



PVP assisted hydrothermal fabrication and morphology-controllable fabrication of BiFeO₃ uniform nanostructures with enhanced photocatalytic activities



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ABSTRACT

Bismuth ferrite (BiFeO₃) nanostructures with various morphologies (spindles, cubes and plates) have been successfully synthesized via a convenient one-pot hydrothermal method. The results show that three kinds of BiFeO₃ products were obtained in this polyvinylpyrrolidone (PVP)-assisted hydrothermal reaction under different alkaline conditions. The resulting nanostructures were characterized using XRD and SEM. Possible formation mechanism for BiFeO₃ nanostructures was proposed on the basis of our results. The experiments showed that the visible light absorptive capacity of the BiFeO₃ nanostructures was significantly influenced on the size and morphology. Notably, the as-prepared BiFeO₃ plates with (104) facets exposed exhibit high efficiency for the degradation of methyl orange (MO) under visible light irradiation, suggesting potential applications in photocatalytic and related areas under visible light.

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1. Introduction

Perovskite ferroelectric oxides have attracted much attention over the past decade due to their fascinating physical properties and potential in applications [1–3]. As a typical multiferroic material [4–6], perovskite-type bismuth ferrite (BiFeO₃), with simultaneous ferroelectric and ferromagnetic ordering at room temperature, has attracted great attention due to its suitable band gap (~2.2 eV) and excellent chemical stability [7,8]. Morphology control for achieving preferential exposure of reactive crystal facets has received extensive attention [9,10]. The latest investigations on

crystal facet engineering of semiconductors have demonstrated that photogenerated charge transfer to distinct crystal facets is closely related to their corresponding geometric and electronic properties [11]. Therefore, control of the shape and size of BiFeO₃ nanoparticles plays very important roles in determining magnetic, electrical, optical and catalytic properties due to the spatial geometry effect [12,13].

It is well known that phase pure BiFeO₃ is very difficult to synthesize because several impurity phases (Bi₂Fe₄O₉, Bi₂₅FeO₄₀ et al.) are often present, which would affect the electrical and magnetic properties of the overall material [14]. Relatively, the hydrothermal approach is a convenient route to fabricate the nanostructures [15–17]. Moreover, several reaction conditions, such as the mineralizer and the surfactant, can be employed to adjust the crystal nucleation and growth. In recent years, Fei et al. have successfully synthesized perovskite BiFeO₃ crystallites with different predominantly exposed facets via a facile one-pot hydrothermal approach under the presence of potassium hydroxide (KOH) and polyethylene glycol (PEG) [18]. The phase-pure BiFeO₃ pills and rods with highly exposed {111}c facets show an obviously

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enhanced visible light response when compared with {100}c dominant BiFeO₃ cubes. Yang et al. have proposed another simple hydrothermal process to prepare single-crystal BiFeO₃ microplates, where the precursor (C₆H₁₀BiNO₈) acts both as reactant and as surface modifier in the formation of the BiFeO₃ microplates [19]. The dielectric constant of the BiFeO₃/poly-vinylidene fluoride (PVDF) film is much higher than the pure BiFeO₃ at room temperature. Besides, Zhang et al. have successfully prepared nanoparticles-assembled one-dimensional BiFeO₃ microrods via a mild polymer directed solvothermal route [20]. The obtained BiFeO₃ microrods exhibit smaller saturation magnetizations and larger coercive force than the nanoparticles.

In spite of some studies focus on the morphology control and characterization, it is necessary to fabricate different-shaped BiFeO₃ nanostructures from the view of their morphology and size-dependent physical and chemical properties and wide practical applications [21–23]. In this work, we find a simple and controllable one-pot hydrothermal approach to create well defined perovskite BiFeO₃ with different morphologies. An inexpensive organic stabilizer like polyvinylpyrrolidone (PVP) is used as a surfactant in the synthesis of BiFeO₃ nanostructures which can react at relatively low temperature [24]. A possible formation mechanism for BiFeO₃ nanostructures was also proposed. The as-prepared BiFeO₃ nanostructures were characterized by XRD, FE-SEM, HRTEM, FTIR and UV–vis spectra. The photocatalytic activity of the catalysts was evaluated by degrading methyl orange (MO) dye solution under visible light irradiation.

2. Experimental section

2.1. Fabrication of BiFeO₃ nanostructures

Bismuth nitrate (Bi(NO₃)₃·5H₂O) and ferric chloride hexahydrate (FeCl₃·6H₂O) were purchased from Guangdong Xilong Chemical Co., Ltd., P. R. China. Sodium hydroxide (NaOH), methyl orange (MO) and Polyvinylpyrrolidone K-30 (PVP) were obtained from Sinopharm Chemical Reagent Corp, P. R. China. All chemicals were used as received without further purification.

BiFeO₃ nanostructures were synthesized by a simple hydrothermal method. In a typical synthesis, Bi(NO₃)₃·5H₂O (2.425 g) and FeCl₃·6H₂O (1.352 g) in a stoichiometric ratio (1:1 in molar ratios) were mixed in acetone (50 mL, 99.8%) and sonicated for 30 min. Then deionized (D.I.) water (200 mL) and concentrated ammonia were added under vigorous stirring until the pH value of the solution reached 10–11. The sediment was centrifuged out and washed with D.I. water several times until the pH value was neutral. Next, the red co-precipitate was redispersed in D.I. water. Under vigorous stirring, a certain amount of PVP and NaOH (5 mL) were added into the suspension. Then, the solution was placed inside a stainless steel autoclave with a Teflon liner and heated at 180 °C for 72 h. After cooling down to room temperature, the precipitate was harvested by filtration, washed with D.I. water and absolute ethanol for three times, respectively, and dried at 80 °C for 2 h.

2.2. Characterization

The morphologies of BiFeO₃ nanostructures were observed via scanning electron microscopy (SEM, S-4800, Hitachi; accelerating voltage = 10 kV). The obtained samples were characterized by XRD on a Bruker D8 Advance x-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of 20°–60° with a step size of 0.002° and a scan speed of 0.5 s per step. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. High-resolution transmission electron microscopy (HRTEM) images were

performed using a JEOL JEM-2100 instrument at the accelerating voltage of 200 kV. The fourier transforms infrared (FTIR) spectra were taken with a PerkinElmer Spectrum Two infrared spectrophotometer. The specific surface area was determined by V-Sorb 2800P (Gold APP Instruments Corporation, China) through the BET method. UV–vis absorption spectra were obtained using a PerkinElmer Lambda 35 spectrophotometer. The visible light ($\lambda > 420 \text{ nm}$) was obtained using a 500 W Xe lamp with a 420 nm cutoff filter to completely remove any radiation below 420 nm.

2.3. Photocatalytic tests

The photocatalytic activities of BiFeO₃ nanostructures were evaluated by degradation of MO aqueous solution under visible light irradiation. A 500 W Xe lamp was used as the light source, and visible-light irradiation was realized by attaching a 420 nm cutoff filter. In a typical photocatalytic test, 50 mg catalyst was dispersed in 50 mL MO aqueous solution with a concentration of 5 mg L⁻¹. Prior to irradiation, the suspensions were magnetically stirred in the dark for 1 h to ensure the establishment of an adsorption-desorption equilibrium. Then, at selected time intervals, samples were collected and filtered to remove the photocatalyst particles by centrifugation. After that, the solution was analyzed using an ultraviolet–visible light spectrophotometer. A blank test was also carried out on an aqueous MO solution without photocatalyst under the same condition.

3. Results and discussion

3.1. Characterization of samples

As an important surfactant, PVP is usually used to control the morphologies of bismuth-containing nanomaterials [25]. SEM was performed to characterize the morphology of all BiFeO₃ samples. Fig. 1 shows SEM images of the as-synthesized BiFeO₃ nanostructures obtained with 0.5 M NaOH. It is well known that PVP is a nonionic surfactant and the amount of PVP could markedly affect the morphology of the final product [26,27]. When quite a few PVP (0.02 g) was introduced into the reaction system, a large amount of inhomogeneous BiFeO₃ products were synthesized, as shown in Fig. 1a. Fig. 1b–c shows the size of the BiFeO₃ decreased by increasing the amount of PVP. Interestingly, when the amount of PVP is further increased to 0.5 g, well-defined and uniform BiFeO₃ spindle-like nanostructures can be obtained, as shown in Fig. 1d. It can deduce that a suitable amount of PVP is crucial for the synthesis of BiFeO₃ nanostructures in our experiments.

Further investigations showed that the morphological and dimensional changes in the as-synthesized BiFeO₃ nanostructures strongly depend on the NaOH concentration. The amount of PVP is fixed 0.5 g according to the above results. When the concentration of NaOH is 0.5 M, the BiFeO₃ product shows pure spindle-like particles in a large scale with average length of about 200 nm and average width of about 100 nm, as depicted in Fig. 2a. Owing to consisting of large amounts of small particles ~50 nm, the surfaces of these spindles are quite rough, and the specific surface area would be increased. With further increase of the NaOH concentration to 2 M, a number of BiFeO₃ cubes with edge lengths ranging from 100 nm to 200 nm can be observed as shown in Fig. 2b. According to the symmetries of perovskite BiFeO₃ and other relevant works [28,29], all the surfaces of cubes can be ascribed to {100} c crystal faces. For 4 M, irregular plates with the length ranging from 200 nm to 500 nm, showed a hexagonal shape on its front surface as the outline showed, and the thickness was ca. 50 nm, as shown in Fig. 2c. More interestingly, one side of the hexagonal plates with different degrees of truncation at edges is concave, which resulted

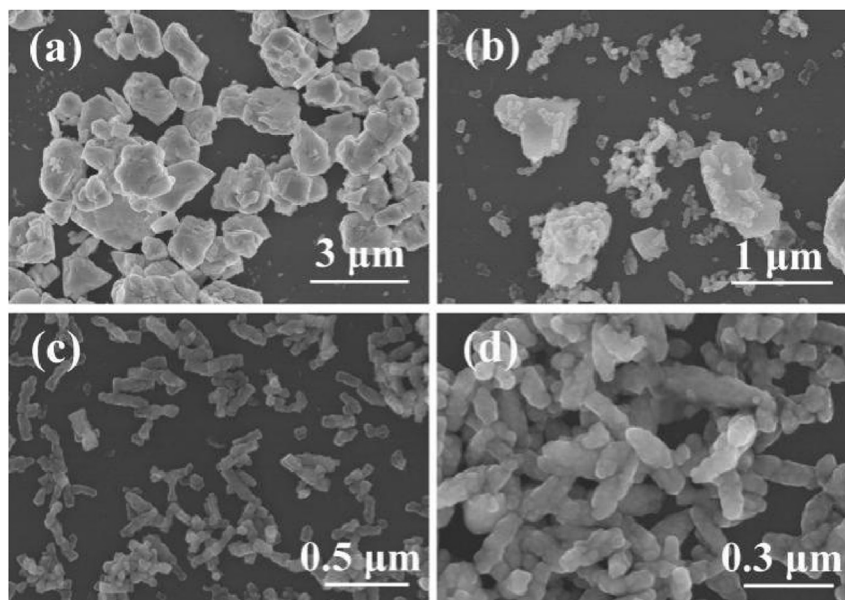


Fig. 1. SEM images of the BiFeO₃ nanostructures (0.5 M NaOH) obtained with various amount of PVP. (a) 0.02 g, (b) 0.1 g, (c) 0.2 g and (d) 0.5 g.

in exposing different facets. The surfaces of these BiFeO₃ plates are quite flat and the well-developed morphology suggests undoubted high crystallinity. The lateral thickness is less than 50 nm, which is much thinner, compared with the previously reported BiFeO₃ microplates dominated by (012) facets with the lateral length of 8 μm and a thickness of 510–550 nm [19]. Nanostructured materials have special physical and chemical properties, which is due to their anisotropic properties and a unique size effect.

The crystal phase of the materials is determined by XRD, as shown in Fig. 3. All the diffraction peaks can be indexed on the basis of a BiFeO₃ rhombohedral phase with the space group *R3c* (JCPDS card No. 86-1518). The intensity of the peaks for BiFeO₃ plates was clearly strengthened, which indicate that the sample is highly crystalline. As for the other two samples, a slight impurity phases (marked with “*”) can be observed, and no secondary phase is observed. The inset of Fig. 3 is the enlarged version of the XRD patterns in the range of 2θ 31°–32.5°. It is worth noting that the (104) diffraction line of the BiFeO₃ plates intensified compared with the standard card, suggesting that the BiFeO₃ plates predominantly exposed the (104) facet. The results indicate that the diffraction peak intensity ratio of (104) to (110) crystal facets for the products can be delicately controlled by simply adjusting the addition amount of NaOH and PVP, suggesting that the anisotropic growth is perhaps preferential. The different exposed facets of all samples indicate that the products may have undergone a morphological evolution, which could lead to the difference in photocatalytic activity.

High-resolution transmission electron microscopy (HRTEM) was employed to analyze the crystalline structures of the BiFeO₃ samples and the images are shown in Fig. 4a–c. The rhombohedral structure of the BiFeO₃ spindles and cubes was confirmed by HRTEM analysis from the measured lattice distance of 3.96 Å along the (012) plane, as can be seen in Fig. 4a and b. From the HRTEM images, the observed lattice of the BiFeO₃ plates is 2.82 Å, which is consistent with the (104) crystal planes of a rhombohedral phase BiFeO₃ crystal (JCPDS No. 86-1518), as shown in Fig. 4c. Fig. 4d–f are the corresponding selected electron diffraction (SAED) pattern. The diffraction rings (Fig. 4d) are discontinuous and consist of sharp spots which indicate good crystallinity of BiFeO₃ spindles. The SAED pattern from an individual cube grain (Fig. 4e) shows very sharp

diffraction spots, indicating the formation of well-developed single-crystalline BiFeO₃. The SAED pattern shows clear lattice planes, again confirming the pure crystallinity of the as-synthesized nanocrystals. Diffraction spots corresponding to the secondary and impurity phases were not present.

3.2. Optical and photocatalytic performance

Considering the potential optoelectronic applications of BiFeO₃ in photodetectors or solar cells, the optical properties of the as-prepared BiFeO₃ samples were investigated by UV–vis diffuse reflectance spectroscopy (DRS). As can be seen from Fig. 5, the broad absorption band indicated that all BiFeO₃ products can absorb considerable amounts of visible light, which suggest their potential applications as visible-light driven photocatalysts. It is well documented that the morphologies of semiconductors affect the light absorbance and band-gap energies [30]. Compared with that of spindles and cubes sample, the absorption edge of the plates distinctively broadened from visible to near-infrared region. Different from the three-dimensional materials (BiFeO₃ spindles and cubes), the electronic properties of two-dimensional materials are modulated in plane. Hence the photocatalyst of the plates could absorb more visible light to produce electron–hole pairs, which could be favorable for a photocatalytic reaction.

The FTIR spectra of the BiFeO₃ samples were studied, as shown in Fig. 6. The broad peak between 550 and 600 cm⁻¹ in the FTIR spectrum is related to the Fe–O stretching and bending vibration of the octahedral FeO₆ groups in perovskite structures, which implying the formation of BiFeO₃ phase. The broad band at 3436 cm⁻¹ (Fig. 6c) possibly arose from the antisymmetric and asymmetric stretching of H₂O and OH⁻ groups.

In contrast, therefore, we also investigated the catalytic activities of BiFeO₃ with various shapes. The photocatalytic performance of BiFeO₃ nanostructures was evaluated by the photodegradation of methyl orange (MO) aqueous solution under visible light irradiation after adsorption/desorption equilibration. The C/C₀ ratio graph is shown in Fig. 7. It was found that the BiFeO₃ cubes and the spindles degraded 38.7% and 49.8% of the dye, respectively, after 180 min radiation, while the plates degraded 69.1% of the dye under the same experiment condition. The specific surface area was

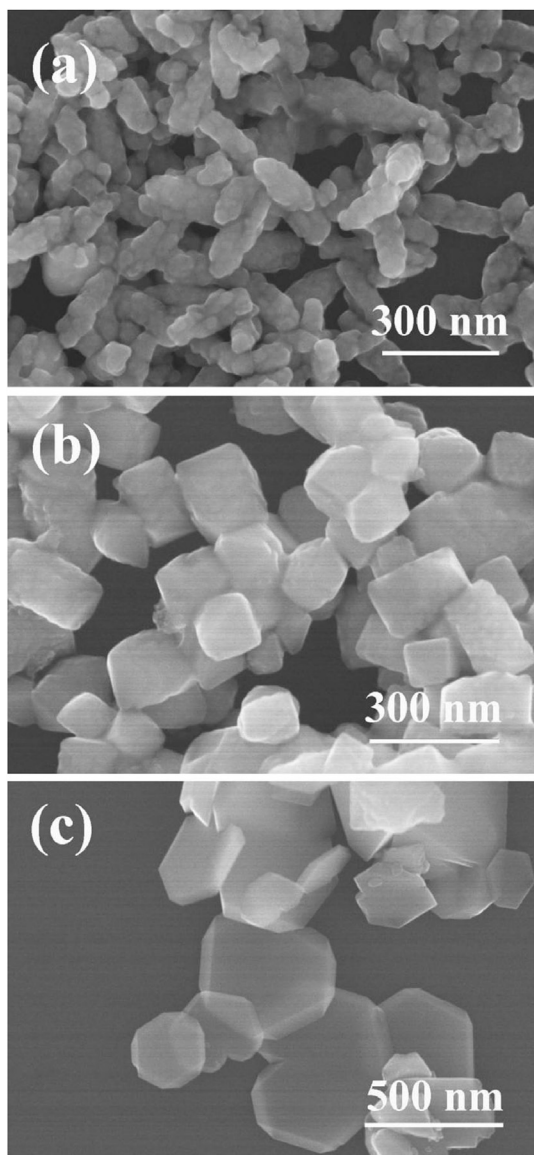


Fig. 2. SEM images of the BiFeO₃ nanostructures obtained with various concentration of NaOH: (a) 0.5 M, (b) 2 M and (c) 4 M.

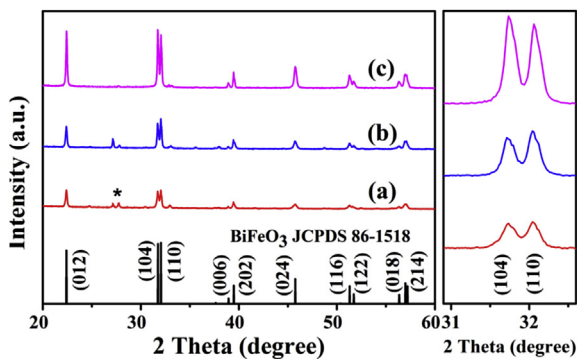


Fig. 3. XRD patterns of the BiFeO₃ samples: (a) spindles, (b) cubes and (c) plates.

obtained and the result showed that the specific surface area of spindles, cubes and plates is 0.874 m²/g, 0.526 m²/g and 0.766 m²/g,

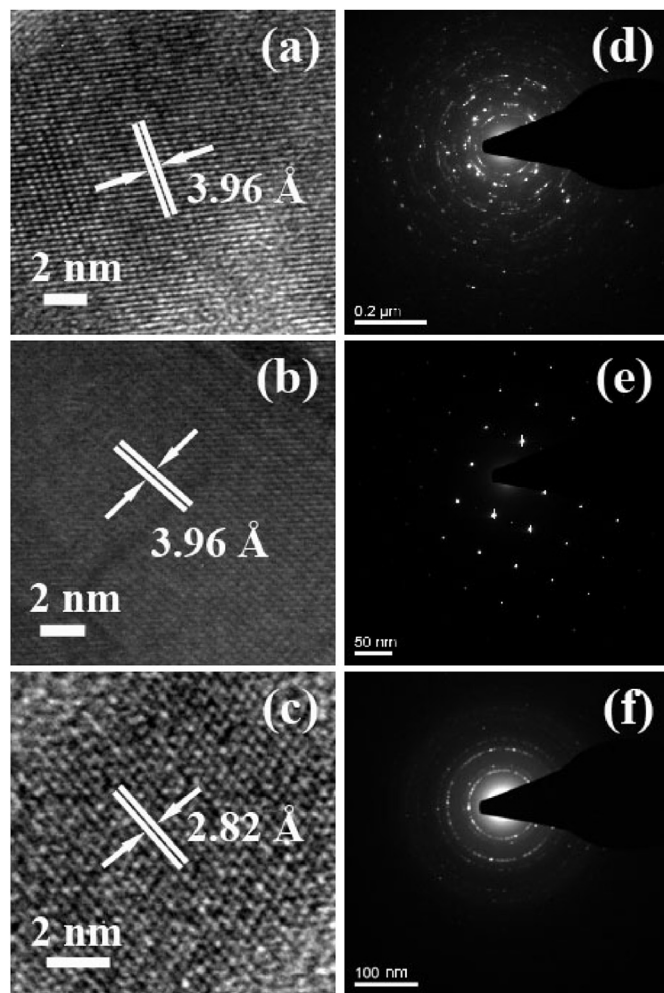


Fig. 4. HRTEM images of the BiFeO₃ samples: (a) spindles, (b) cubes and (c) plates, and corresponding SAED patterns: (d) spindles, (e) cubes and (f) plates.

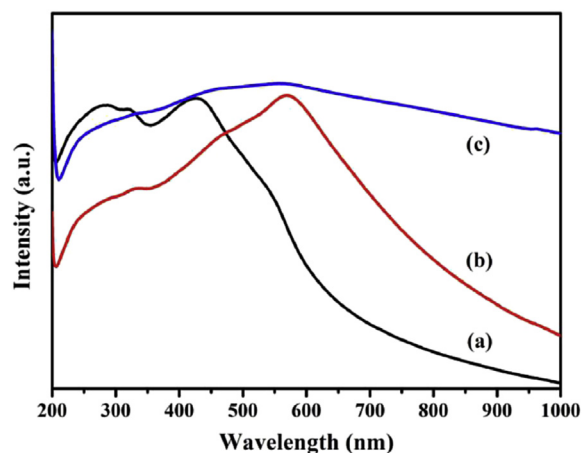


Fig. 5. UV–vis spectra of BiFeO₃ nanostructures: (a) spindles, (b) cubes and (c) plates.

respectively. Although the specific surface area of plates is not the maximum value among of them, the photocatalytic activity is the highest. The results showed that the optical properties of the BiFeO₃ nanostructures were strongly related to their shape and exposed facet. The possibility, which would enhance the catalytic

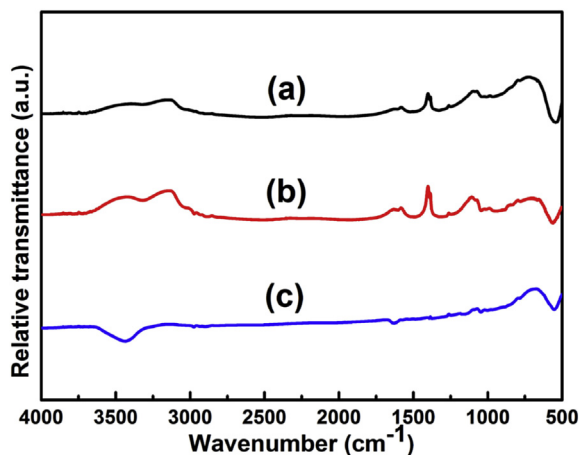


Fig. 6. FTIR spectrum of BiFeO₃ nanostructures: (a) spindles, (b) cubes and (c) plates.

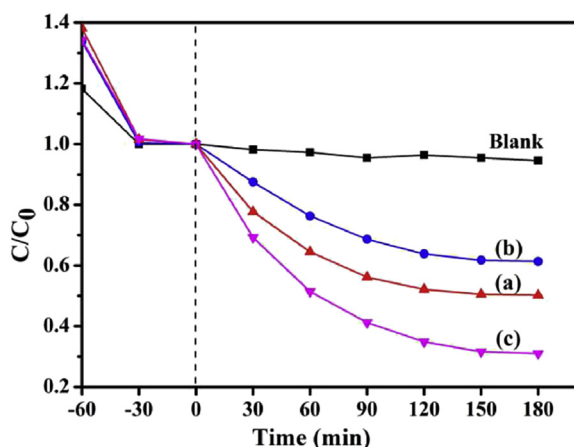


Fig. 7. Photocatalytic activity of different catalysts for the degradation of MO solution at room temperature: (a) spindles, (b) cubes and (c) plates.

activity in the plate structures, is excited photocatalytic species reaching to different exposed facets. Meanwhile, based on Fig. 3, it can be deduced that the exposed (104) facet was pivotal for achieving the high photocatalytic activity of the BiFeO₃ plates.

3.3. Growth mechanism

On the basis of the above results, a proposal formation mechanism of BiFeO₃ nanostructures is suggested as follows. The shape evolution of BiFeO₃ nanostructures are illustrated in detail in Fig. 8. Firstly, as we all know, Bi(NO₃)₃ hydrolyzed easily in water to

produce slightly soluble irregular shaped BiONO₃ [31], while Fe(OH)₃ is resulted from the reaction between ferric chloride hexahydrate and ammonia. As a surface modifier, the PVP polymer could selectively absorb on the (012) and (104) facets of these nanoparticles due to its large number of carbonyl groups and amide ligands in the NaOH solution of various concentration. Bi ion combines easily with PVP by the chelating effect owing to the much higher stability constant than Fe ion. Then BiFeO₃ amorphous colloids are formed by a slow aggregation and crystallization of primary small seed particles [32,33]. Secondly, in the alkaline conditions, BiFeO₃ nanoparticles had a tendency to aggregate along a certain direction in order to minimize the overall energy of the reaction system. The alkaline concentration significantly influences the morphology of the products which has been discussed before. The preferential growth of the BiFeO₃ nanoparticles can be attributed to the different nanoparticle-aggregation potentials [34], leading to the anisotropic growth rates in different directions. For BiFeO₃ plates, BiFeO₃ nanoparticles aggregated along (104) direction more quickly than along (102) direction. The self-assembly and anisotropic growth process could be explained by the “oriented attachment” mechanism [35,36]. In the present work, PVP is not only as a surfactant, but also as the structure-directing reagent in the formation of BiFeO₃ nanostructures. The nuclei grew only along the directions unoccupied by PVP [37]. Compared with previous reports, it also indicates that the PVP is beneficial to reduce the size of products. Thirdly, the primary self-aggregate nanoparticles recrystallized according to the well-known Gibbs–Thomson law [38]. With the assistance of Ostwald ripening, the surface energy will be further decreased, thus the as-prepared BiFeO₃ nanostructures become much more stable [39].

4. Conclusions

In summary, we have successfully synthesized uniform BiFeO₃ nanostructures with tunable morphology via a facile PVP-assisted hydrothermal method under the presence of sodium hydroxide. The effect of the surfactant and alkaline concentration was investigated, indicating the role of these parameters to achieve controlled morphology. PVP is beneficial to not only reduce the size of products as a surfactant, but also control the direction of growth as the structure-directing reagent in the formation of BiFeO₃ nanostructures. The photocatalytic activity of the as-prepared BiFeO₃ plates with (104) facets exposed is the best among the three samples for methyl orange (MO) photodegradation under visible light irradiation. It is believed from the present work that the BiFeO₃ nanostructures are an economically viable perovskite oxide and a promising candidate with great potential for environment remediation application.

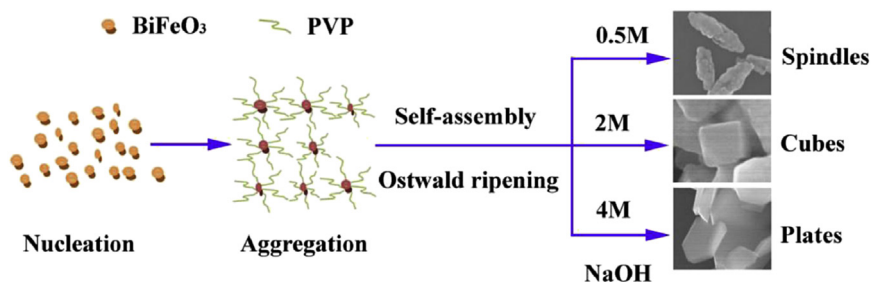


Fig. 8. Schematic illustration of the formation mechanism of BiFeO₃ nanostructures.

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