

# Optical Properties of Soluble Polythiophene for Flexible Solar Cell

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**ABSTRACT:** Polythiophene-TiO<sub>2</sub> composite was synthesized with different molar ratios of thiophene and titaniumisopropoxide (Ti(OPr)<sub>4</sub>) for flexible solar cell application as a flexible electrode or an active material. The Ti(OPr)<sub>4</sub> was stabilized by thiophene. The thiophene was polymerized by ferric chloride catalyst. The synthesized polythiophene exhibited strong UV-visible absorption in the range of the wavelength shorter than 500 nm. Field emission scanning electron microscope (FESEM) image of low concentration of TiO<sub>2</sub> film showed smooth surface. However, FESEM image of high concentration of TiO<sub>2</sub> film exhibited relatively rough surface. Polythiophene concentration dependent strong photoluminescence quenching of surfrhodamine-B was observed.

**Key words:** Polythiophene, TiO<sub>2</sub>, Composite, Photoluminescence quenching

## 1. Introduction

Since TiO<sub>2</sub> has unusual electrical<sup>1)</sup>, optical<sup>2)</sup>, magnetic properties<sup>3)</sup>, many researchers has been focused on TiO<sub>2</sub> research during the last decades. The TiO<sub>2</sub> has been developed wide applications including photoluminescence devices<sup>4)</sup>, energy efficient windows<sup>5)</sup>, dye-sensitized solar cells<sup>6)</sup>, and water and air purifications<sup>7)</sup>. Functional metal oxide and organic conducting polymer composites have been extremely interest for various application fields including dye sensitized solar cells<sup>8)</sup>, sensors<sup>9)</sup>, and electrochromic devices<sup>10)</sup>. Conducting polymers including polypyrrole, polythiophene, polyaniline and poly (3,4-ethylenedioxythiophene) and TiO<sub>2</sub> nano- or micro-structures have been exhibited promising application devices.

Many researchers have been studied the conducting polymer and TiO<sub>2</sub> composites including conducting polyaniline-nano-TiO<sub>2</sub> composites for smart corrosion resistant coatings<sup>11)</sup>, polyaniline/urchin-like mesoporous TiO<sub>2</sub> nanosphere composite for supercapacitors<sup>12)</sup>, 20 nm of polypyrrole layer and 10 nm TiO<sub>2</sub> layer for memory device<sup>13)</sup>, and nanocomposites of TiO<sub>2</sub> with polypyrrole for lithium batteries<sup>14)</sup>. Among the conducting polymers, polythiophene is one of the most important conjugate polymers. Even though polythiophene has such a large application fields, insolubility in common solvent is a major

drawback. We report synthetic method to fabricate soluble polythiophene and TiO<sub>2</sub> composite (PThTiO<sub>2</sub>) and characteristics of TiO<sub>2</sub> and polythiophene composite including, field emission scanning electron microscope (FESEM) images, UV-visible absorption spectra, and photoluminescence (PL) quenching spectra of sulfrhodamine-B by PThTiO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

Titaniumisopropoxide (Ti(OPr)<sub>4</sub>, 97 %), thiophene (99.5 %), ferric chloride (97 %) and 2-propanol (99.5 %) were purchased from Sigma Aldrich CO. Ltd. and used without further purification.

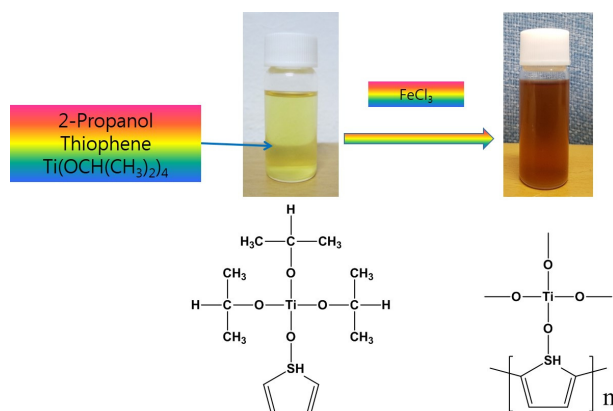
### 2.2. Synthesis

Schematic view of the synthetic process was shown in Fig. 1. To the 25 ml of a vial with a magnetic stirring bar, 10 ml of 2-propanol, and 3 g of thiophene and 1.2 g of acetic anhydride were added, and then 0.3 g or 0.5 g of Ti(OPr)<sub>4</sub> was added to the vial with stirring. Finally, 1.0 g of ferric chloride was added to the vial with vigorous stirring to polymerize the thiophene.

### 2.3. Measurement

The PThTiO<sub>2</sub> was spin coated to a silicon wafer for FESEM images. FESEM images were obtained with field emission scanning electron microscope (JEOL ISM-7401F). Methanol

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**Fig. 1.** Schematic representation of the synthetic process and possible chemical structures

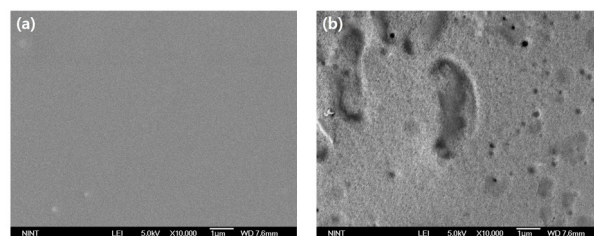
(approximately 6 ml) was filled in the UV-visible spectrometer cuvette and added PThTiO<sub>2</sub> drop by drop and recorded UV-visible absorption spectra each time using Thermo Scientific Genesys 10S UV-visible spectrometer. For PL quenching spectra, methanol (approximately 6 ml) was added to the UV-visible cuvette and added surfrhodamine-B. The PL quenching spectra were obtained by adding various amount of PThTiO<sub>2</sub>.

### 3. Results and discussion

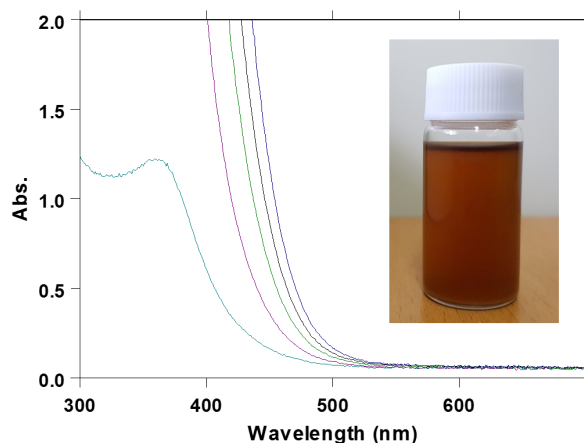
The  $\text{Ti}(\text{OPr})_4$  is very quickly hydrolyzed and precipitated from the solution with trace of water. Therefore, many researchers use diethanolamine as a  $\text{Ti}(\text{OPr})_4$  stabilizer. In this research, thiophene was used as a  $\text{Ti}(\text{OPr})_4$  stabilizer. The initial solution color was weak yellow and turned intense brown color after ferric chloride addition as shown in Fig. 1. The composite was stable at room temperature for long time.

The FESEM images of PThTiO<sub>2</sub> films synthesized with 0.3 and 0.5 g of  $\text{Ti}(\text{OPr})_4$  are shown in Fig. 2 (a) and (b), respectively. Although the surface of FESEM image of PThTiO<sub>2</sub> film synthesized with 0.3 g of  $\text{Ti}(\text{OPr})_4$  shows smooth surface without particles, the surface of FESEM image synthesized with 0.5 g of  $\text{Ti}(\text{OPr})_4$  exhibits rough surface with small holes with extremely small irregular patterns. Addition of more  $\text{Ti}(\text{OPr})_4$  exhibited rough surface of the film, which could be a partial aggregation of titanium oxide.

The synthesized PThTiO<sub>2</sub> has deep yellow-brown color as shown in inset Fig. 3. Concentration dependent UV-visible spectra of PThTiO<sub>2</sub> synthesized with 0.3 g of  $\text{Ti}(\text{OPr})_4$  was shown in Fig. 3. The UV-visible absorption spectra were recorded with each addition 1 drop of PThTiO<sub>2</sub> solution. The first spectrum shows maximum absorption peak at approxi-



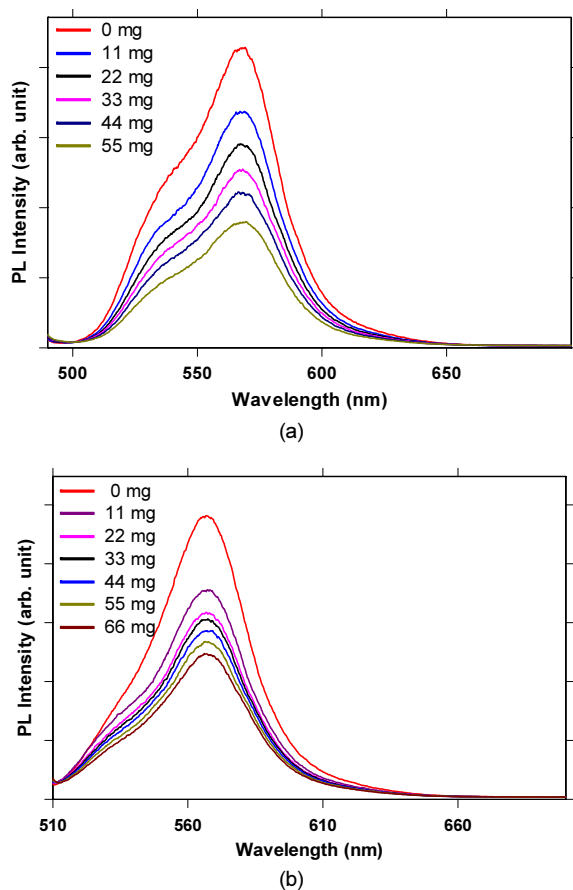
**Fig. 2.** FESEM images of PThTiO<sub>2</sub> synthesized with (a) 0.3 g of  $\text{Ti}(\text{OPr})_4$  and (b) 0.5 g of  $\text{Ti}(\text{OPr})_4$



**Fig. 3.** UV-visible absorption spectra with various amount of PThTiO<sub>2</sub> solution.

mately 3.44 eV (360 nm). The spectra for more than 2 drops show strong absorption in the range between 300 nm and 500 nm. These unusually strong absorption near visible region could be advantageous for solar cell application.

The degree of exciton dissociation in a bulk heterojunction due to the luminescence process competes with nonradiative process and exciton dissociation, which is closely related with luminescence quenching. Therefore, large amount of luminescence quenching implies possible success of efficient solar cell development. The PL spectra of surfrhodamine-B in methanol with excitation wavelength 480 and 500 nm with maximum luminescence peak at 567 nm are shown in Fig. 4 (a, 0 mg) and 4(b, 0 mg), respectively. The synthesized PThTiO<sub>2</sub> was added to the surfrhodamine-B solution drop by drop and obtained luminescence quenching spectra each time. The PThTiO<sub>2</sub> concentration dependent luminescence quenching spectra were shown in Fig. 4(a) and 4(b) with the excitation wavelength at 480 and 500 nm, respectively. Initially large amount of luminescence quenching was observed and significant amount of additional emission quenching was shown by adding additional PThTiO<sub>2</sub>. These result shows that the charge separation process is preferred process than emission process for the PThTiO<sub>2</sub> system.



**Fig. 4.** PL quenching spectra of PThTiO<sub>2</sub> with excitation wavelength of (a) 480 nm and (b) 500 nm

## 4. Conclusions

Polythiophene-TiO<sub>2</sub> composites were fabricated with thiophene, Ti(OPr)<sub>4</sub>, FeCl<sub>3</sub> as a catalyst and 2-propanol as a solvent. Although the FESEM image showed smooth surface for the PThTiO<sub>2</sub> synthesized with 0.3 g of Ti(OPr)<sub>4</sub>, the surface was rough the the PThTiO<sub>2</sub> film synthesized with 0.5 g of Ti(OPr)<sub>4</sub>. The PThTiO<sub>2</sub> solution had deep yellow-brown color and exhibited strong absorption in the range between 300 and 500 nm. Strong luminescence quenching of surfrhodamine-B was observed with PThTiO<sub>2</sub>, which indicated preferred charge separation process instead of luminescence process.

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