One-step hydrothermal preparation and characterization of ZnO–TiO2 nanocomposites for photocatalytic activity

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Abstract

ZnO–TiO2 nanowire composites with different Zn/Ti molar ratios were prepared by one-step hydrothermal process. The crystal structure, surface morphology and chemical state of the samples were characterized by XRD, SEM, TEM and XPS. The effect of ZnO content on the photocatalytic performance was investigated by degradation of Rhodamine B dye under xenon lamp illumination. The XRD result indicated that Zn/Ti molar ratio significantly affected the crystallinity and phase composition of ZnO–TiO2 composites. SEM images showed that ZnO nanoparticles of smaller size were dispersed on the surface of TiO2 nanowires and aggregated in the TiO2 framework. The optimal Zn/Ti molar ratio of 5% was obtained with highest photocatalytic activity, which could be attributed to the superior charge separation ability.

1. Introduction

Due to the unique properties such as chemical stability, low cost and nontoxicity, TiO2 photocatalyst has been widely used in environmental protection [1–3]. It is well known that TiO2 generally exists in three crystalline phases namely anatase, rutile, and brookite. The photocatalytic activity of TiO2 strongly depends on the crystallite phase and morphology [4]. One-dimensional (1D) nanostructure TiO2 related to nanotubes, nanorods, and nanowires [5–7] has a particular advantage due to their high aspect ratio as well as high specific surface and efficient charge transfer, which are beneficial to improve photocatalytic activity. However, anatase TiO2 with a large bandgap of 3.2 eV can only absorb the ultraviolet (UV) light of the solar spectrum during photocatalysis [8, 9]. The photocatalytic application of pristine TiO2 is greatly limited by its fast recombination of photoinduced electron-holes and poor visible light absorption [10, 11]. Thus, various effective strategies have been developed to enhance the photocatalytic efficiency of TiO2. It has been reported that TiO2 coupling with other semiconductors to form a heterojunction could accelerate transfer of photoinduced charge carriers and extend the photoresponse of TiO2 into the visible light region [12, 13]. Typical coupled composites including ZnO/TiO2 [14], CdS/TiO2 [15], WO3/TiO2 [16], SnO2/TiO2 [17], Fe2O3/TiO2 [18] and MoS2/TiO2 [19] have been extensively investigated to demonstrate better photocatalytic properties than pure TiO2. Among these semiconductors, the modification of TiO2 with ZnO is considered to be a promising strategy which can promote the transfer of photogenerated electrons from ZnO to anatase and holes transfer in the opposite direction [20–22]. Thus the quantum efficiency of TiO2 could be significantly enhanced. In this study, One-dimensional structure ZnO–TiO2 nanowire composites with various Zn/Ti molar ratios were synthesized by a facile hydrothermal method. The influence of Zn/Ti molar ratio on the crystal structural, morphological and photocatalytic properties was investigated in detail. The optimal Zn/Ti molar ratio was obtained to achieve superior photocatalytic activity.

2. Experimental

2.1. Synthesis

In a typical synthesis, the precursor of TiO2 (8 ml titanium butyrate) was dissolved in ethanol with a volume ratio of 1:2. Then different calculated amounts of Zn (NO3)2 · 6H2O (Zn/Ti molar ratio of 0, 1%, 3%, 5% and 7%,
respectively) were added into the mixed solution under a magnetic stirring. 3 ml of 10 M NaOH solution was added drop by drop into the mixed solution with continuous stirring. After that, the mixture was moved to a Teflon-lined stainless steel autoclave of 50 ml and heated at 180 °C for 24 h. The products were repeatedly washed with 0.1 M HCl solution and deionized water until the pH value reached 7, and then dried at 80 °C. Finally, the products were annealed in a muffle furnace at 450 °C for 2 h. The samples were labeled as pureTiO2, Zn-1, Zn-3, Zn-5, Zn-7, respectively.

2.2. Characterization
The crystal phase and composition of the samples were analyzed by x-ray diffraction (XRD, DX 2700B, Dandong) with Cu Kα radiation. The morphologies of synthesized powders were observed by field-emission scanning electron microscopy (FESEM, Hitachi SU8220 and FEI Quanta 450) and high-resolution transmission electron microscope (HRTEM, JEM 2100F, Jeol). The chemical states of ZnO–TiO2 nanocomposites were investigated by x-ray photoelectron spectra (Escalab 250Xi, Thermo Scientific).

2.3. Photocatalytic performance
The photocatalytic activity of ZnO–TiO2 nanocomposites was investigated under a 350 W Xenon lamp (Solar-350, Beijing Nbet) using Rhodamine B solution (RhB, 20 mg l⁻¹) as target pollutant at room temperature. Prior to irradiation, 0.1 g of photocatalysts were dispersed in 100 ml of RhB solution and stirred for 30 min in dark to ensure adsorption–desorption equilibrium. At given intervals of irradiation times, the suspension was centrifuged and measured with the UV-Vis spectrophotometer (UV-6100A, Shanghai Metash).

3. Results and discussion

3.1. Crystal structure
Figure 1 shows the XRD patterns of ZnO–TiO2 composites with different Zn/Ti molar ratios. After hydrothermal treatment and calcination at 450 °C, the peaks of the pristine TiO2 at 24.8°, 28.8°, 33.5°, 43.8°, 48.5° and 58.1° can be indexed to the TiO2 (B) phase (JCPDS No. 46-1237) with typical monoclinic structure, which is consistent with the previous report [23]. As the addition of zinc nitrate, a mixture of anatase and rutile phase is observed. The characteristic peaks at 25.3° and 27.5° correspond to (101) and (110) planes, respectively. With an increase in the Zn/Ti molar ratio, the intensity of rutile peaks is weakened while the anatase peaks become stronger. When the concentration of ZnO reached 5%, the rutile peaks completely disappear. It is evident that the composite of ZnO could improve the crystallinity of TiO2 nanowires and the percentage of rutile phase depends on the content of ZnO. The result that the content of rutile phase decreases with increasing Zn/Ti molar ratio is in agreement with previous study [24]. However, there were few explanations on the difference of rutile phase proportion with the addition of zinc nitrate during the formation of TiO2 nanowires. According to the report [25], the type of dopants, dopant concentration, distribution, chemical environment and oxidation state all affect the anatase transformation.

3.2. XPS analysis
As the low concentration of zinc nitrate, there are no zinc-related phases observed from XRD patterns. In order to explore the elemental composition and chemical state of ZnO–TiO2 composites, XPS was carried out with 5%...
ZnO–TiO₂ sample. As shown in figure 2(a), the signals of Ti, O, Zn and C elements can be found in the XPS survey spectrum. Figure 2(b) shows the XPS spectrum of Ti 2p. The two peaks at 458.3 eV and 464.0 eV, corresponding to the Ti 2p3/2 and Ti 2p1/2, respectively, reveal the existence of Ti⁴⁺ state in TiO₂. The O 1s spectrum is depicted in figure 2(c). The peaks at 529.9 eV and 532.5 eV are ascribed to the lattice oxygen and surface adsorbed oxygen, respectively. The two peaks observed in figure 2(d) at 1021.1 eV and 1044.3 eV are assigned to Zn 2p3/2 and Zn 2p1/2, respectively, indicating the presence of Zn²⁺ state. The XPS results further confirm the existence of ZnO in ZnO–TiO₂ nanowire composites.

3.3. Morphology analysis

Figure 3 depicts the surface morphology of pure TiO₂ nanowires and ZnO–TiO₂ composites samples. As shown in figure 3(a), typical nanowires structure of pure TiO₂ prepared by hydrothermal method under alkaline condition has been obtained. The average diameter of TiO₂ nanowires ranges from 20–50 nm with the length of several micrometers. It can be seen clearly in figure 3(b) the nanowires structure has no great change with a lower content of ZnO at 1%. The surface of nanowires is smooth and the structure is uniform. As the concentration of ZnO reaches 3%, a small amount of ZnO nanoparticles is observed in figure 3(c). The ZnO nanoparticles with smaller particle size around 10 nm are dispersed randomly over the TiO₂ nanowires. With increasing ZnO content, the surface of TiO₂ nanowires are covered with a large number of ZnO nanoparticles and only a few nanowires can be seen in figure 3(d). Notably, comparing with SEM images of Zn-1 and Zn-3 samples under the same magnification times, the length of ZnO–TiO₂ composites is decreased obviously when the addition of ZnO is up to 5%.

The TEM images of pristine TiO₂ nanowires, Zn-5 and Zn-7 samples are shown in figure 4. A similar observation that the nanowire structure decreases with the increasing ZnO content is found. These ZnO nanoparticles are not only diffused on the surface of TiO₂ nanowires, but also aggregated in the TiO₂ framework.

3.4. Photocatalytic activity

The photocatalytic activity of synthesized samples was evaluated by degradation of RhB aqueous solution. Figures 5(a)–(e) shows the UV-Vis absorption spectra of RhB dye solution under different irradiation times with various photocatalysts. The strong peak at 554 nm is the characteristic peak of RhB dye and the peak intensity
can be used to calculate the decolorization rate. It can be seen clearly that the absorbance of RhB solution decreases gradually with increasing reaction time for all the samples. Comparing with other samples, Zn-5 sample shows a very weak and nearly disappeared peak after the same irradiation time of 60 min, which implies that RhB dye has been completely degraded.

The comparison of photocatalytic decolorization between synthesized samples is displayed in figure 6. The changes in concentration of RhB dye with irradiation time are shown in figure 6(a) and the degradation rate kinetics curves are represented in figure 6(b). It is found that the degradation rate of RhB dye with all the samples almost follows the first-order reaction kinetics. The photocatalytic degradation efficiency and reaction rate are listed in table 1. Comparing with pure TiO$_2$ nanowires, ZnO–TiO$_2$ composites demonstrate superior
degradation behavior except Zn-1 sample. The lower degradation rate of Zn-1 sample than pure sample can be attributed to the large content of rutile phase, which exhibits lower photocatalytic capability than anatase phase. When the Zn/Ti molar ratio exceeds 1% the degradation rate of ZnO–TiO₂ composites increases with the ZnO.
content. It is obvious Zn-5 sample shows the highest photocatalytic activity than other samples. After illumination of 60 min, the degradation efficiency of RhB dye solution reaches 100%. With further increase in ZnO content, the decrease of degradation rate is observed. It is well known that the photodegradation ability is mainly affected by charge transfer. As n-type semiconductors, ZnO and TiO2 can be triggered under illumination and produce photogenerated electron-hole pairs. Due to the heterojunctions formed in ZnO–TiO2 composites, the photogenerated electrons were transferred from the conduction band (CB) of ZnO nanoparticles to the CB of TiO2 and the holes were transferred from the valence band (VB) of TiO2 to the VB of ZnO. Therefore, the charge separation improves efficiently and the recombination of photogenerated electron-hole pairs reduces remarkably, resulting in the increase of the number of electrons and holes. Based on the photodegradation mechanism [26], the holes in the VB can react with water molecule and produce hydroxyl radicals (·OH), which promotes the degradation of organic dye molecule. However, with increasing ZnO content, TiO2 nanowires were covered with a large number of ZnO nanoparticles which could hinder the contact between TiO2 and oxygen–containing species [27], leading to the decrease of photodegradation ability. Thus, the content of ZnO plays an important role in photocatalytic performance. In this study, anatase phase ZnO–TiO2 composites prepared with the optimal Zn/Ti molar ratio of 5% were achieved to display highest photodegradation ability.

4. Conclusion

TiO2 nanowires with different contents of ZnO nanoparticles were prepared by adjusting the Zn/Ti molar ratio during hydrothermal process. The Zn/Ti molar ratio affected the percentage of rutile phase. XPS result confirmed the existence of ZnO in the ZnO–TiO2 composites. It was found that ZnO nanoparticles around 10 nm were diffused on the surface of TiO2 nanowires and aggregated in the TiO2 framework. The heterojunctions formed in ZnO–TiO2 composites could improve charge transfer and reduce recombination of photogenerated electron–hole pairs, which is beneficial to photodegradation ability. ZnO–TiO2 composites synthesized with Zn/Ti molar ratio of 5% exhibited highest photocatalytic activity. After 60 min of irradiation, 100 ml of RhB dye solution with concentration of 20 mg l−1 has been completely degraded.

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Table 1. Comparison of photocatalytic degradation efficiency and reaction rate.

| Samples     | pureTiO2 | Zn-1 | Zn-3 | Zn-5 | Zn-7 |
|-------------|----------|------|------|------|------|
| Degradation efficiency (%) | 65.2 | 47.9 | 94.0 | 100 | 85.5 |
| Reaction rate (min⁻¹) | 0.0181 | 0.0119 | 0.0491 | 0.0815 | 0.0394 |
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