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Polyaniline as a new type of hole-transporting material to significantly increase the solar water splitting performance of $BiVO_4$ photoanodes

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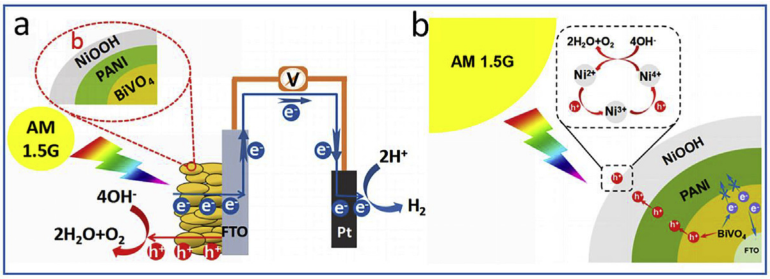
HIGHLIGHTS

- PANI as a hole-transporting layer was used to fabricate $NiOOH/PANI/BiVO_4$ photoanode.
- NPB showed higher PEC water splitting performance than most $BiVO_4$-based photoanode.
- $NiOOH/PANI/BiVO_4$ exhibited excellent stability with high Faraday efficiency.
- PANI transported holes to NiOOH for water oxidation reaction and isolated electrons.
- PANI had great potential as a hole-transporting layer for water splitting photoanode.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyaniline (PANI), with its low cost, chemical stability and high conductivity, is used as a hole transporting layer to fabricate $NiOOH/PANI/BiVO_4$ (NPB) photoanode, of which the photoelectrochemical (PEC) water splitting performance is significantly enhanced. The remarkable water oxidation photocurrent of NPB photoanode achieves $3.31\ mA\ cm^{-2}$ at 1.23 V vs. RHE under AM 1.5G solar light irradiation, which is greatly increased compared with that of pristine $BiVO_4$ ($0.89\ mA\ cm^{-2}$ under the same condition). The maximal incident photon-to-current conversion efficiency achieves 83.3% at 430 nm at 1.23 V vs. RHE and the maximal applied bias photo-to-current efficiency reaches 1.20% at 0.68 V vs. RHE, which are nearly five and ten times higher than that of pristine $BiVO_4$ photoanode, respectively. This NPB photoanode exhibits excellent stability with about 97.22% Faraday efficiency after PEC water splitting for 3 h. The exciting results demonstrate that PANI shows great potential as a hole-transporting layer for photoanode and NPB is an efficient and stable photoanode material with a great potential application in PEC water splitting. Overall, this work provides an excellent reference on designing and fabricating photoanode materials for the future.

1. Introduction

With the rapid development of industrialization, the dwindling fossil fuels have been insufficient to meet the growing energy demand for human, which causes a severe challenge for human existence and the sustainable development of the economy and society. Thus, it is extremely urgent to develop alternative renewable energy sources. Hydrogen, as a clean and renewable energy with a high energy density, is considered to be ideal to meet these energy challenges. Splitting water by PEC methods to produce hydrogen has received increasing

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attention and is thus an important technology for the future. The properties of photoelectrodes have been suggested as the most important factor which affects the efficiency of PEC water splitting. Therefore, many semiconductor metal oxides with high photoactivities have been explored and widely used as photoanodes materials, such as TiO_2 [1], SnO_2 [2], ZnO [3], WO_3 [4] and Fe_2O_3 [5].

Monoclinic $BiVO_4$, with a suitable band gap of ~2.4 eV for visible light absorption and an appropriate valance band position for oxygen evolution (1.23 eV vs. RHE), has emerged as a promising photoanode material for PEC solar water oxidation and attracts considerable interest. Assuming the quantum efficiency is 100%, the maximal water oxidation photocurrent could theoretically achieve 7.5 mA cm^{-2} under solar illumination [6–8]. However, the values reported in previous papers are still far below this value up to now, due to its low photo-generated electron-hole separation yield and poor surface photo-generated carrier transfer efficiency [9–11]. As a result, a series of research activities that aimed to enhance the PEC water splitting performances were carried out by improving the separation efficiency and surface transfer capability of photo-generated carriers of $BiVO_4$ photoanode. Doping (such as in W, Mo-$BiVO_4$) [12,13], nanostructuring (such as nanoporous $BiVO_4$) [14], heterojunctions (such as $WO_3/BiVO_4$) [15], and homojunctions (such as W-$BiVO_4/BiVO_4$) [12] were reported. PEC water splitting capabilities of these photoanodes were enhanced by suppressing the photo-generated electron and hole recombination. NiFe-(oxy) hydroxide and Co-Pi were employed as oxygen evolution catalyst (OEC) for $BiVO_4$ photoanode, such as NiOOH/FeOOH/$BiVO_4$ [14], N-$BiVO_4$/FeOOH/NiOOH [16], WO_3/(W, Mo)-$BiVO_4$/FeOOH/NiOOH [17], Co-Pi/$BiVO_4$ [10] and Co-Pi/W:$BiVO_4$ [12], in which surface charge transfer was improved to enhance the performance for PEC water splitting. However, the water oxidation photocurrents of these photoanodes are still much lower than the ideal maximum 7.5 mA cm^{-2}, which may be enhanced by improving the efficiency of both charge separation and surface charge transfer simultaneously.

PANI, a conducting polymer of extended π-conjugated electron system, with its excellent stability and hole transporting capability, has recently attracted considerable attention. For example, Han et al. [18] proved that nano PANI films electrodeposited as hole transporting layers and applied in P3HT/PCBM-based organic solar cells could enhance their power conversion efficiency. Bejbouji et al. [19] used PANI as a hole injection layer which was inlaid between P3HT:PCBM and ITO to increase photovoltaic efficiencies for organic photovoltaic cells. In addition, Alonso et al. [20] corroborated that electrodepositing PANI as a hole transporting layer between PVK and ITO could optimized turn-on voltage in polymer lightemitting devices. All of these reports indicates that PANI is a good hole-transporting material, which will be a promising candidate for photoelectrochemical devices.

With these motivations, in this work, we prepared an integrated NPB photoanode, in which a thin interlayer of PANI was incorporated between the $BiVO_4$ core and the OEC NiOOH shell. Accordingly, as schematically illustrated in Figure S1, an integrated PEC solar water splitting system was employed, which was composed of NPB photoanode for oxygen evolution reaction (OER), Ag/AgCl electrode for reference and Pt cathode for hydrogen evolution reaction (HER). During the water splitting process, electrons and holes were generated by $BiVO_4$ under solar light irradiation and subsequently electrons transferred to the Pt cathode for HER and holes to the NiOOH layer for OER (Fig. 1).

The exciting result showed that the NPB photoanode achieved a remarkable water oxidation photocurrent of 3.31 mA cm^{-2} at 1.23 V vs. RHE under AM 1.5G solar light irradiation, which was significantly improved compared with that of the pristine $BiVO_4$ (0.89 mA cm^{-2} at 1.23 V vs. RHE) in KH_2PO_4 aqueous solution without a hole scavenger (pH = 7). Moreover, incident photon-to-current conversion efficiency (IPCE) of NPB photoanode achieved 83.3% at 430 nm, which was nearly 5-fold higher than that of pristine $BiVO_4$ (17.7% at 430 nm) under the same condition. Our investigation demonstrates the crucial role of PANI for improving the separation of electrons and holes by transporting holes from $BiVO_4$ to the OEC NiOOH layer, finally accelerating the water oxidation kinetics. The excellent PEC performance confirms PANI to be an effective material modifying inorganic semiconductor-based photoanodes due to its excellent hole transporting capability, and qualifies the great potential of NPB to be a promising photoanode material for PEC water splitting.

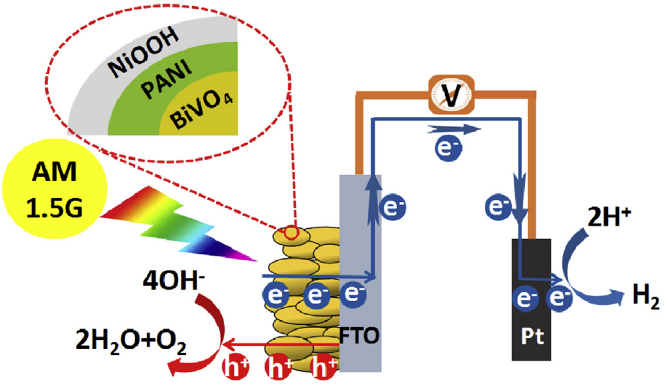

Fig. 1. Mechanism diagram showing the separation and directional movement of photo-excited electrons and holes in the PEC water splitting system.

2. Experimental section

2.1. Electrodeposition of BiOI electrodes

50 mL of mixed solution (pH = 1.7 by adding HNO_3) containing 0.04 M $Bi(NO_3)_3{\cdot}5H_2O$ (99.0%) and 0.4 M KI (99.0%) solution was mixed with 20 mL of C_2H_5OH (99.7%) containing 0.23 M p-benzoquinone (99.0%) with vigorous stirring. A typical three-electrode cell was used for electrodeposition. A F-doped SnO_2 (FTO, area of 1 × 2.0 cm^2), an Ag/AgCl electrode and a Pt electrode served as the working electrode (WE), the reference electrode (RE) and the counter electrode (CE), respectively. The crystalline BiOI was deposited on transparent FTO under cathodic bias of −0.1 V vs. Ag/AgCl at room temperature (RT) for 200 s.

2.2. Preparation of $BiVO_4$ electrodes

0.2 mL of dimethyl sulfoxide (DMSO, ≥99%) solution containing 0.2 M vanadyl acetylacetonate ($VO(acac)_2$, 99%) was placed on the BiOI electrode, and then annealed in a muffle furnace at 450 °C (ramping rate = 2 °C/min) for 2 h in air to convert BiOI to $BiVO_4$. Lastly, the as-obtained samples were soaked in 1 M NaOH solution for 30 min with gentle stirring to remove excess V_2O_5, and subsequently rinsed with deionized (DI) water and dried at RT to obtain pure $BiVO_4$ electrodes.

2.3. Photoelectrodeposition of PANI on $BiVO_4$ electrodes

Firstly, 0.1 M aniline ($C_6H_5NH_2$, AR) solution (pH = 3 by adding HCl) was prepared as a electrolyte by dissolving $C_6H_5NH_2$ in 100 mL of DI water which was further dispersed by ultrasonication (KQ-100DE). Then, an undivided three-electrode cell was used for photoelectrodeposition, which was composed of a $BiVO_4$ WE, an Ag/AgCl RE, and a Pt CE. An AM 1.5G solar simulator (100 mW cm^{-2}, Newport, LCS 100 94011A-ES) was used as the light source to assist electrodeposition (an anodic bias of +0.60 V vs. Ag/AgCl) which was carried out on $BiVO_4$ electrode to fabricate PANI/$BiVO_4$ electrode for various deposition times (10, 30 and 50 s). Finally, an electrodeposition of PANI was carried out in the same solution by applying +2.0 V vs. Ag/AgCl for 1 min to obtain PANI/$BiVO_4$-10 (30, 50) s electrodes.