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Sunlight responsive WO_3/ZnO nanorods for photocatalytic degradation and mineralization of chlorinated phenoxyacetic acid herbicides in water

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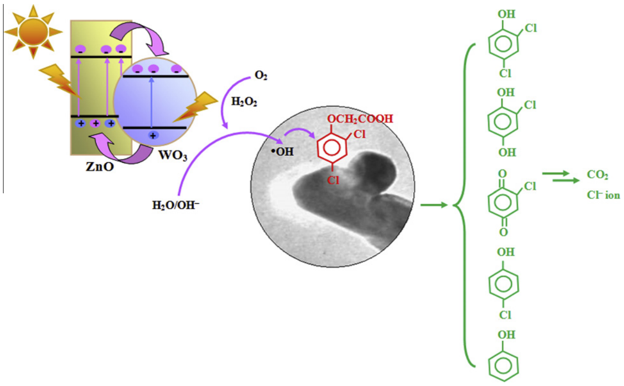
GRAPHICAL ABSTRACT



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ABSTRACT

Highly effective WO_3/ZnO nanorods (NRs) were synthesized via a hydrothermal–deposition method for degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) under natural sunlight. The structural properties of WO_3/ZnO NRs such as morphology, crystal structure, porous properties and light absorption characteristics were investigated in detail. The X-ray diffraction and X-ray photoelectron spectroscopy results indicated that the prepared samples were two-phase photocatalysts consisted of WO_3 and ZnO NRs. The UV–vis diffuse reflectance spectroscopy result showed that the addition of WO_3 altered the optical properties of the photocatalysts. In contrast with the pure ZnO NRs, commercial anatase TiO_2 and commercial WO_3, the WO_3/ZnO NRs showed excellent sunlight photocatalytic activities in degrading 2,4-D. The optimal WO_3 loading and calcination temperature were also determined. Based on the band position, the synergetic effect of WO_3 and ZnO NRs was the source of the enhanced photocatalytic activity as validated by PL and terephthalic acid-photoluminescence measurements. The reaction intermediates and degradation pathways of 2,4-D were elucidated by a HPLC method. In addition, the extent of mineralization during the 2,4-D degradation was also estimated using total organic carbon (TOC) and ion chromatography (IC) analyses.

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1. Introduction

In modern society, the applications on conversion of solar energy and remediation of toxic pollutants in environment by employing photocatalysts have attracted extensive attention. TiO_2 is by far most widely used photocatalyst because it comprises the best balance of properties among the known semiconductors. As an alternative semiconductor material for TiO_2, the band gap of ZnO is similar to that of TiO_2. ZnO is a good semiconducting material due to its high photocatalytic capability, environmental stability and low cost. In some cases, ZnO exhibited higher photocatalytic degradation of organic pollutants than that of TiO_2 [1–3]. In this regard, ZnO has been synthesized with a variety of well-defined nanostructures with various morphologies such as nanowires [4], nanorods [5], nanonails [6], nanotubes [7] and nanobelts [8].

Nevertheless, owing to its large band gap (~3.3 eV), ZnO only activated under irradiation with ultraviolet (UV) light, which greatly impeded its practical applications. Many efforts have been made to extend the optical response of ZnO into visible light region by doping with transition metal elements to the Zn sites, or N, C and S to the oxygen sites, or coupling of ZnO with other narrow band gap semiconductors [9–11].

WO_3 is a narrow band gap semiconductor with band gap of ~2.8 eV [12,13]. It is a promising photocatalyst for opto-electronic applications, viz. transparent electrodes, solar cells, phototransistors, photodiodes and gas sensors. In literature, successful preparation of TiO_2 coupled with WO_3 and their applications in photocatalytic degradation under UV light have been reported [14,15]. There were also few reports on the coupling of ZnO nanoparticles with WO_3 [16]. In WO_3 coupled ZnO composites, the conduction band (CB) of ZnO was positioned to a more negative side than that of WO_3. Irradiated by solar light, ZnO can be excited and the photogenerated electrons can be injected into the CB of WO_3 because the CB level of WO_3 was lower than that of ZnO. The electron transfer behavior effectively reduced the probability of light-induced corrosion on ZnO and facilitated the separation between the photogenerated holes and electrons of ZnO-based photocatalysts.

The chlorinated phenoxyacetic acid herbicide 2,4-D is extensively used for control of broadleaf weeds in cereal crops. It has been used for weed control on wheat, barley, oats, rice, maize and raps crops and is typically applied to cereals at a rate (active ingredient) of 0.5 kg ha^{-1} [17,18]. 2,4-D is considered to be potentially dangerous to both animals and humans and is a well-known endocrine disruptor [19]. Its biodegradability is extremely low and it has been detected as a major contaminant in effluents from both subterranean and superficial waters [19,20]. Thus, several methods including adsorption [21], electrochemical oxidation [22], a combination of ozonation and photocatalysis [23] and photocatalysis [24] have been employed to remove 2,4-D from water. Since 2,4-D is termed recalcitrant pollutant, it must therefore be destroyed and photocatalysis which can bring a complete destruction or mineralization of the pollutant is well suited for this task.

On the basis of the above consideration, this work focuses on the synthesis of WO_3 coupled with ZnO nanorods (NRs) by a hydrothermal-deposition method for the sunlight photocatalytic degradation of 2,4-D. The one-dimensional ZnO NRs were selected as investigation materials because of their advantages over nanoparticles including high surface-to-volume ratio, enhancement of light scattering and absorption as well as rapid diffusion of reactive species transport along the long direction [5,25]. According to above discussion, it was expected that WO_3/ZnO NR composites have the potential to avoid the photocorrosion of ZnO due to their different interfacial potentials and special structures, which promoted the electron transfer from ZnO NR and WO_3 to reactive species. It was also worth noting that the enhanced photocatalytic mechanism of WO_3/ZnO NRs was discussed. To get a better picture for the sunlight degradation process of 2,4-D, intermediate products and chloride ions measurements were finally presented.

2. Experimental

2.1. Materials

All the reagents used in this work were of analytical grade without further purification. Hydrogen peroxide (H_2O_2, Assay 30 vol%), ammonium metatungstate ($(NH_4)_6{\cdot}(H_2W_{12}O_{40}){\cdot}nH_2O$, Assay 99%), 2,4-D (Assay ⩾ 99.5%), terephthalic acid (TA, Assay 99%), sodium hydroxide (NaOH, Assay 98%), commercial ZnO powders, commercial WO_3 powders, chlorohydroquinone (Assay 90%), chlorobenzoquinone (Assay 90%) and phenol (Assay ⩾ 99%) were purchased from ACROS Organics. Commercial TiO_2 powders (whose XRD pattern is shown in Fig. S1), 2,4-dichlorophenol (Assay ⩾ 99%) and 4-chlorophenol (Assay ⩾ 99%) were purchased from Merck. Deionized water was used throughout this study.

2.2. Preparation of WO_3/ZnO NRs

Pure ZnO NRs were fabricated by a hydrothermal method from commercial ZnO powder and H_2O_2 at 180 °C for 24 h. The detailed synthesis process was reported in our previous study [25]. WO_3/ZnO NRs were prepared by a chemical-deposition method. The typical procedure for the preparation of WO_3/ZnO NRs was as follows: 1.0 g of pure ZnO NRs was dispersed in 50 mL deionized water and the suspensions were ultrasonicated for 30 min. The pH of the mixture was adjusted to about 6.5 using ammonia solution. After that, ammonium metatungstate with different W/Zn molar ratios (0.5%, 1.0%, 2.0% and 5.0%) was added into above mixture, followed by stirring for 12 h. Subsequently, the as-formed precipitates were filtrated, washed with deionized water and ethanol for several times, dried in air at 60 °C for 12 h and finally calcined at different temperatures (300 °C, 400 °C and 500 °C) for 2 h. As a comparison, the pure ZnO NRs were also calcined at 300 °C for 2 h without the addition of ammonium metatungstate.

2.3. Analytical methods

The samples were characterized using X-ray diffraction (XRD) analysis on a Philips PW1820 diffractometer equipped with Cu Kα radiation at a scanning rate of 2° min^{-1} in the range of 20–80°. The field emission-scanning electron microscopy (FESEM) was carried out using a Quanta FEG 450 together with an energy dispersive X-ray (EDX) analysis. Transmission electron microscopy (TEM) image was captured using a Philips CM-12 operated at 120 keV. High resolution transmission electron microscopy (HRTEM) image was taken on a Fei Tecnai 20. The specific surface area of the sample was determined through nitrogen adsorption–desoprtion at 77 K on the basis of BET equation using a micrometrics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) spectra were obtained with a Omicron els 5000 spectrophotometer using Al Kα at 1480 kV as radiation source. UV–vis diffuse reflectance spectrum (DRS) was recorded on a Perkin Elmer Lambda 35 UV–vis spectrophotometer with $BaSO_4$ as a reference. The photoluminescence (PL) measurement was performed on a Perkin Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm at room temperature.

HPLC analysis was performed using HPLC model: Perkin Elmer Series 200, a *C18* column (150 mm-length × 4.6 mm-ID × 5 μm

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