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Article

Amorphous ferric oxide as a hole-extraction and transfer layer on nanoporous bismuth vanadate photoanode for water oxidation

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ABSTRACT

An amorphous ferric oxide layer was prepared on a bismuth vanadate photoanode. This resulted in improved charge carrier separation and surface catalytic performance compared with the photoanode without the oxide layer. The photocurrent of the oxide-layer-containing photoanode was 2.52 mA/cm² at 1.23 V versus the reversible hydrogen electrode, in potassium phosphate buffer (0.5 mol/L, pH = 7.0). The amorphous ferric oxide layer on the photoanode contained low-valence-state iron species (Fe^{II}), which enabled efficient hole extraction and transfer.

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1. Introduction

The direct capture and storage of solar energy via the formation of chemical bonds is a promising approach to realizing alternative energy sources [1,2]. Various approaches for solar energy storage have been reported. Photoelectrochemical (PEC) water splitting is one of the most promising approaches for hydrogen evolution [3–5]. n-Type bismuth vanadate (BiVO₄) is a promising photoanode in PEC systems, because of its narrow bandgap, appropriate conduction band energy level, and sufficient abundance [6]. However, typical incident photon-to-current conversion efficiencies (IPCE) of unmodified BiVO₄ have been unimpressive, because of the rapid recombination of photogenerated electron-hole pairs, poor electrical

conductivity, and slow hole transfer kinetics for water oxidation. Much effort has focused on enhancing the performance of BiVO₄-based water splitting, by coupling with dedicated electron collectors [7], oxygen-evolution catalysts (OEC) [8], and forming homo- or hetero-junctions [9]. A synergetic enhancement of surface reaction kinetics and bulk charge separation should be an ideal way to improve the PEC performance of BiVO₄. Chang et al. [10] prepared Co₃O₄ nanoislands on BiVO₄ to suppress the formation of recombination centers, but the coverage of Co₃O₄ on BiVO₄ was insufficient for long-term performance.

In the current study, we prepared an amorphous ferric oxide layer (FeO_x) on a BiVO₄ photoanode, to enhance the PEC performance of BiVO₄. The resulting photoanode (denoted Bi-

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VO_4/FeO_x) exhibited a photocurrent of 2.52 mA/cm^2 at 1.23 V versus the reversible hydrogen electrode (RHE) in 0.5 mol/L potassium phosphate buffer (0.5 mol/L , $\text{pH } 7.0$) under AM 1.5G simulated solar irradiation.

2. Experimental

2.1. Chemicals

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), dimethyl sulfoxide (DMSO), sodium hydroxide (NaOH, AR) and hexane were purchased from Sinopharm Chemical Reagent Co., Ltd. Vanadyl acetylacetonate ($\text{VO}(\text{acac})_2$, 99%) was purchased from J&K.

2.2. Preparation of nanoporous BiVO_4 photoanode

The nanoporous BiVO_4 photoanode was prepared in two steps: electrodeposition of a BiOI nanoarray, and subsequent conversion to nanoporous BiVO_4 by annealing and soaking treatment. Typically, 0.4 mol/L KI solution (0.4 mol/L) was adjusted to $\text{pH} = 1.7$ by adding HNO_3 . Then, 20 mmol of KI was added to give a transparent orange-red solution. This solution was mixed with 20 mL of absolute ethanol (99.99%) containing 0.23 mol/L p-benzoquinone, and the resulting solution was vigorously stirred for 15 min . Electrodeposition was carried out using a three-electrode system with a fluorine-doped tin oxide (FTO) substrate ($2.5 \text{ cm} \times 1 \text{ cm}$) as the working electrode, platinum foil ($2 \text{ cm} \times 2 \text{ cm}$) as the counter electrode, and a saturated Ag/AgCl electrode as the reference electrode. Cathodic deposition was performed potentiostatically at -0.1 V versus Ag/AgCl at room temperature for 5 min . BiVO_4 electrodes were obtained by depositing 0.1 mL of a DMSO solution containing 0.4 mol/L $\text{VO}(\text{acac})_2$ on the BiOI film, followed by annealing in a muffle furnace at 450°C for 2 h . After soaking in 0.5 mol/L NaOH solution for 30 min to remove excess V_2O_5 , the resulting yellow BiVO_4 film was rinsed in pure water and allowed to dry.

2.3. Preparation of $\text{BiVO}_4/\text{FeO}_x$ photoanode

Iron (III) 2-ethylhexanoate (50% (w/w) in mineral spirits, J&K) was dissolved in hexane to give a 10% (w/w) solution. $5 \mu\text{L}$ of this solution was deposited onto the BiVO_4 photoanode using a pipette. The electrode was irradiated by an ultraviolet light-emitting diode for 50 h to achieve decomposition of precursor complex, and was then annealed in an oven at 100°C for 1 h . A similar procedure was used to prepare the FTO/FeO_x samples.

2.4. Characterization

The crystal structures of the samples were determined using X-ray diffraction (XRD, Bruker D8 Advanced diffractometer, $\text{Cu K}\alpha$ radiation, 40 kV). The morphologies and microstructures of the samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S4800, Japan) and high-resolution transmission electron microscopy (HRTEM,

JEOL JEM-2010F, F20, 200 kV).

2.5. Photoelectrochemical measurements

PEC experiments were conducted by back-side illumination using a three-electrode configuration. The sample electrode, platinum foil, and Ag/AgCl in saturated KCl solution were used as the working, counter, and reference electrodes, respectively.

Simulated solar radiation was provided by a solar simulator (Oriel, 91160, AM 1.5 globe), the power of which was calibrated to be 100 mW/cm^2 using a Newport Oriel PV reference cell system (model 91150V). A potassium phosphate (KPi) buffer solution (0.5 mol/L , $\text{pH} = 7.0$) with and without Na_2SO_3 (1 mol/L) as a hole scavenger was used as the electrolyte. The IPCE was measured by a solar simulator (Newport 70525) coupled with a filter (Newport 70625) and an aligned monochromator (Newport 7400). All experiments were performed using an electrochemical workstation (Parstat 2237, Princeton, UK).

Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC amplitude of 50 mV with a frequency range from 10^5 to 0.01 Hz , in KPi buffer (0.5 mol/L) under the open-circuit potential. Mott-Scotky plots were obtained under the same solution and scanned from 0 to 1 V versus RHE. The AC potential frequency was 5000 Hz under dark conditions, with an amplitude of 3 mV .

The potential versus Ag/AgCl was converted to the RHE scale using the Nernst equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + 0.1976$$

3. Results and discussion

Fig. 1(a) shows that the gossamer-like amorphous FeO_x was uniformly deposited on the surface of the BiVO_4 nanoparticles, without obvious aggregation. Energy dispersive X-ray spectroscopy was used to confirm the presence of the ferric oxide layer (Fig. 1(b)). The mapping images show the uniform distribution

Fig. 1. (a) Top-view SEM image of the $\text{BiVO}_4/\text{FeO}_x$ photoanode; (b) Elemental mapping images of the $\text{BiVO}_4/\text{FeO}_x$ photoanode; (c) HRTEM image and corresponding SAED pattern of the $\text{BiVO}_4/\text{FeO}_x$ film; (d) XRD pattern of the $\text{BiVO}_4/\text{FeO}_x$ photoanode.

bution of Fe throughout the BiVO_4 nanoparticles. The selected area electron diffraction (SAED) pattern and HRTEM image in Fig. 1(c) indicated a lattice spacing of ~ 0.31 nm. The angle of 50° between the two lattice fringes was consistent with the angle between the (130) and (121) planes. The crystal structure of $\text{BiVO}_4/\text{FeO}_x$ was investigated by XRD (Fig. 1(d)). Obvious diffraction peaks corresponded to monoclinic BiVO_4 , while diffraction peaks of Fe_2O_3 or FeO were not observed, confirming the presence of amorphous ferric oxide.

Fig. 2(a) shows current-potential curves of the BiVO_4 and $\text{BiVO}_4/\text{FeO}_x$ photoanodes under back-side illumination. FeO_x is capable of evolving O_2 in basic solution at moderate overpotentials [11], when not coupled with a semiconductor for photooxidation of water in neutral aqueous solution. Adding FeO_x enhanced the photocurrent over the entire potential range. The $\text{BiVO}_4/\text{FeO}_x$ photoanode exhibited an AM 1.5G photocurrent of 2.52 mA/cm^2 at 1.23 V versus RHE for water splitting. The photocurrent of the BiVO_4 photoanode was 0.8 mA/cm^2 .

Fig. 2(b) shows chronoamperometry measurements of the $\text{BiVO}_4/\text{FeO}_x$ and BiVO_4 photoanodes at 0.6 V versus RHE, under chopped AM 1.5G simulated solar radiation at 100 mW/cm^2 . Under irradiation, a photocurrent spike was observed for the BiVO_4 photoanode at an applied potential of 0.6 V versus RHE.

This was due to the rapid generation and subsequent recombination of charge carriers. When irradiation ceased, an obvious cathodic transient was observed, which was caused by the accumulation of holes [12]. The cathodic and anodic transients were barely observed in the measurements for the $\text{BiVO}_4/\text{FeO}_x$ photoanode. This indicated that the FeO_x coating decreased charge recombination and hole accumulation in the BiVO_4 surface [13]. This observation suggested that the recombination of photogenerated charge carriers was suppressed in the $\text{BiVO}_4/\text{FeO}_x$ photoanode compared with in the BiVO_4 photoanode [10].

EIS can provide information about the interfacial properties of electrodes. The diameter of the semicircle in the EIS curve indicates the electron transfer resistance within the electrode interface [14]. Fig. 2(c) shows typical EIS curves for the BiVO_4 and $\text{BiVO}_4/\text{FeO}_x$ photoanodes under irradiation in KPi buffer. A smaller diameter was observed for the curve of the $\text{BiVO}_4/\text{FeO}_x$ photoanode under irradiation compared with the BiVO_4 photoanode. This indicated that the resistance within the FeO_x /electrolyte interface was much smaller than that within the BiVO_4 /electrolyte interface. Thus, the presence of FeO_x decreased the charge transfer barrier at the electrode interface, so the oxygen-evolution reaction was enhanced as reported pre-

Fig. 2. (a) Current-potential curves of the BiVO_4 and $\text{BiVO}_4/\text{FeO}_x$ photoanodes under AM 1.5G simulated solar radiation (100 mW/cm^2), in potassium phosphate buffer (0.5 mol/L, pH = 7.0). (b) Chronoamperometry measurements of the photoanodes at 0.6 V versus RHE, under AM 1.5G simulated solar radiation (100 mW/cm^2) in 0.5 mol/L potassium phosphate buffer (0.5 mol/L, pH = 7.0). (c) Electrochemical impedance spectra of $\text{BiVO}_4/\text{FeO}_x$ and BiVO_4 photoanodes under open-circuit potential in dark. (d) The incident photon conversion efficiencies of $\text{BiVO}_4/\text{FeO}_x$ and BiVO_4 photoanodes at 1.23 V vs. RHE.

viously [10]. Water oxidation occurred more readily because of the lower reaction barrier, so a cathodic shift was observed in the onset potential.

The IPCE values of the $\text{BiVO}_4/\text{FeO}_x$ and BiVO_4 photoanodes are plotted as a function of wavelength in Fig. 2(d). The IPCE spectra of the BiVO_4 and $\text{BiVO}_4/\text{FeO}_x$ photoanodes exhibited photoresponses up to 520 nm. The BiVO_4 photoanode exhibited a maximum IPCE of 11% at 400 nm, while the $\text{BiVO}_4/\text{FeO}_x$ photoanode exhibited an IPCE of 38% at the same wavelength. The IPCE results indicated that the photocurrent response resulted from photon absorption solely by BiVO_4 (i.e. no photon absorption by amorphous FeO_x). Thus, the enhanced photochemical performance of the $\text{BiVO}_4/\text{FeO}_x$ photoanode was attributed to enhanced charge transfer and catalysis kinetics, rather than to enhanced light absorption.

The FeO_x layer was characterized by X-ray photoelectron spectroscopy (XPS), to understand its composition. The Bi 4f state exhibited splitting peaks at 159.0 and 164.5 eV (Fig. 3(a)), and the V 2p state exhibited peaks at 516.9 and 523.9 eV (Fig. 3(b)). Fig. 3(c) shows the XPS spectrum of the Fe 2p_{3/2} and 2p_{1/2} region for the $\text{BiVO}_4/\text{FeO}_x$ sample. The $\text{BiVO}_4/\text{FeO}_x$ sample exhibited an obvious satellite peak at around 716 eV, which corresponded to Fe^{II} [15]. The Fe 2p_{3/2} peaks of Fe^{III} and Fe^{II} were both centered at ~711 eV. A satellite peak of the Fe^{III} main line was observed at ~719 eV, which indicated the presence of Fe^{III} . The asymmetric O 1s peaks (Fig. 3(d)) indicated different oxygen species present near the surface. Three O 1s binding

energies (529.3, 530.6 and 532.2 eV) were observed in the spectrum of the $\text{BiVO}_4/\text{FeO}_x$ sample, which were assigned to O^{2-} species in FeO , Fe_2O_3 , and adsorbed H_2O , respectively. These results suggested that Fe^{II} sites formed in the amorphous FeO_x . These Fe^{II} sites acted as shallow donors for the layer of FeO_x , which increased conductivity and promoted carrier transfer [16,17].

To understand the role of Fe^{II} in the PEC process, X-ray absorption fine structure spectra were measured under ex-situ and in-situ conditions [18]. Fig. 4 shows the X-ray absorption near-edge structure (XANES) spectra. The edge position of FeO_x (7121.8 eV at half-height of the normalized edge-jump) was 1.2 eV lower than that of standard Fe_2O_3 . This suggested a slightly lower oxidation state of Fe in the $\text{BiVO}_4/\text{FeO}_x$ film, compared with that in Fe_2O_3 (Fig. 4(a)). The shape of the XANES spectrum reflects the ligand type and coordination geometry of the X-ray-absorbing transition metal [19]. Compared with the spectrum of Fe_2O_3 , the FeO_x spectrum was shifted to lower energy, but was otherwise similar. This suggested that the Fe coordination was largely similar to that in Fe_2O_3 . In-situ XANES spectra were then recorded. Fig. 4(b) shows that under open-circuit conditions, the edge position of FeO_x was at ~7121.8 eV, at half-height of the normalized edge-jump. After applying a bias of 1.2 V to the photoanode, the edge position exhibited a 0.6 V anodic shift compared with that of the photoanode under open-circuit conditions. Simultaneously irradiating and applying a 1.2 V bias to the photoanode caused the

Fig. 3. XPS profiles of the (a) Bi 4f, (b) V 2p, (c) Fe 2p, and (d) O 1s regions for $\text{BiVO}_4/\text{FeO}_x$. The Fe^{II} satellite peak at 716 eV in the Fe 2p region and the O 1s peak at 529.3 eV indicated the presence of Fe^{II} .

Fig. 4. (a) K-edge XANES spectra of Fe foil (grey), Fe₂O₃ (dark grey), FeO_x on FTO (red), and BiVO₄/FeO_x before (black) and after (blue) irradiation and applied bias. (b) In-situ K-edge XANES spectra of BiVO₄/FeO_x under 1.2 V bias (red), under 1.2 V bias and irradiation (orange), and under open-circuit conditions (black). (c) In-situ K-edge XANES spectra of BiVO₄/Fe₂O₃ under 1.2 V bias (blue), under 1.2 V bias and irradiation (black), and under open-circuit conditions (red); (d) Current-potential curves of FTO under irradiation (blue) and FTO/FeO_x in the dark (black) and under AM 1.5G simulated solar radiation (100 mW/cm², red) in potassium phosphate buffer (0.5 mol/L, pH = 7.0).

edge position to anodically shift by ~ 1 V, compared with that of the sample under a bias of 1.2 V. The shift in edge position indicated an in-situ change in the valence state with FeO_x. This was consistent with the hole transfer process in the FeO_x layer during photochemical reaction. In-situ X-ray absorption spectra of the BiVO₄/Fe₂O₃ film were also recorded. XANES spectra of the film prepared by annealing at 450 °C at a potential of 1.2 V are shown in Fig. 4(c). The edge position of the BiVO₄/Fe₂O₃ showed no change upon irradiation under an applied bias. To rule out the oxidation of Fe species under bias and irradiation without the contribution of BiVO₄, linear scan tests of amorphous FeO_x in the dark and under irradiation were performed (Fig. 4(d)). The results indicated that oxidation occurred at ~ 1.6 V versus RHE. Thus, a bias of 1.2 V versus RHE was insufficient to oxidize the Fe species.

These results suggested that photogenerated holes in BiVO₄ could be captured and transferred at the ferric oxide layer. Scheme 1 shows how trace Fe^{II} species played a subtle but profound role as a shallow dopant during the PEC process. Under irradiation and an applied bias, Fe^{II} species were oxidized to Fe^{III} or Fe^{IV} by holes, and then acted as active sites for water oxidation. This could be considered a self-repair and self-activation recyclable reaction mode. The anodic shift in the

EXAFS edge position of the BiVO₄/FeO_x photoanode under irradiation and bias was consistent with hole transfer in the amorphous ferric oxide layer (Scheme 1). The near absence of anodic or cathodic peaks indicated the high efficiency of hole transfer and catalysis in the presence of the FeO_x layer. When irradiation and the bias ceased, the edge position of FeO_x reverted to the previous position. Fe^{II} sites reportedly act as donors and therefore increase the density of charge carriers. The formation of Fe^{II}/Fe^{III} mixed valence states could have significantly enhanced the conductivity, by way of the hopping mechanism [20].

Scheme 1. Mechanism of charge separation for the BiVO₄/FeO_x heterojunction.

Graphical Abstract

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Amorphous ferric oxide as a hole-extraction and transfer layer on nanoporous bismuth vanadate photoanode for water oxidation

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An amorphous ferric oxide layer was deposited on bismuth vanadate in a photochemical process. Species in this layer enhanced charge carrier separation and surface catalytic performance.

4. Conclusions

Forming an amorphous FeO_x layer on the BiVO_4 photoanode significantly improved its photoactivity for water oxidation compared with the BiVO_4 photoanode without the FeO_x layer. The $\text{BiVO}_4/\text{FeO}_x$ photoanode exhibited a photocurrent density of 2.5 mA/cm^2 at 1.23 V versus RHE. The enhanced photoactivity resulted from the increased conductivity and surface catalytic kinetics, which in turn resulted from the formation of Fe^{II} sites. This study reports a simple and effective method for preparing photoactive BiVO_4 for use in PEC water oxidation at low activation temperature, without requiring dopants.

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无定形氧化铁层在纳米多孔 BiVO_4 的光电化学分解水反应中的作用

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摘要: 通过“人工光合成”过程, 将太阳能转化成氢能的形式加以存储和利用, 是替代传统化石能源的清洁能源的制备有效途径。其中, 光电化学分解水是氢能制备的最有潜力的路径之一。n型 BiVO_4 由于具有丰富的储量、较窄的带隙以及合适的能带位置, 被称为光电化学领域的研究热点。然而, 未修饰的 BiVO_4 光阳极性能并不理想, 主要原因在于载流子复合严重、导电性差以及表面催化动力学低等性质的制约。科研工作者们针对这些方面已进行了非常多的研究, 例如与电子传输层的复合、产氧电催化剂的负载以及异质结的构建等。其中表面动力学和电荷分离的同时提升是更理想的改善 BiVO_4 光阳极

性能的方法. 我们在上述研究基础上, 采用光化学沉积法在纳米多孔 BiVO_4 电极表面担载无定形氧化铁层, 将电极在1.23 V vs. RHE电位下的光电流提升至 2.52 mA/cm^2 , 是初始光电化学性能的3倍. 采用间歇光照计时电流(*i-t*)测试, 电化学交流阻抗谱(EIS), X射线光电子能谱(XPS), 原位和非原位的X射线精细结构能谱(in-situ and ex-situ XAFS)等表征手段研究了无定形氧化铁层的成分和光电化学反应过程中的价态变化, 从而分析出光电化学性能提升的原因.

间歇光照*i-t*测试和EIS测试结果表明, 无定形氧化铁沉积在 BiVO_4 使电荷累积减少, 复合率降低. XPS测试结果发现无定形氧化铁层存在少量的二价铁成分. 通过原位XAFS测试发现, $\text{BiVO}_4/\text{FeO}_x$ 电极中Fe原子的价态在光照和施加外加偏压条件下会有价态的升高, 而撤去光照和偏压后Fe原子的价态状态与最初非原位的测试结果重合. 这样的结果证明了无定型氧化铁层在光电化学反应过程中由于二价铁成分的存在, 能够很好的通过价态改变实现空穴的吸附和传输, 即吸附空穴, 被空穴氧化成三价或四价, 同时结合自身电催化活性, 促进表面分解水反应的进行. 而水的氧化反应结束时, 则伴随着二价铁离子的再生成. 这种反应机理为开发更高效电催化剂, 匹配光电极使用, 有着重大的指导意义.

关键词: 氧化铁层; 无定形; 钒酸铋; 光阳极; 氧生成

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For Author Index:

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