



Novel nanocomposites based on polythiophene and zirconium dioxide



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ABSTRACT

This paper reports charge transport mechanism of polythiophene (PT) and its nanocomposites having various weight of zirconium dioxide (ZrO_2). Fourier transform infrared (FT-IR) spectral studies showed that the Zr ions mostly affected the C—S bond of the polythiophene. X-ray diffraction (XRD) patterns indicated that ZrO_2 powder was a mixture of monoclinic (64.62%) and tetragonal (35.38%) phase. XRD measurements revealed that crystallinity of PT decreased with increasing doping level. Significant morphological differences were observed in scanning electron microscopy (SEM) images of PT depending on the doping process. Thermal analysis carried out by differential scanning calorimetry (DSC) indicated that the doping processes increased glass transition temperature of PT. The alternating current (ac) conductivity mechanism analysis by universal power law indicated that charge transport mechanism of both PT and PT/ ZrO_2 nanocomposites was consistent with correlated barrier hopping (CBH) model. The doping process and frequency affected the hopping distance between the sites.

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1. Introduction

Metal oxide nanoparticles have attracted much attention due to their unique optical, electronic and magnetic properties, low cost and environmentally friendly features [1–3]. Zirconium dioxide, one of the important transition metal oxides, has extensively been studied because of its remarkable applications in oxygen sensors, optical coatings, electroceramics, fuel cells, electrochromic devices, catalysts and gate dielectrics [4–6].

With the rapid development of nanotechnology, especially conducting polymer matrix nanocomposites are currently being widely studied [7,8]. Conducting polymers have also attracted great deal of attention in the last two decades due to their potential applications as chemical sensors, corrosion protection, electrochemical super capacitors, electrochromic devices, photovoltaics, light-emitting diodes, optical computers and batteries [9,10]. However, conducting polymers have some disadvantages such as poor processability and stability [11,12]. Doping of various inorganic materials into the conducting polymers has increased the application areas by decreasing those disadvantages of the conducting polymers. Hence, in recent years, focus of the researches have become a combination of semiconducting properties of conducting polymers and the properties of metal oxides to produce novel polymeric nanocomposites with exciting

physical and chemical properties [13–15]. Many investigations have been carried out with the aim of understanding the structural and electronic properties of the nanocomposites. In these studies, the experimental parameters such as polymerization method, temperature, doping material, oxidant and solvent types used during preparation of the nanocomposites are very important in terms of their morphological and electrical properties [16–18].

In this study, polythiophene was doped by various weights of zirconium dioxide nanoparticles. Chemical oxidative polymerization method has been preferred for the sample preparation process due to its low cost, shorter time and adjustable weight control. Among the conducting polymers, polythiophene has attracted much attention due to its excellent thermal, chemical and environmental stabilities, facile synthesis and high electrical conductivity that exhibit some unique advantages of polythiophene for the development of various applications such as electrochromic devices, solar cells, sensors and light emitting diodes [19–21]. Recently various nanocomposites of polythiophene with inorganic metal oxide particles have been synthesized. Guo et al. [22] showed that polythiophene composites with lithium vanadium oxide can be used as a cathode material for lithium ion batteries. Huang et al. [23] proved that polythiophene/ WO_3 nanocomposites can be potentially used as gas sensor material for detecting the low concentration of NO_2 at low temperature. Zhu et al. [24] indicated that polythiophene/ TiO_2 nanocomposites showed good photocatalytic activity.

As far as it is known, there is only one study in the literature regarding polythiophene/zirconium dioxide which was made by

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Dongmei et al. [25]. This study is patented and includes a research on the sensitivity of polythiophene–zirconia composite film, which is prepared by sol–gel process, against SO_2 gas. In our study, polythiophene/zirconium dioxide (PT/ZrO₂) nanocomposites in powder state with various amounts of zirconium dioxide were synthesized by first time using in-situ oxidative polymerization process. Structural and thermal properties of PT and its nanocomposites were investigated via FT-IR, XRD, SEM-EDX and DSC. Temperature dependent ac conductivity mechanisms of the samples were analyzed by LCR meter measurements. The understanding of charge transport mechanism in the conducting polymer matrix composites is very important for the production of electronic devices such as transistor, biosensor, organic and hybrid photovoltaics. Since the mechanism of charge transports in conducting polymeric composites is not yet fully understood, the temperature dependent conductivity properties of PT/ZrO₂ nanocomposites may be crucial in improving device performance for various applications mentioned above. Furthermore, the experimental results can also contribute to the literature studies.

2. Experimental

2.1. Materials

Thiophene (C₄H₄S), anhydrous iron(III)-chloride (FeCl₃), and chloroform (CHCl₃) were supplied by Merck (Germany). Methanol (CH₃OH) and Zirconium dioxide (ZrO₂, <100 nm) were purchased from Sigma–Aldrich. These materials were used without undergoing any processing.

Chemical abstracts service (CAS) numbers of C₄H₄S, FeCl₃, CH₃OH, CHCl₃ and ZrO₂ are 110-02-1, 7705-08-0, 67-65-1, 67-66-3 and 1314-23-4, respectively.

2.2. Preparation of PT and its nanocomposites

PT and its nanocomposites were synthesized by chemical oxidative polymerization using FeCl₃, as oxidant, in CHCl₃. Molar ratio of $n_{\text{FeCl}_3}/n_{\text{C}_4\text{H}_4\text{S}}$ was 3.

0.06 mol (9.732 g) FeCl₃ in 40 mL CHCl₃ and 0.02 mol (1.587 mL) C₄H₄S in 30 mL CHCl₃ was separately mixed for 30 min with magnetic stirrer. Various amounts of ZrO₂ nanoparticles (0.1; 0.2; 0.3 g or 0.8; 1.6; 2.4 mmol) were stirred separately in 30 mL CHCl₃ for 1 h in ultrasonic bath. In order to provide the adsorption of the nanoparticles on the monomer, ZrO₂ and C₄H₄S bearing CHCl₃ solutions were combined and stirred for 30 min in ultrasonic bath. This solution was taken into ice bath and FeCl₃ was added drop wise. Polymerization process continued for 5 h by mixing with magnetic stirrer inside ice bath and under argon atmosphere. After filtration, the nanocomposites were washed with 2 × 50 mL chloroform and 2 × 50 mL methanol, respectively. After washing process, the samples were dried in vacuum oven at 70 °C for 48 h and brown colored PT/Zr nanocomposites were obtained. The nanocomposites having 0.1 g, 0.2 g and 0.3 g weight of ZrO₂ will be tagged as samples PT/0.1Zr, PT/0.2Zr and PT/0.3Zr, respectively, for the remainder of this paper.

For the synthesis of polythiophene, same experimental processes were applied as described above. However, since ZrO₂ was not used, the volume of C₄H₄S solution was adjusted to 100 mL by the addition of chloroform.

2.3. Measurements

Samples were characterized by an FT-IR (Shimadzu FT-IR 8201, Japan) spectrophotometer between 4000 and 400 cm⁻¹ using the KBr pellet method and X-ray (RIGAKU MINIFLEX-2 Diffractometer with Cu K α radiation) diffraction patterns were collected in 2 θ

range of 10–80° with scanning step width of 0.02 deg (2 θ)/min. Thermal properties were determined by DSC (PerkinElmer DSC 4000) between –50 and 400 °C with 20 °C/min heating rate under nitrogen atmosphere. Surface morphologies of the samples were examined with SEM-EDX (JEOL 50 A, Japan). The images were taken at 20 kV and no conducting layer was used before imaging. For the dielectric measurements, pellets with 13 mm diameter were prepared by applying a pressure of 10 MPa using a hydraulic press. Dielectric measurements were performed by an LCR meter (Sourcetronic ST2826A, Germany) in the temperature range of 300–400 K at a frequency range of 10 kHz–1 MHz under vacuum ($\sim 10^{-3}$ Torr). Copper plates with 13 mm diameter and 1 mm thickness were used as electrodes. The temperature was controlled by using a temperature controller (Lakeshore 335, USA). The alternating current (ac) conductivity was calculated by $\sigma_{\text{ac}} = \omega C_p \text{d} \tan \delta / A$ relation, where ω is the angular frequency, C_p is the capacitance of the sample, d is the sample thickness, $\tan \delta$ is the dielectric loss factor and A is the electrode area.

3. Results and discussion

3.1. Characterization

Fig. 1 shows FT-IR spectra of ZrO₂, PT and nanocomposites. The adsorption bands of the samples matched well with results reported in literature. The absorption peaks of PT at 3416, 1634, 1389 and 1331 cm⁻¹ are due to the O–H stretching, asymmetric, C=C asymmetric stretching vibration, C=C symmetric stretching vibration and C–H bending vibration, respectively. The bands at 1109 and 1034 cm⁻¹ for PT are related to C–H in plane bending

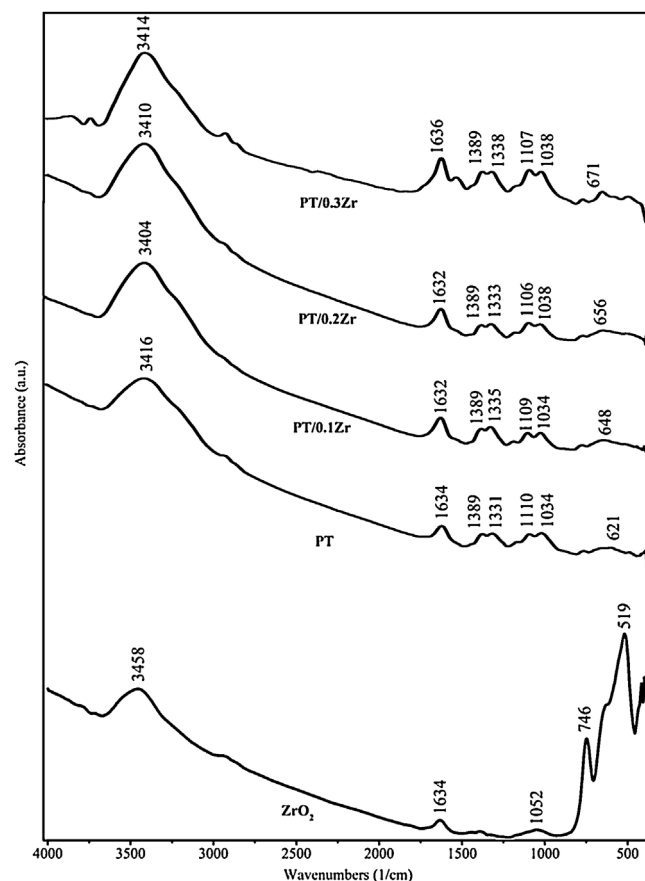


Fig. 1. FT-IR spectra of ZrO₂, PT and its nanocomposites.

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