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Investigation of ZnTiO₃/TiO₂ composites and their application in photocatalysis

 Zhenzhao Pei ^{*}, Pei Wang  and Zhiguo Li 

 Department of Chemical Engineering, Faculty of College of Materials Science and Engineering, Hebei University of Engineering, Handan, 056038, China
peizhenzhaophd@126.com (A.P.), wangpeihbgcdx@126.com (P.W.), 18231024595@163.com (Z.L.)

^{*} Corresponding author at: Department of Chemical Engineering, Faculty of College of Materials Science and Engineering, Hebei University of Engineering, Handan, 056038, China.

 Tel: +86.0310.3161792 Fax: +86.0310.3161792 e-mail: peizhenzhaophd@126.com (Z. Pei).

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ABSTRACT

In this work, we report that ZnTiO₃/TiO₂ composites, which were synthesized by hydrothermal method possessed photocatalytic and potential spraying properties. The obtained ZnTiO₃/TiO₂ composites were characterized by scanning electron microscopy (SEM) and X-ray diffraction techniques (XRD). Photocatalytic activities of ZnTiO₃/TiO₂ composites were evaluated by using Rhodamine B (RhB) as a model pollutant under visible light irradiation. The experimental results showed that the as-prepared ZnTiO₃ (2%)/TiO₂ composite exhibited better photocatalytic activity than that of pure TiO₂.

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1. Introduction

Over the past decades, titanium dioxide (TiO₂) has attracted considerable scientific interest in the field of photocatalysis, due to the outstanding properties such as low cost, photochemical stability and security [1,2]. However, due to its large band gap (TiO₂ ~3.2 eV) [3], TiO₂ can only work under UV irradiation, which greatly restricts the use of sunlight as an energy source for photoreactions since only about 3-4% of the solar spectrum falls within the UV range [4-6]. In addition, high recombination rate of electron-hole pairs lowers its photocatalytic efficiency [7]. Up to now, many methods have been proposed to extend the spectral response of TiO₂ to the visible-light region, including doping with metal/non-metal ions [8-10] and coupling with other oxide semiconductors [11-15]. In general, doping with metal/non-metal ions can affect the band gap and extend the light absorption range [16], coupling with an oxide semiconductor can improve the charge separation and extend its photo-responsive range [17].

After years of research, many composite systems have been successfully synthesized, such as V₂O₅/TiO₂, SnO₂/TiO₂, CdO/TiO₂, and ZnO/TiO₂ [18]. Liang and his coworkers

synthesized ZnTiO₃-TiO₂ heterojunction exhibiting photocatalytic activity [19]. Subsequently, ZnTiO₃-TiO₂ was synthesized by solid state dispersion method and sol-gel technique, which could degrade 4-chlorophenol under sunlight [20,21]. Then, Tian *et al.* [22] found that ZnTiO₃-TiO₂ could be used for photocatalytic H₂ production under visible light.

To date, spraying process has been successfully applied to produce many protective coatings for wear, erosion and heat resistance [23,24]. In recent years, numerous studies have been conducted to synthesize spraying materials, such as Al₂O₃-Al composite, Fe₂O₃-Al composite, Cr₂O₃, Al₂O₃-Cr₂O₃ composite and ZrO₂-Al₂O₃ composite. Song *et al.* [25] reported that the FeAl-Al₂O₃ composite showed excellent wear resistance under dry sliding wear test conditions. Tao and his coworkers [26] found that the coexistence of metal Al phase and Al₂O₃ ceramic phase could effectively improve the toughness, strength and wear resistance of coatings. However, compared to the gained great progress on spraying materials and photocatalysis, there are no research reports that ZnTiO₃/TiO₂ composite possessed photocatalytic and spraying properties.

In this paper, it was firstly found that ZnTiO₃/TiO₂ composites showed photocatalytic activity and potential

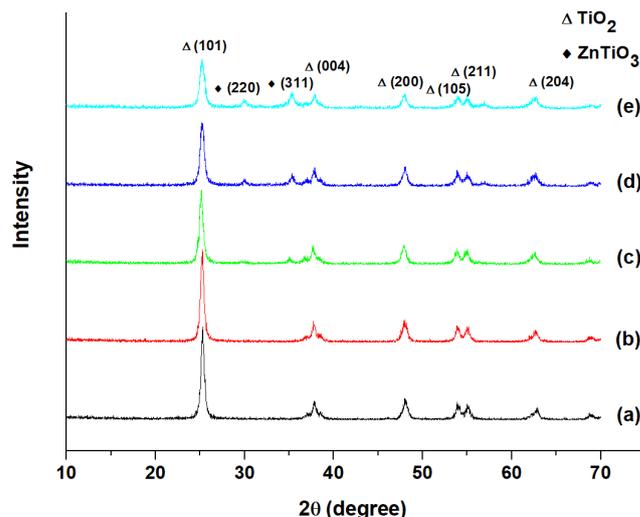


Figure 1. XRD patterns of the corresponding powder samples of pure TiO_2 (a) and ZnTiO_3 (2, 10, 20 and 30%)/ TiO_2 composite (b-e).

spraying properties. The hydrothermal method was employed to synthesize $\text{ZnTiO}_3/\text{TiO}_2$ composites. Rhodamine B was selected as a model hazardous dye to evaluate the photocatalytic activity of $\text{ZnTiO}_3/\text{TiO}_2$ composites under visible light irradiation. The experimental results suggested that these $\text{ZnTiO}_3/\text{TiO}_2$ composites could be a promising class of photocatalyst candidates for organic contaminant degradation and spraying material for wear resistance and metal corrosion prevention.

2. Experimental

2.1. Preparation of $\text{ZnTiO}_3/\text{TiO}_2$

Titanium(IV) sulfate ($\text{Ti}(\text{SO}_4)_2$, CP) was purchased from Sinopharm Chemical Reagent Co., Ltd., Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, AR) was purchased from Tianjin Zhiyuan Reagent Co., Ltd., and hexamethylene tetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, AR) was purchased from Beijing Chemical Reagent Co., Ltd. All chemicals applied to the experiment were used fully as received without further purification. Deionized water used was self-made.

$\text{ZnTiO}_3/\text{TiO}_2$ composites were synthesized by a relatively simple hydrothermal method. $\text{Ti}(\text{SO}_4)_2$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were used as the source of titanium and source of zinc, respectively. Different $\text{ZnTiO}_3/\text{TiO}_2$ composites varying in the content of ZnTiO_3 in the composite were obtained by adding different amounts of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ into a certain amount of $\text{Ti}(\text{SO}_4)_2$. In a typical procedure, a known amount of $\text{Ti}(\text{SO}_4)_2$ and a certain amount of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 35 mL distilled water. The mole fractions of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ used for synthesizing $\text{ZnTiO}_3/\text{TiO}_2$ composites were 0, 2, 10, 20 and 30%, respectively. Then 2 g $\text{C}_6\text{H}_{12}\text{N}_4$ was added into the distilled water. Subsequently, the mixed solution was transferred to a 50 mL Teflon lined stainless-steel autoclave under vigorous stirring at ambient temperature, and kept at 220 °C for 5 h in an oven. After cooling to room temperature, the precipitates were collected by centrifugation, washed several times with absolute ethanol and distilled water. The precipitates were dried at 105 °C for 8 h and then calcined in air at 600 °C for 2 h. The as-prepared $\text{ZnTiO}_3/\text{TiO}_2$ composites were correspondingly denoted as pure TiO_2 , ZnTiO_3 (2%)/ TiO_2 , ZnTiO_3 (10%)/ TiO_2 , ZnTiO_3 (20%)/ TiO_2 , and ZnTiO_3 (30%)/ TiO_2 .

2.2. Characterization of phase and microstructure

The morphologies of the as-prepared $\text{ZnTiO}_3/\text{TiO}_2$ composites with varying ZnTiO_3 content were observed by a scanning electron microscopy. The powder X-ray diffraction patterns of the powders were recorded on apparatus (D/Max-2200, Rigaku) using $\text{CuK}\alpha$ irradiation ($\lambda = 1.5408 \text{ \AA}$) in the range of 2θ , 10-70°.

2.3. Measurements of photocatalytic performance

The photocatalytic activities of the as-prepared $\text{ZnTiO}_3/\text{TiO}_2$ composites were evaluated by photocatalytic decolorization of Rhodamine B in aqueous solution under visible light irradiation. A 500 W Xenon lamp equipped with a special cut-off filter to remove ultraviolet irradiation ($\lambda < 380 \text{ nm}$) was used as a visible light source. Before exposure to the visible light irradiation, 40 mg of the powder photocatalyst was combined with 40 mL of the dye solution in a 50 mL quartz test tube and was stirred for 40 min to reach the adsorption-desorption equilibrium. The samples were then irradiated by a 500 W Xenon lamp. Eight milliliter aliquot was withdrawn at certain time intervals and then centrifuged (8000 rpm, 30 min) to remove the particles. The change of the solution absorbance with the extension of irradiation time was measured by an UV-vis spectrophotometer.

3. Results and discussion

3.1. X-ray diffraction analysis

The crystal structures of the corresponding pure TiO_2 and as-prepared $\text{ZnTiO}_3/\text{TiO}_2$ composites were measured by XRD characterization. XRD pattern of pure TiO_2 (Figure 1a) revealed the typical peaks at around $2\theta = 25.3, 37.8, 48.0, 53.9, 55.1$ and 62.7° , which were attributed to the (101), (004), (200), (105), (211) and (204) planes of TiO_2 (JSPDS 21-1272). These peaks conformed to the presence of anatase structure in the pure TiO_2 [27]. The pure TiO_2 had anatase (101) plane peak but no rutile (100) plane peak was observed, clearly indicating that only the anatase crystalline phase was present. When the ZnTiO_3 molar fraction was 2%, no obvious diffraction peak assigned to the crystal phase of ZnTiO_3 could be observed in Figure 1b.

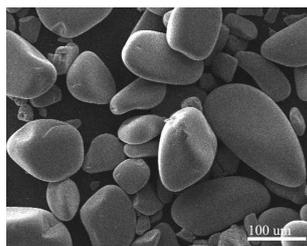


Figure 2. SEM image of pure TiO₂.

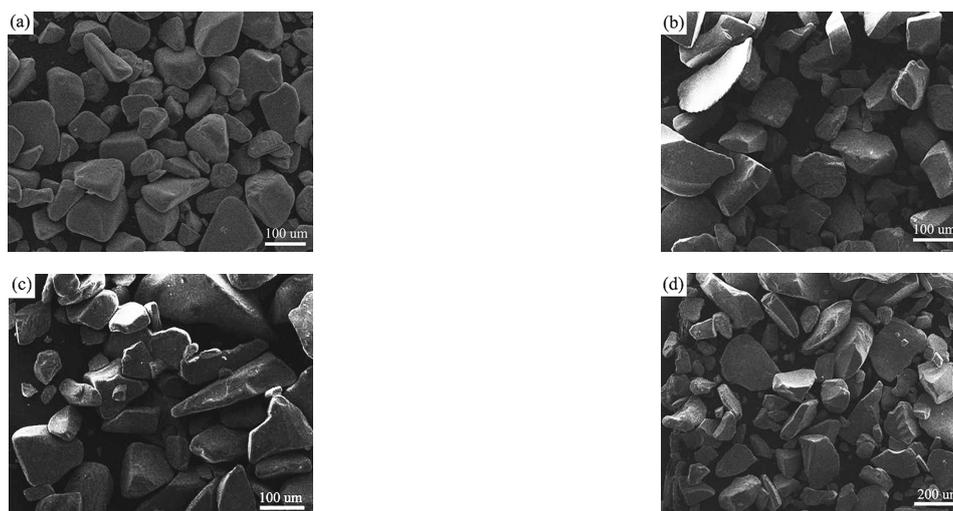


Figure 3. SEM images of as-prepared ZnTiO₃ (2, 10, 20 and 30%)/TiO₂ composites (a-d).

However, with the larger content of ZnTiO₃ in the ZnTiO₃/TiO₂ (from 10 to 30% molar fraction), it could be seen that the characteristic peak of anatase TiO₂ gradually decreased, which was shown in Figure 1c-e. XRD patterns of ZnTiO₃/TiO₂ composites (Figure 1c-e) demonstrated that the diffractions at around $2\theta = 30.0$ and 35.4° were assigned to the (220) and (311) planes of ZnTiO₃ (JSPDS 39-0190). Such results clearly indicated that two components (TiO₂ and ZnTiO₃) coexisted in the composites.

3.2. Morphology and microstructure analysis

The morphologies of pure TiO₂ and ZnTiO₃/TiO₂ composites were examined by SEM (Figure 2 and 3). As shown in Figure 2, pure TiO₂ exhibited smooth surfaces and ellipsoid-like shape, with an average size diameter around 60.54 μm. Figure 3a-d showed SEM images of ZnTiO₃/TiO₂ composites prepared by introducing different amounts of ZnSO₄ into Ti(SO₄)₂ to reach a ZnTiO₃ molar content of 2, 10, 20 and 30% in the ZnTiO₃/TiO₂ composites. The morphology depended on the ZnTiO₃ content. As the molar content of ZnTiO₃ was 2% (Figure 3a), the average size diameter (appropriately 64.12 μm) of ZnTiO₃/TiO₂ composite became larger, compared to that of pure TiO₂. When the ZnTiO₃ molar fraction was increased to 10 and 20%, larger average size diameter could be observed, compared to that of ZnTiO₃ (2%)/TiO₂. Figure 3d illustrated that average size diameter became different with larger diameters and smaller diameters in the composite containing 30% ZnTiO₃. Actually, as clearly shown in Figure 3, the as-prepared ZnTiO₃/TiO₂ composites owned a relatively big particle size, which enabled them to be employed as promising spraying materials for metal corrosion prevention and wear resistance.

3.3. Enhanced photocatalytic performance

RhB was used as the target probe molecule for photocatalytic degradation reactions to evaluate the photocatalytic capability of pure TiO₂ and as-prepared ZnTiO₃/TiO₂ composites under visible light irradiation. Figure 4 displayed the photodegradation of RhB as a function of irradiation time over pure TiO₂ and ZnTiO₃ (2, 10, 20 and 30%)/TiO₂ composites. As clearly shown in Figure 4f, based on a blank experiment without any catalyst, the self-photolysis of RhB under visible light irradiation could be ignored, corroborating the degradation reaction was truly driven by the photocatalytic process. It could be seen from Figure 4 that 62.2, 87.5, 52.5, 27.8 and 36.5% of RhB had been effectively degraded over pure TiO₂ and ZnTiO₃ (2, 10, 20 and 30%)/TiO₂ for 5 h, respectively. It was found that pure TiO₂ exhibited photocatalytic activity under the visible light irradiation, the reason might be that added C₆H₁₂N₄ in the experiment not only provided an alkaline environment, meanwhile added C₆H₁₂N₄ acted as the nitrogen source for nitrogen doping into TiO₂, so the as-prepared TiO₂ exhibited photocatalytic activity under visible light irradiation. ZnTiO₃ (2%)/TiO₂ exhibited the highest photocatalytic activity among the as-prepared ZnTiO₃/TiO₂ composites, which increased photodegradation efficiency by 25.3% compared to the pure TiO₂. As the molar fraction of ZnTiO₃ increased from 2 to 10%, a decrease in the photocatalytic activity of ZnTiO₃ (10%)/TiO₂ composite was observed. With the 20 and 30% content of ZnTiO₃, the photocatalytic activities of ZnTiO₃ (20%)/TiO₂ and ZnTiO₃ (30%)/TiO₂ could be seen from Figure 4d-e.

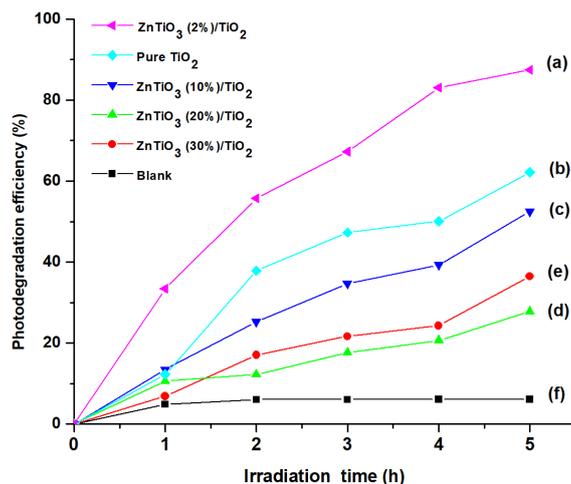


Figure 4. Photocatalytic activities of blank (without catalyst), pure TiO₂, and as-prepared ZnTiO₃/TiO₂ composites on the degradation of RhB under visible light irradiation.

3.4. Photocatalytic reaction mechanism of ZnTiO₃/TiO₂

The reason for the improved photocatalytic performance might be that electrons and holes induced in ZnTiO₃ were separated and pushed to the side of TiO₂, and those generated active electrons and holes could act in the reduction of oxygen molecules to radicals and oxidation of water molecules to hydroxyl radicals [28]. Generally, organic molecules such as RhB could be efficiently degraded by these generated active radicals. So, ZnTiO₃ (2%)/TiO₂ exhibited higher photocatalytic activity than pure TiO₂. However, the increase of molar fraction of ZnTiO₃ led to the increase of particle size, which could be seen from Figure 3a-c. The larger particle size resulted in the longer migration distance of photo-generated electrons and holes, which could improve the recombination of photo-generated carriers and decrease the photocatalytic activity. The particle size of ZnTiO₃ (30%)/TiO₂ became different with larger diameters and smaller diameters, which led to lower photodegradation efficiency than ZnTiO₃ (10%)/TiO₂ and higher photodegradation efficiency than ZnTiO₃ (20%)/TiO₂.

4. Conclusions

In summary, ZnTiO₃/TiO₂ composites were synthesized via a facile hydrothermal method exhibited photocatalytic activity. By tuning the different amounts of ZnSO₄, different ZnTiO₃/TiO₂ composites were successfully obtained. ZnTiO₃ (2%)/TiO₂ composite exhibited the superior photocatalytic activity with 87.5% RhB degradation rate (compared to pure TiO₂ of 62.2%) under the visible light irradiation. Therefore, use of ZnTiO₃/TiO₂ composites showed advantages of low cost, re-usability and enhanced photocatalytic activity. In addition, the as-prepared ZnTiO₃/TiO₂ composites owned a relatively big particle size, which enabled them to be employed as promising spraying materials for metal corrosion prevention and better photocatalytic applications. This study could promote the synthesis of photocatalysts that exhibited high photodegradation efficiency and further application in the spraying fields.

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Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.

Author contributions: All authors contributed equally to this work.

Ethical approval: All ethical guidelines have been adhered.

Sample availability: Samples of the compounds are available from the author.

ORCID

Zhenzhao Pei

<http://orcid.org/0000-0003-4298-7539>

Pei Wang

<http://orcid.org/0000-0001-6382-6182>

Zhiguo Li

<http://orcid.org/0000-0002-9446-2091>

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