



# Effects of V and Zn codoping on the microstructures and photocatalytic activities of nanocrystalline TiO<sub>2</sub> films

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## Abstract

To enhance the photocatalytic activity of TiO<sub>2</sub>, V and Zn co-doped TiO<sub>2</sub> films were synthesized by the sol–gel method. The experimental results indicated that the films were composed of round-like nano-particles or aggregates. V and Zn codoping could not only obviously increase the specific surface area of TiO<sub>2</sub> but also result in the narrowed band gap of TiO<sub>2</sub> sample. The photocatalytic activities of the TiO<sub>2</sub> films were evaluated by the photocatalytic decomposition of organic dyes in aqueous solution. Compared with undoped TiO<sub>2</sub> film or single doped TiO<sub>2</sub> film, V and Zn co-doped TiO<sub>2</sub> film exhibited excellent photocatalytic activities under both UV light and visible light. The improvement mechanism by V and Zn codoping was also discussed.

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**Keywords:** TiO<sub>2</sub> film; V and Zn codoping; Microstructure; Photocatalytic activity

## 1. Introduction

Wide band gap transition metal oxide semiconductor materials have attracted considerable research interest in the past few decades because of their unique properties. Among these heterogeneous semiconductors, TiO<sub>2</sub> is the most widely used photocatalytic material because of its strong oxidizing power, photo-stability, non-toxicity, chemical and biological inertness, as well as its low cost [1–3]. However, wide application of TiO<sub>2</sub>-based photocatalytic technology has been restricted by three major factors [4]: (a) tedious operation to recover the powder catalyst; (b) low photocatalytic efficiency due to recombination of photogenerated electrons and holes; and (c) low visible light utilization efficiency due to the wide band gap of TiO<sub>2</sub> (3.2–3.4 eV). To overcome these drawbacks, many techniques were proposed to improve photocatalytic

activity of TiO<sub>2</sub>, such as various preparations, composite semiconductors [5], metal or nonmetal doping [6,7], etc.

Metal ion doping is one of the most effective ways to enhance the photocatalytic activity of TiO<sub>2</sub>. Compared with noble metals and lanthanide metals, modification of TiO<sub>2</sub> with transition metals provides a successful and cost effective alternative. Transition metal ions are doped into the TiO<sub>2</sub> lattice to modify its microstructures and electronic structures. Chang and Liu [8] reported that vanadium doped titanium dioxide films in the surface lattice could separate charge carriers and promote the photocatalytic activities of micrometer-sized TiO<sub>2</sub>. Lu et al. [9] prepared an efficient photocatalyst Zn<sup>2+</sup>-TiO<sub>2</sub> by the sol–gel method. Experiment indicated that Zn<sup>2+</sup>-doping reduced the crystallite size of TiO<sub>2</sub> and the agglomeration of TiO<sub>2</sub> powder, thus displayed higher photocatalytic activity and regeneration ability than TiO<sub>2</sub>. Although single metal doping can enhance the visible light response, single dopant has to be used in small quantity to avoid recombination of photogenerated electrons and holes. Therefore, the higher dye decomposition cannot be achieved by using

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single dopant with higher amount. Recently, a low concentration codoping of ions are reported to have higher photocatalytic activity than that of TiO<sub>2</sub> doped with single ions [10,11]. Up to now, few studies focus on V and Zn co-modified TiO<sub>2</sub> films for degradation of organic pollutants.

In this paper, we adopted a sol-gel process to prepare V and Zn co-doped TiO<sub>2</sub> films on common glass substrates. The photocatalytic activity was evaluated by photodegradation of organic dyes in solution. The mechanism of photoactivity enhancement was also discussed.

## 2. Experimental

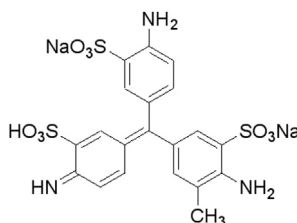
### 2.1. Preparation of TiO<sub>2</sub> film

All chemicals used in this study were analytical-grade. Deionized water was used throughout in all experiments. TiO<sub>2</sub> film was prepared by the following steps. Firstly, colloidal TiO<sub>2</sub> was prepared by the sol-gel method. Tetra-butyl titanate (TiO(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>) was added dropwise to ethanol absolute in a clean vessel, and 0.2 M diluted nitric acid was added to the above solution at the speed of 1 drop/sec. under vigorous stirring. The composition of the starting solution was TiO(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>:C<sub>2</sub>H<sub>5</sub>OH:HNO<sub>3</sub> = 1:20:20 in volume ratio. After 48 h aging, the colloidal TiO<sub>2</sub> was obtained. Secondly, we used a controllable dip-coating device to prepare colloidal TiO<sub>2</sub> film on the surface of common glass substrate (25 mm × 25 mm × 1 mm) in an ambient atmosphere. The speed withdrawal was controlled at 3 mm s<sup>-1</sup>. Then, 0.1 mL 5.0 × 10<sup>-3</sup> M ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>), 0.1 mL 5.0 × 10<sup>-3</sup> M zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>), 0.05 mL 1.0 × 10<sup>-3</sup> M NH<sub>4</sub>VO<sub>3</sub> and 0.05 mL 9.0 × 10<sup>-3</sup> M Zn(NO<sub>3</sub>)<sub>2</sub> aqueous solution was doped into the surface layer of TiO<sub>2</sub> gel-film, respectively. Finally, the doped TiO<sub>2</sub> gel-films were calcined in air at 450 °C for 1 h. In our experiments, the thickness of the film was about 0.6 μm measured using a profilometer

### 2.2. Characteristic test of TiO<sub>2</sub> film

The identity of crystalline phase was identified by DX-2500 X-ray diffraction (XRD) with a diffractometer employing Cu Kα radiation at a scan rate (2θ) of 0.05 °S<sup>-1</sup>. Surface morphology of the film was detected using SUPRA 55 high-resolution field emission scanning electron microscopy (FE-SEM). The photoluminescence (PL) emission spectra were recorded at room temperature by a FLS 920 spectrometer with a 300 nm line of 450 W Xenon lamps as excitation source. The emission was scanned in the region of 300–600 nm. The widths of both the excitation slit and the emission slit were set to 3.0 and 2.0 nm, respectively. The Brunauer–Emmett–Teller (BET) surface area of the TiO<sub>2</sub> powders was analyzed by nitrogen adsorption/desorption apparatus (ASAP 2020). UV-vis diffuse reflectance spectra of the film was recorded on a UV-vis spectrophotometer (TU-1901) with an integrating sphere accessory (IS 19-1) using blank glass plate as a reference.

The photocatalytic activity was evaluated by the degradation of acid naphthol red (ANR) dye in aqueous solution under UV-lamp irradiation or visible light irradiation. Structure of acid naphthol red is as following:



Its formula is C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub>, and its maximum of absorption wavelength is about 540 nm. Acid naphthol red is usually used in textile industry due to its good pigmentation. It is well-known that some of dyes are lost during the dyeing process and are released into the environment as textile effluent. Therefore, heightened concerns over public health and associated environmental hazards due to the presence of toxic organic compounds such as dyes in wastewater have been reported.

Ions doped or undoped TiO<sub>2</sub> film was settled in 5 mL acid naphthol red (ANR) aqueous solution with a concentration of 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>. A tungsten halogen lamp equipped with UV cut-off filters (λ > 400 nm) was used as a visible light source whose average light intensity was 40 mW cm<sup>-2</sup>, and the wavelength of 365 nm was used as a UV light source. UV-vis Spectrometer (TU-1901) was adopted to assess the photodegradation activity of the film photocatalysts. The degradation rate of photocatalysis can be calculated by formula  $D = (A_0 - A) / A_0 \times 100\%$ , as previously reported [12].

## 3. Results and discussion

### 3.1. Microstructures

FE-SEM can be used to examine the surface morphology of the doped or un-doped TiO<sub>2</sub> film. Fig. 1 shows the surface morphology of the un-doped TiO<sub>2</sub> or V/Zn co-doped TiO<sub>2</sub> film calcined at 450 °C in air for 1.0 h. It is clear that the films are composed of round-like nanoparticles or aggregates. Compared with un-doped TiO<sub>2</sub> film (1a), the surface of V/Zn co-doped TiO<sub>2</sub> film (1b) is relatively uniform and smooth without cracks. It is well-known that a good dispersion or reduced aggregation among particles may increase the active site-reactant contact area, thus enhance photocatalytic degradation of organic dyes. X-ray energy dispersive spectroscopy (EDS) element analyses indicate that the atomic ratio of Ti/O/V/Zn in doped TiO<sub>2</sub> film is 37.62/58.99/1.61/1.86. According to the literature [13,14], chemical states of V and Zn are +5, +4 and +2, 0, respectively. The presence of V<sup>4+</sup> or Zn<sup>0</sup> in the catalysts may be due to the reduction of V<sup>5+</sup> or Zn<sup>+2</sup> by the organics from starting materials.

XRD can be used to investigate the phase structure of the doped and un-doped TiO<sub>2</sub> samples. The XRD patterns of un-

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