

## Synthesis of High-Activity TiO<sub>2</sub>/WO<sub>3</sub> Photocatalyst via Environmentally Friendly and Microwave Assisted Hydrothermal Process

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**Summary:** This work focused on the synthesis of high-activity TiO<sub>2</sub>/WO<sub>3</sub> photocatalysts through an environmentally friendly and novel process. A high energy-efficient microwave assisted hydrothermal method was employed to prepare TiO<sub>2</sub>/WO<sub>3</sub> from TiCl<sub>4</sub> and Na<sub>2</sub>WO<sub>4</sub> without using any organic species. The properties of the synthesized catalysts were characterized by XRD, TEM and BET. The size of the obtained TiO<sub>2</sub>/WO<sub>3</sub> photocatalyst was about 10 nm with high specific surface areas larger than 150 m<sup>2</sup>/g. Compared with pure TiO<sub>2</sub>, the TiO<sub>2</sub>/WO<sub>3</sub> nanoparticles exhibited better photocatalytic activity for the degradation of Rhodamine B under visible light irradiation.

### Introduction

Among the various oxide semiconductor photocatalysts, research has mainly focused on titanium dioxide (TiO<sub>2</sub>) as photocatalyst in diverse areas ranging from water and air treatment to self-cleaning surfaces because of its high photoreactivity, biological and chemical inertness, cost effectiveness, non-toxicity, and long-term stability against photocorrosion and chemical corrosion [1]. Such photocatalyst, as we know, has some shortcomings. Firstly, TiO<sub>2</sub> is a high-energy band material that can only be excited by high energy UV irradiation. This practically rules out the use of sunlight as an energy source for the photoreaction. Secondly, a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs result in a low quantum yield rate and also a limited photooxidation rate [2]

In order to improve photocatalytic activity of TiO<sub>2</sub> for wide range applications, it can be achieved via coating with Ag, Au, Pt, Pd and other transition metals or doping with a lot of nonmetal elements [3-5]. Coupling TiO<sub>2</sub> with other semiconductors is an approach that has received much attention for improving the photocatalytic properties of TiO<sub>2</sub>, including TiO<sub>2</sub>/CdS, TiO<sub>2</sub>/SnO<sub>2</sub>, TiO<sub>2</sub>/ZnO, TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/WO<sub>3</sub>. Among these, WO<sub>3</sub> coupling has been widely studied to improve the photocatalytic performances of TiO<sub>2</sub>, since WO<sub>3</sub> can be served as an electron accepting species [6-8]. As a basic function, WO<sub>3</sub> has a suitable conduction band potentially to allow the transfer of photo-generated electrons from TiO<sub>2</sub> facilitating effective charge separation. Additionally, formation of a monolayer of WO<sub>x</sub> species on TiO<sub>2</sub> can significantly increase the surface acidity as WO<sub>3</sub> is 15 times more acidic than TiO<sub>2</sub> [9]. Because of this increased acidity, TiO<sub>2</sub>/WO<sub>3</sub> can absorb more hydroxyl groups and simultaneously more organic reactants on its surface. Thus,

significant improvement of the photocatalytic activity has been achieved in comparison with the pure TiO<sub>2</sub> photocatalysts. To date, TiO<sub>2</sub>/WO<sub>3</sub> has been prepared by sol-gel, impregnation, microemulsion, hydrothermal and mechanical methods [10-13].

Common Ti sources used in hydrothermal synthesis usually include titanium tetrachloride, titanium isopropoxide and titanium butoxide, etc [14, 15]. Ti(OPr)<sub>4</sub> and Ti(OBu)<sub>4</sub> are very stable, but the cost is much more and organic solvents are usually used during the synthesis, which would make it difficult for industry use, due to the necessity of waste water treatment.

In this study, TiCl<sub>4</sub> was applied as precursor substance. In comparison with above organic Ti sources, it would be much cheaper and it is a commercially available raw material. Na<sub>2</sub>WO<sub>4</sub> was employed as W source. The TiO<sub>2</sub>/WO<sub>3</sub> nanoparticles were synthesized through a novel microwave assisted hydrothermal process without using any organic species. Under visible light irradiation, photocatalytic experiments indicated that this composite catalyst shows far superior activity to pure TiO<sub>2</sub> in the degradation of Rhodamine B (RhB).

### Results and Discussion

XRD was used to investigate the changes of phase structure of TiO<sub>2</sub> samples prepared with different amounts of sodium tungstate addition (Fig. 1). It can be seen that the structure of pure TiO<sub>2</sub> powder is mainly rutile crystal (JCPDS card No. 21-1276). But the diffraction peaks of all TiO<sub>2</sub>/WO<sub>3</sub> powders are ascribed to the anatase phase (JCPDS card No. 21-1272). As doping quantity increased, the characteristic peaks were broadened. Using Scherrer equation, the particle sizes of TiO<sub>2</sub>/WO<sub>3</sub> powder are

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about 10.8, 10.2, 9.2 and 6.8 nm corresponding to 1%, 3%, 5% and 10% mol  $\text{WO}_3$ , respectively, which indicate that the average crystal sizes decrease with the increase of the added  $\text{WO}_3$ . Those results suggested that W-doped  $\text{TiO}_2$  could not only hinder the phase transformation from anatase to rutile, but also prevent the growth of the catalyst crystallites.

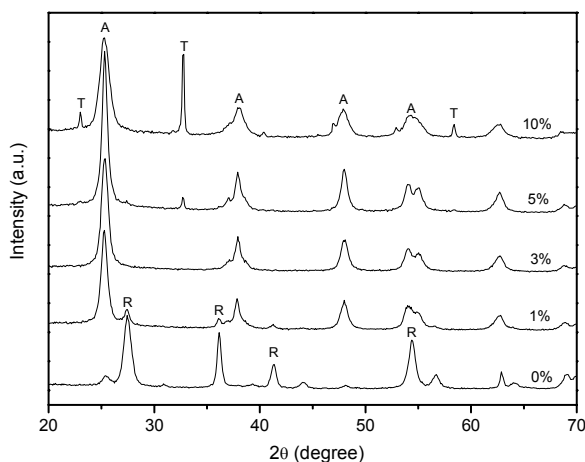


Fig. 1: XRD patterns of  $\text{TiO}_2/\text{WO}_3$  nanocomposites (A = anatase, R = rutile, T =  $\text{WO}_3$ ).

However, anatase  $\text{TiO}_2$  was obtained when sulfate or fluoride was used as a raw material [16, 17]. As we all know  $\text{Cl}^-$  ions are easily to be volatilized in the hydrothermal treatment, which will weaken the resistance to form high crystallinity. Moreover, its adsorption in titanium oxygen octahedron can reduce the connection strength between the crystal particles, which is favorable for the formation of rutile [18, 19]. It is worth noting that no  $\text{WO}_3$  phase could be observed in the XRD patterns, even the doping amount reached 3 mol%. Thus we can propose that all the  $\text{W}^{6+}$  may be incorporated into the titania lattice and replaced  $\text{Ti}^{4+}$  to form  $\text{W-O-Ti}$  bonds or located at interstitial sites [20]. The  $\text{WO}_3$  is present either in the form of highly dispersed  $\text{WO}_3$  clusters or as an amorphous layer on  $\text{TiO}_2$  [9]. When the tungsten concentration exceeds the minimum amount for monolayer formation, the  $\text{WO}_3$  crystal structures will be formed (JCPDS card No. 72-0677).

Fig. 2 shows the TEM images of pure  $\text{TiO}_2$  and 3.0 mol% W- $\text{TiO}_2$  photocatalysts prepared under different reaction conditions. The average particle sizes are 17, 13 and 9 nm corresponding to sample (a), (b) and (c), respectively. Obviously, doping W element into  $\text{TiO}_2$  would prevent the growth of crystallites. Moreover, during the microwave assisted hydrothermal process, the temperature of the reaction

solution is raised so rapidly that a large amount of nuclei can be generated in a very short time, which inhibited the crystal growth of the product.

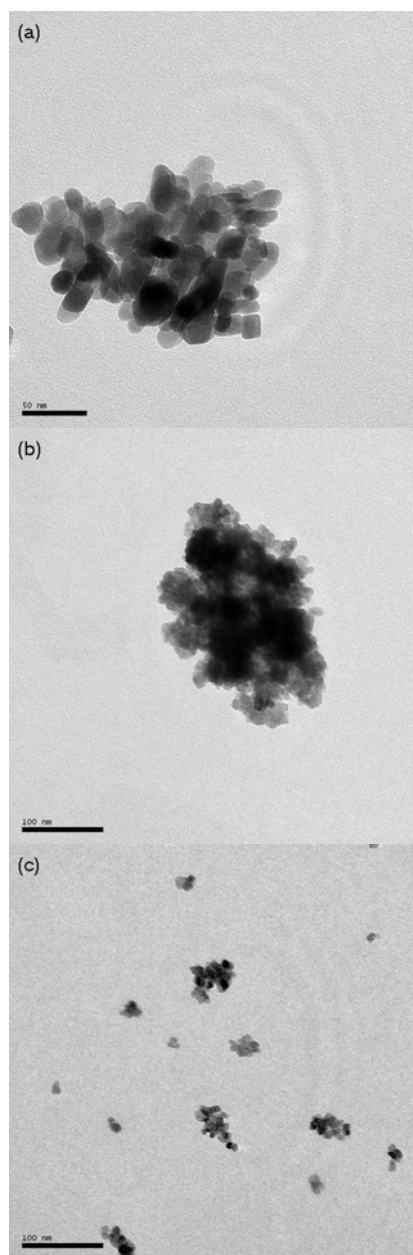


Fig.2: SEM images of samples. (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2/\text{WO}_3$  synthesized by hydrothermal method, (c)  $\text{TiO}_2/\text{WO}_3$  synthesized by microwave assisted hydrothermal method.

Specific surface areas of undoped and W-doped  $\text{TiO}_2$  powders are given in Table-1. The results show an increase of the W-doped  $\text{TiO}_2$  compared with the pure  $\text{TiO}_2$  synthesized by hydrothermal method. On the other hand, the specific

surface area of W-doped sample synthesized by microwave assisted method is larger than  $150 \text{ m}^2/\text{g}$ , which is about 2 times as that of the sample synthesized by hydrothermal method.

Table-1: Specific surface area of photocatalysts.

Sample	W content (mol %)	Synthetic method (m <sup>2</sup> /g)	Specific surface area
TiO <sub>2</sub>	0	hydrothermal	44.94
3.0% W-TiO <sub>2</sub>	3.0	hydrothermal	79.08
3.0% W-TiO <sub>2</sub>	3.0	microwave hydrothermal	153.70

In order to investigate the photocatalytic activity of W-doped TiO<sub>2</sub> samples, degradation experiments of RB were performed under visible light irradiation. The same amount of each sample (120 mg sample in 120 ml solution) was used for an easy comparison in our experiments. Photodegradation result of RB is presented in Fig. 3, where (a) shows the blank reaction, indicating that RB degraded about 12% after visible light irradiation for 90 min. This is because of RB's self-photosensitization. The degradation rate of 3.0 mol% W-doped TiO<sub>2</sub> sample synthesized by microwave assisted hydrothermal could be more than 97% under visible light irradiation. Under the same circumstance, the pure TiO<sub>2</sub> sample was only about 57%. In addition, the microwave assisted process could enhance the activity of the catalyst significantly, comparing with the hydrothermal condition without microwave.

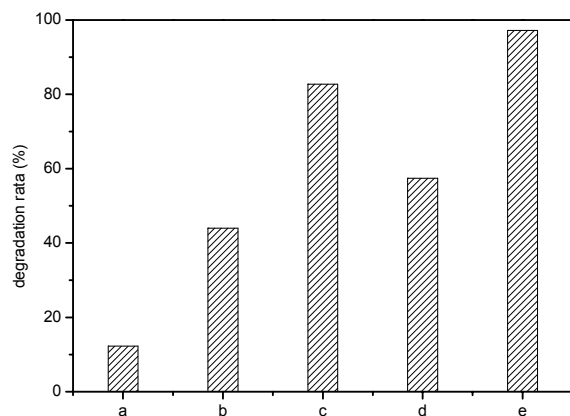


Fig.3: Photocatalytic decomposition of RB under visible light illumination for 90 min. (a) blank, (b) TiO<sub>2</sub> and (c) TiO<sub>2</sub>/WO<sub>3</sub> synthesized by hydrothermal method, (d) TiO<sub>2</sub> and (e) TiO<sub>2</sub>/WO<sub>3</sub> synthesized by microwave assisted hydrothermal method.

The effect of photocatalytic activity of W-doped TiO<sub>2</sub> samples synthesized at different contents of tungsten on the rate of destruction of RB is shown in Fig. 4. Compared with Fig. 3 (a), pure WO<sub>3</sub> did not show any photocatalytic activity towards RB under the operating conditions used. The

nanocomposites containing 3% mol WO<sub>3</sub> showed up to 97% higher hotocatalytic activity compared with that of other samples. The enhancement in the rate can therefore be attributed to the improved charge separation. However, at WO<sub>3</sub> loadings of 10% mol or higher, the activity reduced as a result of the dilution effect of the inactive WO<sub>3</sub> phase [21]. When WO<sub>3</sub> was doped into TiO<sub>2</sub>, the photogenerated electrons can be transferred to the lower-lying conduction band of tungsten oxide, while the holes can accumulate in the valence band of titania, and effectively scavenged by the oxidation, while the photo-generated electrons can be transferred onto the surface of tungsten oxide rather than undergoing bulk recombination [22].

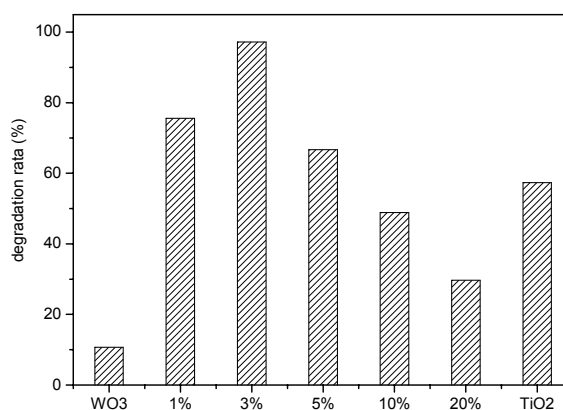


Fig.4: Reaction rates of TiO<sub>2</sub> samples having different WO<sub>3</sub> contents.

## Experiment

### Materials Preparation

A typical synthesis process for the preparation of TiO<sub>2</sub>/WO<sub>3</sub> (molar ratio 97:3) nanocomposite oxides was as follows: 5.14g Titanium tetrachloride (TiCl<sub>4</sub>) was added into 5M HCl under vigorous stirring for 1h at room temperature. 0.27g Sodium tungstate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O) was dissolved in distilled water, and was added dropwise into solution in the ice salt bath. And then, NH<sub>3</sub>·H<sub>2</sub>O was used to adjust the solution pH to 1. The solution was transferred into a Teflon tube, sealed and heated by microwave irradiation at  $2 \times 10^5 \text{ Pa}$  for 10min, then kept at 160°C for hydrothermal treatment. After 24h, the resulting product was separated by centrifugation, and washed with distilled water for several times. Finally, it was dried at 80°C for 5h. As a comparison, the synthesis process was also carried out without microwave irradiation.

Similarly, 1.0, 5.0, 10.0mol% TiO<sub>2</sub>/WO<sub>3</sub> and

pure TiO<sub>2</sub> samples were also prepared by repeating the above procedure. All chemicals used in this work were of analytical grade, and doubly distilled water was used for the solution preparation.

#### Characterization

The crystalline structure of samples was measured by an X-ray diffractometer (XRD, XRD-6000, Shimadzu) using graphite monochromatic copper radiation (Cu K $\alpha$ ) at 40 kV, 30 mA and  $\lambda=1.5406 \text{ \AA}$  over the  $2\theta$  range of 20-70° with a scan rate of 2° per min. The crystallite size was estimated from the X-ray patterns using the Scherrer formula. The morphology of the samples was examined using a transmission electron microscopy (TEM, JEM-1400, JEOL). Specific surface areas of the products were measured with a surface area analyzer (NOVA 3000e, Quantachrome).

#### Evaluation of Photoactivity

In photocatalytic experiments, an aqueous solution of Rhodamine B (RB, 120 ml,  $1.25 \times 10^{-5}$  mol dm<sup>-3</sup>, pH 6.91) containing 1g/L TiO<sub>2</sub> samples was used. The solution was stirred overnight in the dark to obtain the adsorption/desorption equilibrium among the photocatalyst, the organic substrates, the solubilized oxygen, and the atmospheric oxygen. A 250W medium mercury lamp with a 450 nm cutoff filter used as a visible light source was positioned within a cylindrical Pyrex vessel; water was circulated through the cylindrical Pyrex vessel to avoid lamp overheating. Three millilitres of aliquots were taken from the solutions irradiated for different time and separated through a centrifugal precipitator (4000 r min<sup>-1</sup>) prior to analysis. Variations in the concentration of the organic substrates in each degraded solution were monitored by measuring the UV-vis absorption at 554 nm with a UV-vis spectrophotometer (TU-1901, Pgeneral).

#### Conclusions

In summary, a novel and environmentally friendly process for the preparation of high activity photocatalyst was presented in this study. The TiO<sub>2</sub>/WO<sub>3</sub> composites with different contents of tungsten oxide were prepared by microwave assisted hydrothermal method. No organic solvents or species were employed throughout the synthesis, which greatly simplified the procedures of waste treatment, and reduced the effect of pollution on the environment. These W-doped TiO<sub>2</sub> nanoparticles possess good crystallinity and exhibit the highest activity for the degradation of RB organic pollutants under visible

light irradiation, making them promising candidates for environmental applications in wastewater treatment.

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