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BaZrO₃ hollow nanostructure with Fe (III) doping for photocatalytic hydrogen evolution under visible light

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ABSTRACT

Visible-light-responded BaZrO₃ hollow nanostructure with Fe (III) doping was prepared through facile solvothermal reaction using ethanediamine (EDA) as solvent. Fe doping in BaZrO₃ as an efficient way of reducing its wide band gap (~4.96 eV) is realized in order to achieve visible light response. The corresponding trapping center introduced by Fe³⁺ doping contributes to the lower recombination of photo-induced holes and electrons. Meanwhile, the special hollow structure with larger specific area is also a key factor to increase optical absorption, charge carrier migration rate and redox reaction sites. Hence, the participation of Fe and hollow nanostructure are responsible for the visible-light-driven photocatalytic hydrogen evolution.

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Introduction

Recently, immense interests have been attracted on visible light driven photocatalytic hydrogen production, which is regarded as a potential solution to the aggravating energy crisis [1,2]. To enhance the conversion efficiency of solar fuel, feasible way is to develop photocatalysts with wide range spectrum response under visible light [3]. Perovskite oxides (ABO₃) have been deemed as promising materials for photocatalysis due to their tunable electronic structures [4,5]. For example, LaFeO₃ [6–8], ATiO₃ (A = Ca, Sr, Ba) [9,10], ATa(Nb)O₃ (A = K, Na) [11,12] and other perovskite-type oxides [13,14]

show higher efficiency in water splitting [15]. In addition, composition diversity and facile chemical substitution in both A and B sites of ABO₃ render it a potential material to broaden photo-responded ranges, restrict the recombination of photo-induced carriers and further improve photocatalytic performance under visible light irradiation [16,17]. Kudo et al. reported the noble metals (e.g. Mn, Ru, Rh, and Ir) doped SrTiO₃ show photocatalytic activities under visible light [18]. Sun et al. synthesized a new type of perovskite SrTiO₃–Ba₂FeNbO₆ (STO-BFNO) nanocrystals with strong visible light response [19]. While progress has been made in recent years on perovskite based photocatalysts, huge potentials remain unexplored.

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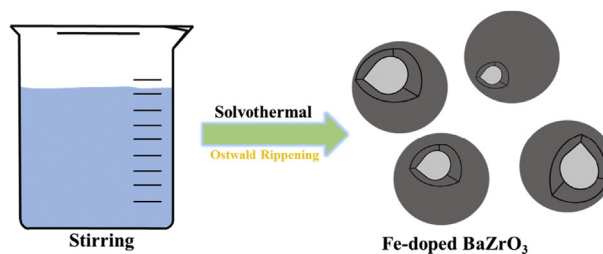
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Barium zirconate (BaZrO_3), first reported by Zou et al., is an ideal perovskite oxide with cubic structure, exhibiting pure water splitting without any co-catalysts under UV light [20]. The bottom of the conduction band (CB), controlled by Zr 4d orbitals locates at around -1.8 eV versus E (NHE) and the top of the valence band (VB) contributed by O 2p orbitals situates in 3 eV. Hence, the photo-excited holes and electrons pairs have enough energy to reduce and oxidize water compared with that of H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox couple in 0 and 1.23 eV, respectively [20,21]. It is well known that the photocatalytic performance is affected by the efficiency of separation and migration for photo-induced carriers. Previous researches reported that the closer to 180° bond angle of M-O-M in MO_6 octahedron, the easier for photo-generated carriers to be delocalized [22–25]. And BaZrO_3 , an ideal cubic perovskite oxide with 180° Zr–O–Zr bond angle, is believed to provide perfect conditions for easy carrier delocalization and transfer to surface sites for redox reaction. Also, the large dispersion in CB for BaZrO_3 means larger energy of electrons, implying more efficient mobilization of electrons according to the equation of $v = \frac{v_{\text{max}} E(k)}{h}$ [26,27]. Therefore, BaZrO_3 can be considered as a potential candidate in photocatalysis.

Many attempts have been carried out to improve the photocatalytic efficiency of BaZrO_3 . Qiu and Zou et al. tuned the band gap and electronic structure of BaZrO_3 by Sn substitution [28]. Domen et al. reported a series of works about BaZrO_3 – BaTaO_2N solid solution for water splitting [29–32]. Qureshi et al. studied the Ta doped BaZrO_3 for efficient hydrogen generation [33]. The charge separation of meso-crystalline BaZrO_3 hollow nanospheres is affected by crystallinity effect confirmed by Chen et al. [34] Also, Zou et al. converted the CO_2 into hydrocarbons using BaZrO_3 as photocatalyst under UV light [35]. However, the wide band gap of BaZrO_3 limits solar absorption, especially visible light region, and no satisfactory solution has been proposed so far. In general, BO_6 octahedron tilting distortions from the ideal cubic ABO_3 perovskite structure have a strong impact on electronic and optical properties according to previous theoretical study [36–38]. Therefore, narrow band gap for ABO_3 structure is possible to be established by different ionic radius replacement in B sites, which is also confirmed by Rapper et al. [16] And defect introduced by non-equivalent doping in B sites have also influenced the band edge positions and carriers trapping [39–42]. Whereas theoretical basis to develop visible light response BaZrO_3 -based photocatalysts is solid [43], few works have been reported in improving the photocatalytic efficiency of BaZrO_3 in visible light regions.

Hence, in this work, we synthesize a novel hollow nanostructure BaZrO_3 photocatalyst with visible light response ($\lambda > 420$ nm) for hydrogen evolution by substituting Fe (III) into Zr sites. The highest hydrogen generation rate is $9.45 \mu\text{mol g}^{-1} \text{h}^{-1}$ with enhanced visible light absorption up to 436.6 nm ($E_g = 2.84$ eV) compared with pure BaZrO_3 with a band energy of 4.96 eV. This tunable band gap with visible light absorption through Fe-doping breaks the limit of wide gap for BaZrO_3 . The Zr cations with +4 are replaced by Fe (+3), and this introduction plays a key role in trapping center to restrict the recombination of photo-induced carriers. Meanwhile, the special hollow structure with higher specific area is also important to affect optical absorption, charge carriers



Scheme 1 – Schematic presentation of the synthesis process of Fe-doped BaZrO_3 hollow nanostructures.

migration and redox reaction sites, thus promoting the photocatalytic hydrogen evolution performance.

Experimental section

Preparation

Fe-doped BaZrO_3 photocatalysts with a series of doping concentration from 0% to 25% were chemically synthesized by solvothermal process (Scheme 1). All reagents were analytical stage without further purification. Typically, calculated amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were firstly dissolved in 10 mL deionized water, followed by the addition of 30 mL ethanediamine (EDA). An exact stoichiometric amount of $\text{Ba}(\text{CH}_3\text{COO})_2$ aqueous solution (2 mL, 2.5 M, and Ba: (Zr + Fe) = 1:1) and 2 mL KOH with 25 M concentration were put into this solution with continuous stirring at room temperature for 30 min. The prepared solution was transferred into a 50 mL Teflon lined autoclave, heated to 200°C for 12 h and cooled to room temperature naturally. The product was washed by ethanol and 2 vol% acetic acid several times and dried at 80°C in the oven for about 12 h. The hollow Fe-doped BaZrO_3 nanoparticles could be collected for next characterization after grinding. According to the doping concentration of the Fe, the samples are named as FBZOn ($n = 0, 5, 10, 15, 20, 25$).

Characterization

X-Ray powder diffraction (XRD) of as-obtained Fe-doped BaZrO_3 powders were collected on a PANalytical X'Pert PRO X-ray powder diffractometer with monochromatic Cu $K\alpha$ radiation. The morphologies and structures of Fe-doped BaZrO_3 products were observed by field emission scanning electron microscopy (SEM: Hitachi SU-70) and transmission electron microscopy (TEM: Tecnai G² F20, FEI) with an energy dispersive X-ray spectrometer (EDX) for elemental analysis. The chemical composition was also determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES: ICP-OES 8000, PerkinElmer). UV–vis diffuse reflectance spectra were collected over the spectral range 190–800 nm with a spectrophotometer (Persee TU-1900) using BaSO_4 as the reflectance standard. Photoluminescence (PL) spectra were obtained by fluorescence spectrometer (Edinburgh instruments FLS920) with an

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