PREPARATION, REDUCTION AND TRANSPARENT CONDUCTING FILM APPLICATION OF LARGE GRAPHENE OXIDE SHEETS

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Introduction

Transparent conductive films (TCFs) have a wide range of technological applications in modern society such as flat displays, solar cells, optical communication devices, and solid-state lighting [1]. Graphene has been considered to be an ideal material for the use of TCFs because of its unique two-dimensional structure, remarkable electronic conductivity, optical transparency and excellent mechanical properties [2]. Chemical exfoliation starting from the oxidation of graphite is widely considered to be an efficient process to produce graphene in a large scale and at low cost, combining with post-reduction process [3]. However, the graphene oxide (GO) sheets prepared by chemical exfoliation is electrical insulator and usually have a small size, which hinder their applications especially for TCFs and flexible electronic film devices because of the large intrinsic and contact resistances. Here, we propose a modified Hummers method for the synthesis of large GO sheets with a mean size larger than hundred micrometers, and develop a HI reduction method to obtain high electrical conductive grapheme films with enhanced mechanical property. Based on these results, we measured the TCF properties of reduced GO films made by different sizes of GO sheets.

Experimental

To prepare large GO sheets, three modifications have been made: 1) using large natural flake graphite with an average size of 500-600 μm as starting material; 2) Applying mild oxidation and sonication to avoid the cracking of GO sheets during oxidation and exfoliation processes; 3) A two-step centrifugation was used to remove thick multilayer flakes and small flakes. The GO films were fabricated by heating GO hydrosol at 60 °C (from 5min to 15min to obtain membranes with different thicknesses) in a water bath. Then the obtained GO films on the surface of aqueous dispersion (i.e., at the air-water interface) were collected onto glass substrates by dip coating, followed by drying at 80 °C for 3 h. In order to recover the electrical conductivity of GOs for the application as TCFs, the obtained GO films were dipped in HI solution at 90 °C for 1 h, and then washed by ethanol followed by heating at 400 °C for 1 h. The electrical conductivity of reduced GO film-based TCFs was measured by a four-probe configuration with an electrochemical workstation, and their transparency at 550 nm wavelength was evaluated with a UV–Vis spectroscope.

Results and Discussion

Fig. 1 shows the typical SEM and AFM images of GO sheets obtained by modified chemical oxidation method. It is worth noting that most of the GO sheets are on the order of 80 μm × 80 μm in size (Figure 1a and b), which is much larger than those reported in the literature [4-6], typically smaller than 50 μm×50 μm. The largest GO sheet we observed can reach 200 μm×200 μm (Figure 1c). A large number of AFM measurements shows that most of our GO sheets obtained are 0.8-1.2 nm in thickness, as shown in Figure 1d, indicating that such GO sheets are monolayer [3].

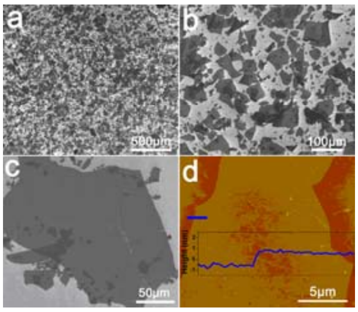

Fig.1 (a),(b),(c) SEM and (d) AFM images of large GO sheets. The inset of (d) shows that the thickness of the measured GO sheets is ~1 nm.

In addition, we found that the size of GO sheets can be tuned simply by changing the oxidation conditions. For sample I (Figure 2a), ~56% sheets are larger than 7000 μm^2, and the biggest sheet achieved is ~30000 μm^2 (Figure 2a'). When an additional high-temperature oxidation at 90 °C was used (sample II, Figure 2b), the size of GO sheets becomes smaller, with ~52 % sheets having an area of ~1000-3000 μm^2 (Figure .2b'). If we further enhance the oxidation by double the amount of $KMnO_4$ (sample III, Figure 2c), the mean size of GO sheets becomes much smaller than that of GO sheets in sample II. In this case, ~41% of GO sheets have an area of ~100-300 μm^2 (Figure 2c').

Fig. 3 shows the reduction of GO films by different agents. After 1h reduction in *HI* acid at 100 °C, the GO film changes from yellow to shining metallic luster in colour, and shrinks from 5 μm to about 2.5 μm in thickness. More importantly, the reduced GO film has a volume conductivity of ~298 S/cm, much higher than that of GO films reduced by other chemical routes reported by now [3] In addition, the *HI* acid reduced GO film shows a 21% increase in tensile strength. As a contrast, the GO films reduced by $N_2H_4 \cdot H_2O$ and $NaBH_4$ solutions become friable (Figure 3e and 3f). The hydrazine vapor reduced GO film (Figure 3d) keeps good integrity, but became too rigid to be rolled, and the film thickness expands more than 10 times (Figure 2i). According to these comparative studies, the GO films reduced by *HI* acid have high electrical conductivity and maintain the original high flexibility and integrity of GO films at the same time.

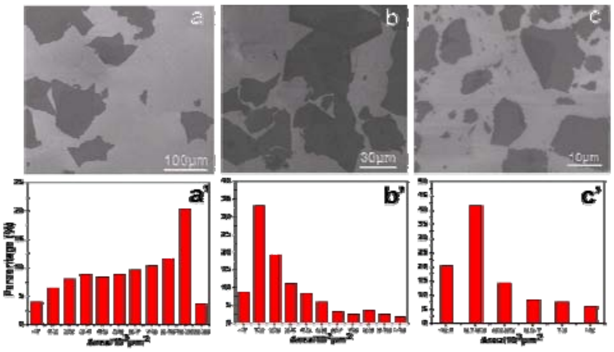

Fig.2 (a), (b) and (c) are typical SEM images of GO sheets in sample I, II and III, respectively, and (a'), (b') and (c') are the corresponding statistic results of the area of GO sheets.

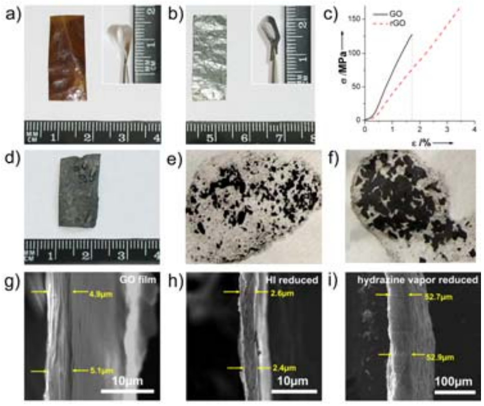

Fig. 3 Characterization of reduced GO films with different agents: (b) *HI* acid, (d) hydrazine vapor, (e) 85% $N_2H_4 \cdot H_2O$, and (f) 50mM $NaBH_4$ solution.

The properties of TCFs made by different sizes of GO sheets are shown in Fig. 4. Generally, TCFs assembled with bigger GO sheets has lower surface resistance than that of the films made by smaller sheets at the same transparency. For example, at the transparency of 85%, film sample I (graphene average size of 80 μm has a surface resistance ~1.2 kΩ/sq, while film sample II (graphene average size of 45 μm) ~12 kΩ/sq. Film sample III (graphene average size of 15 μm) has a surface resistance of 23 kΩ/sq with a transparency of 83%. Considering the same reduction conditions used for the three types of films, we believe that the higher electrical conductivity of film sample I is mainly attributed to the large sheet size comparing with the other two types of GO samples, which leads to a great decrease in contact resistance between neighboring sheets.

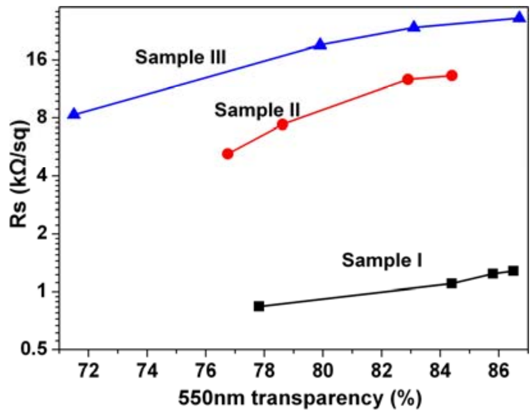

Fig.4 The properties of TCFs assembled with sample I (■), sample II (●) and sample III (▲) GO sheets.

Conclusions

We have proposed a modified oxidation method to produce large GO sheets. By using mild oxidation, sonication and two-step centrifugation, GO sheets with average size of 80 μm×80 μm were obtained, and the maximum size of GO sheets can reach 200 μm×200 μm. GO sheets with average area of ~100-300, ~1000-3000 and ~7000 μm^2 were synthesized only by changing oxidation conditions. In addition, we developed a HI reduction method to efficiently obtain high electrical conductive graphene films with enhanced mechanical property. The reduced films made by large GO sheets is ~840 Ω/sq at 78% transmission at 550nm wavelength, which is much better than that of films made by small sheets, 19.1kΩ/sq at 79% transmission.

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