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Simultaneously improving solar water oxidation kinetics and passivating surface states of hematite by loading an amorphous Ni doped cobalt phosphate layer

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ABSTRACT

High surface states density of hematite photoanodes results in their low water oxidation kinetics and high surface electrons-holes recombination. To overcome these inherent drawbacks, various methods have been adopted, especially loading oxygen evolution catalysts and depositing oxide passivation layers. We report here an efficient way to promote the photocurrent of Fe₂O₃ photoanodes via depositing a thin layer of Co_{0.84}Ni_{0.16}-Pi. With the Co_{0.84}Ni_{0.16}-Pi deposit on its surface, the photocurrent density of Fe₂O₃ increases by ca. 42% at 0.23 V vs. Ag/AgCl, and the onset potential shifts 200 mV cathodically. In contrast, Co-Pi@Fe₂O₃ photoanode shows only 20% enhancement in photocurrent density under otherwise identical condition. The dark current densities of the photoanodes give an evidence that both Co_{0.84}Ni_{0.16}-Pi and Co-Pi are good oxygen evolution catalysts. Moreover, different from sparsely distributed Co-Pi nanoparticles, a 2–3 nm amorphous Ni doped cobalt phosphate layer can be also an effective passivation layer for surface states of hematite, which has been demonstrated by the analyses of Mott-Schottky plots and electrochemical impedance spectroscopy. This work demonstrates the dual roles of an amorphous oxygen evolution co-catalyst on hematite photoanodes and provides a simple method for designing highly efficient photoanodes.

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Introduction

Due to greenhouse effect and environmental pollution, clean energy has greatly attracted world's attention [1]. Hydrogen is

customarily viewed as clean and efficient energy substitute of fossil oil and gas [2, 3]. Since TiO₂ electrode was found the ability of water oxidation, photoelectrochemical (PEC) water splitting has been considered as one of potential techniques for hydrogen production [4,5]. Many semiconductors have

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been applied in solar water splitting, including TiO_2 [6–11], WO_3 [12–15], ZnO [16,17], BiVO_4 [18–22], Cu_2O [23,24], Ta_3N_5 [25–28], TaON [29,30], etc. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has been extensively investigated as photoanode for water splitting because of its narrow band gap (2.1 eV), excellent visible light absorption efficiency and ready availability [5,31–34]. However, the reported solar-to-hydrogen efficiency (STH) of hematite is much lower than the theoretically predicted value because its high surface states density results in poor water oxidation kinetics and high surface electrons-holes recombination [35–37]. It is well accepted that the surface states of hematite electrode consist of low valent iron-aqua or iron hydroxyl species. The photo-generated holes from the valance band of hematite will firstly oxidizes the low valent iron-aqua or iron hydroxyl species to a high valent Fe-oxo chemical species at the surface. This will cripple the oxygen evolution kinetics [38]. Two of deeply investigated and effective methods to reduce surface charge loss are loading water oxidation co-catalyst and depositing a passivation layer on semiconductors [39–41]. Therefore, various water oxidation co-catalysts and passivation layer have been explored in photoelectrochemical cells, especially metallic oxides or phosphates catalysts, such as FeOOH [42], NiOOH [43], Co-Pi [44,45], Co_3O_4 [46], and oxide passivation layer, including TiO_2 [47], Al_2O_3 [48], Ga_2O_3 [49], SiO_x [50], etc. It is more interesting to explore an adsorbent structure not only passivating the surface states of hematite, but also catalysing oxygen evolution reaction to improve the water oxidation kinetics. Kim et al. have found an ultrathin amorphous FeOOH overlayer deposited on hematite nanostructure combines the two functions of an excellent water oxidation co-catalyst and a passivation layer so that the water oxidation photocurrent can be greatly enhanced [35]. Moreover, the hydrothermal deposition of FeOOH on hematite in faintly acid environment can also suppress the back reaction [51]. Naldoni et al. loaded a thin layer of amorphous NiOOH on Fe_2O_3 by photo-assisted electrodeposition [43] and demonstrated that a thin layer of NiOOH could improve the photo-generated charge injection efficiency into the electrolyte by reduction of charge transfer resistance at electrode/electrolyte interface and serve as a passivation layer for scavenging holes from hematite surface traps as well. Thus, an amorphous oxygen evolution catalyst (OEC) layer may simultaneously improve the water oxidation kinetics and passivate the surface states of photoanodes.

Co-Pi catalyst, composed of layered Co oxo/hydroxo with molecular dimensions and stabilized at neutral pH by the PO_4 groups [52–56], have been widely applied in many photoanodes. Irregular Co-Pi nanoparticles will be formed on photoanodes when deposited with thin coverage in most cases [50,55], So Co-Pi overlayer cannot serve as an efficient passivation layer for passivating surface states of semiconductors. In contrast, nickel phosphate (Ni-Pi) usually deposits as an amorphous layer with a good hydrophilic ability [56,57], and acts as a good passivation layer for scavenging holes from hematite surface traps [57]. In this sense, Ni-doped Co-Pi may be a good candidate combining both merits of Co-Pi and Ni-Pi to promote water oxidation photocurrent of hematite. On the other hand, the additional active site can be also created by doping, evidenced by higher catalytic activity of Fe doped Ni-Pi than FeOOH or Ni-Pi [56] and the

superior PEC performance of Ni-Doped $\text{CoO}_x/\text{BiVO}_4$ to $\text{CoO}_x/\text{BiVO}_4$ [58]. To our knowledge, Ni doped cobalt phosphate (refer to $\text{Ni}_x\text{Co}_{1-x}\text{-Pi}$) has not been investigated in PEC water splitting up to date.

In this work, $\text{Ni}_x\text{Co}_{1-x}\text{-Pi}$ has been deposited on Fe_2O_3 nanorod arrays by photo-assisted electrodeposition. The $\text{Co}_{0.84}\text{Ni}_{0.16}\text{-Pi}$ exhibits the highest oxidation activity among all $\text{Ni}_x\text{Co}_{1-x}\text{-Pi}$ samples with the same charges passed ($2.1 \times 10^{-4} \text{ C/cm}^2$). The photocurrent density of Fe_2O_3 photoelectrode increases by ~42% at 0.23 V vs. Ag/AgCl and its onset potential shifts 200 mV toward cathodical direction after decoration with $\text{Co}_{0.84}\text{Ni}_{0.16}\text{-Pi}$ layer. Moreover, the constant current density of $\text{Co}_{0.84}\text{Ni}_{0.16}\text{-Pi}/\text{Fe}_2\text{O}_3$ photoelectrode indicates $\text{Co}_{0.84}\text{Ni}_{0.16}\text{-Pi}$ is as stable as Co-Pi in 1 M NaOH electrolyte. The detailed electrochemical analysis confirms the dual role of an ultrathin $\text{Co}_{0.84}\text{Ni}_{0.16}\text{-Pi}$ layer as passivation layer and oxygen evolution catalyst, which is beneficial for PEC performance enhancement of Fe_2O_3 photoelectrode. Such a dual role of Ni doped Co-Pi may simplify the fabrication of photoanodes combining the virtues of a high photocurrent density and a low photocurrent onset potential, different from those decorated with two or more catalysts and/or passivation components via complex procedures.

Experimental section

Materials

Fluorine doped tin oxide (FTO) glass (F:SnO_2 , 14 Ω per square) were purchased from Nippon Sheet Glass (Japan). Ultrapure water (18.2 $\text{M}\Omega/\text{cm}$) was used throughout the experiments. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$), Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), phosphoric acid (H_3PO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

Synthesis of Fe_2O_3 and $\text{Ni}_x\text{Co}_{1-x}\text{-Pi}/\text{Fe}_2\text{O}_3$ photoelectrodes

The synthesis and decoration procedures of Fe_2O_3 photoelectrodes are illustrated in Scheme 1. FeOOH films were directly grown on fluorine-doped tin oxide substrates (FTO) without a seed layer using a hydrothermal method (step 1). Typically, 3.75 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3.75 mmol of urea were dissolved in 25 mL ultrapure water and then transferred into a 45 mL Teflon-liner. Two substrates (1.5 cm \times 2 cm) were placed at an angle against the wall of Teflon-liner with conducting side facing down. After 12 h of reaction at 100 $^\circ\text{C}$, yellow films appeared on FTO substrate. The substrates were thoroughly rinsed in ultrapure water and blow-dried with N_2 gun. After annealing at 550 $^\circ\text{C}$ with ramping rate of 5 $^\circ\text{C}/\text{min}$ under air for 2 h, FeOOH was transformed into red hematite (step 2). Afterwards, the samples were further annealed at 800 $^\circ\text{C}$ for 10 min to obtain Fe_2O_3 photoanode (step 3).

Photo-assisted electrodeposition of Co-Pi or Ni-Pi onto $\alpha\text{-Fe}_2\text{O}_3$ nanorod arrays was performed from electrolyte of 0.5 mM cobalt or nickel nitrate in 0.1 M potassium phosphate buffer at pH 7, with 1 sun AM 1.5 simulated sunlight illumination (step 4). $\text{Ni}_x\text{Co}_{1-x}\text{-Pi}$ was photo-assisted electrodeposited in

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