FABRICATION OF HIGHLY CONDUCTING AND TRANSPARENT GRAPHENE FILMS

Shu Jun Wang, Yan Geng, Qingbin Zheng, Jang-Kyo Kim

Hong Kong University of Science & Technology
Department of Mechanical Engineering, Clear Water Bay,
Kowloon, Hong Kong

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 [1,2]. Indium tin oxide (ITO) has been the predominant material for the fabrication of TC because of its high electrical conductivity and optical transparency. Graphene is a new material, which has attracted significant attention only recently. 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. This paper reports synthesis of graphene films on a cellulous ester (CE) filter membrane through vacuum filtrating graphene aqueous colloid which was made by chemical reduction of graphene oxide.

Experimental

Natural graphite flakes were exfoliated in a formic acid through ultrasonication to produce graphene oxide (GO) using the modified Hummer's method [3]. The as-prepared graphene oxide was exfoliated in water by ultrasonication followed by centrifugation at 4000 rpm to remove the precipitates, yielding GO colloid [4]. The GO colloid was reduced to graphene colloid using hydrazine and ammonium hydroxide solutions. Chemically converted graphene films were prepared on a CE filter membranes and the thickness of film was controlled by varying the volume of colloids. The graphene films were pasted onto the quarts substrates and a pressure was applied to obtain flat graphene films. The CE membrane was dissolved in acetone, leaving the graphene films on the quartz substrates. The graphene films were heat treated to remove the residual oxygen functional groups in a tube furnace: initially at 400 ºC and followed by further treatment at 1100 ºC for 30 min.

The thickness and the surface roughness of film were measured using an atomic force microscopy. The elemental compositions and the assignments of the carbon peaks were characterized using the X-ray photoelectron spectroscopy. The transparency of the graphene films was characterized using the UV/VIS spectroscopy and the Fourier transform infrared spectroscopy. Raman spectroscopy was used to analyze the effects of heat treatments on the crystal quality of graphene films. The electrical conductivity of the graphene films was measured using the four-point probe method.

Results and Discussion

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. 1 shows the AFM image of the chemically reduced graphene sheets. Fig. 2 summaries the roughness of graphene films plotted as function of thickness after different treatments. The surface roughness measured before thermal treatment was influenced by the roughness of filter paper, which in turn affected the final roughness after thermal treatment. 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.

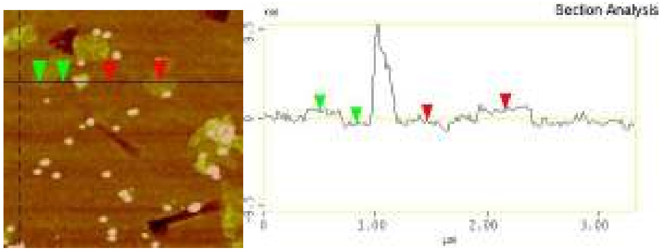

Fig. 1 AFM images of chemically reduced graphene single sheets on the quartz substrate (the height of the sheet being around 1.2 nm).

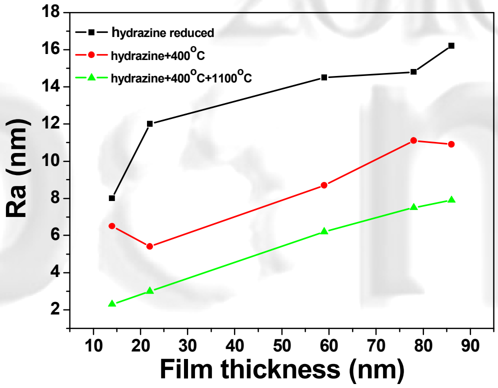

Fig. 2 Surface roughness plotted as a function of film thickness at different stages of treatment

The chemical reduction and the following heat treatments resulted in significant improvements in electrical conductivity of graphene films. Fig. 3 shows the 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 about 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 KΩ/sq). The highest electrical conductivity obtained was 649 S/cm (R_s= 181.2 Ω/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]. Heat treatment had two major effects that were responsible for the improvement of electrical conductivity, namely i) restoration of sp^2 C-C bonds; and ii) cross-linking between chemically-reduced graphene sheets.

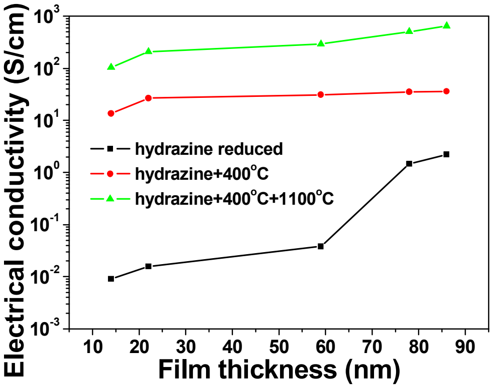

Fig. 3 Electrical conductivity of graphene sheets as a function of film thickness at different stages of treatment

There were strong correlations between the electrical conductivity and transmittance measured at a wavelength of 550 nm, as well as the thickness of grapheme film, as shown in Fig. 4. The wavelength 550 nm is known as typical of indicating the transparency of TCs. It 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 Ω/sq (or electrical conductivity = 649 S/cm) with a transmittance around 35% at a wavelength of 550 nm.

4. Conclusions

Highly transparent conducting graphene films with improved electrical conductivity and transparency were produced 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. These observations confirmed that the synthesis technique devised in this study could yield transparent conducting films with acceptable quality and functional performances.

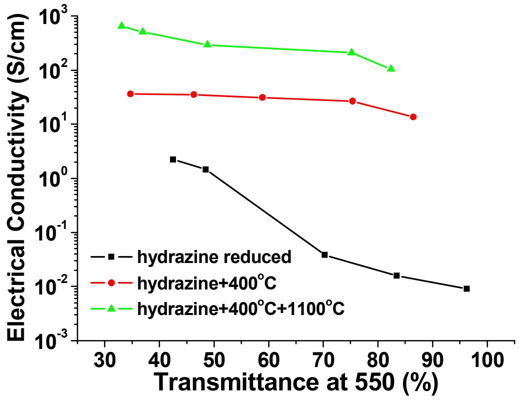

Fig. 4 Electrical conductivity as a function of transmittance at a wavelength of 550 nm

Acknowledgements. This project was financially supported by Henkel International (Project number: ICIPLC001.07/08). Technical assistance from the Materials Characterization and Preparation Facilities (MCPF) of HKUST is appreciated.

References

[1] Rowell MW, Topinka MA, McGehee MD, Prall HJ, Dennler G, Sariciftci NS, et al. Organic solar cells with carbon nanotube network electrodes. Appl Phys Lett 2006; 88(23): 233506.
[2] Wang X, Zhi LJ, Tsao N, Tomovic Z, Li JL, Mullen K. Transparent carbon films as electrodes in organic solar cells. Angew Chem Int 2008; 47(16): 2990-2.
[3] Hummers WS, Offeman RE. Preparation of graphitic oxide. J Am Chem Soc 1958; 80(6): 1339.
[4] Geng Y, Wang SJ, Kim JK. Preparation of graphite nanoplatelets and graphene sheets. J Colloid Interf Sci 2009; 336: 592–598
[5] Gruner G. Carbon nanotube films for transparent and plastic electronics. J Mater Chem 2006; 16(35): 3533-9.