Fabrication of highly conducting and transparent graphene films

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A B S T R A C T
Graphene-based transparent conducting films were prepared using the following method. A chemically-reduced graphene dispersion was synthesized and graphene films were prepared from it by transfer printing, followed by thermal treatment. The resulting graphene films possessed an excellent electrical conductivity with a high transparency. A sheet resistance lower than ~2 kΩ/sq and a transparency well over 80% were achieved at a typical wavelength of 550 nm. These properties are considered quite sufficient for many applications, such as transparent conductor films for touch panels.

1. Introduction

A transparent conductor (TC) is a critical component in many photoelectronic devices such as liquid crystal displays (LCD), organic solar cells, organic light emitting diodes (OLED), smart windows, etc. [1–3]. Indium tin oxide (ITO) has been the predominant material for the fabrication of TC because of its high electrical conductivity and optical transparency. However, there are several disadvantages of using ITO: (1) the cost of indium has gone up continuously, making ITO an increasingly expensive material, (2) ITO itself falls short in meeting property requirements for new applications such as flexible devices (i.e. flexible LCD, organic solar cell) due to its brittle nature and (3) ITO is inherently incapable of undergoing etching and high temperature processing, which makes patterning of ITO films difficult to realize.

Considerable research has been conducted on the possibility of applying carbon nanotubes (CNTs) as a material for TC [1–9]. In one approach, TC was prepared in the form of composite thin film where CNTs are incorporated into a polymer. The transparent thin films prepared with multi-walled carbon nanotube (MWCNT) reinforced poly(2-vinylpyridine) composite showed optimal transmittance ~70% and sheet resistance ~90 kΩ/sq [10]. Another approach was through direct fabrication of neat CNT films on a substrate, which yielded TCs of more applicable quality. The thin neat single-walled carbon nanotube (SWCNT) films [11] had visible light transmittance 90–97% and sheet resistance 200–500 Ω/sq, which approached those of practical ITO films. Although the above finding opened the potential of replacing ITO with neat SWCNTs for TC applications, SWCNTs are prohibitively too expensive to make profits for low-cost consumable electronic products.

Graphene is a new material, which has attracted significant attention only recently [12]. Due to its unusual physical and mechanical properties such as high carrier concentration and mobility [13] along with a room temperature quantum Hall effect [14], high thermal conductivity [15,16], and highest mechanical strength measured to date [17], it holds a number of promising applications [18]. One encouraging aspect of graphene is to replace CNTs as a cheaper but better solution in various applications including TCs because the naturally abundant and cheap graphite flakes are used to produce graphene. Since chemical oxidation method has been regarded as the most promising way to produce graphene sheets from both scale and cost perspectives [19,20], one typical approach to fabricate graphene TC is to coat graphite oxide (GO) films on a substrate, followed by converting GO...
films into graphene films through thermal or vapor chemical reduction [21,22]. Several techniques have been devised to fabricate the GO films, such as spin- or spray-coating, transfer printing and electrophoretic deposition. Spin-coating is a procedure used to deposit uniform thin films on flat substrates. Individual graphene oxide sheets were incorporated into silica sols followed by spin-coating, chemical reduction, and thermal curing [23]. However, the electrical conductivity of such TC films, compared to the requirement of optoelectronic devices, was relatively low, typically ranging from $10^{-3}$ to 1 S/cm. Blake et al. [24] fabricated graphene TC film based on spray-coating, showing that its high transparency and low resistivity were ideally suitable for electrodes in LCDs. In transfer printing method, the GO aqueous dispersion was first vacuum filtrated through a membrane and then transferred onto a substrate by placing the membrane with the film side down to the substrate and applying force. The GO film can be finally obtained after dissolving the membrane in a solvent [25]. Recently, researchers reported a new technique, namely electrophoretic deposition, to fabricate graphene TC films [26,27]. The graphene oxide was reduced to graphene nanosheets in a strongly alkaline solution and the reduced graphene sheets were electrophoretically deposited onto a substrate. The film thickness can be controlled by changing the deposition time. Different starting materials, such as giant polycyclic aromatic hydrocarbons (PAHs) that contained ‘nanographene molecules’ bonded to alkyl side chains, have also been used to produce graphene films. It was claimed that the ‘nanographene molecules’ would form a large-size graphene film on a substrate through cross-linking upon the decomposition of alkyl side chains during the thermal treatment. TCs obtained thereby had a transmittance of 85% and a sheet resistance of 18 KΩ/sq [2], which was still quite high.

This paper is part of a larger project on the development and applications of graphene and graphite nanoplatelets (GNPs) [19,28–31]. In this paper, graphene films are initially prepared on a cellulose ester (CE) filter membrane through vacuum filtrating graphene aqueous colloid which was made by chemical reduction of graphene oxide. Not only being able to produce films with well-packet graphene sheets, the vacuum filtration technique employed here has a flexibility to control the thickness by varying either the concentration or volume of the graphene aqueous colloid. In contrast, the conventional spin-coating method can produce only very thin films.

2. Experimental

2.1. Preparation of graphene aqueous colloid

First of all, natural graphite flakes (Asbury Graphite Mills) were exfoliated in a formic acid (HCOOH, 98%, supplied by BDH) through ultrasonication (Bransonic 1510-DTH) to obtain GNPs, according to the procedure described previously [19]. The GNPs were processed to produce GO using the modified Hummer’s method [32]: GNPs were put into a flask, and nitric acid (69–72%, supplied by Fisher), sulfuric acid (95.5–96.5%, supplied by General Chemical) as well as potassium permanganate (>99%, supplied by RDH) were added into the flask sequentially while magnetically stirring the mixture in an ice bath. After diluting the mixture with distilled water, the resulting slurry was subjected to dialysis for purification over a week. Upon the completion of dialysis, GO was stored either in a colloidal state or in the form of solid after drying in a vacuum oven.

Prior to reduction, the as-prepared GO was first exfoliated in water by ultrasonication for 2 h and followed by centrifugation at 4000 rpm for 1 h to remove the precipitates, yielding GO colloid [33]. The GO colloid was subsequently reduced to graphene colloid in the presence of hydrazine solution (N2H4 in water, Aldrich) and ammonium hydroxide solution (NH3·H2O, 28–30 wt.%, Wako), similar to a recent study [19,20]. Fig. 1 shows the images of the as-prepared GO colloid and the corresponding graphene colloid.

2.2. Preparation of graphene films on quartz substrates

Substrates for graphene films were prepared using 2 mm thick × 25 mm square quartz slides, which were washed in an acetone bath by ultrasonication to remove any organic contamination. The quartz pieces were pretreated with a trithoxysilane solution (3% in toluene). The silane treatment allowed the substrate surface to become more adhesive to the transferring graphene film. The clean substrates were stored in a vacuum oven at 80 °C before being used in the next step.

Chemically converted graphene films were prepared on CE filter membranes (Roshi Kaisha) through vacuum filtration of the chemically converted graphene colloid. The thickness of film was carefully controlled by varying the volume of colloids. The CE membranes with graphene films on were cut into appropriate sizes when they were still wet and subsequently pasted onto the quartz substrates with the film surface against the substrate surface. A dead weight of 1 kg was applied overnight in vacuum to assure that the graphene films firmly stuck to the substrate surface and any entrapped air bubbles could be eliminated. The CE membrane was dissolved in an acetone bath, leaving the graphene films on the quartz substrates.

To further remove the residual oxygen functional groups and thus improve the electrical conductivity, the as-produced graphene films were heat treated as follows. A tube furnace
The thermal treatment was aimed at eliminating the oxygen functionality by decomposition. Through this process, it is expected that the graphene sheets would reorient and thus the film becomes denser and smoother. Fig. 3(a) shows the AFM image of the chemically-reduced graphene sheets. The images of Fig. 3(b)–(e) are the 3D surface morphologies of the graphene films. The surface roughness of the 22 nm thick film were $R_a \sim 9$ and $\sim 3$ nm before and after the thermal treatment (Fig. 3(b) and (c)), respectively; whereas for the 78 nm thick film the corresponding surface roughness values became much higher, i.e. $R_a \sim 15$ and $\sim 7$ nm, respectively (Fig. 3(d) and (e)). Fig. 4 summaries the roughness of graphene films plotted as function of thickness after different treatments. As chemically-reduced graphene films were prepared through vacuum filtration, the surface roughness measured before thermal treatment may have been influenced by the roughness of filter paper, which in turn affected the final roughness after thermal treatment. The pore size of the filter paper employed here was 0.2 $\mu$m. It is envisaged that the final surface roughness could have been considerably reduced if a filter paper with a much smaller pore size had been chosen.

### 3. Results and discussion

#### 3.1. Surface morphology of graphene films

The thermal treatment was aimed at eliminating the oxygen functionality by decomposition. Through this process, it is expected that the graphene sheets would reorient and thus the film becomes denser and smoother. Fig. 3(a) shows the AFM image of the chemically-reduced graphene sheets. The images of Fig. 3(b)–(e) are the 3D surface morphologies of the graphene films. The surface roughness of the 22 nm thick film were $R_a \sim 9$ and $\sim 3$ nm before and after the thermal treatment (Fig. 3(b) and (c)), respectively; whereas for the 78 nm thick film the corresponding surface roughness values became much higher, i.e. $R_a \sim 15$ and $\sim 7$ nm, respectively (Fig. 3(d) and (e)). Fig. 4 summaries the roughness of graphene films plotted as function of thickness after different treatments. As chemically-reduced graphene films were prepared through vacuum filtration, the surface roughness measured before thermal treatment may have been influenced by the roughness of filter paper, which in turn affected the final roughness after thermal treatment. The pore size of the filter paper employed here was 0.2 $\mu$m. It is envisaged that the final surface roughness could have been considerably reduced if a filter paper with a much smaller pore size had been chosen.

#### 3.2. Crystallization of graphene films after heat treatments

Fig. 5 shows the Raman spectra obtained for four different graphite materials, and the corresponding intensity ratios of the prominent bands, namely D and G bands at wave numbers of 1356 and 1586 cm$^{-1}$, are given in Table 1. It is well-known that the G band indicates sound graphite carbon structure (sp$^2$), whereas the D band is typical of defects in carbon materials [34]. The intensity ratio of D ($I_D$) to G band ($I_G$) can be used as an indication of defects quantity: a low $I_D/I_G$ corresponds to a small defect quantity. The intensity ratio, $I_D/I_G$, decreased consistently when graphene oxide was reduced by hydrazine and subsequently heat treated at 400 and 1100 $^\circ$C to produce the final product. Along with the XPS findings in Section 3.3, it can be said the thermal treatments restored the carbon–carbon bonds thereby reducing the defect quantity when the oxygen functional groups were decomposed, which in turn promoted the crystallization of graphene films.

#### 3.3. Surface chemistry

The high oxygen content in the form of functional groups contained by graphene oxide inevitably makes it an insulator. Reduction is necessary to enable electrical conduction. Chemical reduction (in the presence of hydrazine) could effectively reduce the oxygen contents of graphene oxide. However, due to the electrostatic repulsion introduced by residual charged functional groups [20], the chemically-reduced graphene sheets remain in an aqueous colloidal state in water. As noted in Section 1, thermal annealing is a very effective method capable of removing oxygen from GO, where reduction is accomplished by decomposition of oxygen-containing groups and simultaneous restoration of carbon–carbon bonding.

The XPS analysis can trace the chemical elements of the films throughout the whole process of different treatments. Fig. 6 presents the oxygen to carbon ratios measured after heat treatments at varying temperatures. The O/C ratio decreased from 0.4 in the original GO to less than 0.02 in the finished graphene films, confirming the effectiveness of heat treatments. Fig. 7 illustrates curve fitting of the C1s peak of XPS spectra and Table 2 summarizes the relative percentages of these carbon structures and those containing functional groups. They signify the gradual reduction of oxygen con-
The intensities of the peaks 1 and 2 (corresponding to sp²- and sp³- C–C, respectively) increased, whereas the intensities of the peaks 3 and 4 (corresponding to C–O and –C=O, respectively) were reduced significantly when the graphene oxide was reduced to graphene and was further treated thermally. Chemical reduction in the presence of hydrazine was proven to be effective in reducing the oxygen content of graphene oxide. Annealing at elevated temperatures further removed the residual oxygen from GO. The reduction process was accomplished by decomposition of oxygen containing species.
groups and the simultaneous restoration of sp\(^2\) C–C bonds as the change in C–C concentration indicates (Table 2).

### 3.4. Enhanced electrical conductivity

The chemical reduction and the following heat treatments resulted in significant improvements in electrical conductivity of graphene films. Fig. 8 shows the sheet resistance and the corresponding electrical conductivity of graphene films plotted as a function of film thickness after different treatments. The electrical conductivity increased by approximately three orders of magnitude for a given thickness after thermal annealing of hydrazine-reduced graphene films at 400 °C. The final thermal annealing at 1100 °C further enhanced the conductivity by approximately one order of magnitude. It is shown that the 14 nm thick graphene film possessed an acceptable transparency of 80% and an electrical conductivity of 209 S/cm (or sheet resistance \(R_s = 2 \Omega/\text{sq}\)). The highest electrical conductivity obtained was 649 S/cm (\(R_s = 181.2 \Omega/\text{sq}\)) with a transparency of 35% at a wavelength of 550 nm. In general, the electrical conductivity increased with increasing the thickness of films, which was attributed to improved orientation and structure of the film as for the spin-coated GO films [2,22].

There were two possible mechanisms responsible for the remarkable, four orders of magnitude improvement in electrical conductivity due to the heat treatments. They are: (1) restoration of sp\(^2\) C–C bonds and (2) cross-linking between chemically-reduced graphene sheets. The heat treatments accelerated the reduction process by decomposing the oxygen functionalities and simultaneous restoration of sp\(^2\) C–C bonds that ubiquitously exist in graphitic structures. The sp\(^2\) bond structure can provide \(p\) electrons that are loosely constrained by the nucleus than common electrons and thus can easily escape from the nucleus to become free electrons if there is external electric field. Hence, the more are the restored sp\(^2\) C–C bonds, the higher is the carrier concentration that graphene films will possess, and consequently the higher is the electrical conductivity.

Another potential mechanism behind the enhanced conductivity is cross-linking between chemically-reduced graphene sheets during the thermal annealing process. It is assumed that during the vacuum filtration of graphene colloid the graphene films were formed through continuous stacking of the individual graphene sheets on top of each other, similar to producing graphene oxide papers [35]. Alkyl chains are decomposed upon heat treatment at elevated temperatures, and cross-linking takes place between the PAHs cores [36]. 1100 °C is known as the graphitization temperature of carbon materials [21] and therefore similar cross-linking

<table>
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<tr>
<th>Treatments</th>
<th>(\text{Intensity Ratio (I_D/I_G)})</th>
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<tbody>
<tr>
<td>GO</td>
<td>0.921</td>
</tr>
<tr>
<td>Hydrazine-reduced</td>
<td>0.916</td>
</tr>
<tr>
<td>Hydrazine + 400 °C</td>
<td>0.908</td>
</tr>
<tr>
<td>Hydrazine + 400 °C + 1100 °C</td>
<td>0.890</td>
</tr>
</tbody>
</table>
mechanisms would occur among the adjacent graphene sheets, which may contribute to the improvement of electrical performance.

3.5. Transparency of graphene films and correlation with electrical conductivity

Figs. 9 and 10 present the UV–vis spectra and IR spectra, respectively, of graphene films with different thicknesses prepared at three different stages, showing the changes in transmittance in the wavelength range from 200 to 3000 nm. There were two observations regarding transparency of graphene films. As expected, the transparency of the film decreased with increasing film thickness for a given treatment. The increase in thickness increased both the back reflection and absorption of light, resulting in the reduction in transparency. The other phenomenon was that the heat treatment had a detrimental effect on transparency of the graphene film. All transmittance curves in both the UV–vis (Fig. 9) and FTIR spectra (Fig. 10) exhibited an obvious tendency to shift downward along the transmittance axis upon heat treatments, suggesting that the transparency decreased after annealing at 400 °C and further decreased after subsequent graphitization at 1100 °C. The degradation of transparency in graphene films during thermal treatment was attributed to the improvement of reduction level [21].

Special note should be made on the FTIR spectra for the graphene film of thickness 14 nm obtained after the heat treatment at 1100 °C (Fig. 10(c)). The transmittance was recorded well over ~85% throughout the whole wavelength range.

Table 2 – Summary on relative percentages of the functional groups (%).

<table>
<thead>
<tr>
<th>Binding energy (eV) and assignation</th>
<th>1: 284.49</th>
<th>2: 286.70</th>
<th>3: 287.78</th>
<th>4: 290.66</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C</td>
<td>46.9</td>
<td>34.5</td>
<td>15.8</td>
<td>2.8</td>
</tr>
<tr>
<td>C–O</td>
<td>71.4</td>
<td>16.1</td>
<td>9.5</td>
<td>3</td>
</tr>
<tr>
<td>–C=O</td>
<td>77.6</td>
<td>7.9</td>
<td>8.9</td>
<td>5.6</td>
</tr>
<tr>
<td>–COO–</td>
<td>80.1</td>
<td>6.7</td>
<td>6.7</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Fig. 7 – Curve fitting of C1s peaks in XPS spectra for materials at different stages of treatment: (a) GO, (b) hydrazine-reduced, (c) hydrazine + 400 °C and (d) hydrazine + 400 °C + 1100 °C. (Peaks 1–4 are assigned to different carbon chemical states specified in Table 2).
studied between 1100 and 3000 nm. This is a remarkable observation because a recent work on conductive graphene electrodes for dye-sensitized solar cells showed only about 70% transmittance for a 10 nm thick graphene film for the same range of wavelength [22]. ITO and fluorine tin oxide (FTO) that have been widely used as window electrodes in optoelectronic devices showed much lower transmittance especially at high wavelengths. This indicates that the graphene films developed in this study are of particular importance for applications in solar cells and other optoelectronic devices.

Further analysis was made to establish the correlation between the electrical conductivity and transmittance measured at a wavelength of 550 nm, as well as the thickness of graphene film, as shown in Fig. 11. The wavelength 550 nm is known as typical of indicating the transparency of TCs. It

Fig. 8 – (a) Sheet resistance and (b) electrical conductivity of graphene sheets as a function of film thickness at different stages of treatment.

Fig. 9 – UV–vis spectra of graphene films obtained at different stages of treatment: (a) hydrazine-reduced, (b) hydrazine + 400 °C and (c) hydrazine + 400 °C + 1100 °C.
is clearly seen that the electrical conductivity gradually decreased as transmittance increased, suggesting an inverse relationship between the conductivity and optical transparency. This observation has practical importance in that applicable TCs can be obtained by controlling the film thickness to balance these two properties. As exhibited in this study, transparent conducting films with transparency well over 80% and electrical conductivity over 200 S/cm (or a sheet resistance 1–2 KΩ/sq) were successfully produced. These properties are sufficient for many important applications, including the TCs for touch panels [5]. The lowest sheet resistance achieved in this study was 181.2 KΩ/sq (or electrical conductivity = 649 S/cm) with a transmittance around 35% at a wavelength of 550 nm.

4. Conclusions

Vacuum filtration method was used to fabricate transparent conducting graphene films with improved electrical conductivity and transparency from the chemically-reduced graphene colloids. The chemically-reduced graphene films were transferred onto the quartz substrates, which were subjected to annealing and graphitization at elevated temperatures. The transparent conducting films obtained possessed remarkable properties: the transparency was well over 80% and the electrical conductivity was over 200 S/cm (or a sheet resistance 1–2 KΩ/sq) at a typical wavelength of 550 nm. These properties are sufficient for many important applications, including the TCs for touch panels [5]. These observations confirmed that the synthesis technique devised in this study could yield transparent conducting films with acceptable quality and functional performances.

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REFERENCES


