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Enhancing and stabilizing α-Fe_2O_3 photoanode towards neutral water oxidation: Introducing a dual-functional NiCoAl layered double hydroxide overlayer

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ABSTRACT

Hematite (α-Fe_2O_3) is a promising candidate as photoanode for photoelectrochemical (PEC) water splitting. However, it still suffers from low efficiency and serious hydrolysis in neutral pH electrolyte. Herein, NiCoAl layered double hydroxides (NiCoAl-LDH) is successfully *in situ* constructed onto hematite (α-Fe_2O_3) nanoarrays. The resulting NiCoAl-LDH/α-Fe_2O_3 photoanode exhibits an onset potential as low as 0.55 V *vs.* reversible hydrogen electrode (RHE) and a significantly enhanced photocurrent density of 2.56 mA cm^{-2} at 1.23 V *vs.* RHE for PEC water oxidation in neutral electrolyte, which is *ca.* 13, 2 and 1.4 times as high as that of α-Fe_2O_3, NiAl-LDH/α-Fe_2O_3 and CoAl-LDH/α-Fe_2O_3. Comprehensive electrochemical and structural analysis reveal the synergistic effect of Ni and Co should be responsible for the enhanced PEC performance. Ni and Co could cause local structure distortion of MO_6 (M = Ni or Co) in NiCoAl-LDH, which (1) improve the conductivity of MAl-LDH, thus enhance the separation and the transfer of photogenerated charges and (2) slightly change the chemical environment of Co and Ni and facilitate the formation of low-valent oxidation states, thus lower the energy barrier of Co^{2+} or Ni^{2+} to high oxidation states and accelerate the kinetics of water oxidation. The versatile skeleton and interlayered anions as well as the thicker decoration of NiCoAl-LDH enable NiCoAl-LDH/α-Fe_2O_3 to possess excellent stability in neutral electrolyte. This work reveals the partial substitution of Co (or Ni) with Ni (or Co) in MAl-LDH could produce more efficient materials toward high PEC water splitting and will stimulate further development on ternary LDHs as excellent cocatalysts for other electrode in neutral electrolyte.

1. Introduction

The increasing energy demands and environmental issues generated from the fossil fuels have forced people to explore alternative and clean energy sources, such as hydrogen energy and solar energy. Photoelectrochemical (PEC) water splitting, which converts solar energy to chemical energy based on semiconductor electrodes, offers an efficient and green carbon-free route to produce hydrogen energy from water ($2H_2O \rightarrow 2H_2 + O_2$) [1,2]. However, the slow kinetics of oxygen evolution reaction (OER) greatly limits the efficiency of overall water splitting. Therefore, designing highly active catalysts and thus photoanodes toward efficient OER attracts enormous research interests.

Up to now, various photoanodes, including TiO_2, ZnO, WO_3 and hematite (α-Fe_2O_3), have been explored for high efficient PEC water splitting [3]. Among these photoanode materials, α-Fe_2O_3 was considered to be one of the most promising candidates, due to its narrow bandgap of 1.9–2.2 eV, elemental abundance, nontoxicity, eco-friend, and 12.6 mA cm^{-2} of theoretical photocurrent density at 1.23 V *vs.* reversible hydrogen electrode (RHE) [4,5]. However, to date only 4.68 mA cm^{-2} of the photocurrent was achieved, which was based on a vertical α-Fe_2O_3 nanosheet modified with Ag and Co-Pi cocatalyst [6]. The low efficiency for overall water splitting of α-Fe_2O_3 is principally related to the complex and kinetically sluggish four-electron, four-proton transfer of OER process ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$) [7,8]. On the other hand, the huge deviation at timescale of photogenerated carriers in bulk α-Fe_2O_3 (ps-ms) and OER (ms-s) resulted in serious surface recombination and scarce utilization of the short-lived photogenerated holes [9]. Thus, accelerating OER kinetics becomes an attractive strategy towards highly efficient PEC systems. In view of this, vigorous OER electrocatalysts have been integrated to fabricate highly efficient α-Fe_2O_3 photoanode. For instance, cobalt-phosphate (Co-Pi) complexes, CoOx, NiOOH and FeB have been proved with high

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efficiency that enhanced PEC performance of α-Fe_2O_3 and accelerated OER kinetics [10–15]. These OER electrocatalysts played important roles that facilitated the separation of photogenerated charges, prolonged the lifetime of photogenerated holes, provided active sites, thus retarded the recombination of photogenerated charges and speeded up OER kinetics.

Besides that, another crucial drawback of α-Fe_2O_3 is the serious hydrolysis and corrosion by the dissociated H^+ from OER [16,17]. To achieve good stability, harsh alkaline electrolytes were commonly employed. However, such strong alkaline condition would cause corrosion to the device and thus increase the cost and shorten long-time stability of PEC system. Moreover, the alkaline condition has also limited the application of α-Fe_2O_3 in PEC tandem cells, where the photocathodes worked well in acidic or neutral electrolytes [18–20]. To extend the practical applications, stable α-Fe_2O_3 in neutral and weakly acidic electrolytes are highly desired. Recently, Kim fabricated a Pi-Fe_2O_3 by modifying α-Fe_2O_3 with phosphate ions, which exhibited superior stability and efficiency in neutral electrolyte [17]. To enhance PEC performance of Pi-Fe_2O_3, our group further decorated Pi-Fe_2O_3 with nickel-phosphate and achieved significantly enhanced PEC activity of Pi-Fe_2O_3 towards glycerol oxidation in neutral electrolyte [21]. Nevertheless, highly stable and highly efficient α-Fe_2O_3 based photoanode for PEC water splitting remains great challenges.

Layered double hydroxides (LDHs) are a kind of layered anionic clays with the general formula as $[M^{2+}_{1-x}M^{3+}_x(OH)_2](A^{n-})_{x/n}{\cdot}mH_2O$, in which M^{2+} and M^{3+} are di- and trivalent metal cations, and A^{n-} are counter anions [22,23]. Recent reports have demonstrated LDHs possessed great potential to be used as OER catalysts due to their versatile composition and abundant active sites [24,25]. For instance, Co- and Ni-based LDHs have emerged as a very promising cocatalysts that enhanced PEC water splitting for photoanodes, such as ZnO@CoNi-LDH, NiFe-LDH/Ta_3N_5, ZnCo-LDH/α-Fe_2O_3, NiFe-LDH/Mn:α-Fe_2O_3, CoAl-LDH/$BiVO_4$ and CoFe-LDH/$BiVO_4$ [26–31]. In addition, our previous work suggested CoAl-LDH would also be as an effective protector to inhibit the hydrolysis of α-Fe_2O_3 in neutral pH electrolyte [32]. In that work, the enhanced PEC performance of α-Fe_2O_3 was assigned to the synergistic effect between Co^{2+}, which provided active catalytic sites for OER, and Al^{3+}, which offered support for the layered skeleton. Co^{2+} could trap the photogenerated holes thus promoted charge separation, lower onset potential and accelerated OER kinetic rates, while the layered skeleton facilitated the fast transfer of protons and the rapid migration of counter anions thus prevented the corrosion of α-Fe_2O_3 from electrolyte. Nevertheless, binary-component LDHs still suffered from low electrical conductivity, due to the fully occupied bonding t_{2g} orbitals of MO_6 center [33]. Recent investigations demonstrated that ternary-component LDHs containing two kinds of transition metal exhibited faster charge-carrier transportation and better electronic conductivity [34–38]. For example, NiCoAl-LDH showed excellent specific capacitance, rate capability and cycling stability as pseudocapacitor electrode material, comparing to that of CoAl-LDH and NiAl-LDH [36]. Moreover, NiCoAl-LDH also displayed relatively stronger catalytic activity for OER than that of Co-Al and Co-Ni [37]. Other ternary-component LDHs like NiCoFe LDH also demonstrated superior OER activity to the outstanding NiFe LDH, which was assigned to the synergistic effect of the unique hierarchical architecture and the intrinsically high activity of NiCoFe LDH nanoplates [38]. In spite of these progress, mechanisms for the enhanced electrical performance of ternary-component LDHs still remained much efforts to reveal the roles of LDHs during the electrochemical reactions.

This work reports an experimental study on ultrathin NiCoAl-LDH nanosheets decorated α-Fe_2O_3 to develop highly efficient and stable photoanode in neutral pH electrolyte. A simple hydrothermal method was utilized to *in situ* growth of NiCoAl-LDH on α-Fe_2O_3 surface. As photoanode, NiCoAl-LDH/α-Fe_2O_3 exhibits a superior electrocatalytic activity with onset potential as low as 0.55 V *vs.* RHE and an almost 13-fold enhancement in photocurrent density at 1.23 V *vs.* RHE toward OER to that of α-Fe_2O_3. Moreover, NiCoAl-LDH/α-Fe_2O_3 also shows an excellent durability with almost 100% retention of photocurrent within 2 h test in neutral pH electrolyte. Further comprehensive electrochemical measurements reveal NiCoAl-LDHs possess relatively higher conductivity, lower charge transfer resistance, and lower the energy barrier of water oxidation. Meanwhile, layered skeleton with suitable thickness allows for fast transfer of protons and counter ions thus prevent the corrosion of α-Fe_2O_3. Our results will open a way to develop new efficient ternary-component LDHs toward enhanced water splitting based semiconducting photoanodes.

2. Experimental

2.1. Preparation of α-Fe_2O_3 based films

α-Fe_2O_3 film was prepared by using our previous method [32]. Typically, $FeCl_3{\cdot}6H_2O$ (15 mmol, 4.055 g) and urea (15 mmol, 0.9008 g) were dissolved successively into 50 mL deionized water in a glass beaker and then the mixture was heated at 100 °C for 6 h. Before being heated, FTO was placed vertically in the beaker with the conducting edge facing wall. The film formed on FTO was washed with high purity water followed by annealed at 500 °C for 3 h. Finally, the film was further annealed at 750 °C for 15 min to produce α-Fe_2O_3 film. NiCoAl-LDH/α-Fe_2O_3 film were fabricated by *in situ* growth of NiCoAl-LDH on the α-Fe_2O_3 film using a simple hydrothermal method. Typically, $Ni(NO_3)_2{\cdot}6H_2O$ (0.375 mmol, 0.1091 g), $Co(NO_3)_2{\cdot}6H_2O$ (0.375 mmol, 0.1091 g), $Al(NO_3)_3{\cdot}9H_2O$ (0.25 mmol, 0.0938 g), urea (2.5 mmol, 0.1501 g), and NH_4F (1 mmol, 0.0370 g) were dissolved in 50 mL deionized water to form a solution. The solution was then transferred into a 100 mL Teflon-lined stainless-steel autoclave in which a piece of α-Fe_2O_3 film was placed with the α-Fe_2O_3 side facing the wall. The hydrothermal process was carried out at 100 °C for 2 h. The resulting NiCoAl-LDH/α-Fe_2O_3 was rinsed with high purity water thoroughly and dried at 80 °C for 1 h. CoAl-LDH/α-Fe_2O_3 and NiAl-LDH/α-Fe_2O_3 were prepared by replacing $Ni(NO_3)_2{\cdot}6H_2O$ or $Co(NO_3)_2{\cdot}6H_2O$ with $Co(NO_3)_2{\cdot}6H_2O$ or $Ni(NO_3)_2{\cdot}6H_2O$ under the same conditions.

2.2. Materials characterization

XRD was performed on a Bruker D8 Advance powder diffractometer using Cu Kα radiation (operating voltage: 40 kV, operating current: 20 mA, scan rate: 5°/min). UV–vis DRS were collected on a UV–vis spectrophotometer (UV-2600, SHIMADZA) and calibrated by using Kubelka-Munk method. SEM were examined on a JSM-7610F scanning electron microscopy at an accelerating voltage of 15 kV. EDS (OXFORD X-act) attached in the SEM was used to obtain elemental mappings (accelerating voltage: 20 kV, probe current: 0.02 μA, Time: 300 s). TEM and HRTEM were carried out on a JEOL JEM-2010 TEM (Japan) with the accelerating voltage of 200 kV. The sample was scraped from FTO and then the obtained power was dispersed on a TEM grid. IR spectra were recorded on a Bruker VERTEX 70 Spectrometer in 4000–400 cm^{-1} using pressed KBr pellets, which contained 0.70–0.75% ground powders shaved from the films. The chemical states were characterized on a VG ESCALab 220i XL X-ray photoelectron spectroscopy (XPS) and the binding energies were calibrated with respect to C1s (284.8 eV).

2.3. PEC and electrochemical characterizations

PEC measurements were performed on a CHI 760D electrochemical workstation (Shanghai) with a three-electrode configura-