A simple and efficient electrochemical reductive method for graphene oxide

YANYUN LIU, DONG ZHANG*, YU SHANG and CHAO GUO

School of Material Science and Engineering, Tongji University, Caoan Road, Shanghai 200092, People's of Republic of China

MS received 29 July 2013; revised 1 October 2013

Abstract. The electrochemical reduction of graphene oxide typically involves complicated procedures, such as modification of electrodes and preparation of electrolytes, which is often needed in previous reports. In this paper, a simple and efficient electrochemical process is described for the synthesis of high-quality reduced graphene oxide. The main procedures involve the electrophoretic deposition of graphene oxide onto positive electrode and the subsequent *in situ* electrochemical negative reduction when the electrode changes from positive to negative. This approach opens up a new, practical and green reducing method to prepare large-scale graphene.

Keywords. Graphene oxide; electrophoretic deposition; negative reduction.

1. Introduction

The synthesis of graphene has been one of the hottest topics in scientific community in recent years because of its remarkable physical and chemical properties (Novoselov *et al* 2004; Lee *et al* 2008; Geim 2009) and its great promising application in devices or composites (Qu *et al* 2010; Wu *et al* 2010; Zhu *et al* 2010). During the past years, diverse procedures have been established for producing graphene, such as mechanical exfoliation (Novoselov *et al* 2004), epitaxial growth (Emtsev *et al* 2009; Kim *et al* 2009) and chemical or thermal reduction of graphene oxide (GO) (Stankovich *et al* 2007; Fan *et al* 2008). The synthesis route from graphite oxide is considered to be the most economical way for mass production of graphene (Geim *et al* 2009). However, it often employs hazardous chemicals (e.g. hydrazine) as reductants or rapid heat treatment at high temperature. The 'green synthesis' of graphene under mild conditions is preferred (Fan *et al* 2008). Electrochemical methods are a promising green strategy for graphene synthesis, and several research works have been reported (Ramesha and Sampath 2009; Zhou *et al* 2009). For example, An *et al* (2010) prepare graphene thin films by electrophoretic deposition of GO and simultaneous positive reduction. Zhou *et al* (2009) synthesized graphene films by coupling negative reduction and spray coating in various electrolytes. However, these methods would suffer from the limits of tedious procedures or want of special equipment. It is not suitable for large-scale production.

Moreover, the obtained products existed in the form of films absorbed on the electrode, which made the output very less efficient. Therefore, it is imperative to explore a simpler and more efficient electrochemical method to synthesize graphene.

In this paper, a simple and an efficient electrochemical process is described for the synthesis of graphene. The main procedures involve the electrophoretic deposition of GO on to positive electrode and the subsequent *in situ* electrochemical negative reduction when the electrode changes from positive to negative. Compared with the reported electrochemical reduction methods, our method has the following significant advantages: (1) It is simple to operate. In this method, several complicated procedures such as modification of electrodes and preparation of electrolytes are not needed. (2) It is highly efficient. The products can be collected not just from electrode, but also from the solution. It provides a promising method for large-scale fabrication of graphene.

2. Experimental

The GO used in this study was synthesized by the modified Hummers and Offeman (1958) method. It was dispersed in water (1 mg/mL) and sonicated for 2 h at room temperature. As much as 50 mL GO aqueous dispersion (1 mg mL⁻¹) was loaded in a 75 mL glass container. Copper electrodes were used in the experiment. The electrode separation was 5 mm. Figure 1 shows the electrochemical reaction process. The GO platelets migrated towards the positive electrode when a direct current (d.c.) voltage was applied. The adsorptive voltage and absorptive time were 30 V

*Author for correspondence (zhangdng@tongji.edu.cn)

Figure 1. Schematic illustration of electrochemical reaction.

Table 1. Samples prepared at different reductive voltages and time.

Sample	Reductive voltage (V)	Reductive time (min)
a-1	60	60
a-2	60	120
a-3	60	180
a-4	60	240
b-4	45	240
c-4	30	240

and 30 min, respectively. Then, adsorptive GO sheets were *in situ* reduced at certain reductive voltage and time, when the electrodes changed from positive to negative. The obtained samples were taken out from the solution and the electrode and thoroughly washed with deionized water and dried at 50 °C. We marked the samples as a-1, a-2, ..., c-4 according to different reductive voltage and time as in table 1.

The UV–Visible (UV–Vis) absorption spectra of the GO and graphene suspension were recorded with a Hitachi U-3310 spectrophotometer. The X-ray diffraction (XRD) images of the samples were measured using an X-ray diffractometer (D/max2550VB3+/PC, Rigaku, Japan) with reference target: CuK α radiation. Fourier transform infrared (FT–IR) spectra were obtained through a Bruker Equinoxss spectrometer use the attenuated total reflectance. X-ray photoelectron spectroscopy (XPS) studies were conducted on an RBD-upgraded PHI-5000C ESCA system (Perkin Elmer) with MgK α radiation ($h\nu = 1253.6$ eV). Raman scattering (Raman) was performed on an INVIA Raman spectrometer using a 488 nm laser source.

3. Results and discussion

The UV–Vis absorption peak of GO dispersion and the obtained graphene at different times are shown in figure 2(A). The peak of GO around 230 nm could be ascribed to the K-band absorption of aromatic compounds. It redshifted towards 260 nm after electrochemical reduction for 60 min and gradually redshifted to

270 nm after 240 min. This suggests that the electronic conjugation within the graphene nanosheets had been mainly restored after 240 min of reduction.

FT–IR spectra of GO dispersion and the obtained graphene at different times are shown in figure 2(B). The most characteristic features of GO are at 1060 cm^{-1} (C–O stretching vibrations), 1706 cm^{-1} (C=O stretching vibrations from carbonyl and carboxylic groups), 1650 cm^{-1} (C=C stretching vibrations from unoxidized graphitic domains), 1340 cm^{-1} (C–H bending vibration) and 3390 cm^{-1} (O–H stretching vibrations). After 60 min of reduction, the strongest vibrational absorption bands of O–H became weak (figure 2B(a-1)). The intensities of the peaks corresponding to the oxygen functionalities all decreased dramatically or even disappeared, when the reductive time reached 240 min (Figure 2B(a-4)). These data reveal that the GO have been successfully reduced with the time increased.

X-ray diffraction (XRD) of GO dispersion and the obtained graphene at different times are shown in figure 2(C). GO exhibited a very sharp diffraction peak at $2\theta = 11.4^\circ$. After 60 min of reduction, the intensities of peak became weak at $2\theta = 11.4^\circ$. Meanwhile, a new peak of graphene at $2\theta = 23.9^\circ$, weak and broad, was observed. The regular stacks of GO were destroyed and their diffraction peaks at $2\theta = 11.4^\circ$ became weaker or even disappeared, when the reductive time reached 240 min, indicates that the oxygen-containing group of GO had been efficiently removed. Meanwhile, interlayer *d*-spacing became small.

Figure 2(D) shows Raman spectra of GO dispersion and the obtained graphene at different reductive times. In carbonaceous material, the D and G bands correspond to sp^2 and sp^3 carbon-stretching modes and their intensity ratio (I_D/I_G) is a measure of the amount of disorder present within the materials. The bands of GO associated at ~ 1350 and ~ 1610 cm^{-1} correspond to D and G modes, respectively (Kudin *et al* 2008). The G band starts shifting towards lower wavenumbers, indicating the beginning of the reduction process when the reductive time is changed from 60 to 180 min. It is observed around ~ 1590 cm^{-1} after 240 min. The D band also shows a similar variation in its position, from ~ 1350 to 1340 cm^{-1}

Figure 2. (A) UV-Vis absorption spectra, (B) FT-IR spectra, (C) X-ray diffraction and (D) Raman spectra of GO dispersion and the obtained graphene at 60 V reductive voltage and different reductive times (a-1: 60 min, a-2: 120 min, a-3: 180 min and a-4: 240 min).

in the same potential range. This is similar to the data reported by Stankovich *et al* (2007) for the chemical reduction of GO to RGO. The Raman spectra showed an increase in the D/G ratio with the reductive time increased, indicating the increased defects or edge areas from GO to graphene. The defects might be due to the smaller size of graphene sheets (Stankovich *et al* 2007).

The UV-Vis absorption peak of the obtained graphene at different reductive voltages are shown in figure 3(A). The absorption peak around 267 nm was found when the reductive voltage was 30 V. Then it gradually redshifted to 270 nm with the reductive voltage increased to 60 V, indicating that the electronic conjugation is restored. FT-IR spectra of obtained graphene at different reductive voltages are shown in figure 3(B), the intensities of the peaks corresponding to the oxygen functionalities, all decreased dramatically or even disappeared with the reductive voltage increased to 60 V. These data reveal that the GO has been successfully reduced with increase in reductive voltage. XRD images of obtained graphene at different reductive voltages are shown in figure 3(C). A very sharp diffraction peak at $2\theta = 11.4^\circ$ and a weak peak at 23.9° were found when the reductive voltage was 30 V. The intensities of peak became weak at $2\theta = 11.4^\circ$, with

the reductive voltage increased to 60 V. Meanwhile, a broad peak of graphene at $2\theta = 23.9^\circ$ was observed. These give evidence that the graphite oxide was reduced to graphene and as such restored the ordered crystal structure. Figure 3(D) shows the Raman spectra of the obtained graphene at different reductive voltages. The D and G bands are shifted to lower wavenumbers with the reductive voltage increased. For example, the G band is at 1605 cm^{-1} for c-4 (30 V), but is at 1590 cm^{-1} for a-4 (60 V).

We can infer that sample a-4 has a better reductive effect compared with other samples from this research. It means that the optimal reductive time and reductive voltage were 240 min and 60 V, respectively, in our experiment. We can obtain high-quality graphene in that condition. Figure 4(A and B) shows the C 1s X-ray photoelectron spectroscopy (XPS) spectra of GO and sample a-4. Five different peaks centered at 284.7 (C=C), 285.5 (C-C), 286.8 (C-O), 287.8 (C=O) and 288.9 eV (O=C-OH) were detected in the GO sample. After electrochemical reduction for 240 min, the intensities of all C 1s peaks of the carbons binding to oxygen decreased obviously, revealing that the most oxygen-containing functional groups were removed. The result was consistent with the research above.

Figure 3. (A) UV-Vis absorption spectra, (B) FT-IR spectra (C) X-ray diffraction and (D) Raman spectra of the obtained graphene at different reductive voltages (a-4: 60 V, b-4: 45 V and c-4: 30 V) for 240 min.

Figure 4. XPS spectra of C 1s of GO and sample a-4 (reductive time and reductive voltage were 240 min and 60 V, respectively).

4. Conclusions

In conclusion, this paper provides a simple and an efficient electrochemical method to obtain high-quality graphene. The main procedures involve the electrophoretic deposition

of graphene oxide on to positive electrode and the subsequent *in situ* electrochemical negative reduction, when the electrode changes from positive to negative. The reducing degree of GO was determined with UV-Vis absorption spectroscopy, X-ray diffraction, Fourier

transform infrared spectroscopy and Raman spectra. This approach opens up a new, practical and green reducing method to prepare graphene on a large-scale.

Acknowledgements

The authors thank the National High Technology Research and Development Program of China (No. 2012AA030303) and Basic Research Key Program of Shanghai (No. 12JC1408600).

References

- An S J, Zhu Y W, Lee S H, Stoller M D, Emilsson T, Park S, Velamakanni A, An J and Ruoff R S 2010 *J. Phys. Chem. Lett.* **1** 1259
- Emtsev K V *et al* 2009 *Nat. Mater.* **8** 203
- Fan X B, Peng W C, Li Y, Li X Y, Wang S L, Zhang G L and Zhang F B 2008 *Adv. Mater.* **20** 4490
- Geim A K 2009 *Science* **324** 1530
- Hong W J, Xu Y X, Lu G W, Li C and Shi G Q 2008 *Electrochem. Commun.* **10** 1555
- Hummers W S and Offeman R E 1958 *J. Am. Chem. Soc.* **80** 1339
- Kim K S *et al* 2009 *Nature* **457** 706
- Kudin K N, Ozbas B, Schniepp H C, Prud'homme R K, Aksay I A and Car R 2008 *Nano Lett.* **8** 36
- Lee C, Wei X, Kysar J W and Hone J 2008 *Science* **321** 385
- Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Crigorieva I V and Firsov A A 2004 *Science* **306** 666
- Qu L T, Liu Y, Baek J B and Dai L M 2010 *ACS Nano* **4** 1321
- Ramesha G K and Sampath S 2009 *J. Phys. Chem. C* **113** 7985
- Stankovich S *et al* 2007 *Carbon* **45** 1558
- Stankovich S, Dikin D A, Piner R D, Kohlhaas K A, Kleinhammes A, Jia Y, Wu Y, Nguyen S T and Ruoff R S 2007 *Carbon* **45** 1558
- Wu Q, Xu Y X, Yao Z Y, Liu A R and Shi G Q 2010 *ACS Nano* **4** 1963
- Zhou M, Wang Y, Zhai Y, Zhai J, Ren W, Wang F and Dong S 2009 *Chem. Eur. J.* **15** 6116
- Zhu Y W, Stoller M D, Cai W W, Velamakanni A, Piner R D, Chen D and Ruoff R S 2010 *ACS Nano* **4** 1227