

Few-layer graphene obtained by electrochemical exfoliation of graphite cathode

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ABSTRACT

Few-layer graphene has been prepared by electrochemical intercalation of graphite cathode using Na⁺/dimethyl sulfoxide complexes as intercalation agent. By adding thionin acetate salt into the electrolyte, the exfoliated graphite is stabilized and further exfoliated into few-layer graphene. Raman and X-ray photoelectron spectra indicate that the graphene material has lower content of defects and oxygen functional groups compared with that obtained by chemically reducing graphene oxide. The graphene paper produced by filtration shows an electrical conductivity of 380 S m⁻¹, which is forty times larger than that of the graphene material produced by chemical reduction of thionin-stabilized graphene oxide.

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1. Introduction

Graphene [1], owing to its excellent physical and chemical properties [2], is promising to be used in a wide range of devices such as high speed transistors [3–5], transparent conducting films [6,7], lithium ion batteries [8–10], and supercapacitors [8,10,11]. The electrical conductance of graphene, which is sensitive to the content of defects and functional groups [12], affects strongly the performance of these devices. How to prepare graphene with low content of defects and functional groups is an important issue for applications of this material.

Chemical exfoliation by oxidation is one of the most widely used methods to obtain graphene [13–15]. This method involves oxidation of graphite to produce hydrophilic graphite oxide, which can be exfoliated as individual graphene oxide sheets by sonication in water. The hydrophilicity of graphene oxide comes from the oxygen functional groups such as –OH, C–O–C, and –COOH produced during oxidation of graphite [16,17]. Although most of these groups are removed in subsequent reduction, the electrostatic repulsion forces between graphene sheets induced by ionization of the remaining –COOH and phenolic –OH in alkaline condition make graphene well dispersed [18]. As a result, when graphite is oxidized vigorously, the graphene product without further thermal treatment has inevitably many oxygen functional groups and structural defects, resulting in poor electrical conduction.

Preparation of graphene by electrochemical exfoliation of graphite anode was first reported by Liu et al. in 2008 [19]. They used a mixed solution containing ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate and water as electrolyte. Through intercalation of PF₆⁻ ions into the graphite anode assisted by oxidation of graphite edges by hydroxyl radicals, a dispersion containing graphene was obtained. Subsequently, others also obtained successfully graphene using this method by changing the recipe of the electrolyte [20–22]. Although this method is easy to implement and to prepare graphene, the obtained graphene still has a lot of oxygen functional groups and structural defects due to the oxidation reactions at the graphite anode. On the other hand, it has also been reported that high yield production of few-layer graphene was achieved by intercalation of graphite cathode with Li⁺/propylene carbonate complex [23]. After brush painting of this graphene onto a commercial paper, a sheet resistance as low as 15 Ω/□ was obtained. Given the reported amount of deposited graphene and assuming less than 50% packing of graphene in the film, this value corresponds to an electrical conductivity of about 7000 S m⁻¹. By adjusting the voltage between working and counter electrodes, Morale et al. controlled the intercalation of hydrogen ions into graphite cathode in perchloric acid electrolyte. Combined with posterior microwave irradiation and sonication, graphene with few defects was successfully prepared [24].

Herewith we report the preparation and characterization of few-layer graphene by electrochemical exfoliation of graphite cathode using an electrolyte containing NaCl, dimethyl sulfoxide (DMSO), thionin acetate, and water. We demonstrate that the intercalation of Na⁺/DMSO complexes will lead to exfoliation of graphite. These edge-exfoliated graphite particles can be stabilized

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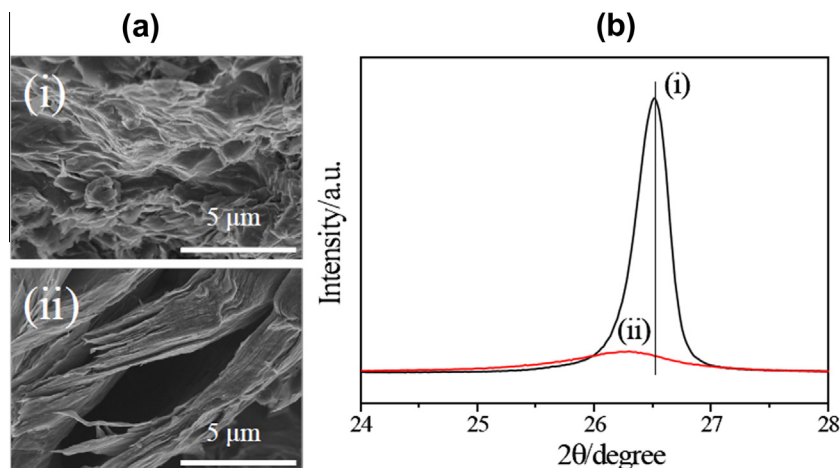


Figure 1. (a) SEM images and (b) the graphitic (002) peak in XRD of (i) natural graphite and (ii) electrochemically exfoliated graphite.

in situ by thionin acetate and be further exfoliated into few-layer graphene with mild sonication in water.

2. Experimental

2.1. Preparation of graphene

In our experiment, graphite rods were used as both anode and cathode. The electrolyte contained deionized water, NaCl, DMSO, and thionin acetate salt. Exfoliation of graphite cathode began after a DC voltage of 5 V was applied. The electrolyte containing edge-exfoliated graphite was first filtered using porous nylon membrane. After washing with ethanol and deionized water before ultrasonic treatment, the obtained suspension was shelved overnight to make most of the unexfoliated graphite settle to the bottom. Finally, the supernatant was separated by decantation and centrifugation to remove large graphite flakes. Graphene film was prepared by filtration of the aqueous graphene suspension.

2.2. Characterization

Morphology of the material sample was characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The interlayer spacing of both natural graphite and the edge-exfoliated graphite was examined by X-ray diffraction (XRD) for comparison. Electrical conductivity of graphene film was measured with a standard physics property measurement system (PPMS) (Quantum Design Model-9). The UV-vis spectrum was recorded on a Perkin Elmer Lambda 900 UV/vis/NIR Spectrometer. Raman and X-ray photoelectron spectroscopy (XPS) measurements were also performed.

3. Results and discussion

3.1. Preparation of graphene and mechanism of formation

In our method, a mixed solution containing NaCl and DMSO was used as the electrolyte for electrochemical exfoliation of the graphite cathode. It has been reported that the sodium ions tend to combine with four or five DMSO molecules to form Na^+/DMSO complexes [25]. After a DC voltage was applied, these complexes would intercalate into the interlayer space of graphite to form ternary graphite intercalation compound ($\text{Na}^+(\text{DMSO})_y\text{C}_n^-$). The interlayer spacing of this compound was reported to be 1.246 nm, which was nearly four times as large as that of natural graphite

(0.34 nm) [26]. The huge internal stress induced by the intercalation of Na^+/DMSO complexes led to the expansion of graphite cathode. For comparison, natural graphite obtained from the electrode was also examined. Figure 1a shows the SEM images of both natural graphite and electrochemically treated graphite. We can see that, relative to natural graphite, the electrochemically treated graphite has obviously been exfoliated. Figure 1b shows the XRD pattern of the two samples. The shift of the graphitic (002) peak in the electrochemically treated graphite to a lower angle relative to natural graphite indicates the expansion of graphite particles after electrochemical intercalation of Na^+/DMSO complexes. The intensity of the (002) peak for electrochemically treated graphite decreased by more than ten times than natural graphite and it reveals that the long-range periodicity associated with the stacking of graphene in the *c*-axis in graphite has also been destroyed by electrochemical intercalation.

The mechanism for the formation of exfoliated graphene is illustrated in Figure 2. Let us assume that there were three graphite particles named Particle 1, Particle 2, and Particle 3, which were not arranged in parallel on the surface of graphite cathode. After the Na^+/DMSO complexes intercalated into Particles 1 and 3, the extraction of graphene layers in these two particles will produce stress F_1 and F_2 to Particle 2. By examining the mechanical forces, we can see that the resultant force of the two stresses F_1 point to the direction opposite to graphite cathode. Therefore, Particle 2 would fall off the electrode. When stresses F_1 and F_2 are large enough to cause Particle 2 fall off the electrode before its inner space is completely intercalated by Na^+/DMSO complexes, edge-exfoliated graphite Particle 2 will be obtained. As the edge-exfoliated graphite has relatively weak cohesion between the graphene layers, graphene was obtained by subsequent sonication of the edge-exfoliated graphite flakes in water.

In order to stabilize the obtained graphene, thionin acetate salt was added to the electrolyte. Thionin ion has a planar aromatic structure with two hydrophilic $-\text{NH}_2$ symmetrically distributed on each side and it has been demonstrated to stabilize aqueous graphene dispersion due to its amphiphilic nature [27]. As the thionin ion is positively charged, it can migrate to graphite cathode during electrochemical charging. Due to its strong interactions with graphene through synergistic noncovalent charge-transfer and π - π stacking forces, thionin ion would be adsorbed onto the surface of the exposed graphene layers in the edge-exfoliated graphite. The electrostatic repulsion forces due to the positive charges of thionin ions would prevent the graphene sheets from aggregation. In addition, the hydrophilic $-\text{NH}_2$ functional groups in thionine would facilitate the dispersion of graphene sheets in

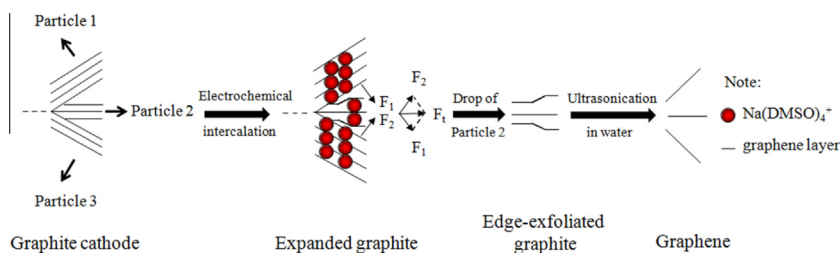


Figure 2. Illustration of the mechanism for production of few-layer graphene from exfoliation of graphite. Electrochemical intercalation of graphite led to exfoliation of the graphite edges and graphene is obtained by subsequent sonication of edge-exfoliated graphite (Particle 2).

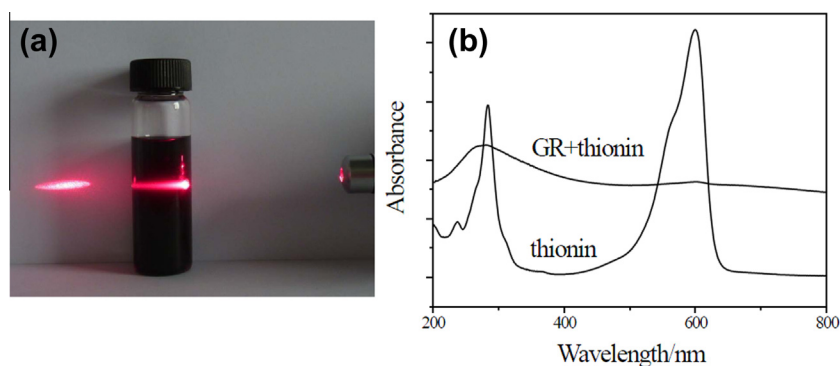


Figure 3. (a) Photograph of aqueous graphene dispersion. (b) UV-vis absorption spectra of both graphene aqueous dispersion and thionin acetate solution.

water. The presence of characteristic absorbance peak of thionin ions in the UV-vis spectrum at 283 and 600 nm, corresponding to the π - π^* transitions of aromatic rings and the n - π^* transitions of the C=N bond, respectively, of aqueous graphene dispersion is

shown in Figure 3b and it confirms the adsorption of thionin ions on graphene. After sonication of the edge-exfoliated graphite in water and posterior centrifugation, aqueous graphene dispersion was obtained (Figure 3a). The Tyndall effect observed with a laser

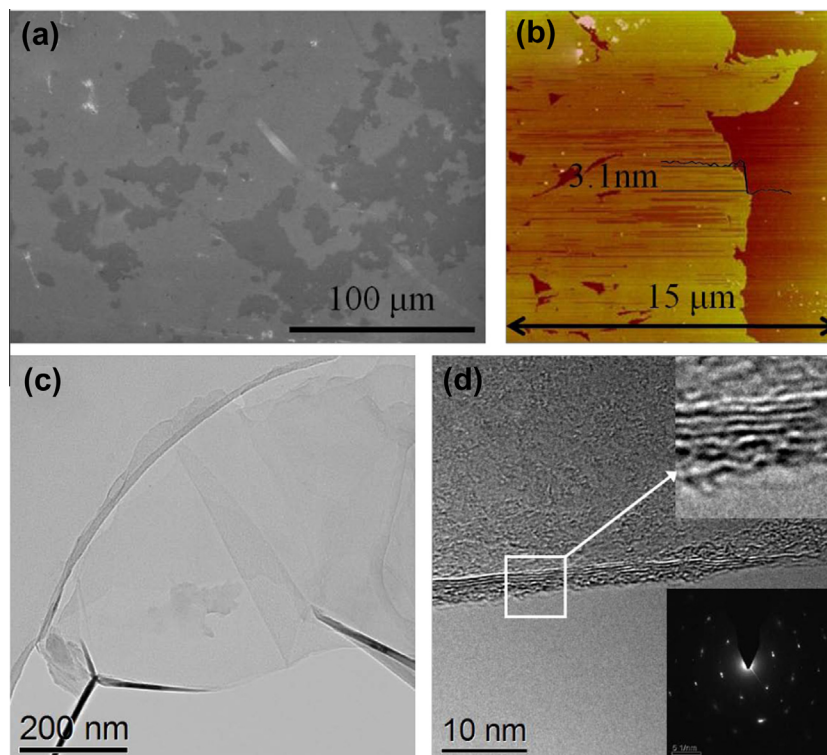


Figure 4. (a) SEM image and (b) AFM image of graphene flakes deposited on Si substrate. (c) TEM image and (d) HRTEM image of a graphene flake. The inset is electron diffraction pattern and magnified portion of the edge of the graphene flake.

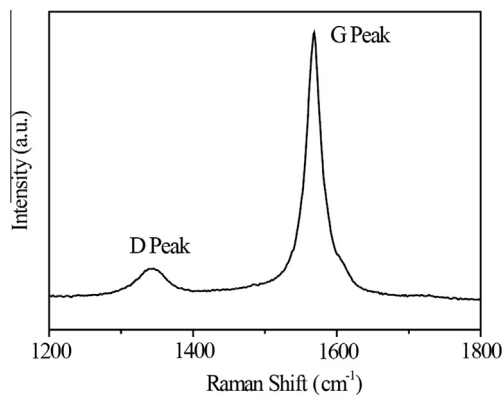


Figure 5. Raman spectrum of few-layer graphene prepared by electrochemically exfoliation of graphite cathode.

passing through the dispersion indicated that the graphene sheets were dispersed homogeneously in the solvent. This dispersion showed excellent stability without sedimentation even after it was shelved for three weeks.

3.2. Structural characterization

Figure 4a shows an SEM image of graphene flakes deposited on a Si substrate. It can be seen that most of the graphene flakes have large lateral size and macro-pores are present which are considered important for supercapacitor applications since the macro-pores can facilitate the diffusion of electrolyte into the space between graphene sheets. Figure 4b displays an AFM image of a graphene flake. As the lateral size is far beyond the AFM scan range, only part of the flake is shown here. The height profile in Figure 4b indicates that the graphene flakes have an average thickness of 3.1 nm. Taking into account the gap of 0.3 nm between stabilizer and graphene [28] and that the one-atom-thick thionin molecules are adsorbed onto both sides of graphene with face-to-face orientation [29], the layer number of this graphene flake is about seven with the interlayer spacing of graphene layers of 0.335 nm included.

To further characterize the graphene flakes, TEM analysis was conducted. It can be seen from Figure 4c that our graphene is surface clean without contaminant. The high resolution TEM image taken from the edge of the flake shown in Figure 4d indicates that it is composed of seven layers of graphene. This typical result is in agreement with that obtained from AFM measurement. The regular hexagonal diffraction pattern in Figure 4d indicates that this graphene flake is highly crystalline.

To detect the amount of defects and oxygen functional groups in our sample, Raman and XPS measurements were performed.

Table 1

Atomic weight percentage of elements in few-layer graphene material obtained from XPS spectrum.

Elements	C (wt%)	O (wt%)	N (wt%)	S (wt%)
Contents	85.60	6.81	4.14	3.45

There are two peaks in the Raman spectra for graphene in the range of 1200–1700 cm^{-1} , typically at 1350 cm^{-1} and 1580 cm^{-1} . These peaks are the D peak and G peak, which correspond to the TO phonons around the K point of the Brillouin zone and the E_{2g} phonons at the Brillouin zone center, respectively [30,31]. The D peak is related to the amount of defects, while the G peak is related to the amount of sp^2 hybrid carbon atoms. Therefore, the ratio between the intensity of D and G peak is often used to examine the amount of defects in graphene sample [22,32,33]. From the Raman spectrum shown in Figure 5, it can be seen that this ratio is about 0.1, which is much smaller than that of chemically reduced graphene oxide with many defects [15] and is comparable to that of small graphene flakes with perfect C–C bonding prepared by liquid-phase exfoliation of graphite in *N*-methyl-2-pyrrolidone [34], indicating the low concentration of defects in our graphene material. Besides, it was reported that larger disorder in graphite will lead to a broader G peak [35]. Since the G peak of the graphene material in the Raman spectrum is very sharp, a low concentration of defects in our graphene material is further confirmed. Figure 6 shows the wide scanning XPS spectra of the graphene sample along with its C 1s peak. The emergence of the N 1s, S 1s and S 2p peaks in the wide scanning XPS spectra indicates that the thionin cations were adsorbed on the graphene surface as stabilizer. The separated C 1s peak as seen in Figure 6b shows that the peaks corresponding to the C–O bond and the C=O bond occurring at 286.2 and 287.6 eV, respectively, were present, indicating that the graphene is still somewhat oxidized. Table 1 shows the weight percentage of all elements present in the sample obtained from the wide scanning XPS spectra. It can be seen that the mass-content ratio of oxygen to carbon atoms in the graphene is about 1:12.5, which is significantly lower than that of chemically reduced graphene oxide [36], indicating the low content of oxygen functional groups in our sample.

3.3. Electrical properties

For electrical conductivity measurement, the as-prepared graphene aqueous dispersion was filtered to form a film. From the image shown in Figure 7a, we can see that the graphene film is smooth and shows metallic flamboyance.

From the cross-sectional SEM image, the thickness of the film is obtained to be 5.5 μm . After cutting the film into a $5.0 \times 2.8 \text{ mm}^2$ piece, conductivity measurement was conducted on a standard physics property measurement system (PPMS). From the obtained

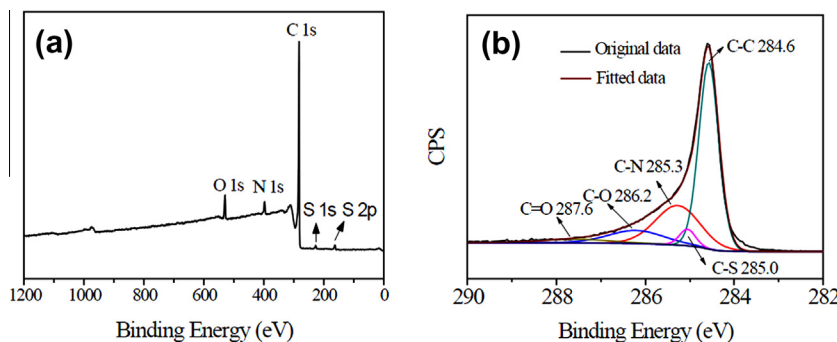


Figure 6. (a) Wide scanning XPS spectrum of the graphene prepared by electrochemical exfoliation of graphite cathode and (b) its C 1s spectrum with separated peaks.

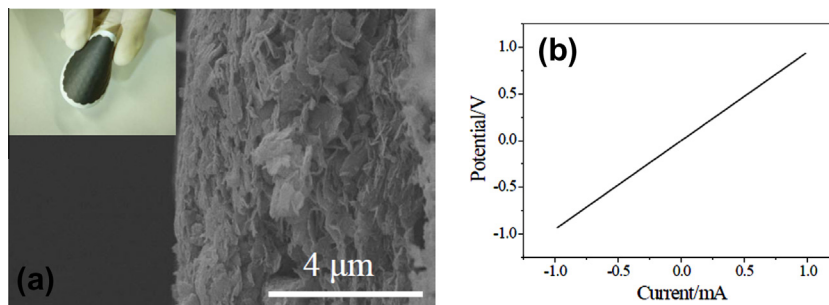


Figure 7. (a) Cross-sectional SEM image of graphene film. The inset is a digital photograph of the film. (b) Current–voltage plot of a $5.0 \times 2.8 \text{ mm}^2$ graphene film.

current–voltage plot shown in Figure 7b, the electrical conductivity of this film was calculated to be 380 S m^{-1} . This value is about forty times higher than that of thionin ion coated chemically-reduced graphene oxide paper [25]. It is worth noting that this electrical conductivity is still low compared with many other values obtained from graphene materials prepared by oxidative exfoliation and electrochemical exfoliation methods without using stabilizers [13,14,21,22]. This may be partially because the stabilizer (thionin) layers hinder the electrical contacts between neighboring graphene sheets and hence lower the electrical conductivity of the graphene film. On the other hand, it has been reported that the electrical conductivity of few-layer graphene decreases with the number of graphene layers and 7–8 is the critical layer number for transition in the electronic behavior from graphene to graphite [37]. Further investigations on reducing the number of graphene layers is in progress.

4. Conclusions

We have studied few-layer graphene produced by exfoliation and electrochemical intercalation of graphite cathode using Na^+ /DMSO complexes as intercalant and thionin acetate salt as stabilizer. The obtained graphene material has lower content of defects and oxygen functional groups compared with chemically reduced graphene oxide. The graphene paper obtained by filtration shows a forty times higher electrical conductivity than that of thionin-stabilized chemically reduced graphene oxide.

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