A simple post-synthesis conversion approach to Zn(OH)F and the effects of fluorine and hydroxyl on the photodegradation properties of dye wastewater

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Abstract

In this work, Zn(OH)F is prepared by an initiative, simple post-synthesis method, in which the molar ratio of F/Zn (R_F) was varied to investigate the effect of the NH_4F amounts added on the samples. Further, we have mainly investigated their energy bands and photochemical properties. Under UV light irradiation ($\lambda \leq 420\text{nm}$), the samples ($R_F=0,1,2$) show the high degradation activities of methylene blue (MB) dye, namely, 80% of MB can be degraded after 8 min. It is found that the hydroxyl and fluorine have greatly down shifted the conduction band (CB, 0.99 eV) and valence band (VB, 4.17 eV) of Zn(OH)F, compared with ZnO (CB=-0.31 eV, VB=2.89 eV),

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but with the nearly same band gap. For the degradation of MB dye, the main oxidative species are holes and hydroxyl radicals for ZnO and Zn(OH)F, respectively. This study suggests that this simple post-synthesis fluorination approach could be extended to develop the other photocatalysts; moreover, we can facilely tune the band structure and photocatalytic activity by introducing or removing hydroxyl and fluorine, which could benefit to develop new photocatalysts.

Keywords: Dye wastewater; Fluorine; hydroxyl; Energy band; Zn(OH)F

1. Introduction

Since the first report by Fujishima and Honda [1], solar energy-driven photocatalytic degradation technology of organic pollutant has been studied intensively. However, the practical applications of photocatalysis are greatly limited by the low quantum efficiency, light utilization efficiency and photo-activity. Specifically, the low photochemistry activities for most of visible light and near-infrared light responsive semiconductors and the low utilization of solar energy for ultraviolet light responsive ones are still big challenges for photocatalysis [2-6]. Thus, it is necessary to well understand crystal structure and to reveal the essential structure-property relationship, so as to develop an excellent photocatalyst.

Among various zinc-containing materials, ZnO has a direct band gap (3.37 eV) and a large exciton binding energy (60 eV), which has been widely used in photocatalysis [2], sensors [3], solar cell [4], optical wave guides [5], room-temperature UV laser [6]. Besides, Zn(OH)F has been reported as selective oxidation catalysts, photoluminescence, optoelectronics devices, and so on [7-18]. For example, Huang *et al.* [9] have prepared Zn(OH)F nanowires by the hydrothermal method; Peng *et al.* [11] have reported that Zn(OH)F has a higher photocatalytic activity than that of commercial TiO₂; Peng *et al.* [18] have also report that the Zn(OH)F possess a high photocatalytic activity and 85% of MO can be degraded after 60 min. Herein, Zn(OH)F and ZnO are typically selected as the objectives to the influence of OH and F on the band structure and photochemical properties of a semiconductor. To the best of our knowledge, however, less work has reported the effect of chemical atomic group on the photochemical properties of a semiconductor. Therefore, this work could benefit to develop new photocatalysts.

In this work, Zn(OH)F was prepared by an initiative post-synthesis method using NH_4F as the fluorination agent under hydrothermal conditions. The as-prepared samples have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and electron diffraction (ED), UV-vis diffused reflectance spectra (UV-DRS), surface pressure (SPV), FT-IR spectra and photoluminescence spectra (PL). Further, the effect of the NH_4F amount added upon the product has been mainly investigated. Moreover, we have mainly revealed the influences of hydroxyl and fluorine on the band structure and photochemical properties of Zn(OH)F and ZnO .

2. Experimental

2.1. Sample preparation

All reagents were of analytical grade, purchased from Beijing Chemical Reagents Industrial Company of China, and were used without further purification.

Synthesis of ZnO . In a typical process, 1.75 mmol ZnCl_2 and 21.0 mmol NaOH were dissolved in 5ml ethanol/30ml distilled water. After being stirred for 20 min at room temperature, the mixture was transferred into a 50-ml Teflon-lined stainless steel autoclave, and then was heated and kept at 140 °C for 12 h. After the autoclave was cooled to room temperature naturally, the sample was separated by centrifugation, washed with distilled water and ethanol several times, and dried at 60 °C for 12 h. Finally, the as-prepared sample was heated at 400 °C for 2 h in air in a muffle furnace.

Synthesis of Zn(OH)F . The as-synthesized ZnO (1 mmol) and different amounts of NH_4F (1, 2, 4, 8 and 16 mmol) were added in 35ml distilled water, and the mixture was stirred at room temperature for 15 min. The mixture was transferred into

a 50-ml Teflon-lined stainless steel autoclave, then was heated and kept at 180 °C for 24h. After being cooled to room temperature naturally, the sample was separated by centrifugation, washed with distilled water and ethanol several times, and dried at 60 °C for 12h. Herein, the molar ratio of F/Zn (R_F) was varied to investigate the effect of the NH_4F amounts added on the samples.

2.2. Characterization

The crystal structures of the samples were determined by X-ray powder polycrystalline diffractometer (Rigaku D/max-2550VB), using graphite monochromatized Cu K_α radiation ($\lambda = 0.154$ nm), operating at 40 kV and 50mA. The XRD patterns were obtained in the range of 10-80° (2 θ) at a scanning rate of 7 ° min⁻¹. The samples were characterized on a scanning electron microscope (SEM, Hitachi SU-1510) with an acceleration voltage of 15 keV. The samples were coated with 5-nm-thick gold layer before observations. The fine surface structures of the samples were determined by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) equipped with an electron diffraction (ED) attachment with an acceleration voltage of 200 kV. UV-vis diffuse reflectance spectra of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO_4 was used as a reflectance standard in a UV-vis diffuse reflectance experiment. Fourier transform infrared spectra (FT-IR) were recorded on a Fourier transform infrared spectrometer (FT-IR, KBr disk method; Thermo Scientific Nicolet iS5). Photoluminescence (PL) spectra were measured on a fluorescence spectrophotometer (Japan, Shimadzu RF-5301PC) excited with a Xe lamp as the excitation source. Nitrogen sorption isotherms were performed at 77 K and $< 10^{-4}$ bar on a Micromeritics ASAP2010 gas adsorption analyzer. Each sample was degassed at

120 °C for 5 h before measurements. Nitrogen adsorption–desorption isotherms were obtained at 77 K using the Autosorb-iQ physicoadsorption apparatus (Quantachrome). Surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

An electrochemical system (CHI-660B, China) was employed to measure the electrochemical impedance spectroscopy (EIS) and photocurrent. EIS was performed from 0.1 Hz to 100 kHz at an open circuit potential of 0.3 V and alternating current (AC) voltage amplitude of 5 mV. The data were analyzed by Zsimwin software. Photocurrent measurement was carried out in a conventional three-electrode system, in which indium-tin oxide (ITO) glass was used as the current collector to fabricate photo electrode, and 0.1M Na₂SO₄ was used as the electrolyte solution. The sample/ITO photo electrodes were prepared by a dip-coating method. The photo electrode was implemented as the photo anode in a photoelectrochemical cell (PEC).

The surface photovoltage (SPV) measurement system is consists of a monochromatic light source, a lock-in amplifier (SR830-DSP) with a light chopper (SR540), a photovoltaic cell and a computer. The monochromatic light is provided by a 500 W xenon lamp (CHFXQ500 W, Global Xenon Lamp Power) and a double-prism monochromator (Zolix SBP500). During the SPV measurement, the samples were test without further treatment. While the measurement of surface photovoltage was performed, the contact between the samples and the indium tin oxide (ITO) electrode was not ohmic. The construction of the photovoltaic cell is a sandwich like structure, which consist of steel timber, sample and ITO. We placed the powders on the steel timber electrode, then, the powder was pressed to obtain a film with ITO electrode.

2.3. Photocatalytic activity measurements

The catalytic activity of the sample was performed under UV light irradiation ($\lambda \leq 420$ nm) 0.1 g of catalyst was dispersed in 200 mL of 5 mg/L MB aqueous solution, which was irradiated with a 500-W high pressure Xe lamp as light source. The reaction system was placed in a sealed black box with the top opened, and the distance between the reaction system and light source was 15 cm. Before the lamp was turned on, the suspension was continuously stirred for 30 min in the dark to ensure the establishment of an adsorption–desorption equilibrium between the catalyst and MB. During degradation, 3-5 mL of the solution was collected using a pipette at intervals of irradiation, and subsequently centrifuged to remove the catalyst. UV-vis spectra were recorded using a Spectrumlab 664sp spectrophotometer to determine the concentration of MB.

3. Results and discussion

3.1 Crystal structure and morphology of the samples

Fig. 1 shows the XRD patterns of the samples prepared at different F/Zn molar ratios (R_F). At $R_F=0$, the sample can be indexed to phase-pure ZnO (JCPDS36-1451). At $R_F=1$, the sample is mainly composed of ZnO (JCPDS36-1451), along with a small amount of Zn(OH)F (JCPDS74-1816). At $R_F=2$, the amount of Zn(OH)F has increased obviously. Moreover, all the samples at $R_F=4, 8$ and 16 are the pure-phase Zn(OH)F, and no ZnO peaks can be detected. It is obvious that the addition amount of fluorine has a great effect on the formation of Zn(OH)F.

Fig. 2 shows the scanning electron microscopy (SEM) of the samples. Fig. 2a shows that the ZnO flowers form at $R_F=0$, which are assembled by the 3~5- μm microrods. From Fig. 2b, we can see that at $R_F=1$, a few of nanoparticles are attached on the surfaces of ZnO microrods, which could be Zn(OH)F. Fig. 2c shows that at $R_F=2$, the formed microrods are 50 μm long, and some of ZnO flowers are still present. At $R_F=4$, ZnO flowers have disappeared completely, and the fan-like microstructures have formed (Fig. 2d). At $R_F=8$, the uniform short microbelts have formed (Fig. 2e). Fig. 2f shows that at $R_F=16$, the Zn(OH)F flowers consisting of 5-10 μm microbelts have formed. It is clear that the R_F value has also an obvious influence on the particles morphology. Also, a simple growth mechanism of Zn(OH)F has been discussed in electronic supporting information (ESI).

Typically, Fig. 3 (a-c) shows the high-resolution electron emission microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns of the sample at $R_F=1$. Fig. 3a shows that the Zn(OH)F nanoparticles are attached on the ZnO microrods. In Fig. 3b, the lattice fringe spacings of 0.432 nm and 0.245 nm can

be indexed to the (110) crystal plane of Zn(OH)F and the (002) crystal plane of ZnO, respectively. In Fig. 3c, the typical diffraction spots can be indexed to the (110) Bragg reflections of Zn(OH)F and the (002) Bragg reflections of ZnO, respectively. The results reveal the single-crystalline properties of both ZnO and Zn(OH)F, and also confirm the formation of ZnO/Zn(OH)F at $R_F=1$. Further, Fig. 3 (d-f) shows the typical HRTEM and SAED patterns of the sample ($R_F=16$). Fig. 3d shows that the nanobelt is 220 nm wide. Fig. 3e shows the lattice fringe spacings of the sample are determined to be 0.217 nm and 0.335 nm, which correspond to (220) and (210) crystal planes of Zn(OH)F, respectively. Fig. 3f shows that the typical diffraction spots can be indexed to the (220) and (210) Bragg reflections of Zn(OH)F, also revealing the single-crystalline property of Zn(OH)F.

3.2 Optical properties of the samples

Fig. 4a shows the UV-Vis absorption spectra of the as-prepared samples. The absorption edges of Zn(OH)F and ZnO are determined to be at about 384 and 388 nm. Typically, Fig. 4b shows Tauc plots of absorption² *versus* energy and absorption^{1/2} *versus* energy of Zn(OH)F ($R_F=4$) in the absorption edge region. For a direct optical transition semiconductor, the square of absorption coefficient is linear with energy, whereas the square root of absorption coefficient linear with energy for an indirect optical transition one [19]. Obviously, the plot of absorption² *versus* energy is nearly linear, whereas the plot of absorption^{1/2} *versus* energy deviates from the fitted straight line. Thus, we could infer that Zn(OH)F is a direct optical transition semiconductor. Fig. 4c suggests that ZnO is also a direct optical transition semiconductor. The band gap of a semiconductor can be determined by the following equation (1) [20,21]:

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

where α , ν , A and E_g represent absorption coefficient, light frequency, proportionality constant and band gap, respectively; and n is dependent on the optical transition type of a semiconductor ($n=1$ for a direct optical absorption; $n=4$ for an indirect optical absorption). From the plot of absorption² *versus* energy, the band gaps of Zn(OH)F and ZnO are estimated to be 3.23 eV and 3.2 eV, respectively.

Moreover, we have calculated the positions of conduction band (E_{CB}) and valence bands (E_{VB}) using Equations (2) and (3) as follows [22].

$$E_{CB} = \chi - E_e - 0.5E_g \quad (2)$$

$$E_{VB} = \chi - E_e + 0.5E_g \quad (3)$$

where χ and E_e , represent the geometric mean of Mulliken's electronegativities of constituent atoms and energy of free electrons on the hydrogen scale (~ 4.5 eV), respectively. For Zn(OH)F, the χ value is calculated to be 7.08 eV, and E_{VB} and E_{CB} are calculated to be 4.2 and 0.97 eV, respectively. For ZnO, the χ value is calculated to be 5.79 eV, E_{VB} and E_{CB} of ZnO are calculated to be 2.89 and -0.31 eV, respectively. It is obvious that compared with that of ZnO, E_{VB} and E_{CB} of Zn(OH)F have down shifted, and their energy bands are matched well, suggesting that an efficient heterojunction can form, which would favors for the charge separation.

3.3 Influences of hydroxyl and fluorine on energy band and electronic structure of the samples

Fig. S1 (seeing ESI) shows the FT-IR spectra of Zn(OH)F and ZnO. It is observed that the absorption bands at 3373 and 3431 cm^{-1} correspond to the lattice stretching vibration mode of the associated O-H, which is due to the presence of the

absorbed water on the solid surface. The absorption band at 3555 cm^{-1} corresponds to the lattice vibration stretching modes of the dissociated O-H. The bending vibration bands of O-H appear at 1384 and 1636 cm^{-1} for both Zn(OH)F and ZnO samples. In addition, the absorption bands of Zn-O appear at 881 and 1020 cm^{-1} of ZnO. And the band of Zn-O of Zn(OH)F also appear at 473 , 523 , 881 and 1020 cm^{-1} . Summarily, the FT-IR spectra also demonstrate the presences of hydroxyl and Zn-O in Zn(OH)F.

Further, the *ab initio* density function theory (DFT) calculations have been carried out to investigate the energy band and electronic structures of Zn(OH)F and ZnO. Fig. 5a shows that valence band maximum (VBM) and conduction band minimum (CBM) converge at the G point, confirming the direct band gap property of ZnO. It can be found that the band gap between VBM and CBM is 2.80 eV , which is narrower than the UV-DRS result (3.2 eV). This difference is a common feature of DFT calculations that usually underestimates the band gap [23,24]. Fig. 5b shows the total and partial density of states (TDOS, PODS). It can be seen that the valence band (VB) of ZnO is mainly composed of both Zn 3d and O 2p orbits, and the conduction band (CB) of ZnO is mainly composed of Zn 4p and Zn 4s orbits.

The energy band structures of Zn(OH)F are shown in Fig. 5c. Obviously, the VBM and CBM converge at the G point, showing that Zn(OH)F is also a direct band gap semiconductor. The band gap between VBM and CBM is 2.89 eV , which is also narrower than the UV-DRS result (3.23 eV). Fig. 5d shows that the VB of Zn(OH)F is mainly composed of Zn 3d, O2p and F 2p orbits; and its CB is not only composed of O2p and F 2p orbits, but also of a small part of H1s orbit. Compared with the E_{VB} (2.89 eV) of ZnO, the E_{VB} of Zn(OH)F increases to 4.2 eV , which could be caused by the O 2p orbital of hydroxyl. However, the E_{CB} (0.97 eV) of Zn(OH)F becomes more positive than that (-0.31 eV) of ZnO, which could be induced by the H 1s orbital of

hydroxyl. It is clear that hydroxyl and F have significant influences on the energy band structure of a semiconductor. The similar results have been demonstrated in our previous report on $\text{Bi}_2\text{O}(\text{OH})_2\text{SO}_4$ and $\text{Bi}_6\text{S}_2\text{O}_{15}$ [25].

Moreover, in order to understand the effects of OH and F on energy band structure, we have constructed the super cell of ZnO and Zn(OH)F (Figure 6). Fig. 6a shows that ZnO has a hexagonal space group ($P63mc$), with the cell parameters of $a = 3.25\text{\AA}$, $b = 3.25\text{\AA}$ and $c = 5.21\text{\AA}$. It is observed that the bond length between O(1)-Zn(1) is $1.98\text{\AA}$, and the bond angle of O(1)-Zn(1)-O(1) is 108.06° . Fig. 6(b,c) present the super cell of Zn(OH)F. It has an orthorhombic space group ($PNA21$), with the cell parameters of $a = 10.13\text{\AA}$, $b = 4.76\text{\AA}$ and $c = 3.12\text{\AA}$. It is interesting that the O and F atoms both locate at the same position. In the ZnO unit cell, only O(1)-Zn(1)-O(1) bonds are contained, but in the Zn(OH)F unit cell, both [O(1)/F]-Zn(1)-[O(1)/F] and [O(1)/F]-Zn(1)-[O(2)/F] bonds are contained. The higher electronegativity of F than that of O suggests that F has a higher ability of attracting electron than O. Thus, the attracting electron ability of the O/F is higher than O, which could be responsible for the formation of [O(1)/F]-Zn(1)-[O(1)/F] and [O(1)/F]-Zn(1)-[O(2)/F] bonds in Zn(OH)F. Furthermore, the distance between O(1)/F and Zn(1) in the Zn(OH)F super cell increases to 2.03, 2.06 and $3.72\text{\AA}$, respectively; and the distance between O(2)/F and Zn(1) is $2.12\text{\AA}$. The bond angle of [O(1)/F]-Zn(1)-[O(1)/F] changes from 108.06° in ZnO to 56.23° , 98.26° , respectively; and the bond angle of [O(1)/F]-Zn(1)-[O(2)/F] is 54.39° . Compared with ZnO, Zn(OH)F shows a different crystal structure due to the presences of hydroxyl and fluorine.

3.4 Photo catalytic properties of the samples

Fig. 7a shows the degradation of methylene blue (MB) under UV light irradiation ($\lambda \leq 420\text{nm}$) by the samples synthesized at different R_F . ZnO ($R_F=0$) and Zn(OH)F/ZnO ($R_F=1$) samples have the higher catalytic activities than the others; and after irradiation for 8 min, 80% of MB can be degraded. At $R_F=2$, the Zn(OH)F/ZnO sample also has a high catalytic activity: after 12 min, 78% of MB can be degraded. At $R_F=4, 8$ and 16 , nevertheless, the Zn(OH)F samples have lower photocatalytic activities, and after irradiation for 105 min, 77% of MB can be degraded by Zn(OH)F ($R_F=16$). In Fig. 7b, the apparent reaction rate constants (k_a) of the samples are 0.172 ($R_F=0$), 0.191 ($R_F=1$), 0.116 ($R_F=2$), 0.018 ($R_F=4$), 0.015 ($R_F=8$) and 0.014 ($R_F=16$) min^{-1} . It is clear that the k_a value of the Zn(OH)F-ZnO sample ($R_F=1$) is 12.6 times higher than that of the Zn(OH)F sample ($R_F=16$). This also show that the degradation activities of the Zn(OH)F samples at higher F/Zn molar ratios ($R_F=4, 8, 16$) are not obviously different, indicating that Zn(OH)F has a lower activity than ZnO.

Typically, the trapping experiments have been performed to explore the active oxidative species over ZnO ($R_F=0$, Fig. 8a) and Zn(OH)F ($R_F=4$, Fig. 8b), in which 1 mmol ammonium oxalate and 5mL dimethyl sulfoxide (DMSO) are used as the hole scavenger²¹ and the hydroxyl radical scavenger [26,27], respectively. For ZnO, the degradation activity of MB decreases when adding DMSO, whereas the degradation activity of MB has been nearly inhibited when adding ammonium oxalate. The results demonstrate that for ZnO, hydroxyl and hole are both oxidative species, and hole plays a more important role than hydroxyl. In contrast, Fig. 8b shows that the degradation activity of Zn(OH)F has been greatly inhibited after adding DMSO, but the degradation activity has almost not decrease while adding ammonium oxalate. The result shows that the hydroxyl radical is the major active oxidative species for

Zn(OH)F. It is obvious that the oxidative species are different over ZnO and Zn(OH)F.

Generally, the surface area of catalyst has an important influence on the photocatalytic activity [28]. In Tab. 1, the BET areas of the as-prepared samples at $R_F=0, 1, 2, 4, 8$ and 16 are $8.3, 10.2, 4.6, 7.2, 5.9$ and $6.7\text{m}^2/\text{g}$, respectively. The BET areas of the samples at $R_F=0$ and 1 are obviously larger than those of the others, leading to the higher catalytic activities. But with increasing R_F to $2, 4, 8$ and 16 , we cannot find a direct relationship between the activity and the BET area. It could be the other factor that mainly governs the photocatalytic activities of the samples ($R_F=2, 4, 8$ and 16).

Then, we have measured the surface photovoltage (SPV) spectra over ZnO and Zn(OH)F (Fig. 9). Under light irradiation, the photoinduced charges are separated in bulk space and transfer to the irradiation surface. When the photo generated holes transfer to the irradiation surface, a positive SPV signal will be produced, since the holes are positively charged. On the contrary, when the photogenerated electrons transfer to the irradiation surface, a negative SPV signal will be produced, since the electrons are negative charged. A negative SPV signal suggests that the photoinduced electrons mainly transfer to the irradiation surface of a solid, whereas a positive SPV signal suggests that the photoinduced holes mainly move to the irradiation surface of a solid [29]. For ZnO, a strong negative SPV signal appears, indicating that the photogenerated electrons are easier to transfer to the irradiation surface than holes. Thus, these accumulated electrons on the surface of ZnO could be captured by the dissolved oxygen in solution to form superoxide radical. Thus, we could assume that the electrons may be mainly involved in dye degradation process. For Zn(OH)F, on the contrary, the photoinduced holes is easier to transfer to the surface than electrons,

leading to a positive SPV signal. Similarly, we could assume that these accumulated holes, and/or then produced hydroxyls, may be mainly involved in dye degradation process. Moreover, the photodegradation reaction has been performed in the absence of dissolved O_2 (*i.e.* bubbled with N_2). Fig. S2 (seeing ESI) shows that after 8 min, 71% of MB can be degraded by ZnO in the presence of O_2 , but only 55.6% of MB can be degraded while bubbling N_2 . It is obvious that ZnO in the presence of O_2 exhibits a higher activity than under bubbling N_2 . During the photocatalytic reaction, the amount of dissolved oxygen decreases under bubbling N_2 , which would inhibit the formation of superoxide radicals, resulting in a lower photocatalytic activity. Further, the SPV signals for ZnO are greatly stronger than those for Zn(OH)F, also indicating that more electrons and holes have separated, compared ZnO with Zn(OH)F. Thus ZnO shows a higher activity than Zn(OH)F. Further, the photocurrent analyses have been further investigated to study the charge separation and transfer (Fig. 10). When light-on, the extremely lower photocurrent can be observed for the samples at $R_F=4, 8$ and 16 , which are only about one percent of those for the samples at $R_F=0, 1$ and 2 . Usually, a higher transient photocurrent indicates a higher transfer and separation efficiency of charges, which favors for a higher photocatalytic activity [30]. Moreover, we can see from the Figure 10a that the sample at $R_F=1$ has a largest photocurrent amongst, which may result from the formation of ZnO/Zn(OH)F heterojunction due to the matched energy bands [31]. Besides, the electrochemical impedance spectra (EIS) are measured to investigate the electron transfer ability of the samples. Usually, a smaller semicircle radius in a Nyquist plot means a smaller electrical resistance [32]. In Fig. 10c, the semicircle radius of the ZnO ($R_F=0$) and Zn(OH)F/ZnO ($R_F=1$) samples are obviously smaller than the other samples, indicating a smaller electron transfer resistances. A higher electron transfer ability favors for the efficient charge separation,

thus leading to the higher photocatalytic activities of ZnO ($R_F=0$) and Zn(OH)F/ZnO ($R_F=1$).

Moreover, Fig. S3 (seeing ESI) shows the photoluminescence spectra (PL), which could reflect the recombination probability of photogenerated electrons and holes [33,34]. PL spectra of the ZnO ($R_F=0$) and Zn(OH)F/ZnO ($R_F=1$ and 2) samples are excited at 325 nm (Figure S2a), and PL spectra of the Zn(OH)F samples ($R_F=4$, 8 and 16) are excited at 285 nm (Fig. S2b, seeing ESI). From Fig. S3a (seeing ESI), the emission peaks of the samples are at about 362, 388, 393, 408, 421 and 445 nm, of which the PL peak at 421nm is resultant from the band edge free excitons [35] and the peak at 388nm is attributed to the excitonic recombination of the near-band edge emission [36]. In Fig. S3b (seeing ESI), the emission peaks are at about 358, 428 and 461nm, indicating that the Zn(OH)F could be a good near-ultraviolet material [11].

Finally, the cycle stability is one of the most important parameters for a photocatalyst. Typically, Fig. 11 shows the cycle stability of Zn(OH)F ($R_F=4$) for the degradation of MB under UV light irradiation ($\lambda \leq 420\text{nm}$). After five cycles, the degradation activity over Zn(OH)F does not decrease. Further, Fig. S4 (seeing ESI) shows the XRD patterns of Zn(OH)F sample after five cycles. It is obvious that the diffraction peaks of Zn(OH)F sample have not changed after five cycles. Fig. S5 (seeing ESI) shows the SEM images of Zn(OH)F sample before and after five cycles. Obviously, the morphology of the Zn(OH)F sample has also not changed. The results demonstrate a high stability of Zn(OH)F.

4. Conclusions

Zn(OH)F can be facilely prepared by a simple post-synthesis method. The

introductions of hydroxyl and fluorine have greatly down shifted conduction and valence bands at a nearly same extent, and Zn(OH)F and ZnO have nearly same band gap. Although the photocatalytic activity of Zn(OH)F is lower than that ZnO, this work suggests that we could tune the band structure by introducing or removing functional chemical group, so as to develop the other photocatalysts.

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Title list of Tables and Figures

Table 1

Band gap (E_g), valence band maximum (E_{VB}), conduction band minimum (E_{CB}) and BET areas of the samples

Sample	Phase composition	χ^* (eV)	E_g (eV)	E_{VB} (ev)	E_{CB} (eV)	BET area (m ² g ⁻¹)
R _F =0	hexagonal ZnO	5.79	3.20	2.89	-0.31	8.3
R _F =1	ZnO + less Zn(OH)F	/	/	/	/	10.2
R _F =2	ZnO + Zn(OH)F	/	/	/	/	4.6
R _F =4	orthorhombic Zn(OH)F	7.08	3.23	4.2	0.97	7.2
R _F =8	orthorhombic Zn(OH)F	/	/	/	/	5.9
R _F =16	orthorhombic Zn(OH)F	/	/	/	/	6.7

Notes: χ , geometric mean of Mulliken's electronegativities; R_F, F/Zn molar ratio

Fig. 1.

Fig. 1. X-ray diffraction patterns (XRD) of the samples prepared at different F/Zn molar ratios (R_F): (a) $R_F = 0, 1, 2$; (b) $R_F = 4, 8, 16$

Fig. 2.

Fig. 2. Scanning electron microscopy (SEM) images of the samples prepared at different R_F : (a) $R_F=0$; (b) $R_F=1$; (c) $R_F=2$; (d) $R_F=4$; (e) $R_F=8$; (f) $R_F=16$.

Fig. 3.

Fig. 3. High-resolution electron emission microscopy (HRTEM) images and selected area electron diffraction pattern (SAED) of the samples:

(a-c) $R_F=1$, $\text{ZnO} + \text{Zn(OH)F}$; (d-f) $R_F=16$, Zn(OH)F .

Fig. 4.

Fig. 4. (a) Ultraviolet-visible diffuse reflectance spectra (UV-DRS) of the samples prepared at different R_F ; (b) Tauc plots ($\alpha^{1/2}$ and α^2 vs. energy) of the Zn(OH)F sample prepared at $R_F = 4$; (c) Tauc plot (absorption² vs. energy) of ZnO sample prepared at $R_F = 0$

Fig. 5.

Fig. 5. Energy band structures and total and partial densities of states (TDOS, PDOS) of the samples: (a,b) ZnO; (c,d) Zn(OH)F

Fig. 6.

Fig. 6. Super crystal cells of (a) ZnO and (b,c) Zn(OH)F: Gray, Zn; red, both O and F locate at one same location.

Fig. 7.

Fig. 7. Degradation curves (a) and apparent reaction kinetic curves (b) of MB over the samples prepared at different R_F under UV light irradiation ($\lambda \leq 420 \text{ nm}$).

Fig. 8.

Fig. 8. Degradation curves of MB while adding different trapping chemicals under UV light irradiation ($\lambda \leq 420\text{nm}$): (a) ZnO ($R_F=0$); (b) Zn(OH)F ($R_F=4$).

Fig. 9.

Fig. 9. Room temperature surface photovoltage (SPV) of the samples: ZnO and Zn(OH)F ($R_F=4$).

Fig. 10.

Fig. 10. Photocurrent response spectra (a,b) of the samples under UV light irradiation ($\lambda \leq 420\text{nm}$) and Nyquist plots (c) of the samples prepared at different R_F .

Fig. 11.

Fig. 11. Cycle stability test of Zn(OH)F sample under UV light irradiation

($\lambda \leq 420\text{nm}$).

Graphic Abstract

Compared with ZnO, OH and F have greatly down shifted the conduction band and valence band of Zn(OH)F.