Enhanced visible-light-driven photocatalytic activities for assembled hierarchical Bi$_2$WO$_6$ microspheres by fluorine substitution

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Abstract. The different compositions of Bi$_2$WO$_6$ by fluorine substitution have been successfully synthesized via a two-step hydrothermal process in the absence of a surfactant. The morphology of all F-doped Bi$_2$WO$_6$ samples was similar with pure Bi$_2$WO$_6$ samples. On the basis of maintaining good morphology, the introducing fluorine element only replaced the O atoms of WO$_6$ octahedron in Bi$_2$WO$_6$. The effects of F-substitution on the crystal structure and photocatalytic activity of Bi$_2$WO$_6$ were investigated. For the Bi$_2$WO$_6$ samples with the different Fluorine content, their band gaps have changed obviously. All F-doped Bi$_2$WO$_6$ samples exhibited good photocatalytic activity in degradation of RhB under 500W Xe lamp light irradiation. It shows that photocatalytic activities of F-doped Bi$_2$WO$_6$ samples are relevant to band gap and F content.

1. Introduction
On account of the rising level of environmental pollution, the researchers paid more and more attentions to environmentally friendly materials of photodegradation catalysts [1, 2]. Since Bi$_2$WO$_6$ has many excellent intrinsic physical and chemical properties such catalytic behavior, oxide anion conduction and luminescent properties [3-8], it can be used as an excellent photocatalyst splitting water and mineralization of organic pollutants under visible-light irradiation [1, 2, 9].

Although the semiconducting photocatalysts have been carried out extensive research by the researchers, they were restricted by their structure, morphology and immanence properties over the past decade. The semiconductors photocatalytic activity depends on photogenerated carriers generation and separation [10]. Therefore, it is important for maximizing the photocatalytic efficiency to maximize the separation efficiency and increase the oxidation power of photogenerated carriers as far as possible. A few researchers have reported that the photocatalytic activity of semiconductor photocatalysts can be improved by surface fluorine modification or fluorine doping [11-16]. The fluorine ions could increase the coordination sphere around the W atom in a WO$_6$ octahedron and cause the distortion of the WO$_6$ octahedron in a Bi$_2$WO$_6$ crystal, resulting in an increased transfer rate of photogenerated electrons to the photocatalyst surface and the enhanced photoactivity for rhodamine B degradation. Meanwhile, F-doped Bi$_2$WO$_6$ presented enhanced photoactivity for RhB degradation, which could be a synergetic effect of the surface fluorination and the doping of the crystal lattice [17]. On the basis of these results, it can be inferred that the introduction of fluorine, irrespective of the approaches of fluorine doping, really enhanced the photocatalytic activity of semiconductor...
photocatalysts. On account of the special morphologies, higher surface areas and so on, the microspheres containing nanosheets usually had better photocatalytic activities. Experimental observations and theoretical calculations also indicate that anisotropic metal nanostructures exhibit shape-dependent optical properties [9, 18]. So, it is very important for photocatalysts to control the morphology of Bi$_2$WO$_6$ microspheres [19–21]. Meanwhile, Bi$_2$WO$_6$ microspheres should be maintained when fluorine was doped in the different samples. Herein, in these cases above, we exhibit the F-doped Bi$_2$WO$_6$ samples of the different RF value (RF = 0, 0.125, 0.25, 0.5, 1) synthesized by the two-step hydrothermal process. The visible light (λ>400nm) photocatalytic activities have also been investigated, and we found that the photocatalytic performances of the F-doped Bi$_2$WO$_6$ samples are greatly different and are strongly dependent on the concentration of fluorine substitution. Our principal aim is not only to investigate the role of F-substitution on the structure and photocatalytic activity of Bi$_2$WO$_6$ crystal but also how to get high crystallinity and good morphology of Bi$_2$WO$_6$ samples. Moreover, our work may be further extended to the design F-doped samples and understand on the photocatalytic mechanisms of F substitution.

2. Experimental

2.1. Synthesis of Bi$_2$WO$_6$ hierarchical microspheres

All chemicals were analytical grade and used as received without further purification. The one-step hydrothermal process was similar to that in the Ref. [2, 9]. On the basis of the literature, the different concentrations of NaF were added into the precursor. Then it was heated at 200 °C for 24 h.

A two-step hydrothermal process: First, 3 mmol of Bi(NO$_3$)$_3$·5H$_2$O and 1.5 mmol of citric acid were added to 60 mL deionized water. After 20 min of magnetic stirring, Na$_2$WO$_4$·2H$_2$O and NaHCO$_3$ were added into the mixed solution apiece 3 mmol. After being further stirred for 10 min, the above mixed solution was poured into a stainless steel autoclave with the 100 ml Teflon liner. It was heated at 200 °C for 24 h. The as-synthesized samples were separated centrifugally and washed three times separately with deionized water and absolute ethanol when the autoclave cooled to room temperature. Subsequently, the samples were dried under vacuum at 80 °C for 10 h.

2.2. Synthesis of Bi$_2$WO$_6$ hierarchical microspheres by fluorine substitution

Following the above procedures, high purity of Bi$_2$WO$_6$ hierarchical microspheres were synthesized on a large scale. Then, 0.5mmol as-synthesized samples were dispersed into a mixture of 40mL ethanol and 20mL deionized water. After 20 min of magnetic stirring, different concentrations of NaF were added to the above solution. In the process, the value of RF was used to describe the molar ratio of NaF to Bi$_2$WO$_6$, these were 0, 0.125, 0.25, 0.5 and 1 nominal ratios, respectively. After being further stirred for 20 min, the suspension was transferred into a stainless steel autoclave with a 100 ml Teflon liner, and heated at 180°C for 20h. After the autoclave had cooled to room temperature, the products were separated centrifugally and washed three times separately with deionized water and absolute ethanol, respectively. Subsequently, the products were dried under vacuum at 60 °C for 10 h.

2.3. Characterization

The purity and crystallinity of the as-synthesized samples were characterized by X-ray diffractometer (XRD, Bruker D8) using Cu Kα radiation (λ = 1.5418 Å). The morphology and characterization of the products were performed by field emission scanning electron microscopy (FE-SEM, JSM-6700F) and transmission electron microscopy (TEM, HITACH H-600). The optical diffuse reflectance spectra were recorded on a Japan Shimadzu UV-2550 (Japan) using BaSO$_4$ as reference.

2.4. Photocatalytic experiments

The visible light photocatalytic activities of Bi$_2$WO$_6$ samples containing the different RF value (RF = 0, 0.125, 0.25, 0.5, 1) were evaluated by the decomposition of rhodamine B (RhB) under a 500 W Xe arc lamp light (λ>400 nm). The photocatalytic reaction procedures were similar to that in the Ref. [1,2] In every experiment, RhB solutions (30 mL, 10$^{-5}$ mol/L) containing the different F-doped Bi$_2$WO$_6$ samples (100mg) were added into test tube. Before illumination, the above solutions were
magnetically stirred in the dark for 2 h to ensure an adsorption-desorption equilibrium between the as-synthesized samples and RhB. After that, the test tubes were taken at the given time intervals, and then centrifuged to remove the photocatalyst particles. Then, the filtrates were analyzed by recording variations of the absorption band maximum (553 nm) by a Shimadzu UV-2550 spectrophotometer.

3. Results and discussion

3.1. Effect of F substitution on the morphology of Bi$_2$WO$_6$ samples

As shown in Figure 1, the FE-SEM images of Bi$_2$WO$_6$ was synthesized for different R$_F$ values via one-step hydrothermal process. With the increasing of fluorine content, the construction of Bi$_2$WO$_6$ hierarchical microspheres caused more and more destruction. It indicates that one-step hydrothermal process is disadvantaged to photocatalysts because the bad morphology was unsuited to the scattering and reflecting of the light in the 3D construction of Bi$_2$WO$_6$ samples. So, two-step hydrothermal process was employing for F-doped Bi$_2$WO$_6$ microspheres.

![Figure 1](image)

Figure 1. FE-SEM images of Bi$_2$WO$_6$ samples synthesized for different R$_F$ values via one-step hydrothermal process. a-b) R$_F$=0; c-d) R$_F$=0.125; e-f) R$_F$ =0.25; g-h) R$_F$ =0.5; i-j) R$_F$ =1.

3.2. Effect of F substitution on the structure of Bi$_2$WO$_6$ hierarchical microspheres

Figure 2a shows XRD patterns of the samples with different R$_F$ values prepared by the two-step hydrothermal process at 200 °C for 20 h. The diffraction peaks of all of the as-prepared samples were
in accordance with phase-pure orthorhombic Bi$_2$WO$_6$ (JCPDS No. 39-0256). Further observation showed that the peak intensities of the F-doped Bi$_2$WO$_6$ samples were almost not change with increasing R$_F$ value. It indicates that the substitution of different R$_F$ values doesn’t result in the development of new crystal orientations or changes in preferential orientations. In other words, nothing to do with the presence or absence of F, the diffraction peak of the as-synthesized samples with different R$_F$ values were in keeping with the pure Bi$_2$WO$_6$. No other peaks can be detected in Figure 2a, indicating the high purity of the samples. As shown in Figure 2b, with an increase of F content, a comparison of the (131) diffraction peaks in the range of $2\theta = 26$~30° shows that the peak position of different F-doped Bi$_2$WO$_6$ samples with increasing R$_F$ values shifts slightly toward a higher 2$\theta$ value. According to Bragg’s law, the increase in 2$\theta$ value should result in the decrease in lattice parameters ($d$(131) value). Therefore, the shift of the diffraction peak with increasing R$_F$ values toward higher angle could be due to the substitution of one O$^2-$ by two F in order to maintain an electroneutrality condition.

![Figure 2](image.png)

**Figure 2.** XRD patterns of the Bi$_2$WO$_6$ microspheres with different R$_F$ values. (a) R$_F$ = 0, (b) R$_F$ =0.125, (c) R$_F$=0.25, (d) R$_F$ = 0.5, and (e) R$_F$ = 1. (b) Comparison of 2$\theta$ peaks from 26° to 30° for the as-synthesized samples of different RF values.

3.3. Effect of F- substitution on the morphology of Bi$_2$WO$_6$ hierarchical microspheres

Figure 3 gives the FE-SEM images of Bi$_2$WO$_6$ hierarchical microspheres synthesized for different R$_F$ values. As shown in Figure 3, the samples are composed of many microspheres which are regular in shape and uniform in size with the average diameter length of 2–4μm. With the increase of the F content, it can be found that the shape and superstructure of Bi$_2$WO$_6$ microspheres with different R$_F$ values almost has no changes by contrasting from Figure 3a to Figure 3j. Comparing with one-step hydrothermal process (as shown in Figure 1), the morphology of Bi$_2$WO$_6$ microspheres may maintain better by two-step hydrothermal process (as shown in Figure 3). It indicates that two-step template-free approach employing a hydrothermal process is beneficial to photocatalysts because high crystallinity and good morphology generally means fewer traps, bigger specific surface area and stronger photocatalytic activity.
Figure 3. FE-SEM images of Bi$_2$WO$_6$ hierarchical microspheres synthesized for different R$_F$ values.
a-b) R$_F$=0; c-d) R$_F$=0.125; e-f) R$_F$=0.25; g-h) R$_F$=0.5; i-j) R$_F$=1.

3.4. Chemical compositions of Bi$_2$WO$_6$ microspheres
The oxidation states and surface chemical composition of the F-doped Bi$_2$WO$_6$ were characterized by X-ray photoelectron spectroscopy (XPS). Typical survey XPS spectrum and Bi 4f, W 4f, O 1s XPS spectra of F-doped Bi$_2$WO$_6$ could all be detected as shown in Figure 4. The high resolution spectra of W 4f, Bi 4f, O 1s are provided in Figure 4b-d. Compared to that of pure Bi$_2$WO$_6$, the binding energies of the W peaks of F-doped Bi$_2$WO$_6$ samples have significant changes (as shown in Figure 4c) that should be ascribed to the alteration of the chemical coordination environment of W surroundings, meanwhile it indicated that F atom succeeded in the substitution of O atom in WO$_6$ octahedron.[22] The binding energies of Bi peaks of F-doped Bi$_2$WO$_6$ samples changed almost nothing (as shown in Figure 4b) which indicated that the coordination environment of Bi surroundings was not influenced by F substitution. [23] Therefore, the F atoms only replaced the O atoms of WO$_6$ octahedron in Bi$_2$WO$_6$ and it suggested that the method successfully introduced the fluorine element on the basis of maintaining good morphology.
Figure 4. XPS of Bi$_2$WO$_6$ and F-doped Bi$_2$WO$_6$ samples. (a) survey, (b) Bi 4f, (c) W 4f and (d) O 1s.

3.5. Optical properties of the F-doped Bi$_2$WO$_6$ microspheres

Figure 5 displays the diffuse reflectance spectra of the F-doped Bi$_2$WO$_6$ samples. When the wavelengths are shorter lower than about 470nm, the Bi$_2$WO$_6$ samples with different $R_F$ values presented the photoabsorption abilities, which is in good agreement with the previous report (3). It is outstanding that the edges of the catalysts are dependent strongly on the $R_F$ value. Although all Bi$_2$WO$_6$ samples show the similar absorption edges, the absorption edges of the Bi$_2$WO$_6$ samples are red shift apparently with the increase of $R_F$ values from 0 to 1. The band gap of the Bi$_2$WO$_6$ samples with different $R_F$ values is estimated to be 2.81, 2.79, 2.75, 2.72, and 2.69 eV from the onset of the absorption edge, corresponding to $R_F = 0$, 0.125, 0.25, 0.5, and 1, respectively. We concluded that the difference of the absorbance edges could arise from the fluorination of Bi$_2$WO$_6$ catalyst. The band gap of the F-doped Bi$_2$WO$_6$ samples can be related closely with two factors [24, 25]: (i) the degree of F 4s and W 5d orbitals being involved in the conduction band of the F-doped Bi$_2$WO$_6$ samples, (ii) the degree of delocalization of excitation energy due to lattice deformation arising from F substitution. With increasing of the $R_F$ value, the change of the band gap energy was not necessarily proportional with the $R_F$ value, but the band gap had the outstanding red shifts. Therefore, the results indicated that Bi$_2$WO$_6$ samples containing the different $R_F$ value had a suitable band gap for photocatalytic decomposition of organic contaminants under the visible-light irradiation.
3.6. Photocatalytic performance of the F-doped Bi$_2$WO$_6$ samples

The photocatalytic activities of RhB mediated by the Bi$_2$WO$_6$ samples with different concentration of fluorine substitution as well as without photocatalyst (the blank test in the inset of Figure 6) under visible light irradiation ($\lambda >400$ nm) are displayed in Figure 6. The blank test demonstrates that the degradation of RhB is extremely few without a photocatalyst under visible light irradiation. As shown in Figure 6, the visible-light irradiation of the aqueous RhB/photocatalyst dispersions lead to vastly different photodegradation rates of RhB, and it is obviously that the photodegradation efficiency of RhB is increasing with the concentration of fluorine substitution in the Bi$_2$WO$_6$ samples. After 105 minutes irradiation, it is found that the photocatalytic performances of all samples are greatly different and are strongly dependent on the concentration of fluorine substitution. The fluorine is integrate into the Bi$_2$WO$_6$ crystal, it may improve the photocatalytic performances of Bi$_2$WO$_6$ samples. The enhanced photocatalytic activity came from the following factor. Comparing with O$^2^-$ ions, F$^-$ ions have the stronger attraction for electrons. Therefore, the electronic cloud can deviate from the original position in the Bi-O polyhedron, meanwhile, the bonds could be weakened between Bi and O in F-doped Bi$_2$WO$_6$ samples. So, plenty of oxygen vacancies can be easily produced under visible light irradiation, and they could induce the OH• radicals to take part in the photocatalytic process. Undoubtedly, it could improve the photocatalytic efficiency. In addition, the fluorinated process could probably increase defects which are beneficial to the photocatalytic activity.

Figure 5. Uv-vis diffusive reflectance spectra of the Bi$_2$WO$_6$ samples with different R$_F$ values.
Figure 6. Photocatalytic degradation of RhB solution by the F-doped Bi$_2$WO$_6$ samples. inset: the degradation of RhB solution in the absence of Bi$_2$WO$_6$ samples.

4. Discussions
The Bi$_2$WO$_6$ samples containing the different R$_F$ value (R$_F$ = 0, 0.125, 0.25, 0.5, 1) have been successfully synthesized through a two-step hydrothermal process in the absence of a surfactant. With increasing of the R$_F$ value from n$_w$ = 0 to n$_w$=1, the morphology of all F-doped Bi$_2$WO$_6$ samples are similar. The results of XRD and FE-SEM indicate that the morphology of F-doped Bi$_2$WO$_6$ microspheres may maintain better via a two-step hydrothermal process comparing with one-step process. On the basis of maintaining good morphology, the two-step hydrothermal process successfully introduced the fluorine element replaced the O atoms of WO$_6$ octahedron in Bi$_2$WO$_6$. For the Bi$_2$WO$_6$ samples with the different R$_F$ value, their band gaps have changed obviously. Under 500W Xe lamp light irradiation, the F-doped Bi$_2$WO$_6$ samples exhibit good photocatalytic activity in degradation of RhB. Comparing with Bi$_2$WO$_6$, the photocatalytic activity of the samples with different R$_F$ value (R$_F$ = 0.125, 0.25, 0.5, 1) increased outstandingly. Therefore, our work provides new possibilities to keep better morphology with different doped elements for future materials.

5. References
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