

# Preparation of Polyaniline/TiO<sub>2</sub> Composite Nanotubes for Photodegradation of AZO Dyes

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**Abstract:** Polyaniline (PANI) composite nanotubes (90-130 nm in diameter) containing titanium dioxide (TiO<sub>2</sub>) nanoparticles (about 10 nm in diameter) were synthesized through a self-assembly process in the presence of  $\alpha$ -naphthalenesulfonic acid ( $\alpha$ -NSA) as the dopant. It was found that PANI-TiO<sub>2</sub> composites and PANI nanotubes both behaved with significant photocatalytic activities towards AZO dyes, during 2 h photocatalytic processes under natural light, the degradation ratio was 94.2% and 97.2% respectively (methyl orange and orange II). The morphology of such products was characterized by SEM. The specific surface area of such composite nanotubes was 14.7 m<sup>2</sup>/g compared to normal polyaniline which was 0.27 m<sup>2</sup>/g. IR and X-ray diffraction characterizations showed that the chemical chain of the composite nanotubes was identical to that of the doped PANI. It may provide a new way for photodegradation of organic contaminants by using conjugated polymer with dimensional structure.

**Key words:** polyaniline; TiO<sub>2</sub>; nanotube; photocatalysis

## 1 Introduction

Heterogeneous photocatalysis, a new water and air purification technique, has attracted great attention in the past decade<sup>[1,2]</sup>. A number of research topics in photocatalysis have emerged and offered the potentials for commercial development and environmental protection, such as splitting water to produce hydrogen fuel and decomposing<sup>[1,2]</sup>, selective synthesis of organic compounds<sup>[3]</sup>, removal of organic or inorganic pollutants<sup>[4,5]</sup>, solar cells and sensors<sup>[6]</sup>. Although titanium dioxide is widely accepted as the most promising photocatalyst for its high photocatalytic activity, chemical stability, nontoxicity and low price<sup>[7-11]</sup>, there are still some difficulties hampering its wide application because of its low quantum yield, low adsorption capacity and so on.

Semiconductors have been incorporated in polymers matrix to achieve the desired objectives because of their semiconductor band structure, tunable absorption spectra, and high stability under irradiation of solar light<sup>[12,13]</sup>. For example, TiO<sub>2</sub> containing Ppy (polypyrrole) films were found to catalyze the degradation of dyes such as methylene blue and methyl orange under UV radiation<sup>[14]</sup>. The Ppy/TiO<sub>2</sub> composite films were found to enhance the degradation reactions better than a mere suspension of TiO<sub>2</sub> nanoparticles<sup>[14]</sup>. TiO<sub>2</sub> in polyethylene and poly(vinyl chloride) (PVC) composites containing non-conducting polymers degrades these polymers under UV radiation<sup>[15,16]</sup>. However, conducting polymers do not undergo degradation in the presence of TiO<sub>2</sub> under UV radiation.

One-dimensional conducting polymer nanostructures, including nanotubes or nanowires, have received great attention because of their unique properties and promising potential applications in electrical nanodevices. Conducting polyaniline (PANI) is one of the promising conducting polymers due to its high conductivity, ease of preparation, and good environmental stability. In addition, the multifunctionalized PANI nanotubes or nanowires

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have also been synthesized either by doping with a functional dopant or by blending with inorganic electrical, optic, and magnetic nanoparticles to form composite nanostructures. Although many papers on PANI/TiO<sub>2</sub> composites have been published in the literature<sup>[17]</sup>, no paper dealing with the photocatalytic activities of PANI/TiO<sub>2</sub> composite nanotubes has been published yet. On the fact that such nanostructure has a large specific surface area and a high pore volume, if the concentration of the pollutant on the surface of TiO<sub>2</sub> could always be kept high with polymer nanotubes, the degradation rate of the pollutant would be greatly increased. Research on the photocatalytic activities of polyaniline-TiO<sub>2</sub> composites nanotubes showed special interests.

In this paper, we conducted the photodegradation of orange II and methyl orange under UV irradiation using PANI/TiO<sub>2</sub> composite nanotubes as photocatalyst. In fact, the polymer nanotubes with and without TiO<sub>2</sub> both exhibited photo-chemical activities. The as-prepared materials were characterized by IR spectra, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The photo-degradation rates of organic dye in such courses were analyzed by UV-Vis spectra.

## 2 Experimental

### 2.1 Materials

The aniline monomer was distilled under reduced pressure. APS was used as received without further treatment. Ammonium hydroxide (NH<sub>3</sub>•H<sub>2</sub>O), orange II, methyl orange (MO),  $\alpha$ -naphthalenesulfonic acid ( $\alpha$ -NSA), TiO<sub>2</sub> nanoparticles were all purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd (China). The above reagents were of analytical grade and used as received without further treatment. The MO and orange II solutions (1 000 ppm) were prepared by mixing 0.1 g MO and orange II powders in 100 mL distilled water separately.

### 2.2 Synthesis of PANI-TiO<sub>2</sub> and PANI composites nanotubes

The typical synthesis process of the nanotubes by STFM was as follows<sup>[17]</sup>: 0.2 mL of aniline (2.0 mmol) was dissolved in 15 mL of de-ionized water with magnetic stirring at room temperature for 0.5 h, and cooled in an ice bath. Then a solution of pre-cooled APS (2.0-4.0 mmol) in 15 mL of de-ionized water was added to the above solution. The mixture was allowed to react at 0-5 °C for 12 h. The precipitates were

collected, washed several times by de-ionized water, methanol and ether. Finally, the product was dried in vacuum at room temperature for 24 h.

### 2.3 Photocatalytic experiments

The photocatalytic oxidation of methyl orange (MO) and Orange II in PANI/TiO<sub>2</sub> suspension under UV illumination was investigated in order to evaluate the photocatalytic activity of the as-prepared PANI/TiO<sub>2</sub>. Orange II and MO, were chosen as simple models of a series of common azo dyes, widely used in the industry.

A 40 W high pressure mercury vapor lamp (Institute of Electric Light Source, Beijing) was used for the degradation reactions. The lamp radiated predominantly at 365 nm corresponding to the energy of 3.4 eV. The details of the photochemical reactor employed in this study have been reported elsewhere<sup>[18]</sup>.

An aqueous PANI/TiO<sub>2</sub> suspension was prepared by adding 2 mg PANI/TiO<sub>2</sub> to a 50 mL distilled water solution and stirring in the dark for 30 min under constant air-equilibrated conditions to reach an adsorption/desorption equilibrium before photocatalytic reaction. Control experiments conducted without the catalyst in UV reaction system also have been presented here. Samples were collected at regular intervals for subsequent analysis. The reactions were carried out under natural pH conditions (no adjustment of pH was made during the reaction).

MO and orange II were analyzed with a Perkin-Elmer UV-vis spectrophotometer. The degraded MO and orange II samples were filtered through Millipore membrane filters (0.45  $\mu$ m pore size) and centrifuged to remove the catalyst particles prior to analysis. The characteristic absorption wavelength of the MO and orange II solution was 471 and 367 nm, respectively. The degree of dyes decolorization could be calculated according to the equation  $C(\%) = (A_0 - A)/A_0 \times 100$ , where  $C$  is the decolorization degree,  $A_0$  the initial absorbance of methyl orange solution, and  $A$  the absorbance of the dyes solution after photocatalysis. In fact, there exists a linear relationship between the absorbance and concentration of the dyes solution under the same condition in our experiments. Therefore, the degree of dyes decolorization indicated its photodegradation<sup>[18]</sup>.

### 2.4 Characterization

The structure of the sample was examined using a D/max-A X-ray diffractometer (Cu-K $\alpha$  radiation,  $\lambda = 0.154\ 056$  nm). The average crystal size of the nanocrystal was calculated according to

Scherrer's formula. The morphology of the sample was observed using Tecnai G2-20 transmission electron microscopy (TEM, Ev=200 kV). Infrared spectra of the nanocomposite sample palletized with KBr were recorded by Fourier transform infrared (FTIR) spectrometer (Perkin-Elmer Model 1600). The microstructure of the nanocomposite was determined by scanning electron microscope. The electrical contacts were made by silver paint. UV-visible spectra of the diluted nanocomposite dispersions in the 200–1 000 nm range were obtained using a Perkin-Elmer instrument.

### 3 Results and discussion

#### 3.1 Morphology and its formation

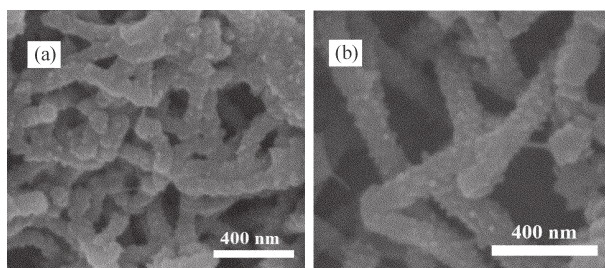


Fig.1 The as-prepared PANI-TiO<sub>2</sub> composite nanotubes using simplified template method

The morphology of PANI-TiO<sub>2</sub> and PANI composites nanotubes obtained by template-free method has been characterized using scanning electron microscopy studies. The details of polymer nanotubes' formation has been described as that a micelle composed of the aniline monomer itself in aqueous solution served as a soft-template in forming nano-spheres at the initial stage. These nano-spheres were then linearly aggregated to form nanotubes by coordination of polymerization and elongation process as well as hydrogen bonds as the driving forces<sup>[17]</sup>. The representative scanning electron microscopic (SEM) images in Fig.1(a) and (b) show that the size of such PANI-TiO<sub>2</sub> and PANI composites nanotubes was ca. 90–130 nm in diameter with a narrow size distribution. Additionally, the polymer nanotube composites were dispersed well in the mixture solution, providing an ideal mutual distance for further photocatalytic investigation. In addition, according to the ASAPS measurement on the specific surface areas of both polymer materials, the results are 0.27 m<sup>2</sup>/g (polyaniline nanotubes) and 14.7 m<sup>2</sup>/g(PANI-TiO<sub>2</sub>), respectively.

#### 3.2 IR analysis of PANI-TiO<sub>2</sub> and PANI composites

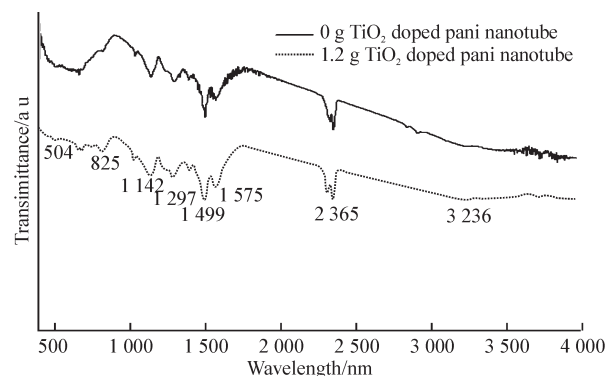


Fig.2 FTIR spectra of the as-prepared PANI-TiO<sub>2</sub> composite nanotubes and PANI nanotubes using simplified template-free method

The chemical structure of PANI-TiO<sub>2</sub> and PANI composites nanotubes were confirmed by FT-IR analysis. The symmetric N–H stretching bands at 3 236 cm<sup>-1</sup> are observed in the spectra of both samples. And the relatively strong absorption peaks at 1 499 and 1 575 cm<sup>-1</sup> correspond to C=C in aromatic ring stretching vibration of the benzenoid and quinoid rings, respectively. The lower frequency bands at 1 297 cm<sup>-1</sup> are assigned to the C–N vibration<sup>[19]</sup>, the aromatic C–H in-plane bending at 1 142 cm<sup>-1</sup> is observed, and peaks at 825 cm<sup>-1</sup>, 504 cm<sup>-1</sup> are due to the out-of-plane deformation C–H in the benzene ring. The FT-IR spectra of PANI-TiO<sub>2</sub> and PANI composites nanotubes are similar. There is no change in the IR spectra of the polymers before and after catalysis indicating that the polymers do not undergo degradation upon exposure to UV radiation.

#### 3.3 XRD analysis of PANI-TiO<sub>2</sub> and PANI composites

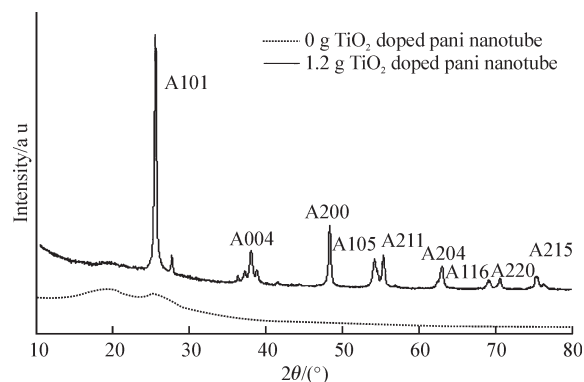


Fig.3 XRD patterns of PANI-TiO<sub>2</sub> and PANI composite nanotubes

Fig.3 shows the XRD patterns of PANI-TiO<sub>2</sub> and PANI composite nanotubes. Identification of titania phases, confirmed by comparison to accepted standard peaks from JCPDS was obtained from X-ray diffraction

(XRD)<sup>[19-21]</sup>. The grain size was calculated using the Scherrer equation  $D = K\lambda / \beta \cos\theta$ , where  $\beta$  is the width of the XRD peak at half height,  $\theta$  is the angle,  $\lambda$  is the X-ray wave length ( $1.54 \text{ \AA}$ ), and  $K$  is a shape factor, about 0.89 for  $\text{TiO}_2$ . The crystal size of  $\text{TiO}_2$  in PANI- $\text{TiO}_2$  composites nanotubes was estimated to be 20.0 nm in diameter. Comparing with the weak diffraction peaks of PANI at about  $25^\circ$  and  $35^\circ$  in Fig.2(a), it confirmed that the  $\text{TiO}_2$  nanocrystal was successfully doped into polymer nanotubes.

### 3.4 Photo-degradation of AZO dyes

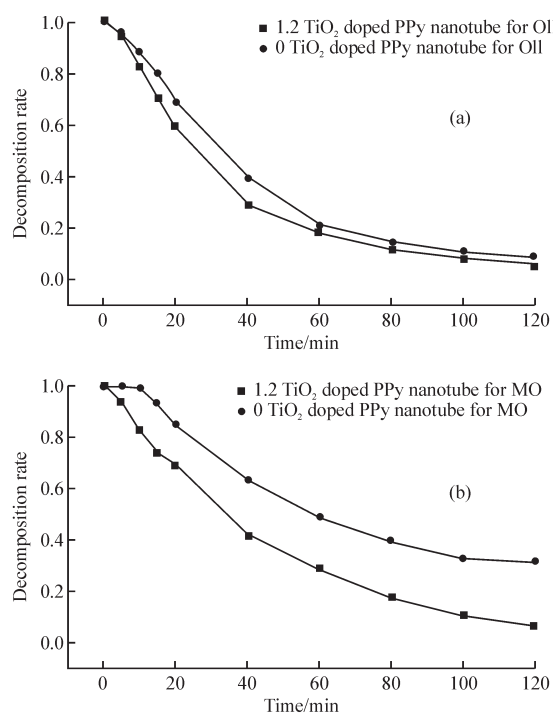


Fig.4 Discolorization of (a) orange II and (b) methyl orange (0.05 mM) under UV irradiation using PANI- $\text{TiO}_2$  nanotubes and PANI nanotubes as photo-catalyst, respectively

PANI- $\text{TiO}_2$  composites nanotubes were successfully prepared in this work. In Fig.4(a), it can be clearly seen that after 2 h photocatalytic process, the discoloration rate is 91.3% and 94.2% by using PANI- $\text{TiO}_2$  nanotube composites and PANI as photocatalyst respectively. Fig.5(a) shows the kinetics of orange II photocatalytic degradation using PANI- $\text{TiO}_2$  composites nanotubes and normal PANI. Ought to be noted here, all of them exhibited significant photocatalytic behavior under UV irradiation. The photocatalytic degradation reaction simply followed a pseudo first-order reaction kinetics<sup>[18]</sup>. The rate constants of PANI- $\text{TiO}_2$  composites nanotubes and normal PANI were relatively lower than  $\text{TiO}_2$ , which are 0.023, 0.021  $\text{min}^{-1}$  respectively, it is mainly because the specific

surface areas of the both former were quite small. The same process also executed to Methyl orange for photocatalytic investigation. In Fig.4(b), it can be clearly seen that after 2 h photocatalytic process, the discoloration rate is 69.5% and 97.2% by using PANI- $\text{TiO}_2$  nanotube composites and PANI as photocatalyst respectively. Fig.5(b) shows the kinetics of methyl orange photocatalytic degradation using PANI- $\text{TiO}_2$  composites nanotubes and normal PANI. Similarly, all of them exhibited significant photocatalytic behavior under UV irradiation. The photocatalytic degradation reaction also followed a pseudo first-order reaction kinetics. The rate constants of PANI- $\text{TiO}_2$  composites nanotubes and normal PANI were 0.027, and 0.012  $\text{min}^{-1}$  respectively.

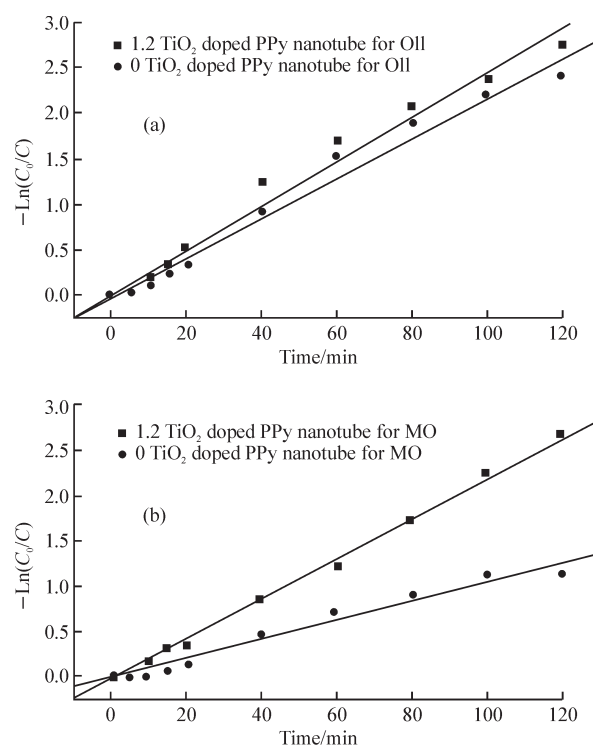
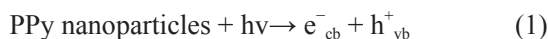


Fig.5 Pseudo first-order reaction kinetics of (a) orange II (0.05 mM) under UV irradiation using PANI- $\text{TiO}_2$  nanotubes and (b) PANI nanotubes as photocatalyst, respectively

It is noted here that the degradation rate of methyl orange slows down much more remarkably than orange II, It is mainly because photo-induced radicals' energy from the narrower band gap (about 2.5 eV) of PANI is much lower than inorganic semiconductor  $\text{TiO}_2$  (about 3.2 eV)<sup>[1]</sup>. As a result, the degradation of MO is more difficult than Orange II because such photo-degradation course is mainly decided by broken of chemical bond with different bond energy. The above catalysis reaction could be described as Eqs.(1-3) below:





## 4 Conclusions

We have described the photocatalytic properties of conjugated polymers normal PANI and PANI-TiO<sub>2</sub> composites nanotubes, which were synthesized through a self-assembly process in the presence of  $\alpha$ -naphthalenesulfonic acid ( $\alpha$ -NSA) as the dopant. We successfully obtained normal PANI and PANI-TiO<sub>2</sub> composites nanotubes with a narrow size distribution from 200-400 nm with good dispersity. Degradation studies of commonly used textile dyes as orange II and methyl orange under UV irradiation indicate higher rates in the presence of PANI nanoparticles in accordance to its higher specific surface area than normal polymer materials. We believe that further studies using conjugated polymer in photocatalysis will throw more light on the reaction mechanisms and extend our understanding about the emerging of photo-electron and photo-hole in the conjugated polymers.

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