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Author affiliations:

Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran

✉ To whom correspondence to be addressed:

Fax: +98 41 3333458
Tel: +98 41 33396024
E-mail: babazadeh@iaut.ac.ir

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ARTICLE

Conductive Polythiophene/Titanium Dioxide Nanocomposites: Synthesis and Investigation of Physical Properties

Mirzaagha Babazadeh[✉]

ABSTRACT

This work describes an efficient method to synthesize and characterization of polythiophene/titanium dioxide (PTP/TiO₂) nanocomposites by one-step *in situ* polymerization of thiophene, using FeCl₃ as an oxidant in the presence of different amount of TiO₂ nanoparticles. The obtained nanocomposites were characterized by Fourier-transform infrared, X-ray diffraction, thermogravimetric analysis, scanning electron microscope and the conductivity by four point probe technique. The obtained results confirmed that TiO₂ nanoparticles are encapsulated by polythiophene.

KEYWORDS

Nanocomposite, Conducting polymers, Polythiophen, Titanium dioxide, *in situ* Polymerization.

INTRODUCTION

Recently, nanocomposites in comparison with pure polymers due to having better mechanical, physical and chemical properties got wide application in different fields of industry and research [1-3]. Furthermore, nanocomposites because of having proper mechanical properties with respect to similar polymers have long life, thus decrease related environmental problems of waste materials [4]. Novel properties of nanocomposites can be obtained by the successful combination of the characteristics of parent constituents into a single material. Encapsulation of inorganic nanoparticles inside the shell of conducting polymers is the most popular and interesting aspect of nanocomposites synthesis. These materials differ from both pure polymers and inorganic nanoparticles in some of the physical and chemical properties [5,6]. Titanium dioxide (TiO₂) is an important inorganic nanoparticle in preparing conducting polymer composites because of its excellent physical and chemical properties, as well as extensive applications in diverse areas, such as coatings, solar cells and photocatalysts [7-9]. As one kind of conducting polymers, polythiophene (PTP) and its derivatives have attracted considerable attention for their easy and excellent environmental and thermal stability. However, the principal problems with the practical utilization of conducting polymers like polythiophene

include its poor mechanical properties like brittleness and low processibility and this limitation can be overcome by application of nanocomposites [10-13]. The present work describes an efficient method to synthesize and indicates characterization of PTP/TiO₂ nanocomposites by one step *in situ* polymerization of thiophene by TiO₂ nanoparticles. The characteristics of the molecular structure, crystallinity, electrical properties, thermal stability and morphology of the PTP/TiO₂ nanocomposites are also discussed.

EXPERIMENTAL

Thiophene monomer was purchased from Merck and distilled in vacuum until a colourless liquid was obtained. The distilled thiophene was stored at lower than 5 °C in the absence of light. TiO₂ nanoparticles (anatase) with an average particle size of 15 nm was obtained from Degussa and used as received. All other chemicals were reagent grade or purer.

X-ray diffraction (XRD) patterns of neat TiO₂, polythiophene and PTP/TiO₂ nanocomposites were measured in the range of 2θ = 10-80° by step scanning on the Simens X-ray diffraction D5000 with CuK_α radiation (λ = 0.154 nm). Fourier-transform infrared (FTIR) spectra nanocomposites were recorded on a Bruker Spectrometer Tensor 27 FT-IR with KBr pellets. The morphology of neat TiO₂, polythiophene and PTP/TiO₂ nanocomposites was investigated by scanning electron microscopy (SEM, LEO-440i). Thermal stability was investigated by thermal gravimetric analyzer (Perkin-Elmer, TGA-7) under a nitrogen flow (35 mL/min) and heating rate of 10 °C/min. The electrical conductivity of the samples was measured using a PCI-DAS6014 (measurement computing) as a current source and temperature controller following a standard four point probe method.

Preparation of PTP/TiO₂ nanocomposites: PTP/TiO₂ nanocomposites were synthesized according to the following method. Different amounts of TiO₂ nanoparticles (0.05, 0.10, 0.15 and 0.20 g) were separately suspended into 50 mL chloroform and sonicated in an ultrasound bath for 20 min to get well dispersed. Then, thiophene (1 mL) was added into the suspension at room temperature with constant stirring. After that, FeCl₃ (7.3 g) was dissolved in 50 mL of chloroform and added drop wise into the above mixture as oxidant. The *in situ* polymerization was carried out with the stirring speed of 600 rpm at room temperature for 24 h. The colour of the mixture changed from gray to deep black. After stirring for 24 h, the product was extracted with methanol to remove the residual iron chloride. During this procedure, the colour of composites changed from black (polythiophene in oxide state) to red (polythiophen in reduced state), which indicated the successful reduction of polythiophen shell. A series of PTP/TiO₂ nanocomposites were obtained after washing with methanol several times and drying at 80 °C for 3 h. Pure polythiophene was prepared by similar method as the preparation of the PTP/TiO₂ composites, but TiO₂ nanoparticles were not required.

RESULTS AND DISCUSSION

The FTIR spectra of polythiophene and PTP/TiO₂ were recorded using KBr pellets in the range of 4000-500 cm⁻¹. FTIR spectra of polythiophen and PTP/TiO₂ nanocomposites

are respectively shown in Figs. 1 and 2. The peaks of 3100-2800 and 1650 cm⁻¹ can be attributed to the C-H stretching vibrations and C=C characteristic peak, respectively. The absorption peak at 692 cm⁻¹ was assigned to the C-S bending mode, which indicated the presence of thiophene. In Fig. 2, a new peak appeared at 648 cm⁻¹, which indicated the presence of TiO₂ nanoparticles. The peak at 786 cm⁻¹ in Fig. 1, should be ascribed to the C-H out-of-plane stretching vibration mode of polythiophen, which after addition of TiO₂ shifts to 787 cm⁻¹ in Fig. 2. This shows that polythiophene has incorporated with TiO₂ successfully.

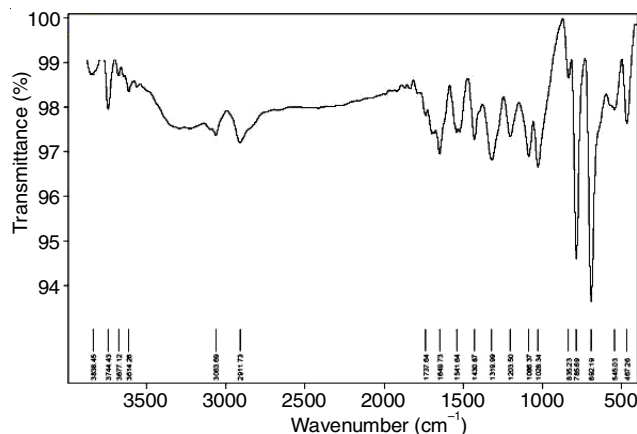


Fig. 1. FTIR spectra of pure polythiophene

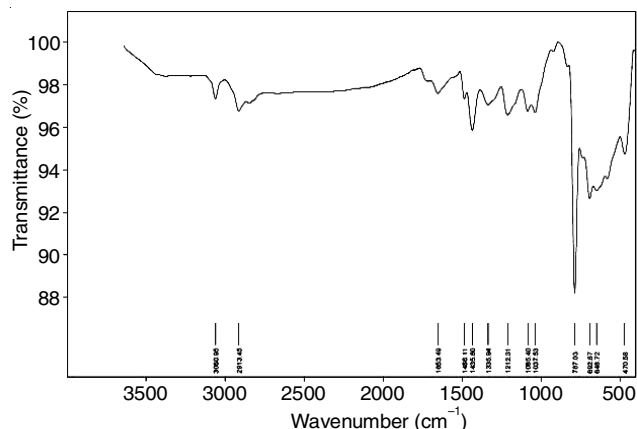
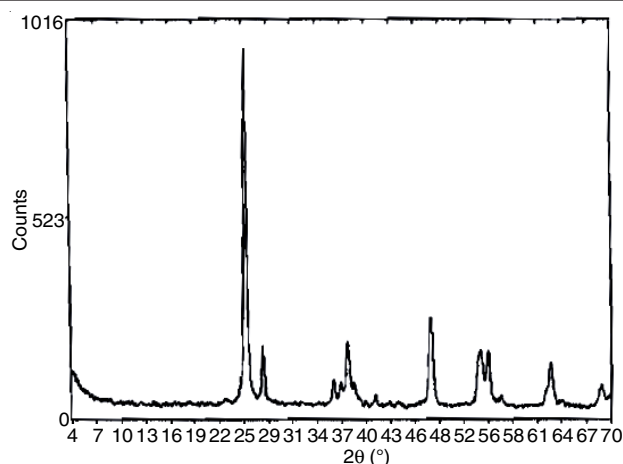
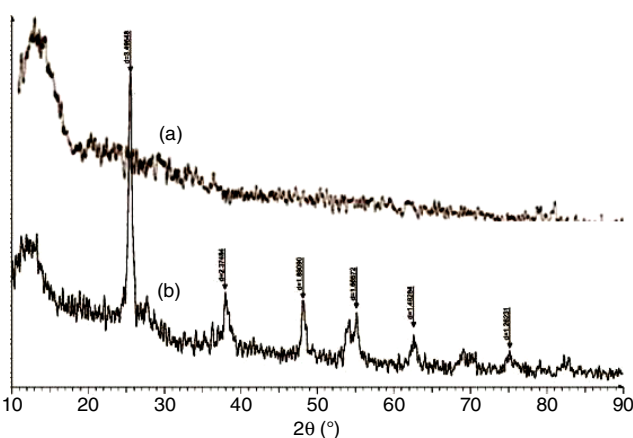


Fig. 2. FTIR PTP/TiO₂ nanocomposites

X-ray diffraction patterns of pure TiO₂, polythiophene and the synthesized PTP/TiO₂ nanocomposites are presented in Figs. 3 and 4. The broad peak in the region of 2θ = 10-30° in XRD pattern of pure polythiophene (curve a) shows that the synthesized polythiophen in the absence of TiO₂ nanoparticles is amorphous. Also, the main diffraction peaks of pure anatase TiO₂ nanoparticles are appeared at 25°, 38° and 48° (Fig. 3). It can be seen from curves (b) that the main peaks of PTP/TiO₂ nanocomposites are similar to those of neat TiO₂ nanoparticles. XRD patterns of PTP/TiO₂ nanocomposites show that the broad weak diffraction peak of polythiophene still exists, but its intensity has been decreased. It implies that when polythiophene is polymerized on TiO₂, each phase maintains his initial structure. The mean size of TiO₂ nanoparticles and PTP/TiO₂ nanocomposites was calculated by Scherrer's formula. The size of nanocomposites is smaller than that of nanoparticles TiO₂.

Fig. 3. XRD pattern of TiO₂ nanoparticlesFig. 4. XRD pattern of (a) pure polythiophene, (b) PTP/TiO₂ nanocomposites

Thermogravimetric curves for pure polythiophene and PTP/TiO₂ nanocomposite are shown in Figs. 5 and 6, respectively. The composite was initially stable up to 145 °C and decomposed in 909 °C about 68 % of sample. The TiO₂ particles were comparatively stable in the range of 0-700 °C. So, the weight loss in TGA curve was due to degradation of polythiophene. Polythiophene was stable up to 130 °C and decomposed at 500 °C about 87 % of polythiophene. These data indicated that the PTP/TiO₂ composites decomposed at higher temperature than that of pure polythiophene. The thermal stability increased with the decrease of polythiophene mass percent.

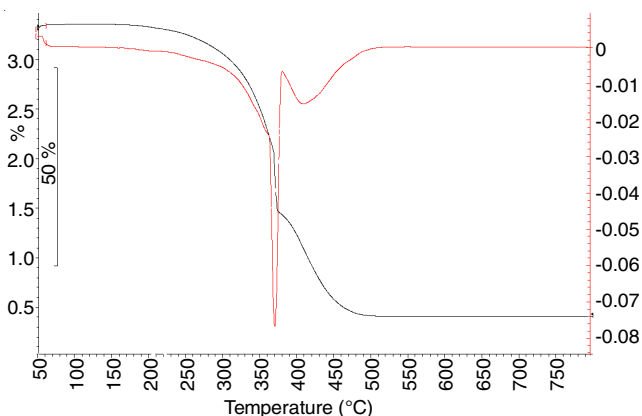
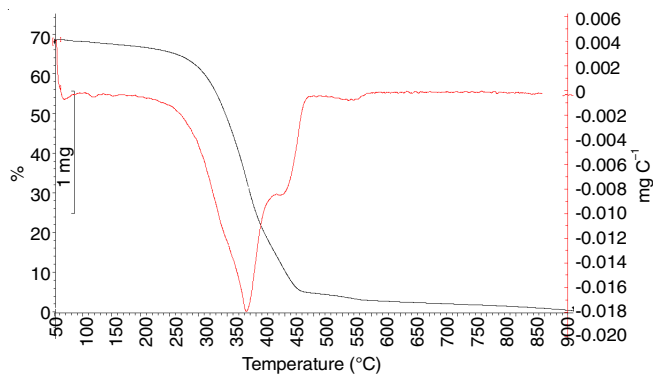
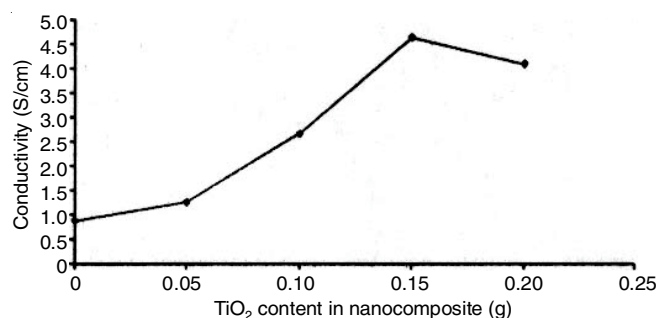


Fig. 5. TGA diagrams of polythiophene

Fig. 6. TGA diagrams of PTP/TiO₂ nanocomposites

The electrical conductivity was measured by four point probe technique (Fig. 7). The obtained conductivity results showed that with increasing TiO₂ content in nanocomposite structure, the conductivity increases slightly, but excess TiO₂ content causes decreasing of conductivity. This decreasing conductivity showed that with introducing excess TiO₂ nanoparticles in nanocomposite structures, the transport of carriers between different molecular chains of polythiophene is hindered and the conductivity decreases. On the other hand, the interaction at the interface of polythiophene and TiO₂ probably led to the reduction of the conjugation length of polythiophene in nanocomposites.

Fig. 7. Electrical conductivity versus the contents of TiO₂ in PTP/TiO₂ nanocomposites

The morphology and shape of neat polythiophene and PTP/TiO₂ nanocomposites were characterized by SEM and the obtained images are presented in Figs. 8 and 9. With increasing contents of TiO₂, the morphology of nanocomposites changed. It indicates that the TiO₂ nanoparticles have a nucleus effect on the polythiophene polymerization and caused a homogeneous polythiophene shell around them. SEM study shows that TiO₂ nanoparticles have a strong effect on the morphology of PTP/TiO₂ nanocomposites. This employed method is very simple and inexpensive and it can be easily applied industrially strong effect on the morphology of PTP/TiO₂ nanocomposites.

Conclusion

Conducting PTP/TiO₂ nanocomposites in CH₃Cl solution were successfully prepared by one-step *in situ* chemical oxidative polymerization of thiophene using FeCl₃ as oxidant in the presence of ultra fine grade powder of anatase nano-TiO₂ particles. The obtained results from XRD, FT-IR, TGA and SEM data confirmed that TiO₂ nanoparticles are encap-

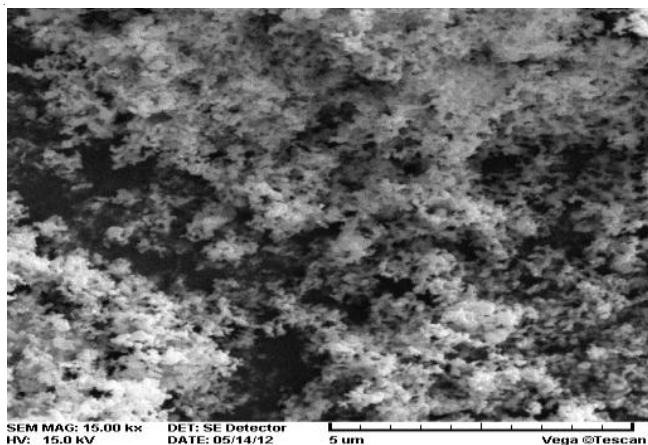
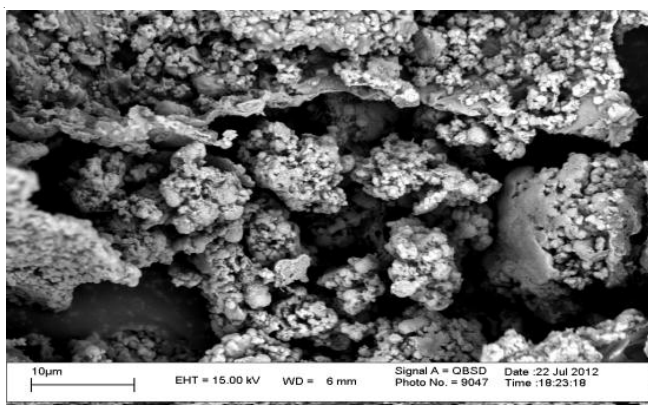


Fig. 8. SEM image of pure polythiophene

Fig. 9. SEM image of PTP/TiO₂ nanocomposites

sulated by polythiophene. Electrical conductivity measurements indicate that the conductivity of nanocomposites at low TiO₂ content is much higher than that of neat polythiophene, while

with the increasing contents of TiO₂, the conductivity shows an orderly decrease. TGA investigation shows that thermal stability of PTP/TiO₂ nanocomposites is higher in comparison with pure polythiophene.

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