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Fabrication of conductive network formed by polyaniline–ZnO composite on fabric surfaces

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ABSTRACT

A conductive network consisting of polyaniline (PANI) and PANI/nm-ZnO immobilized on the surfaces of poly (ethylene terephthalate) (PET) fabrics was synthesized by a route involving a wet-chemical technique and in-situ chemical oxidative polymerization procedures. Morphological, structural, thermal and electrical properties of the PET fabrics modified with PANI–ZnO composites were analyzed. X-ray diffraction (XRD) measurements of the composites revealed that the crystal structure of incorporated ZnO undergone a weak distortion during the polymerization reaction and the XRD pattern of PANI was predominate. Attenuated total reflection Fourier transform infrared spectroscopic studies indicated the presence of interaction between ZnO nanorods and molecular chains of PANI in the ZnO/PANI layers. Field emission scanning electron microscope images implied the thin composite layers showed a submicro-sized rod like network and the homogeneous distribution on the substrates. Thermogravimetric studies exhibited that the PET-ZnO/PANI composite had a higher thermal stability than anyone of PET and PET-PANI. The surface resistance of ZnO/PANI conductive films was found to be smaller than the PANI film, which was declined as aniline concentration in adsorption bath increased and reached a relatively low value when $Zn(NO_3)_2$ concentration was at 0.03 mol/L in the precursor solution.

1. Introduction

Intrinsically conductive polymers have aroused a great interest among the researchers due to high mobility of the charge carriers, which also can be the excellent hosts for the trapping of metals and semiconducting nanoparticles as stabilizers or surface capping agents [1,2]. Amongst conductive polymers, polyaniline (PANI) has been widely studied owing to relative ease in preparation, good environmental stability and tunable conductivity, and showed its promising applications in many technologic fields, such as sensors, electromagnetic interference shielding, electrostatic discharge, conducting materials and corrosion inhibitors, etc. Incorporation of nanostructured inorganic compounds into PANI polymers will facilitate the combination of different features of inorganic and organic species, and the inorganic fillers in the nano-form are expected to modify the properties of the conducting polymers leading to the development of multifunctional devices [3,4]. Among the modified properties, the enhanced conductivity was displayed due to the change in morphology of the conductive PANI in the hybrids [5,6].

Several reports on the synthesis of the composites of PANI with a variety of metal oxides such as TiO_2, ZnO, Fe_3O_4, NiO and MnO_2 have been described [7–11]. Among the nano-crystaline inorganic semiconductors, nanostructured ZnO has been currently attracted worldwide interest as a representative II–VI group compound semiconductor with a wide direct band gap (3.37 eV) and a large exciton binding energy (60 meV) and become excellent electronic and photonic material. Distinct nanostructures ZnO have been demonstrated, for example, nanowires, nanorods, nanotubes, nanobelts, and nanoflowers, among which ZnO nanorods are of particular interest due to their electrical and optical properties [12,13].

With the aim of gaining the properties attributing to the molecular level interaction of two dissimilar chemical components, we intended to fabricate the composites of PANI and ZnO nanorods. Although many papers on the composites of PANI with inorganic nanoparticles, few reports have been focused on the synthesis, morphological, electrical and optical studies of PANI/nm-ZnO composites and efforts reported in the literature for the formation of PANI/ZnO thin films have mainly utilized a complicated chemical process [14,15]. This study deals with the fabrication of conductive network layers consisting of micro-structured PANI/nm-ZnO and PANI by a wet-chemical technique and in-situ chemical polymerization method.

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2. Experimental details

2.1. Materials

Poly(ethylene terephthalate) (PET) fabrics (87 ± 2 g/m^2) were cut into a rectangular shape 40 mm × 50 mm in size. All chemicals used including Aniline (C_6H_7N, An), ammonium persulfate ($(NH_4)_2S_2O_8$, APS), hydrochloric acid (HCl), zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), sodium hydroxide (NaOH), zinc nitrate hexahydrate ($Zn(NO_3)_2$), methanol (CH_3OH), acetic acid (CH_3COOH) and hexamethylenetetramine ($C_6H_{12}N_4$) were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. Sample preparation methods

2.2.1. Fabrication of ZnO nanorods on fabric surface

The fabric was pretreated in a 20 g/L NaOH solution at 95 °C for 90 min. The nanosized ZnO coatings on fabrics were prepared by a modified seeds-guided hydrothermal method. ZnO colloid was synthesized according to the method that 0.12 mol/L NaOH/ CH_3OH solution (50 ml) was slowly added to a 0.04 mol/L $Zn(CH_3COO)_2$/ CH_3OH solution (50 ml) and stirred vigorously at 60 °C for 2 h. Then, the textile samples were dipped into the ZnO colloid for 10 min, padded with a laboratory padder and then cured at 170 °C. The fiber samples covered with ZnO nanocrystals were then immersed into a mixed solution of 0.025 mol/L $Zn(NO_3)_2$ and 0.025 mol/L $C_6H_{12}N_4$ were oscillated continuously at 90 °C for 3 h, then taken out and dried.

2.2.2. Synthesis of the films of polyaniline (PANI) and PANI/nm-ZnO composites

The fabrics modified with PANI and PANI/nm-ZnO composites were synthesized by a process including monomer sorption and oxidation polymerization in the presence of nanosized zinc oxide coatings on the fabrics surface. The typical two-step formation process for PANI film was as follows: the substrates were soaked in 0.5 mol/L An and 0.5 mol/L HCl solution for 2 h at 80 °C, dipped in 0.2 mol/L APS and 0.2 mol/L HCl solution for 30 s then immediately squeezed by a padder and then cooled to 0 °C. Finally, the composite fabrics were rinsed by ethanol and distilled water for several times and dried. The liquor ratios applied in our study were all 50:1.

2.3. Characterization

The structural characterization of the as-prepared textile samples were analyzed by X-Ray diffraction (XRD, Rigaku D/max-2550) spectra with the Cu Kα line of 1.54 Å.The distributions of the composites were characterized by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, ThermoNicolet Nexus 670 with variable angle horizontal ATR accessory).The thermal gravimetric analysis (TG) measurements were carried out using a Netzsch TG 209 thermogravimetric analyzer in 25–800 °C range at heating rate 10 °C/min in N_2 atmosphere. The morphologies of the films grown on textile samples were observed by scanning electron microscope (SEM, JSM-5600LV, operating at 15 kV) and field-emission scanning electron microscope (FESEM, Hitachi S-4800, operating at 10 kV). Elemental analysis (Zn) was carried out using a Prodigy inductively coupled plasma atomic emission (ICP-AES). The surface electrical resistance (ρ_s) of the composite fabric was measured by a two-probe method with a multimeter. It is noted that the control substrates used was the alkali pre-treated PET when the samples prepared were characterized and compared.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The X-ray diffraction (XRD) patterns of pure PET (curve a), PET-PANI (curve b), PET-ZnO (curve c) and PET-ZnO/PANI (curve d) composites are shown in Fig. 1. The X-ray diffractogram of PET (curve a) indicates characteristic diffraction peaks between 10° and 30°, which are also present in the XRD pattern of PET-ZnO composites (curve c). The XRD patterns of PET-PANI (curve b) and PET-ZnO/PANI (curve d) composite specimens exhibit three distinguished peaks at 17.7°, 22.4° and 25.9°, which are much sharper than the PET characteristic diffraction peaks (curve a). The two peaks at 2θ angles around 22.4° and 25.9° get sharpened and intensified significantly, which can be assigned to the characteristics of the PANI crystal, indicating that the polymer chains are parallel and arranged in an orderly manner in a close-packed array [16,17].

The ZnO nanorods grown on PET substrates (curve c) showed typical crystallinity remarkably, with diffraction peaks at 2θ values of 31.9°, 34.3° and 36.4°, corresponding to the (100), (002) and (101) reflections of the hexagonal wurtzite structure [18,19]. Weak XRD characteristic peaks of ZnO nanorods in PET-ZnO/PANI composite (curve d) shows that the crystallinity of ZnO nano particles is disturbed by the growing of PANI molecular chains on the surface of ZnO nanorods.

3.2. ATR-FTIR spectroscopy studies

Fig. 2 shows the ATR-FTIR spectra of PET, PET-PANI, PET-ZnO, PET-ZnO/PANI samples. Comparing the characteristic peaks of PET and PET-PANI in Fig. 2a, a new peak at 3417 cm^{-1} is attributed to N-H stretching mode and the peaks appear at 1641 cm^{-1}, 1579 cm^{-1}, 1474 cm^{-1}, 1182 cm^{-1}, and 1050 cm^{-1} correspond to C=N of imonoquinone, C=C stretching mode of quinoid rings, C=C stretching mode of benzenoid rings, stretching mode of N=Q=N where Q represents the quinoid ring and the aromatic C–H in plane bending modes, respectively [20,21]. There is a broadened band at 790–990 cm^{-1} in the case of PET-PANI sample related to the C-H bonding mode of aromatic rings in polyaniline structures. It is evident from Fig. 2b that the FTIR spectrum of PET-ZnO/PANI composite contains contributions from both the PET-ZnO and polyaniline. A broad band at 3438 cm^{-1} is observed in the spectrum of PET-ZnO sample, which is assigned to the vibration mode of water OH group for presence of amount of water adsorbed on the ZnO nanocrystal surface [22]. The broadness and intensity of this peak is observed in case of PET-ZnO/PANI composite due to N-H stretching mode in PANI structures, which indicates the coating of

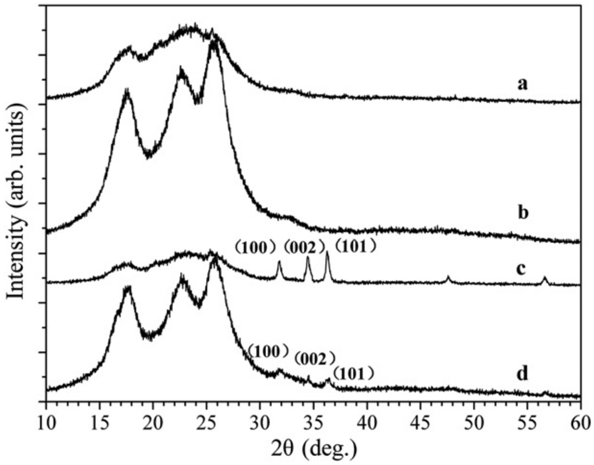

Fig. 1. X-ray diffraction patterns of (a) pure PET (b) PET-PANI (c) PET-ZnO (d) PET-ZnO/PANI composites.