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Structuring porous "sponge-like" $BiVO_4$ film for efficient photocatalysis under visible light illumination

Lu Dong, Xiufang Zhang *, Xiaoli Dong *, Xinxin Zhang, Chun Ma, Hongchao Ma, Mang Xue, Fei Shi

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China

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ABSTRACT

The porous "sponge-like" $BiVO_4$ films were prepared with the polystyrene (PS) as pore forming material and F-doped SnO_2 (FTO) glass as substrate. SEM observation displayed that "sponge-like" $BiVO_4$ film with interconnect pore structure was successfully obtained. DRS analysis indicated the light absorption ability of $BiVO_4$ film was enhanced by constructing porous structure. The measurement of surface area showed that porosity could elevate the surface area of the $BiVO_4$ film. The experiment of PEC degradation of phenol showed that the degradation rate on the porous $BiVO_4$ film (with 200 μL) was 2.68 times as much as that on the $BiVO_4$ film. The enhanced PEC performance was attributed to the increased photo absorption ability, elevated surface area, and more efficient reactant transfer.

1. Introduction

During the past decades, semiconductor photocatalytic (PC) process has been proven a promising method in the destruction of organic pollutants in wastewater due to its strong oxidation power, moderate operation temperature, and relative "green" final products [1–3]. Recently, considerable research was focused on the development of photocatalysts with visible light response in order to obtain high utilization efficiency of solar energy [4–8]. Monoclinic scheelite-type $BiVO_4$, one kind of visible light photocatalyst with the energy of band gap (E_g) of 2.4 eV, has also attracted a great deal of attention for water splitting and pollutant elimination [9,10]. However, low efficiency is the bottle neck that holds up the application progress. Some efforts have been pursued to enhance the PC efficiency such as deposition of noble metals and constructing the heterojunction [11,12]. Despite all the advances in the modifications, a nonporous photocatalyst still suffers from limited light penetration, which partly accounts for its poor photoactivity [13]. One solution to solve this problem is to construct the porous material as the photocatalyst [14–17]. The channels in the porous photocatalyst could serve as light-transfer paths for the distribution of photon energy onto the large surface of inner photocatalyst particles. As a result, the light penetration distance could be lengthened, and the efficiency of photo absorption, one of the most important factors of the photocatalysis, could be enhanced. Furthermore, porosity enhances diffusion process and decreases diffusion resistance of the pollutant throughout the channels in the photocatalyst [15]. At last, appropriate pore diameter can elevate the surface area of the photocatalyst, which is a basic requirement for an efficient photocatalyst, both to enhance the adsorption of reactants and to offer a large number of reactive sites [18,19]. Otherwise, applying a bias potential to the reaction compartment is a promising way to improve the efficiency of PC process [20]. The photogenerated electron can be drawn from work electrode (photo-anode) to the counter electrode, and the separation efficiency of photogenerated electron-hole pairs can be enhanced.

Template procedures are an ideal way to control material structure including the outer morphology and size and the inner pore size and distribution [21,22]. Organic materials are commonly used as template, which are easily removed with solvent or heating procedures. Polystyrene (PS) ball has been proved useful for the formation of porous materials [23].

Herein, porous $BiVO_4$ films were produced with the PS as the template for enhanced PC performance. The preparation and the photoelectrochemical property, especially their photoelectrocatalytic (PEC) ability in pollution controlling, was described. Phenol, a common pollutant in the industry wastewater, was chosen as a test substance to evaluate the PEC performance of the porous $BiVO_4$ films under visible light.

2. Experimental

2.1. Preparation of porous $BiVO_4$ films

Vanadium (V) tri-i-propoxy oxide was purchased from Strem Chemicals, USA. All of the other reagents (analytical grade purity) were bought from Tianjin Kermel Chemical Reagents Development

* Corresponding authors. Fax: +86 411 86323736.
E-mail addresses: zhangxf@dlpu.edu.cn (X. Zhang), dongxl@dlpu.edu.cn (X. Dong).

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Centre, China, and were used without further purification. F-doped SnO_2 (FTO) glass with a thickness of 2.2 mm, which was purchased from Geao Co., China, was employed as a substrate.

The porous $BiVO_4$ films were prepared with PS as pore forming material. The procedure for preparing porous $BiVO_4$ films was illustrated in Scheme 1. In detail, $Bi(NO_3)_5{\cdot}5H_2O$ was dissolved in acetic acid (CH_3COOH), and the solution was named as A, Triisopropoxyvanadium (V) Oxide was dissolved in acetylacetone ($C_5H_8O_2$), and the solution was named as B. Then, B was added into A drop by drop with a 1:1 stoichiometric ratio of V to Bi, and the concentration of Bi (or V) in the obtained sol was 0.02 mol/L. And then, 25 μL, 50 μL, 100 μL, 200 μL, and 300 μL of PS balls (240 nm) were added to 10 ml sol and recorded by S_{25}, S_{50}, S_{100}, S_{200}, and S_{300}, respectively. The sol was vigorously stirred for 0.5 h. The $BiVO_4$ film and porous $BiVO_4$ films were obtained by coating certain quantity of the above sol onto FTO glass and annealed in air at 500 °C for 2 h. The $BiVO_4$ film was prepared by the same process without PS balls and was recorded by S_0.

2.2. Characterization of the prepared samples

The morphology of the samples was observed using a scanning electron microscopy (SEM, Hitachi S-4800); The crystal structure of the films was investigated by XRD (Rigaku D/MAX-2400) with Cu Kα radiation, accelerating voltage of 40 kV, current of 30 mA, and UV–vis absorption spectra of the samples were recorded on a UV–vis spectrophotometer (Shimadzu, UV-2450) in the range of 300–600 nm. The specific surface area was determined by an adsorption instrument (Tristar 3000) and calculated using the linear portion of the Brunauer–Emmett–Teller (BET) model.

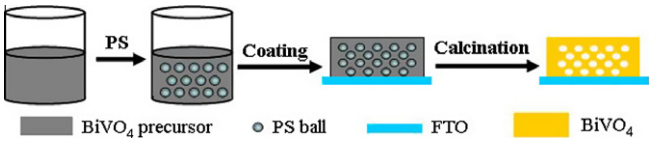
2.3. PEC degradation of phenol

The experimental cell was a standard three-electrode configuration with the porous $BiVO_4$ film electrode as photo-anode, a platinum foil as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The light from a 500 W Xe lamp (Shanghai Jiguang Light, China) was passed through a glass filter, which allowed wavelength above 400 nm to be incident on the photo-anode at a measured intensity of 50 mW cm^{-2}. The initial concentration of phenol was 5 mg L^{-1}. The potential applied to the experimental cell was 0.5 V. The concentration of phenol was determined by high-performance liquid chromatography (HPLC, Waters 2695, Photodiode Array Detector 2996) with a Sun-Fire C 18 (5 μm) reverse-phase column at 30 °C. Methanol and water (v:v = 0.55:0.45) at a flow rate of 1.0 mL min^{-1} served as the mobile phase.

3. Results and discussion

3.1. XRD

The XRD patterns of $BiVO_4$ film and porous $BiVO_4$ film were shown in Fig. 1. The crystal form of the $BiVO_4$ film could be identified to the monoclinic scheelite type by the diffraction pattern according to JCPDS Card No. 14-0688. Compared with that of the



Scheme 1. Schematic procedure for preparing porous the $BiVO_4$ film.

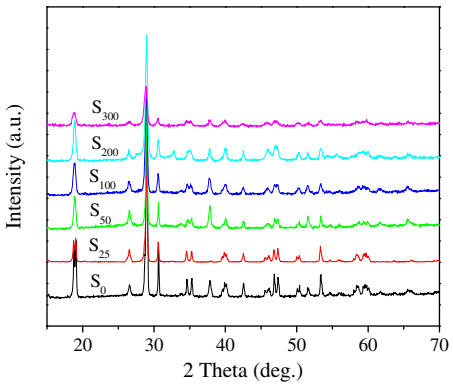


Fig. 1. XRD patterns of $BiVO_4$ film and porous $BiVO_4$ films.

$BiVO_4$ film, it was obvious that no characteristic peaks were observed in the patterns of porous $BiVO_4$ films.

3.2. SEM

Fig. 2 showed SEM images of the $BiVO_4$ film and porous $BiVO_4$ films. From Fig. 2a, the particle of S_0 was big, and the size of them was micron grade. The particle size of all the porous $BiVO_4$ films was decreased to the nanometer level (Fig. 2b–f). The particle size reduced demonstrated that the introduction of PS prevented the generation of the particle in the anneal process. It could be clearly seen that the PS quantity added to the sample affected the pore quantity and structure. The pores of S_{25} and S_{50} did not connect and separated to each other. But, the pores of S_{100} and S_{200} interconnected due to the increased PS quantity in sol. S_{200} showed the porous "sponge-like" morphology. This interconnected pore structure may provide convenient and efficient path for the photo and reactant transfer and expose more active sites on the surface of the $BiVO_4$ particle to the object substance, and these two excellent features were the basic advantage to efficient PC performance. When 300 μL of PS was added, and some pores in the $BiVO_4$ film collapsed. From the morphology of films, there was not clear template effect. The reason that the size of $BiVO_4$ gel was larger than PS balls was speculated [24]. The balls were supposed to be present separated from the gel domains or present between the interlamellar spaces formed by the gel. After burning off the PS balls, the spaces maintained by the spheres are mostly lost, leaving only the stacks of crumpled $BiVO_4$ particles.

3.3. DRS

It is well known that the optical absorption property, which can exhibit the spectrum range the photocatalyst can absorb and the value of absorption coefficient of the photocatalyst, is recognized as the key factor in determining the PC performance of the photocatalyst. The UV–vis diffuse reflectance spectra of the $BiVO_4$ film and porous $BiVO_4$ films were illustrated in Fig. 3. All the films showed intense absorption in the visible light region (from 400 to 500 nm). The absorption value of all the porous films was bigger than that of the $BiVO_4$ film, indicating that the porous structure in the film was benefit to the absorption of the light. This enhanced light-trapping effect was attributed to the multiple scattering by pores in $BiVO_4$ films. Furthermore, the channels in the porous $BiVO_4$ film could serve as the light-transfer paths for the distribution of more photons onto the large surface of the photocatalyst particles and promote the next photon absorption. A similar effect was reported in other porous materials [15,25,26]. The band gap absorption edges of all the films were nearly same.