



Solvothermal synthesis of spindle-like $\text{WO}_3\text{-TiO}_2$ particles with enhanced photocatalytic activity

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ABSTRACT

Spindle-like $\text{WO}_3\text{-TiO}_2$ composite particles were synthesized through a facile one-step solvothermal method. The as-synthesized spindle-like $\text{WO}_3\text{-TiO}_2$ composite particles with center diameter of ca. 150 nm and length of ca. 300 nm were assembled by numerous $\text{WO}_3\text{-TiO}_2$ nanorods of ca. 20 nm in diameter. It is found that the photo-responding range was extended and the specific surface area of the composite was increased. Such spindle-like $\text{WO}_3\text{-TiO}_2$ composite exhibited much higher photocatalytic activity than that of single phase TiO_2 or WO_3 in the degradation of methyl orange dye under illumination with simulated sunlight.

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1. Introduction

Photocatalytic degradation of organic pollutants is one of the promising processes for environmental purification [1]. TiO_2 is considered to be an effective, environmentally friendly and most popular photocatalyst due to its various merits, such as excellent photocatalytic activity, low cost, nontoxicity, and chemical and biological inertness [2,3]. However, TiO_2 has a high band gap energy (for anatase is 3.2 eV), which limits its wide application in visible light range of solar spectrum. Moreover, the recombination of photo-generated electron-hole pairs also leads to low photo quantum efficiency of TiO_2 photocatalysts [4]. To solve these shortcomings much effort has been directed toward the modification of TiO_2 by metal/nonmetal ion doping, coupled semiconductor oxide and noble metal depositing [5–7], etc. Among them, coupling TiO_2 with other semiconductor oxide is considered as a good way because coupling semiconductor oxide can not only promote the separation of photo-generated electrons and holes, but also achieve visible light response [8–10]. In general, high hybrid of the different semiconductors could be beneficial to the separation of photo-generated electrons and holes, and then improve the photocatalytic activity.

WO_3 is an exceptionally important semiconductor, which has drawn more attention in the applications of electrochromic devices,

gas sensors and photocatalysts because of its relative narrower band gap (2.6–2.8 eV) [11,12]. Coupling TiO_2 with WO_3 can achieve an efficient charge separation because WO_3 has a suitable conduction band potentially to allow the transfer of photo-generated electrons from TiO_2 [13–15]. In recent years, the development of $\text{WO}_3\text{-TiO}_2$ composite photocatalyst that can work effectively under visible light illumination with photochemical stability is one of the hot topics in photocatalyst research. To date, $\text{WO}_3\text{-TiO}_2$ composites have been synthesized by several methods like sol-gel, hydrothermal, precipitation and microemulsion methods [16–20]. Furthermore, it is known that the morphology and microstructure play important roles in determining the catalytic properties. Many studies to deal with some specific morphologies of photocatalysts, such as nanowires, nanorods, nanotubes, and so on, have been involved [21–24].

In the present work, spindle-like $\text{WO}_3\text{-TiO}_2$ composite particles with a very uniform distribution for principal components of W and Ti were synthesized through a facile one-step solvothermal method at 180 °C. The as-prepared samples exhibit high photocatalytic activity of degraded methyl orange (MO) dye under simulated sunlight illumination of a 300 W Xe lamp.

2. Experimental

2.1. Starting materials

All major chemicals were AR grade and used without further purification. Titanyl sulfate ($\text{TiOSO}_4 \cdot x \text{H}_2\text{SO}_4 \cdot x \text{H}_2\text{O}$) was supplied

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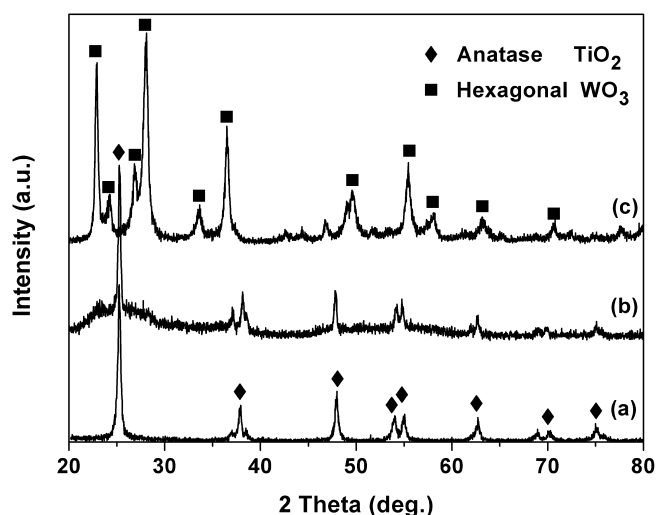


Fig. 1. XRD patterns of: (a) TiO_2 ; (b) $\text{WO}_3\text{-TiO}_2$; (c) WO_3 synthesized solvothermally at 180°C for 12 h.

by Tianjin Jinke Chemical Reagent Co., Ltd., China. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) was purchased from Xilong Chemical Co., Ltd., China. Absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and Sulfuric acid (H_2SO_4) were all obtained from Beijing Chemical Works, China. Distilled water was used in all experiments.

2.2. Catalyst synthesis

In a typical synthesis, 2 g of $\text{TiOSO}_4 \cdot x\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ was mixed with 15 mL absolute ethanol and then stirred for 30 min to get an emulsion. 0.72 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (36 wt% in a weight ratio of $\text{Na}_2\text{WO}_4\text{:TiOSO}_4$) was dissolved in 15 mL distilled water under magnetic stirring. During stirring, a certain amount of H_2SO_4 was introduced into the above solution, resulting in a yellow tungsten acid precipitation to adjust the pH value to 1. Subsequently, 1 g of $\text{H}_2\text{C}_2\text{O}_4$ was added into the precipitation. After 10 min of stirring, a settled solution was obtained. Then the settled solution was added into the emulsion of TiOSO_4 , and then stirred for 20 min to form a homogeneous mixture. Afterward, the resulting homogeneous mixture was transferred into 50 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 180°C for

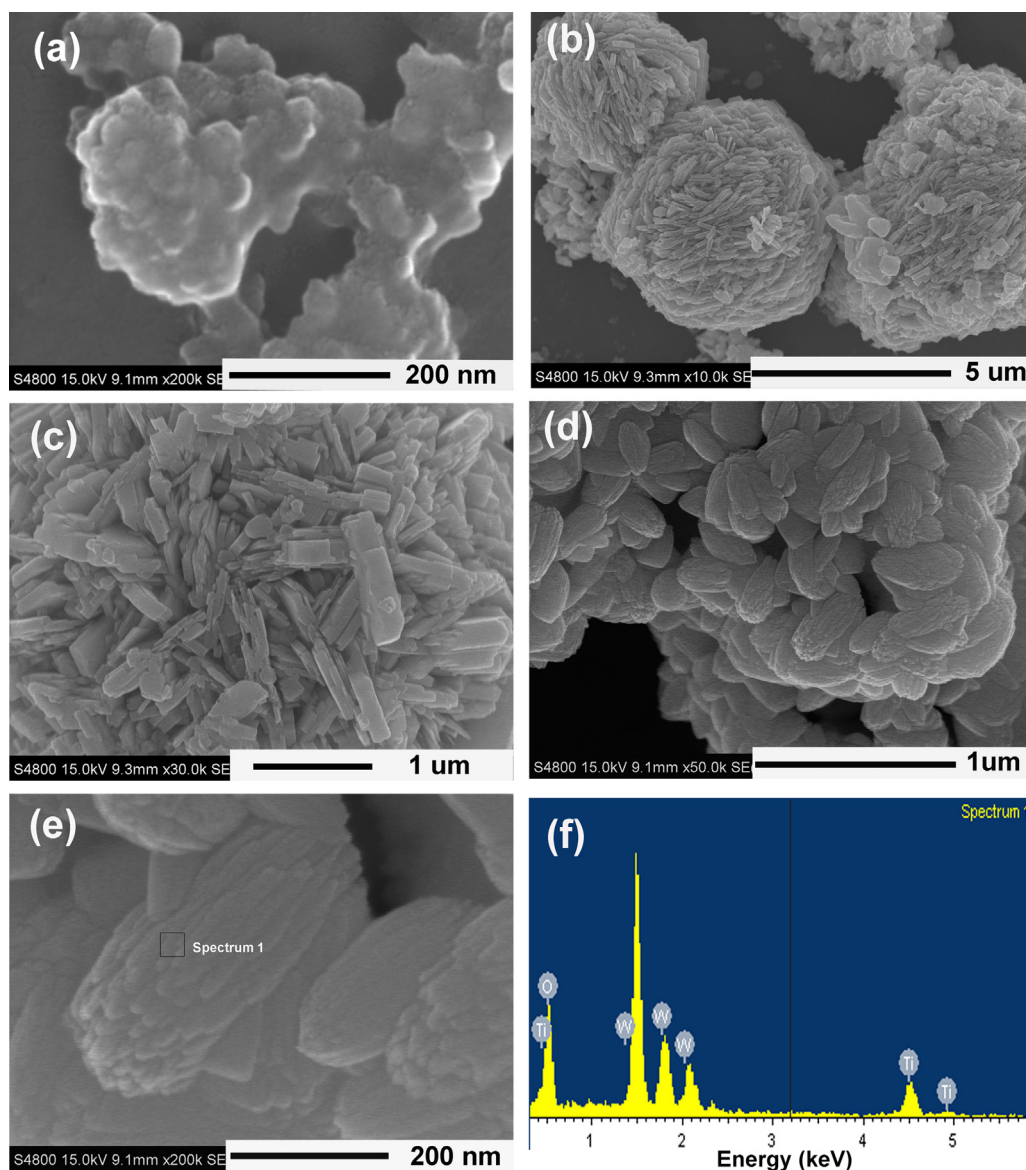


Fig. 2. SEM images of: (a) TiO_2 ; (b) and (c) WO_3 ; (d) and (e) $\text{WO}_3\text{-TiO}_2$; (f) EDS of $\text{WO}_3\text{-TiO}_2$ synthesized solvothermally at 180°C for 12 h.

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