available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

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

Yawen Li, Yuzhen Bu, Qian Liu, Xia Zhang, Junli Xu *

College of Science, Northeastern University, Shenyang 110004, Liaoning, China

ARTICLE INFO

Article history:

Received 9 July 2017

Accepted 12 November 2017

Published 5 January 2018

Keywords:

Zinc oxide nanotube

Tungsten trioxide

Photocatalytic degradation

Electrodeposition

Electronic property

ABSTRACT

Well-aligned zinc oxide (ZnO) nanotube arrays loaded with tungsten trioxide (WO₃) nanoparticles were synthesized by a process involving chemical bath deposition in combination with pyrolysis. The prepared ZnO–WO₃ 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–WO₃ composite photocatalysts with different WO₃ contents for the degradation of the herbicide chlorinated phenoxyacetic acid (MCPA-Na) under simulated sunlight irradiation were systematically evaluated. It was found that the WO₃ content had a great effect on the photocatalytic activity of the ZnO–WO₃ composites. The composite with 3% WO₃ 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 WO₃ to ZnO. The high relative content of defects on the surface of the ZnO–WO₃ composites was beneficial to their photocatalytic activity in the degradation of chlorinated phenoxyacetic acid.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

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

* Corresponding author. Tel/Fax: +86-24-83684533; E-mail: jl Xu@mail.neu.edu.cn

This work was supported by the National Natural Science Foundation of China (51574071).

DOI: 10.1016/S1872-2067(17)62977-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 1, January 2018

[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 ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$) 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 ($\text{Zn}(\text{NO}_3)_2$), 0.013 mol/L ammonium acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$), and 0.01 mol/L hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) 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 $\text{C}_2\text{H}_4(\text{NH}_2)_2$ 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 $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ 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 $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$. Pristine WO_3 powder was also prepared by calcination of $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ 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 ($\lambda = 1.5406 \text{ \AA}$). 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.

tron microscopy (HRTEM) images were captured using a Tecnai G² 20 microscope (FEI, USA) at an accelerating voltage of 200 kV. UV-vis diffuse reflectance spectroscopy (DRS) was recorded on a Perkin Elmer Lambda 35 UV-vis spectrophotometer (Wellesley, USA) using BaSO₄ as a reference over the scan range of 200–800 nm. Photoluminescence (PL) measurements were performed on a Hitachi F7000 fluorescence spectrophotometer (Japan) with an excitation wavelength of 325 nm at room temperature. Mott-Schottky (MS) measurements were performed in 0.5 mol/L Na₂SO₄ solution using an electrochemical workstation (CHI660E, China) with a three-electrode system at room temperature. The obtained ZnO, WO₃, and ZnO–WO₃ nanotube array samples served as the working electrode. A Pt plate and saturated Ag/AgCl were used as the counter and reference electrodes, respectively. Fourier transform infrared (FTIR) spectra were measured using a Thermo Scientific Nicolet IS10 spectrometer (USA) over the scan range from 400 to 4000 cm^{−1} using KBr disks. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250Xi spectrometer (USA) with an Al K_α excitation source.

2.3. Photocatalytic activity tests

The photocatalytic activities of the samples were evaluated by the degradation of MCPA-Na aqueous solution under simulated sunlight irradiation. In each experiment, the sample was put into water (100 mL) containing MCPA-Na (20 mg). A 300-W xenon lamp with a power density of 20.15 mW/cm² (Beijing Science and Technology Co, Ltd., Park Philae) was set inside a cylindrical reactor and surrounded by a circulating water jacket to cool the lamp and minimize infrared radiation. UV-Vis spectroscopy was used to determine the solution concentration of residual MCPA-Na at room temperature (TU-1900, Beijing Purkinje General Instrument Co, Ltd.). The absorbance accuracy was ±0.002 Abs (0–0.5 Abs) and ±0.004 Abs (0.5–1.0 Abs). The total organic carbon (TOC) remaining in the solution after the photodegradation process was measured using a Jena Multi C/N 3100 analyzer.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 2 shows the microstructure of the obtained ZnO and ZnO–WO₃ (3%) nanotube arrays. The pristine ZnO nanotubes (Fig. 2(a)) possess a hollow hexagonal structure with an internal diameter of 400 nm and thickness of 80 nm. The pristine ZnO nanotubes have a smooth surface. The ZnO nanotubes after loading WO₃ (Fig. 2(b)) have a smaller internal diameter than that of the pristine ZnO nanotubes. The elemental maps of ZnO–WO₃ (3%) recorded by EDS are shown in Fig. 2(c–e). These elements are all distributed uniformly on the surface. Element contents of the samples are listed in Table 1. Only Zn and O were detected in the pristine ZnO nanotubes. However, the atomic ratio of Zn to O was not exactly equal to 1; the atomic ratio of Zn was slightly higher than that of O. Table 1 reveals that the W contents in ZnO–WO₃ (2%), ZnO–WO₃ (3%), and

Fig. 2. FESEM images of ZnO (a) and ZnO–WO₃ (3%) (b). (c) Corresponding elemental mapping images of Zn, O (d), and W (e) in ZnO–WO₃ (3%). (f) TEM image of ZnO–WO₃ (3%). (g) HRTEM image of ZnO–WO₃ (3%).

ZnO–WO₃ (5%) are 12 at%, 11 at%, and 20 at%, respectively. Higher W contents were found in the ZnO–WO₃ samples than present in the precursor solution, indicating that most of the WO₃ in solution was loaded on the surface of the ZnO nanotubes. Moreover, the W content of ZnO–WO₃ (3%) was slightly lower than that detected for ZnO–WO₃ (2%), indicating more WO₃ was inside the ZnO nanotubes in the ZnO–WO₃ (3%) sample than in ZnO–WO₃ (2%).

Fig. 2(f) displays a typical TEM image of the ZnO–WO₃ (3%) sample, which clearly indicates that it has a tubular structure with some substance in the tube and on its surface. Fig. 2(g) shows a HRTEM image of the same sample, in which two single-crystalline phases can be distinguished. The insets are the fast Fourier transformation (FFT) of the marked areas. The FFT spots corresponded to the (1 0 3) crystalline plane of ZnO with an interlayer spacing of around 0.15 nm as well as the (0 1 1) and (2 0 2) crystalline planes of WO₃ with interlayer spacings of around 0.54 and 0.26 nm, respectively.

Fig. 3 shows the XRD patterns of the pristine ZnO, WO₃, and ZnO–WO₃ (3%) samples. The peaks at 34.422° (002), 36.253°

Table 1
Element contents in ZnO and ZnO–WO₃ samples.

Sample	Element content (at%)		
	Zn	O	W
ZnO	53	47	0
ZnO–WO ₃ (2%)	49	39	12
ZnO–WO ₃ (3%)	51	38	11
ZnO–WO ₃ (5%)	44	36	20

Fig. 3. XRD patterns of pristine ZnO, WO₃, and ZnO-WO₃ (3%) samples.

(101), 47.539° (102), 56.603° (110), 62.864° (103), 67.963° (112), 69.100° (201), and 72.562° (004) were indexed to ZnO with a hexagonal wurtzite structure (JCPDS Card No. 00-036-1451). The peaks observed at 34.730° (020), 23.172° (002), 24.104° (110), 28.341° (102), 36.292° (221), 50.726° (114), and 56.785° (412) (JCPDS Card No. 01-083-0950 and 01-087-2401) were consistent with monoclinic WO₃, indicating that WO₃ can be obtained by annealing (NH₄)₆H₂W₁₂O₄₀·xH₂O. No obvious diffraction peaks from WO₃ were observed for the ZnO-WO₃ (3%) sample, which is probably because of its low

content of WO₃. Because the samples were fabricated on ITO glass substrates, In₂O₃ (JCPDS Card No. 03-065-3170), SnO₂ (JCPDS Card No. 00-046-1242), and SiO₂ (JCPDS Card No. 00-046-1242) were also detected for these samples.

XPS measurements were conducted to obtain insight into the composition of the ZnO-WO₃ (3%) sample; the results are shown in Fig. 4. The survey spectrum (Fig. 4(a)) revealed the presence of W, O, and Zn. As illustrated in Fig. 4(b), the W 4f spectrum contains typical W⁶⁺ peaks at binding energies of 35.4 and 37.5 eV, which are very close to the values reported for WO₃ [31]. In Fig. 4(c), the Zn 2p peaks at 1022.0 and 1045.2 eV indicated that Zn existed as Zn²⁺, which was consistent with the values reported for ZnO [10]. Figure 4(d) shows that the O 1s peak can be deconvoluted into two individual peaks at the binding energies of 530.3 and 531.6 eV, which correspond to the lattice oxygen of ZnO and hydroxide (OH⁻), respectively [10].

Fig. 5 presents the FTIR spectra of pristine ZnO and ZnO-WO₃ samples. The peak at 491 cm⁻¹ is ascribed to the stretching of Zn-O bonds [32]. The peak at 1636 cm⁻¹ is assigned to aromatic and -OH bending vibrations, and the peak at 3428 cm⁻¹ corresponds to the stretching of surface OH⁻ groups [33]. Compared with that of pristine ZnO, the FTIR spectra of the ZnO-WO₃ samples contained new peaks at around 870 and 989 cm⁻¹, which belonged to W-O-W stretching, bending, or lattice modes [34]. Moreover, the peak at 3428 cm⁻¹ for the ZnO-WO₃ composites is stronger than that for pristine ZnO, indicating more OH⁻ groups were present in the ZnO-WO₃

Fig. 4. XPS analysis of ZnO-WO₃ (3%). (a) Survey; (b) W 4f; (c) Zn 2p; (d) O 1s.

Fig. 5. FTIR spectra of pristine ZnO and ZnO-WO₃ samples.

composites than in ZnO. It has been reported that a higher amount of OH⁻ groups in the catalyst may result in higher photocatalytic activity because OH⁻ can capture photogenerated holes and transform into reactive hydroxyl radicals [31].

3.2. Optical properties

UV-vis DRS is an effective technique to determine the light absorption ability of a semiconductor at different wavelengths. Fig. 6(a) shows the UV-vis DRS obtained for all the samples. Pristine ZnO exhibited strong light absorption from 200 to 420 nm and little absorption in the visible light range. In comparison, the absorption spectra of the ZnO-WO₃ (3%) and ZnO-WO₃ (5%) composites displayed an apparent, red shift of the band edge, which may be caused by the aggregation of WO₃ particles [35]. Fig. 6(a) reveals that the absorption intensity in the visible region increases with the content of WO₃ in the ZnO-WO₃ samples, which indicates that the coupling of WO₃ with ZnO can enhance the absorption of ZnO in the visible-light region. This increased intensity may be attributed to the interaction between W⁶⁺ and crystal lattice oxygen resulting in an unsaturated bond and surface vacancy on ZnO [28].

The optical bandgap of the composites is calculated using the fundamental absorption, which corresponds to electron

excitation from the valance band to conduction band. The absorption coefficient (α) is calculated using the Eq. (1):

$$\alpha = 2.303A/d \quad (1)$$

where A is the absorbance, and d is the film thickness. The absorption coefficient (α) and the incident photon energy ($h\nu$) are related by Eq. (2):

$$\alpha h\nu = C(h\nu - E_g)^{1/2} \quad (2)$$

where h , ν , C and E_g are plank's constant, light frequency, proportionality constant, and the optical band gap, respectively. From the plot of $(\alpha h\nu)^2$ vs. $h\nu$ (Fig. 6(b)), the band gap energy is obtained by extrapolating the linear portion of the curve to the $h\nu$ axis. The pristine ZnO and WO₃ exhibited the E_g of 3.15 and 2.8 eV, respectively, while the ZnO-WO₃ (2%, 3%, and 5%) composites displayed narrower E_g of about 2.96, 2.85, and 3.10 eV, respectively. E_g of the ZnO-WO₃ samples initially decreased and then increased with the WO₃ content. ZnO-WO₃ (3%) possesses the narrowest E_g , which indicates that it can absorb more visible light than the other samples.

PL spectroscopy is an effective technique to evaluate the efficiency of charge carrier trapping, transfer, and separation in semiconductor materials and surface defects of samples [36–39]. Fig. 7 shows the room-temperature PL spectra of the ITO-supported ZnO and ZnO-WO₃ nanotube arrays obtained with an excitation wavelength of 325 nm. The emission at 380 nm is caused by the recombination of photogenerated electrons and holes [28,40,41]. High PL intensity at 380 nm is observed for the pristine ZnO nanotubes sample, indicating the rapid recombination of electrons and holes. The intensities of this emission peak for the ZnO-WO₃ composites are dramatically decreased compared with that of the pristine ZnO nanotubes. Very weak emission intensity is observed for the ZnO-WO₃ (2% and 3%) photocatalysts, which implies that a large number of photogenerated electrons and holes were trapped and their recombination was prohibited for these samples. Moreover, there is an extra emission peak at 600 nm for the ZnO-WO₃ (2% and 3%) composites. It has been reported that the visible emission peaks at around 420–620 nm observed for ZnO are related to defects and doubly charged oxygen vacancy states in the nanostructures [28,42,43]. The stronger the intensity of this luminescence, the more intrinsic defects (oxygen and zinc vacancies or interstitials) present in the sample [44]. As shown

Fig. 6. (a) UV-vis DRS of pristine ZnO, WO₃, and ZnO-WO₃ samples. (b) Plots of transformed Kubelka-Munk function versus light energy.

Fig. 7. PL spectra of pristine ZnO and ZnO-WO₃ samples.

in Fig. 7, the visible emission peak at 600 nm is much more intense for the ZnO-WO₃ (2% and 3%) samples compared to the case for ZnO-WO₃ (5%) and pristine ZnO samples, which indicates there are more defects in the former two samples than in the latter two samples. It has been reported that surface defects can improve the photocatalytic performance of metal oxide semiconductors because defects can act as charge carrier traps, where the charges are transferred to adsorbed species, preventing the recombination of photogenerated electrons and holes [42].

3.3. Photocatalytic properties

Fig. 8(a) depicts the relationship between the MCPA-Na degradation efficiency and irradiation time of the prepared ZnO

nanotubes and ZnO-WO₃ composites. After 200 min of simulated sunlight irradiation, about 58% of MCPA-Na was degraded by pristine ZnO nanotubes, while about 92%, 98.5%, and 49% of MCPA-Na was degraded by ZnO-WO₃ (2%), ZnO-WO₃ (3%), and ZnO-WO₃ (5%), respectively. Increasing the content of WO₃ in ZnO from 2% to 3% effectively enhanced the photo-degradation efficiency of the ZnO nanotubes. However, further increasing the WO₃ content had an adverse effect. The TOC contents of MCPA-Na solution were also measured, as shown in Fig. 8(b). The TOC content decreased to almost zero after 200 min of photocatalytic degradation, which means the herbicide pollutant was almost totally removed.

The pseudo-first-order model expressed by the equation $-\ln(C/C_0) = kt$ was used to quantitatively explain the reaction kinetics of MCPA-Na degradation. Here, C_0 and C are the initial pollutant concentration and pollutant concentration at any time, respectively, k is the pseudo-first-order rate constant, and t is the reaction time. According to this equation, k can be obtained from a linear plot of $-\ln(C/C_0)$ against t . The kinetic plots for photocatalytic degradation of MCPA-Na over composites with different WO₃ loading are presented in Fig. 8(c) and the calculated k values are shown in Fig. 8(d). The highest k was 0.0148 min⁻¹ for ZnO-WO₃ (3%), and it was 0.0145, 0.003, and 0.007 min⁻¹ for ZnO-WO₃ (2%), ZnO-WO₃ (5%), and ZnO, respectively.

Cycling stability is an important factor to evaluate the performance of a photocatalyst. Herein, the cycling stability of the prepared ZnO and ZnO-WO₃ (3%) thin films was evaluated. As shown in Fig. 8(e), the pristine ZnO sample exhibited poor cycling stability. The ZnO photocatalyst achieved 58% MCPA-Na degradation in the first run, which decreased markedly to 7% and 6% in the second and third runs, respectively. This poor

Fig. 8. (a) Photocatalytic degradation of MCPA-Na under simulated sunlight irradiation. (b) Variation of MCPA-Na and TOC concentrations using ZnO-WO₃ (3%) as a catalyst. (c) Kinetic plots for the photocatalytic degradation of MCPA-Na. (d) Pseudo-first-order rate constants of MCPA-Na photocatalytic degradation. (e) Reuse of ZnO and ZnO-WO₃ (3%) for photocatalytic degradation of MCPA-Na.

cycling stability of the ZnO photocatalyst is mainly caused by photoinduced corrosion [45]. In contrast, the ZnO-WO₃ (3%) composite degraded 98%, 63%, and 41% of MCPA-Na in the first, second, and third runs, respectively. Thus, photocatalytic stability was improved by the coupling of WO₃ with ZnO. However, it still needs to be further improved for practical use of this composite catalyst.

3.4. Mechanistic study

The electronic properties of a semiconductor can be investigated by MS analysis of its capacitance measurements. The type of semiconductor can be determined from the plot of $1/C_{sc}^2$ versus E , where C_{sc}^2 is the space-charge capacitance and E is the scanning potential. A negative slope indicates a p-type semiconductor, while a positive slope indicates an n-type semiconductor. Moreover, the intercept of a linear plot at $1/C_{sc}^2 = 0$ gives the flat band potential (E_{FB}). Fig. 9(a) shows the MS plots for the ZnO-WO₃ (3%) sample at different frequencies. The derived E_{FB} were almost the same at different frequencies. Therefore, the capacitance measurements for MS analysis of all samples were collected at 1000 Hz; the results are presented in Fig. 9(b). The slopes of the MS plots are positive for all the samples, indicating their n-type nature. To estimate E_{FB} , the linear part of each plot was extrapolated to $1/C_{sc}^2 = 0$. The E_{FB} values for ZnO, ZnO-WO₃ (2%), ZnO-WO₃ (3%), ZnO-WO₃ (5%), and WO₃ samples estimated from their MS plots are -0.23, -0.25, -0.46, -0.19, and -0.52 V (vs. Ag/AgCl), respectively. Because the Fermi level of NHE at 25 °C is -4.5 eV with respect to the vacuum level [46], the energy positions of band edges on the electrochemical scale can be converted from the values on the absolute vacuum energy scale using Eq. (3):

$$E_{(NHE)} = -E_{(AVS)} - 4.50 \quad (3)$$

The calculated E_{FB} on the absolute vacuum energy scale for ZnO, ZnO-WO₃ (2%), ZnO-WO₃ (3%), ZnO-WO₃ (5%), and WO₃ are -4.47, -4.45, -4.24, -4.50, and -4.18 eV, respectively. Because E_{FB} lies just below the conduction band (CB) edge energies (E_c) for n-type semiconductors and just above the valence band (VB) edge energies (E_v) for p-type semiconductors, it could be assumed that E_c is equal to E_{FB} for n-type semiconductors. Combined with the results of UV-vis DRS, the E_v values of ZnO and the ZnO-WO₃ composites were calculated using Eq.

Table 2

Electronic properties of ZnO and ZnO-WO₃ samples.

Semiconductor	Potential of the conduction band (eV)	Potential of the valence band (eV)	Band gap energy (eV)
ZnO	-4.47	-7.62	3.15
ZnO-WO ₃ (2%)	-4.45	-7.41	2.96
ZnO-WO ₃ (3%)	-4.24	-7.09	2.85
ZnO-WO ₃ (5%)	-4.50	-7.60	3.10
WO ₃	-4.18	-6.98	2.80

(4); the results are summarized in Table 2.

$$E_v = E_c - E_g \quad (4)$$

Based on the positions of the CB, VB, and E_g of WO₃ and ZnO, we speculate that the possible energy storage mechanism of the ZnO-WO₃ composites is as follows (Fig. 9(c)). When WO₃ and ZnO are irradiated with solar light, electrons are excited to the CB, leaving holes in the VB. Because both the bottom of the CB and top of the VB of ZnO are lower than those of WO₃, ZnO can act as a sink for the photogenerated electrons in the coupled oxides. In addition, the photogenerated holes in ZnO might be trapped within the WO₃ particle, making charge separation more efficient. Therefore, the recombination of the photogenerated carriers is suppressed, leading to an increase in photo-oxidation efficiency. However, if WO₃ content of the composite is too high, the dispersion of WO₃ becomes poor and the aggregated WO₃ can behave as recombination centers, resulting in a decrease in photocatalytic activity.

4. Conclusions

WO₃ was successfully loaded onto ZnO nanotube arrays by chemical bath deposition. The addition of WO₃ changed the band structure of the ZnO nanotube arrays, allowing the recombination of photogenerated electrons and holes to be suppressed at a proper loading content of WO₃. About 98.5% of MCPA-Na in solution was degraded by ZnO-WO₃ (3%) under simulated sunlight irradiation, and the degradation rate of MCPA-Na by ZnO-WO₃ (3%) was about twice that of the pristine ZnO nanotube array sample. The high relative content of surface defects on the ZnO-WO₃ composite increased its photocatalytic activity in MCPA-Na degradation.

Fig. 9. (a) MS plots of ZnO-WO₃ (3%) at frequencies of 500, 1000 and 1500 Hz in 0.5 mol/L Na₂SO₄ aqueous solution. (b) MS plots of ZnO, WO₃, and ZnO-WO₃ samples in 0.5 mol/L Na₂SO₄ aqueous solution at a fixed frequency of 1000 Hz. (c) Schematic diagram illustrating the principle of charge transfer between ZnO and ZnO-WO₃ (3%).

Graphical Abstract

Chin. J. Catal., 2018, 39: 54–62 doi: 10.1016/S1872-2067(17)62977-2

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

Yawen Li, Yuzhen Bu, Qian Liu, Xia Zhang, Junli Xu*
Northeastern University

ZnO nanotubes loaded with WO₃ particles exhibited enhanced photocatalytic activity for the degradation of the herbicide chlorinated phenoxyacetic acid because of the improved separation of photogenerated charges and visible light absorption.

References

- [1] E. Grabińska-Sota, E. Wisniewska, J. Kalka, *Crop Protection*, **2003**, 22, 355–360.
- [2] A. Lopze-Pineiro, D. Pena, A. Albarran, J. Sanchez-Lerena, D. Becerra, *J. Contam. Hydrol.*, **2013**, 152, 137–146.
- [3] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [4] A. Zaleska, J. Hupka, M. Wierowski, M. Biziuk, *J. Photochem. Photobiol. A*, **2000**, 135, 213–220.
- [5] S. O. Fatin, H. N. Lim, W. T. Tan, N. M. Huang, *Int. J. Electrochem. Sci.*, **2012**, 7, 9074–9084.
- [6] A. Akyol, H. C. Yatmaz, M. Bayramoglu, *Appl. Catal. B*, **2004**, 54, 19–24.
- [7] F. A. Catano, S. H. Valencia, E. A. Hincapie, G. M. Restrepo, J. M. Marin, *Lat. Am. Appl. Res.*, **2012**, 42, 33–38.
- [8] J. Z. Huang, S. Liu, L. Kuang, Y. D. Zhao, T. Jiang, S. Y. Liu, X. J. Xu, *J. Environ. Sci.*, **2013**, 25, 2487–2491.
- [9] S. M. Lam, J. C. Sin, A. Z. Abdullah, A. R. Mohamed, *J. Colloid Interface Sci.*, **2015**, 450, 34–44.
- [10] Z. Q. Liu, X. H. Xie, Q. Z. Xu, S. H. Guo, N. Li, Y. B. Chen, Y. Z. Su, *Electrochim. Acta*, **2013**, 98, 68–273.
- [11] C. Q. Zhu, B. A. Lu, Q. Su, E. Q. Xie, W. Lan, *Nanoscale*, **2012**, 4, 3060–3064.
- [12] D. D. Nguyen, D. T. Do, X. H. Vu, D. V. Dang, D. C. Nguyen, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, **2016**, 7, 015004/1–015004/6.
- [13] Y. Miao, H. J. Zhang, S. Yuan, Z. Jiao, X. D. Zhu, *J. Colloid Interface Sci.*, **2016**, 462, 9–18.
- [14] Z. Lou, J. N. Deng, L. L. Wang, L. J. Wang, T. Fei, T. Zhang, *Sens. Actuators, B*, **2013**, 176, 323–329.
- [15] Y. Sun, G. M. Fuge, N. A. Fox, D. J. Riley, M. N. R. Ashfold, *Adv. Mater.*, **2005**, 24, 77–81.
- [16] J. Elias, R. Tean-Zaera, G. Y. Wang, C. Levy-Clement, *Chem. Mater.*, **2008**, 20, 6633–6637.
- [17] X. Y. Gan, X. M. Li, X. D. Gao, W. D. Yu, *J. Alloys Compd.*, **2009**, 481, 397–401.
- [18] J. Y. Yang, Y. Lin, Y. M. Meng, Y. H. Liu, *Ceram. Int.*, **2012**, 38, 4555–4559.
- [19] C. H. Hsu, D. H. Chen, *Int. J. Hydrogen Energy*, **2011**, 36, 15538–15547.
- [20] A. I. Hochbaum, P. D. Yang, *Chem. Rev.*, **2010**, 110, 527–546.
- [21] C. L. Yu, W. Q. Zhou, J. C. Yu, H. Liu, L. F. Wei, *Chin. J. Catal.*, **2014**, 35, 1609–1618.
- [22] J. D. Li, C. L. Yu, W. Fang, L. H. Zhu, W. Q. Zhou, Q. Z. Fan, *Chin. J. Catal.*, **2015**, 36, 987–993.
- [23] H. B. He, S. S. Xue, Z. Wu, C. L. Yu, K. Yang, G. M. Peng, W. Q. Zhou, D. H. Li, *Chin. J. Catal.*, **2016**, 37, 1841–1580.
- [24] X. H. Zhang, X. H. Lu, Y. Q. Shen, J. B. Han, L. Y. Yuan, L. Gong, Z. Xu, X. D. Bai, M. Wei, Y. X. Tong, Y. H. Gao, J. Chen, J. Zhou, Z. L. Wang, *Chem. Commun.*, **2011**, 47, 5804–5806.
- [25] H. D. Zheng, J. Z. Ou, M. S. Strano, R. B. Kaner, A. Mitchell, K. Kalantar-Zadeh, *Adv. Funct. Mater.*, **2011**, 21, 2175–2196.
- [26] D. Li, H. Haneda, *J. Photochem. Photobiol. A*, **2003**, 160, 203–212.
- [27] D. Li, H. Haneda, N. Ohashi, S. Hishita, Y. Yoshikawa, *Catal. Today*, **2004**, 93, 895–901.
- [28] C. L. Yu, K. Yang, Q. Shu, C. Yu Jimmy, F. F. Cao, X. Li, *Chin. J. Catal.*, **2011**, 32, 555–565.
- [29] J. Xie, Z. Zhou, Y. W. Lian, Y. J. Hao, X. Y. Liu, M. X. Li, Y. Wei, *Ceram. Int.*, **2014**, 40, 12519–12524.
- [30] S. Adhikari, D. Sarkar, G. Madras, *RSC Adv.*, **2015**, 5, 11895–11904.
- [31] L. Y. Huang, H. Xu, Y. P. Li, H. M. Li, X. N. Cheng, J. X. Xia, Y. G. Xu, G. B. Cai, *Dalton Trans.*, **2013**, 42, 8606–8616.
- [32] S. Sharma, S. Singh, N. Khare, *Int. J. Hydrogen Energy*, **2016**, 41, 21088–21098.
- [33] K. Z. Lv, J. Li, X. X. Qing, W. Z. Li, Q. Y. Chen, *J. Hazard. Mater.*, **2011**, 189, 329–335.
- [34] S. Y. Zhang, H. Li, Z. F. Yang, *J. Alloys Compd.*, **2017**, 722, 555–563.
- [35] Y. P. He, Z. Y. Wu, L. M. Fu, C. R. Li, Y. M. Miao, L. Cao, H. M. Fan, B. S. Zou, *Chem. Mater.*, **2003**, 15, 4039–4045.
- [36] J. C. Sin, S. M. Lam, K. T. Lee, A. R. Mohamed, *Mater. Sci. Semicond. Process.*, **2013**, 16, 1542–1550.
- [37] A. K. Sajjad, S. Shamaila, B. Z. Tian, F. Chen, J. L. Zhang, *Appl. Catal. B*, **2009**, 91, 397–405.
- [38] M. V. Limaye, S. B. Singh, R. Das, P. Poddar, S. K. Kulkarni, *J. Solid State Chem.*, **2011**, 184, 391–400.
- [39] D. Y. Fu, G. Y. Han, C. F. Meng, *Mater. Lett.*, **2012**, 72, 53–56.
- [40] B. Subash, B. Krishnakumar, B. Sreedhar, M. Swaminathan, M. Shanthi, *Superlattices Microstruct.*, **2013**, 54, 155–171.
- [41] S. Stojadinovi, R. Vasili, N. Radi, N. Tadi, P. Stefanov, B. Grbic, *Appl. Surf. Sci.*, **2016**, 377, 37–43.
- [42] R. Mohammadzadeh, Kakhki, R. Tayebbe, F. Ahsani, *J. Mater. Sci. Mater. Electron.*, **2017**, 28, 5941–5952.
- [43] J. D. Ye, S. L. Gu, F. Qin, S. M. Zhu, S. M. Liu, X. Zhou, W. Liu, L. Q. Hu,

- R. Zhang, Y. Shi, Y. D. Zheng, *Appl. Phys. A*, **2005**, 81, 759–762.
- [44] S. K. Panda, N. Singh, J. Hooda, C. Jacob, *Cryst. Res. Technol.*, **2008**, 43, 751–755.
- [45] H. J. Zhang, G. H. Chen, D. W. Bahnemann, *J. Mater. Chem.*, **2009**, 19, 5089–5121.
- [46] Y. Xu, M. A. A. Schoonen, *Am. Mineral.*, **2000**, 85, 543–556.

WO₃纳米颗粒修饰ZnO纳米管的光催化性能

李亚文, 布玉珍, 刘 倩, 张 霞, 徐君莉*

东北大学理学院, 辽宁沈阳110004

摘要: 二甲四氯钠(MCPA-Na)是一种广泛用于牧场和果园的除草剂, 但由于其生物降解性极低, 已成为地下水和浅水中的主要污染物. 研究发现, 半导体可以有效地辅助降解转化危险化学品. ZnO纳米管因其中空结构和较大的比表面积, 而在光催化降解有机物方面备受关注. 但是, ZnO只能吸收紫外光, 如果将其与窄带隙半导体进行复合, 可以有效降低带隙, 增强其在可见光区域的光吸收, 表现出更好的光催化性能. WO₃是一种具有稳定物理化学性质及耐光腐蚀窄带隙半导体. 采用WO₃修饰ZnO纳米管, 能扩展ZnO吸收光的范围以及提高ZnO纳米管的耐光腐蚀性能. 本文首先通过电化学合成的方法制备了ZnO纳米管, 然后按照不同的W/Zn摩尔比将(NH₄)₆H₂W₁₂O₄₀·XH₂O滴加在纳米管表面, 并在450 °C下退火2 h制得ZnO-WO₃纳米管阵列. 研究了不同WO₃含量的ZnO-WO₃纳米管光催化降解MCPA-Na性能, 并且通过X射线光电子能谱(XPS)、傅里叶红外光谱仪(FTIR)、紫外可见光谱(UV-Vis)和光致发光光谱(PL)等手段研究了复合WO₃纳米颗粒后ZnO纳米管半导体光催化性能提高的原因.

XPS结果表明, W元素在ZnO-WO₃纳米管阵列中以W⁶⁺的形式存在. FTIR结果表明, 复合WO₃后的ZnO-WO₃复合半导体上比纯ZnO纳米管表面具有更多的OH⁻基团. 由于OH⁻可以捕获光生空穴, 并转化为具有反应活性的·OH自由基, 因此复合WO₃能在一定程度上提高ZnO纳米管的光催化活性. UV-Vis结果表明, WO₃的复合使得光谱发生明显红移, 但随着WO₃含量的增加, ZnO-WO₃的吸光度明显增加. 另外, PL结果表明, 适当的复合WO₃可以抑制光生电子-空穴的复合. 这是因为W⁶⁺和晶格氧的相互作用产生了较高不饱和键和表面缺陷, 而表面缺陷可以作为光生载流子的陷阱, 促进了光生电子和空穴的分离, 因而光催化性能提高.

在模拟太阳光下研究了不同WO₃含量的ZnO纳米管对光催化降解MCPA-Na溶液的性能. 发现W/Zn摩尔比为3%的ZnO-WO₃样品表现出最好的光催化活性, 200 min内其降解率为98.5%. 与纯ZnO纳米管相比, 其光催化循环性能也有所提高. 利用Mott-Schottky测试方法并结合UV-vis结果, 我们计算得到不同WO₃含量的ZnO-WO₃复合半导体导带价带位置. 由于WO₃导带位置和价带位置都比ZnO的更高, WO₃上产生的光生电子会向ZnO的导带移动, 而ZnO光生空穴向WO₃的价带移动, 从而促使光生电子和空穴的分离, 提高了光催化性能. 但是如果WO₃复合的量太大, 则在ZnO纳米管上分散性不好, 反而成为光生空穴和电子复合中心, 导致其光催化活性降低.

关键词: 氧化锌纳米管; 三氧化钨; 光催化降解; 电沉积; 电学性质

收稿日期: 2017-07-09. 接受日期: 2017-11-12. 出版日期: 2018-01-05.

*通讯联系人. 电话/传真: (024)83684533; 电子邮箱: jlxu@mail.neu.edu.cn

基金来源: 国家自然科学基金(51574071).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).