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The polar solvent effect of transparent conductive films composed of graphene/PEDOT:PSS nanohybrids

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ABSTRACT

Novel transparent conductive films were successfully fabricated by forming graphene/PEDOT:PSS nanohybrids and then spin-coating the mixture onto glass substrates. The mechanism and characterization of graphene nanosheets dispersed at various concentrations of polar solvents (isopropanol, IPA) to improve the conductivity of the nanohybrids are evaluated using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), four-point probe sheet resistance measurements, and UV/vis spectroscopy. The results show that the conductivity of the graphene/PEDOT:PSS nanohybrids significantly improves upon addition of 50 wt.% IPA (the optimum conditions). The sheet resistance of the nanohybrids was reduced by ~95% from 16.6 kΩ/□ by addition of 0 wt.% IPA to 0.85 kΩ/□ by addition of 50 wt.% IPA, whereas the transparency still remained up to 82%. The conductivity could then be rapidly enhanced (from 0.85 kΩ/□ to 0.64 kΩ/□) by a second treatment of H_2SO_4, with a concomitant loss of transmittance. The correlations among the roughness, hydrophilicity, conductivity, and transparency also are investigated in detail in this paper. It is anticipated that graphene/PEDOT:PSS nanohybrids can be potentially used in an electronic and biomedical platform, such as biosensors.

1. Introduction

Recently, transparent conductive films have become an important component of electronic devices, including OLEDs, LCDs, and solar cells [1–6]. Most transparent conductive films are composed of indium tin oxide (ITO). However, indium is an expensive, brittle, and non-environmentally friendly material. In addition, ITO cannot be coated onto a flexible substrate. Therefore, organic conductive polymers, such as poly(3,4-ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS), are receiving more attention for use as transparent conductive thin films due to their superior optical and electronic properties, which enable potential applications in electronic devices [7–11]. PEDOT:PSS is a conjugated polymer that can be used to produce a flexible organic electronic coating. However, PEDOT:PSS is very expensive; thus, determining how to reduce the expense of the organic conductive polymers for industrial application is a critical issue.

Graphene nanosheets [12–15] are single layers of sp^2-bonded carbon atoms exfoliated from graphite sheets. In 2004, graphene nanosheets were characterized by Andre Geim and Konstantin Novoselov, who successfully exfoliated graphene nanosheets from graphite using 3 M tapes. The resistivity of graphene nanosheets is lower than that of copper and silver, making it the lowest resistivity at room temperature; graphene nanosheets display excellent electrical properties and have been used in electronic and biosensor devices [16–18]. In addition, graphene nanosheets exhibit outstanding optical properties, with the transparency of a single-layer graphene nanosheet of over 96% on a glass substrate. Therefore, we plan to blend the two forms of outstanding materials, graphene and PEDOT:PSS, to fabricate novel organic conductive nanohybrids. Although many works regarding the use of nanohybrids of graphene/PEDOT:PSS to fabricate novel transparent conductive nanohybrids have been reported [3,19–20], few reports discuss the solvent effects in the blending system of graphene and organic conducting polymer. To homogenously blend graphene and PEDOT:PSS, it is important to choose a suitable co-solvent to disperse the two compounds. IPA can be used for the dispersion of graphene and PEDOT:PSS to increase the conductivity of the graphene/PEDOT:PSS nanohybrids.

Secondary treatments, such as the application of H_2SO_4 or UV-ozone, to enhance the conductivity of graphene and PEDOT:PSS have been developed by several groups [7,21]. Y. Xia et al. [7] reported secondary treatments using various concentrations of H_2SO_4 to increase the conductivity of a transparent electrode of optoelectronic devices. With an increasing concentration of H_2SO_4, the conductivity of the conducting polymer films (PEDOT:PSS) increases and then saturates as the concentration of H_2SO_4 approaches 1.5 M. Further, C.W. Chen [21] demonstrated that the sheet resistance of a graphene thin film decreases with UV-ozone secondary treatment. The optimum sheet resistance was obtained with ozone exposure for 6 min at 300 °C, confirming that UV-ozone secondary treatment is an effective and simple process for enhancing the conductivity of graphene.

In this study, the solubility and optic/electronic characterization of graphene and PEDOT:PSS nanohybrids in the various concentrations

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Table 1
The fabrication parameters of graphene (GE)/PEDOT:PSS films with various weight fractions (wt.%) of IPA/water co-solvent and the transmittance (T%), roughness, and sheet resistance of the graphene (GE)/PEDOT:PSS films.

IPA/water (wt.%)	GE (mg)	PEDOT:PSS (ml)	IPA (ml)	Water (ml)	T%	Roughness (RMS, nm)	Sheet resistance (kΩ/□)	Resistivity (Ω × cm)
0	7	3	0	7	89.1	8.7	16.6	0.266
17	7	3	2.1	7	88.9	8.6	11.3	0.184
28	7	3	3.5	5	88.8	8.8	5.5	0.091
39	7	3	4.9	3	86.4	8.7	3.0	0.052
50	7	3	6.3	1	83.7	10.2	0.85	0.015
52	7	3	6.65	0.5	84.2	13.5	1.3	0.024
H_2SO_4-secondary treatment (IPA50%)	–	–	–	–	70.3	28.8	0.64	0.011

of IPA/DI-water co-solvent are evaluated using scanning electron microscopy (SEM), atomic force microscopy (AFM), four-point probe sheet resistance measurements, and UV/vis spectroscopy. The effects of secondary treatment using H_2SO_4 in the graphene/PEDOT:PSS nanohybrids are also investigated in this paper.

2. Experimental section

2.1. Chemicals and reagents

Graphene nanosheets (few layers) were purchased from Allightec Co., Taiwan. Poly(3,4-ethylenedioxythiophe):poly(styrenesulfonate) (PEDOT:PSS, 170 Ω/square) was purchased from Polychem Co., Taiwan. Isopropyl alcohol (IPA) (≥99.5%) was purchased from Acros Co., USA.

2.2. Fabrication of graphene/isopropyl/PEDOT:PSS nanohybrids

Graphene/PEDOT:PSS nanohybrids were prepared by blending and self-assembled graphene nanosheets and PEDOT:PSS with various weight fractions of IPA/water co-solvent, as shown in Table 1 and Fig. 1a. Graphene/PEDOT:PSS nanohybrids were sonicated for 5 min to homogenously disperse in the IPA/water co-solvent. The chemical structure of PEDOT:PSS is shown in Fig. 1b.

2.3. Preparation of transparent conductive films

Each graphene/PEDOT:PSS solution was spin-coated onto a glass substrate at 1000 rpm for 10 s and then at 3000 rpm for 30 s. The resulting graphene/PEDOT:PSS films were heated for 5 min at 100 °C to remove the residual solvent. Finally, the resultant films were post treated by sulfuric acid solutions by spin-coating and then dried at 110 °C for 5 min.

2.4. Characterization of the films

The atomic force microscopy (AFM) images of graphene/PEDOT:PSS films were obtained using a Dimension 3100 microscope (Veeco Instruments Inc.) in tapping mode. XRD patterns of graphene/PEDOT:PSS films were evaluated using an X-ray diffractometer (Bruker D8) equipped with a Cu-Kα radiation (1.5406 Å) source. Field emission scanning electron microscopy (FE-SEM) images of graphene/PEDOT:PSS films were obtained using a JEOL 6701F instrument. The transmittance (T%) was characterized by UV–vis spectrophotometry (Thermo Scientific Co.).

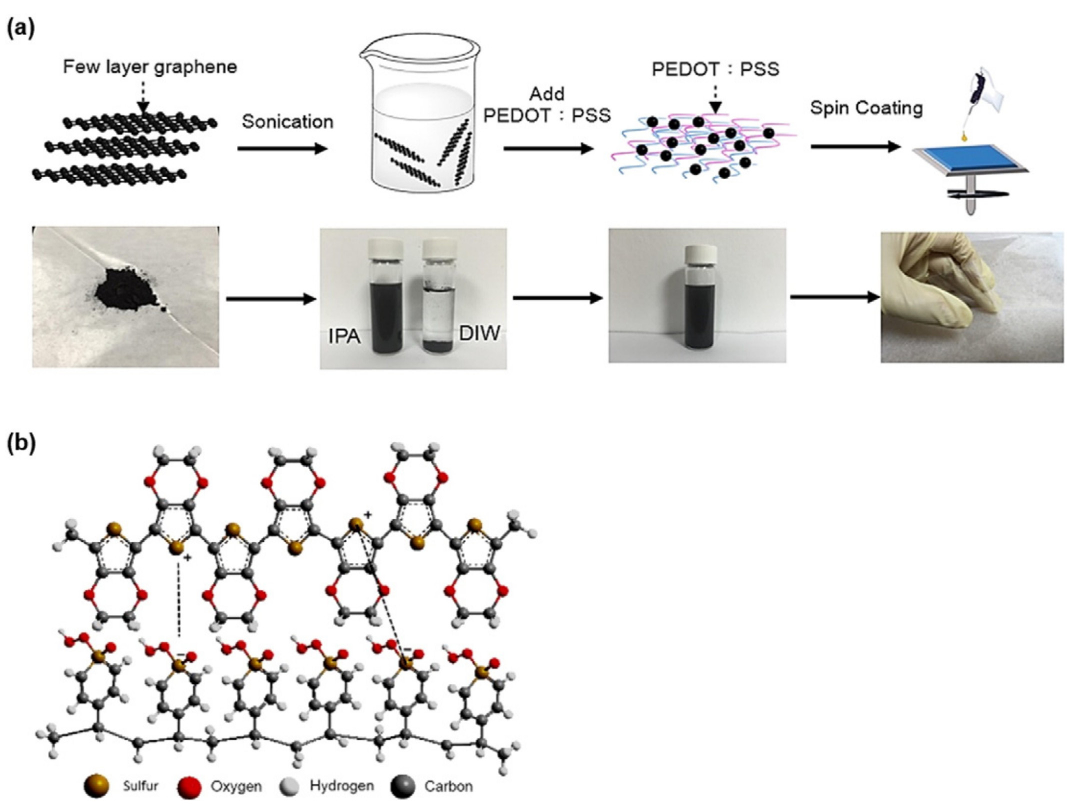

Fig. 1. (a) Schematic process of transparent graphene/PEDOT:PSS conducting films; (b) the chemical structure of PEDOT:PSS.