

Rapid Communication

# Synthesis and photocatalytic activity of poly(3-hexylthiophene)/TiO<sub>2</sub> composites

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Received 18 May 2007; received in revised form 17 July 2007; accepted 17 July 2007

Available online 7 August 2007

## Abstract

An heterogeneous conducting polymer composite, poly(3-hexylthiophene)/TiO<sub>2</sub> (P3HT/TiO<sub>2</sub>), was synthesized. The photocatalytic activity of P3HT alone and the composite was investigated for the first time by degrading a common dye under UV exposure. It was shown that the photocatalytic activity of the nanocomposites was higher compared to either the polymer or TiO<sub>2</sub> alone. A simple mechanism was proposed to explain this observed synergetic effect.

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**Keywords:** Nanocomposites; Photocatalysis; Titania; P3HT

## 1. Introduction

Heterogeneous conducting polymer composites (organic/inorganic) have been attracting attention owing to their applications in various fields [1–16] such as charge storage materials, catalysts, solar cells [8–10], immunodiagnostic assays and electrorheological ER fluids [16]. Several composites of polyaniline (PANI), polypyrrole (Ppy), polyphenylene vinylene (PPV) and polythiophene (PTh) with inorganic materials such as LiMnO<sub>2</sub>, Pt, Cu, SiO<sub>2</sub>, WO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, MnO<sub>2</sub> have been studied in this context [17]. Conducting polymers have also been used as the supporting matrix in different composites for intercalation of catalytically important nanoparticles so that catalytic activity is retained in the composite [17].

Yet another important property of conducting polymer nanocomposites is electrocatalysis. Dispersion of Pt particles in PANI matrix has been shown to oxidize methanol [18]. Athawale et al. [8] have described the oxidation of methanol and formic acid by a series of monometallic and bimetallic electrodes in which Pd, Cu,

Pd/Cu, and Cu/Pd have been combined with PANI. Recently, we reported that conjugated polymers exhibit photocatalytic activity [19]. A study on the degradation of various textile dyes under UV radiation in the presence of the conjugated polymers such as poly(3-hexylthiophene) (P3HT) and poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene (MEH-PPV) showed higher activity in the case of the polymers than Degussa (commercial titania). Since both TiO<sub>2</sub> and the conducting polymers are independently photocatalytic in nature, nanocomposites of (P3HT) and (MEH-PPV) with TiO<sub>2</sub> are expected to show higher degradation rates than the mere polymers. To the best of our knowledge, there is only one report on the photocatalytic activity of polymer nanocomposites [20] and no reports on the use of P3HT as a nanocomposite material. This article reports the preparation of P3HT/TiO<sub>2</sub> nanocomposites in various ratios and photocatalytic degradation studies.

## 2. Experimental

P3HT was synthesized by the reported procedure [21]. To chloroform solutions (15 mL) of P3HT (0.005 kg/m<sup>3</sup>), 5 mL suspensions of Degussa P-25 titania in chloroform were mixed in various mass percentages of 10%, 20%,

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30%, and 50%. The solutions were ultrasonicated for about 30 min and then the solvent was slowly evaporated under vacuum. The resultant nanocomposites formed films along the sides of the glass beakers. Then, aqueous solutions of Orange G ( $10^{-4}$  M), were added to each flask and the flasks were subjected to UV radiation. The materials were characterized by X-ray diffraction (XRD), FTIR, SEM, and photoluminescence. The XRD patterns were recorded on a Philips X'pert Pro Diffractometer with  $\text{CuK}\alpha$  radiation in the  $2\theta$  range from  $20^\circ$  to  $80^\circ$  with a scanning rate of  $1^\circ/\text{min}$ . FT-IR studies were carried out with Perkin-Elmer (FT-IR-Spectrum-1000) spectrometer in the frequency range of  $400\text{--}4000\text{ cm}^{-1}$  in the transmission mode. Compositional analysis was done for all samples with the help of energy-dispersive X-ray (EDX) micro-analysis on a JEOL JSM-840 SEM/EDAX machine. The photoluminescence measurements were performed in a luminescence spectrophotometer (Perkin-Elmer 55) operated at room temperature. A high-pressure mercury vapor lamp (125 W, Philips, India) was used for the degradation reactions. The details of the photochemical reactor employed in this study have been reported elsewhere [22]. The lamp radiated predominantly at 365 nm. The degradation reactions were performed in a photochemical reactor with various initial concentrations with constant polymer concentration of  $0.005\text{ kg/m}^3$ . Samples were collected at regular intervals for subsequent analysis. Control experiments conducted without the catalyst under UV radiation and with the catalyst without UV radiation did not show any appreciable degradation indicating that both the catalyst and UV radiation are required for the degradation reactions. There was no reduction in the concentration of the Orange G (OG) dye solution when a solution of  $10^{-4}$  M was stirred with the catalysts for 12 h in dark. The reactions were carried out at natural pH conditions and were monitored by change in the UV-visible spectra.

### 3. Results and discussion

Powder XRD studies confirm the presence of  $\text{TiO}_2$  in the composites (Fig. 1). The highest intense peak at  $5.38^\circ$  is representative of the polymer. The  $\text{TiO}_2$  (Degussa, P-25) contains anatase and rutile phases in a ratio of about 3:1.

SEM images of the P3HT/20% $\text{TiO}_2$  and P3HT/50% $\text{TiO}_2$  nanocomposites are shown in Figs. 2a and b. The  $\text{TiO}_2$  particles are homogeneously dispersed into the polymer folds. The particle size of  $\text{TiO}_2$  in both the cases was estimated to be in the range of approximately 30–40 nm, consistent with the size of Degussa P-25 particle size of 27 nm. Point EDX analysis on several spots on the  $\text{TiO}_2$  particles confirmed the presence of titanium on the polymer as confirmed by powder XRD. The  $\text{TiO}_2$  particles appear to be well dispersed on the polymer. The PL spectra indicate quenching as the content of  $\text{TiO}_2$  in the composites increases (Fig. 3). The quenching is due to the presence and distribution of titania in a polymer matrix because charge transfer occurs from the polymer to titania.

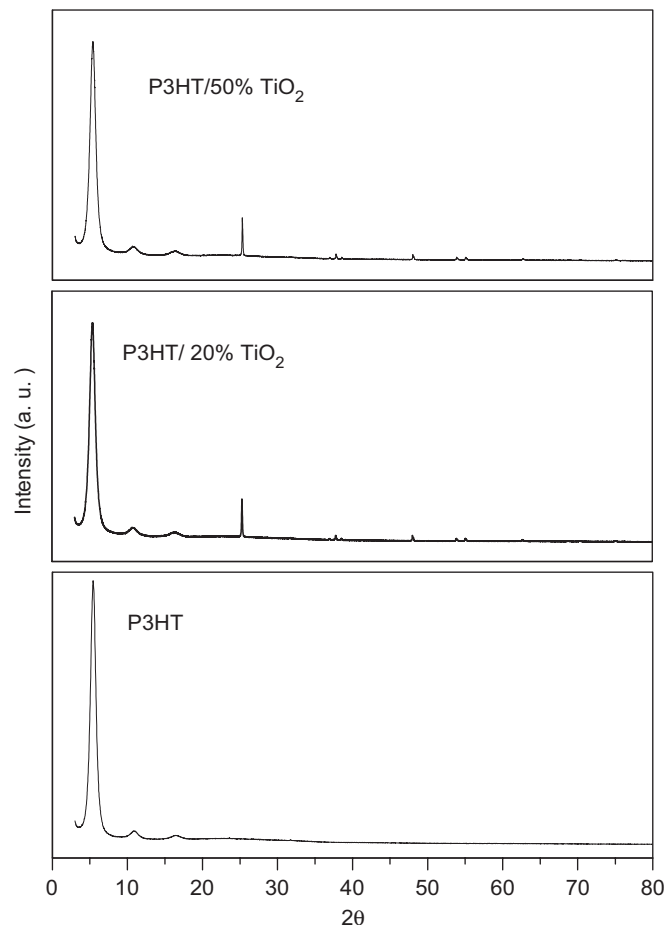


Fig. 1. Powder X-ray patterns of the P3HT/ $\text{TiO}_2$  composites.

The P3HT composites containing 10%, 30%, and 50% of  $\text{TiO}_2$  were investigated for their photocatalytic activity. Photocatalytic degradation of a commonly used textile dye, OG was performed in the photocatalytic reactor described earlier. The decrease in concentration of OG at various concentrations of  $\text{TiO}_2$  in the nanocomposites with respect to time is shown in Fig. 4. The degradation profiles indicate higher degradation rates with an increase of the  $\text{TiO}_2$  content in the nanocomposites. The maximum rate was observed for the P3HT/50% $\text{TiO}_2$  composite, among the composites investigated.

Solid phase degradation of polymer substrate has been reported to occur under UV radiation in the presence of  $\text{TiO}_2$ . Polymer matrices such as polystyrene [23] and polyvinyl chloride [24] have been studied for degradation. Interestingly, the P3HT matrix does not undergo degradation under UV radiation in the presence of  $\text{TiO}_2$  nanoparticles. The films were found to be quite stable to 2 h of exposure to UV radiation that was further confirmed by no change in the UV-visible and IR spectra (Fig. 5) before and after the degradation reactions. A comparison of the degradation profiles with that of mere polymer and  $\text{TiO}_2$  independently indicates higher degradation rates for

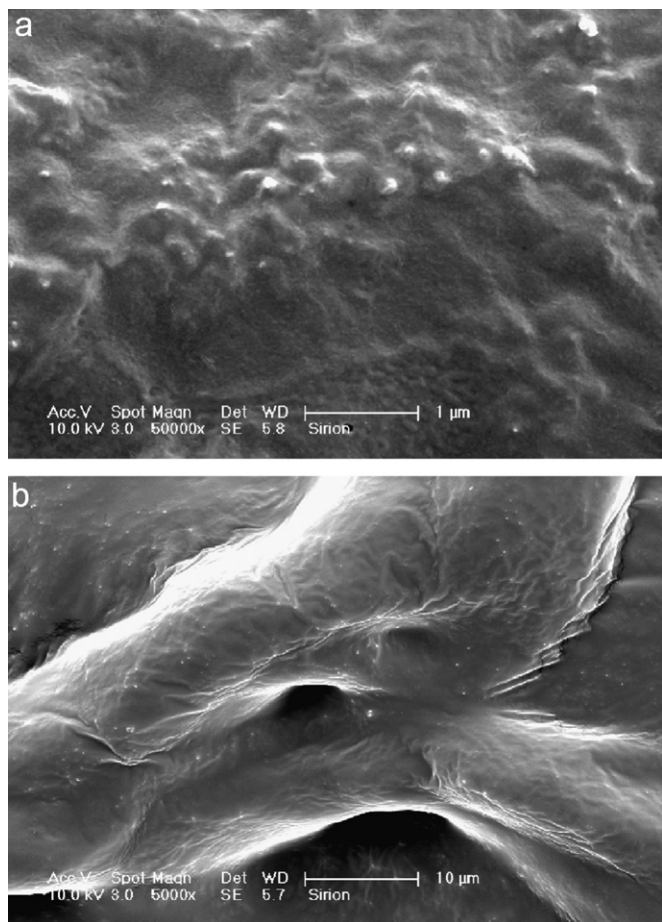


Fig. 2. SEM images of (a) P3HT/20%TiO<sub>2</sub> and (b) P3HT/50%TiO<sub>2</sub>.

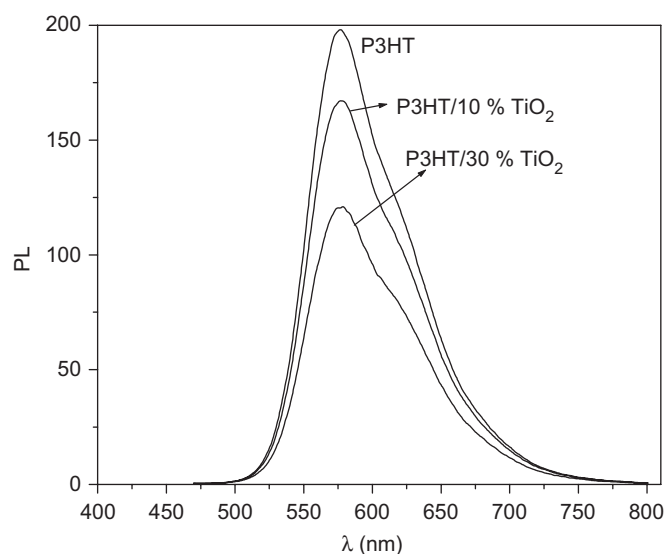


Fig. 3. PL spectra of the P3HT/TiO<sub>2</sub> composites.

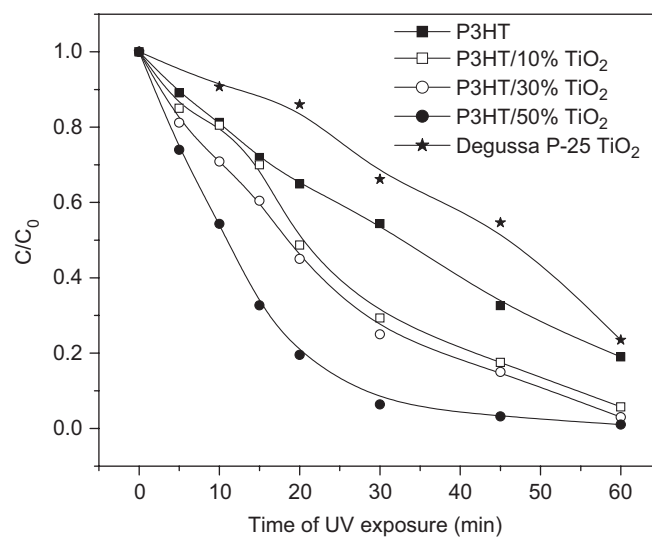


Fig. 4. Photocatalytic degradation profiles of OG in the presence of P3HT/TiO<sub>2</sub> nanocomposites.

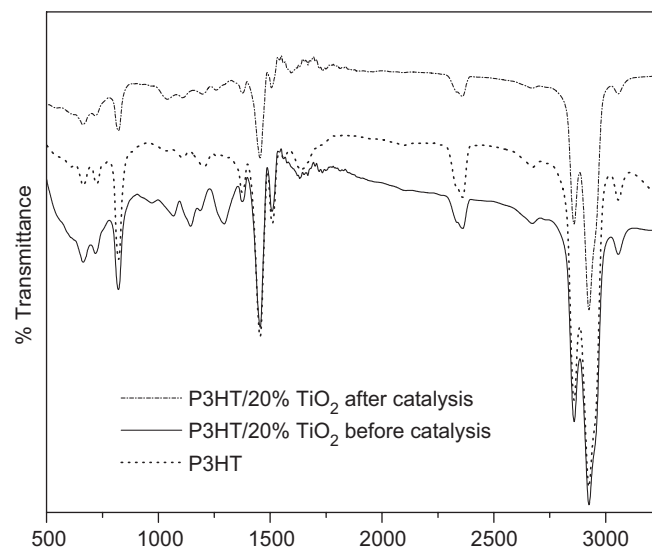


Fig. 5. IR spectra of the P3HT/TiO<sub>2</sub> composites before and after photocatalytic degradation.

the composites (Fig. 4). The degradation rates remained unaltered on repetition of the reactions in the same volumetric flask indicating the stability of the material.

Chowdhury et al. [20] observed that the photocatalytic activity of PANI itself was not significant. However, in an earlier study [19], we observed that the degradation rate of the polymer was greater than a mere suspension of TiO<sub>2</sub> itself. Hence, a combination of the conducting polymer and TiO<sub>2</sub> further enhances the degradation rate of the conducting polymer. The mechanistic pathway for the degradation reactions is via the formation of hydroxyl radicals, as observed in our earlier studies [19]. The degradation reactions occur primarily through the electron-mediated mechanism though the formation of <sup>•</sup>OH radicals by the hole-mediated pathway remains unaffected. The increase in degradation rate with an increase in the

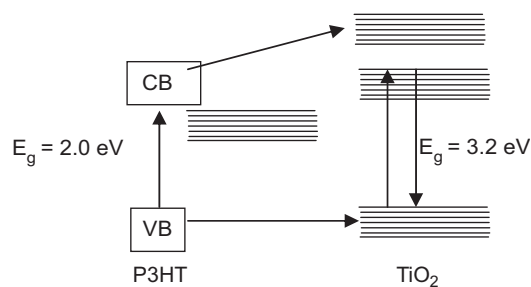


Fig. 6. Scheme of the possible mechanism of enhancement of photocatalytic degradation rate in a conducting polymer nanocomposite.

TiO<sub>2</sub> content indicates a synergistic effect of both TiO<sub>2</sub> and the polymer in the degradation reactions. The band gap of P3HT (2.0–2.1 eV) is much lower than that of TiO<sub>2</sub> (3.2 eV). On excitation, an electron from the conduction band of TiO<sub>2</sub> may go up to the empty states in P3HT (Fig. 6). This in turn enhances the oxidative property of TiO<sub>2</sub> by making the valence band hole of TiO<sub>2</sub> stable. On the other hand, P3HT may also absorb UV radiation allowing an energy transfer to the TiO<sub>2</sub> nanoparticles followed by the creation of the valence band hole and conduction band electron.

The latter mechanism seems plausible owing to the lower band gap of the polymer compared to that of TiO<sub>2</sub>, as reported in the literature [9]. It can be inferred that a combination of both TiO<sub>2</sub> and conducting polymers as in a nanocomposite enhances the degradation rates owing to the synergistic effect. This is based on the observation that the degradation rates are higher in the presence of either the polymer or TiO<sub>2</sub> independently. A charge transfer could occur between the conjugated polymer into the empty states of TiO<sub>2</sub>. The mechanism of degradation however, is through the hydroxylated pathway. Further experiments with visible light can be carried out to confirm the mechanism.

### Acknowledgments

The authors thank the Department of Science and Technology, India, for financial support.

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