Influence of Fluorine on Structure, Morphology, Optical and Photocatalytic Properties of ZnWO₄ Nanostructures

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We report on the synthesis of Fluorine (F) doped ZnWO₄ photocatalysts and the influence of F-doping on their structure, morphology, optical and photocatalytic properties. A two-step process was used to produce F-doped ZnWO₄ photocatalysts. The quality of synthesized materials was characterized using different analytical methods, such as X-ray diffraction analysis, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDS), Fourier transform infrared spectra (FTIR), as well as photoluminescence (PL) measurement. It was found that the photocatalyst morphology and band gap energy strongly depend on the F-doping concentration. The band gap energy of the photocatalysts decreased when increasing F-doping concentration, and reached a lowest value at a concentration of 4 mol%, and then increased thereafter. At 4 mol% of F-doping, nanowires were formed with approximately 1 μm in length and 50 nm in diameter. On the contrary, others F-doped ZnWO₄ samples were obtained in the shape of nanorods or a mixture of nanorods and granular particles. Moreover, it was demonstrated that F-doped ZnWO₄ enhanced photocatalytic activity by a factor of three, as compared to that of undoped ZnWO₄. This enhancement can be explained by the nanowire shape of synthesized F-doped ZnWO₄, its narrow band gap energy and the small recombination rate of photogenerated electron-hole pairs, which was indirectly proved by PL spectra. 

Keywords: photocatalytic, nanorod, recombination, electron-hole pair

1. Introduction

Nowadays environment safety has become one of the hottest-debated issues, which hold the interest of the science community. The application of photocatalytic technology has been proved to be a promising - but challenging - method of treating environmental pollution due to its low cost, high efficiency degradation, simplicity in technology and high stability⁵. Zinc Tungstate ZnWO₄ (ZWO), an important member of Tungstates, is recently shown to be photocatalyticaly active under UV irradiation, sufficient chemical stability and environmentally friendly⁶,⁷. However, its photocatalytic efficiency is restricted by the fast recombination rate of photogenerated electron-hole pairs⁸. Moreover, ZWO presents relatively low photocatalytic efficiency under visible light due to its large band gap energy⁹. Therefore, many studies have been conducted to improve the photocatalytic property of ZWO, especially under the visible light excitation. These studies mainly focused on three following strategies: (1) to increase the specific surface area of ZWO catalyst via controllable morphology⁶; (2) to narrow the band gap energy by the doping of nonmetal elements or transition metals⁸,⁹, by controlling morphology¹⁰,¹¹; or by coupling with other semiconductors¹²,¹³; and (3) to reduce the recombination rate of photogenerated electron-hole pairs¹⁴,¹⁵. Fluorine (F) was believed to be a promising dopant to enhance photocatalytic activity of TiO₂ and non-TiO₂ photocatalysts due to its ability in reducing the recombination rate of photogenerated electron-hole pairs, creating oxygen vacancies, and increasing effective electron mobility¹⁶,¹⁷. The influence of F on the photocatalytic activity of ZWO was reported by Huang et al.¹⁸ An enhanced photocatalytic activity was ascribed to accelerate the transfer-rate of photogenerated electrons to the photocatalyst surface, which resulted in a large number of electrons and holes participating in the photocatalytic process. Later, a study of Sun et al.¹⁹ based on density functional theory calculations showed two different mechanisms for improving photocatalytic activity in different types of F-doped ZWO. When the lattice O atom is substituted by one F atom, a reduced W⁵⁺ center adjacent to the doped F atom will act as a trap for the photo-induced electrons. In case of the interstitial F-doped model, partial F (2p)-states mixing with O (2p)-states localize above the top of the valence band. Electronic transitions from these localized states induce a red shift of about 54 nm of the optical absorption edge, therefore increasing the photocatalytic activity in the UV region.

In this work, we demonstrated a facile two-step process to elaborate F-doped ZWO photocatalysts and systematically studied the influence of F concentration (0–10 mol%) on the structure, morphology, optical and photocatalytic properties of the F-doped photocatalysts. Different experimental methods were used to characterize the quality of synthesized materials, such as X-ray diffraction analysis, field emission scanning electron microscopy (FE-SEM), Fourier transform infrared spectra (FTIR), as well as photoluminescence (PL) measurement. We hope that the presented results will be useful for understanding the mechanisms of F-doping in ZWO crystal lattice and the physical mechanism of the enhancement of F-doped ZWO photocatalytic activity.
2. Experimental Procedure

2.1 Synthesis of F-doped ZnWO4 samples

The experimental process used to synthesize F-doped ZnWO4 photocatalysts consists of two steps: (1) producing a required ionic powder mix and (2) annealing powder for crystallization of the materials. Firstly, a stoichiometric amount of Zn(COOCH3), Na2WO4·2H2O, and NH4F (Sigma-Aldrich) were weighted and dissolved separately in three cups containing 30 ml of distilled water each. The homogeneous solutions were obtained after 30 minutes of magnetic stirring. Solutions containing Zn2+ and W6+ were then poured into a container containing F−. The mixture was again stirred magnetically for 30 minutes and then washed once with ethanol and twice with distilled water to remove remaining Na, using ultrasonic vibration and centrifuge at 4000 rpm. The wet powder obtained was dried in an oven at 60 °C for 5 h to get a white powder. The powder was then milled for 1 hour in a mortar and transferred to an alumina crucible with a lid. Finally, the crucible was heated at a temperature of 700 °C in a tube furnace for 2 hour. Samples doped with various F-doping concentration were labeled as ZFx with x being the mole fraction of F (x = 2, 4, 6, 8, and 10).

2.2 Characterization

A D8 Advance diffractometer (Bruker) with Cu-Kα radiation was used to record X-ray diffraction (XRD) patterns of F-doped ZnWO4 samples. Field-emission scanning electron microscopy (FE-SEM) images were obtained using S-4800 NHIE microscope (Hitachi). A Jasco V670 UV-vis spectrometer was used to measure Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) of the samples. Fourier transform infrared spectra (FTIR) were collected on an IR Prestige-21 FTIR/NIR spectrometer (Shimadzu). Photoluminescence (PL) spectra were performed on a Nanolog iHR 320 fluorescence spectrometer (Horiba) at an excitation wavelength of 325 nm.

2.3 Photocatalytic experiment

Photocatalytic activity of F-doped ZnWO4 materials was evaluated based on the photodegradation of 10 ppm methylene blue (MB) solution. Firstly, 0.1 g of F-doped ZnWO4 was dispersed in a glass cup containing 50 ml of distilled water using magnetic stirrer for 1 h. Then, 50 ml of 20 ppm MB aqueous solution was added to the solution of F-doped ZnWO4. The suspension was stirred in the dark for 30 minutes to reach the equilibrium state of adsorption-desorption. The irradiation of 300 W mercury vapor lamp was used as exciting photons for the generation of electron-hole pairs in ZnWO4. Mercury source is placed approximately 6 cm from reactor. For each measurement, 5 ml of suspension was taken every 1 h and centrifuged to remove F-doped ZnWO4. The degradation rate of MB was evaluated by investigating the change in peak intensity of UV-vis absorbance at 668 nm-wavelength.

3. Results and Discussion

XRD patterns of pure ZWO and all F-doped ZWO samples shown in Fig. 1(a) indicate that all of the as-synthesized samples are pure wolframite-type monoclinic phase ZWO (JCPDS card No. 15-0774). The uniform incorporation of F− ions into the ZWO lattice can be inferred from the fact that no signal for any other phase was detected in F-doped ZWO samples. The detailed XRD scan in the 2θ range of 2θ = 29.7–31.5° and 2θ = 35.8–37.2° is presented in Fig. 1(b). A careful observation of the diffraction peaks shows that the intensities of the (111) and (-111) peaks became weaker as F-doping concentration increases from 0 to 4 mol%, indicating that the crystallinity tends to decrease. In addition, XRD-peak position shifted slightly toward a lower 2θ value. Huang group’s studies3) reported that shifting to lower 2θ angle indicates an interstitial doping configuration of F− ion into ZWO crystal. This is appropriate to explain the lowering crystallization, which can be assigned to the increase of lattice distortion in interstitial doping configuration. When F-doping concentration exceeds 4 mol%, the corresponding peaks intensities become much stronger and also narrower, indicating a better crystallization. On the other hand, the peak position shifted toward higher 2θ values. This illustrates that beside the existence in the interstitial configuration, F− ions begin to replace into the lattice sites of ZnWO4.

Fig. 1 (a) X-ray diffraction patterns of as-synthesized F-doped ZnWO4 photocatalysts with different F-doping concentrations. (b) Zoom in of diffraction peaks in the range of 2θ = 29.7–31.5° and 2θ = 35.8–37.2°.
in substitutional configuration when F concentration exceeds 4 mol%. The better crystallization of F-doped ZWO with F-doping concentration exceeded 4 mol% was also illustrated by the splitting of (021) and (002) peaks at 2θ angle of 36.4°, as shown in Fig. 1(b).

The results of FE-SEM measurements are shown in Fig. 2. It shows that morphologies of F-doped ZWO strongly depend on F-doping concentration. As shown in Fig. 2(a) and 2(b), undoped ZWO and ZF2 sample represented a mixture of granular and rod-shaped nanocrystals. The number of rod-shaped particles in ZF2 sample was larger than in ZWO sample and rod-shaped particles in ZF2 was also larger in diameter and length. For ZF4 sample, most crystal particles grew into nanowire microstructure. Figure 2(c) shows homogeneous morphology of the ZF4 crystallites with nanowires of 1 μm in length and 50 nm in diameter. However, nanowire microstructure was no longer observed for ZF6 sample. Figure 2(d) exhibits short nanorods morphology of ZF6 crystallites about 500 nm in length and 50–150 nm in diameter. Finally, granular-like morphology of ZF8 and ZF10 crystallites can be observed in Fig. 2(e,f). The elements existed in the synthesized samples can be identified from EDS analysis. All samples exhibit the high intense peaks of Zn, W, and O which came from the ZnWO4. ZF4 and ZF10 photocatalysts present a weak peak at about 0.70 keV which can be assigned to the presence of F in the F-doped samples.

The FTIR absorption spectra of as-prepared F-doped ZWO photocatalysts with different F-doping concentrations are shown in Fig. 3. The broad band at 3200–3600 cm$^{-1}$ and the peak at 1639 cm$^{-1}$ were attributed to the stretching vibration and bending vibration of OH groups localized on the...
samples surface, and the peak at 1381 cm\(^{-1}\) corresponds to an OH absorption of hydrogen-related defects\(^{(19)}\). Shi et al.\(^{(10)}\) demonstrated that the surface hydroxyl groups would easily form on ZWO (100) surface. Figure 3 shows that the intensities of 1639 and 3419 peaks first decreased as F-doping concentration increases, and almost disappeared at ZF4 sample, and then increased with higher F-doping concentration. This implies that the number of (100) planes decreases as F-doping concentration increases from 0 to 4 mol\%, and then increased thereafter. This reveals that F-doped ZWO crystallites grew into nanorods and nanowires with a highly [100] preferred orientation. In addition, Shi et al.\(^{(10)}\) also showed that the decrease of the intensities of 1381 cm\(^{-1}\) peaks corresponds to the decrease of the number of hydrogen-related defects, which may act as recombination centers for photocatalytic electrons and holes. The sharp decrease of 1381 cm\(^{-1}\) peak as F-doping concentration increases can be assigned to the decrease of hydrogen-related defects. Therefore, it can be believed that F-doped ZWO samples with F-doping concentration in the range of 4–10 mol\% will exhibit higher photocatalytic activity in comparison to undoped and F-doped ZWO with lower F-doping concentration.

The UV-vis DRS of F-doped ZWO photocatalysts with different doping concentrations are shown in Fig. 4(a). It can be clearly seen that samples absorb mainly in UV range below 400 nm. The band gap energy (\(E_g\)) can be estimated from the Tauc plots of the dependence of \((\alpha h \nu)^2\) on photon energy, as shown in Fig. 4(b). The band gap energy of ZWO sample was found at 3.23 eV, smaller than that in previous studies where materials were synthesized by hydrothermal route\(^{(20,21)}\). As F-doping concentration increases, the absorption edge first slightly shifted to the right up to 4 mol\% and then shifted to the left with further doping. As a consequence, the band gap energy first decreased with increasing F-doping concentration, reaching a lowest value of 3.20 eV for ZF4, and then increased with further increasing of F-doping concentration, as shown in inset figure in Fig. 4(a). Sun et al.\(^{(18)}\) reported that the red shift of optical absorption edge was a consequence of interstitial configuration of F. Hence, observed variation of band gap energy also demonstrated the interstitial configuration of F\(^-\) ions in ZWO crystal lattice for the low range 0–4 mol\% of F-doping content, agreeing with above XRD discussion.

To investigate the photocatalytic performance of as-synthesized F-doped ZWO photocatalysts with different doping contents, MB was used as the target of photocatalytic degradation under irradiation of mercury vapor lamp. The rate of change in MB concentration \(C/C_0\) can be determined from the decrease of the absorbance at 668 nm peak of the MB solution by comparing to the standard curve expressing the change of absorbance as a function of MB concentration. Figure 5(a) presents the photocatalytic activities of the F-doped ZWO photocatalysts for degradation of MB. With an increase of F-doping concentration, the photocatalytic activity of F-doped ZWO increased and reached to a maximum and then decreased with further increasing of F-doping concentration. At 4 mol\% of F concentration, ZF4 photocatalyst reached to the highest visible photocatalytic activity, 85\% of MB content can be degraded in 5 h, which is three times larger than that of undoped ZWO sample. However, with further increasing of F-doping concentration, photocatalytic efficiency decreased from 85\% for ZF4 sample to 62\% for ZF10 sample. The observed trend in photocatalytic efficiency is consistent with the report of Lin et al.\(^{(22)}\). The researchers reported that the [100] preferred orientation growth of ZnWO\(_4\) nanorods can enhance the photocatalytic efficiency. Based on the analysis results of XRD, FTIR, FE-SEM, and DRS measurements, the enhanced photocatalytic activity can be attributed to: (i) the increase of the specific surface area of adsorption substance due to the formation of nanorods and nanowires, which leads to the faster rate of photocatalysis reaction; (ii) the decrease of the number of hydrogen-related defects which act as the electron-hole recombination centers; and (iii) the narrowing of band gap energy, resulting in the increase of absorbance at the wavelength of mercury irradiation which can stimulate the generation of electron-hole pairs.

Photoluminescence spectrum measurement is an effective method to investigate the separation and recombination of photogenerated carriers. The photoluminescence intensity determines the number of electron-hole recombination. In order to compare the recombination rate of electron-hole
pairs between ZWO, ZF2, ZF4, and ZF10 samples, PL spectra were carried out in the same measurement condition (see Fig. 5(b)). The PL intensity of ZWO sample was relatively higher, indicating that the photogenerated electrons and holes were easy to recombine together. In contrast, the PL intensity of F-doped ZWO samples decreased strongly with decreasing of F concentration, illustrating that F-doping induced a separation of photogenerated carriers and hence a reduction of electron-hole recombination. The decrease of PL intensity of F-doped ZWO samples can be attributed to the decrease of the number of hydrogen-related recombination centers as discussed above in FTIR analysis. In addition, the remarkable reduce of PL intensity in ZF10 sample compared to that of others can be assigned to the much higher crystallization as shown in XRD result. This result confirms that the origin of photocatalytic enhancement is partly contributed from the decrease of the recombination rate of photogenerated electron-hole pairs.

4. Conclusions

F-doped ZWO photocatalysts with varying doping concentration were synthesized by a simple two-step process and experimentally characterized by different optical methods. With the increasing of F-doping concentration, F\textsuperscript{-} ions were introduced into ZWO matrix by a two-stage mechanism. Doping of F\textsuperscript{-} ions was predominantly in the interstitial configuration when the concentration of F\textsuperscript{-} impurity was low, whereas in impurity concentration range greater than 4 mol\% the substitutional configuration was exhibited significantly. The incorporation of F into ZWO matrix allowed controlling the morphology, band gap energy, and photocatalytic property of ZWO photocatalyst. Experimental results confirmed that sample with F-doping concentration of 4 mol\% exhibited a highest photocatalytic efficiency, which was explained by the nanowire shape of the synthesized materials, its narrow band gap energy, and the decrease of the recombination rate of photogenerated carriers.

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