Effect of Ce dopant on structure, morphology, photoabsorbance and photocatalysis of ZnWO₄ nanostructure

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The effect of Ce dopant on phase, morphology, optical property and photocatalytic activity of ZnWO₄ was investigated in this research. The products were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy and UV–visible spectroscopy. The results showed that the pure product was monoclinic ZnWO₄ nanorods with the growth direction of [021] and that Ce³⁺ and W⁶⁺ ions contained in the Ce-doped products. The photocatalytic activities of the photocatalysts were evaluated through the degradation of methylene blue (MB) solutions under UV-light illumination. The results showed that the efficiencies for MB photocatalytic degradation were influenced by Ce dopant. The photocatalytic activities of the Ce-doped ZnWO₄ samples were higher than that of the pure ZnWO₄.

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1. Introduction

ZnWO₄ is one of the most promising photocatalysts due to its optical and electronic properties, stability, non-toxicity and low cost. It can be applied to eliminate persistent organic pollutants in water, and exhibits relatively high photocatalytic and photoelectrocatalytic activities for the mineralization of organic compounds.^{1)–6)}

Doping materials are the effective way to improve properties of ZnWO₄ photocatalyst. Lanthanide doped photocatalysts have drawn much attention due to their special 4f electron configuration.^{7)–9)} Among them, cerium dopant has received much attention due to its important properties including: (1) the Ce³⁺/Ce⁴⁺ redox couples that result cerium oxide in shifting between CeO₂ and Ce₂O₃ under oxidizing and reducing conditions and (2) the easy formation of labile oxygen vacancies with relatively high mobility of bulk oxygen species.^{7),8)} Thus, cerium can modify photoresponsivity of the Ce-doped ZnWO₄. In this research, Ce-doped ZnWO₄ photocatalyst was synthesized. Phase, morphology and optical properties of products were characterized. Photocatalytic activity of the photocatalyst was evaluated by monitoring through the degradation of methylene blue (MB) under UV radiation.

2. Experimental procedure

Zinc tungstate (ZnWO₄) and cerium doped zinc tungstate (Ce-doped ZnWO₄) were prepared by hydrothermal method. Na₂WO₄·2H₂O (2 mmol) and Zn(NO₃)₂·6H₂O (2 mmol) were added to a 50 ml of deionized water under stirring. Subsequently, 25 ml of 0–3% by mole Ce(NO₃)₃·6H₂O was added to the mixtures. The pH was adjusted to 8 by 3 M NaOH solution. Then, the mixtures were transferred into 100 ml Teflon-lined stainless steel

autoclaves which were heated at 200°C under autogenous pressure for 24 h and left the autoclaves cooling to room temperature in ambient atmosphere. White precipitates were washed with ethanol and distilled water three times, dried at 80°C under vacuum for 24 h and collected for further characterization.

The photocatalytic activities of photocatalysts were estimated by monitoring the degradation of methylene blue (MB) under UV light. Each of 0.05 g photocatalysts was added to 100 ml of 1×10^{-5} M MB solution in 250 ml Pyrex glass beakers. Before UV illumination, the MB solutions containing the catalysts were kept in the dark for 1 h for adsorption/desorption equilibrium of MB molecules on surfaces of photocatalysts. Then the mixed solution was irradiated by UV radiation of 11 W low pressure mercury lamp. During testing, each 5 ml of the dye solution was sampled every 10 min interval and was centrifuged to separate the photocatalysts from MB solutions. The concentrations of MB solutions were analyzed by a UV–vis absorption spectrometer (Perkin Elmer, Lambda 25 UV–vis spectrometer) to determine the degradation efficiency of MB by the equation

$$\text{Decolorization efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where C_0 is the initial concentration of MB and C_t is the concentration of MB after visible light irradiation within the elapsed time (t).

3. Results and discussion

The XRD patterns of ZnWO₄ doped with different Ce contents are shown in Fig. 1. All diffraction peaks of the prepared ZnWO₄ sample were indexed to the pure monoclinic ZnWO₄ structure corresponding to JCPDS No. 15-0774.¹⁰⁾ The cell parameters were determined: $a = 4.6907 \text{ \AA}$, $b = 5.7192 \text{ \AA}$ and $c = 4.9245 \text{ \AA}$. The sharp diffraction peaks indicate that the ZnWO₄ sample has high crystallinity. Upon Ce doping, the XRD peaks of 1–3 mol % Ce-doped ZnWO₄ samples are similar to the pure ZnWO₄ phase

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Fig. 1. XRD patterns of the 0–3 mol % Ce-doped ZnWO_4 samples at 2θ of (a) $10\text{--}70^\circ$ and (b) $29\text{--}33^\circ$.

Fig. 2. TEM images, HRTEM image and SAED pattern of pure ZnWO_4 sample.

confirming that Ce dopant did not change the phase of monoclinic ZnWO_4 structure. An expand view for the peaks at $2\theta = 29\text{--}33^\circ$ shows that the diffraction peaks are slightly shifted to lower angle because the ionic Ce^{3+} ($1.03 \text{ \AA}$)^{11,12} is bigger than Zn^{2+} ($0.74 \text{ \AA}$).¹¹ This phenomenon suggests that Ce^{3+} ions were homogeneously incorporated into the lattice of ZnWO_4 and the successful substitute for Zn^{2+} by Ce^{3+} .

Figure 2 shows transmission electron microscopy (TEM) images and SAED pattern of the pure ZnWO_4 sample. They show the formation of well-dispersed ZnWO_4 nanorods. The length and width of these ZnWO_4 nanorods varied from 1–2 μm and 100–150 nm, respectively. SAED pattern of single ZnWO_4 nanorod shows a spot pattern which confirms the single crystalline product. This SAED pattern was interpreted to have an electron beam in the $[01\text{--}2]$ direction of the monoclinic ZnWO_4 nanorod.^{13,14} A typical high-resolution transmission electron microscopic (HRTEM) image of a straight single ZnWO_4 nanorod clearly reveals only the fringe of (100) plane with a lattice spacing of about 0.459 nm, indicating that the ZnWO_4 nanorod is single crystalline in nature. Furthermore, it indicated that $[021]$ is the growth direction of the ZnWO_4 nanorod.^{13,14}

Figure 3 shows TEM and SAED results of 1 and 3 mol % Ce-doped ZnWO_4 nanorods. The Ce-doped ZnWO_4 shows uniform and perfect crystalline nanorods with straight and curve shapes. The 1 and 3 mol % Ce-doped ZnWO_4 nanorods with the average diameter of 20 nm and length up to 300 nm were observed by TEM. SAED patterns were taken from each of a single ZnWO_4 nanorod. They show spot patterns which confirm that 1 and 3 mol % Ce-doped ZnWO_4 nanorods are single crystal. These SAED patterns recorded by electron beam normal to the long axis

Fig. 3. TEM images and SAED patterns of (a and b) 1 mol % Ce-doped ZnWO_4 and (c and d) 3 mol % Ce-doped ZnWO_4 .

Fig. 4. XPS spectra of (a) Ce 3d and (b) W 4f of 3 mol % Ce-doped ZnWO_4 .

Fig. 5. UV–visible spectra of ZnWO_4 and 3 mol % Ce-doped ZnWO_4 .

of nanorods revealed that the products were monoclinic ZnWO_4 single crystal. These SAED patterns were interpreted to have the electron beam in the $[0\text{--}12]$ direction of the monoclinic Ce-doped ZnWO_4 nanorods.^{13,14}

Figure 4 shows XPS spectra of Ce 3d and W 4f of 3 mol % Ce-doped ZnWO_4 . It can be seen that Ce $3d_{3/2}$ and Ce $3d_{5/2}$ displayed characteristic peaks at 902 and 884 eV which indicated that the Ce ions were tetravalent.^{15,16} The XPS peaks of W $4f_{5/2}$ and W $4f_{7/2}$ were detected at 38 and 36 eV, respectively. They confirm the presence of W^{6+} ions in the sample.^{17,18} Thus, Ce ions were homogeneously incorporated into the ZnWO_4 lattice.

The optical absorption of the as-synthesized ZnWO_4 and 3 mol % Ce-doped ZnWO_4 nanorods was measured by a UV–vis spectroscopy as the results shown in **Fig. 5**. The spectra appear in the range of 200–350 nm with two absorption shoulders at 259

Fig. 6. Photodegradation of MB by 0–3 mol% Ce-doped ZnWO₄ samples under UV light illumination within 60 min.

and 289 nm for ZnWO₄ attributed to direct excitation from the occupied O 2p orbital to the empty W 5d orbital in ZnWO₄.^{4),14),19)} Comparing to pure ZnWO₄, the absorption edge of 3 mol% Ce-doped ZnWO₄ nanorods appears remarkably blue-shifted resulting from broadening band gap. UV–visible absorption of 3 mol% Ce-doped ZnWO₄ shows shoulder peak at 263 nm due to the f–d electron transition of Ce³⁺ in the ZnWO₄ lattice.^{20),21)} The energy level for Ce³⁺ shows three electron transitions: $^2F_{5/2} \rightarrow ^2F_{7/2}$, $^2F_{5/2} \rightarrow ^2D_{3/2}$ and $^2F_{5/2} \rightarrow ^2D_{5/2}$. The lowest energy transition ($^2F_{5/2} \rightarrow ^2F_{7/2}$) is a Laporte forbidden μ to μ transition corresponding to the $^n f$ to $^n f$ transition. The other two electron transitions ($^2F_{5/2} \rightarrow ^2D_{3/2}$ and $^2F_{5/2} \rightarrow ^2D_{5/2}$) are Laporte allowed $^n f$ to $(n-1)f$ -d transitions. The shoulders peak of 3 mol% Ce-doped ZnWO₄ at 263 is assigned to be $^2F_{5/2} \rightarrow ^2D_{5/2}$ of Ce³⁺ ions.^{20),21)}

The photocatalytic activities of the as-synthesized ZnWO₄ and Ce-doped ZnWO₄ nanostructures were tested by monitoring the degradation of MB under UV light illumination from 11 W low pressure mercury lamp with wavelength of 254 nm. The degradation of MB was monitored using UV–visible spectroscopy at $\lambda_{\max}$ of 663 nm. Before UV light illumination, the MB solutions containing the catalysts were kept in the dark for 1 h for adsorption/desorption equilibrium of MB molecules on surface of photocatalysts. The MB contents adsorbed on photocatalytic surfaces are 10.12, 12.43, 15.62 and 16.23% for ZnWO₄, 1 mol% Ce-doped ZnWO₄, 2 mol% Ce-doped ZnWO₄ and 3 mol% Ce-doped ZnWO₄, respectively. **Figure 6** shows the photodegradation of MB vs time intervals. Under UV irradiation, pure ZnWO₄ shows the MB photodegradation of 63.5%. It can be seen that the efficiency of photocatalyst to degrade the MB was improved by Ce doping and was increased by the increase of Ce content. The 3 mol% Ce-doped ZnWO₄ photocatalyst exhibits the highest photocatalytic activity. The efficiency of 3 mol% Ce-doped ZnWO₄ photocatalyst to degrade MB was 99.13% within 60 min under UV light irradiation. Ce³⁺ dopant can play a role in enhancing the photocatalytic activity of ZnWO₄ due to the presence of defects on the surface of Ce-doped ZnWO₄ nanocrystal. The Ce⁴⁺ ions on the surface of ZnWO₄ trap electrons in the conduction band by transforming Ce⁴⁺ into Ce³⁺ ions.^{16),22)} After that Ce³⁺ ions are oxidized by transferring the electron to the adsorbed O₂ molecules which produce the O₂^{•−} radical.²²⁾ Thus the recombination of electrons and holes in the Ce-doped ZnWO₄ photocatalyst was suppressed and the photocatalytic activity in Ce-doped ZnWO₄ was enhanced.

4. Conclusions

0–3 mol% Ce-doped ZnWO₄ samples as UV-light-responsive photocatalyst have been synthesized by hydrothermal method. In this research, the products are monoclinic ZnWO₄ nanorods with the growth direction of [021]. The photocatalytic activities of as-prepared samples were tested by monitoring through the degradation of MB under UV light illumination. The photodegradation efficiency of 3 mol% Ce-doped ZnWO₄ is as high as 99.13% within 60 min of UV illumination.

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