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Short Communication

Controlled synthesis of anatase/tungstite heterogeneous nanomaterials induced by oxalic acid

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ABSTRACT

A series of anatase/tungstite heterogeneous nanomaterials with various molar ratios were synthesized by hydrothermal method with oxalic acid as additive, in which the nucleation and growth of tungstite grains were controlled effectively. In our experiments, tungstite grains grew on the surface of TiO_2 grains, which was significant for obtaining heterogeneous composites, and the grain boundaries in composites were considered to promote photocatalytic ability effectively. It was demonstrated that heterogeneous nanomaterials synthesized had obviously better photocatalytic ability than the physical mixture of homogeneous nanomaterials (pure anatase and tungstite) no matter if under ultraviolet irradiation or visible light.

1. Introduction

As well known functional materials, titanium oxide (TiO_2) has been extensively investigated for more than three decades [1,2]. However, its application is restricted by the absence of visible light photoactivity and low photocatalytic efficiency [3,4]. WO_3 is a promising additive since it modifies photochemical properties of TiO_2 by both reducing photogenerated electron–hole recombination rate and expanding its useful range into visible light wavelengths [5].

Lots of methods have been used to synthesize TiO_2/WO_3 hybrids, such as sol–gel [6,7], impregnation [8], microemulsion [9], solvothermal [10,11] and mechanical methods [12]. Among them hydrothermal synthesis is the most commonly used method to synthesize nanomaterials. Several researches [13,14] reported a typical hydrothermal synthesis of TiO_2/WO_3 heterogeneous photocatalyst, in which the alcohol solution of titanyl sulfate was mixed with an aqueous solution of soluble tungstate (such as sodium tungstate or ammonium tungstate). In most of hydrothermal synthesis method reported, the flocculent amorphous Ti/W species had been rapidly formed before hydrothermal treatment. Thus the morphology and grain sizes of products were largely determined by pretreatment process and the nucleation and growth of composite grains were difficult to be controlled. Moreover, the uncontrolled rapid reaction incurred massive homogeneous nucleation, which is severely bad for the synthesis of heterogeneous composites.

Recently, several literatures [15–17] mentioned a hydrothermal synthesis of WO_3 using oxalic acid as additive, in which WO_3 grains were controlled to nucleate slowly and grow from the transparent aqueous solution containing tungstic acid during the hydrothermal process. Besides, it was reported that WO_3 grains could be controlled to have various morphologies with the help of oxalic acid, such as amorphous particles [15], regular spindle [16] and nanoflowers assembled of nanoplates [17]. It is demonstrated that oxalic acid played an important role in controlling the nucleation and growth of nanomaterials containing WO_3. However, oxalic acid was seldom reported to be used in the hydrothermal synthesis of TiO_2/WO_3 heterogeneous photocatalyst.

Here, we report a hydrothermal synthesis of anatase/tungstite heterogeneous nanomaterials with the help of oxalic acid, in which tungstite grains were controlled to nucleate slowly and grow during the relatively long hydrothermal procedure. Thus the morphologies and grain sizes of composites were effectively controlled. In our experiments, tungstite grains grew on the surface of TiO_2 grains, which was significant for obtaining heterogeneous composites, and the grain boundaries in composites were inferred to promote the photogenerated charge transfer between anatase grains and tungstite grains. Then, it was demonstrated in the degradation of methylene blue (MB) and salicylic acid (SA) that heterogeneous nanomaterials synthesized had obviously better photocatalytic ability than the physical mixture of

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homogeneous nanomaterials (pure anatase and tungstite) no matter if under ultraviolet irradiation or visible light.

2. Experimental

2.1. Photocatalyst preparation

Anatase/tungstite heterogeneous photocatalysts were synthesized by direct hydrothermal method with oxalic acid as additive. All the chemicals were of analytic grade and used without further purification or modification. Sodium tungstate dehydrate ($Na_2WO_4 \cdot 2H_2O$) was dissolved in 20 mL double distilled water and nitric acid was added dropwise to get a pH of 1. During the procedure of acidification, a yellow precipitate was obtained, and then it was dissolved after adding 30 mL saturated oxalic acid solution and vigorously stirring. After that, Tetrabutyl Orthotitanate (TBOT) was directly added and hydrolyzed in the obtained transparent solution. The final solution was then transferred into a 100 mL teflon-lined stainless steel autoclave and heated to 180 °C for 24 h. The obtained powders were filtered with double distilled water for several times and then dried at 80 °C. Different dosages of $Na_2WO_4 \cdot 2H_2O$ and TBOT were added in the preparation, while the total amount of $Na_2WO_4 \cdot H_2O$ and TBOT was controlled to be 0.02 mol. According to the molar contents of TBOT (20%, 40%, 60%, and 80%) added in the solution, the obtained composites were identified as Com-20%, Com-40%, Com-60% and Com-80% respectively. For comparison, pure WO_3 powder (labeled as sample A) was prepared with a similar procedure without TBOT, and pure TiO_2 (labeled as sample B) was also prepared with a similar method without $Na_2WO_4 \cdot 2H_2O$.

2.2. Characterization and photocatalytic activity measurement

The morphological and structural investigations of the samples were carried out using X-ray diffraction (XRD, RIGAKU D/max2550) and transmission electron microscopy (TEM, JEOL 2010F). Specific surface area calculations were made using Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP 2020M surface area analyzer. The photocatalytic activities were measured using the decomposition rate of methylene blue (MB) and salicylic acid (SA) by dispersing and stirring 100 mg samples in 100 mL of 10 mg/L MB or SA aqueous solution under a 300 W mercury lamp or 500 W xenon lamp with filter.

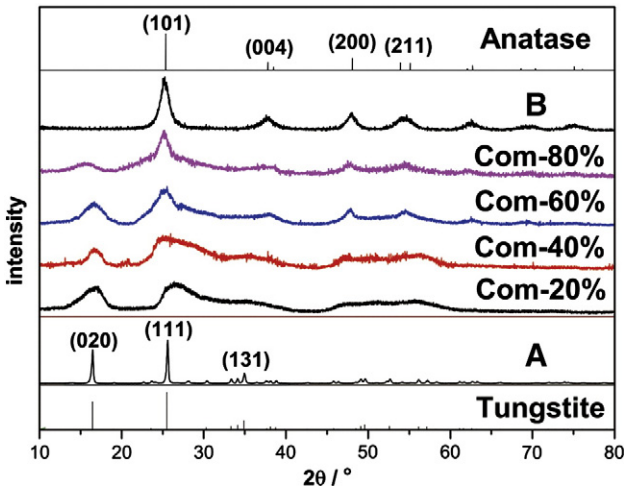

Fig. 1. XRD patterns of pure tungstite samples (A), pure anatase samples (B), and synthesized heterogeneous nanomaterials (Com-20%, Com-40%, Com-60% and Com-80%).

Table 1
Contents, crystallinity, grain sizes and surface areas of various samples.

Samples	Contents (molar percent)		Crystallinity	Grain sizes (nm)	Surface areas (m^2/g)
	Tungstite	Anatase			
A	100%	0	94.1%	29.4	5.2
Com-20%	80%	20%	24.2%	1.4	64.7
Com-40%	60%	40%	27.3%	2.4	82.2
Com-60%	40%	60%	31.1%	4.4	213.9
Com-80%	20%	80%	41.3%	5.1	132
B	0	100%	82.5%	7.2	116.5

3. Results and discussion

3.1. XRD characterization

The XRD patterns shown in Fig. 1 reveal that the samples A and B are pure tungstite (JCPDS 18-1418) and anatase (JCPDS 04-0477) respectively and other samples are anatase/tungstite hybrids. The diffraction peak at 16.4°, corresponding to tungstite (020) facet, decreases along with the increasing content of anatase in samples obtained. Moreover, the diffraction peaks of pure tungstite are obviously different from samples containing anatase.

The contents of anatase and tungstite calculated from dosages of $Na_2WO_4 \cdot 2H_2O$ and TBOT, crystallinity, grain sizes and surface areas were exhibited in Table 1. Grain sizes were calculated using Scherrer equation from XRD patterns. In this work, the degree of crystallinity was specified as the percentage of the volume of crystalline and calculated from the XRD patterns. The concept of crystallinity and its calculation method were detailed in Supplementary data.

As exhibited in Table 1, the crystallinity and average grain sizes of hybrids were slowly increasing with the content of anatase, however far less than pure tungstite and anatase. Thus, it could be inferred that the growth of tungstite and interaction between tungstite and anatase during hydrothermal treatment had a severe influence on the crystallization and growth of nanomaterial grains. On the other hand, the surface areas of hybrid samples first increased and then decreased along with the content of anatase. Especially, the surface area of Com-60% was far greater than that of pure tungstite and anatase.

For better comparison with as-prepared hybrids, a physical mixture (labeled as Mixture) consisting of 1 g sample A (4 mmol pure tungstite)

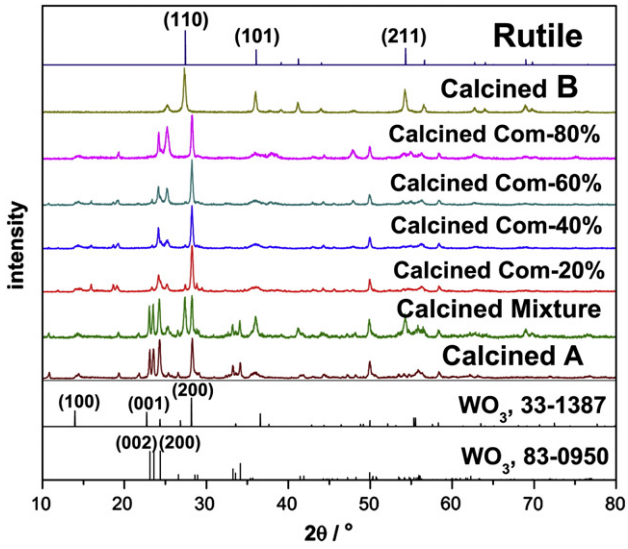

Fig. 2. XRD patterns of samples calcined at 600 °C for 6 h: WO_3 (Calcined A), rutile and anatase (Calcined B), heterogeneous nanomaterials (Calcined Com-20%, Calcined Com-40%, Calcined Com-60% and Calcined Com-80%) and physical mixture of pure anatase and tungstite (Calcined Mixture).