

## Photocatalytic Activities of TiO<sub>2</sub> Modified by Poly(flourene-co-bithiophene) under Visible Light

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**Abstract**—Photocatalytic removal of phenol was studied using the photocatalyst poly(flourene-co-bithiophene) (PFB)/TiO<sub>2</sub> under visible light. After two hours irradiation with a three watts GaN LEDs (light emitting diode) cluster, about 75% removal of phenol. the degradation reaction showed the first-order behavior and the reaction rate constants (*k*) of PFB/TiO<sub>2</sub> was calculated to be 0.0169 min<sup>-1</sup>. Diffuse reflectance spectra showed that the absorbance range of PFB/TiO<sub>2</sub> was expanded from 387 nm (TiO<sub>2</sub>) to above 500 nm. Photoluminescent spectra and photoluminescent quantum efficiency indicated that electrons were transferred from PFB to the conduction band of TiO<sub>2</sub>. The surface modification using PFB did not decrease the photocatalytic activity of TiO<sub>2</sub> under the UV light irradiation.

**Keywords**- Photocatalytic; TiO<sub>2</sub>; Polymer; Photosensitizer; Visible light

### I. INTRODUCTION

The inorganic semiconducting material TiO<sub>2</sub> has attracted great attention because it can photocatalytically split water [1] and degrade the organic pollutions [2-6]. Nevertheless, the wide band gap (3.2 eV) of TiO<sub>2</sub> limits the absorption of solar light (<4%). Recently many studies have been devoted to improving photocatalytic activity under the visible light by surface modifying TiO<sub>2</sub> using dyes. Great success was achieved in the field of dye-sensitized solar cell [7, 8] as well as the dye-sensitized TiO<sub>2</sub> for photocatalytic degradation of the organic pollutions [9-11]. Three basic processes are involved in the dye sensitizing semiconductor. First, dye sensitizer adsorbs onto the surface of TiO<sub>2</sub>; second, adsorbed dye is excited by visible light; and finally, electrons are injected from the excited dye with high mobility into the conduction band of TiO<sub>2</sub> [12, 13].

It should be pointed out that the simple physical absorption of the dyes on the surface of TiO<sub>2</sub> is not tight enough because the dyes are always readily dissolved in water, the change in degradation induced by change of pH value of the reactive solution was linear with the concentration of dye adsorbed onto TiO<sub>2</sub> [14]. A costly way is to synthesize the modified TiO<sub>2</sub> with chemical bond formation between dye and TiO<sub>2</sub> [15, 16]. We developed another simple way of using conjugated polymers Poly(flourene-co-thiophene)s (PFT) as photosensitizer [17] and attracted wide attention [18]. Recently, it was reported that Polypyrrole [19], Polythiophene [20], polyaniline [21, 22] and polyvinyl alcohol [23] modified TiO<sub>2</sub> showed

photocatalytic activity in the degradation of methyl orange, phenol, and so on.

In our previous study we use poly(flourene-co-thiophene) (PFT) as photosensitizer to modified TiO<sub>2</sub> [17]. In this study we use poly(flourene-co-bithiophene) (PFB), which use bithiophene instead of thiophene as one of copolymers, as the photosensitizer. The photodegradation of phenol under the irradiation of the GaN LEDs cluster using PFB modified TiO<sub>2</sub> as photocatalyst was investigated.

### II. EXPERIMENTAL SECTION

#### A. Materials

Poly (flourene-co-bithiophene) [24] shown in Fig. 1 were purchased from Canton OLEDKING Optoelectric Materials Co. Ltd. TiO<sub>2</sub> (Degussa P25: 80% anatase, 20% rutile; BET ca. 50 m<sup>2</sup>/g) and Al<sub>2</sub>O<sub>3</sub> (Degussa, 100 m<sup>2</sup>/g) were both pre-dried at a temperature of 393K under vacuum before use. All other chemicals were analytical grade and used without further purification.

#### B. Measurements

A UV-2501 UV-visible spectrophotometer (SHIMADZU, Japan) with an integrating sphere was used to directly record diffuse reflectance spectra of the polymer/TiO<sub>2</sub> photocatalyst. Baseline correction was done using a calibrated sample of barium sulphate.

Photoluminescent (PL) spectra were obtained with a Fluorolog JY luminescence spectrometer. PFB 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).

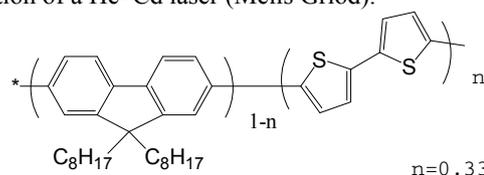


Figure 1. Structure of polymer poly(flourene-co-bithiophene).

Phenol concentration was measured using a UV-1700 spectrophotometer (SHIMADZU, Japan). Total organic

carbon (TOC) was determined using a TOC-VSH analyzer (SHIMADZU, Japan).

### C. Photodegradation experiments

The sensitization of TiO<sub>2</sub> by PFB was conducted by adopting the processes in the literature [17]. The photodegradation experiments were carried out in a column glass reactor. A three watts GaN LEDs cluster with a radiation wavelength of 450-475 nm was used as visible light source. The reactor was open to air to ensure enough oxygen in the reaction solution. Prior to the photoreaction, the solution containing the photocatalyst and the pollutant was magnetically stirred in darkness for 30 min to establish adsorption-desorption equilibrium. After 2 h irradiation, 5 mL of the reaction mixture was centrifuged, filtered, and measured spectrophotometrically at 510 nm by the 4-aminoantipyrine method. The reaction mixture was stirred throughout the reaction to keep in suspension.

## III. RESULTS AND DISCUSSION

### A. Diffuse reflectance spectra (DRS)

The photocatalyst (sign as PFB/TiO<sub>2</sub> following) exhibited as greenish or yellowish powder. The absorption of them should be demonstrated via DRS (as shown in Fig. 2). It can be seen that this polymer expand the absorption range of the TiO<sub>2</sub> from 380nm to over 500 nm although their weight ratio to TiO<sub>2</sub> is only 1:100. In fact, the spectra of PFB/TiO<sub>2</sub> were the spectra of polymer PFB adsorbed onto the surface of the powders. It is a vital prerequisite for photo-sensitization that the photosensitizer be adsorbed onto the surface of semiconductor. PFB/TiO<sub>2</sub> seemed capable of responding to visible light.

### B. Photoluminescent (PL) spectrum and PL quantum

Fig. 3 shows the photoluminescent spectra of the PFB film and PFB/TiO<sub>2</sub> powder. No major difference was observed between the spectral shapes of these two samples, which indicated that TiO<sub>2</sub> had no great influence on the electron structure of the polymer. Since the mobility of electrons in polymer is much less than that of dyes, it is suggested that the conjugation length of the polymer is not changed by TiO<sub>2</sub>.

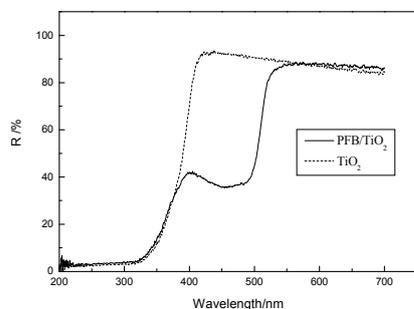


Figure 2. The DRS spectra of pure TiO<sub>2</sub> and TiO<sub>2</sub> modified with PFB.

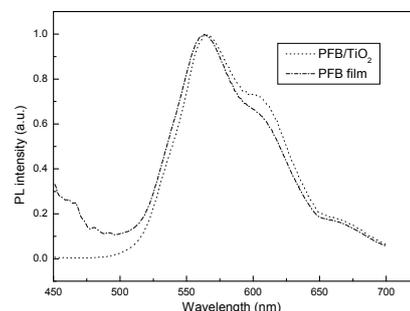


Figure 3. The PL spectra of PFB film and PFB/TiO<sub>2</sub> powder

It is reported that PL quantum yields decrease abruptly if there is electron transfer from dyes to a semiconductor [25, 26]. Our earlier results [17] showed that PFT/TiO<sub>2</sub> had PL quantum yields that were only 40% of those of PFB/Al<sub>2</sub>O<sub>3</sub>, which indicated that many electrons on the conduction band of the polymer were transferred into the conduction band of TiO<sub>2</sub>. These electrons may play an important role in the photocatalytic degradation of organic pollutants.

It has been reported that the reductive potential of PFB is about -1.33V, which is lower than that of TiO<sub>2</sub> (-0.2V), so, it is thermodynamically possible for electrons to be injected from the conduction band of the polymer to the conduction band of TiO<sub>2</sub>. And in this study, PL quantum yields of PFB-modified TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were measured carefully in integrating sphere IS080 with 405 nm excitation of a He-Cd laser (Mells Grid). A similar result was observed in the case of PFB/TiO<sub>2</sub> (Table 1), indicating that electrons were transferred between PFB and TiO<sub>2</sub>.

### C. Photocatalytic removal of phenol

A series of blank experiments revealed that less than 10% of the concentration of phenol was absorbed on the surface of TiO<sub>2</sub> in the dark under specified conditions, and no appreciable degradation of phenol was observed.

The degradation of phenol under the irradiation of GaN LEDs for two hours was demonstrated in Fig. 4. It showed that little phenol was decomposed with pure TiO<sub>2</sub> under visible light, while with PFB/TiO<sub>2</sub> nearly 75% of the phenol was removed. It is suggested that PFB is an effective photosensitizer, as has been reported for some dyes [9-11]. Kinetically, the degradation reaction showed the first-order behavior. The data can be rationalized by the first-order equation:

$$-\ln(C/C_0)=kt \quad (1)$$

TABLE I. THE PL QUANTUM YIELDS OF PFB/TiO<sub>2</sub>, PFB/AL<sub>2</sub>O<sub>3</sub> AND PFB FILM

	Abs. edge (nm)	PL max (nm)	Band gap (eV)	E <sub>red</sub> (V)	PL quantum yields (%)
PFB film	504nm	570, 610	2.46	-1.33	8.7

TiO <sub>2</sub> /PFB	525nm	570, 610	—	—	3.9
Al <sub>2</sub> O <sub>3</sub> /PFB	525nm	570, 610	—	—	7.3

The reaction rate constants ( $k$ ) of PFB/TiO<sub>2</sub> was calculated to be 0.0169 min<sup>-1</sup>.

The concentration of total organic carbon (TOC), which was mostly contributed by the phenol, was determined (as shown in Fig. 4). The loss of TOC via mineralization was lower than the amount of phenol that was degraded. This discrepancy occurred because phenol was photooxidized to benzoquinone, and further degradation to CO<sub>2</sub> and H<sub>2</sub>O took place more slowly. Therefore, the concentration of phenol declined more rapidly than did that of TOC.

The PFB-modified non-conducting material alumina (PFB/Al<sub>2</sub>O<sub>3</sub>) was prepared, and photodegradation experimental results showed that a little of the phenol was degraded (Fig. 4). Just like other research results with phthalocyanine/Al<sub>2</sub>O<sub>3</sub>, about 5% degradation of phenol in this experiment should be induced completely by PFB adsorbed on the surface of Al<sub>2</sub>O<sub>3</sub> particles, because no electrons can be transferred from the conduction band of the excited PFB to the conduction band of Al<sub>2</sub>O<sub>3</sub> [27]. This can be explained by the difference between TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub> is a semiconductor with a special energy band structure, while Al<sub>2</sub>O<sub>3</sub> is not. Electrons which were promoted from the  $\pi$ - $\pi^*$  absorption band of the conjugated polymer under natural light were easily injected into the conduction band of TiO<sub>2</sub>. This indicated that interactions between TiO<sub>2</sub> and PFB were responsible for the photocatalytic degradation, because neither TiO<sub>2</sub> nor PFB alone is effective. It is generally believed [10, 11] that upon visible light irradiation, the photosensitizer adsorbed onto the surface of TiO<sub>2</sub> gets excited and injects an electron into the conduction band of TiO<sub>2</sub>. This conduction band electron is subsequently captured by dioxygen adsorbed onto the surface of TiO<sub>2</sub> and induces the generation of  $\cdot\text{O}_2^-$  /HO $\cdot$  radicals which attack organic pollutants to yield the ultimate products.

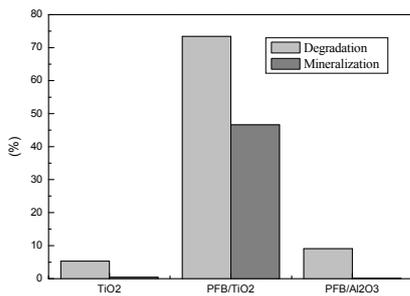


Figure 4. Photocatalytic activity of PFB/TiO<sub>2</sub> under the visible light. [phenol]<sub>i</sub> = 10 mg·L<sup>-1</sup>, [photocatalyst] = 1.0 g·L<sup>-1</sup>.

#### D. Photocatalytic removal of phenol under different light source

Some researchers adopted metal/metal oxide or metal ion doping into TiO<sub>2</sub> to expand the absorption of TiO<sub>2</sub> to visible light region. But this method could decrease the activity of TiO<sub>2</sub> under the UV light irradiation [28]. The stability of TiO<sub>2</sub> after modification attracted wide attention. The photo-degradation of phenol using PFB/TiO<sub>2</sub> as photocatalyst under different light source was carried out and shown in Table 2. UV irradiation was provided by a low-pressure mercury lamp.

TABLE II. PHOTODEGRADATION RATE CONSTANT OF PHENOL IN DIFFERENT SYSTEM

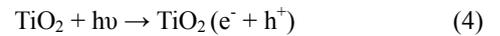
Reaction system	$k$ (min <sup>-1</sup> )	$t_{1/2}$ (min)
phenol+UV+TiO <sub>2</sub>	0.0216	32.91
phenol+UV+PFB/TiO <sub>2</sub>	0.0327	23.62
phenol+Vis+PFB/TiO <sub>2</sub>	0.0169	89.93

Under the UV irradiation, The reaction rate constants ( $k$ ) of PFB/TiO<sub>2</sub> was higher than that of TiO<sub>2</sub>. It indicated the modification did not decrease the activity of TiO<sub>2</sub> quondam. The reductive potential of PFB is about -1.33V, which is lower than conduction band potential of TiO<sub>2</sub> (-0.2V). And the oxidative potential of PFB is about 1.28V, lower than valence band potential of TiO<sub>2</sub> (3.0V).

Therefore, when the irradiation wavelength was longer than 387 nm, only polymer PFB was excited and electrons transferred from PFB to TiO<sub>2</sub>:



When when the irradiation wavelength was shorter than 387 nm, not only PFB but also TiO<sub>2</sub> were excited. The electrons transferred from PFB to TiO<sub>2</sub>, and holes (h<sup>+</sup>) transferred from TiO<sub>2</sub> into valence band of PFB [11]:



As presented above, either only PFB was excited or both excited, electron-hole couple generated could be transferred effectively, and the photocatalytic activity of TiO<sub>2</sub> was enhanced.

#### IV. CONCLUSION

The results of the present study demonstrate that the synthesized conjugated polymer poly(fluorene-co-bithiophene), which has strong absorbance in the visible region, can photosensitize TiO<sub>2</sub> to catalyze the degradation and mineralization of phenol under visible light. Compared

with the photocatalytic activity of the PFB surface-modified non-conducting material alumina, an electron transition was likely to occur in the PFB/TiO<sub>2</sub> system. The surface modification using PFB did not decrease the photocatalytic activity of TiO<sub>2</sub> under the UV light irradiation.

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