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Article

High photocatalytic activities of zinc oxide nanotube arrays modified with tungsten trioxide nanoparticles

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ABSTRACT

Well-aligned zinc oxide (ZnO) nanotube arrays loaded with tungsten trioxide (WO_3) nanoparticles were synthesized by a process involving chemical bath deposition in combination with pyrolysis. The prepared ZnO–WO_3 composites were characterized by X-ray diffraction, energy dispersive spectrometer, field emission scanning electron microscopy, X-ray photoelectron spectroscopy, photoluminescence spectroscopy, Fourier transform infrared spectroscopy and UV–vis diffuse reflectance spectroscopy. The photocatalytic activities of the ZnO–WO_3 composite photocatalysts with different WO_3 contents for the degradation of the herbicide chlorinated phenoxyacetic acid (MCPA-Na) under simulated sunlight irradiation were systematically evaluated. It was found that the WO_3 content had a great effect on the photocatalytic activity of the ZnO–WO_3 composites. The composite with 3% WO_3 showed the highest photocatalytic activity, with a degradation rate of chlorinated phenoxyacetic acid of 98.5% after 200 min with 20 mg of photocatalyst. This photodegradation rate was about twice that of the pristine ZnO nanotube array. The recombination of photogenerated electrons and holes was increasingly suppressed with the addition of WO_3 to ZnO. The high relative content of defects on the surface of the ZnO–WO_3 composites was beneficial to their photocatalytic activity in the degradation of chlorinated phenoxyacetic acid.

1. Introduction

Chlorinated phenoxyacetic acid (denoted MCPA-Na) is one of the oldest and most readily available herbicides in the world, and is widely used as a weed killer on cereal crops, pasture, and orchards. However, MCPA-Na is considered potentially dangerous to both animals and humans and is a well-known endocrine disruptor [1]. The biodegradability of MCPA-Na is extremely low and it has been detected as a major contaminant in effluents released into both subterranean and superficial water bodies [2].

Semiconductor-assisted photocatalysis can complement conventional approaches to degrade or transform hazardous chemical waste [3,4]. Zinc oxide (ZnO) is one of the most extensively studied semiconductor photocatalysts because it is environmentally friendly, cheap, and has a large exciton binding energy [4–7]. Various morphologies of ZnO including nanorods [8,9], nanotubes [10], hollow nanospheres [11], nanoplates [12], and nanoflower-like structures [13,14] have been prepared. In particular, the “one-dimensional” tubular morphology of ZnO has attracted interest because of its special hollow structure and large surface area, which are crucial for optimizing the performance of dye-sensitized solar cells, sensors, and hydrogen devices [15–18]. Moreover, the “one-dimensional” morphology can facilitate transport of charge carriers and minimize the loss of charge carriers at grain boundaries

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[19,20].

Most reported ZnO nanotubes are wide-band-gap semiconductors and can only absorb ultraviolet (UV) light. Therefore, it is necessary to functionalize ZnO nanotubes so that they absorb the visible component of sunlight. Coupling a narrow-band-gap semiconductor with a wide-band-gap semiconductor is a useful approach to capture visible light because the coupling of different semiconductor oxides can narrow the band gap of the resulting composite. Moreover, higher photocatalytic activity may be achieved for semiconductor composites because electron–hole pairs maybe separated efficiently under irradiation. It has been reported that the construction of heterostructures is an effective strategy to improve photocatalytic performance [21–23].

Tungsten trioxide (WO_3) is a promising photocatalyst that has an appropriate band gap of 2.8 eV to enable absorption in the visible region, stable physicochemical properties, and high resistance to photocorrosion [24,25]. It has been reported that the coupling of ZnO nanoparticles with WO_3 resulted in composites with higher photocatalytic activity than those of pristine ZnO and pristine WO_3 [26–30]. However, the photocatalytic properties of ZnO nanotubes loaded with WO_3 have not been reported yet. Therefore, we decided to couple WO_3 nanoparticles with ZnO nanotube arrays in the present work. ZnO nanotube arrays are first synthesized by electrodeposition. Composites with different contents of WO_3 are obtained by the addition of ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}\cdot XH_2O$) to the prepared ZnO nanotube arrays and annealing at 450 °C in air for 2 h. The photocatalytic properties of the prepared ZnO–WO_3 nanotube arrays with different contents of WO_3 nanoparticles are evaluated by their ability to degrade MCPA-Na. Based upon the results of activity evaluation and characterization, a photocatalytic mechanism for the composites is proposed.

2. Experimental

2.1. Synthesis of ZnO nanotubes and ZnO–WO_3 arrays

Electrodeposition of ZnO nanotubes was carried out in a conventional three-electrode cell using a Pt electrode with an area of about 3.0 cm^2 as the auxiliary electrode. The working electrode was indium tin oxide (ITO)-coated glass with a sheet resistance of 6–8 Ω/cm^2. A saturated Ag/AgCl electrode was used as the reference electrode. The ITO glass substrate with dimensions of 3 × 4 cm was cleaned ultrasonically in distilled water, ethanol, acetone, and 6 vol% hydrochloric acid in sequence for 5 min each, and then rinsed in distilled water before electrodeposition. ZnO crystal seeds were grown on the ITO substrate in solution containing 0.02 mol/L zinc nitrate ($Zn(NO_3)_2$), 0.013 mol/L ammonium acetate ($CH_3CO_2NH_4$), and 0.01 mol/L hexamethylenetetramine ($C_6H_{12}N_4$) under a cathodic voltage of –1.8 V (vs. Ag/AgCl) for 300 s at 90 °C. The cathodic voltage was switched to –1.2 V to prepare the ZnO nanorod arrays. After electrodeposition for 60 min at this applied potential, a uniform white film was obtained. The film was washed with distilled water and then used as the working electrode in 0.07 mol/L $C_2H_4(NH_2)_2$ at –0.2 V for 60 min at 70 °C to prepare pristine ZnO nanotube arrays.

To prepare ZnO–WO_3 nanotube arrays, the required amount of $(NH_4)_6H_2W_{12}O_{40}\cdot XH_2O$ was first dispersed in acetone. The solution was added dropwise onto the prepared ZnO nanotube surface. The substrate was annealed in a muffle furnace at 450 °C in air for 2 h. The composite fabrication process is illustrated in Fig. 1. All reagents used in this study were of analytical grade and used directly without any purification. The obtained ZnO–WO_3 samples are denoted as ZnO–WO_3 (2%, 3%, or 5%) according to their W/Zn molar ratio of 2%, 3%, and 5%, respectively, in the precursor solution. For comparison, annealed pristine ZnO nanotube arrays were prepared under the same conditions without the addition of $(NH_4)_6H_2W_{12}O_{40}\cdot XH_2O$. Pristine WO_3 powder was also prepared by calcination of $(NH_4)_6H_2W_{12}O_{40}\cdot XH_2O$ at 450 °C in air for 2 h in a muffle furnace.

2.2. Characterization

The crystal structures of the prepared ZnO and ZnO–WO_3 nanotube arrays were characterized by X-ray diffraction (XRD) using a PANalytical B.V. MPDDY2094 X-ray diffractometer (Almelo, the Netherlands) with Cu K_α radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) images and quantitative standard microanalyses were obtained using a Zeiss ultra plus field-emission scanning electron microscope (Germany) (FE-SEM) equipped with energy-dispersive X-ray spectrometer (EDS) analysis apparatus. High-resolution transmission elec-

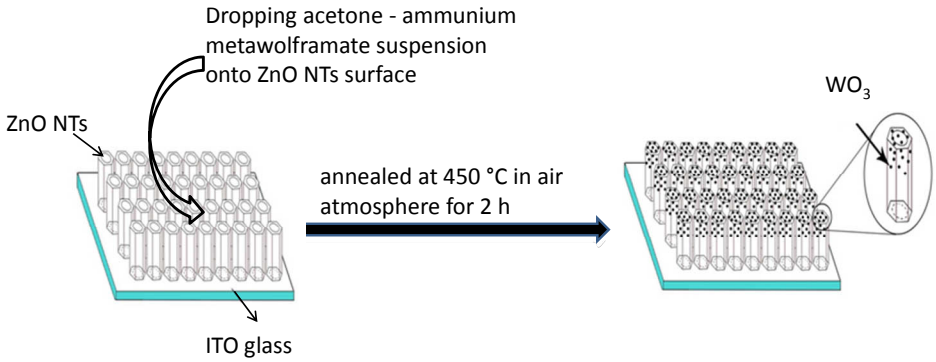

Fig. 1. Schematic illustration of the fabrication process of the ZnO–WO_3 nanotube arrays.