PEG-assisted hydrothermal synthesis of novel flower-like hierarchical BiVO₄ with enhanced visible light photocatalytic activity

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Abstract. Pizza-like BiVO₄ powders were successfully synthesized by hydrothermal route, while novel flower-like hierarchically structured BiVO₄ sample was obtained with adding PEG. X-ray diffraction, scanning electron microscopy and UV-vis light reflectance were employed to characterize the as-prepared products. The photocatalytic performance of the BiVO₄ samples was evaluated by degrading RhB under visible light irradiation. The results display that nanoflake-assembled flower-like BiVO₄ sample showed an excellent photocatalytic performance. The possible reasons for the enhanced photocatalytic activity were discussed.

1. Introduction
In recent years, visible light photocatalysts have received considerable attention, which offer a desirable way to address the increasing energy and environmental issues by utilization of solar energy. To date, numerous efforts have been made to explore metal oxide semiconductors such as α-Fe₂O₃ [1], Ag₃PO₄ [2], and BiVO₄ [3], for the purpose of efficient degradation of harmful organic pollutants under visible light illumination. Among these, monoclinic BiVO₄ has emerged as one of the most promising visible light photocatalysts, owing to its narrow bandgap of 2.4 eV [4]. However, it was founded that the photocatalytic activity of pure BiVO₄ is usually poor due to the low charge-transfer rate and rapid recombination of photoinduced electron-hole pairs, which significantly limits its practical applications [5]. Numerous strategies have been developed to improve the photocatalytic activity, such as nanostructuring [6-8], morphology controlling [9-12], and forming heterojunction structures [13-16].

It is generally founded that the photocatalytic performance of nanostructured catalysts strongly depended on their sizes and shapes. Therefore, relativity efforts have focused on achieving controllable synthesis of BiVO₄ hierarchical nanostructures for enhanced photocatalytic activity. Herein, we reported novel hierarchical BiVO₄ micro-flowers which were prepared by PEG-assisted hydrothermal method and showed excellent photocatalytic activity in Rhodamine B (RhB) degradation under visible light irradiation. Moreover, the relationship between the morphology and photocatalytic activity of BiVO₄ was discussed.
2. Experimental

2.1. Preparation of the BiVO₄ samples
In a typical procedure, 0.29 g of NH₄VO₃ was dissolved in 15 mL of 2 M NaOH solution, followed by the addition of 1.00 g of EDTA under stirring to form solution A. Secondly, 1.21 g of Bi(NO₃)₃·5H₂O and 1 g of polyethylene glycol (PEG, average Mn 4000) were initially dissolved in 15 mL of diluted nitric acid (2 M) to form solution B. Thirdly, solution A was added dropwise into solution B with continuous stirring for 0.5 h. The pH of the mixture was adjusted to 3 by slowly adding 2 M NaOH solution. The obtained mixture was then transferred into a 40 mL Teflon-lined stainless-steel autoclave, heated at 180 °C for 24 h, and naturally cooled to room temperature. The obtained precipitates were collected after centrifugation, washed with water and absolute ethanol repeatedly, and then dried at 80 °C for 8 h.

2.2. Characterization
Powder X-ray diffraction (XRD) patterns were recorded on Philips X'Pert Pro X-ray diffractometer with Cu Kα radiation. The product morphology was observed with a scanning electron microscope (SEM, JEOL-6610-LV). UV-vis diffuse reflectance spectra of the products were measured by a UV/vis/NIR spectrophotometer (PerkinElmer, Lambda 950).

2.3. Photocatalytic performance
Photocatalytic activity was evaluated by the degradation of RhB under visible light irradiation using a 150 W Xe lamp with a cutoff filter (λ > 420 nm). Typically, 50 mg of photocatalyst was dispersed into 100 mL of 10 mg/L RhB solution. Before illumination, the suspensions were magnetically stirred in dark for 30 min to achieve an adsorption-desorption equilibrium. At given time intervals, 5 ml aliquots were sampled and centrifuged to remove photocatalysts. The filtrates were analyzed according to the absorption intensity at 554 nm in the UV-vis spectrum of RhB using a UV-vis spectrophotometer.

3. Results and discussion
Fig. 1 shows the XRD patterns of the as-prepared BiVO₄ samples fabricated via hydrothermal strategy under different conditions. It was clear that all the diffraction peaks are well assigned to monoclinic BiVO₄ (JCPDS No. 14-0688), indicating that pure BiVO₄ powders were obtained without or with adding PEG. The strong and sharp peaks indicated that all these BiVO₄ crystals had a high degree of crystalline.

![Fig. 1 XRD patterns of BiVO₄ samples synthesized (a) without and (b) with PEG.](image-url)
Fig. 2 SEM images of BiVO$_4$ samples synthesized (a), (b) without and (c), (d) with PEG.

SEM images of the as-prepared BiVO$_4$ powders are shown in Fig. 2. It can be seen from Fig. 2(a) that the BiVO$_4$ sample prepared without adding PEG is primarily composed of pizza-like particles with average sizes of about 7 μm. Close investigation of the pizza-like BiVO$_4$ powders through the high magnification image reveals that some micro-sized BiVO$_4$ particles were closely attached to the surface of the BiVO$_4$ plates, as shown in Fig. 2(b). Fig. 2(c) shows the novel hierarchical BiVO$_4$ micro-flowers with average sizes of about 4 μm, which were obtained in the presence of PEG. As demonstrated in the magnification image (Fig. 2(d)), the BiVO$_4$ micro-flowers were composed of numerous nanoflakes. These nanoflakes have a thickness of about 100 nm and closely attached layer by layer to form the novel flower-like hierarchical structure. The above results suggested that novel flower-like hierarchically structured BiVO$_4$ sample could be easily obtained via PEG-assisted hydrothermal method.

The optical properties of the as-prepared BiVO$_4$ samples were evaluated by a UV/vis/NIR spectrometer (Fig. 3(a)). The spectra were transformed from the corresponding diffuse spectra. Both samples exhibited absorption bands at around 410-650 nm, indicating that the as-prepared BiVO$_4$ samples can absorb considerable amounts of visible light in this range. However, an enhanced visible light absorption was observed for the flower-like BiVO$_4$ sample, which may result from its unique flower-like hierarchical structure. Furthermore, compared with pizza-like BiVO$_4$ sample, the absorption edge of the flower-like BiVO$_4$ crystals shifted to longer wavelengths. Additionally, according to the intercept of the tangents to the plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$), the bandgaps of pizza- and flower-like BiVO$_4$ samples were estimated to be 2.43 and 2.40 eV, respectively, as shown in Fig. 3(b). The bandgaps are comparable to the values previously reported [4]. The smaller bandgap of flower-like BiVO$_4$ sample is probably because the thickness of nanoflakes in the BiVO$_4$ micro-flowers was smaller than the grain size of micro-sized particles in the pizza-like sample [14].

Fig. 3 (a) UV-vis absorption spectra and (b) plots of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) of the as-prepared pizza- and flower-like BiVO$_4$ samples.
The photocatalytic performance of the BiVO$_4$ photocatalysts was measured by degrading RhB under visible light irradiation. As shown in Fig. 4, both the pizza- and flower-like BiVO$_4$ samples can efficiently photodegrade RhB. When the pizza-like BiVO$_4$ particles were used as photocatalyst, up to 63% RhB was decolorized under visible light illumination after 3 h. In contrast, more than 86% RhB was degraded by the flower-like BiVO$_4$ photocatalyst under the same experimental conditions. The higher visible light photocatalytic activity of the flower-like BiVO$_4$ sample may result from the following several reasons. Firstly, the flower-like BiVO$_4$ displayed enhanced light harvesting efficiencies and smaller bandgap, indicating that more photons can be absorbed and be utilized for the photocatalytic reaction. Secondly, hierarchical BiVO$_4$ micro-flowers were composed of nanoflakes, which may lead to larger surface area and provide more reaction sites, thereby facilitating surface photocatalytic reactions. In addition, the nanosized thickness of nanoflakes is also beneficial for migration of photogenerated charge carriers to the surface, which reduces the possibility of recombination, eventually leading to higher activity. To confirm the decreased recombination of electron-hole pairs in flower-like BiVO$_4$, room temperature PL emission spectra of the BiVO$_4$ samples were measured, as displayed in Fig. 5. It can be seen that the PL spectrum of pizza-like BiVO$_4$ shows a strong emission, which indicates that the electrons and holes recombine rapidly. By contrast, the flower-like BiVO$_4$ sample displays a lower emission intensity, indicating that the recombination rate of electron-hole pairs was slow.

![Fig. 4 Photocatalytic activity of the pizza- and flower-like BiVO$_4$ samples for the degradation of RhB under visible light.](image_url)

![Fig. 5 PL spectra of the pizza- and flower-like BiVO$_4$ samples.](image_url)
4. Conclusion
In summary, pizza-like and novel flower-like hierarchical BiVO$_4$ samples were obtained via hydrothermal method without or with adding PEG, respectively. The nanoflake-assembled flower-like BiVO$_4$ sample showed excellent photocatalytic performance towards RhB under visible light illumination, which relevant to its effective light absorption, smaller bandgap, larger surface area and nanosized thickness of nanoflakes.

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