

Photocatalytic activity of polymer-modified ZnO under visible light irradiation

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Abstract

Photocatalytic removal of phenol, rhodamine B, and methyl orange was studied using the photocatalyst ZnO/poly-(fluorene-*co*-thiophene) (PFT) under visible light. After 2 h irradiation with three 1 W LED (light-emitting diode) lights, about 40% removal of both phenol and methyl orange was achieved; rhodamine B was completely degraded to rhodamine. Diffuse reflectance spectra showed that the absorbance range of PFT/ZnO was expanded from 387 nm (ZnO) to about 500 nm. Photoluminescent spectra and photoluminescent quantum efficiency indicated that electrons were transferred from PFT to the conduction band of ZnO. Electron spin resonance (ESR) signals of spin-trapped paramagnetic species with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) evidenced that the OH[•] radicals were indeed formed in the PFT/ZnO system under visible light irradiation. A working mechanism involving excitation of PFT, followed by charge injection into the ZnO conduction band is proposed.

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1. Introduction

Recently it has been demonstrated that semi-conducting materials capable of mediating photocatalytic oxidation of organic compounds can be an alternative to conventional methods for the removal of organic pollutants from water. Advantages of the photocatalytic process include its mild operating conditions and the fact that it can be powered by sunlight, thus reducing significantly the electric power required and therefore the operating costs. Scientists are investigating many semiconductors that can utilize visible light to degrade a high number of recalcitrant materials in aqueous system [1–6]. Among the semiconductors whose photocatalytic properties have been studied, TiO₂ is the most commonly used, because it is effective, stable, harmless, and inexpensive [7]. However, another semi-conducting oxide, ZnO, has recently been receiving attention

from researchers. ZnO is well known to semiconduct under solar irradiation, and its photocatalytic mechanism has been proven to be similar to that of TiO₂, although it shows less vigorous oxidation states [8]. ZnO has sometimes been reported to be more efficient than TiO₂. The biggest advantage of ZnO is that it absorbs over a larger fraction of the solar spectrum than TiO₂ [9]. For this reason, ZnO is the most suitable photocatalyst for photocatalytic removal in the presence of sunlight. Since the minimum energy required for excitation of an electron for ZnO is 3.2 eV, which corresponds to 387.5 nm, and UV light (<387 nm) in solar light is less than 4%, the application of ZnO is limited. To extend the photoresponse of ZnO to the visible region, surface modification and dye sensitization are effective methods that are similar to previously reported TiO₂ modification techniques.

In the present paper, a conjugated polymer was used as a photosensitizer to modify the ZnO surface. Conjugated polymers have already been widely used as sensitizers in photovoltaic devices such as solar cells [10,11]. Moreover, polythiophene has been used to degrade fungicide [12], which indicated that polythiophene is quite stable under photoirradiation in the air.

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Therefore, the copolymer poly-(fluorene-*co*-thiophene) (PFT hereafter) was chosen in this work. In our earlier study [13–15], PFT-modified TiO₂ (PFT/TiO₂) had substantial photocatalytic activity under visible light. This paper provides results describing the photocatalytic activity of PFT-modified ZnO (PFT/ZnO).

2. Experimental

2.1. Materials

ZnO (Shanghai Caiyu Nanometer-technology Co. Ltd., China, BET $\geq 45 \text{ m}^2/\text{g}$) and Al₂O₃ (Degussa, BET = $100 \text{ m}^2/\text{g}$) were both pre-dried at a temperature of 393 K under vacuum. The conjugated polymer PFT, whose chemical structure is seen in literature [13], was synthesized according to the literature [16]. Purified water was obtained from a Millipore filtration system (Millipore ZLXS50020). The spin trap reagent 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from Sigma. All other chemicals were analytical grade and used without further purification.

2.2. Measurements

A UV-2501 UV-vis spectrophotometer (SHIMADZU, Japan) with an integrating sphere was used to directly record diffuse reflectance spectra of the PFT/ZnO. Baseline correction was done using a calibrated sample of barium sulphate.

Photoluminescent (PL) spectra were obtained with a Fluorolog JY luminescence spectrometer. PFT solution (1% in toluene) was dripped on the glass template to form a thin film. Powder samples (prepared as described below) were packed in a 1 mm-thick quartz cell. PL quantum yields were determined in integrating sphere IS080 with 405 nm excitation of a He–Cd laser (Mells Grid).

Electron spin resonance (ESR) signals of spin-trapped paramagnetic species with DMPO were recorded with a Bruker ESP 300E spectrometer to examine the formation of active radical species. The settings for ESR spectrometer were center field 3480.0 G, sweep width 100.0 G, microwave frequency 9.78 Hz, modulation frequency 100 kHz, and power 5.05 mW.

Phenol concentration and spectrum of dyes were measured using a UV-2450 spectrophotometer (SHIMADZU, Japan). Total organic carbon (TOC) was determined using a TOC-V CSH analyzer (SHIMADZU, Japan). Light intensity was measured by a UV-A Ultraviolet Meter equipped with two probes with wavelengths of 420 nm and 365 nm, respectively.

2.3. Procedures

Sensitization of ZnO and Al₂O₃ using PFT was followed by the process below: a mixture composed of 5 mg of PFT and 5 ml of tetrahydrofuran (THF) was stirred for 1 h in darkness to form a clear solution. A 500-mg quantity of ZnO or Al₂O₃ powder was added to 50 ml of ethanol solution and stirred for 2 h in darkness to obtain a uniform suspension. The PFT solution was added dropwise into the stirring ZnO or Al₂O₃ suspension and stirred for another 30 min to insure the suspension

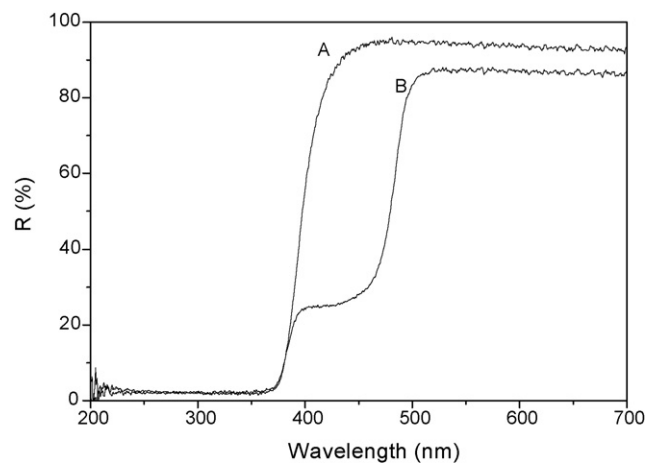


Fig. 1. The Diffuse reflectance spectra of ZnO and PFT/ZnO. Curves A and B represent the spectra of ZnO and PFT/ZnO, respectively.

uniform. Then the solvent was removed by a rotary evaporator (RE-100, QUICKFIT, England) in the darkness, yielding a greenish powder. Finally, the greenish powder was dried at 333 K under vacuum before use.

The photocatalytic experiments were carried out in a column glass reactor. Three 1 W LED (light-emitting diode, Shenzhen Lanbaoli Photo-electricity Technology Co. Ltd. China) lights with a radiant wavelength of 450–475 nm were used as the visible light source. The lights were placed tightly against the reactor, and were spaced 120° from each other. The reactor was open to air to ensure enough oxygen in the reaction solution. Prior to photoreaction, the solution containing photocatalyst and pollutant was magnetically stirred in darkness for 30 min to establish adsorption–desorption equilibrium. After a specified interval of irradiation time, a 5 ml aliquot of the reaction mixture was centrifuged and filtered through a 0.22 μm filter (Millipore). The change in the concentration of phenol was monitored spectrophotometrically at a wavelength of 510 nm through 4-aminoantipyrine method, and the dye concentration was monitored by the spectral change. The reaction mixture was stirred throughout the reaction to keep the mixture in suspension.

3. Results and discussion

3.1. Diffuse reflectance spectra (DRS)

Fig. 1 shows the DRS of ZnO and PFT/ZnO. The photosensitizer PFT was a co-polymer of fluorene/thiophene (70/30 in molar ratio), with maximum absorption at a wavelength of about 400 nm [16]. As shown in Fig. 1, there is no absorption above 400 nm for pure ZnO, while PFT/ZnO shows light absorption from 360 nm to about 500 nm. A similar result was observed previously for pure Al₂O₃ and PFT/Al₂O₃ [13]. It is a vital prerequisite for photosensitization that the photosensitizer be adsorbed onto the surface of semiconductor. The results indicate that PFT/ZnO should be capable of responding to visible light.

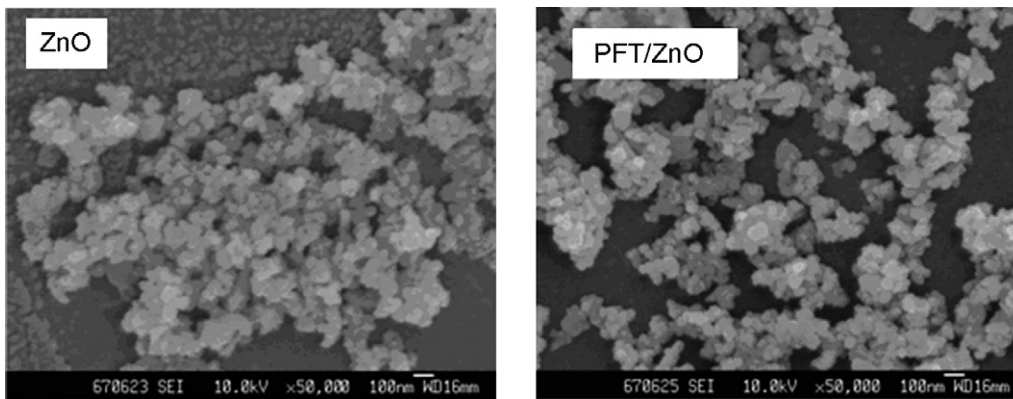


Fig. 2. SEM images of ZnO and PFT/ZnO.

3.2. Scanning electron microscopy (SEM)

Typical SEM images of ZnO and PFT/ZnO are shown in Fig. 2. The SEM images indicate that there was little change in the particle size of ZnO after modification by PFT. The PFT was evenly dispersed on the surface of ZnO without apparent agglomeration. It is important for photocatalytic reaction that the particle size of the photocatalyst be homogeneous.

3.3. Photoluminescent (PL) spectrum and PL quantum yields

Fig. 3 shows the photoluminescent spectra of PFT film and PFT/ZnO powder. No major difference was observed between the spectral shapes of these two samples, which indicated that ZnO had no great influence on the electron structure of the polymer. Since the mobility of electrons in conjugated polymers is much less than that of dyes, it is suggested that the conjugation length of the polymer is not changed by ZnO.

It is reported that PL quantum yields decrease abruptly if there is electron transfer from dyes to a semiconductor [10,11]. Our earlier results [13] showed that PFT/TiO₂ had PL quantum yields that were only 40% of those of PFT/Al₂O₃, which indicated that many electrons on the conduction band of the

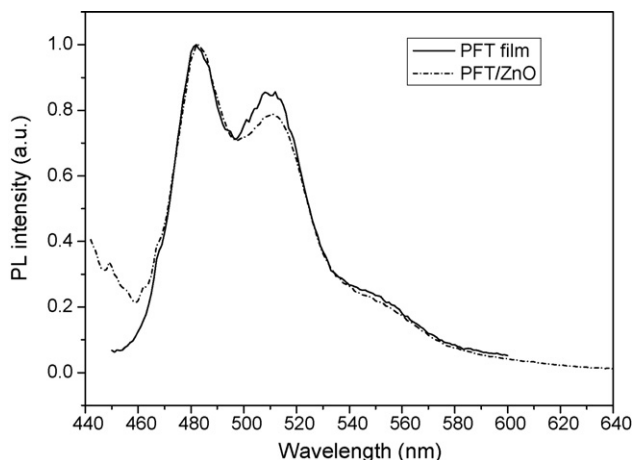


Fig. 3. Photoluminescent spectra of PFT and PFT/ZnO.

polymer were transferred into the conduction band of TiO₂. These electrons may play an important role in the photocatalytic degradation of organic pollutants. It is suggested that PFT behaves like an organic semiconductor. It has been reported that the reductive potential of PFT is about -1.35 V, which is lower than that of TiO₂ (-0.65) and ZnO (-0.76), so it is thermodynamically possible for electrons to be injected from PFT into the conduction band of these semiconductors. A similar result was observed in the case of ZnO (Table 1), indicating that electrons were transferred between PFT and ZnO.

3.4. ESR measurements

It is reported that the active oxygen radicals play a very important role in the initial photooxidation stage of the organic pollutants under visible light irradiation in the presence of photocatalysts. In order to examine and confirm the active oxygen radicals formed in the photooxidation of phenol and dye under visible light irradiation as we proposed above, ESR spectra of DMPO spin-trapping adducts were in situ recorded following irradiation of PFT/ZnO by the LED lights at 450–475 nm.

Fig. 4 shows the ESR spectra signals of spin-trapped DMPO–OH• radicals formed under visible light irradiation of an aqueous PFT/ZnO dispersion, the characteristic peak intensity of 1:2:2:1 evidenced that OH• radicals are indeed formed in the photocatalytic system [17]. However, the intensity of signals of spin-trapped DMPO–OH• radicals was a little weak at the irradiation time of 10 min, and became much stronger at 30 min, which indicated that the generation of OH• in PFT/ZnO dispersion under visible light irradiation was much slower compared with that in modified TiO₂ [17–19].

Table 1
The PL quantum yields of PFT, PFT/ZnO and PFT/Al₂O₃

	Abs. edge (nm)	PL max (nm)	Band gap (eV)	E_{red} (V)	PL quantum yields (%)
PFT film	480	480, 510	2.58	-1.28	14.7
PFT/ZnO	490	480, 510	–	–	6.62
PFT/Al ₂ O ₃	490	480, 510	–	–	13.3

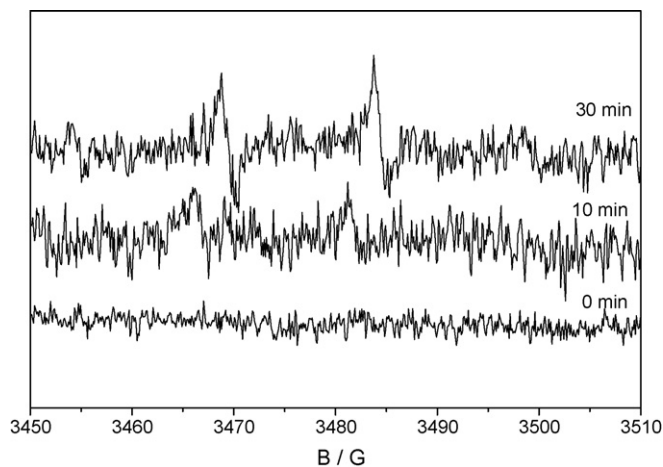


Fig. 4. ESR spectral of the DMPO-OH• in the aqueous of PFT/ZnO.

3.5. Photocatalytic removal of phenol

A series of blank experiments revealed that about 10% of the concentration of phenol was adsorbed on the surface of ZnO in the dark under specified conditions, and no appreciable removal of phenol was observed. Fig. 5 shows that little phenol was decomposed with pure ZnO under visible light, while with PFT/ZnO nearly 40% of the phenol was removed. It is suggested that PFT is an effective photosensitizer, as has been reported for some dyes [17–21]. However, loss of TOC (total organic carbon) via mineralization was much lower than the amount of phenol that was removed. This discrepancy occurred because phenol was photooxidized to benzoquinone, and further degradation of benzoquinone to CO₂ and H₂O took place more slowly. Therefore, the concentration of phenol declined more rapidly than did that of TOC.

3.6. Photocatalytic removal of dyes

Control experiments were carried out on rhodamine B and methyl orange solutions containing no ZnO and PFT/ZnO in the dark, under otherwise identical experimental conditions,

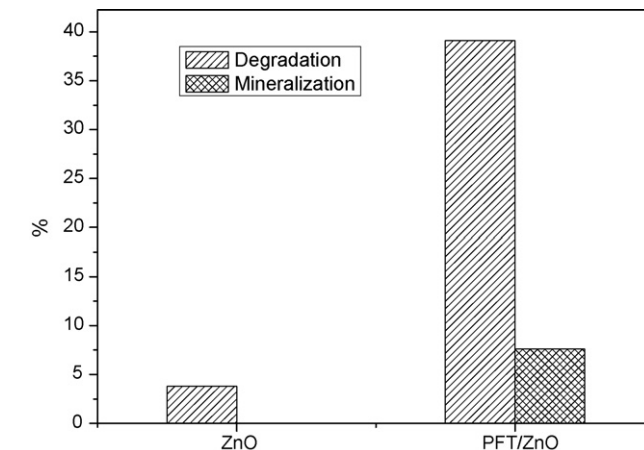
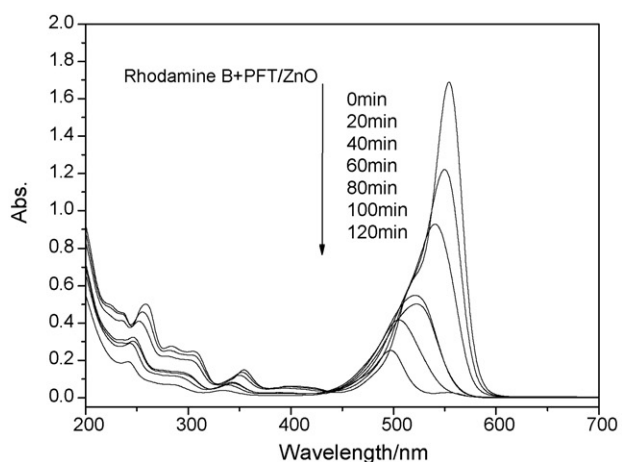


Fig. 5. Photocatalytic removal of phenol in different systems under visible light. [phenol]_i = 10 mg/L, [photocatalyst] = 1.0 g/L, irradiation time = 2 h.

showed that in the absence of photocatalyst there was no change in absorption peak intensity and no peak shifts with irradiation time. Results of the photocatalytic removal of dyes are shown in Fig. 6. In the presence of PFT/ZnO, absorption by both dyes decreased with time, implying that the dyes were being degraded. Rhodamine B in solution containing PFT/ZnO disappeared completely after irradiation for 2 h. From Fig. 6, it is observed that the absorption peak intensity decreased gradually, and at the same time there was a hypsochromic shift in the spectrum from 554 nm to 497 nm. The decrease in absorbance was probably caused by the destruction of the dye chromogen [22]. The hypsochromic shift was reported as de-ethylation of rhodamine B, leading to the formation of rhodamine, which has a maximum absorption peak at 497 nm [23,24].

The photocatalytic removal of methyl orange differed from that of rhodamine B. There was a decrease in the absorption peak of the spectrum, but no hypsochromic shift. The removal ratio calculated from the spectrum was 41.3% in 2 h, and there was little further change with increased irradiation time. Since methyl orange is an azo dye, and the conjugative system made up of azo group and aryl rings is the main chromophore of methyl

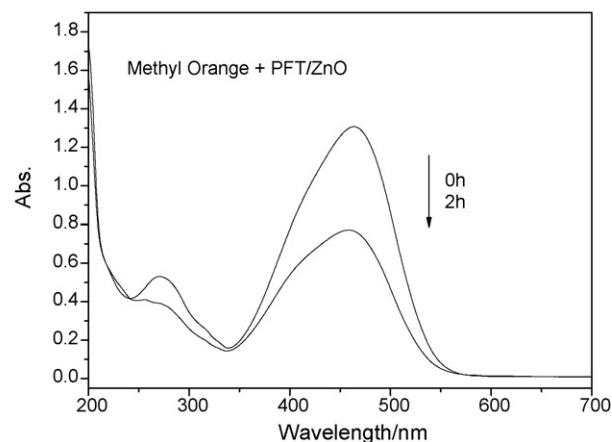
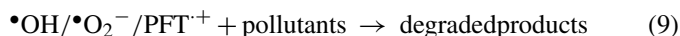
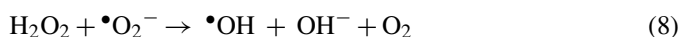
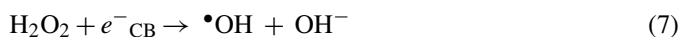
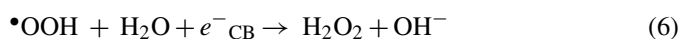
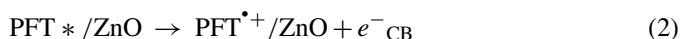


Fig. 6. Absorption spectra of rhodamine B and methyl orange solutions during irradiation in a PFT/ZnO system. [rhodamine B]_i = 10 mg/L, [methyl orange]_i = 20 mg/L, [photocatalyst] = 1.0 g/L

orange, the decoloration of methyl orange was mainly caused by damage to the conjugative system [25]. However, since it is difficult to destroy the $-N=N-$ bond completely under our experimental conditions, much of the dye was still present after 2 h of irradiation.

3.7. Photocatalytic reaction mechanism

Based on the results above and considering earlier reports of ZnO as a photocatalyst [26–32], the following working mechanism is proposed (Eqs. (1)–(9)):



In the PFT/ZnO system, irradiation with visible light results in the excitation of the surface-adsorbed photosensitizer PFT (Eq. (1)), which, acting as an organic semiconductor, effects charge transition into the conduction band of ZnO in the excited state (Eq. (2)). The electron in the conduction band (e^-_{CB}) is transferred to molecular oxygen, leading to the formation of a series of radicals, which are active oxidizers capable of degrading organic pollutants in the system (Eqs. (3)–(8)). Subsequently, the pollutants can be degraded through a variety of paths (Eq. (9)).

4. Conclusion

In this work, the photocatalytic removal of phenol, rhodamine B and methyl orange was studied under visible light. It was observed that the synthesized conjugated polymer PFT can photosensitize ZnO effectively to degrade organic pollutants. Hydroxyl radicals (OH^\bullet) were detected through ESR method. The photocatalytic reaction mechanism, involving production of a series of radicals, was also discussed.

Acknowledgements

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