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Study on stability of poly(3-hexylthiophene)/titanium dioxide composites as a visible light photocatalyst

Jianling Zhang, Shaoqiang Cao, Shoubin Xu, Haigang Yang, Long Yang, Yuanqing Song, Long Jiang*, Yi Dan*

State Key Laboratory of Polymer Materials Engineering of China (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, China

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ABSTRACT

Conjugated polymer/TiO_2 composites are promising visible light photocatalysts for solar chemical conversion processes in the field of environmental chemistry for decomposition of organic compounds in water and air. In consideration of the fact that conjugated polymers are also organic substances, particular attention must be focused on the stability of conjugated polymer/TiO_2 composites, which has not been laid enough emphasis upon so far. Poly(3-hexylthiophene)/titanium dioxide ($P3HT/TiO_2$) composites, as a representative of conjugated polymer/TiO_2 photocatalysts, were prepared by combining chemical oxidative polymerization method and physical blending technique. The stability of the composites was systematically studied by comparative analysis of the physical and chemical structure of $P3HT/TiO_2$ composites before and after the photocatalytic reaction. As confirmed by the results of high-resolution transmission electron microscopy (HRTEM), scanning electron microscope (SEM), ultraviolet-visible diffuse reflectance spectroscopy (UV–vis DRS), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), the $P3HT/TiO_2$ composites were quite stable to 10 h of photodegradation of methyl orange (MO) under visible light, maintaining both their physical and chemical structure.

1. Introduction

Due to the growing global energy crisis and environmental problems, heterogeneous photocatalysis has attracted considerable attention owing to its ability to purify water and air, and to split water with the use of solar light [1–7]. Conjugated polymer/TiO_2 photocatalysts hold great promise for solar chemical conversion processes by combining the advantages from both the conjugated polymer and the inorganic semiconductor, overcoming the serious drawbacks of fast charge recombination and the limited visible light absorption of inorganic semiconductor. Polythiophenes [8–10], polypyrroles [11–13], polyanilines [14–17] and their derivates [18–23] have been widely incorporated with TiO_2, resulting in conjugated polymer/TiO_2 photocatalysts with not only efficient visible light activity but also improved ultraviolet light activity by extending the response spectrum of TiO_2 to visible light region and facilitating the separation of photogenerated carriers.

Based on the previous studies [22,24–26], the conjugated polymers can be excited by visible light irradiation and the excited electrons simultaneously reach the interface by exciton diffusion before injected to the conduction band of TiO_2. The conduction band electrons subsequently transport to the surface of photocatalyst to react with absorbed O_2 and H_2O to generate $\cdot O_2^-$ and $\cdot OH$, who are the most potent oxidizing agents to degrade organic pollutants. However, the conjugated polymers are also organic substances that can be oxidized as that happened to pollutants, for the oxidizing agents are of high activity and almost choiceless for reactants. We have studied the influence of the oxidation degree of poly(3-hexylthiophene) on the photocatalytic activity of poly(3-hexylthiophene)/TiO_2 composites, finding that although moderate oxidation degree of P3HT is beneficial for the photocatalytic activity of $P3HT/TiO_2$ composites, the excessive oxidation of P3HT will decrease the photocatalytic activity of $P3HT/TiO_2$ composites [27]. Meanwhile, the change of physical morphology and optical properties during the photocatalytic reaction may result in the decrease of photocatalytic activity. The decrease of photocatalytic activity will lead to deactivation of conjugated polymer/TiO_2 photocatalysts until totally loss of their performance, which is a critical problem need to be considered. However, not enough emphasis has been laid so far upon the stability of conjugated polymer/TiO_2 photocatalysts and most of researchers prefer to invest their efforts in increasing the quantum efficiency rather than fighting against deactivation.

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* Corresponding authors. Tel.: +86 28 85407286; fax: +86 28 85402465.
E-mail addresses: jianglong@scu.edu.cn (L. Jiang), danyichenweiwei@163.com (Y. Dan).

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As far as we know, there have been no studies carried out to systematically examine the stability of conjugated polymer/TiO_2 photocatalysts during degradation of organic compounds, especially about the structure of the polymers.

With higher charge carrier mobility, dissolubility and processability, long-term stability and broad and strong absorption in visible region [28], poly(3-hexylthiophene) (P3HT) has been reported as the effective sensitizer of TiO_2 [9,10,20]. In present study, poly (3-hexylthiophene)/titanium dioxide (P3HT/TiO_2) composites, as a representative of conjugated polymer/TiO_2 photocatalysts, were prepared and through comparative analysis of the physical and chemical structure of the composites before and after the photocatalytic reaction, the stability of the composites was systematically evaluated.

2. Experimental

2.1. Materials

1-Bromohexane, chemical grade, was purchased from Changzhou Xinhua Active Material Research Institute (Changzhou, China). Anatase titanium dioxide (TiO_2, HR-3), with specific surface area (SET) of 240.30 $m^2\,g^{-1}$, corresponding to a mean particle size of ca. 15 nm, nonporous, was obtained from Zhoushan Mingri Nanometre Material Co., Ltd. (Zhoushan, China). 3-Bromine thiophene, magnesium bar (Mg), [1,3-Bis(diphenylphosphino) propane] nickel(II) chloride (Ni(dppp)Cl_2), anhydrous iron(III)-chloride ($FeCl_3$), n-hexane, methanol (CH_3OH) and methyl orange (MO) were all bought from Chengdu Kelong Chemical Reagents Factory (Chengdu, China) and used without further purification. Diethyl ether was purified by distillation from Na in argon atmosphere after 15 h refluxing. Chloroform ($CHCl_3$) was purified by washing with de-ionized water twice to remove traces of alcohol, and then distilled over $CaCl_2$.

2.2. Synthesis and preparation

3-hexylthiophene (3-HT) monomer was synthesized by coupling n-hexylmagnesium bromide with 3-bromothiophene in the presence of nickel catalyst [29]. P3HT was synthesized by a typical chemical oxidative in $CHCl_3$. 0.03 mol anhydrous $FeCl_3$ and 50 ml $CHCl_3$ was added to a 250 three-necked, round-bottom flask equipped with a magnetic, Teflon-coated stirrer. Subsequently, 0.01 mol 3-HT was added to the mixture with constant stirring. The reaction was carried out in an ice bath for 4 h. Then, the mixture was precipitated in methanol and the resultant product was extracted in methanol to remove iron ion. P3HT was obtained by collecting the soluble part.

The P3HT/TiO_2 composites were prepared by the following procedure: a certain amount of TiO_2 particles (dried at 120 °C for 4 h before use) was added to 100 ml of chloroform, sonicated for 20 min to ensure that the TiO_2 particles were totally dispersed, and then 20 ml of P3HT chloroform solution (5 mg/ml) was added into above suspension. After stirred for 1 h, the solvent was removed by rotary evaporation (bath temperature 30 °C, vacuum), then the damp solid was transferred to an oven to dry at 40 °C under vacuum for 12 h and the P3HT/TiO_2 composites were obtained.

2.3. Characterization

UV-vis absorption spectra were recorded on a UV-2300 UV–Vis spectrophotometer (Techomp Co.). Fourier transform infrared spectra (FTIR) of samples were measured on a Nicolet 560 FTIR spectrometer in the range of 400 cm^{-1} to 4000 cm^{-1} with 1 cm^{-1} resolution, using KBr as reference sample. Fluorescence spectra were collected from a Hitachi F-4600 spectrophotometer using a xenon lamp (500 W) as the excitation source at room temperature. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded on a TU-1901 spectrophotometer equipped with an integrating sphere attachment (IS 19-1). Scanning electron microscopic (SEM) analyses were performed with a field emission scanning electron microscope (JSM-5900LV, JEOL). High-resolution transmission electron microscopy (HRTEM) micrograph was obtained using a JEOL 2100F microscope at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a XSAM-800 spectrometer (KRATOS Co.) using Mg-Kα radiation (12 kV, 11 mA) as excitation sources.

2.4. Evaluation of photocatalysis

MO aqueous solution was used as model contaminant for studying the adsorption performance and photocatalytic activity of P3HT/TiO_2 composites. The adsorption experiments were performed by adding 200 mL of MO solution (10 mg/L) and 200 mg of photocatalyst in a 500 mL beaker. The suspension was magnetically stirred in dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and MO. A portion of the samples were then withdrawn at regular times, filtered immediately for separation of any suspended solid and kept in the dark. The change in the concentration of MO was monitored by measuring the absorbance at λ_{max} (464 nm) with a UV-2300 UV–Vis spectrophotometer (Techomp Co., China).

Photocatalytic experiments under visible light irradiation were carried out just after the adsorption experiments. A 500 W tungsten-halogen lamp (OSRAM, Germany), used as the VL irradiation source, was positioned over the solution to maintain on irradiance of 40 Mw/cm^2. A 420 nm cut-off filter was used to cut off UV light below 420 nm. The change in the concentration of MO was monitored by the same method described in adsorption experiments. The first sample was taken out at the end of the dark adsorption period, just before the light was turned on and the concentration of MO was set as the initial concentration for photocatalytic experiments. In this paper, the decolorization ratio of MO was calculated as follows:

$$\eta = \frac{A_0 - A_t}{A_0} \times 100\% \qquad (1)$$

Where A_t is the absorbance of the contaminant solution at different reaction time t, A_0 is the absorbance of initial contaminate solution.

2.5. Evaluation of stability of P3HT/TiO_2 composites

To evaluate the photocatalytic stability of P3HT/TiO_2 composites, the photocatalyst used for 10 h of photocatalytic degradation of MO under visible light, without another MO added, was recollected by centrifugation at 5000 rpm for 5 min. Then, the composites were washed by distilled water repeatedly to remove the remained molecules and dried in a vacuum at 40 °C for 24 h to obtain used P3HT/TiO_2 composites (labeled as U-P3HT/TiO_2 composites). The structure of U-P3HT/TiO_2 composites was characterized by SEM, UV-vis DRS, FTIR and XPS to study both the physical and chemical structure change of them to that of original P3HT/TiO_2 composites.

3. Results and discussion

3.1. Characterization and photocatalytic performance of the P3HT/TiO_2 composites

The high-resolution TEM images of TiO_2 and P3HT/TiO_2 composites are presented in Fig. 1(a) and (b). The distance between TiO_2 lattice planes is measured to be 0.351 nm, corresponding to the interplanar spacing of anatase TiO_2 (1 0 1) plane. A polymer layer