

Hydrothermal synthesis and photocatalytic properties of titanium acid $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ nanosheets

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Abstract

Titanium acid $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ with nanosheet morphology has been prepared by doping Zn^{2+} into Ti–O crystal structure through the hydrothermal method. The products were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscope (XPS), transmission electron microscopy (TEM), and ultraviolet–visible (UV–vis) spectroscopy. It indicated that Zn^{2+} doping plays an important role in formation of layered $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$. The photo-catalytic activity of the samples was characterized by the depigmentation of methyl orange solution by UV light irradiation. It demonstrated that $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ possess good photocatalytic properties in water purification and may find potential application in related fields.

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1. Introduction

TiO_2 have attracted a great deal of attention because of its high photocatalytic activity which may find potential application in environmental purification [1–4]. In the first instance, people devoted themselves to the synthesis of TiO_2 with nano-scale dimensions. This was motivated by a known concept that photocatalytic activity of TiO_2 will be enhanced due to quantum-size effect and specific surface effect. With the development of researches, it is found that the properties of some semiconductor nanomaterials are markedly affected by impurities, and consequently these constituents also affect applications and economic value [5], the researches of doping Zn^{2+} into TiO_2 have been widely unfolded [6] and gotten some initial results [7–9]. In spite of this, the research is farther away to complete and the synthesis conditions have not been investigated in detail.

In recent years, layered compounds have been extensively studied [10–12] in this domain due to its unique structure and chemical activity [13,14]. Titanium acid, as one

of the layered compounds, attracted wide attentions due to its compositional similarity to that of TiO_2 . Some authors have obtained $\text{H}_2\text{Ti}_3\text{O}_7$ type through the alkali treatment of commercial TiO_2 [15], however, the uniformity of the products produced in this manner might be destroyed because its final transformation to $\text{H}_2\text{Ti}_3\text{O}_7$ was dynamically unfavorable although thermodynamically favorable [16]. Other authors got $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ form by the ion-exchange reaction between H^+ and prepared alkali titanates [17] which needed two steps to get the final product.

In this work, we have obtained layered titanium acid which proved to be $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ form by doping Zn^{2+} into Ti–O structure through hydrothermal method. Some reaction parameters in the hydrothermal conditions were studied in detail. The products showed nanosheet morphology and possessed the potential to be a photocatalyst in water purification according to the photocatalytic experiments.

2. Experimental

All the reagents were of analytical grade and without further purification before utilization. Firstly, different molar

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ratio of titanium sulfate and zinc sulfate were mixed evenly as initial reactants. Afterwards, they were transferred to a 50 ml Teflon-lined autoclave, where corresponding quantity of alkali solution ($n_{\text{NaOH}} = 4n_{\text{Ti}} + 2n_{\text{Zn}}$) was added. Then the autoclave was sealed and heated under auto-generated pressure at 200 °C for different reaction times. The as-formed solid precipitate was centrifuged, washed with distilled water and then dried at 80 °C for 2 h to give the products.

The structure of the products was examined by X-ray diffractometry (XRD, Bruker Advance D-8) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The elements composition was detected by X-ray photoelectron spectroscope (XPS), XPS measurements were performed on a MK II system with Mg K α radiation as the exciting source, where the binding energies were calibrated by referencing the C 1s peak to reduce the sample charge effect. The morphology of the samples was investigated by transmission electron microscopy (TEM, Model Hitachi H-700H, 200 kV). Optical absorption studies were carried out using a UV–vis–NIR spectrophotometer (Shimadzu UV-3101PC).

The photocatalytic property of the products was tested in our house-made instruments. A commercial 400 W high-pressure Hg lamp was used as the light source. Before illumination was turned on, the suspension with methyl orange and photocatalyst was magnetically stirred in a dark condition for 30 min to establish an adsorption–desorption equilibrium. The first sample was taken out at the end of the dark adsorption period, just before the light was turned on, in order to determine the methyl orange concentration in solution, which was hereafter considered as the initial concentration after dark adsorption. Samples were then withdrawn regularly from the reactor and centrifuged immediately for separation of the suspended solids. The clean transparent solution was analyzed with UV–vis spectroscopy.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products obtained from alkali treatment of titanium sulfate and zinc sulfate sep-

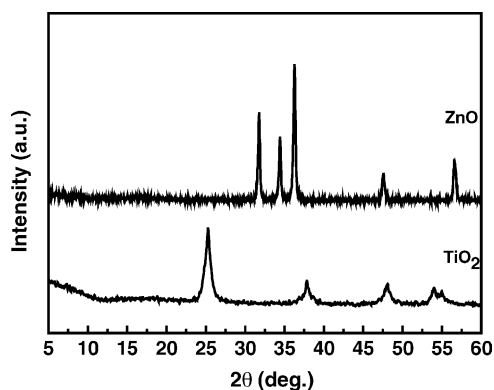


Fig. 1. The XRD patterns of pure TiO₂ and ZnO prepared at 200 °C for 12 h.

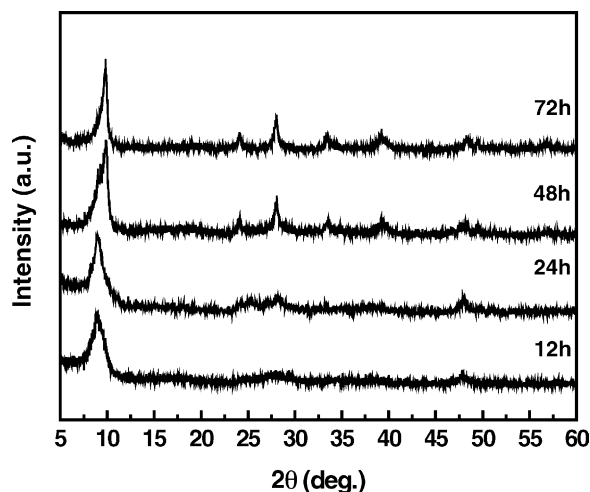


Fig. 2. The XRD patterns of as-prepared products with 5% Zn/Ti + Zn molar ratio at 200 °C for different time.

arately at 200 °C for 12 h. Seen from the pattern, pure TiO₂ and ZnO products can be obtained under this reaction conditions according to JCPDS 21-1272 and JCPDS 36-1451, respectively. However, when titanium sulfate and zinc sulfate were mixed with different molar ratio together, there happened some change. All of the XRD results showed the products are amorphous.

To quest for the doping technique, we kept the molar ratio of Zn/Ti + Zn be 5% and prolonged the reaction time. Fig. 2 gives the products synthesized at 200 °C for 12–72 h. It is obvious that the variation of reaction time causes a change in the XRD patterns of the resulting products. When the time exceeded 24 h, the product became crystallized and when the time was prolonged to 48 h, the product got crystallized well. When the reaction time was further prolonged to 72 h, there was no obvious change relative to the sample for 48 h. According to JCPDS card 47-0124, the crystallized product proved to be H₂Ti₂O₅·H₂O and no any peaks which belong to TiO₂ or ZnO appear.

To characterize the role of Zn²⁺ in the process of synthesizing H₂Ti₂O₅·H₂O, some experiments with different molar ratio of Zn/Ti + Zn were taken under 200 °C for 48 h. Fig. 3

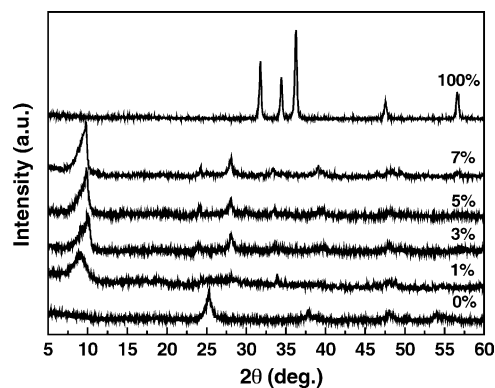


Fig. 3. The XRD patterns of as-prepared product with different Zn/Ti + Zn molar ratio at 200 °C for 48 h.

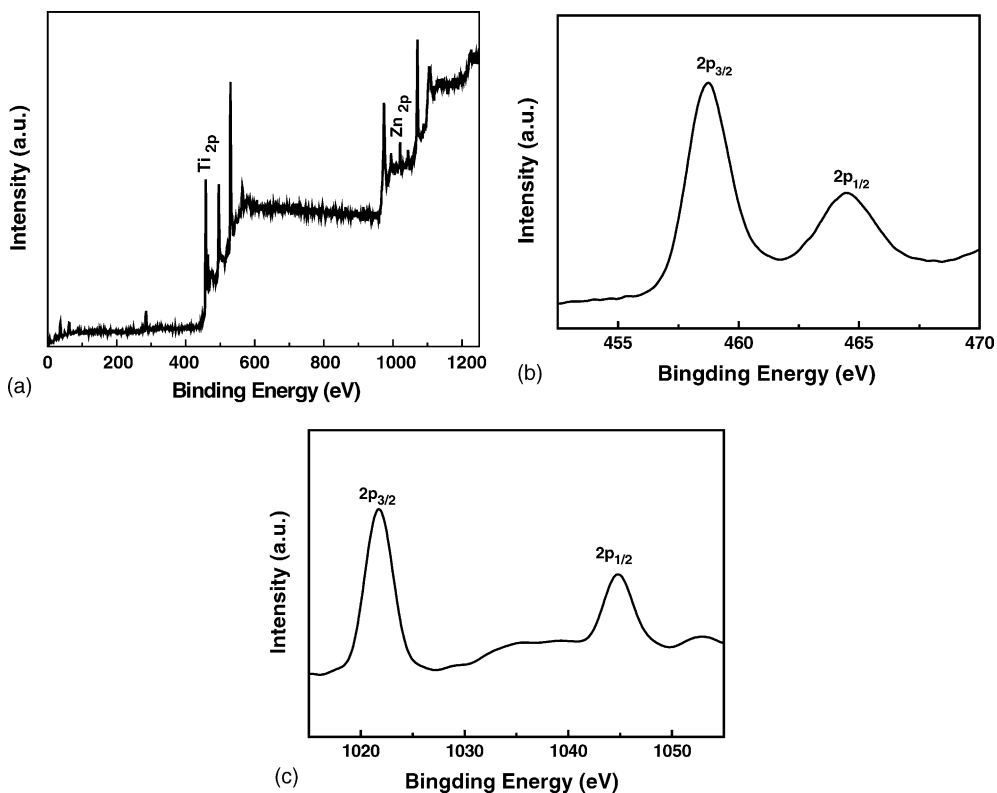


Fig. 4. The XPS patterns of as-prepared $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$ whose Zn/Ti + Zn molar ratio is 5%.

shows the final results. Seen from the XRD patterns, when no Zn^{2+} was added, the product showed to be pure TiO_2 . While when the molar ratio of Zn/Ti + Zn was 1%, the $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$ product became amorphous. Until the ratio reached to 3%, the product became crystallized, and kept the ratio increasing to 5%, even to 7%, there was no obvious change except a slightly shift of the main peaks which may be caused by superfluous Zn^{2+} situated between the layers.

Fig. 4(a) shows the XPS survey spectra of the as-synthesized product whose Zn/Ti + Zn molar ratio is 5%. Seen from its local chart, the binding energy of Ti 2p_{3/2} (Fig. 4(b)) for the as-synthesized product is 458.7 eV which agrees with the literature value of TiO_2 [18], and the binding energy of Zn 2p_{3/2} (Fig. 4(c)) is 1021.8 eV which accords with the literature value of ZnO [19]. However, there were not any characteristic peaks about ZnO appeared in the XRD patterns of $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$. So we perfumed that Zn^{2+} entered into the Ti–O crystal structure and replaced partially Ti^{4+} due to their similar ionic radius when they were mixed together in hydrothermal process, and the progress needs a longer time than 48 h at 200 °C. When Zn^{2+} replaced Ti^{4+} in amorphous state, some H^+ may be adsorbed into the crystal structure to keep whole charge conservation. Pre-formed product acted as the crystal seeds and induced the continuous reaction. Consequently, the final product $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$, formed.

Fig. 5 gives the TEM image of the as-synthesized products whose Zn/Ti + Zn molar ratio is 5%. Seen from the figure, the sample shows nanosheet shape whose width is about 200 nm

and length is near to 500 nm. It was thought that this kind of morphology was suitable to transform to some new types of nanostructure such as nanotube, multi-nanofilm and nano-compound materials [20,21]. The inset SAED pattern taken

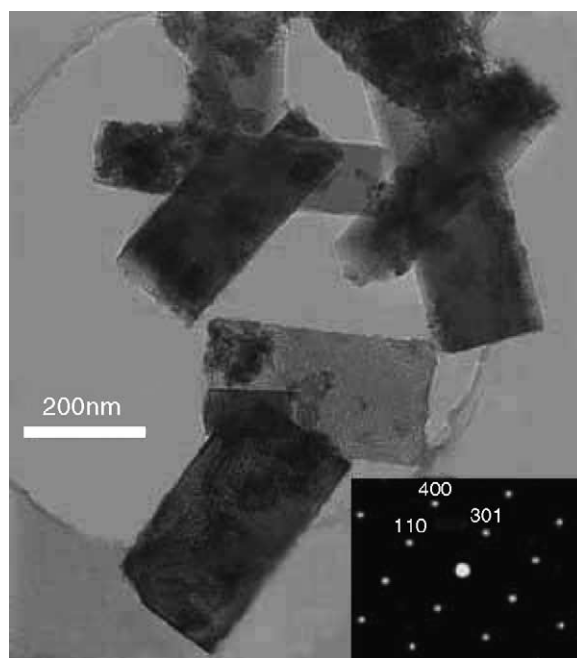


Fig. 5. TEM and SAED patterns of as-prepared $\text{H}_2\text{Ti}_2\text{O}_5\cdot\text{H}_2\text{O}$ whose Zn/Ti + Zn molar ratio is 5%.

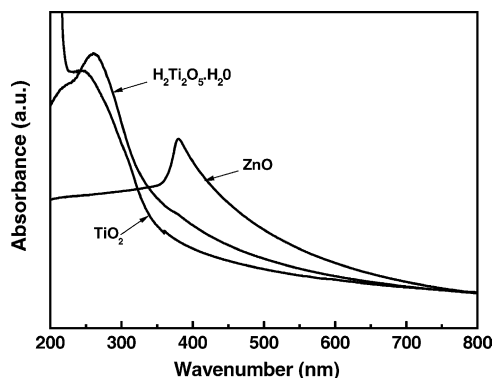


Fig. 6. UV-vis patterns of as-synthesized TiO_2 , ZnO and $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ whose Zn/Ti + Zn molar ratio is 5%.

from individual nanosheet confirms the products are well-crystallized single crystals.

Fig. 6 shows the whole UV-vis spectra of the as-synthesized TiO_2 , ZnO and $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ whose Zn/Ti + Zn molar ratio is 5%. The as-synthesized TiO_2 is of anatase structure with the particle size of about 10 nm. The average size of ZnO particles is about $2 \mu\text{m}$. Usually ZnO would grow to micron size under hydrothermal condition if no template or surfactant was adopted [22]. As can be seen from the figure, the absorbance edge of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is closer to the one of TiO_2 which indicates that $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ has similar optic quality with TiO_2 . The difference of the two Ti-based compounds lies that $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ has a little shift to visible area comparative to TiO_2 . It may due to the effect of implanted Zn^{2+} . The as-synthesized ZnO in our experiments has an absorbance in the visible area which can be seen from the spectra.

Fig. 7 gives the depigmentation curves of methyl orange solutions with the addition of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ whose Zn/Ti + Zn molar ratio is 5% under ultraviolet light. The concentration of the catalyst is 2 g/L. Curve A shows the depigmentation curve of absolute methyl orange solution without any $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ irritated under ultraviolet light

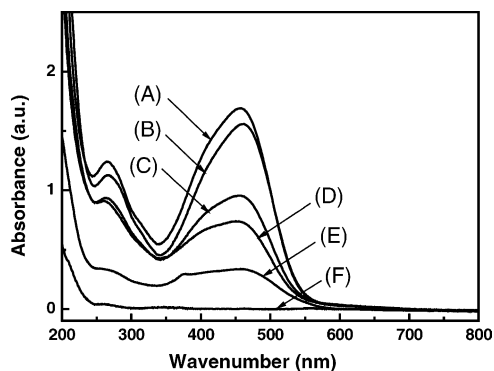


Fig. 7. Depigmentation curves of methyl orange solutions under ultraviolet light: (A) without $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 50 min; (B) with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 10 min; (C) with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 20 min; (D) with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 30 min; (E) with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 40 min; (F) with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ for 50 min.

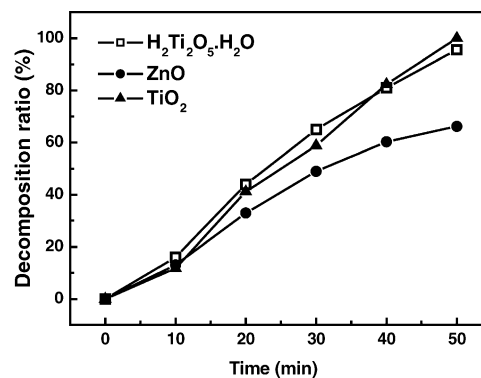


Fig. 8. Methyl orange solution decomposition ratio with different photocatalysts under ultraviolet light for different time.

for 50 min, while other curves denote methyl orange solution with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ irritated under ultraviolet light for different time. Seen from the pattern, $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ played the role of photocatalyst in the depigmentation of methyl orange solution. Under its role, the solutions with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ depigmented gradually and were almost decolorized totally when the irritated time was up to 50 min.

Fig. 8 shows the decomposition ratio of methyl orange solution with the role of 2 g/L as-synthesized TiO_2 , ZnO and $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ under ultraviolet light for different time. Seen from the results, all the solutions depigmented gradually with elonged irritation time, and after 50 min, the decomposition ratio of methyl orange solution with TiO_2 has reached nearly to 100%. At this time, the depigmentation ratio of solution with $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ is 95.6% which is lower slightly than TiO_2 . In spite of this, $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ may still find potentially much wider application than TiO_2 due to its unique layered structure. Although ZnO also took the role of photocatalyst in the depigmentation of methyl orange like the above two, however, its ability is weaker comparatively, the decomposition ratio is just 66.2% after 50 min. It may due to its large size which is about $2 \mu\text{m}$ in our hydrothermal growth atmosphere.

Fig. 9 shows the effect of concentration of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ on the depigmentation activity of methyl orange under the

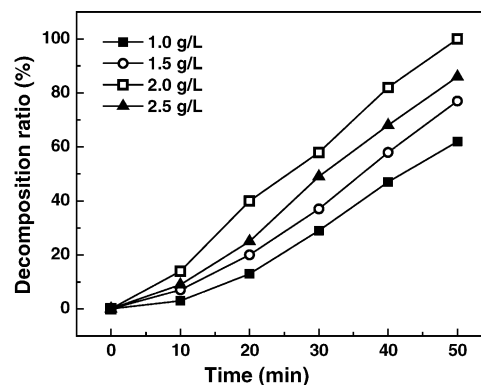


Fig. 9. The effect of concentration of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ catalysts on the depigmentation activity of methyl orange under the irradiation of UV light.

irradiation of UV light. The concentration of methyl orange decreased negligibly over the time span of these experiments in the absence of photocatalysts. A blank experiment in the absence of irradiation but with the prepared catalysts demonstrates that no significant change in the concentration was found. As shown in Fig. 9, the concentration of $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ catalysts has a great effect upon its ability to depigment the aqueous methyl orange. The decomposition rate of methyl orange increases with the increasing concentration of photocatalysts, reaches the higher value at 2 g/L and then decreases. This phenomenon attributed to the so-called shielding effect; after exceeding the optimal amount, the suspended catalysts reduce the penetration of the light in the solution [23]. Similar phenomena were found in the study of the TiO_2 and $\text{Bi}_2\text{Ti}_2\text{O}_7$ photocatalysts [23,24], the catalysts concentration were all shown having an optimal amount, to support the catalysts showing the highest activity.

4. Conclusion

In summary, layered titanium acid $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ nanosheet has been synthesized via doping Zn^{2+} into the Ti–O crystal structure in hydrothermal process. The as-synthesized products were characterized by XRD, XPS, TEM, and UV–vis spectroscopy. In this route, Zn^{2+} played an important role in the formation of final product. Layered titanium acid $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ synthesized by this method has shown superior photocatalytic property in water purification and may find much wider applications due to its unique structure.

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