Materials Letters 211 (2018) 171–174

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Facile synthesis and photocatalytic performance of $BiVO_4$ with controllable pumpkin-like microstructure

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A R T I C L E   I N F O

Article history:
Received 3 August 2017
Received in revised form 13 September 2017
Accepted 27 September 2017
Available online 28 September 2017

Keywords:
$BiVO_4$
Microstructure
Hydrothermal method
Photocatalysis
Antibiotics
Visible light irradiation

A B S T R A C T

The controllable synthesis of novel pumpkin-like microstructure $BiVO_4$ has been successfully obtained via a facile hydrothermal method with the aid of surfactant PVP(K30) in the present study. The effects of amount of PVP on the structure, morphology, optical and photocatalytic activity were investigated. The results revealed that the amount of PVP added in reaction mixture played a significant role in formation of pumpkin-like morphology of $BiVO_4$. The as-prepared $BiVO_4$ with 1.0 g PVP exhibited highest photocatalytic activity for degradation of doxycycline under visible light irradiation at room temperature. Based on the evolution process of morphology, a possible formation mechanism was proposed based on the PVP working as a soft template.

1. Introduction

In recent decades, semiconductors have been considered as the most promising materials for environmental remediation through the radicals such as •OH and O_{2-}, which were produced by semiconductors through light irradiation [1,2]. Among them, considerable research have been focused on increasing the photoactivity of wide band gap semiconductors (eg. TiO_2, $SrTiO_3$, ZnO, $ZnWO_3$ and so on) for their response only to ultraviolet (UV) light, hindered their practical application outdoor [3–6]. Meantime, A class of Bi-based semiconductor oxides stand out exhibiting novel photocatalytic activity in the range of visible light with the narrow band gap. $BiVO_4$ with a 2.4 eV band gap has been recognized as one of the outstanding visible-light responsive photocatalysts [7–10]. Especially, the monoclinic scheelite structure $BiVO_4$ shows superior photocatalytic performance over the other two crystalline (the scheelite tetragonal and zircontetragonal structure) under visible-light irradiation [11]. There have been a lot of $BiVO_4$ prepared successfully with various morphology, and the most important thing is that the photocatalytic activity of semiconductor photocatalysts is strongly dependent on their shape, size, specific surface area, crystal structure and morphology [12–17]. While in several approaches developed for the synthesis of $BiVO_4$ with different morphology and size, the hydrothermal route could generally satisfied the needs since the micro/nano-structure and surface morphology can be easily controlled by adjusting the experimental conditions such as the concentrations of reactants, the pH values, the temperature, and the reaction medium.

Herein, we demonstrate a facile low-temperature hydrothermal route for the controllable synthesis of a pumpkin-like $BiVO_4$ microstructure only with the assistance of PVP without other additives. PVP, a widely used surfactant and a capping agent, can be utilized as a soft template offering microemulsion condition as well as the pyrrole moiety of PVP might be negatively charged making it possible to coordinates with Bi^{3+}, finally control the concentrations of reactants to obtain the required morphology.

2. Experimental

2.1. Synthesis of pumpkin-like $BiVO_4$ microstructures

All chemicals reagents were of analytical grades and used without further treatments. The pumpkin-like $BiVO_4$ microstructures were synthesized via a facile hydrothermal process. In the first step, both 5 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and a certain amount of PVP were dissolved in 20 ml deionized water. Afterwards, 5 mmol NH_4VO_3 was added into the above solution. A homogeneous

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https://doi.org/10.1016/j.matlet.2017.09.109
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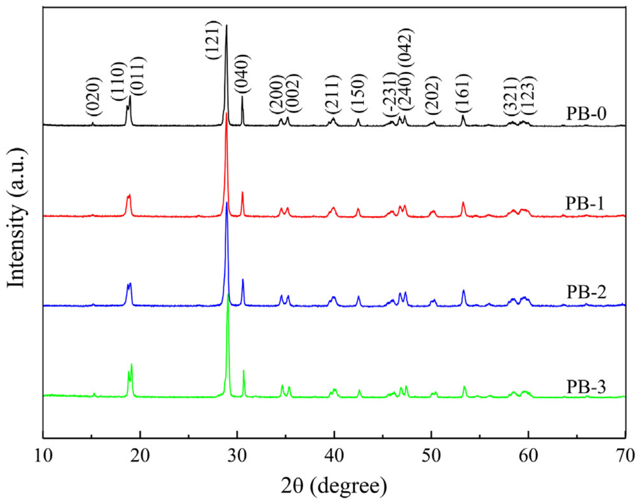

Fig. 1. XRD patterns of $BiVO_4$ microstructures prepared with different amount of PVP.

solution was obtained after magnetic stirring and then ultrasound dispersed evenly for 30 min at room temperature. The resulting mixture was transferred into a 40 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 6 h under autogenous pressure. After that the Teflon-lined stainless steel autoclave was cooled down. The precipitate was filtered, washed with distilled water and absolute ethanol for several times, and dried in the oven at 80 °C for 12 h, then calcined at 500 °C for 3 h in a muffle furnace to remove the residual additions. According to the amount of PVP controlled in the reaction, 0 g, 0.5 g, 0.75 g and 1.0 g, the as-prepared $BiVO_4$ products were named respectively PB-0, PB-1, PB-2, and PB-3 for convenience.

2.2. Characterization

The prepared products were characterized by X-ray diffractometer (XRD) patterns. The equipment is Rigaku D/MAX-2000 diffractometer with Cu Kα radiation (λ = 1.5418 Å), at 60 kV and 80 mA. Surface morphology and size distribution of the products were carried out on field emission scanning electron microscopy (Hitachi, S-4800, Japan). Diffuse reflectance (DR) UV-vis spectra of the products were recorded by a Shimadzu 2450 spectrophotometer.

3. Result and discussion

Fig. 1 shows the XRD patterns of $BiVO_4$ microstructures fabricated by hydrothermal technique using different amount of PVP. It is confirmed that the resulting $BiVO_4$ is monoclinic scheelite-type structure [18], which is in accordance with the standard card (JCPDS card No. 14-0688). In addition, there was no secondary phase or impurities detected in the products suggesting the purity of $BiVO_4$ microstructures.

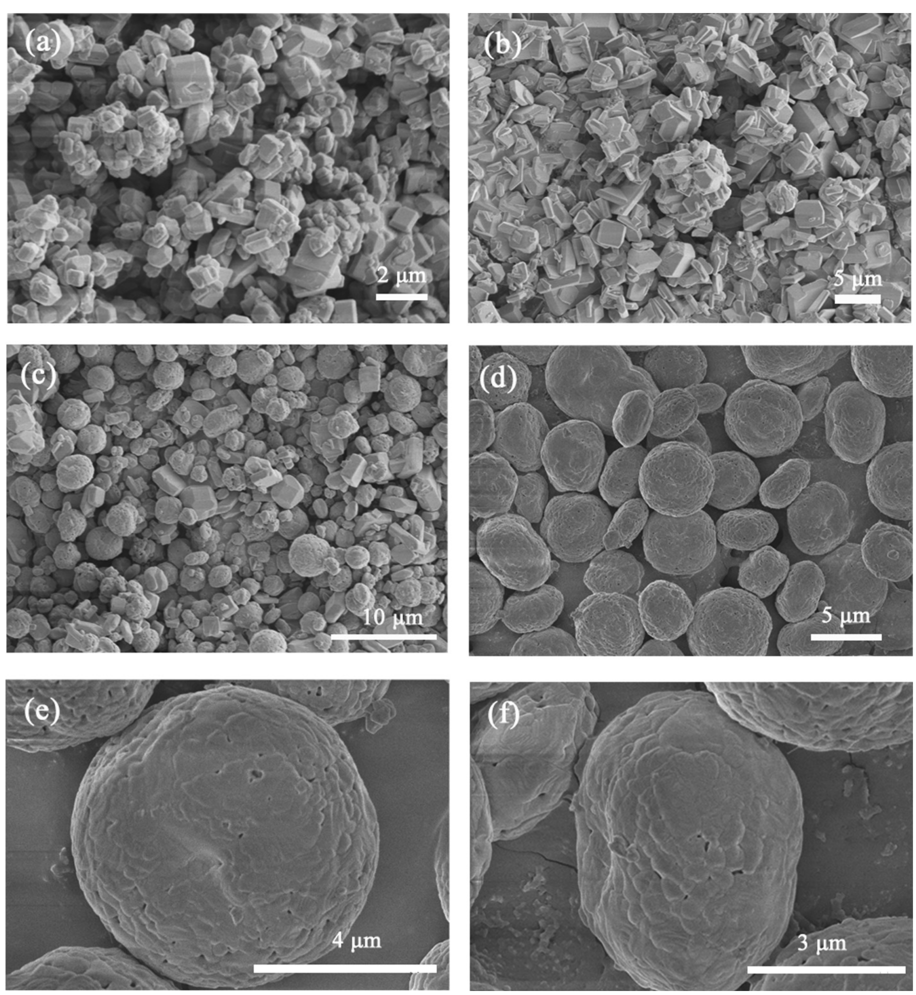

Fig. 2. SEM images of $BiVO_4$ products (a) PB-0, (b) PB-1, (c) PB-2 (d) PB-3 and the enlarged front (e) and profile (f) images of PB-3.