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Synthesis of dendritic-like $BiVO_4$:Ag heterostructure for enhanced and fast photocatalytic degradation of RhB solution

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ABSTRACT

Dendritic-like $BiVO_4$:Ag heterostructure was formed in the process of visible light-irradiated photocatalysis using dendritic-like $BiVO_4$ as photocatalyst, $AgNO_3$ as additive and photocatalytic degradation of Rhodamine B (RhB) solution as model reaction. In the coexistence of $BiVO_4$ and $AgNO_3$, Ag islands (nanoparticles) could be formed on the surface of dendritic-like $BiVO_4$ crystals after Ag^+ ions captured the photo-generated electrons, and hence the $BiVO_4$:Ag heterostructure was obtained. The formation of Ag islands can be directly confirmed by TEM technique. The synergistic effect of the formation of $BiVO_4$:Ag heterostructure and Ag^+ ions as electron capture agent leads to prominent improvement of the photocatalytic activity, i.e., the decolor efficiency of the dendritic-like $BiVO_4$ photocatalysts for degradation of RhB solution was prominently improved from 34.4% to 91.4% under visible light irradiation only for 20 min.

1. Introduction

With the intense need of people for a healthy environment, the elimination of pollutant chemicals has received extensive attention. Photocatalysis technique based on some semiconductor materials such as TiO_2, ZnO, etc. can be used to eliminate many pollutant chemicals [1–4]. However, due to the wide bandgap of these materials, only ultraviolet light (a small fraction of the sun's energy spectrum) can excite electrons from valence band to conduction band and thus generate effective photocatalysis, which limits the application of these kinds of photocatalysts in many fields [1,3]. As a result, various investigations have been undertaken to exploit novel and efficient photocatalysts (such as N-doped TiO_2, g-C_3N_4, SnS_2-based photocatalysts, $BiVO_4$, etc.) for pollutant degradation and water splitting under visible light irradiation [5–12]. Among of many photocatalysts, those contained Bi compounds have been studied extensively [13,14], such as carbon-modified $BiVO_4$ microtubes [15], flower-like Bi_2MoO_6 hollow spheres [16], g-C_3N_4/$BiIO_4$ [17], Bi_2WO_6 [18,19], Ag and graphene co-modified Bi_2WO_6 nanosheets [20], $Bi_{12}TiO_{20}$ [21], $Bi_4O_5I_2$ [22], BiOI/TiO_2 nanotube arrays [23], hierarchical graphene-$Bi_2O_2CO_3$ composites [24], etc. Due to its narrower band gap (2.4 eV), monoclinic $BiVO_4$ is a promising photocatalyst under visible light irradiation [25–28]. Tan et al. prepared $BiVO_4$ powders via microwave hydrothermal method and reported that their photocatalytic activity was not only related to the crystal structure but also to its morphology and specific surface area [29]. $BiVO_4$ microspheres have been prepared and investigated the degradation of methylene blue (MB) under visible light irradiation [30]. However, it is thought that pure $BiVO_4$ photocatalysts still have some drawbacks like low efficiency in separating photo-generated electron-hole pairs and weak visible light absorptive performance, which limits its practical applications [31–33]. In order to overcome these drawbacks, loading metal, metal oxide or other compounds on $BiVO_4$ could improve the photocatalytic activity through suppressing the recombination of photo-generated electron-hole pairs and reducing the photocatalysts' band gaps [34–37]. For example, Obregon et al. obtained a ternary Er^{3+}-$BiVO_4$/TiO_2 complex heterostructure with high photocatalytic activities for degradation of phenol [38]. Li et al. fabricated the monoclinic porous $BiVO_4$ networks decorated by g-C_3N_4 nano-island and demonstrated that the heterojunction photocatalyst could decompose MB under visible light irradiation [39]. Yang et al. synthesized $BiVO_4$@β-$AgVO_3$ composite by an *in-situ* or *ex-situ* growth method

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and discussed the mechanism of enhanced photocatalytic activities [40]. Other heterojunction structure including $BiVO_4$-TiO_2 [41], Mo:$BiVO_4$ [42], $BiVO_4$-Ru/$SrTiO_3$:Rh [43], CoPi/$BiVO_4$-$CH_3NH_3PbI_3$ [44], C_3N_4-$BiVO_4$ [45], $BiVO_4$-YVO_4 [46], Co/$BiVO_4$ [47], Ag-$BiVO_4$/$InVO_4$ [48], $BiVO_4$/BiOI [49], BiOBr-BiOI [50], etc., were also investigated in recent years.

Metal Ag or Ag compound and $BiVO_4$ complexes have attracted much attention for its high photocatalytic activity. Chen et al. have developed Ag/$BiVO_4$ composites by a one-step method, and the possible growth mechanism of these composites was proposed [51]. Kohtani et al. investigated Ag-loaded $BiVO_4$ photocatalysts' photo-oxidative degradation for nine polycyclic aromatic hydrocarbons and discussed the corresponding mechanism [52]. Li et al. synthesized a homotype heterojunction photocatalyst Ag_3PO_4/$BiVO_4$ with Ag_3PO_4 nanoparticles selectively deposited on the high-active $BiVO_4$ (040) facets with excellent photocatalytic activity [53]. In this work, the monoclinic $BiVO_4$ with various morphologies was synthesized by hydrothermal method, and then the dendritic-like $BiVO_4$:Ag heterostructure was formed in the process of visible light-irradiated photocatalytic degradation of RhB solution using dendritic-like $BiVO_4$ as photocatalyst, with the presence of $AgNO_3$. The photocatalytic activity was prominently improved after a certain amount of $AgNO_3$ was added into the reaction system, which is due to the synergistic effect of the formation of $BiVO_4$:Ag heterostructure and Ag^+ ions as electron capture agent.

2. Experimental section

2.1. Preparation of $BiVO_4$ photocatalyst

All reagents were analytical grade and used without any further purification. Ammonium metavanadate (NH_4VO_3, >99.0%) was supplied by Chengdu Chemical Reagent Factory. Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99.0%) was supplied by Tianjin Bodi Chemical Industry Co., Ltd. Silver nitrate ($AgNO_3$) was purchased from Zhengzhou Xipaike Chemical Co., Ltd.

$BiVO_4$ with different morphologies was prepared by hydrothermal method, similar to a reported procedure with some modifications [28]. Firstly, 0.5 mol/L of $Bi(NO_3)_3$ and NH_4VO_3 solutions were obtained by dissolving the certain amount of $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 powders in 2 mol/L of HNO_3 and NaOH solutions, respectively. Secondly, the $Bi(NO_3)_3$ and NH_4VO_3 solutions were mixed under vigorous stirring, with the molar ratio of 1:1. The pH value of the mixed solution was adjusted by HNO_3 or NaOH solutions. Then, the above mixture was sealed in a 50 mL of Teflon-lined stainless steel autoclave and heated at 180 °C for 24 h. After the autoclave was cooled to room temperature, the powders were separated by centrifugation, washed with deionized water and absolute ethanol for several times, dried at 80 °C for 24 h. Finally, $BiVO_4$ photocatalysts with nanorod or dendritic-like morphology were obtained.

2.2. Characterizations

X-ray diffraction (XRD) patterns were determined by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation source (λ = 0.15406 nm). An FEI Quanta 200 scanning electron microscope (SEM) was used to examine the morphology. TEM images and EDS were recorded through a JEM 2100F (field emission) scanning transmission electron microscope equipped with an Oxford INCA x-sight EDS Si (Li) detector at an acceleration voltage of 200 kV. The diffuse reflection spectrum (DRS) was obtained using a UV–vis spectrophotometer equipped with an integrating sphere, with $BaSO_4$ as a reflectance standard.

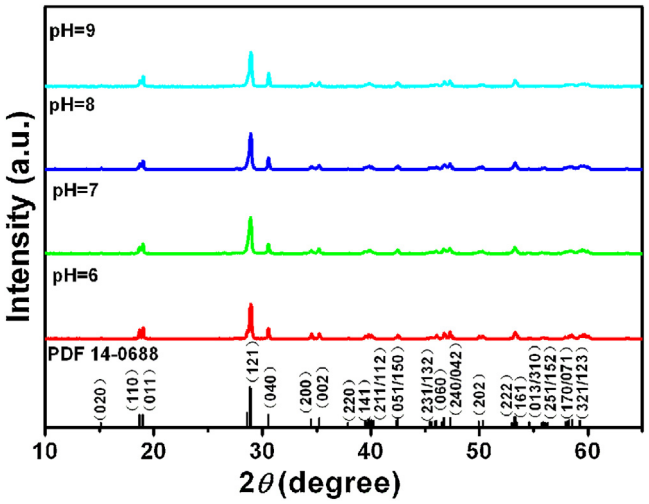

Fig 1. XRD patterns of $BiVO_4$ synthesized at different pH values and the standard data for $BiVO_4$ powders (JCPDS card No. 14-0688).

2.3. Photocatalysis experiments

Photocatalytic activities of the as-prepared samples were evaluated by the degradation of RhB in aqueous solution under simulated sunlight (A 500 W metal halogen lamp with a 400 nm cut-off filter was used as light source) in XPA photochemical reactor. The obtained $BiVO_4$ powders (0.1 g) were dispersed in an aqueous RhB solution (5 mg/L, 50 mL) and then the suspension was transferred into a 80 mL cylindrical quartz reactor with constant magnetic stirring, equipped with a water circulation facility. To reach an adsorption-desorption equilibrium before irradiation, the suspensions were first stirred for 30 min in dark condition. Then the light was switched on, and the solutions were kept stirring. At given time intervals, 5 mL of the suspension was sampled and centrifuged to remove the photocatalysts from the aqueous solution so as to obtain the supernatant for the analysis of RhB. The concentrations of RhB were monitored with a UV–vis spectrometer in terms of the absorbance at 553 nm.

To obtain dendritic-like $BiVO_4$:Ag heterostructure, a certain amount of $AgNO_3$ powders (The mass ratio to $BiVO_4$ are 0.1%, 0.5%,

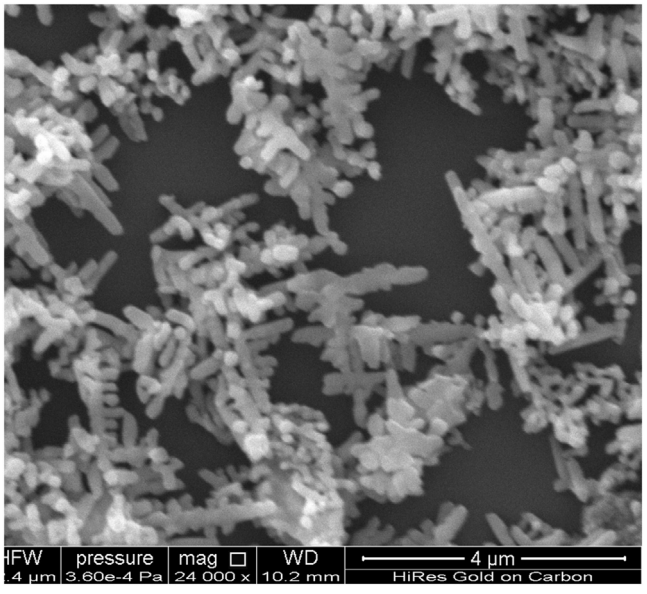

Fig. 2. SEM image of dendritic-like $BiVO_4$.