Research Article

Characterization of Conjugated Polymer Poly(fluorene-co-thiophene) and Its Application as Photosensitizer of TiO$_2$

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The copolymer poly(fluorene-co-thiophene) (PFT) has strong absorption in the visible light region. In this paper, PFTs with four different thiophene contents were evaluated for their suitability as photosensitizers of TiO$_2$. All four of the PFTs were capable of being excited by light with wavelengths above 455 nm, and all had reductive potentials more negative than the conduction band potential of TiO$_2$. Consequently, it was deemed that transfer of electrons from the excited PFTs to the conduction band of TiO$_2$ was thermodynamically possible. PFTs with higher thiophene content had more electron transitions in the excited state, resulting in increased photocatalytic activity of PFT-sensitized TiO$_2$. The method used to prepare the combined PFT/TiO$_2$ photocatalyst affected its photocatalytic activity. Best results in this study were achieved by dropwise addition of a tetrahydrofuran solution of PFT to a stirred TiO$_2$/ethanol suspension.

1. INTRODUCTION

Photosensitization of the semiconducting oxide TiO$_2$ is a method for extending its photoresponse in the visible light region by physically combining it with another semiconductor that acts as a photosensitizer. As p-type semiconductors, photosensitizers, which are commonly organic dyes, have strong absorption in the visible light region and can inject electrons into the conduction band of TiO$_2$ when excited by visible light, giving rise to a series of photochemical processes and allowing the photocatalytic reactions mediated by TiO$_2$ to operate under visible light irradiation.

Conjugated polymers composed of repeated small aryl ring molecules such as benzene, thiophene, and pyrrole are other types of organic semiconductors. Although the energy level difference between π-bonding and antibonding orbits in a single aryl ring is large, it is found that as the number of repeated units increases, π orbits overlap each other, causing the energy level difference between π-conjugated bonding and antibonding orbits to decrease sharply and fall eventually to less than 4 eV. Energy level differences of this magnitude make these polymers suitable for use as semiconductors. In addition, some of these polymers have a number of optical properties, such as electroluminescence and nonlinear optical behavior, that make them especially useful as photovoltaic materials. At present, conjugated polymers such as poly(3-methylthiophene) [1], poly(phenylene vinylene) [2], polyaniline [3], polypyrrole [4], poly(o-methoxy aniline) [5], poly(3-undecyl-2,2′-bithiophene) [6], and poly[2-(3-thienyl)-ethoxy-4-butylsulfonate] (PTEBs) [7] are being increasingly used in the field of photovoltaics as solid electrolytes and electrode sensitizers [8].

Methods for sensitizing semiconductors are similar to those for sensitizing electrodes of solar energy cells. However, little work has been done to date on the use of conjugated polymer-sensitized semiconductors to photocatalyze the degradation of organics under visible light irradiation, in part because of limitations of the polymers themselves. One problem is that the HOMO energy level of polymers is generally higher than those of inorganic materials and dyes, so polymers tend to be unstable and easily oxidized. In addition, the electron mobility of polymers is relatively poor. Finally,

it can be difficult to physically combine polymers and inorganic semiconductors, because most polymers are not soluble in water or ethanol. However, as research in this area continues, more and more polymers with improved characteristics are being synthesized. For example, the wide band gap polymer polyfluorene (PF) and the narrow band gap polymer polythiophene have improved antioxidative ability. Moreover, electron transfer takes place easily in thiophene-based polymers.

In this paper, a series of conjugated copolymers containing fluorene and thiophene [9] were investigated to evaluate their suitability as photosensitizers of TiO_2.

2. EXPERIMENTAL

2.1. Materials

A series of copolymer PFTs with thiophene contents of 5%, 15%, 30%, and 50% (so called PFT5, PFT15, PFT30, and PFT50, resp.) were provided by College of Material Science and Engineering, South China University of Technology; the chemical structure is presented in Figure 1, TiO_2 (Degussa P25: 80% anatase, 20% rutile; BET $\sim 50\,m^2/g$). Purified water was obtained from a Millipore filtration system (Millipore ZLXS50020). All other chemicals were analytical grade and used without further purification.

2.2. Measurements and procedures

An HP 8453 diode array UV-Vis spectrophotometer (Agilent, USA) was used to directly record the UV-Vis spectra of the copolymer PFTs using chloroform as solvent. The electrochemical properties of PFTs were obtained with a CHI 660 A electrochemical workstation. Phenol concentration was monitored by UV-2450 spectrophotometer (Shimadzu, Japan) at a wavelength of 510 nm.

Sensitization of TiO_2 was performed according to the literature [10]. The photocatalytic degradation experiment was carried out by adding 50 mg photocatalyst into 50 mL phenol aqueous solution with 10 mg/L initial concentration. A 250 W GaI_3 lamp (DJG250, Shanghai Hualun Lighting Co. Ltd., China) with maximum radiant wavelength matched to the absorption wavelength of PFT was used as the visible light source. UV and IR cutoff filters were placed between the lamp and the glass reactor to ensure irradiation by visible light (400–700 nm) only. Light intensity was measured by a UV-A ultraviolet meter equipped with two probes with wavelengths of 420 nm and 365 nm, respectively. The glass reactor was open to air to ensure enough oxygen in the reaction solution. Prior to irradiation, the solution containing photocatalyst and phenol was magnetically stirred in darkness for 30 minutes 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), and the change in the concentration of phenol was monitored spectrophotometrically.
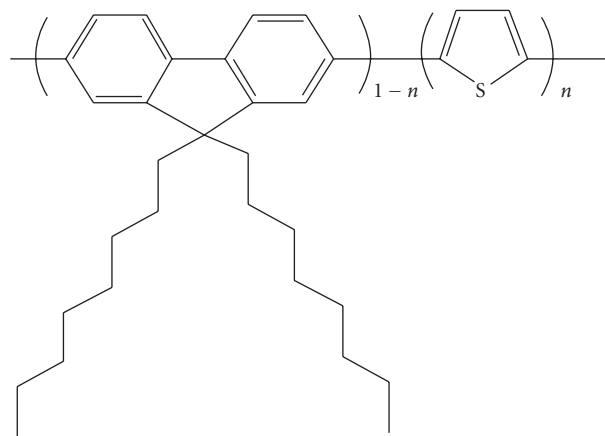

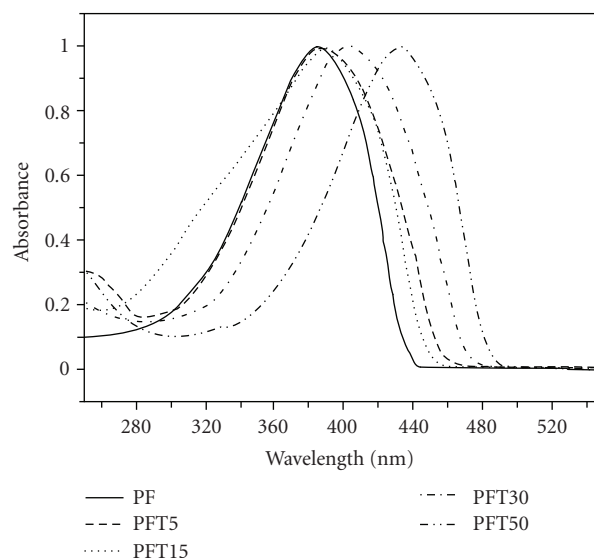FIGURE 1: Structure of conjugated polymer poly(fluorene-co-thiophene).

FIGURE 2: UV-Vis spectra of the different copolymers.

3. RESULTS AND DISCUSSION

3.1. Electrochemical properties of PFTs

Having strong absorption in the visible light region is the most important property of a photosensitizer. Figure 2 shows the UV-Vis spectra of the copolymers PF, PFT5, PFT15, PFT30, and PFT50 in chloroform. These polymers all have strong absorption in the visible light region. As expected, the intensity and maximum absorption peaks progressively increased and were red-shifted with increasing content of thiophene in the PFTs. The maximum absorption peaks are at 384 nm, 384 nm, 390 nm, 400 nm, and 433 nm, respectively. From Figure 2 it is observed that the absorption peaks of PFT5 and PFT15 were little changed from that of PF, while their spectra were slightly red-shifted toward the visible light region. The absorption peak of PFT30 was red-shifted from 384 nm (PF) to 400 nm, and its absorption edge

TABLE 1: Wavelength at peak absorption and electrochemical properties of PFTs.

Copolymers	$\lambda_{\mathrm{absmax}}$ (nm)	E_{ox} (V)	E_{red} (V)	E_g (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
PTF5	455	1.38	−1.35	2.73	−5.78	−3.05
PTF15	470	1.31	−1.33	2.64	−5.71	−3.07
PTF30	480	1.30	−1.28	2.58	−5.70	−3.12
PTF50	490	1.22	−1.31	2.53	−5.62	−3.09

was red-shifted to 480 nm. In the case of PFT50, the red shifting was more obvious; the absorption peak and edge were red-shifted to 433 nm and 490 nm, respectively. The increased red shifting that was associated with increased thiophene content of the PFTs was due to strong absorption of visible light by the thiophene units of the polymer. Compared with PF oligomers, the blocks of spatial configuration between thiophene ring and benzene ring in PFTs are smaller than those between benzene rings in PF, and twists between thiophene ring and benzene ring take place more easily, leading to higher coplanarity and a larger conjugated system in PFTs. In addition, the lone pair electrons of the sulfur atom in thiophene units increase the electron cloud density in the PFT chain, thereby increasing its ability to act as an electron donor and decreasing its band gap. Thus, higher thiophene content of a PFT is associated with higher coplanarity, lower band gap, and red shifting of its absorption spectrum.

The second most important property of a photosensitizer of TiO$_2$ is that its energy level matches that of TiO$_2$. Only if the reductive potential of the photosensitizer is more negative than the energy level of the conduction band of TiO$_2$, it is thermodynamically possible for excited electrons to be injected from the conduction band of the photosensitizer to the conduction band of TiO$_2$.

Table 1 presents the wavelength at peak absorption and electrochemical properties of the PFTs used in this study. The peak and onset of absorption wavelength of PFTs were obtained from Figure 2, and the band gaps (E_g) were estimated by (1) [11]:

$$E_g = 1240/\lambda_{\mathrm{onset}}, \tag{1}$$

$$E_{\mathrm{red}} = (E_g E_{\mathrm{ox}}), \tag{2}$$

$$E_{\mathrm{HOMO}} = e(E_{\mathrm{ox}} + 4.4), \ (\mathrm{eV}) \tag{3}$$

$$E_{\mathrm{LUMO}} = e(E_{\mathrm{red}} + 4.4), \ (\mathrm{eV}). \tag{4}$$

All oxidative potentials (E_{ox}) of PFTs were measured by a CHI 660 A electrochemical workstation, using a platinum electrode as working electrode, a saturated calomel electrode (SCE) as reference electrode, and a platinum wire as assistant electrode in 0.1 mol/L of tetra-n-butylammonium tetrafluoroborate (Bu$_4$NPF$_6$) in anhydrous acetonitrile as a supporting electrolyte with a scan rate of 50 mV/s. The reductive potentials (E_{red}), HOMO, and LOMO energy levels were calculated by empirical equations (2)–(4) [12], respectively.

The results in Table 1 indicate that the band gaps of these PFTs were less than or equal to 2.73 eV, which corresponds
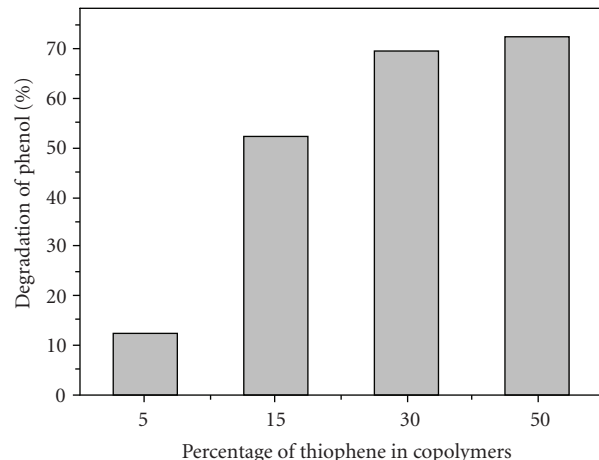

FIGURE 3: Photodegradation of phenol using PFT-sensitized TiO$_2$ [phenol]$_i$ = 10 mg/L, [photocatalyst] = 1 g/L, irradiation time = 10 hours.

to excitation by wavelengths at or above 455 nm. The reductive potentials were approximately −1.30 V and were all more negative than the energy level of the conduction band of TiO$_2$. Thus, transfer of electrons from excited PFTs to the conduction band of TiO$_2$ is thermodynamically possible. It was also found that with increasing thiophene content in the main chain of the polymer, the oxidative potential gradually decreased from 1.38 V (for PFT5) to 1.22 V (for PFT50). These oxidative potentials are higher than those of many polymers, and lead to stronger antioxidative ability.

3.2. Photodegradation of phenol using PFT-sensitized TiO$_2$

The photodegradation of phenol by PFT-sensitized TiO$_2$ is presented in Figure 3. During the photodegradation experiment, the light intensity was $E_{420} = 11.1 \times 100\ \mu\mathrm{w/cm}^2$ and $E_{365} = 1.4\ \mu\mathrm{w/cm}^2$. The maximum absorption wavelength of phenol is about 270 nm and phenol has no response for visible light. Our earlier experimental results showed that no phenol decomposes under visible light irradiation. From Figure 3, all of the PFTs were able to photosensitize TiO$_2$. The photocatalytic activity of sensitized TiO$_2$ excited by visible light increased with increasing thiophene content of the PFT. The relatively small increase in catalytic activity between PFT30- and PFT50-sensitized TiO$_2$ was attributed to two factors. First, addition of 50% thiophene reduced the molecular weight of the PFTs from above 20 000 to about 6000. As a result, there was less entwisting between PFT chains, so, the polymer film was weaker and did not adsorb as well onto the TiO$_2$ powder. Second, it was observed that PFT50 had lower solubility in tetrahydrofuran (THF) than the other polymers, which interfered with the physical process of combining it with the TiO$_2$. Thus, we used PFT30 as sensitizer in the following experiments.

Commonly, PF has a larger band gap than PFT, with maximum absorption in the UV region [13, 14]. With increasing thiophene content in the main chain of PF, its band

gap decreases and its absorption spectrum is gradually red-shifted. It was found that PFT with a higher thiophene content had more electron transitions when excited by visible light, which resulted in greater photocatalytic activity of PFT-sensitized TiO_2. Hara and coworkers [15] reported for the first time a new kind of sensitizers based on introducing thiophene moieties into a coumarin backbone, and then bonded it to the surface of TiO_2 with $-COOH$ bonds. Using this new compound in dye-sensitized solar cells, they achieved a remarkable solar energy-to-electricity conversion efficiencies of up to 7.7% under simulated solar irradiation ($100\,mW\cdot cm^{-2}$), which was the highest efficiency obtained among solar cells based on organic dye photosensitizers in the past decades. Luo and coworkers [16], studying the properties of oligothiophene carboxylic acid sensitized TiO_2 films, found that oligothiophene carboxylic acid could be used as a cosensitizer with N3 [Ru complex, $Ru(II)L_2(SCN)_2$, L = $2,2'$-bipyridyl-$4,4'$-dicarboxylate] dye, extending its spectrum and improving its photoelectric properties. Thiophene has also been used to improve the properties of porphyrin photosensitizers [17, 18]. Ha and coworkers [19] investigated singlet oxygen generation efficiencies of porphyrin and thiophene-modified porphyrin using time-resolved and steady-state spectroscopic methods. They found that the introduction of the sulfur atom from thiophene into the porphyrin core greatly increased the intersystem crossing rate due to spin-orbit coupling enhancement, resulting in enhanced triplet and singlet oxygen quantum yields. These results suggested that thiophene can improve the photophysical efficiency of photosensitizers. From the above, it is clear that addition of thiophene directly affects the properties of combinative photosensitizers.

Additionally, PFTs showed higher stability than other small molecular dyes such as rhodamine B and eosin Y under irradiation because of the higher oxidative potentials. Reused after 10 hours irradiation, PFT30 still had efficient photosensitization to TiO_2, and the photocatalytic activity of PFT30-sensitized TiO_2 slightly decreased less than 10% under the same experiments conditions.

3.3. Effect of photosensitization method on photodegradation of phenol

In studies of organic pollution degradation using dye-sensitized TiO_2, the primary methods used for combining dye with TiO_2 are simple adsorption [20, 21], chemical bonding [22], and LB (Langmuir-Blodgett) film technology [23]. The combining of TiO_2 with polymers depends primarily on adsorption and wrapping by polymer long chains. The conjugated polymer PFTs used in this paper have high solubility in aromatic solvents, begin to precipitate in ethanol, and have very low solubility in water. Thus, in the combining method that we designed, PFTs were first dissolved in THF, a good solvent, and then the solution was added to ethanol, a worse solvent, in order to initiate a gradual precipitation of PFT via wrapping of long chains. Finally, the solvents were removed by a rotary evaporator (RE-100, QUICKFIT, England), leaving the PFT coated on the surface of the TiO_2. The precipitation of PFT and its bonding to TiO_2 are af-
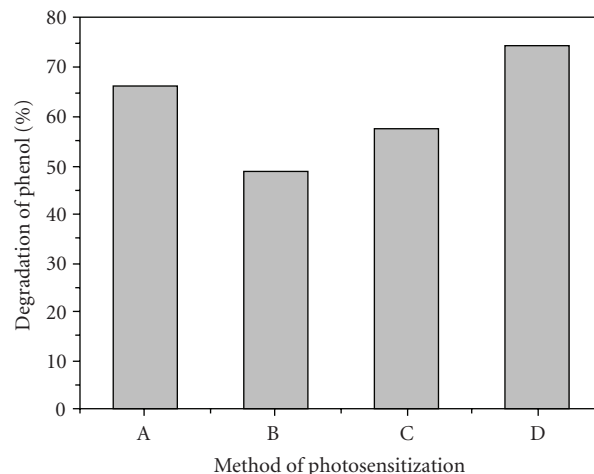

FIGURE 4: Photodegradation of phenol using PFT30-sensitized TiO_2 with different methods of photosensitization. A: PFT30/THF solution added to TiO_2/ethanol suspension quickly. B: TiO_2/ethanol suspension added to PFT30/THF solution quickly. C: PFT30/THF solution added to TiO_2/ethanol suspension in two parts. D: PFT30/THF solution added dropwise to TiO_2/ethanol suspension.

fected by the physical parameters of the combining process, including the method of mixing the solvents, the mixing time, and the method of adding the TiO_2 powder. These parameters must be optimized in order to avoid uneven deposition of PFT or premature agglomeration of TiO_2, both of which can adversely affect configuration and separateness of the combinative photocatalyst and impair its photocatalytic activity. Figure 4 shows the results of an experiment in which the photodegradation of phenol was catalyzed by PFT30-sensitized TiO_2 prepared using four different methods. The photodegradation experiments conditions were the same with Section 3.2 in this paper.

Figure 4 indicates that addition of PFT30/THF solution to a TiO_2/ethanol suspension produced a more active photocatalyst than addition of TiO_2/ethanol suspension to the PFT30/THF solution. The best results were obtained by dropwise addition of PFT30/THF solution to the TiO_2/ethanol suspension, which ensured that the PFT precipitated slowly enough to evenly coat the surface of the TiO_2.

4. CONCLUSION

Four copolymers, consisting of poly(fluorene-co-thiophene) (PFT) with a range of thiophene content, were evaluated as photosensitizers of TiO_2. All of the PFTs had strong absorption in the visible light region and had band gaps less than or equal to 2.73 eV, which corresponds to excitation by wavelengths above 455 nm. The reductive potentials of the PFT copolymers were approximately $-1.30\,V$, which was more negative than the energy level of the TiO_2 conduction band. Thus, transfer of electrons from the excited PFTs to the conduction band of TiO_2 is thermodynamically possible. All of the PFTs were capable of photosensitizing TiO_2. Photocatalytic activity of PFT-sensitized TiO_2 increased with

increasing thiophene content of the PFT. The method of preparation of the combined PFT/TiO$_2$ photocatalyst affected its photocatalytic activity. The best method of photocatalyst preparation in our study was dropwise addition of a solution of PFT in tetrahydrofuran to a stirred suspension of TiO$_2$ in ethanol.

ACKNOWLEDGMENT

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