

Preparation and properties of composite particles made by nano zinc oxide coated with titanium dioxide

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Abstract In this paper, composite particles of nano zinc oxide coated with titanium dioxide were prepared and characterized by TEM, XRD, XPS and FT-IR, and the properties of the composite particles for photo catalysis and light absorption were studied. Tetrabutyl titanate (TBT) was hydrolyzed in an alcoholic suspension of nano zinc oxide with diethanolamine (DEA) as an additive, resulting in a film with a thickness of 20–30 nm being coated on the surface of nano zinc oxide, and the composite particles contained $ZnTiO_3$ after drying and calcination. Photocatalysis capabilities of the composite particles for the degradation of phenol in an aqueous solution were greatly improved as compared with nano zinc oxide particles before coating, with pure nano ZnO and nano TiO_2 with similar average sizes, or with the mixture of nano ZnO and TiO_2 with the similar composition as the composite particles. The light absorption scope of the composite particles was enlarged when compared to nano titanium dioxide with same average size.

Introduction

The coatings of materials with different compositions are usually carried out in order to modify or improve properties of the coated materials, such as chemical, magnetic, optical, etc [1, 2]. Such materials are also of economic interest because precious reactants can be coated on inexpensive cores. Finally, if a material cannot be prepared in a desired shape, one may coat it on a core of different composition but of the required morphology.

As important inorganic materials, nano zinc oxide and nano titanium dioxide have respective properties and application limitations. For example, as sunscreens, nano titanium dioxide can shield against UVB but nano zinc oxide can not only shield against UVB but also UVA [3–5]. As photocatalysis materials, the degradation capabilities of nano titanium dioxide for organic contaminants are usually better than that of nano zinc oxide under sodium lamp and direct sunlight, but nano zinc oxide is found to be as reactive as titanium dioxide under concentrated sunlight. Moreover, nano zinc oxide is a low cost alternative as solar photocatalyst for degradation of organic contaminants in aqueous solutions compared to titanium dioxide [6, 7]. The composite particles made by nano zinc oxide coated with titanium dioxide are expected to be a novel material having the merits of both compositions. There are a few publications about composite particles consisting of titanium dioxide coated with zinc oxide that were used to improve anti-pulverization of titanium dioxide and the mixture of nano titanium oxide and nano zinc oxide that was used as a photo catalyst of organic contaminants [8–10]. Few publications up to now were about the preparation and properties of

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composite particles made by nano zinc oxide coated with titanium dioxide [11]. In this paper, the composite particles were prepared by a sol-gel method. The properties of composite particles for photo catalysis and light absorption were studied as compared to pure nano titanium oxide, pure nano zinc oxide particles and mixed particles consisting of nano titanium oxide and nano zinc oxide.

Experimental

Reagents and samples

Analytical grade tetrabutyl titanate produced by Beijing Chemical Reagent Company was applied as the precursor of titanium dioxide. Chemical grade ethanol from Beijing Chemical Factory was used as the solvent. Analytical grade diethanolamine from Beijing Yili Fine Chemicals Ltd. was used as an additive. Polyacrylic acid 5100 sodium salt purchased from Fluka Company was used as dispersant of nano zinc oxide powder.

Nano zinc oxide powders with diameters of 40–60 nm and an average of 80 nm (ZnO-80) were prepared by the reaction of ammonia gas and zinc nitric aqueous solution. Nano titanium dioxide powders of anatase crystal with average diameters of 80 nm (TiO₂-80) and 20 nm (TiO₂-20) were synthesized by the hydrolysis of titanium tetrachloride. The preparation of nano zinc oxide and nano titanium dioxide were performed in a rotating packed bed reactor in our lab. The basic principles of preparing nano powders with a rotating packed bed reactor were described in reference [12].

Experimental process

Five gram of nano zinc oxide powder and 0.015 g of polyacrylic acid 5100 sodium salt were added to 200 mL of ethanol and dispersed mechanically for 12 h with 600 rpm in a 70 °C water bath. The ethanol solution containing 0.18 mol/L of tetrabutyl titanate and 0.09 mol/L of diethanolamine was prepared in a three-necked flask by stirring for 30 min in a 60 °C water bath. After the as-prepared nano zinc oxide suspension was added into the flask, 30 mL of a mixture of distilled water and alcohol with a 1:2 volume ratio was added dropwisely at a rate of 0.00025 L/min by peristaltic pump, then stirred for another 2 h in a 60 °C water bath. The whole process was protected by N₂ gas. After being separated by a centrifuge, the cakes were dried at 80 °C in vacuum for 6 h and calcined at 600 °C for 4 h to get the composite particles.

The characterizations

The absorbencies of powders and phenol aqueous solutions were measured by a UV-2501PC Ultraviolet and Visible Light Spectrophotometer (Japan). A HITACHI-800 Transmission Electron Microscopy (TEM) was used to characterize the morphologies and sizes of particles. An XRD-600 X-Ray Diffractometer (XRD, Japan) was applied to characterize the crystal phase and compositions of powders. A Nicolet60SXB Fourier Transform Infra-Red Spectrometer (IR) was employed to characterize the compositions of powders. A MICROLB-MKII X-ray Photoelectron Spectrometer (XPS) was used to characterize the bonding states and compositions of surface atoms.

The investigations of particles photo catalysis ability were performed in a self-made setup with an ultraviolet lamp as the light source, and phenol as the degraded target. The absorbencies of phenol aqueous solutions with different known concentrations were measured to get the function relationship between absorbency and phenol concentration.

One gram of powder was dispersed into 100 mL of phenol solution with known concentrations and radiated by ultraviolet lamp for 6 h at 60 °C. The samples were taken in 1-h intervals and separated by a centrifuge; the absorbencies of the supernates were measured. The phenol concentrations from different degradation times were calculated according to the as-obtained function relationship. Accordingly, the degradation rates in different degradation times can be obtained.

Results and discussions

The functions of diethanolamine during the preparation of composite particles

The surface coatings may be formed either by surface nucleation and growth that create a uniform and dense film or by coagulation of pre-formed coating material with the core particles that creates incompact film.

The relationship of free energies for hetero-phase surface nucleation (ΔG_h^*) and homo-phase particle nucleation (ΔG_r^*) are as follows [13]:

$$\Delta G_h^* = f(\theta)\Delta G_r^* \quad (1)$$

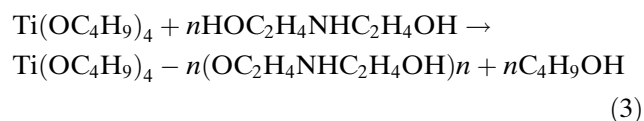
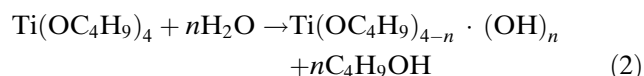
where $f(\theta)$ is related to the contact angle between new phase and nucleating matrix. Generally, $f(\theta) \leq 1$, and hetero-phase surface nucleation is easier than homo-phase particle nucleation. In order to achieve a

homogenous coating of one substance on another substance, the reaction rate usually needs to be controlled.

Because nano zinc oxide is an amphoteric substance, the pH value during coating must be strictly controlled. Accordingly, the TBT was selected as the precursor of titanium dioxide and coating was conducted in an ethanol medium.

Generally, the reaction for the hydrolysis of TBT to create titanium dioxide is very quick. In order for titanium dioxide to be coated on the surface of nano zinc oxide in the form of surface nucleation, the hydrolysis rate of TBT must be retarded.

If no DEA is added in the system, the main reaction to form TiO₂ is expressed as Eq. 2; while adding DEA, the main reaction is altered to Eq. 3.



where $1 \leq n \leq 4$. Due to the molecular size of DEA the hydrolysis rate of TBT is reduced which increases the probability of surface nucleation coating. Figure 1 shows the XRD patterns of composite particles in different molar ratios of DEA and TBT and the positions of main X-ray characteristic peaks of ZnTiO₃ and ZnO. It can be seen from Fig. 1 that there were ZnTiO₃ diffraction peaks in composite particles when the ratio was 0.5; as the ratio increased, the ZnTiO₃

diffraction peaks weakened, showing the important function of DEA in reducing the reaction rate.

The morphologies and structure of the composite particles

Figure 2 is the TEM photographs of nano zinc oxide and composite particles. The sizes of nano zinc oxide are approximately 40–60 nm. After being coated, the sizes of composite particles are approximately 60–90 nm and the thickness of the coated layer is approximately 20–30 nm. Because the zinc atomic number is larger than that of titanium, the TEM photograph shows that the cores color is darker than that of shells; a layer of film coated on the surface of nano zinc oxide is illuminated.

As demonstrated by the XRD patterns in Fig. 1, nano zinc oxide is hexagonal crystal phase. There are diffraction peaks of ZnTiO₃ besides zinc oxide diffraction peaks in XRD patterns of composite particles. For the formation of ZnTiO₃, there are two mechanisms: (1) nano zinc oxide particles and nano titanium dioxide particles created from the hydrolysis of tetrabutyl titanate react to produce ZnTiO₃ at high temperatures; (2) titanium dioxide hydrates are coated on the surfaces of zinc oxide, and then the interface reactions take place to create ZnTiO₃. Seen from the TEM picture of composite particles, the later mechanism is closer to the reality.

The surface characteristics of composite particles

Table 1 shows the XPS results of nano zinc oxide and composite particles. Compared with the nano zinc

Fig. 1 XRD patterns of samples with different molar ratios of DEA and TBT: 1. DEA/TBT = 1.5; 2. DEA/TBT = 1; 3. DEA/TBT = 0.5; 4. the main X-ray characteristic peaks of ZnO; 5. the main X-ray characteristic peaks of ZnTiO₃

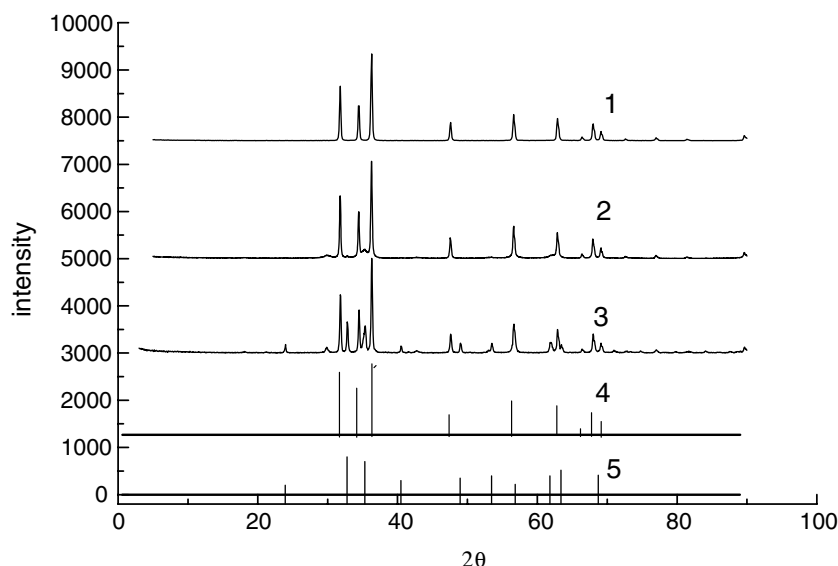


Fig. 2 TEM micrographs: (a) nano zinc oxide; (b) composite particles

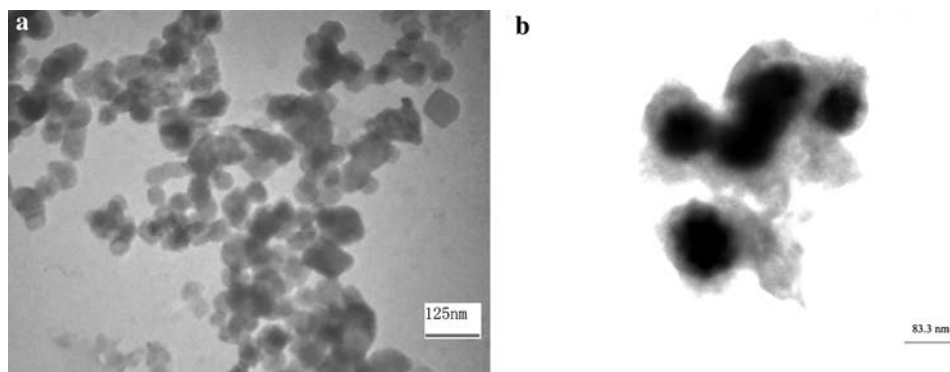


Table 1 The analyzing results of XPS

Samples	Element	Chemical Shifts	Shift Changes	Peak Areas	Ratios of relative atom contents	Remarks
Zinc oxide	Zn	1021.33	0	448898.58	Zn:O = 1:1.56	Zn–O
	O1s	530.06	0	46583.76		OH
		531.29	0	54229.45		Zn–O
Composite particles	O1s	529.88	–0.12	38382	Zn:O:Ti = 1:1.66:0.29	Zn–O
		531.34	0.05	9387.53		OH
		532.26	2.2	9633.46		Zn–O reacting with TiO ₂
	Zn	1021.31	–0.02	239734.47		
	Ti	458.41	0	16140.22		Ti–O of TiO ₂
		460.31	1.9	1708.86		Ti–O reacting with ZnO

oxide, the number of zinc atoms, oxygen atoms and hydroxide groups are reduced significantly except the titanium atoms in the composite particles. Moreover, the chemical shift of oxygen increases relative to those in nano zinc oxide. And the chemical shift of titanium atoms also enhances in comparison with that in titanium dioxide.

Figure 3 shows the FT-IR spectrums of nano zinc oxide and composite particles. There are distinct

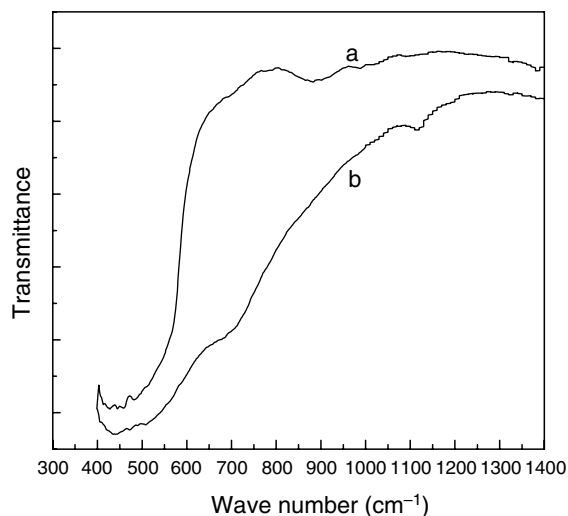


Fig. 3 FT-IR spectrums: (a) nano zinc oxide; (b) composite particles

differences between that of nano zinc oxide and composite particles; the pattern of composite particles is also different from that of the IR standard pattern of nano titanium dioxide. It can be concluded that there is new substance created in the composite particles in comparison with nano zinc oxide and nano titanium dioxide.

During the preparation of composite particles, the following processes may take place: Firstly, titanium dioxide hydrates are deposited on the surfaces of zinc oxide, where many hydroxide groups exist; secondly, on the interfaces of zinc oxide and titanium dioxide hydrates, condensation reactions between OH groups take place to produce ZnTiO₃ during the drying and calcining. Because most of titanium dioxide hydrates are deposited on the surfaces of zinc oxide and transformed to ZnTiO₃, no obvious diffraction peaks of titanium dioxide appear on the XRD pattern of composite particles. The reactions of parts of the Zn–OH and Ti–OH bonds to produce Zn–O–Ti bonds make the increases of chemical shifts for oxygen and titanium.

The properties of composite particles

The ultraviolet absorptions of composite particles

Figure 4 shows the ultraviolet absorption curves of nano zinc oxide before coating, TiO₂-80 and ZnO-80

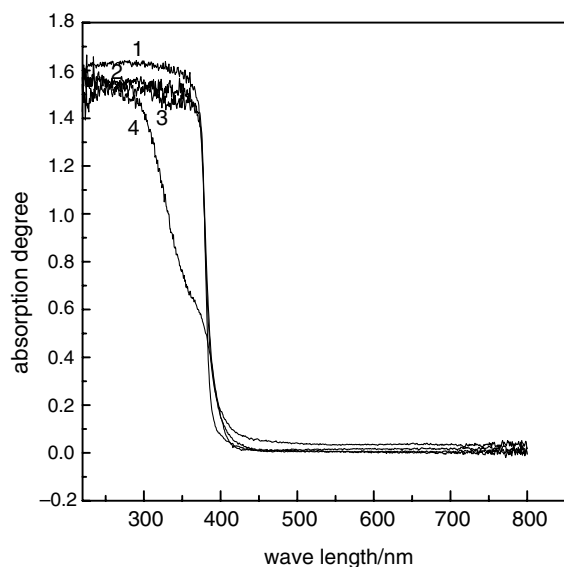


Fig. 4 Ultraviolet absorption curves of different powders: 1. nano zinc oxide before coating; 2. nano zinc oxide with an average diameter of 80 nm, being close to composite particles; 3. composite particles; 4. nano titanium dioxide with an average diameter of 80 nm, being close to composite particles

whose average diameters are close to composite particles and composite particles powders. It can be seen from Fig. 4 that the ultraviolet absorption capability of composite particles is closer to that of nano zinc oxide with approximate average size, but weaker than that of nano zinc oxide before coating. The curve shape for composite particles is similar to that of nano zinc oxide but totally different from that of nano titanium dioxide. The absorption capability of composite particles is corresponded to that of nano titanium dioxide with close size in the wavelength bands of less than 260 nm. The absorption capability is stronger than that of nano titanium dioxide with close size in the wavelength bands between 260–380 nm. The light absorption scope of composite particles is enlarged when compared to nano titanium dioxide due to the existence of ZnTiO_3 film that modifies the optical absorption edge [14].

The photo catalysis properties of composite particles

Figure 5 shows the results of photo degrading phenol for nano zinc oxide before coating, TiO_2 -80 whose average diameter is close to that of composite particles, mixing particles of nano zinc oxide before coating and TiO_2 -20, whose compositions are close to composite particles, ZnO -80 whose average diameter is close to composite particles, and composite particles. The capability for composite particles to degrade phenol is greatly improved in comparison with that of the mixed

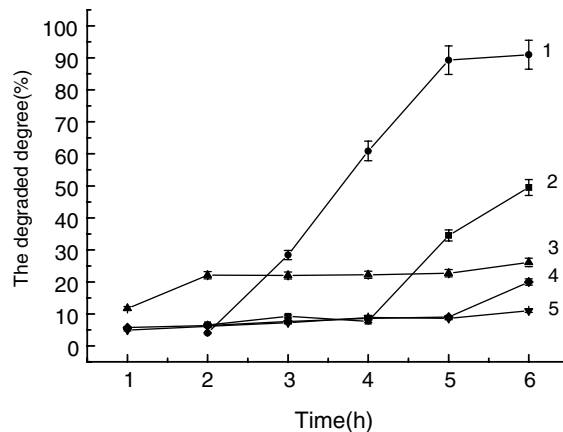


Fig. 5 The results of different powders used to degrade phenol: 1. composite particles; 2. nano zinc oxide before coating; 3. mixed particles consisting of 80 wt% of zinc oxide with an average diameter of 60 nm and 20 wt% of titanium dioxide with an average diameter of 20 nm, whose composition is close to composite particles; 4. nano titanium dioxide with an average diameter of 80 nm, being close to composite particles; 5. nano zinc oxide with an average diameter of 80 nm, being close to composite particles

particles, ZnO -80, TiO_2 -80 and nano zinc oxide before coating, showing that the composite particles are not simple mixture of the two substances and can substitute for TiO_2 and ZnO with close average sizes to be applied to the prevention of environmental organic pollutants. Compared to the mixed particles, the nano ZnTiO_3 films coated on the surfaces of nano ZnO may take effect on enhancing photo catalysis capability. The reductions of capabilities for nano ZnO to degrade phenol along with the sizes increase are caused by different surface activities. The photo degrading capability of nano TiO_2 is stronger than that of nano ZnO with close average sizes because of different surface structures and components.

Conclusions

In this paper, the composite particles of nano zinc oxide coated with titanium dioxide were prepared. The nano zinc oxide and composite particles were characterized by TEM, XPS, FT-IR, XRD. The powders absorption capabilities of ultraviolet and visible light, and the photo-catalysis degrading capabilities of phenol for composite particles, nano zinc oxide, and nano titanium dioxide were investigated. The following conclusions were obtained:

(1) Tetrabutyl titanate (TBT) was hydrolyzed in an alcoholic suspension of nano zinc oxide with diethanolamine (DEA) as an additive, resulting in a film with a thickness of 20–30 nm being coated on the surface of

nano zinc oxide after drying and calcinations, and the created composite particles contained ZnTiO₃.

(2) The capability of photo-catalysis degrading phenol for composite particles is better than nano zinc oxide before coating, mixed particles whose composition is close to composite particles, nano ZnO and TiO₂ with close average sizes. The light absorption scope of composite particles is enlarged as compared with nano titanium dioxide.

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