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Preparation, characterization and photocatalytic properties of polythiophene-sensitized zinc oxide hybrid nanocomposites

M. Khatamian *, M. Fazayeli, B. Divband

Inorganic Chemistry Department, Faculty of Chemistry, University of Tabriz, C.P. 51664, Tabriz, Iran

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ABSTRACT

The composites of polythiophene (PT)/zinc oxide (ZnO) nanoparticles with different PT wt %, (2%, 4%, 6%, 10% and 20%), were synthesized by an in situ chemical oxidative polymerization method. Zinc oxide nanoparticles, prepared by polymer pyrolysis method, with average particle size of 30 nm were used as inorganic phase of these composites. The particle size of ZnO powder was measured by transmission electron microscopy (TEM). FTIR measurements and X-ray diffraction analyses showed that PT/ZnO composites were successfully synthesized. Optical properties of the prepared composites were investigated by diffuse reflectance spectroscopy (DRS) that showed a broad peak in the visible region. The morphologies of the obtained composites were studied by scanning electron microscopy (SEM). Also Barrett–Emmett–Teller (BET) technique was used to measure the specific surface area of the samples. The photocatalytic activities of the composites were evaluated by degradation of methyl orange (MO) aqueous solution under visible light (9 W LED lamp) and sunlight irradiation.

1. Introduction

In the last decades, organic–inorganic hybrid structures have been widely studied due to their interesting properties. These distinctive structures posses advantages inherited from each component, besides exhibiting novel properties originated from interactions occurring at the molecular level during the formation of the interface between the components [1]. Various types of metal oxide semiconductors such as TiO_2, zinc oxide (ZnO) and SnO_2 have been used in these hybrid materials for different applications including solar cells [2], gas sensors [3], electronic devices [4] and photocatalysts [5].

Recently, the combination of conjugated polymers and semiconductor photocatalysts has attracted considerable attention. Among semiconductor photocatalysts TiO_2 has proven to be the most suitable for widespread photocatalytic applications, but ZnO has sometimes been reported to be more efficient than TiO_2 [6]. ZnO is a II–VI compound semiconductor with a direct band gap around 3.37 eV in the near-UV and a large excitation binding energy of 60 meV [7]. The major advantage of ZnO is that it absorbs a larger fraction of UV spectrum than TiO_2, but the occurrence of photocorrosion and the susceptibility of ZnO to facile dissolution at extreme pH value, have significantly limited its application in photocatalysis [8]. On the other hand both ZnO and TiO_2 can only be excited under UV light illumination [9]. Therefore intensive efforts have been focused on the surface modification of these semiconductors to produce highly active visible light photocatalysts. In most cases doping with metal or nonmetal elements can only cause a

* Corresponding author. Tel.: +98 411 3393129; fax: +98 411 3340191.
E-mail address: mkhatamian@yahoo.com (M. Khatamian).

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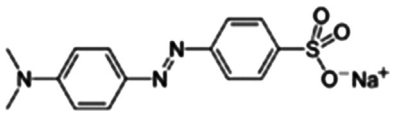
small red-shift in the absorbance spectrum that hardly reaches threshold of 500 nm [10]. In order to improve the solar energy utilization efficiency, researchers have suggested that the conjugated polymers extending π-conjugated electron systems may enhance the visible light absorption of semiconductor photocatalysts. Conjugated polymer/semiconductor photocatalyst combinations can mostly absorb not only UV but also visible light due to high absorption coefficient of these polymers in the visible part of the spectrum. Furthermore π-conjugated polymers are efficient electron donors and good hole transporters upon visible light excitation [11].

Until now most of studies have been published on hybridization of TiO_2 with conjugated polymers to improve its photocatalytic efficiency under UV and visible light. For example Li et al. reported the synthesis of polyaniline/TiO_2 nanocomposite and found that it had higher photocatalytic activity and stability than bare TiO_2 toward the degradation of methyl orange (MO) under both UV and visible light irradiation [12]. Song et al. prepared poly-(fluorene-co-thiophene) (PFT)/TiO_2 composite and investigated its performance in degradation of phenol and rhodamine B under visible light [13]. Poly-(3-hexylthiophene)/TiO_2 nanocomposite was synthesized by Zhu and Dan and photodegradation of methyl orange was measured under visible light [14]. Unlike a lot of works have been done on TiO_2, there are a few studies on modification of ZnO by conjugated polymers in the field of photocatalytic processes. To the best of our knowledge, there are only two composites, poly-(fluorine-co-thiophene) (PFT)/ZnO and polyaniline (PANI)/ZnO, about conjugated polymer-modified ZnO for degradation of organic pollutants [15,16]. However in the case of PANI/ZnO there are different synthetic methods and the composites are the combination of polyaniline and ZnO particles ultimately [17,18]. Among the heterocyclic conjugated polymers, polythiophenes have a special place in photocatalytic applications because of their stability under photoirradiation. Unsubstituted polythiophene has the band gap of 2.1 eV, and can absorb the visible light [19,20]. Dan et al. reported that combination of polythiophene and TiO_2 nanoparticles changed the spectrum of TiO_2 in the visible light range. PT/TiO_2 composites absorbed much more visible light than TiO_2 and they were more efficient in removing methyl orange from solution than pure PT and pure TiO_2 [21].

According to this background, in the present work ZnO nanoparticles were modified by different amounts of polythiophene to improve the photocatalytic activity of nanoparticles under visible light irradiation for the first time. The PT/ZnO composites were synthesized by an in situ chemical oxidative polymerization method. The photocatalytic activities of prepared composites were evaluated by degradation of methyl orange (Scheme 1) under visible and solar light.



Scheme 1. Structure of methyl orange.

2. Experimental

2.1. Materials

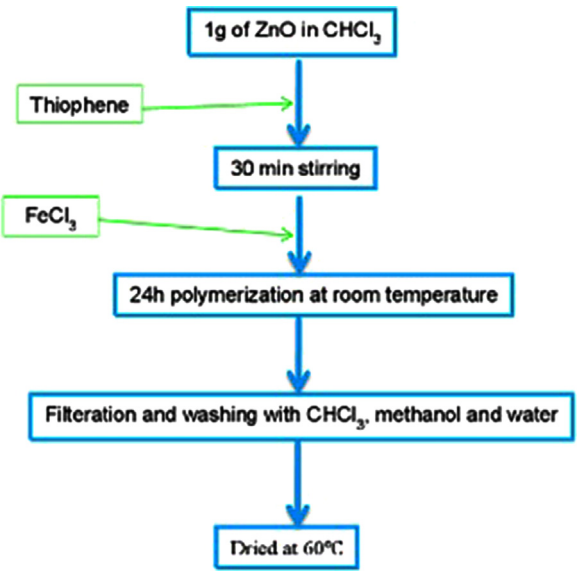
Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), nitric acid ($HNO_3$, 68%), citric acid ($C_6H_8O_7$), acryl amide ($C_3H_5NO$), 2-2′-azoisobutyronitrile (AIBN), chloroform ($CHCl_3$), thiophene, methanol and anhydrous iron (III) chloride were obtained from Merck Chemicals (Germany).

2.2. Preparation of ZnO nanoparticles

ZnO nanoparticles were prepared following the procedure described in our recent work [22,23]. 0.17 g Zn $(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 2 ml dilute nitric acid (2 mol l^{-1}) and 0.3 g citric acid was added in order to accelerate dissolution of $Zn(CH_3COO)_2 \cdot 2H_2O$. The mixture was kept under stirring for 2 h. The final pH was controlled to be 6–7 by using dilute ammonia. Subsequently, the monomers of acrylamide (0.3 g) were added into the solution. The resulting solution was stirred for 20 min, and then was heated in water bath. When the temperature reached about 80 °C, a small amount of compound initiator AIBN ($C_8H_{12}N_4$) was added into the solution and polymerization occurred quickly and polymeric resin was obtained without any precipitation. At last, the gel was dried at 100 °C for 24 h to yield a xerogel. The xerogel was heated at 300 °C for 10 h and calcined at 500 °C for 5 h.

2.3. Synthesis of PT/ZnO composites

Chemical oxidative polymerization was used for the preparation of composites (Scheme 2). 1 g of ZnO nanoparticles were dispersed in 20 ml chloroform and stirred for 30 min. Then according to the thiophene (TP) percentage (2%, 4%, 6%, 10% and 20%), 20 μl, 40 μl, 60.2 μl, 105 μl and 236 μl, respectively, was added into the above suspension.



Scheme 2. Schematic illustration of the synthetic procedure of the PT/ZnO composites.