Flexible transparent electrodes made of electrochemically exfoliated graphene sheets from low-cost graphite pieces

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Graphene has attracted intense interest due to its extremely high aspect ratio and unique physical properties [1], such as high carrier mobility (2 × 10^6 cm^2/Vs; silicon: 1400 cm^2/Vs) [2,3], superior electrical conductivity (10^5 Ω^−1 cm^−1), almost transparent in visible light (97.7%) [4], excellent mechanical strength (Young’s modulus > 1 TPa) [5], and good bendability. Owing to the remarkable properties mentioned above, graphene is a good candidate as transparent electrodes for applications in touch screens [6], flexible displays [7], printable electronics [8], and solar cells [9,10]. The transparent conducting oxides commonly used in portable electronic devices, like indium tin oxide (ITO) or aluminum-doped zinc oxide (AZO), have the drawbacks of brittle nature and growing cost, thus not being compatible with the requirements of next-generation flexible devices [11]. Graphene is highly promising for a replacement of oxide-based conducting materials.

To date several general methods have been developed for the preparation of graphene: (1) Mechanically-exfoliated graphene film exhibits great quality, but is impossible to scale-up production [12,13]; (2) Chemical vapor deposition using copper or nickel as catalysts can grow large-area, high-quality graphene [14–16]. Although more efforts should be made to lower the costs, especially those associated with wet etching of metal catalysts. Using this technique is still impractical to provide graphene with reasonable price; (3) Chemical exfoliation based on Hummers’ method can produce graphene derivatives in a large quantity [17–19]. Oxidation of graphite flakes into graphene oxide (GO), followed by chemical or thermal reduction, has become a common mass-production process due to the benefit of potentially low-cost fabrication. However, the physical property of reduced GO is scarcely comparable to that of graphene; and (4) Few-layer graphene can be synthesized in ethanol/Ar mixture using a substrate-free, plasma-enhanced reactor [20,21]. The system does not require a vacuum chamber and heater, and only needs a plasma generator. The quality is quite good as compared with GO, but the issue is how to create a homogeneous reaction zone for ensuring the uniformity of the products. Table 1 presents a comparative summary of current synthesis methods. According to Table 1, it can be found that on the market there is not an appropriate method to produce high-quality graphene in a large quantity. Thus the development of new technique is necessary to promote the performance of graphene-based products. Moreover, the feasibility of continuous (rather than batch) production, and the need of complicated post-treatment should be taken into account.
Our previous study has demonstrated a one-step process to synthesize graphene thin sheets by electrochemical exfoliation of natural graphite or highly oriented pyrolytic graphite (HOPG) [22]. The lateral size of the samples can be up to several tens μm, and their quality determined by Raman spectroscopy is much better than reduced GO. However, the cost of starting material (single-crystal graphite flake) used in our previous report is extremely high, thus it is not suitable for large-scale production. In this study, artificial graphite was utilized instead of high-cost graphite flakes to prepare the samples. The results indicate that massive graphene sheets can be successfully obtained by exfoliating artificial graphite using the same electrochemical method. The quality, morphology, and size of the products are investigated and discussed. Meanwhile, we also demonstrate that the transparent electrodes can be simply made by spraying graphene dispersions onto a flexible polymer substrate.

2. Experimental

Our samples were synthesized by electrochemical exfoliation method [22]. The experiment was set up with a piece of artificial graphite used as the working electrode and a Pt wire served the purpose of a reference electrode. The graphite was connected to a copper wire by a metal clip and inserted into the electrolyte as an anode. Note that only graphite piece was immersed into the solution. The Pt wire was placed parallel to the graphite with a spacing of ≈3 cm. The electrolyte was a mixture of H2SO4 and KOH (composition: 2.4 g of H2SO4 and 11 ml 30% KOH in 100 ml DI water). The design of the electrochemical system is schematically illustrated in Fig. 1a. The electrochemical reaction was performed at room temperature by applying DC bias on working electrode (±20 V). The voltage program is shown in following steps: (1) +2.5 V for 60 s; (2) +20 V for 5 s; and (3) −20 V for 5 s. Steps (2) and (3) are repeated alternatively until the amount of the product meets our requirement. The products were then vacuum-filtrated by a filter membrane (pore size ≈0.2 μm) and rinsed with DI water/ethanol to remove the residual electrolyte. The purified powder was dried at 100 °C for 5–10 min on hot plate. To obtain well-dispersed samples, 1-min sonication was carried out for the products in N,N-dimethylformamide (DMF). Eventually the dispersion was screened by a sieve to exclude unreacted starting materials. The flowchart of the whole electrochemical process is given in Fig. 1b. The morphologies of the samples were observed by optical microscope (OM) and scanning electron microscope (SEM, JEOL JSM-6500F). The atomic force microscopy (AFM) images were

<table>
<thead>
<tr>
<th>Quality</th>
<th>Size</th>
<th>Cost</th>
<th>Scale-up</th>
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<tbody>
<tr>
<td>Mechanical exfoliation</td>
<td>Good</td>
<td>Tens μm</td>
<td>-</td>
</tr>
<tr>
<td>Chemical vapor deposition</td>
<td>Good</td>
<td>No restriction</td>
<td>High (Thin films)</td>
</tr>
<tr>
<td>Chemical exfoliation (Hummers’ method)</td>
<td>Bad – fair</td>
<td>Hundreds nm</td>
<td>Low – fair</td>
</tr>
<tr>
<td>Plasma-assisted growth</td>
<td>Fair</td>
<td>Tens μm</td>
<td>Low – fair</td>
</tr>
<tr>
<td>Electrochemical exfoliation (this study)</td>
<td>Fair</td>
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Table 1: The comparison of current production routes.

Fig. 1. (a) Schematic illustration of the design of the electrochemical system. (b) Flowchart of the electrochemical exfoliation process and the further characterization.

Fig. 2. (a) Photograph of electrochemically exfoliated graphene dispersed in DMF. (b) OM image of graphene thin sheets. (c) Raman spectra of starting material and the product after reaction.
Fig. 3. SEM images of (a) artificial graphite and (b) electrochemically exfoliated graphene. Typical AFM images of graphene thin sheets deposited on (c) 300 nm SiO$_2$/Si and (d) quartz substrates.

Fig. 4. (a) Photograph of deposition process by airbrush spraying method. (b) A typical optical transmittance spectrum and the picture (inset) of the graphene film deposited on quartz substrate. (c) Sheet resistance as a function of transmittance (evaluated at 500 nm wavelength). The inset shows the bendability of the conducting sample deposited on PET substrate. (d) The change of sheet resistance of the films before and after thermal reduction.
taken in Veeco Dimension-Icon system. The quality of graphene sheets was accessed using Raman spectroscopy (NT-MDT NTEGRA, wavelength: 473 nm). The silicon peak at 520 cm$^{-1}$ was used as reference for calibration.

3. Results and discussions

In the electrochemical exfoliation process, artificial graphite was used as the working electrode to react at the programmed voltage (±20 V) in a mixed electrolyte solution (H$_2$SO$_4$ + KOH). The use of sulfate ions (SO$_4^{2-}$) is to intercalate into graphite layers by applying a positive bias to the working electrode. The addition of hydroxide ions (OH$^-$) is to partially neutralize the acidic electrolyte for avoiding oxidation of the graphene products during reaction. Because the reaction efficiency depends on the nature of the starting materials such as crystallization degree or microstructure, therefore the electrochemical conditions should be fine-tuned to obtain the desired products. For example, if the applied voltage is too low, the exfoliation cannot be triggered, whereas under a very high bias the electrode would be broken because of strong intercalation behavior. After reaction, the residual electrolyte was removed from the products by vacuum filtration and rinsing with DI water/ethanol for several times until the pH is close to neutral. Eventually the purified samples were sonicated in N,N-dimethylformamide for 1 min to form a uniform stable dispersion (called graphene ink), as shown in Fig. 2a. Such dispersion is stable up to several months. In Fig. 2b, the OM image shows the products deposited on 300 nm SiO$_2$/Si substrate by dip-coating. The lateral size of these sheets is several to 20 μm, which is comparable to those exfoliated from single-crystal graphite.

Fig. 2c shows the confocal Raman spectra (excited by 473 nm laser) for the starting material and exfoliated graphene sheets, respectively. The strong G-band (at 1578.4 cm$^{-1}$) and tiny D-band (near 1360 cm$^{-1}$) from artificial graphite indicate a feature of well-structured bulk graphite [23]. After exfoliation, the D-band greatly increases and a blue shift of G-band (at 1591.8 cm$^{-1}$) appears. The I$_D$/I$_G$ ratio is 1.21, suggesting that graphene surface is partially oxidized because of sulfuric acid intercalation. The 2D-band located at ~2700 cm$^{-1}$ is originated from a double-resonance process. It has been reported that the larger I$_D$/I$_G$ ratio (the integrated peak ratio between 2D- and G-bands) represents higher degree of sp$^2$-hybridized carbon–carbon bonding in graphene structure [24–28]. Although our sample is as-prepared and without any reduction treatment, its I$_D$/I$_G$ ratio (0.36) is still higher than that of GO, suggesting a higher quality. Although the same process has been proposed by exfoliation of single-crystal graphite flake in our previous report, the change of starting material greatly decreases the production cost and makes this technique closer to practical applications. Using airbrush spraying method, the transparent electrodes should be bendable without significant loss of conductivity. The bending tests were carried out using graphene films prepared on PET substrate according to the work of Wang et al. [31]. The picture presented in the inset of Fig. 2c demonstrates that the electrical property of our samples can be maintained under deformation conditions. The resistance of the films can be significantly decreased by post-treatment, such as thermal and/or chemical reduction.

For use in flexible displays, the transparent electrodes should be bendable without significant loss of conductivity. The bending tests were carried out using graphene films prepared on PET substrate according to the work of Wang et al. [31]. The picture presented in the inset of Fig. 2c demonstrates that the electrical property of our samples can be maintained under deformation conditions. The resistance of the films can be significantly decreased by post-treatment, such as thermal and/or chemical reduction.

4. Conclusions

We demonstrate that bilayer graphene sheets can be produced by fast electrochemical exfoliation using artificial graphite as starting material. The lateral size of the products can be up to several to 20 μm. The I$_D$/I$_G$ ratio of electrochemically exfoliated graphene is 0.36, which is larger than that of chemically and thermally reduced GO, suggesting a higher quality. Although the same process has been proposed by exfoliation of single-crystal graphite flake in our previous report, the change of starting material greatly decreases the production cost and makes this technique closer to practical applications. Using airbrush spraying method, the transparent electrodes can be formed from graphene dispersion. The Hall mobility of as-prepared films is in the range of 0.3–25 cm$^2$/Vs and the sheet resistance versus transmittance can be well fitted by an exponential equation. The sheet resistance of the samples may decrease to 16–24% after annealing at 450 °C. This work may lower the threshold for the development of graphene-based applications in flexible displays.

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References