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. Among them, cerium dopant has received much attention due to its special 4f electron configuration. 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. 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. 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. The cell parameters were determined: \( a = 4.6907 \AA, b = 5.7192 \AA \text{ and } c = 4.9245 \AA \). 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.
confirming that Ce dopant did not change the phase of monoclinic ZnWO₄ structure. An expand view for the peaks at 2θ = 29–33° shows that the diffraction peaks are slightly shifted to lower angle because the ionic Ce³⁺ (1.03 Å)¹¹,¹² is bigger than Zn²⁺ (0.74 Å).¹¹ This phenomenon suggests that Ce³⁺ ions were homogeneously incorporated into the lattice of ZnWO₄ and the successful substitute for Zn²⁺ by Ce³⁺.

Figure 2 shows transmission electron microscopy (TEM) images and SAED pattern of the pure ZnWO₄ sample. They show the formation of well-dispersed ZnWO₄ nanorods. The length and width of these ZnWO₄ nanorods varied from 1–2 µm and 100–150 nm, respectively. SAED pattern of single ZnWO₄ nanorod shows a spot pattern which confirms the single crystalline product. This SAED pattern was interpreted to have an electron beam in the [01−2] direction of the monoclinic ZnWO₄ nanorod.¹³,¹⁴ A typical high-resolution transmission electron microscopic (HRTEM) image of a straight single ZnWO₄ nanorod clearly reveals only the fringe of (100) plane with a lattice spacing of about 0.459 nm, indicating that the ZnWO₄ nanorod is single crystalline in nature. Furthermore, it indicated that [021] is the growth direction of the ZnWO₄ nanorod.¹³,¹⁴

Figure 3 shows TEM and SAED results of 1 and 3 mol % Ce-doped ZnWO₄ nanorods. The Ce-doped ZnWO₄ shows uniform and perfect crystalline nanorods with straight and curve shapes. The 1 and 3 mol % Ce-doped ZnWO₄ 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 ZnWO₄ nanorod. They show spot patterns which confirm that 1 and 3 mol % Ce-doped ZnWO₄ nanorods are single crystal. These SAED patterns recorded by electron beam normal to the long axis of nanorods revealed that the products were monoclinic ZnWO₄ single crystal. These SAED patterns were interpreted to have the electron beam in the [0−12] direction of the monoclinic Ce-doped ZnWO₄ nanorods.¹³,¹⁴

Figure 4 shows XPS spectra of Ce 3d and W 4f of 3 mol % Ce-doped ZnWO₄. It can be seen that Ce 3d₃/₂ and Ce 3d₅/₂ displayed characteristic peaks at 902 and 884 eV which indicated that the Ce ions were tetravalent.¹⁵,¹⁶ The XPS peaks of W 4f₅/₂ and W 4f₇/₂ were detected at 38 and 36 eV, respectively. They confirm the presence of W⁶⁺ ions in the sample.¹⁷,¹⁸ Thus, Ce ions were homogeneously incorporated into the ZnWO₄ lattice.

The optical absorption of the as-synthesized ZnWO₄ and 3 mol % Ce-doped ZnWO₄ 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
and 289 nm for ZnWO$_4$ attributed to direct excitation from the occupied O 2p orbital to the empty W 5d orbital in ZnWO$_4$.$^{6,14,19}$ Comparing to pure ZnWO$_4$, the absorption edge of 3 mol % Ce-doped ZnWO$_4$ nanorods appears remarkably blue-shifted resulting from broadening band gap. UV–visible absorption of 3 mol % Ce-doped ZnWO$_4$ shows shoulder peak at 263 nm due to the f–d electron transition of Ce$^{3+}$ in the ZnWO$_4$ lattice.$^{20,21}$ The energy level for Ce$^{3+}$ shows three electron transitions: $^2F_{5/2} \rightarrow ^2D_{3/2}$ and $^2F_{5/2} \rightarrow ^2D_{5/2}$ and $^2F_{5/2} \rightarrow ^2D_{3/2}$. The lowest energy transition ($^2F_{5/2} \rightarrow ^2F_{7/2}$) is a Laporte forbidden $\mu \rightarrow \mu$ transition corresponding to the $^4$ to $^4$ transition. The other two electron transitions ($^2F_{3/2} \rightarrow ^2D_{3/2}$ and $^2F_{5/2} \rightarrow ^2D_{3/2}$) are Laporte allowed $\delta \rightarrow (n-1)$-$\delta$ transitions. The shoulders peak of 3 mol % Ce-doped ZnWO$_4$ at 263 is assigned to be $^2F_{3/2} \rightarrow ^2D_{5/2}$ of Ce$^{3+}$ ions.$^{20,21}$

The photocatalytic activities of the as-synthesized ZnWO$_4$ and Ce-doped ZnWO$_4$ 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 $\lambda_{\text{max}}$ 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 samples under UV light illumination within 60 min.

4. Conclusions

0–3 mol % Ce-doped ZnWO$_4$ samples as UV-light-responsive photocatalyst have been synthesized by hydrothermal method. In this research, the products are monoclinic ZnWO$_4$ 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 photocatalytic efficiency of 3 mol % Ce-doped ZnWO$_4$ is as high as 99.13% within 60 min of UV illumination.

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References

1) G. Huang and Y. Zhu, Mater. Sci. Eng., B, 139, 201–2085 (2007).
2) G. Huang, S. Zhang, T. Xu and Y. Zhu, Environ. Sci. Technol., 42, 8516–8521 (2008).
3) R. Shi, Y. Wang, D. Li, J. Xu and Y. Zhu, Appl. Catal., B, 100, 173–178 (2010).
4) J. Li, J. Lu and Y. Zhu, Inorg. Chem., 46, 8372–8378 (2007).
5) H. Fu, J. Lin, L. Zhang and Y. Zhu, Appl. Catal., A, 306, 58–67 (2006).
6) G. Huang, C. Zhang and Y. Zhu, J. Alloys Compd., 432, 269–276 (2007).
7) J. Xie, D. Jiang, M. Chen, D. Li, J. Zhu, X. Lu and C. Yan, Colloids Surf., A, 372, 107–114 (2010).
8) M. Yousefi, M. Amir, R. Azimirad and A. Z. Moshfegh, J. Electroanal. Chem., 681, 106–112 (2011).
9) J. W. Shi, J. T. Zheng and P. Wu, J. Hazard. Mater., 161, 416–422 (2009).
10) Powder Diffract File, JCPDS Internat. Centre Diffract. Data, PA 19073-3273, U.S.A. (2001).
11) J. Jung, B. Y. Noh, Y. S. Lee, S. H. Baek, J. H. Kim and I. K. Park, Nanoscale Res. Lett., 7, 1–5 (2012).
12) A. L. Gal and S. Abanades, J. Phys. Chem. C, 116, 13516–13523 (2012).
13) J. Arin, P. Dumrongrojthan, O. Yayapao, A. Phuruangrat, S. Thongtem and T. Thongtem, Superlattices Microstruct., 67, 197–206 (2014).
14) R. C. Dai, Z. P. Wang, Z. M. Zhang and Z. J. Ding, Surf. Interface Anal., 46, 1151–1155 (2014).
15) J. C. Sin, S. M. Lam, K. T. Lee and A. R. Mohamed, J. Mol. Catal. A, 409, 1–10 (2015).
16) M. Faisal, A. A. Ismail, A. A. Ibrahim, H. Bouzid and S. A. Al-Sayari, Chem. Eng. J., 229, 225–233 (2013).
17) Y. Wang, B. Zhang, J. Liu, Q. Yang, X. Cui, Y. Gao, X. Chuai, F. Liu, P. SUN, X. Liang, Y. Sun and G. Lu, Sens. Actuators, B, 236, 67–76 (2014).
18) P. A. Shinde, V. C. Lokhande, N. R. Chodankar, T. Ji, J. H. Kim and C. D. Lokhande, J. Colloid Interface Sci., 483, 261–267 (2016).
19) G. Huang, R. Shi and Y. Zhu, J. Mol. Catal. A, 348, 100–105 (2011).
20) N. Ekhammamatht, T. Thongtem, A. Phuruangrat and S. Thongtem, Rare Met., 30, 572–576 (2011).
21) A. Phuruangrat, T. Thongtem and S. Thongtem, Rare Met., 34, 301–307 (2015).
22) R. Kumar, A. Umar, G. Kumar, M. S. Akhtar, Y. Wang and S. H. Kim, Ceram. Int., 41, 7773–7782 (2015).