J_{sc} of 2.5 mA/cm² and the largest V_{oc} of 0.56 V [76]. Too few or too much graphene content may result in noncontinuous P3OT/graphene interface or graphene aggregation, which would have negative effects on charge separation and transportation in the active layer of P3OT/graphene [76].

Table 1-4. I-V characteristics of P3OT/graphene (5 wt% graphene) based solar cells [76].

P3OT/graphene devices		J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%]
Temperature (°C)	Time (min)				
No	No	2.5	0.56	23	0.32
160	10	3.2	0.98	32	0.98
160	20	4.2	0.92	37	1.4
210	10	3.2	1.0	31	0.98

To enhance the charge transport properties of graphene and hence improve the performance of the P3OT/graphene based solar cells, annealing of the spin-coated P3OT/graphene can be applied to remove the functional groups of graphene. I-V characteristics of P3OT/graphene based solar cells with annealing treatments at different temperatures and durations are listed in Table 1-4 [76]. The PCE of the P3OT/graphene based solar cell is greatly improved to 0.98% after annealing at 160°C for 10 min and the

PCE further increases to 1.4% after annealing for 20 min. The annealing process does not only enhance the charge transport mobility in graphene but also increases crystallinity of P3OT and improves the charge transport in P3OT [76]. However, annealing at higher temperature of 210°C does not improve the device performance further because of the high-temperature induced coarse phase separation and material decomposition [76]. Moreover, solar cells using the composite of poly(3-hexylthiophene) (P3HT) and graphene as the active layer have been fabricated with the same device configuration, achieving the best efficiency of 1.1% [77,78].

1.2.5.4 Use of GO as a hole-collecting material in solar cells

Figure 1-13. (A) Illustration of the polymer solar cell structure using GO as the hole transport layer. (B) Energy level diagram of the device in (A) [79].

Instead of using graphene as a component in solar cell fabrications, GO can play a role of hole transport layer (HTL) in the devices as well. Li et al. designed a photovoltaic device with the layered structure of ITO/GO/P3HT:PCBM/Al (Figure 1-13) [79]. To

have a comparison, solar cells with a HTL of PEDOT:PSS and without any HTL are built as control devices. Table 1-5 shows the I-V characteristics of the fabricated devices.

The comparable efficiency of GO-based polymer solar cells to PEDOT:PSS based devices suggests the efficient hole transport in GO from P3HT to the ITO electrode. Further investigation of carrier transport mechanism in the as-fabricated devices indicates the lowest recombination rate in GO-based devices, which leads to effective carrier separation and suppression of leakage current. Besides, GO layer could block the electron injection from PCBM LUMO to ITO due to its large bandgap of around 3.6 eV. Gao et al. also reported the application of GO as the hole selective interfacial layer in the inverted polymer solar cells [80].

Table 1-5. I-V characteristics of GO-based solar cells and control devices [79].

Solar cell	J_{sc} [mA/cm ²]	V_{oc} [V]	FF [%]	PCE [%]
GO (2 nm)	11.4	0.57	54.3	3.5 ± 0.3
Control device with PEDOT:PSS	11.15	0.58	56.9	3.6 ± 0.2
Control device without any HTL	9.84	0.45	41.5	1.8 ± 0.2

1.2.6 Biosensors constructed with graphene

Recent studies also focus on the electrochemical properties of graphene (rGO), a new allotrope of carbon. Zhou et al. reported a large potential window of ~2.5 V, a large apparent electrode area of 0.092 cm², and a low charge-transfer resistance of 160.8 Ω on rGO electrodes [81]. All these electrochemical characteristics suggested the high

electrochemical activity of rGO electrodes. In addition, electrochemical behaviors of rGO electrodes have been examined in the representative redox systems, $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ [82-85]. The low peak-to-peak potential separations (ΔE_p) in the cyclic voltammograms of the redox couples, which relates to electron transfer coefficient, suggests the fast electron transfer on rGO electrodes because of its high density of electronic states [86].

Due to its superior electrochemical activity, fast electron transfer rate and large specific surface area, the rGO electrode is promising for biosensing. For example, the direct electrochemistry of glucose oxidase (GOD) has been studied on rGO electrodes [86-89]. The obtained results show the excellent electron transfer between the rGO electrode and the active center of GOD, hence the rGO electrode can be used for glucose detections [87-91]. Wu et al. constructed glucose biosensors using rGO and revealed that the as-constructed rGO-based biosensors exhibited a high sensitivity of $\sim 110 \mu\text{A}\text{mM}^{-1}\text{cm}^{-2}$, a wide linear range from 0.1 mM to 10 mM and a low detection limit of 10 μM [88]. The superior performance of the rGO-based biosensors may be attributed to the high adsorption capacity and the unique electronic structure of rGO [88]. In addition, the surface defects present on rGO which lead to high electronic states density near Fermi level can be one possible reason for the fast electron transfer kinetics of GOD and the high sensitivity of the rGO-based electrodes [88]. Other biosensors based on rGO have been fabricated for detecting H_2O_2 [82, 92], reduced form of β -nicotinamide adenine dinucleotide [82, 93, 94], dopamine [85, 95-98], DNA bases [81, 98] and DNA molecules [99-101].

1.2.7 Short summary

In conclusion, methods to produce graphene, stable dispersion of rGO and the graphene-metal/metal oxide composites have been introduced in this chapter. The synthetic methods to produce the graphene-based composites generally require either the functionalization of graphene or the careful experiment control for GO and metal salts reductions. In addition, these methods show poor control over the composite morphology or composition. Therefore, it is important to develop some simple and robust methods to obtain composites with a well control over the morphology and composition. Moreover, the applications of graphene or graphene oxide for solar cells and biosensors have been reviewed briefly.

CHAPTER 2

AIMS AND MOTIVATIONS

2.1 Objectives and Scopes

Graphene (or reduced graphene oxide, rGO) has shown its experimental and theoretical importance in the research field of carbon nanostructures and demonstrated various unique and remarkable electronic, mechanical and thermal properties for composites fabrications. Therefore, we need to fully understand the structure of rGO through various characterization techniques. Besides, we aim to develop novel strategies to acquire different rGO-based composites since current methods are limited by synthesis conditions, composite morphology and composition control. At the same time, we also intend to investigate the growth mechanism of the crystals on rGO. Moreover, we want to explore the potential applications of as-acquired rGO-based composites.

In order to achieve the abovementioned objectives, we design and conduct the following researches:

- 1) Synthesis of graphene oxide (GO) nanosheets by a modified Hummer method and rGO through chemical reduction of GO. After the synthesis, the as-synthesized GO and rGO can be characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Therefore, the structures of GO and rGO can be compared.
- 2) Synthesis of Cu/rGO and semiconductor oxides (ZnO and Cu₂O)/rGO composites through electrochemical deposition method. The transparent rGO films can be employed as conductive electrodes for the deposition of various nanomaterials with controlled

shape or density. Moreover, the Cu nucleation mechanism on rGO can be studied through various electrochemical methods, such as cyclic voltammetry, Tafel plot and chronoamperometry. In addition, the application of semiconductor oxides/rGO composites for solar cell fabrications can be explored.

3) Synthesis of bifunctional rGO composites with the decoration of Fe_3O_4 and Pt nanoparticles onto the rGO sheets using the solution processing approach. Subsequently, the catalytic properties of the as-synthesized composites towards the reduction of methylene blue can be investigated.

2.2 Hypothesis

Before conducting the experiments, we have following hypotheses:

1) Many researches on rGO films have shown that the high transparency, stability and flexibility of rGO films make them capable to replace indium tin oxide (ITO) electrodes for electronic applications. Electrochemical approach has been widely applied to synthesize various nanomaterials on ITO. Similarly, the nanomaterials can be deposited on conductive rGO films by electrochemical methods to obtain various rGO-based composites.

2) Cu electrodeposition is a common practice in the electronic industry, hence the initial stage of Cu deposition process is critical for the fundamental studies and industrial applications. When rGO, a newly developed carbon form, is used for Cu deposition, the Cu nucleation may be different from other carbon substrates due to its different morphology and electronic properties.

3) If the semiconductor oxide nanomaterials of high crystallinity can be deposited on rGO films, they can be applied for solar cell fabrications. Since the electrochemical approach provides a strong adhesion between the rGO electrode and the deposited metal oxide materials, the charge carrier transport across them can be improved and an enhanced solar cell efficiency based on the electrodeposited metal oxide/rGO composites may be realized.

4) From the literature review, it can be found that the solution processing method has been used to achieve graphene-metal/metal oxide composites in addition to the electrochemical approach. The single-layer rGO sheet with a large surface area is an ideal template to anchor different functional metal and metal oxide nanoparticles. Therefore, bifunctional rGO composites with magnetic Fe_3O_4 nanoparticles and catalytic Pt nanoparticles may be acquired through the green solution processing route.

CHAPTER 3

MATERIALS AND EXPERIMENTAL DETAILS

3.1 Chemicals and Materials

Natural graphite (SP-1, Bay Carbon, Bay City, Michigan, USA) was used to synthesize graphene oxide (GO). Concentrated sulfuric acid (98% H_2SO_4), hydrochloric acid (HCl), phosphorus (V) oxide (P_2O_5), potassium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$), potassium permanganate (KMnO_4), hydrogen peroxide (30% H_2O_2), 3-aminopropyltriethoxysilane (APTES), anhydrous hydrazine (98% N_2H_4), copper (II) chloride (CuCl_2), lactic acid, sodium hydroxide (NaOH), anhydrous iron (III) chloride (FeCl_3 , 98%), potassium hexachloroplatinate (IV) (K_2PtCl_6), sodium borohydride (99%), and methylene blue were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. KCl (99.99% purity), ZnCl_2 (99.99% purity), poly(3,4-ethylene dioxythiophene)/poly(styrene-sulfonate) (PEDOT:PSS), N,N-dimethylformamide (DMF), diethylene glycol (DEG, 99%) and ethylene glycol (EG, 99%) were purchased from Sigma-Aldrich Chemical Co.(Singapore) and used as received. 4002-EE highly regioregular poly(3-hexylthiophene) (P3HT) was purchased from Rieke Metals Inc. (Nebraska, US) and used as received. Copper sulphate (CuSO_4), ethanol (99.9%), and methanol (99%) were purchased from Fisher Scientific (Pittsburgh, PA) and used as received. Silicon oxide (SiO_2) wafers were purchased from Bonda Technology Pte Ltd (Singapore). Fused quartz wafers were purchased from SYST Integration Pte Ltd (Singapore). Indium tin oxide (ITO) coated glass was purchased from Kintec Company (China). Polyethylene terephthalate (PET) film was purchased from 3M

(USA). Ultrapure Milli-Q water (Milli-Q System, Millipore, Billerica, MA, USA) was used in all experiments.

3.2 Sample Preparation

3.2.1 Synthesis of graphene oxide (GO)

Graphite oxide was prepared by a modified Hummer method using natural graphite [34, 102]. Graphite (0.3 g) was mixed with concentrated H_2SO_4 (2.4 mL), $\text{K}_2\text{S}_2\text{O}_8$ (0.5 g), and P_2O_5 (0.5 g). The mixture was under vigorous stirring and maintained at 80 °C for 4.5 h. The resulting pre-oxidized graphite was washed with Milli-Q water to remove the residual acid and dried under ambient condition.

The dried pre-oxidized graphite was then added into the concentrated H_2SO_4 (12 ml). KMnO_4 (1.5 g) was slowly added into the stirring mixture with an ice bath used to prevent the temperature exceeding 20 °C, otherwise overheating or explosion may occur. The mixture was then heated to 35 °C and maintained for 2 h. Subsequently, 25 ml of Milli-Q water was poured into the mixture with an ice bath used again to avoid overheating or explosion. The mixture became brown with bubbling and was stirred for another 2 h. Afterwards, additional 70 ml of Milli-Q water was poured to dilute the solution, and H_2O_2 (2 ml) was injected to react with the excess KMnO_4 . The color of the solution changed to bright yellow immediately.

In the end, the resulted solution was washed with diluted HCl to remove metal ions and Milli-Q water thoroughly to remove HCl. The resulted GO was dried at 60°C in a vacuum oven overnight. The dried GO was exfoliated in water by ultrasonication for 15-20 min to produce various concentrations of GO solution.

3.2.2 Adsorption of graphene oxide (GO) and reduced graphene oxide (rGO) sheets on the SiO₂ substrates

SiO₂ wafer substrates were cleaned in the piranha solution (H₂SO₄/H₂O₂ in volume = 7: 3) at 100 °C for 30 min (CAUTION: strongly corrosive). After that, they were rinsed with water thoroughly and blew dry with nitrogen. The cleaned substrates were immersed in APTES (0.5 wt% in ethanol) solution for 30 min and dried at 120 °C for 2 h. The APTES-modified SiO₂ substrates were then immersed in the prepared GO solution for the absorption of single-layer GO. The rGO sheets were obtained by vapor reduction of the GO sheets adsorbed on APTES-modified substrates with hydrazine at 60 °C overnight.

3.2.3 Reduction of GO in a H₂O/DMF mixture

GO was reduced in the H₂O/DMF mixture using the reported procedures [103]. 18 mL of DMF was added into 2 mL of brown GO aqueous suspension (3 mg/mL) and the volume ratio of DMF:H₂O was hence 9:1. Afterwards, 100 µL of hydrazine was added into the stirring GO suspension. The mixture was heated at 80 °C for 10 h to reduce GO completely. The solution of as-produced stable rGO suspension turned black and no precipitation was observed. If the solution precipitated after several days, mild sonication would exfoliate rGO sheets again.

3.2.4 Fabrication of rGO films

GO films were obtained by the spin coating method using concentrated GO in methanol solution. This solution was prepared according to the following procedures. Firstly, dried GO was exfoliated in water. After that, the solution was centrifuged at 1500

rpm for 30 min to remove any unexfoliated GO sheets. The supernatant solution was centrifuged again at 4500 rpm for 30 min to obtain relatively large GO sheets (bottom precipitate of the solution). Finally, large GO sheets were redispersed in methanol solution by shaking or sonication to produce a homogenous GO solution. The spin speed for the spin coating was 4000 rpm. The volume of GO solution used for spin coating determined the thickness of the GO films. GO films on the substrates (SiO₂, PET, ITO) could be reduced in a hydrazine environment at 60 °C overnight to obtain rGO films. To transfer the rGO films onto quartz, rGO films on SiO₂ were exposed to 0.03 M NaOH and detached in water [104]. The transferred rGO films were then dried at 80 °C for 1 h. To improve the conductivity of rGO films, high-temperature treatment could be used. The detailed process was described below. RGO films on quartz were placed in a crucible and inserted into an oven fitted with gas flows of Ar:H₂ (95%:5%, volume). The temperature was raised at a rate of 5 °C/min till 1100 °C, then maintained at the temperature for 2 h, and finally cooled naturally to room temperature overnight.

3.2.5 Synthesis of Cu/rGO composites through electrochemical deposition method

All the electrochemical experiments were performed by an electrochemical workstation (CHI600C, CH Instrument Inc., USA) under ambient condition. The setup for Cu/rGO composites synthesis was a conventional three-electrode electrochemical cell. The rGO film (ITO glass as the substrates), a Pt mesh, and an Ag/AgCl (3 M NaCl) electrode were used as the working, counter, and reference electrode, respectively. Copper tape was used for the connection between the rGO film and the power source.

CuSO₄ solutions of different concentrations were the deposition electrolytes. The pH of the electrolyte could be adjusted by adding appropriate amount of concentrated H₂SO₄.

3.2.6 Synthesis of ZnO/rGO composites through electrochemical deposition method

The electrochemical deposition of ZnO nanorods on the rGO-quartz wafer or rGO-PET substrate was carried out by the electrochemical workstation (CHI600C). The setup for the experiments was the same as the previous Cu/rGO composites synthesis except that a saturated calomel electrode (SCE) was used as the reference electrode when ZnO was deposited on rGO-PET.

The ZnO deposition on rGO electrodes included two steps [105]. First, a layer of ZnO seeds was formed by a galvanostatic deposition using the oxygen-saturated electrolyte of 5 mM ZnCl₂ and 0.1 M KCl at room temperature. The applied constant current density was 1.0×10^{-4} A/cm² and the charge density was 0.3 C/cm². Second, the ZnO nanorods were grown by a potentiostatic process using the oxygen-saturated electrolyte of 1 mM ZnCl₂ and 0.1 M KCl at 80 °C and the charge density was 2 C/cm².

3.2.7 Fabrication of solar cells using the ZnO nanorods/rGO composite

The preparation of the solar cells based on the ZnO/rGO composite with a layered structure of quartz/rGO/ZnO nanorods/P3HT/PEDOT:PSS/Au contained four steps. First, a layer of P3HT was spin-coated onto the ZnO/rGO composites with a P3HT chloroform solution (15 mg/mL) at 700 rpm, followed by annealing in N₂ at 120 °C for 10 min. Second, a ~50 nm thick layer of PEDOT:PSS was sprayed by a Badger airbrush model 150 onto the previous spin-coated P3HT layer at 70-80 °C using a PEDOT:PSS solution

(filtered through a 0.45 μm filter). Third, ~ 100 nm thick Au electrode was sputtered to form a top contact in a vacuum (10^{-6} mbar). At last, the device was annealed in N_2 at 150 $^\circ\text{C}$ for 15 min and ready for the device measurement.

3.2.8 Synthesis of $\text{Cu}_2\text{O}/\text{rGO}$ and $\text{Cl-Cu}_2\text{O}/\text{rGO}$ composites through electrochemical deposition method

The electrochemical deposition of Cu_2O on rGO films (PET as the substrate) was carried out by the electrochemical workstation (CHI600C). The setup for the experiments was the same as the previous ZnO/rGO composites synthesis except that the SCE was used as the reference electrode. Cu_2O was grown by a potentiostatic process using the electrolyte containing 0.4 M CuSO_4 and 3 M lactic acid at 60 $^\circ\text{C}$ [106, 107]. The applied constant potential was -0.4 V and the charge density was 2 C/cm^2 . The semiconducting type of as-grown Cu_2O could be controlled by the electrolyte pH adjusted by adding 4 M NaOH.

The electrolyte for the deposition of Cl-doped Cu_2O on rGO films (SiO_2 as the substrate) was slightly different, which contained 0.3 M CuSO_4 , 4 M lactic acid and CuCl_2 as chlorine (Cl) precursor with pH adjusted to 8.0 ± 0.2 [108]. The amount of CuCl_2 varied from 0 to 1.6 mmol to study the effects of Cl-doping on the carrier concentration of the deposited Cu_2O .

3.2.9 Synthesis of $\text{Fe}_3\text{O}_4\text{-Pt}/\text{rGO}$ composites through solution processing method

The synthesis of the $\text{Fe}_3\text{O}_4\text{-Pt}/\text{rGO}$ composites consisted of two steps. The first step was to obtain the $\text{Fe}_3\text{O}_4/\text{rGO}$ composite [58, 109]. 10 mg of GO exfoliated in 20 mL of

DEG was mixed with 63 mg of anhydrous FeCl_3 (iron content was equal to 30 mg of Fe_3O_4), hence the mass feed ratio of GO to Fe_3O_4 was 1:3. The mixture was poured into a flask equipped with a condenser and protected under N_2 . It was then heated up to 220 °C and maintained for 30 min with vigorous stirring. 5 mL of NaOH in DEG solution, prepared by dissolving 50 mg of NaOH in 5 mL DEG solution under N_2 at 120 °C for 1h and keeping at 70 °C, was injected into the previously prepared mixture and maintained at 220 °C for 1 h. The as-obtained $\text{Fe}_3\text{O}_4/\text{rGO}$ composite was washed with ethanol and water for several times by centrifugation and vacuum dried at 40 °C overnight.

The second step was to anchor the Pt nanoparticles onto the $\text{Fe}_3\text{O}_4/\text{rGO}$ composite [110]. 10 mL of the $\text{Fe}_3\text{O}_4/\text{rGO}$ dispersed in ethylene glycol (0.6 mg/mL) was mixed with 4 mL of K_2PtCl_6 aqueous solution (1.5 mg/mL, the Pt content was equal to 2.4 mg) in a flask under N_2 atmosphere. The flask was equipped with a condenser, heated up to 140 °C and maintained for 4 h. The final product of $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ was washed with water for several times by centrifugation and vacuum dried at 40 °C overnight.

3.2.10 Catalytic reduction of methylene blue (MB) with $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and sodium borohydride (SB)

The reduction of MB with $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ composite and SB was utilized to evaluate the catalytic activity of the composite [111]. 0.1 mL of MB solution (2.5×10^{-3} M) was added into 2.8 mL of buffer solution (pH 9.5, $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) and purged with N_2 for 5 min. After that, about 8 mg of $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and 0.15 mL of SB solution (0.1 M, stored in ice bath) were added together into the MB solution. UV-visible spectrophotometry was used to monitor the MB reduction process. To confirm the catalytic effect of $\text{Fe}_3\text{O}_4\text{-}$

Pt/rGO, a control experiment of using only 0.15 mL of SB solution to reduce the same MB solution was performed as well.

3.3 Characterizations

3.3.1 Atomic Force Microscopy (AFM)

AFM images were obtained by a Dimension 3100 AFM (Veeco, CA, USA), NSCRIPTOR system with a Si tip (resonance frequency: 320 kHz; spring constant: 42 N/m) in the tapping mode. Images were acquired under ambient conditions with a scanning rate of 1 Hz and scanning line of 512. The AFM images were used to reveal the topographies of GO/rGO sheets/films and determine the thickness of the sheets/films.

3.3.2 Current Density – Voltage (J-V) Measurement

The J-V characteristics of the photovoltaic devices based on the ZnO/rGO composite were determined by a Keithley SMU 2400 unit (Keithley Instruments Inc., US). The quartz side of each cell with an effective area of $\sim 6 \text{ mm}^2$ was illuminated by a Xenon lamp which was used at a power of 100 mWcm^{-2} to simulate the AM 1.5 global sunlight.

3.3.3 Four-point Probe Station

The electrical resistances of rGO films were measured by the manual four-point resistivity probing equipment (Signatone, Gilroy, CA).

3.3.4 Mott-Schottky (MS) and Photocurrent Measurements

MS plots were produced by the electrochemical workstation (CHI600C) using the AC impedance method. For the measurements of ZnO/rGO composites, the amplitude of the ac potential was set to 20 mV, the frequency was 1 kHz and the electrolyte was 0.05 M KCl. For the measurements of Cu₂O/rGO composites, the amplitude of the AC potential was set to 5 mV, the frequency was 1 kHz and the electrolyte contained 0.1 M Na₂HPO₄ with the solution pH adjusted to 10 ± 0.2 by 4 M NaOH. The photocurrent measurements of Cl-Cu₂O/rGO composites were conducted in the electrolyte of 0.5 M Na₂SO₄ when the composites (with an area of ca. 0.3 cm²) were irradiated by a 150-W halogen lamp. The setup for the MS and photocurrent measurement was a conventional three-electrode cell, using the rGO-based composite, a standard Ag/AgCl electrode or SCE, and a Pt mesh as the working electrode, reference electrode and counter electrode, respectively.

3.3.5 Photoluminescence (PL) Measurement

PL measurement of ZnO/rGO was conducted by a UV Nd:YAG laser with an excitation wavelength of 355 nm (LOT-Oriel GmbH & Co. KG, Darmstadt, Germany).

3.3.6 Surface Enhanced Raman Spectroscopy (SERS)

SERS spectra were collected on a WITec CRM200 confocal Raman microscopy system with an air cooling charge coupled device (CCD) as the detector (WITec Instruments Corp, Germany). The excitation line was 488 nm and the Raman band of a silicon wafer at 520 cm⁻¹ was used for calibration.

3.3.7 Scanning Electron Microscopy (SEM)

SEM images were acquired with a JEOL JSM-6340F field-emission scanning electron microanalyzer (accelerating voltage = 5 kV).

3.3.8 Transmission Electron Microscopy (TEM)

TEM images were recorded on a JEOL JEM-2010 or JEM-2100F equipped with the energy-dispersive X-ray spectrometer (EDS) (accelerating voltage = 200 kV). The deposited material on rGO electrodes, ZnO or Cu₂O, was scratched with a needle and sonicated in water to obtain the sample solution. The TEM sample was then prepared by dropping 2 μ L of the obtained sample solution onto a TEM copper grid.

3.3.9 Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis transmittance spectra were obtained on a UV-1800 spectrophotometer (Shimadzu, Asia Pacific Pte Ltd). The reduction process of MB with/without Fe₃O₄-Pt/rGO in the presence of SB was monitored by recording the UV-vis spectra.

3.3.10 Vibrating Sample Magnetometer (VSM)

The magnetic hysteresis curves of Fe₃O₄-Pt/rGO were acquired by a VSM (Lake Shore).

3.3.11 Work Function Measurement

Work function was measured by Kelvin Probe Force Microscopy (KPFM) (KP Technology Ltd, Caithness, UK) in air. Before each measurement, the known relative

work function difference between Au and Al was used to calibrate the KPFM system. The work function value of rGO film electrode was determined from the contact potential difference between the rGO electrode and the reference Au electrode. The average values from four different positions on the surface of rGO (area of $2.5 \times 1.5 \text{ cm}^2$) were used to determine the work function of rGO more accurately.

3.3.12 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns of rGO-based composites were collected by an X-ray diffractometer (Rigaku D/max 2250 V). Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$) was used while the accelerating voltage was 40 mV and the applied current was 40 mA.

3.3.13 X-Ray Photoelectron Spectroscopy (XPS)

XPS survey and high-resolution scan were performed on a Kratos Axis ULTRA spectrometer. A monochromatized Al K_α X-ray source (1486.71 eV) operated at a reduced power of 150 W (15 kV and 10 mA) was used. The base pressure was 2.66×10^{-7} Pa in the analysis chamber. The data was analyzed using a commercial software package CasaXPS. The C1s peak at 284.5 eV was used as a reference to calibrate the XPS spectra of GO and rGO.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preparation and Characterization of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

4.1.1 Introduction

In our study, graphene or rGO has been acquired by chemical reduction of GO produced by oxidation of graphite powder using a modified Hummer method. To obtain a comprehensive understanding of the morphologies and structures of GO and rGO sheets, atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy have been used to characterize them. Afterwards, rGO films have been fabricated by transferring the hydrazine reduced GO films spin coated on SiO₂ onto the 3-aminopropyltriethoxysilane (APTES)-modified quartz. The resistance and transmittance of rGO film electrodes have been investigated using four-point probe station and ultraviolet-visible spectroscopy (UV-vis).

4.1.2 AFM images of GO and rGO sheets

Figure 4-1A shows the AFM image of exfoliated GO sheets adsorbed on APTES-modified SiO₂ substrate. The step height from the Si/SiO₂ substrate to the GO sheet is about 1.2 nm, which matches well with the reported thickness of single layer GO sheets [38] and confirms that monolayer GO sheets have been achieved in the study. AFM

image of rGO sheets produced by reduction of GO on APTES-modified SiO_2 substrate is illustrated in Figure 4-1B. The thickness of rGO sheets (~ 1 nm) suggests the monolayer nature of the obtained rGO sheets. There are some wrinkles appeared on the rGO sheets, which may be resulted from the reduction process at 60°C for a long time.

Figure 4-1. AFM images of monolayer (A) GO and (B) rGO sheets on the APTES-modified Si/SiO₂ substrate with a height profile across one or two sheets.

4.1.3 TEM images of GO and rGO sheets

The morphology and structure of GO and rGO sheets were analyzed by TEM. The wrinkles and ripple-like corrugations can be understood by the thermodynamic stability principle since the 2D material can maximize its stability by wrinkling or bending. Figure

4-2A presents a flake-like GO sheet from which a selected area electron diffraction (SAED) pattern is collected. The ring pattern without resolved diffraction points suggests the amorphous with slightly polycrystalline nature of GO. The disordered structure of GO is resulted from the introduction of oxygen functional groups into the graphitic structure during the oxidation of graphite. Figure 4-2B shows the flat and thin rGO sheet with some overlaps. The SAED pattern from the sheet exhibits clearly resolved diffraction dots, which confirms the ordered crystal structure of obtained rGO after reduction [40].

Figure 4-2. TEM images of (A) GO and (B) rGO sheets. The insets are the corresponding selected area electron diffraction (SAED) patterns from the sheets.

4.1.4 XPS spectra of GO and rGO sheets

XPS spectrum can be used to identify chemical states of element carbon (C) in GO and rGO, hence it could reveal the oxidation degree of graphite. In the C1s XPS spectrum of GO (Figure 4-3A), besides a strong peak at 284.5 eV for C-C bond, oxygenated carbon groups are observed, i.e. C-O and C=O bonds at 286.6 and 288.2 eV, respectively. XPS

spectrum of rGO (Figure 4-3B) displays a strong peak of C-C at 284.5 eV while the intensity of C=O peak decreases significantly and C-O peak disappears. This indicates the removal of most oxygen functionalities and formation of abundant sp^2 bonded carbon atoms after the reduction of GO, which proves the derivation of graphene-based materials. The presence of an additional C-N bond at 285.3 eV is due to the nitrogen incorporation from the reduction process with hydrazine as reported [38].

Figure 4-3. C1s XPS spectra of (A) GO and (B) rGO sheets.

4.1.5 Raman spectra of GO and rGO sheets

Both GO and rGO demonstrate two prominent peaks in their Raman spectra (Figure 4-4). D peak at 1340 cm^{-1} and G peak at 1593 cm^{-1} in the Raman spectrum of GO correspond to the disorder-induced mode and first-order scattering of the E_{2g} optical mode, respectively [38]. The Raman spectrum of rGO contains D band at 1345 cm^{-1} and G band at 1598 cm^{-1} , respectively. The primary difference between Raman spectra of GO and rGO is that the D/G intensity ratio of rGO is higher than that of GO. The higher D/G

ratio suggests smaller sp^2 domain sizes and more disordering in the structure of rGO. Theoretically, GO should have a higher D/G ratio since it contains more oxygen functionalities. However, new sp^2 domains are created with removal of oxygen functional groups during the chemical reduction. Therefore, the total area of sp^2 domains is larger in rGO while the average sp^2 domain size in rGO actually decreases, which results in a higher D/G intensity ratio.

Figure 4-4. Raman spectra of (A) GO and (B) rGO sheets.

4.1.6 AFM images of rGO films on quartz

By adjusting the volume of GO solution used for spin-coating, the thickness of the GO films and hence rGO films on quartz ($2.5\text{ cm} \times 2.5\text{ cm}$) could be controlled. Figure 4-5(A-D) shows the AFM topographic images of rGO films with thickness ranging from 5 to 17 nm. The thickness of the rGO films can be estimated using AFM (Figure 4-5E shows an example for the measurement of 5 nm thick rGO film). From AFM

characterizations, it can be observed that the rGO film shows increasing roughness with increasing film thickness.

Figure 4-5. AFM images ($5 \times 5 \mu\text{m}^2$) of rGO film with thickness of (A) 5, (B) 9, (C) 13 and (D) 17 nm, respectively. (E) AFM image and section analysis of 5 nm thick rGO film.

4.1.7 Sheet resistance and transmittance of rGO films on quartz

Figure 4-6A presents the UV-vis spectra showing the optical transmittance change of rGO films as a function of film thickness. It is obvious that the thicker rGO film exhibits a lower transmittance. Variation of sheet resistance (for the whole film) and optical transmittance of rGO films ($2.5 \text{ cm} \times 2.5 \text{ cm}$) with film thickness is shown in Figure 4-6B. The rGO film resistance decreases with increasing thickness abruptly initially but decreases much slowly at thicknesses larger than 13 nm. The optical transmittance (all above 50%) of rGO films decreases almost linearly with increasing thickness. Compared to 8 nm thick reduced GO film spin coated on the quartz substrate by 1100 °C annealing

with transmittance of $\sim 75\%$ and sheet resistance of $\sim 500 \text{ } \Omega/\text{sq}$ [68], our 9 nm thick rGO film shows a similar transmittance of 72% but a much larger film resistance of $7.5 \text{ k}\Omega/\text{sq}$.

Figure 4-6. (A) UV-vis transmittance spectra of rGO film (on quartz) with thickness of (a) 5nm, (b) 9nm, (c) 13nm and (d) 17 nm, respectively. (B) Film resistance and transmittance at a wavelength of 1000 nm as a function of film thickness.

4.1.8 Short summary

In summary, single layer GO and rGO sheets have been successfully synthesized in our study as verified by AFM images. Through the characterizations of GO and rGO with various techniques, structure of GO and rGO has been compared. Reduction process in a hydrazine vapor could transform the disordered structure of GO to a crystalline structure of rGO and restore the conjugated graphitic network in rGO substantially. The chemical method to synthesize rGO sheets is easy to scale up for productions but introduces impurities inevitably into the rGO structure (e.g. nitrogen incorporation). Furthermore, conductive rGO films have been prepared on quartz substrates and characterized by AFM, UV-vis spectroscopy and four-point probe station. The thinner rGO film with a smoother surface exhibits a larger optical transmittance while it has a larger sheet resistance.

4.2 Synthesis of Cu / Reduced Graphene Oxide (rGO) Composites through Electrochemical Deposition Method: Nucleation Mechanism Study

4.2.1 Introduction

Carbons have been widely applied in analytical and industrial electrochemical studies. They are preferred applying in electrochemistry due to their exceptional properties, such as low cost, excellent conductivity, electrochemical inertness, superior electrocatalytic activity for various redox reactions, low background current and wide potential window [112]. Carbons have various forms for electrode applications including glassy carbon, pyrolytic graphite, pencil graphite and carbon nanotubes. The surface chemistry of these carbon materials determines their electrochemical performance [112]. For example, most polished glassy carbon surfaces are terminated by surface oxides such as carbonyls, lactones, carboxylates, ethers, etc. These oxides influence the adsorption, charge transfer and electrocatalysis in electrochemical reactions [112].

Graphene, a newly developed form of carbon in two-dimension, is a basic building block for the various graphitic structures. It has been already used in electrochemical studies including electrochemical sensing, electrocatalysis, electrochemiluminescence, electrochemical energy conversion, etc [90]. In the previous literature review, the advantageous properties of graphene for electrochemical studies have been mentioned such as superior electrochemical activity, fast electron transfer rate and large specific surface area. Therefore, graphene is stimulating great research interests nowadays and considered as a strong competitor in electrochemical applications. Moreover, graphene can be used as a conductive electrode for electrochemical synthesis.

Electrochemical methods to obtain nanostructures have following competences: 1) it is a low temperature process, which is particularly attractive for applications related to conducting polymers; 2) it is simple to perform with low cost; 3) it has a well control over film composition, uniformity, morphology, and thickness by varying various deposition parameters, such as composition of electrolyte, deposition current, voltage, and temperature; 4) it could produce a layer of conformal coating on the substrate with arbitrary shapes; 5) it can be used to synthesize novel materials that are difficult to be acquired by other methods [113]. The electrochemical technique also has its drawbacks. For example, impurities may be introduced into the deposit during the deposition. Besides, it may produce material with less ordered structure. Additionally, it requires a conductive substrate for the deposition [113].

Cu electrodeposition is important in electronic industry, such as integrated circuits manufacturing, protective and decorative electroplating [114]. In addition, Cu deposition on carbon supports is crucial for catalysts preparation [115]. Hence Cu has been electrochemically deposited on various carbon electrodes, such as glassy carbon [116], pyrolytic graphite [115, 117] and pencil graphite [114]. The Cu structure and properties deposited through Volmer-Weber island growth mainly depend on its nucleation and growth mechanism that the deposition adopts [118]. Therefore, Cu nucleation study is an appropriate model system to investigate the correlation between deposition kinetics and resulted morphology of Cu on a carbon-based substrate, graphene. In this section, Cu/reduced graphene oxide (rGO) composites have been obtained through the electrochemical deposition method. At the same time the Cu nucleation has been investigated on rGO electrodes, which is significant for the fundamental study.

4.2.2 Preparation of rGO electrode

RGO electrodes have been fabricated by reduction of GO thin films (ca. 10 nm-thick) spin-coated on the 3-aminopropyltriethoxysilane (APTES)-modified indium tin oxide (ITO) glasses ($1\text{ cm} \times 0.5\text{ cm}$). Figure 4-7 shows the Raman spectra of ITO and rGO-ITO electrodes. Raman spectrum of ITO electrode does not contain any obvious peaks in the region of $1100\text{--}1800\text{ cm}^{-1}$. Raman spectrum of rGO-ITO exhibits two peaks at 1351 and 1585 cm^{-1} which correspond to D and G bands of rGO, respectively. The higher Raman intensity of D band than that of G band confirms the successful reduction of GO.

Figure 4-7. Raman spectra of ITO and rGO-ITO electrodes.

4.2.3 Cyclic voltammetry and Tafel plot of Cu electrodeposition on rGO electrodes

Cyclic voltammetry (CV) is often used to study electrochemical reactions that occur during a potential scan. Figure 4-8A shows the typical cyclic voltammograms for Cu deposition on rGO electrodes in an electrolyte of 10 mM CuSO_4 at different pH values. Each voltammogram starts from a positive potential of 0.8 V and the scan rate is set as 20 mVs^{-1} . The cathodic current starts to increase until the potential reaches 0.105 V , which

indicates the beginning of Cu deposition. This potential value is more positive than that observed on pencil graphite electrode (-0.055 V) [114] and glassy carbon electrode (-0.034 V) [116]. The reactions for Cu deposition occur through two consecutive one-electron transfer steps: $\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$ (slow) and $\text{Cu}^+ + \text{e}^- = \text{Cu}$ (fast) [114, 119]. A broad reduction peak is formed when the potential goes more negative, suggesting that the Cu deposition process is controlled by the diffusion of copper ions [116, 117]. The reduction peak potential of Cu^{2+} ions depends on the pH value of the electrolyte. This phenomenon is similar to that observed on glassy carbon electrode, which could be explained by the different solution resistances at different pH values [116]. On the reversed potential sweep in CuSO_4 solution (pH 1), an oxidation peak appears at ~ 0.17 V, which corresponds to anodic stripping of previously deposited Cu.

Figure 4-8. (A) Cyclic voltammetry as a function of pH (scan rate = 20 mV/s) and (B) Tafel plot (at pH 1, scan rate = 1 mV/s) of Cu deposition on rGO electrodes in 10 mM CuSO_4 solution.

The kinetics of Cu deposition can be simply described by the Butler-Volmer equation [120]:

$$j = j_0 \left[\exp\left(\frac{\alpha_A n F}{RT} \eta\right) - \exp\left(-\frac{\alpha_c n F}{RT} \eta\right) \right]$$

where j is the current density, j_0 is the exchange current density, α_A and α_c are the anodic and cathodic transfer coefficient, respectively, n is the number of electrons involved in the electrode reaction, F is the Faraday, R is the gas constant, T is the absolute temperature (K), and η is the overpotential. Figure 4-8B displays a typical Tafel plot of Cu deposition on rGO electrodes measured in a 10 mM CuSO₄ solution (pH = 1). There is a small portion of the curve exhibiting a linear relationship in the plot of $\log j$ vs. potential, which confirms the mass transport is the rate-determining step [120].

4.2.4 Chronoamperometry for Cu nucleation mechanism study on rGO electrodes

Chronoamperometry is an electrochemical technique to study the Cu nucleation mechanism [114, 116, 117]. In each of our chronoamperometry measurements, the potential was stepped from the open-circuit potential, at which no deposition occurred, to the deposition potential of -0.4 to -0.6 V. The deposition potential was more negative than the reduction peak potential to ensure each measurement was in the mass-transfer limited regime. The current-time transient curves for the chronoamperometry experiments could be depicted using the Cottrell equation [116, 120]:

$$j = \frac{nFD^{1/2}C_0}{\pi^{1/2}t^{1/2}}$$

where j is the current density, n is the number of electrons involved in the reaction, F is the Faraday constant, D is the diffusion coefficient, C_0 is the concentration of species (*i.e.* Cu^{2+}) in the bulk, and t is the time.

The potentiostatic current transients can be analyzed using the Scharifker and Hills (SH) theory [116, 121], which determines the nucleation mechanism of a diffusion controlled electrochemical reaction. There are two limiting nucleation mechanisms in the SH theory, *i.e.* instantaneous and progressive nucleation. In the instantaneous nucleation, all active surface sites on the electrode surface are converted to nuclei instantaneously. However, in the progressive nucleation [122], the number of nuclei continuously increases with the deposition time.

The instantaneous nucleation is described by the equation [121]:

$$\frac{j^2}{j_m^2} = \frac{1.9542}{t/t_m} \left\{ 1 - \exp \left[-1.2564 \left(\frac{t}{t_m} \right) \right] \right\}^2$$

and the progressive nucleation is described by the equation [121]:

$$\frac{j^2}{j_m^2} = \frac{1.2254}{t/t_m} \left\{ 1 - \exp \left[-2.3367 \left(\frac{t}{t_m} \right)^2 \right] \right\}^2$$

where j is the current density, t is the time, j_m and t_m are the current density and time at the maximum, respectively. To determine the nucleation modes, the experimental potentiostatic current transients should be transformed to the non-dimensional plots of $(j/j_m)^2$ vs. (t/t_m) and compared to the theoretical transients for instantaneous and progressive nucleation mechanisms.

Figure 4-9. Potentiostatic current transients for Cu deposition on rGO electrodes in (A) 1 mM, (B) 10 mM and (C) 50 mM CuSO₄ solution at pH 1. (a), (b) and (c) are the corresponding non-dimensional plots of $(j/j_m)^2$ vs. (t/t_m) . Deposition potential range: -0.4 to -0.6 V.

Figures 4-9 demonstrate the potentiostatic current transients for Cu deposition on rGO electrodes in CuSO₄ solutions (pH = 1) of three different concentrations (1, 10 and 50 mM). The current transients recorded in 10 mM (Figure 4-9B) and 50 mM CuSO₄

(Figure 4-9C) solutions show a non-Faradic current which decreases at the beginning due to the double-layer charging [117, 120]. After the non-Faradic part, the current increases due to the reduction of average diffusion distance with nuclei growth and subsequently the number of nuclei increases on the electrode surface. The diffusion zones around the nuclei continue expanding as nuclei grow and finally overlap with that of the neighboring nuclei. At the point of overlapping of neighboring diffusion zones, the current reaches a maximum. After this point, the current decreases as effective electrode surface area decreases. Simultaneously, a hemispherical mass transfer is changed to a linear transfer from electrolyte to the planar electrode surface. Finally, the current reaches a limiting value as the further deposition of Cu on rGO electrodes is limited by the diffusion of Cu species. However, the transient curves in 1 mM CuSO₄ solution (Figure 4-9A) show a current maximum at the beginning in the absence of the double layer charging and the nuclei growth stages.

Figures 4-9(a-c) show the non-dimensional plots of $(j/j_m)^2$ vs. (t/t_m) , transformed from the curves in Figures 4-9(A-C) and compared with the theoretical curves for instantaneous and progressive nucleations. It can be found that the Cu nucleation on rGO electrodes at pH 1, in 1 mM CuSO₄ solution (Figure 4-9a), is likely to be progressive. The nucleation mode cannot be confirmed because only few data points are presented when the current achieves maximum initially. The Cu nucleation in 10 mM CuSO₄ solution with the applied potential from -0.4 V to -0.6 V (Figure 4-9b) and 50 mM CuSO₄ solution at -0.6 V (Figure 4-9c) is close to the instantaneous mode. However, the experimental data of Cu deposition in 50 mM CuSO₄ solution depart from the instantaneous curve at -0.4 and -0.5 V (Figure 4-9c).

Figure 4-10. Potentiostatic current transients for Cu deposition on rGO electrodes in (A) 1 mM, (B) 10 mM and (C) 50 mM CuSO₄ solution at pH 3. (a), (b) and (c) are the corresponding non-dimensional plots of $(j/j_m)^2$ vs. (t/t_m) . Deposition potential range: -0.4 to -0.6 V.

The effect of pH on chronoamperometry of Cu deposition on rGO electrodes has also been studied in three different concentrations of CuSO₄ solution, 1, 10 and 50 mM (Figure 4-10). The Cu nucleation mode in the electrolyte of pH 3 is inconclusive as the experimental data are far from either of the theoretical nucleation mechanisms.

It can be seen that Cu nucleation mechanisms on rGO electrodes were better defined at pH 1 than those at pH 3, which may be explained by the solution resistance at pH 3 [116]. To compensate the solution resistance and improve the solution conductance at pH 3, background electrolyte of sodium sulfate can be added into the electrolyte [116]. Figure 4-11 illustrates the chronoamperometry of Cu deposition in 10 mM CuSO₄ solution with addition of 1 M Na₂SO₄. Cu nucleation at pH 1 (Figure 4-11) is similar to that at pH 3 with the presence of background electrolyte. Hence the background electrolyte can assist the study of nucleation modes at pH 3.

Figure 4-11. Potentiostatic current transients for electrodeposition of Cu on rGO electrodes in 10 mM CuSO₄ solution with 1 M Na₂SO₄ at (A) pH 1 and (B) pH 3. (a) and (b) are the corresponding non-dimensional plots of $(j/j_m)^2$ vs. (t/t_m) . Deposition potential range: -0.4 to -0.6 V.

4.2.5 Correlation between Cu nuclei morphology and nucleation models

SEM images were taken after Cu was deposited in 10 mM CuSO₄ solution (pH 1) at -0.6 V on rGO electrodes for 1, 4, 10, 30 s to study the Cu nucleation and growth on rGO electrodes. The Cu nuclei formed are particle-like with density of ca. $1.1 \times 10^8 \text{ cm}^{-2}$ (Figure 4-12A) after deposition for 1 s. Nuclei density increases to $9.5 \times 10^8 \text{ cm}^{-2}$ after deposition for 4 s (Figure 4-12B). After deposition for 10 s, the nuclei density remains (Figure 4-12C). At this stage nuclei with small sizes between 60 to 100 nm form newly while some preexisting nuclei continue growing and become large particles with sizes between 200 to 260 nm. Eventually, (Figure 4-12D), nuclei form with a broad Gaussian size distribution and a higher density of $22.4 \times 10^8 \text{ cm}^{-2}$ after deposition for 30 s. Therefore, Cu nucleation behavior on rGO electrodes under the specified condition was almost in a progressive manner at the larger time scale of 30 s, different from the instantaneous nucleation predicted by SH theory at the smaller time scale of <1 s.

To study the Cu electrolyte concentration effect in influencing the reaction mechanism of Cu on rGO electrodes, SEM images were taken on rGO electrodes after Cu had deposited in 50 mM CuSO₄ solution (pH 1) at -0.6 V for 1, 4, 10, and 30 s. Interestingly, Cu forms flower-like nuclei after deposition for 1 s with a density of ca. $1.5 \times 10^8 \text{ cm}^{-2}$ (Figure 4-13A). From the images after deposition for 4, 10 and 30 s (Figure 4-13B-D), it can be inferred that Cu clusters grow with flower-like shape by merging or coalescence of Cu nucleus. Besides, no obvious increase in Cu nuclei density is observed with increasing deposition time. Consequently, the Cu nucleation on rGO electrodes under a high electrolyte concentration of 50 mM resembled the instantaneous nucleation manner, which was the same as the nucleation mode predicted with the SH theory.

Moreover, the instantaneous nucleation on the rGO electrode may be explained by the interaction between Cu^{2+} and the remaining oxygen groups on rGO [123] as most oxygen groups on rGO were bonded to the Cu^{2+} ions at a higher concentration of Cu^{2+} . In addition, an XRD pattern of Cu deposited on rGO was collected at the same day of the experiment (see Figure 4-13E), from which Cu_2O or CuO could not be observed.

Figure 4-12. SEM images of electrodeposited Cu nucleus and histogram analyses of their sizes on rGO electrodes in 10 mM CuSO_4 solution (pH 1) at -0.6 V for (A) 1, (B) 4, (C) 10, and (D) 30 s, respectively.

Figure 4-13. SEM images of electrodeposited Cu nucleus on rGO electrodes in 50 mM CuSO₄ solution (pH 1) at -0.6 V for (A) 1, (B) 4, (C) 10, and (D) 30 s, respectively. (E) XRD pattern of Cu deposited on rGO in 50 mM CuSO₄ solution (pH1) at -0.6 V for 30 s (XRD peaks labeled with * are from ITO underneath the rGO film).

Moreover, SEM images were taken on rGO electrodes after Cu had deposited in 50 mM CuSO₄ solution (pH 1) at -0.4 V for 1, 4, 10, 30 s to study the effect of potential on Cu deposition. Cu forms particle-like nuclei within the first 1 s of electrodeposition and the nuclei density is ca. $2.3 \times 10^7 \text{ cm}^{-2}$ (Figure 4-14A). Cu nuclei start the dendritic growth during a period from 1 to 4 s (Figure 4-14B) and exhibit similar morphology to that formed at -0.6V. When the deposition time is longer (Figure 4-14C, D), Cu clusters grow much larger but the cluster density is much lower compared with Cu deposited at more negative potential. Therefore, the deposition potential did not have evident effects on Cu morphology but affected the cluster density greatly.

Figure 4-14. SEM images of Cu electrodeposited on rGO electrodes in 50 mM CuSO_4 solution (pH 1) at -0.4 V for (A) 1, (B) 4, (C) 10, and (D) 30 s, respectively.

4.2.6 Short summary

In conclusion, composites of rGO and Cu nanostructures have been achieved through electrochemical deposition, and Cu nucleation mechanism on rGO electrodes has been studied as well. The Cu deposition process has been analyzed using cyclic voltammetry, Tafel plot and chronoamperometry. Cyclic voltammetry and the Tafel plot indicate that the rate-determining step of Cu deposition on rGO is the mass transport. Furthermore, chronoamperometry has been applied to predict Cu nucleation modes on rGO while the predictions are not absolutely matched with experimental observations. Effects of CuSO_4 solution concentration and applied potential on Cu deposition have also been investigated. This study opens up an electrochemical platform based on rGO electrodes for the wide applications in the fields of sensing, optoelectronics and energy harvesting.

4.3 Synthesis of ZnO Nanorods / Reduced Graphene Oxide (rGO)

Composites through Electrochemical Deposition Method

4.3.1 Introduction

Electrochemical deposition method has been demonstrated to simply obtain composites of Cu/rGO, it has a great potential to apply in the synthesis of rGO-based composites with other materials, for example, semiconducting oxides. ZnO is one of the most important semiconductor materials with wide band gap of 3.37 eV [124]. Besides, ZnO has great potential in various applications due to its exceptional electrical, optical and chemical properties. It is widely used in optoelectronics [125], field emission [126, 127], solar cells [128, 129], gas sensors [130], etc. One of the mostly studied ZnO nanostructures is the nanorod morphology, which can be achieved by the pulsed laser deposition [123], chemical vapor deposition [131], and hydrothermal method [132].

The electrochemical method to prepare ZnO nanorods is promising since it is a low cost process at low reaction temperatures and facile for the large scale production [133]. In addition, electrochemical technique has a good control over the dimension of ZnO nanorods using different deposition conditions [105, 134]. To synthesize ZnO nanorods on rGO electrodes, it requires a template-free process since it is complicated to grow a template on rGO electrodes. The most frequently-used Zn precursor in the electrolyte for ZnO nanorods deposition is ZnCl_2 [105, 134].

The electrochemical reactions, involved in an oxygen-saturated solution bath to deposit ZnO nanorods, contain two steps: the reduction of O_2 and precipitation of ZnO, i.e. $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ and $\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 = \text{ZnO} + \text{H}_2\text{O}$ [132]. Several parameters would influence the ZnO nanorods deposition, including substrate defects,

potential, zinc concentration, electrolyte pH, temperature, time, etc. Effects of substrate defects, potentials and ZnCl_2 concentration are emphasized in the following paragraphs.

First, GaN substrates with different defect densities influence the nucleation and growth of ZnO [135]. GaN with a defect density of $100 \mu\text{m}^{-2}$ could produce ZnO directly while GaN with a lower defect density of $1 \mu\text{m}^{-2}$ could not produce ZnO unless it is pretreated in hot ammonia for ZnO nucleation [135].

Second, ZnO nanorods can only form on indium tin oxide (ITO) glass when the applied potential is more negative than -0.2 V [132]. Besides, the rod density and length of ZnO increase while average diameter decreases with applied potential from -0.4 to -1.0 V [132]. This is because that when the applied potential is more negative, more hydroxide ions can be generated from oxygen reduction, zinc ions can also more easily diffuse and/or adsorb to the electrode, and eventually the growth rate of ZnO increases [132].

Third, the ZnCl_2 concentration also affects the morphology of ZnO [123]. ZnO nanorods can be formed when the electrolyte is poor in Zn^{2+} and pH increases with the deposition time to produce hydroxide complexes of Zn^{2+} , i.e. $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$. As the electrolyte pH exceeds 7, the lateral growth is completely quenched while the vertical growth can continue since the hydroxide complexes of Zn^{2+} can react with the coordination corner on the reactive (0001) planes of ZnO.

Fourth, the O_2 reduction also plays a major role in ZnO nanorod formation [105]. When the oxygen reduction is faster than the diffusion of Zn^{2+} to the cathode, Zn^{2+} can easily react with the OH^- ions adsorbed on the nanorod tips, hindering the lateral growth of ZnO as Zn^{2+} ions are difficult to access the bottom of nanorods.

In this section, ZnO/reduced graphene oxide (rGO) composites have been achieved through the electrochemical deposition approach. The effects of rGO film thickness/conductivity and deposition potential on ZnO nanorod formation have been investigated, revealing the ZnO nucleation and growth process on rGO electrodes.

4.3.2 Effect of film thickness on electrodeposition of ZnO on rGO-quartz

Transparent and conductive rGO electrodes were prepared by reduction of GO films spin-coated on the quartz substrates (2.5 cm × 2.5 cm) with thickness ranges from 5 to 17 nm as described in the chapter 4.1.6. Figure 4-15 illustrates the SEM images of ZnO deposited at -0.98 V (vs. Ag/AgCl) on rGO films with different thicknesses. At a low thickness of 5 nm, obtained ZnO is more particle-like (diameter ~320 nm) and some are agglomerated with poor crystallinity (Figure 4-15A). As the thickness increases to 9 nm, the ZnO rods (diameter ~350 nm) form with non-flat (round) top surfaces (Figure 4-15B). For film thicknesses of 13 and 17 nm, vertically grown ZnO rods (~230 nm in diameter and 1 μm in length) with well-defined hexagonal top surface and homogeneous crystallite size are acquired (Figure 4-15C,D). This indicates the nucleation of ZnO growth centers on these rGO films is very fast and the nucleation behavior is almost instantaneous. Moreover, ZnO nuclei density was similar (~9.0 μm⁻²) on rGO films of four different thicknesses.

The morphology change from particle-like to nanorod implied the ZnO growth rate along the *c*-axis increased as the thickness/conductivity of the film increases. Therefore, ZnO electrodeposition on rGO film was strongly dependent on the film conductivity. When the film thickness increased, film conductivity increased, hence rGO electrode

current density increased under constant potential. The higher current density accompanied with promoted electrochemical reduction of the molecular oxygen in the solution, resulting in anisotropic growth of ZnO. In addition, surface (oxygen) defects on rGO films would play certain role in affecting ZnO crystal nucleation, as the example of GaN discussed in the introduction.

Figure 4-15. SEM images of ZnO grown on rGO films with thickness of (A) 5 nm, (B) 9 nm, (C) 13 nm and (D) 17 nm. The scale bars in the images and insets are 2 μm and 600 nm, respectively.

4.3.3 Effect of deposition potential on electrodeposition of ZnO on rGO-quartz

The applied potential is an important parameter to control the deposit morphology. Oxygen reduction to generate hydroxide ions occurs at 0.16 V vs. the saturated calomel electrode (SCE). When the cathode potential applied is more negative than this value, more hydroxide ions can be generated.

Figure 4-16. SEM images of ZnO deposited on rGO films at a potential of (A) -0.7 V, (B) -1.0 V, (C) -1.5 V and (D) -1.9 V (vs. SCE). The scale bars in the images are 2 μm .

Figure 4-16 illustrates the SEM images of ZnO deposited at different potentials on ca. 13 nm thick rGO films. At a potential of -0.7 V (Figure 4-16A), only ZnO particles with wide size distribution (particle density $\sim 5.4 \mu\text{m}^{-2}$, diameter ~ 330 nm) are observed. ZnO nanorods with good crystallinity are formed at a potential of -1.0 V (Figure 4-16B) (particle density $\sim 6.8 \mu\text{m}^{-2}$, diameter ~ 230 nm). The rod morphology is resulted from the higher hydroxide ions production rate at the more negative potential. The applied potential of -1.0 V is more negative than the required potential of -0.4 V for ZnO nanorods formation on ITO reported by Guo [132]. This is due to the higher resistance of rGO films ($\sim 3.3 \text{ k}\Omega/\text{sq}$), which is about 3 orders higher than the reported resistance of indium tin oxide (ITO) ($10 \Omega/\text{sq}$). At -1.5 V (Figure 4-16C), ZnO nanorods form with density of $\sim 7.2 \mu\text{m}^{-2}$ and diameter of ~ 220 nm while ZnO nanorods with a higher density of $\sim 9.6 \mu\text{m}^{-2}$ and a smaller diameter of ~ 200 nm are formed at -1.9 V (Figure 4-16D). The increased density and decreased diameter with the increasing deposition potential

can be explained by the increased deposition rates of ZnO at more negative potentials and more absorption of zinc ions on the cathode under the higher electric field gradient [132].

4.3.4 Characterization of the ZnO nanorods / rGO composite

To understand the structure of ZnO/rGO composites, ZnO nanorods deposited on the 13 nm thick rGO film (composite α) have been characterized by X-ray diffraction (XRD), photoluminescence (PL) and transmission electron microscopy (TEM). The XRD pattern of the composite α (Figure 4-17A) reveals the wurtzite structure of ZnO with space group of $P6_3mc$ [136]. The sharp diffraction peaks suggest the good crystallization of ZnO. The higher intensity of the ZnO (002) diffraction peak than other peaks confirms the preferential anisotropic growth of ZnO along the c -axis of the [001] direction and perpendicular to the rGO film, which can also be observed from the SEM images. The room-temperature PL spectrum of the composite α (Figure 4-17 B) exhibits a peak at ~ 390 nm, which agrees with the energy bandgap (3.2 eV) of ZnO crystals [137].

Figure 4-17. (A) XRD pattern and (B) PL spectrum of composite α .

Figure 4-18A shows the high resolution TEM (HR-TEM) image of a random ZnO nanorod (inset of Figure 4-18A) on rGO films. The lattice spacing of 0.26 nm is consistent with the interplanar distance of (002) crystal planes of ZnO. The selected area electron diffraction (SAED) pattern (Figure 4-18B) clearly presents the resolved diffraction spots, confirming the single crystalline characteristic and wurtzite structure of the ZnO nanorod.

Figure 4-18. (A) HR-TEM image of a ZnO nanorod from the composite α . Inset: TEM image of the ZnO nanorod. (B) SAED pattern from the ZnO nanorod in (A).

4.3.5 Effect of annealing on electrodeposition of ZnO on rGO-quartz

Since the conductance of the rGO films is much lower than that of ITO, thermal annealing is required to further remove oxygen functionalities on rGO films and hence improve its conductivity [68]. Figure 4-19A reveals the resistance change of the films upon thermal annealing at 1100 °C for 2 h. About seven times decrease in resistance has been achieved through the thermal treatment. A low resistance of ca. 0.4k Ω /sq rGO films (thickness $\sim$ 13 nm) was attained for the composite fabrication. Many deep wrinkles

forming a microstructure network is observed in the AFM image of the as-annealed rGO film (Figure 4-19B). This could be explained by the different thermal expansion coefficients between rGO and quartz [138, 139] and hence the resulted strains in rGO film from thermal annealing.

Figure 4-19. (A) Annealing effect on rGO film resistance. (B) AFM image of annealed rGO film at 1100 °C for 2 h (thickness ~ 13 nm).

Figure 4-20. SEM images of ZnO formed on (A) nonannealed rGO film and (B) annealed rGO film at 1100 °C for 2 h (thickness ~ 13 nm). The scale bars in the images and insets are 2 μm and 600 nm, respectively.

ZnO rods with well defined hexagonal top surfaces are obtained on nonannealed rGO films (Figure 4-20A) while ZnO rods deposited on annealed rGO films (composite β) are more uniform (Figure 4-20B). The annealing effect is the same as increasing film thickness/conductivity, which promotes nucleation and growth rate of ZnO nanorods.

Raman spectra (Figure 4-21A) of both rGO film and ZnO/rGO (composite β) exhibit peaks at 1350 and 1590 cm^{-1} , which correspond to D and G band of rGO, respectively. Higher intensity of D band than that of G band confirms the derivation of rGO. Three additional peaks at 438, 570, and at 1143 cm^{-1} in the spectrum of ZnO/rGO belong to characteristic signals of E_2 , E_1 (LO) mode, and Raman 2LO mode in the ZnO wurtzite structure, respectively [140].

Figure 4-21. (A) Raman spectra of rGO and ZnO/rGO (composite β), (B) Mott-Schottky plot of composite β in 0.05M KCl aqueous solution.

Mott-Schottky (MS) plot was measured at the ZnO nanorods - electrolyte interface to determine the conduction type and carrier concentration of the ZnO nanorods deposited on rGO films. Figure 4-21B shows the MS plot of composite β in 0.05M KCl solution.

The positive slope of the MS curve suggests n-type semiconducting character of the ZnO nanorods deposited on the rGO film. The donor concentration in ZnO nanorods can be calculated using the following MS equation [107]:

$$\frac{1}{C_{sc}^2} = \pm \frac{2}{e\epsilon\epsilon_0 A^2 N_{D/A}} \left(V - V_{FB} - \frac{kT}{e} \right) \quad (\text{"+" represents n-type, "-" represents p-type})$$

where C_{sc} is the capacitance of the space charge region, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the permittivity of the free space, $N_{D/A}$ is the donor/acceptor concentration, V is the applied potential, and V_{FB} is the flatband potential.

According to the MS equation ($\epsilon = 10$ for ZnO [141], $A = 0.2 \text{ cm}^2$), the donor concentration for ZnO nanorods is $\sim 0.45 \times 10^{20} \text{ cm}^{-3}$, which is close to the value for electrodeposited ZnO nanowires [141] or columns [142] on fluorine-doped tin oxide (FTO). The as-obtained ZnO/rGO composites have great potentials in electro-optical device application, for example, solar cells.

4.3.6 Hybrid solar cells based on ZnO/rGO composites

Inorganic-organic cells based on ZnO/rGO composites were fabricated. The cell contains a layered structure of quartz/rGO/ZnO nanorods/P3HT/PEDOT:PSS/Au (inset of Figure 4-22A). Composites α and β were used for devices I and II, respectively. Electrons from the excited state (lowest unoccupied molecular orbital, LUMO) of P3HT are first injected into the conduction band (E_c) of ZnO and then reach the rGO electrode (Figure 4-22B). Under illumination, the current density-voltage curve for device I (Figure 4-22A) shows an open-circuit voltage (V_{oc}) of 0.52 V, a short-circuit current density (J_{sc}) of 0.92 mA cm^{-2} , a fill factor (FF) of 0.30 and overall power conversion efficiency (η) of 0.14%. Moreover, the current density-voltage curve for device II shows a V_{oc} of 0.66 V, a

J_{sc} of 1.43 mA cm^{-2} , a FF of 0.33 and overall power conversion efficiency (η) of 0.31%. The better performance from device II could be explained by the improved conductivity and modified work function of the annealed rGO film in composite β . The work function decrease from 5.0 eV of nonannealed to 4.7 eV of annealed rGO is observed. This would lead to an increase in V_{oc} and provides a better match between the E_c of ZnO and Fermi level of rGO, which consequently results in better electron-hole separation and improved electron collection efficiency. However, there is still room to improve the performance of the devices based on the ZnO/rGO composites by optimizing the rGO films quality.

Figure 4-22. (A) Current density-voltage curves based on composite α (Device I) and composite β (Device II), the inset shows the device structure, and (B) energy level diagram of solar cells based on ZnO/rGO.

4.3.7 Electrodeposition of ZnO on rGO-based flexible substrate

In the above study, ZnO nanorods were electrodeposited on rGO films spin-coated on quartz wafer while rGO films spin-coated on the easy-bending substrate of polyethylene terephthalate (PET) (rGO-PET) could also be applied for electrochemical synthesis.

The photograph and AFM image of rGO-PET substrate (rGO film thickness ~ 11 nm) are shown in Figure 4-23A and B. It can be observed that the rGO-PET surface is quite rough (RMS = 2.6 nm in $3 \times 3 \mu\text{m}^2$). The Raman spectrum of rGO-PET (Figure 4-23C) exhibits the typical D and G bands of rGO at 1342 and 1571, respectively. The other Raman peaks belong to the PET substrate [143]. The transmittance of rGO-PET substrate is $\sim 47\%$ from the UV-Vis measurement (Figure 4-23D). The as-obtained rGO-PET substrates with a resistance of ca. 15 k Ω /sq are used for ZnO deposition.

Figure 4-23. (A) Photograph, (B) AFM image, (C) Raman spectrum and (D) UV-Vis transmittance spectrum of rGO-PET substrate (thickness ~ 11 nm).

At a low potential of -1 V, the obtained ZnO on rGO-PET shows a poor morphology (Figure 4-24A) due to the lower conductivity of rGO films. ZnO nanorods can be formed with good crystalline structures when the potential is changed to -1.9 V (Figure 4-24B).

Figure 4-24. SEM images of electrochemically deposited ZnO on rGO-PET at (A) -1 V and (B) -1.9 V (vs. SCE), respectively.

Figure 4-25. XRD pattern of (A) ZnO/rGO composites on PET (Inset: Magnified plot in the 2θ region of 30° - 60°) and (B) rGO-PET, respectively (XRD peaks labeled with Δ are from PET).

ZnO/rGO composites on PET substrates have been characterized by XRD (Figure 4-25A), which indicates the wurtzite structure of ZnO. Figure 4-25B presents the XRD pattern of rGO-PET while the peak from rGO cannot be observed due to the overlap of peak position with PET at 26° and its weak signal. Figure 4-26A shows the TEM image of a ZnO nanorod from the composites. The SAED pattern (inset in Figure 4-26A) displays the typical dot pattern, confirming its good crystallinity. The lattice spacing of

0.26 nm in the HR-TEM image of the nanorod (Figure 4-26B) is consistent with the interplanar distance of ZnO (002) crystal planes.

Figure 4-26. (A) TEM image of a ZnO nanorod. Inset: SAED pattern. (B) HR-TEM image at the edge of the ZnO nanorod in (A).

4.3.8 Short summary

In conclusion, ZnO/rGO composites have been achieved by electrochemical deposition. In addition, effects of rGO film thickness, deposition potential and film annealing on ZnO deposition on rGO films have been investigated. N-type ZnO nanorods with high donor concentration deposited on rGO films have been characterized by XRD, Raman, PL, SEM and TEM, showing the wurtzite structure and good crystallinity. As-obtained ZnO/rGO composites have been applied for solar cell fabrications, showing a power conversion efficiency of 0.31%. The composites open up a new avenue for design of inorganic-organic hybrid solar cell with stronger adhesion between the semiconducting nanomaterials and rGO electrodes. Moreover, the synthesis of ZnO/rGO composites has also been realized on flexible substrates of PET, which makes it promising to construct flexible photovoltaic devices with ZnO/rGO composite materials.

4.4 Synthesis of Cu₂O / Reduced Graphene Oxide (rGO) Composites through Electrochemical Deposition Method

4.4.1 Introduction

In addition to abovementioned Cu/rGO, ZnO/rGO composites, electrochemical deposition method can be used to obtain composites of Cu₂O/rGO. Cu₂O is a cheap, non-toxic semiconducting oxide material that can be obtained in large quantities [144]. It is typically obtained as a p-type material [106] with a narrow direct band gap of 1.9-2.2 eV and a relatively high solar absorbance [145]. It is a viable catalyst for water decomposition when illuminated [144-146]. Moreover, it can be used in gas sensors [147], lithium ion batteries [148] and photovoltaic devices [149]. Cu₂O nanostructures can be produced by several different methods, such as the sonochemical method [150], solution-phase method [151, 152], thermal oxidation [153] and so on. Besides the aforementioned methods, electrodeposition is widely used for the synthesis of Cu₂O nanostructures because it can control the deposit morphology and property by tuning the electrolyte pH or the electrode overpotential [106-108, 154,155].

The electrochemical reactions to deposit Cu₂O using CuSO₄ as Cu precursor take place in two steps: the reduction of Cu²⁺ ions and the hydrolysis of Cu₂O, i.e. $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$ and $2\text{Cu}^+ + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O}$ [106-108]. Lactic acid is often added to the deposition bath to form complexes with Cu²⁺ and hence stabilize Cu²⁺ in basic solutions [106]. Effects of one important parameter on Cu₂O electrodeposition, electrolyte pH, are discussed in the following paragraphs.

The electrolyte pH has been found to influence the orientation of the Cu₂O film. Under the conditions of pH = 9, the Cu₂O film deposited on Ti film at 30°C shows a [100]

preferred orientation while it exhibits a [111] orientation under pH = 12 [156]. This is also observed when the Cu₂O film is deposited on stainless steel or ITO or n-InP (001) [106, 155]. The explanation for pH dependent film orientation may be given by the growth kinetics of Cu₂O. The growth rate along different crystallographic direction is pH dependent and correlated with the selective absorption of Cu(II)-lactate complexes on different crystal faces [155].

Moreover, electrolyte pH can influence the conduction type of Cu₂O. It is believed that the typical p-type conductivity of Cu₂O is resulted from the presence of copper vacancies, which introduces an acceptor level above valence band [107, 157]. However, the source for the n-type conductivity in Cu₂O is controversial. Wang et al. suggested the change of Cu₂O conductivity type was due to the suppressed copper vacancies and increased oxygen vacancies by varying solution pH [107]. Later, they claimed the copper antisites were mainly responsible for the n-type Cu₂O formed under strong acidic condition, not the neutral state of oxygen vacancies [158]. However, Scanlon et al. had an opposite opinion and demonstrated that the abovementioned defects cannot be the source of the n-type conduction in Cu₂O from the first-principle calculations [159]. The n-type conductivity may stem from the formation of an inversion layer during electrochemical deposition process [159].

In this section, we have prepared the Cu₂O/rGO composites through the electrochemical deposition method. The effects of solution pH on Cu₂O morphology and conduction type have been discussed. Besides, the n-type Cu₂O by Cl doping has been deposited on rGO electrodes and the effect of Cl doping on Cu₂O properties has also been studied.

4.4.2 Electrodeposition of p-type Cu_2O on rGO-polyethylene terephthalate (PET)

Same as the rGO-PET substrates for ZnO deposition, rGO electrodes for Cu_2O deposition were fabricated by reduction of GO films (ca. 11 nm thick) spin-coated on PET substrates. Figure 4-27A-B shows the SEM images of pyramidal Cu_2O crystallites deposited on rGO-PET at pH 9. The (111) planes at the slope side of the p-type Cu_2O crystal indicate [111] is the slower growth direction [155].

Figure 4-27. (A-B) SEM images of Cu_2O electrodeposited on rGO-PET at pH 9. (C) Mott-Schottky plot of as-obtained p-type Cu_2O on rGO-PET. (D) XRD pattern of p-type Cu_2O on rGO-PET (peaks labeled with Δ are from PET). (E) TEM image of a p-type Cu_2O crystal. Inset: SAED pattern. (F) HR-TEM image at the edge of p-type Cu_2O in (E).

The Mott-Schottky (MS) plot (Figure 4-27C) was measured at the interface between Cu_2O and the Na_2HPO_4 electrolyte to characterize the Cu_2O semiconducting behavior.

The negative slope of MS plot suggests the p-type semiconducting characteristic (referred to as p-type Cu₂O) of Cu₂O grown in the basic solution. According to the MS theory, the acceptor concentration is calculated to be $1.40 \times 10^{20}/\text{cm}^3$ ($\epsilon = 6.3$ for Cu₂O [107], $A = 0.4 \text{ cm}^2$).

XRD pattern of p-type Cu₂O on rGO-PET (Figure 4-27D) confirms the derivation of Cu₂O rather than CuO or Cu [106]. The higher intensity of (200) diffraction peak is observed from the pattern of Cu₂O (compared to the standard XRD data JCPDS 5-667), which may be explained by the deposition current density. It has been reported that Cu₂O deposited at a current density of $5 \times 10^{-5} \text{ A/cm}^2$ exhibited a stronger [100] orientation [160]. The deposition current density in our experiment for p-type Cu₂O was $\sim 7 \times 10^{-5} \text{ A/cm}^2$, similar to the previously reported current density ($5 \times 10^{-5} \text{ A/cm}^2$) [160].

Figure 4-27E shows the TEM image of a p-type Cu₂O crystal scratched from the electrode. The selected area electron diffraction (SAED) pattern (inset in Figure 4-27E) shows the bright individual diffraction dots, confirming the single crystallinity of the p-type Cu₂O crystal grown on rGO-PET. HR-TEM image of a portion of the crystal (Figure 4-27F) shows the lattice spacings of 0.14 and 0.12 nm, corresponding to the interplanar distances of ($\bar{2} 20$) and ($\bar{3} \bar{1} 1$) planes in the Cu₂O lattice, respectively.

4.4.3 Electrodeposition of n-type Cu₂O on rGO-PET

Cu₂O shows a quite different morphology (Figure 4-28A-B) when it is deposited in an electrolyte of pH 7 to form the p-type Cu₂O. The MS plot of the as-deposited Cu₂O (Figure 4-28C) displays a linear relationship between the $(C_{sc})^2$ and the applied potential with a positive slope, which suggests the n-type semiconducting nature of Cu₂O

deposited in the neutral solution (referred to as n-type Cu_2O). The carrier (donor) concentration calculated is ca. $3.50 \times 10^{19}/\text{cm}^3$, which is lower than that of p-type Cu_2O . XRD pattern (Figure 4-28D) confirmed the deposited film is Cu_2O . In addition, the crystal structures of p-type Cu_2O and n-type Cu_2O are the same as both XRD patterns are consistent with the standard XRD data JCPDS 5-667. The lattice parameter of n-type Cu_2O (4.25 Å) calculated from the XRD pattern is slightly larger than that of p-type Cu_2O (4.22 Å). A thin sheet of n-type Cu_2O scratched from the rGO electrode is observed in the TEM image (Figure 4-28E). The SAED pattern (inset in Figure 4-28E) from the sheet exhibits the clearly resolved dot pattern, confirming the good crystallinity of n-type Cu_2O deposited on rGO-PET. Figure 4-28F shows the HR-TEM image at the inner portion of Cu_2O sheets with the lattice spacing of 0.21 nm, which agrees with the interplanar distance between (020) crystal planes.

Figure 4-28. (A-B) SEM images of electrochemically deposited Cu_2O on rGO-PET at pH 7. (C) Mott-Schottky plot of as-obtained n-type Cu_2O on rGO-PET. (D) XRD pattern

of n-type Cu_2O on rGO-PET (XRD peaks labeled with Δ are from PET). (E) TEM image of an n-type Cu_2O crystal. Inset: SAED pattern. (F) HR-TEM image at the edge of n-type Cu_2O in (E).

4.4.4 Electrodeposition of Cl-doped n-type Cu_2O on rGO- SiO_2

Although the electrolyte pH value could influence the conduction type of Cu_2O , it is difficult to prepare n-type doped Cu_2O of high quality. Doping through introducing a new element can be used to tailor the electrical properties of materials [161]. In our study, high-quality n-type doped Cu_2O /rGO composites have been achieved by introducing substitutional n-type dopant of Cl through the electrochemical method. RGO- SiO_2 electrodes were prepared by reduction of GO films spin-coated on the SiO_2 substrate and used for the synthesis of the composites.

Besides the two-step electrochemical reactions involved in the deposition bath of Cu_2O , another reaction ($\text{Cu}^+ + \text{Cl}^- \rightarrow \text{CuCl}$) occurred because of the addition of chlorine (Cl) precursor (CuCl_2) [108]. This reaction induced the incorporation of Cl into Cu_2O due to the limited solubility of CuCl [108]. Doping of Cl is usually substitutional as the radius of Cl^- ions (1.8 Å) is larger than that of O^{2-} ions (1.4 Å).

A typical sample of Cl-doped Cu_2O deposited on rGO electrode in an electrolyte containing 1 mmol CuCl_2 is referred to as Cl- Cu_2O . The XRD pattern (Figure 4-29A) indicates the derivation of Cu_2O and its cubic crystal structure with space group of $\text{Pn}\bar{3}$ (according to the standard XRD data JCPDS 5-667) [106]. No other phases form due to the Cl doping. In addition, the sharp diffraction peaks suggest the good crystallinity of Cl- Cu_2O .

Figure 4-29. (A) XRD pattern and (B) Raman spectrum of Cl- Cu_2O deposited on rGO electrode.

Raman spectrum of Cl- Cu_2O /rGO composites (Figure 4-29B) shows peaks at 1360 and 1594 cm^{-1} , corresponding to D and G band of rGO electrodes, respectively. It also displays peaks at 218, 306, 435 and 625 cm^{-1} , belonging to the second-order overtones $2\Gamma_{12}$, $2\Gamma_{15}^{(1)}$, fourth-order overtone $4\Gamma_{12}$, red-allowed mode $\Gamma_{15}^{(2)}$ (TO) phonon vibration of crystalline Cu_2O [162]. SiO_2 substrate produces the strongest peak, which is calibrated at 520 cm^{-1} . There is an overlapping peak from SiO_2 substrate and the adsorbed sulphate species on the Cu_2O crystals at 980 cm^{-1} due to the presence of CuSO_4 in the Cl- Cu_2O deposition bath contains [163].

Figure 4-30. (A) SEM image and (B) EDX spectrum of electrochemically deposited Cl- Cu_2O on rGO electrode. (C) TEM image of a Cl- Cu_2O crystal. Inset: SAED pattern.

SEM image of the Cl-Cu₂O (Figure 4-30A) shows the micrometer sized crystallites with typical (111) planes at the slope sides and some multifaceted crystallites nucleated on pre-formed large crystallites. The inset exhibits an enlarged view of the crystallites. The elemental composition of Cl-Cu₂O from the EDX spectrum (Figure 4-30B) indicates the successful incorporation of 2.1% Cl (atomic concentration) into the deposited Cu₂O. Figure 4-30C shows the TEM image of a Cl-Cu₂O crystal scratched from the rGO electrode. The SAED pattern (inset in Figure 4-30C) from the crystal presents individual diffraction dots, confirming the good crystallinity of the deposited Cl-Cu₂O.

Figure 4-31. (A) Mott-Schottky plot for Cl-Cu₂O on rGO electrode in 0.1 M Na₂HPO₄ solution at pH 10. (B) Variation of carrier concentration as a function of CuCl₂ amount added into the electrolyte.

MS measurement at the interface between Cl-Cu₂O and the Na₂HPO₄ solution (Figure 4-31A) shows a positive slope, confirming the n-type semiconducting behavior of Cl-Cu₂O. The donor concentration calculated from the slope of the MS plot is about $1 \times 10^{20}/\text{cm}^3$ according to the MS theory ($\epsilon = 6.3$ for Cu₂O). A series of samples were

deposited in the electrolyte with the addition of different CuCl_2 amounts to study the effect of CuCl_2 on the carrier concentration of Cu_2O film. All the samples displayed a positive slope of MS plot and hence they were n-type semiconducting. Figure 4-31B shows the change of carrier concentration with the CuCl_2 amount added into the solution. Till the addition of 1.0 mmol CuCl_2 , the carrier concentration increases slowly with the CuCl_2 amount. When the amount of added CuCl_2 exceeds 1.0 mmol, the carrier concentration decreases rapidly.

Figure 4-32. SEM images of Cl- Cu_2O deposited in the electrolyte with addition of (A) 0.3 (B) 1.0, and (C) 1.3 mmol CuCl_2 .

Theoretically, chlorine (group VII element), as a substitutional dopant for oxygen (group VI element) sites, would contribute electrons to the crystal and hence increase the concentration of charge carriers (electrons) in Cu_2O . However, it was found that Cu_2O crystals were difficult to grow on rGO electrodes when the CuCl_2 amount in the electrolyte exceeded 1.0 mmol in our experiments. The amount of Cl- Cu_2O crystals deposited with 1.3 mmol CuCl_2 on rGO electrode is much lower than those deposited with 0.3 and 1.0 mmol CuCl_2 (as shown in Figure 4-32). This is similar to the situation that Cu electrodeposition is inhibited by the presence of Cl^- ions as its surface is covered

with almost insoluble CuCl [164]. Besides, when the Cl^- ion concentration in the solution exceeds $8.45 \times 10^{-4} \text{ M}$, kinetics and mechanisms of Cu deposition are changed, for example, anodic exchange current density increases [164].

Figure 4-33. Photocurrent measured from Cl- Cu_2O deposited with three different chlorine precursor (CuCl_2) amounts in a solution of 0.5 M Na_2SO_4 .

Figure 4-33 displays the photocurrent measurements at an applied potential of -0.5 V (vs. Ag/AgCl) from Cl- Cu_2O samples deposited with three different amounts of CuCl_2 . All the samples produce the anodic photocurrents that are characteristics of n-type semiconducting material [108]. Obviously, Cl- Cu_2O deposited with addition of 0.3 mmol (referred to as 0.3-Cl- Cu_2O) and 1.0 mmol CuCl_2 (referred to as 1.0-Cl- Cu_2O) shows much larger photocurrent than that deposited with addition of 1.3 mmol CuCl_2 . The larger photocurrent indicates a higher light-to-electrons/holes conversion efficiency or light harvesting efficiency. The surface coverage of the deposited Cl- Cu_2O on rGO electrode is believed to be the main factor that influences the light harvesting efficiency.

The slightly higher photocurrent from 1.0-Cl-Cu₂O than that from 0.3-Cl-Cu₂O can be explained by the higher Cl-doping concentration in 1.0-Cl-Cu₂O although they have similar surface coverage of Cu₂O crystals on rGO electrode.

4.4.5 Short summary

In summary, Cu₂O/rGO composites have been obtained by electrochemical deposition. The pH effects on Cu₂O morphology and semiconducting behavior have been investigated. Comprehensive understanding on the structures of Cu₂O/rGO composites has been realized based on characterizations and analysis. Besides, to get n-type Cu₂O, element Cl has been introduced into the Cu₂O/rGO composites through the electrochemical synthesis techniques. From our work, it has been found that the amount of chlorine precursor (CuCl₂) in the electrolyte influences the growth and surface coverage of Cu₂O crystals on rGO electrode, subsequently affects the carrier concentration and light harvesting efficiency of Cl-Cu₂O/rGO composites. Our study has explored rGO-based composites synthesis using electrochemical methods and promised the potential of various future applications based on these composites.

4.5 Synthesis of Bifunctional Reduced Graphene Oxide (rGO)

Composites (Fe₃O₄-Pt/rGO) through Solution Processing Method

4.5.1 Introduction

With the development of various rGO-based composites, multifunctional composites based on rGO are stimulating a surge in rGO-related researches [165]. In the aforementioned experiments, we have employed rGO films for the composite synthesis through the electrochemical method. However, the electrochemical method still has some limitations for the multifunctional composites fabrication. From the literature review, solution processing methods have been applied for the composite synthesis using single-layer rGO as a suitable support material [53-58] and hence it is highly desired for our bifunctional rGO-based composite synthesis. In this section, we have designed and prepared bifunctional rGO composites of Fe₃O₄-Pt/rGO, which exhibit magnetic property of Fe₃O₄ nanoparticles and catalytic property of Pt nanoparticles at the same time.

The magnetic Fe₃O₄/rGO composites have been prepared by various synthetic strategies, such as chemical precipitation method [166], solvothermal reaction [167], high temperature decomposition of iron precursors [168], etc. These Fe₃O₄/rGO composites have shown excellent performances in electrocatalytic oxidation of guanosine [169], drug delivery [166], and lithium-ion batteries [170]. The preparation of catalytic Pt/rGO composites through solution processing methods has also been reported [16, 20, 171-173]. The as-prepared composites can be used for electrochemical sensing [20], oxygen reduction [171, 172], and methanol oxidation [173]. Therefore, rGO can acquire magnetic and catalytic property simultaneously through the decoration of Fe₃O₄ and Pt nanoparticles on its surface, subsequently the bifunctional rGO composites can be formed.

Moreover, the recycled use of Pt, a typical expensive noble metal catalyst, can be realized by applying an external magnetic field to the composites.

4.5.2 Synthesis and characterization of Fe_3O_4 nanoparticles decorated rGO ($\text{Fe}_3\text{O}_4/\text{rGO}$) sheets

XRD pattern of as-synthesized $\text{Fe}_3\text{O}_4/\text{rGO}$ (Figure 4-34A) proves the derivation of Fe_3O_4 rather than FeO or Fe_2O_3 and reveals its cubic crystal structure with space group of $\text{Fd}\bar{3}\text{m}$ (according to the standard XRD data JCPDS 19-0629). The peak at 21° from rGO corresponding to an interplanar spacing of 0.42 nm suggests GO is partially reduced since the theoretical spacing of graphene is 0.34 nm. The magnetic hysteresis loop of $\text{Fe}_3\text{O}_4/\text{rGO}$ (Figure 4-34B) reveals the magnetic response of the composite to the varying magnetic field with a saturation magnetization of 37.84 emu/g and a low coercivity value of 7.63 Oe.

Figure 4-34. (A) XRD pattern of $\text{Fe}_3\text{O}_4/\text{rGO}$. (B) Magnetic hysteresis loop of $\text{Fe}_3\text{O}_4/\text{rGO}$ and $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ measured at 300 K. Inset: Magnified plot in the square area.

Figure 4-35. (A-B) TEM images of Fe₃O₄/rGO. (C) Size distribution analysis of Fe₃O₄ nanoparticles on rGO. (D) HR-TEM image of Fe₃O₄/rGO. Inset: HR-TEM image of a Fe₃O₄ nanoparticle.

TEM images (Figure 4-35A, B) show the rGO sheet densely decorated with spherical Fe₃O₄ nanoparticles. These Fe₃O₄ nanoparticles have a uniform size of ca. 4.8 nm (Figure 4-35C). The inserted HR-TEM image in Figure 4-35D shows a random Fe₃O₄ nanoparticle on the rGO sheet. The lattice spacing of 0.26 nm may be assigned to the interplanar distance of (311) planes in the cubic magnetite (Fe₃O₄). Figure 4-36 shows the elemental composition of the composite and further confirms the presence of Fe₃O₄ nanoparticles.

Figure 4-36. (A) TEM images of Fe₃O₄/rGO. (B) EDS spectrum collected from the rectangular area in (A).

4.5.3 Synthesis and characterization of Fe₃O₄ and Pt nanoparticles decorated rGO (Fe₃O₄-Pt/rGO) sheets

Figure 4-37. XRD pattern of Fe₃O₄-Pt/rGO.

Pt nanoparticles have been deposited on the pre-synthesized Fe₃O₄/rGO composite by mixing K₂PtCl₆ and Fe₃O₄/rGO. The XRD pattern of Fe₃O₄-Pt/rGO (Figure 4-37) proves the successful deposition of Pt on Fe₃O₄/rGO and reveals the cubic close packed crystal structure of Pt with space group of Fm3m (standard XRD data JCPDS 04-0802). The

sharp diffraction peak of rGO in $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ at a larger angle of 22° compared to that in $\text{Fe}_3\text{O}_4/\text{rGO}$ indicates a smaller interplanar spacing of 0.40 nm and a more ordered structure of rGO. The smaller interplanar distance is resulted from the further reduction of rGO during the synthesis of Pt nanoparticles, which accompanies with removal of more oxygen functional groups in rGO. Besides, after decoration with Pt nanoparticles, the magnetic response of the $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ (Figure 4-34B) composite to the varying magnetic field shows a decreased saturation magnetization of 26.74 emu/g, which is due to the added mass of nonmagnetic Pt nanoparticles.

Figure 4-38. (A) TEM and (B) HR-TEM images of $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$.

It is difficult to distinguish between Pt and Fe_3O_4 nanoparticles from the TEM image of $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ (Figure 4-38A). However, they may be differentiated according to the lattice spacings in the HR-TEM image (Figure 4-38B). The lattice spacing of 0.22 might be assigned to the interplanar distances of (111) planes in the Pt lattice while the lattice spacing of 0.26 nm might be assigned to (311) planes in the Fe_3O_4 lattice. Figure 4-39 presents the EDS spectrum from $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and reveals the successful incorporation of Pt and Fe elements into the composite.

Figure 4-39. (A) TEM image of Fe₃O₄-Pt/rGO. (B) EDS spectrum collected from the rectangular area in (A).

The coverage density of Fe₃O₄ and Pt nanoparticles can be adjusted by changing the amounts of Fe and Pt precursors. Figure 4-40 shows an example of Fe₃O₄/rGO with a lower density of Fe₃O₄ and Pt nanoparticles.

Figure 4-40. (A) TEM images of Fe₃O₄/rGO synthesized with the mass feed ratio of GO to Fe₃O₄ is 1:1. (B-C) TEM images of Fe₃O₄-Pt/rGO synthesized by mixing 0.6 mg of

K_2PtCl_6 and 6 mg of $\text{Fe}_3\text{O}_4/\text{rGO}$ powder as shown in (A). (D) HR-TEM image of a Fe_3O_4 nanoparticle and a Pt nanoparticle on rGO.

4.5.4 Catalytic reduction of methylene blue (MB) with $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and sodium borohydride (SB).

Figure 4-41. (A) UV-vis spectra of MB solution before (black) and after reduction in presence of 0.1 M SB without (blue) and with (green) $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$. (B) Time for complete reduction of MB with recycled $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and SB. Inset: photograph of MB solution before (left) and after (right) reduction with $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and SB. The magnet in right inset is used to recycle the $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ composites.

A model reaction of MB reduced by $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ and SB has been used to study the catalytic activity of the $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ composite [111]. Figure 4-41A shows the UV-vis spectra employed for monitoring the MB reduction. The initial MB solution (black curve) seems unchanged even after mixing with 0.1 M SB for 40 min (blue curve), which indicates that SB is difficult to reduce MB. However, MB can be reduced by $\text{Fe}_3\text{O}_4\text{-}$

Pt/rGO and SB immediately, as observed from the dramatic decrease of absorption peaks at 609 and 663 nm (green curve in Figure 4-41A). Compared to the Pt/SiO_x nanowires composite which took more than 40 min to reduce MB completely [111], our Fe₃O₄-Pt/rGO composite exhibited much better catalytic activity.

The Fe₃O₄-Pt/rGO composite could be recycled within 1 min by applying an external magnetic field and repeatedly used for at least 16 times with minimum loss of the catalytic property. During the recycled use of the composite, only the MB reduction time increases from < 5 s at the 1st cycle to 1 min at the 16th cycle (Figure 4-41B).

4.5.5 Short summary

A bifunctional Fe₃O₄-Pt/rGO composite has been prepared for the first time through a facile solution processing approach and used for catalytic reduction of MB. Importantly, it can be recycled by applying an external magnetic field for at least 16 times with high catalytic activity. Our work shows that rGO, a two-dimensional material with a large surface area, can serve as an excellent template to anchor nanoparticles with different functions. The bifunctional rGO-based composites are promising for various applications such as electrochemical sensing, catalytic reactions, clean energy, *etc.*

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this thesis, graphene oxide (GO) and reduced graphene oxide (rGO) have been successfully synthesized and characterized. Electrochemical methods have been used to synthesize different rGO-based composites, *i.e.* Cu/rGO, ZnO/rGO, Cu₂O/rGO. Moreover, the bifunctional rGO-based composites have been synthesized through the solution processing approach. Several conclusions can be drawn from these works.

Single layer GO sheets can be achieved by a modified Hummers method. The hydrazine reduction process can transform the disordered GO to the crystalline rGO and restore its conjugated graphitic network and hence the conductivity. The conductive rGO films prepared by the reduction of spin-coated GO films show potential to replace indium tin oxide (ITO) in the electrochemical synthesis. The thicker rGO film exhibits a higher conductance but a lower optical transmittance.

During the synthesis of Cu/rGO composites through the electrochemical deposition, the Cu deposition on rGO is determined by the mass transport. The Cu nucleation behaviors in 10 mM and 50 mM CuSO₄ solution at -0.6 V on rGO are different from the experimental observations while they should be the same from the Scharifker-Hills model analysis. Moreover, it can be observed that the solution concentration of CuSO₄ influences the Cu morphology while the applied potential affects the cluster density greatly.

The electrochemical method can be also used to prepare ZnO/rGO composites. Both the film thickness and deposition potential would influence the ZnO morphology. High quality ZnO nanorods can only be obtained on the thicker rGO films with higher conductivity at a potential of more negative than -1.0 V. In addition, the density of ZnO nanorods on rGO films increases but their diameter decreases with increasing of the deposition potential. ZnO deposited on the annealed rGO film with a donor concentration of $\sim 0.45 \times 10^{20} \text{ cm}^{-3}$ has been applied for the solar cell fabrication, showing a power conversion efficiency of 0.31%. Moreover, synthesis of ZnO/rGO composites has been realized on flexible substrates of polyethylene terephthalate (PET), which could be applied for the fabrication of flexible photovoltaic devices.

The Cu₂O/rGO composites have been prepared by the electrochemical deposition as well. The pH value of electrolyte can influence the Cu₂O morphology and its semiconducting behavior. The p-type Cu₂O/rGO can be obtained in a deposition solution of pH = 9 while the n-type Cu₂O/rGO are obtained in a neutral solution. Besides, the chlorine has been introduced into the Cu₂O/rGO composites through the electrochemical method to improve the carrier concentration of n-type Cu₂O. Higher amount of chlorine precursor (CuCl₂) in the electrolyte may improve the carrier concentration of Cl-Cu₂O/rGO composites initially. However when the amount of CuCl₂ exceeds 1.0 mmol in our electrolyte, surface coverage of Cu₂O crystals on rGO electrode is poor and the carrier concentration of Cl-Cu₂O/rGO decreases significantly.

Besides electrochemical methods, the solution processing approach has been applied for the synthesis of bifunctional Fe₃O₄-Pt/rGO composites. As-synthesized composites

show a high catalytic activity towards the reduction of methylene blue. Moreover, it can be recycled by applying an external magnetic field for at least 16 times.

5.2 Recommendations for Future Work

In this thesis, the present work demonstrates the synthesis of rGO-based composites using electrochemical methods or solution processing approach. The electrochemical method shows well control of the deposit morphology and density of synthesized nanomaterials on rGO films while the solution processing approach is favorable for decorating different materials on rGO sheets. Therefore, several future works can be recommended.

First, metal oxides with different semiconducting behaviors have been electrodeposited on the flexible rGO electrode. Therefore, solar cell can be constructed by depositing n-type ZnO and p-type Cu₂O on rGO-PET. Cu₂O/ZnO heterojunctions have been studied extensively for fabrication of thin film solar cells because of the high theoretical conversion efficiency of ca. 18% [174]. In addition, the cheap and non-toxic Cu₂O and ZnO have favorable alignment of conduction band edges and similar atomic arrangements at the heterojunctions with a small lattice mismatch of 7.1% [175]. Therefore, it is possible to construct the flexible solar cells based on Cu₂O/ZnO/rGO-PET. Furthermore, since p-type or n-type Cu₂O can be obtained on rGO by adjusting the electrolyte pH or Cl-doping, solar cells based on p-type Cu₂O/n-type Cu₂O/rGO-PET can be realized in the future.

Second, other semiconducting materials can be prepared on rGO through the electrochemical deposition as well, for example, nickel oxide and cobalt oxide. Since the

electrochemical deposition can lead to strong adhesion between the rGO electrode and the deposited metal oxide materials, an enhanced performance of metal oxide/rGO composite is anticipated. It is known that carbon nanotubes (CNTs) have shown its capability in supercapacitors when the nickel oxide and cobalt oxide are electrodeposited on them [176, 177]. RGO with a large surface area and high electric conductivity has emerged as a competitor of CNTs, and shown a larger specific capacitance of 205 F/g than that from CNT-based supercapacitors [10]. Therefore, the supercapacitor based on nickel-cobalt oxides/rGO is highly expected.

Third, the electrochemical method can be used to reduce GO as well (referred as ER-GO), which has been investigated by Zhou et al. [45]. RGO has shown superior biosensing performance for detections of glucose, nucleic acids and biomolecules because of its large surface area, remarkable electron mobility and high density of electronic states [85-92]. Interestingly, ER-GO has also exhibited good electrocatalytic activity towards biomolecules [178]. Therefore, it is important to study the difference between rGO and ER-GO in structures and properties.

Fourth, the solution process approach for the synthesis of bifunctional $\text{Fe}_3\text{O}_4\text{-Pt/rGO}$ composites can be extended to synthesize other bifunctional rGO-based composites. For example, we can adopt this approach to decorate other magnetic nanoparticles, such as Co, CoO, Ni, and other metal nanoparticles, such as Pd, Ag, Au, onto the single-layer rGO sheets.

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