Applied Surface Science 258 (2012) 5056–5060

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Synthesis, characterization and optical property of graphene oxide films

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ARTICLE INFO

Article history:
Received 10 October 2011
Received in revised form
23 November 2011
Accepted 18 January 2012
Available online 26 January 2012

Keywords:
Graphene oxide films
Self-assembly technique
Electrical property
Optical property
Ag decoration

ABSTRACT

Graphene oxide (GO) sheets were used to build up films via layer-by-layer electrostatic self-assembly technique. GO sheets and poly(diallyldimethylammonium chloride) (PDDA) alternately deposited on the quartz substrate during the self-assembly process. To make the films electrically active, reduction treatment involving the thermal annealing in Ar/H_2 atmosphere at 600 °C was conducted. The microstructure and morphology of the obtained films were investigated by FT-IR, TEM, XPS and SEM. The optical property was examined by UV–vis instrument at room temperature. Results show that the surfaces of the obtained films are uniform. Films with 5 and 10 assembly cycles have transmittances of 74 and 49%, respectively, at a wavelength of 500 nm. To improve the optical and electrical property, Ag particles was decorated into the film and the transmittance at 500 nm was increased to 82% with 5 assembly cycles, while the surface resistance was about 95 kΩ □$^{-1}$, much lower than that of pure film, 430 kΩ □$^{-1}$.

1. Introduction

The fabrication of graphene films with controllable thickness and property is a key subject in modern nanoscience because of their potential applications in many technological fields such as nanoelectronics, nanocomposites and sensors [1–3]. The discovery of isolated graphene obtained from the mechanical cleaving 'Scotch tape method' has made fabrication of devices on individual graphene sheets straightforward [4,5]. In addition to individual sheet devices, efforts to obtain graphene films through bottom-up chemical reaction route and top-down exfoliation route have yield promising results. Transparent graphene-constructed films have been fabricated by the thermal reaction of synthetic nanographene molecules of giant polycyclic aromatic hydrocarbons [6]. Film with thickness of 30 nm has transmittance of 55% at a wavelength of 500 nm and shows a sheet resistance of 1.6 kΩ □$^{-1}$. Recently, the exfoliation of individual to few layered graphene sheets via chemical oxidation and reduction route makes the deposition of graphene from solution possible, allowing devices to be fabricated on virtually and surface. Chhowalla reported that graphene oxide (GO) thin films with thicknesses ranging from a single monolayer to several layers over large areas could be fabricated by vacuum filtration involving the filtration of a GO suspension through a mixed cellulose ester membrane and the obtained films could be used as a transparent and flexible electronic material [7]. The challenging aspect of graphene integration into electronic devices is the fabrication of films in a controlled, scalable, and reproducible way.

The solution-based route is promising because it opens a route for the deposition of graphene film from solution. It is well known that exfoliated GO sheets are highly negatively charged when dispersed in water and form well-dispersed aqueous colloid [8,9], which makes it possible to use the well-known layer-by-layer electrostatic assembly technique to build up graphene-based films. In this paper, GO solution obtained by improved Hummers's method was used as raw material for the fabrication of graphene oxide films by layer-by-layer electrostatic assembly technique. The structure, chemical composition, electrical and optical properties of the obtained films were also studied. It was found that the conductibility and transmittance of the film could not be improved simultaneously, but could be if PDDA was substituted by $AgNO_3$.

2. Experimental

2.1. Synthesis

Graphene oxide (GO) was prepared according to the procedure described in the literature [10]. The quartz slide was firstly immersed in PDDA solution (20 wt%) for 20 min and rinsed with deionized water and dried in air. Then immersed in aqueous GO solution (0.6176 mg/mL) for 20 min, rinsed with deionized water and dried in air. Multilayer film was grown by repeating these adsorption cycles. GO films with different assembly cycles were marked as FO-n (where n = 1, 2, 3, etc.). For Ag substituted film,

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doi:10.1016/j.apsusc.2012.01.105

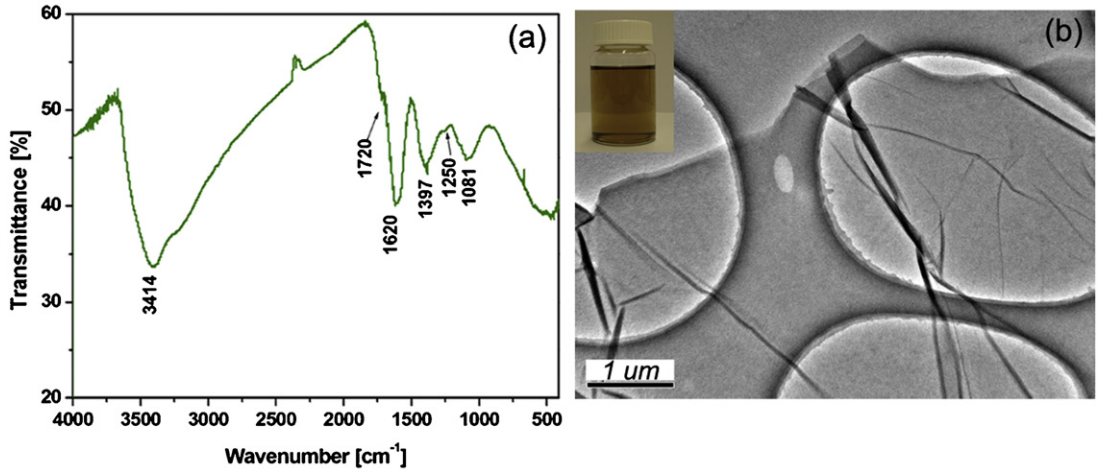

Fig. 1. (a) FTIR spectrum of GO; (b) TEM image of GO. Inset is image taken 15 days after the ultrasonic treatment.

the slide was firstly immersed in PDDA solution and then GO, for the remaining assembly cycles, PDDA was substituted by $Ag(NO_3)$ solution (0.01 mol/L) and the obtained film was marked as FO-Ag-*n*.

The GO films were reduced by chemical method or thermal annealing method. For chemical method, GO film was hung in a 25 mL stainless steel Teflon-lined autoclave with 2 mL hydrazine in the bottom. The autoclave was sealed, kept at 120 °C for 2 h, and then naturally cooled to room temperature. For thermal annealing, GO film was calcined in a tube furnace at 600 °C under Ar/H_2 atmosphere (volume ratio = 5:1) for 2 h and cooled naturally. The obtained films were marked as F-*n* and F-Ag-*n*, correspondingly.

2.2. Characterization

TEM images of GO was obtained on a JEOL 2011 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. Infrared (IR) spectrum of the GO sample was collected on a Nicolet Nexus 470 FTIR Fourier transform infrared (FTIR) spectrometer. The optical property was tested on a Shimadzu UV-2550 spectrophotometer at room temperature. Scanning electron microscopy (SEM) images of the films were taken on a XL-30ESEM scanning electron microscope. The contact angle measurement was done in atmospheric conditions at 25 °C following the sessile drop method (OCAH200, Germany) and the XPS measurements were performed on a Thermo ESCALAB 250 spectrophotometer with Al-K_α radiation. The film surface resistance was tested on RTS-9 four point resistivity test system at room temperature.

3. Results and discussion

An important property of GO, brought about by the hydrophilic nature of the oxygenated graphene layers, is its easy exfoliation in aqueous media. As shown in Fig. 1(a), the relatively broad peak at 3414 cm^{-1} and relatively sharp peak at 1620 cm^{-1} indicate that the sample contain adsorbed water. Peaks at 1397 cm^{-1} and 1081 cm^{-1} can be assigned to the deformation vibration of O—H and stretching vibration of C—O, respectively. Characteristic bands of C=O carbonyl stretching and C—O—C vibration located at 1720 cm^{-1} and 1250 cm^{-1} are very weak, indicating the small amount of these two functional groups [11]. The introduction of above mentioned functional groups during the chemical oxidation process makes the GO hydrophilic. In our work, sufficiently dilute colloidal suspensions of GO prepared with the aid of ultrasound are clear, homogenous, and stable as shown in Fig. 1(b). TEM image of GO exfoliated by the ultrasonic treatment at concentration of 0.1544 mg/mL in water revealed that GO nanosheets tend to congregate together to form multilayer agglomerates.

Li reported that the formation of stable GO colloid should be attributed to electrostatic repulsion, rather than just the hydrophilicity of GO [7]. Given that the exfoliated GO sheets are highly negatively charged, the well-known layer-by-layer electrostatic assembly technique can be used to build up controllable GO-based films. The film formation process was monitored by UV–vis and it can be seen in Fig. 2 that the absorbance increases linearly with an increase of the number of assembly cycles, indicating the successful assembly of GO sheets on the substrate. In Fig. 3(b), one can see that FO-10 is transparent with slightly brown color.

GO film is electrically insulating and the surface resistance is too large to be detected by our test system (listed in Table 1), must be reduced via exposure to hydrazine vapor and/or annealing in inert conditions [12] to render the material electrically conductive. We found that hydrazine vapor treatment led to a reduction in the film resistance (decreased to ~900 $k\Omega\,\square^{-1}$, 10 assembly cycles). But the binding force between the film and quartz was very weak and the film was partially peeled off as shown in Fig. 3(a), which might be caused by the existence of organic PDDA between the GO layers. In our experiments, thermal annealing in Ar/H_2 was applied to reduce GO films.

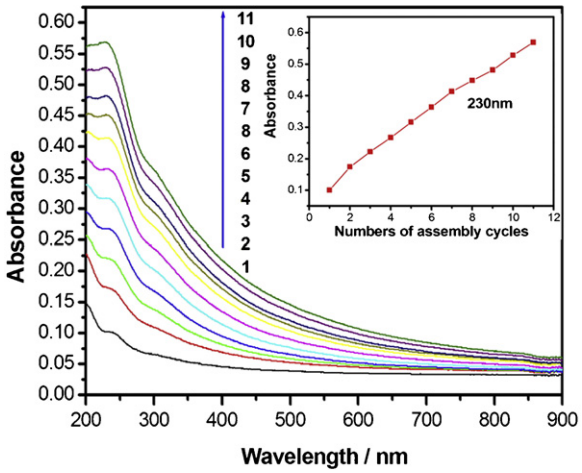

Fig. 2. (a) UV–vis spectra of PDDA/GO films prepared by layer-by-layer electrostatic self-assembly technique, inset shows the linear relationship between the absorbance and the number of assembly cycles.