

Zinc ions surface-doped titanium dioxide nanotubes and its photocatalysis activity for degradation of methyl orange in water

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Abstract

Zn ions surface-doped TiO₂ nanotubes were synthesized via an assembly process based on ligand exchange reaction and with additional thermal treatment. First the ligand exchange reaction between zinc acetylacetonate and hydroxide radicals on TiO₂ surface introduced the Zn ions onto the surface of TiO₂ nanotubes, then the Zn(acac)₂ assembled TiO₂ nanotubes were calcined at an optimal temperature (400 °C) to eliminate the organic ligands. The as-prepared Zn ions surface-doped TiO₂ nanotubes showed a further improvement on the photocatalysis activity for degradation of methyl orange in water.

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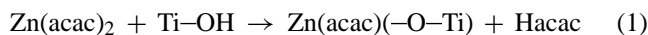
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1. Introduction

Titanium dioxide, as a popular nanomaterial, has numerous potential applications such as photocatalysis [1], liquid solar cell [2], and electroluminescent hybrid device [3]. Its tubular structures, TiO₂ nanotubes have been considered more practical in photocatalysis and optical-electronic devices because of their unique shape, size confinement in radial-direction and large surface-to-volume ratio. Most of the researches in this area are generally directed toward the synthesis and characterization of TiO₂ nanotubes [4–6], with actual application perceived to be years away. For photocatalysis or optical-electronic device applications, it is necessary to follow the proven method of preparing transition metal ions doped TiO₂ nanotubes to effectively enhance the separation of electron/hole pairs and quantum efficiency of TiO₂ [1,7,8]. Although various transition metal ions doped TiO₂ colloids and nanoparticles have been successfully prepared

[7–10], there has been no report on synthesizing transition metal ions doped TiO₂ nanotubes.

Recently, we have developed a simple method to prepare Zn ions surface-doped TiO₂ nanoparticles [11]. Firstly, a ligand exchange reaction between zinc acetylacetonate and hydroxide radicals on TiO₂ surface resulted in the introduction of Zn ions onto the surface of TiO₂ nanoparticles:



Then, a further thermal treatment at 500 °C eliminated the organic ligands to form the Zn ions surface-doped TiO₂ nanoparticles. This method allowed metal ions to be located on the surface of TiO₂ nanoparticles rather than in the lattice. The metal ions on the surface act as a charge separation center to enhance the photocatalysis activity of TiO₂. In this study, we will demonstrate that this approach is applicable to synthesize Zn ions surface-doped TiO₂ nanotubes. Taken into consideration that, on one hand, the calcination at a high temperature may destroy the microstructure of TiO₂ nanotubes, however, on the other hand, the calcination at a low temperature is not favorable for the complete decomposition of zinc complex, an optimal calcination temperature

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is necessary for producing Zn ions surface-doped TiO₂ nanotubes. The thermogravimetric and differential thermal analyses (TGA–DTA), as well as transmission electron microscope (TEM) investigation, were employed here to determine the optimal calcination temperature for Zn(acac)₂ assembled TiO₂ nanotubes. The experiment for degradation of methyl orange in water under UV irradiation was carried out to value their photocatalytic activity.

2. Experimental section

2.1. Synthesis of TiO₂ nanotubes

TiO₂ nanotubes with a diameter of 8–10 nm were synthesized via a hydrothermal chemical process [5]. Typically, 2.5 g pure TiO₂ powders of anatase phase were mixed with 10 M NaOH aqueous solution in a Teflon vessel at 110 °C for 20 h. The resulted product was treated with 0.1 M HCl and further washed with distilled water.

2.2. Synthesis of zinc acetylacetonate

Zinc acetylacetonate was prepared by a general method involving the reaction of acetylacetonate and metal salts [12,13]. Acetylacetonate (99%, Beijing Chemical Factory, Beijing, China) was added to the ethanol solution of zinc acetate (99%, Beijing Chemical Factory, Beijing, China) under stirring for 8 h. The white powder of zinc acetylacetonate was rinsed with ethanol using filtration for several times and finally dried under vacuum.

2.3. Synthesis of TiO₂(–Zn) nanotubes

The procedure used to prepare Zn ions surface-doped TiO₂ nanotubes is shown schematically in Fig. 1. First 0.5 g TiO₂ nanotubes (pH = 7–8) were sonicated in 20 ml of 1 M HCl solution for 3 h to remove residual Na⁺ (pH = 5–6) and washed with distilled water using filtration. Then the resulting TiO₂ nanotubes (Fig. 1b) were mixed with an acetonitrile solution (50 ml) containing 0.1 M zinc acetylacetonate under stirring for 6 h. This step allowed an assembly process based on a ligand-exchange reaction between the ligands of Zn(acac)₂ and the protons of hydroxide radicals on TiO₂ nanotubes (Fig. 1c), which was due to the nucleophile of the ligands of Zn(acac)₂ [14]. The Zn(acac)₂ assembled TiO₂ nanotubes (pH = ~7)

were washed with acetonitrile to remove physical absorbed Zn(acac)₂, and finally calcined at 400 °C for 1 h to eliminate organic ligands.

2.4. Characterization of TiO₂(–Zn) nanotubes

The transmission electron microscope (TEM) investigation was performed on a JEOL-2010 microscope at 200 kV. A Setarm 92A instrument was used for thermogravimetric and differential thermal analysis (TGA–DTA). The samples were heated up to 800 °C with a rate of 10 °C min⁻¹. The elementary composition was determined by an atomic absorption spectrometer (AAS, WFX-10) using flame method. XPS measurements were performed in an X-ray photoelectron spectrometer PHI-5702 using the Al Kα X-ray beam.

2.5. Measurement of photocatalytic activity

Photocatalytic activity experiments of Zn ions surface-doped TiO₂ nanotubes and other catalyst for the degradation of methyl orange in water were performed in a light reactor. The catalysts were dispersed in 100 ml 20 mg/l methyl orange aqueous solution. The weight of the photocatalyst used in each experiment was kept at 0.2 g. The reactor was sparged with air at 0.2 m³/h and illuminated by a 400 W high-pressure mercury lamp. The concentrations of methyl orange solution were quantified by a VIS-7220 spectrophotometer at 464 nm [15].

3. Results and discussion

3.1. Thermogravimetric and differential thermal analysis

Fig. 2 shows the TGA–DTA curves of Zn(acac)₂, TiO₂ nanotubes and Zn(acac)₂ assembled TiO₂ nanotubes. Pure Zn(acac)₂ in Fig. 2a exhibited a weight loss of about 63.5% at 100–250 °C with a corresponding sharp DTA peak at 200 °C, caused by the complex decomposition. No noticeable weight loss occurred at above 250 °C, an indication that the decomposition was completed at 250 °C. Another distinct feature of Fig. 2a is the broad DTA peak at about 370 °C with a shoulder at ~455 °C, which should be assigned to the crystallization of ZnO [16]. TiO₂ nanotubes showed a continual weight loss below 300 °C (about 3.5%) followed by a

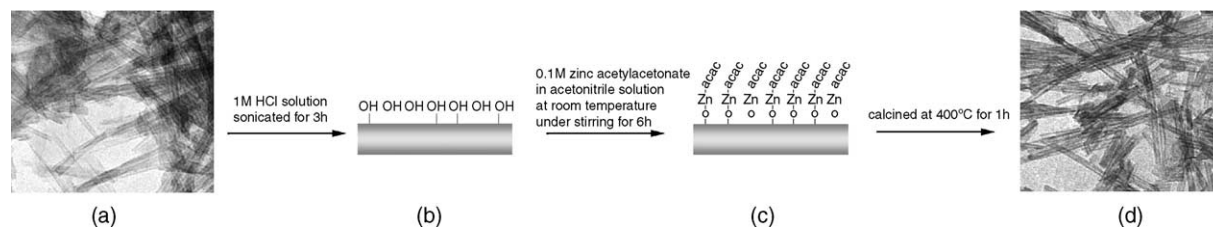


Fig. 1. A schematic diagram showing the steps for the synthesis of Zn ions surface-doped TiO₂ nanotubes.

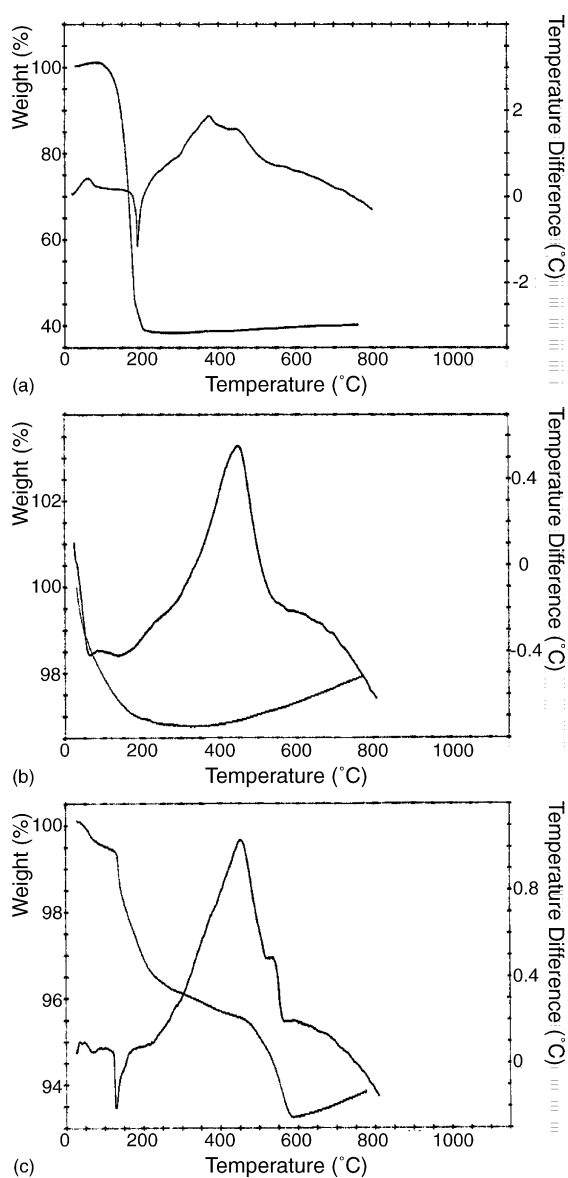


Fig. 2. TGA–DTA curves of (a) pure $\text{Zn}(\text{acac})_2$, (b) TiO_2 nanotubes, and (c) $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes.

continual small amount of weight increase above 370°C (Fig. 2b). The weight fluctuation can be attributed to the release of water adsorbed on/in nanotubes and the further oxidation of TiO_2 nanotubes, respectively. A strong DTA peak at $\sim 450^\circ\text{C}$ should be ascribed to the recrystallization of anatase TiO_2 .

$\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes exhibited two clear weight losses in Fig. 2c, one immediately below 100°C due to the removal of adsorbed water corresponding to a small DTA peak at $60\text{--}70^\circ\text{C}$, and the other at in-between $100\text{--}250^\circ\text{C}$ due to the complex decomposition corresponding to the main DTA peak at 140°C with a shoulder at 155°C . In addition to the strong DTA peak of the recrystallization of TiO_2 at 450°C , the occurrence of weight loss at $470\text{--}580^\circ\text{C}$ (about 2.3%) is difficult to assign compared to the individual TGA curves of $\text{Zn}(\text{acac})_2$ and TiO_2 nanotubes. The possibility of any unexpected phase transition in TiO_2 is eliminated as no DTA peak is observed at $470\text{--}580^\circ\text{C}$ range except for the strong peak at 450°C , similar to that of TiO_2 nanotubes. This particular weight loss may be a result of the release of adsorbed water in nanotubes, which is interfered by the composition change and complex decomposition on nanotube surface.

3.2. Transmission electron microscope investigation

Fig. 3 shows the TEM images of $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes at different calcination temperature. For Fig. 3a, it can be seen that $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes were in good tubular structure and there was no obvious damage caused by calcination at 300°C . Fig. 3b shows that $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes had little sintering damage until the calcination temperature raised up to 400°C . When calcined at 500°C , $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes showed more sintering damages and agglomerated together although most of them retained tubular structure. The insets of each TEM images are the corresponding selective area electron diffraction (SAED) patterns. They indicate that a definite improvement in the crystallization of TiO_2 can be obtained with an increase in the calcination temperature. From the thermal analysis and TEM results, it

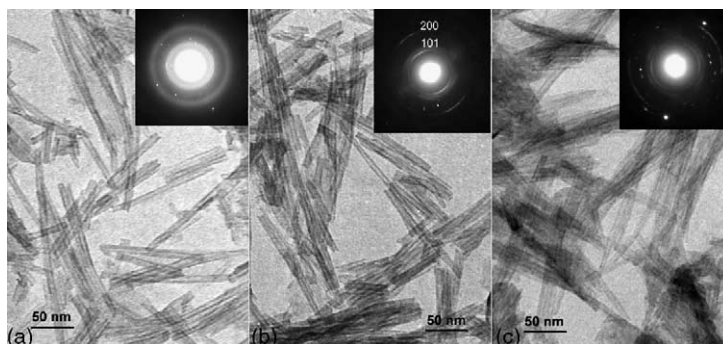


Fig. 3. TEM images of $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes at different calcination temperatures: (a) 300°C , (b) 400°C , and (c) 500°C for 1 h.

can be concluded that the optimal calcination temperature for $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes is 400°C , at which the complex decomposition is completed and nanotubes remain to be in good tubular structures and with a better crystallization.

The diameters of Zn ions surface-doped TiO_2 nanotubes is about 8–10 nm with little variance compared to the uncovered nanotubes (see Fig. 3b). The two tube-sides of ZnO coated TiO_2 nanotubes are darker than that of uncoated TiO_2 nanotubes (Fig. 1a), which is likely due to the sintering during the calcination. Additionally, it can be seen that the long tubes can be broken into shorter segments by calcinations. The SAED patterns of ZnO coated TiO_2 nanotubes present two clear diffraction rings, which can be identified as (1 0 1) and (2 0 0) of the anatase of TiO_2 crystal. The TEM investigations imply that the doping of Zn ions has little effect on the structure of TiO_2 nanotubes, i.e. Zn ions surface-doped TiO_2 nanotubes remained in the good tubular structures despite of the sintering effect by calcination.

3.3. AAS and XPS analysis

The ligand exchange reaction between $\text{Zn}(\text{acac})_2$ and hydroxide radicals on TiO_2 nanotubes resulted in the introduction of Zn ions onto the surface of TiO_2 nanotubes, proven with the results of XPS (PHI-5702) and AAS (WFX-10). The atomic ratio of Zn/Ti in $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes was 0.12 with XPS and 0.02 with AAS. Taken into consideration that XPS result corresponds to the surface composition and AAS analysis provides the average composition of a sample, it can be concluded that Zn ions were primarily located on the surface of TiO_2 nanotubes. The XPS and AAS results of Zn ions surface-doped TiO_2 nanotubes also indicated that Zn ions were located on the surface of TiO_2 nanotube (the atomic ratio of Zn/Ti, 0.13 by XPS and 0.03 by AAS).

3.4. Photocatalytic activity for degradation of methyl orange in water

The percent of residual methyl orange at different UV light irradiation time over $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes calcined at different temperature are shown in Fig. 4. $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes calcined at 300°C showed a very low photocatalysis activity for degradation of methyl orange in water. The solution still remained 19.72, 19.08 and 18.24 mg/l methyl orange after irradiated for 1, 2 and 3 h. Its low photoactivity may be attributed to the uncompleted complex decomposition on nanotubes' surface, which blocked the degradation reaction. For $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes calcined at 400°C , it presented a much higher photoactivity for degradation of methyl orange. The solution contained 13.82, 9.44 and 7.02 mg/l methyl orange as irradiated for 1, 2 and 3 h. $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes calcined at 500°C showed a lower photoactivity than that calcined at 400°C . There remain 15.32, 12.70 and 10.82 mg/l methyl orange after irradiated 1, 2 and 3 h. That

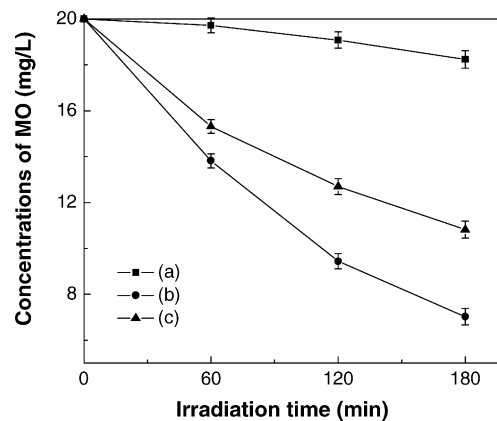


Fig. 4. The residual methyl orange at different irradiation time for $\text{Zn}(\text{acac})_2$ assembled TiO_2 nanotubes calcined at (a) 300°C , (b) 400°C and (c) 500°C .

is probably due to the agglomeration and sintering damage of nanotubes caused by calcination at high temperature.

Fig. 5 shows the residual methyl orange at different irradiation times for different catalysts. For comparison, the pure TiO_2 nanoparticles and Zn ions surface-doped TiO_2 nanoparticles prepared using same method were also present in the photo degradation experiment under same experimental conditions. Pure TiO_2 nanoparticles are more active than pure TiO_2 nanotubes for photo degradation of methyl orange. Its solution remained 16.24, 13.86 and 12.62 mg/l methyl orange after irradiated 1, 2 and 3 h. The Zn ions surface-doped TiO_2 nanotubes had an obvious increase on the photoactivity of TiO_2 nanotubes. In our previous work [11], the Zn ions surface-doped TiO_2 nanoparticles showed an enhancement on the photoactivity of TiO_2 nanoparticles, which is ascribed to that Zn ions on its surface facilitate the charge separation. In this report, Zn ions surface-doped TiO_2 nanotubes showed a further improvement on the photocatalysis activity, which indicates that larger surface area and pore size of nanotubes might be beneficial for the degradation reaction involving contact of organic molecules.

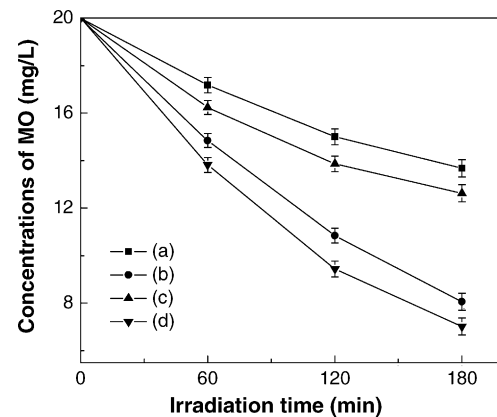


Fig. 5. The residual methyl orange at different irradiation time for (a) pure TiO_2 nanoparticles, (b) Zn ions surface-doped TiO_2 nanoparticles, (c) pure TiO_2 nanotubes, and (d) Zn ions surface-doped TiO_2 nanotubes.

4. Conclusion

In summary, we have demonstrated for the first time the synthesis of metal ions surface-doped TiO₂ nanotubes. TiO₂ nanotubes with Zn ions surface doping can be synthesized via an assembly process based on ligand exchange reaction and with additional thermal treatment. TGA–DTA and TEM results reveal that the optimal thermal treatment temperature should be 400 °C. TEM results also show that Zn ions doping has little effect on the microstructure of TiO₂ nanotubes. XPS and AAS results indicate that Zn ions are primarily located on the surface of TiO₂ nanotubes. The Zn ions surface-doped TiO₂ nanotubes exhibit a further improvement on the photocatalytic activity for the degradation of methyl orange in water. The approach is also applicable to synthesize other transition metals modified TiO₂ nanotubes for the improvement of photocatalysis activity.

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