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In situ growth of ultrathin Co-MOF nanosheets on α-Fe_2O_3 hematite nanorods for efficient photoelectrochemical water oxidation

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ABSTRACT

Efficient charge transport is an important factor in photoelectrochemical (PEC) water splitting. The charge transfer at the semiconductor/electrolyte interface is of great importance, especially for the complex water oxidation reaction. In this study, we explored the feasibility of improving charge transfer efficiency at the interface of semiconductor/electrolyte by in situ growth of Co based Metal-Organic Frame work (Co-MOF) through a facile ion-exchanging method. Under optimized conditions, the Co-MOF nanosheet-modified hematite gave a photocurrent density of 2.0 mA cm^{-2} (200% improvement) at 1.23 V_{RHE} with a cathodic shift of 180 mV in the photocurrent onset potential, in comparison to bare α-Fe_2O_3 (0.71 mA cm^{-2}@1.23 V_{RHE}). To elucidate the role of Co-MOF, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy and Mott-Schottky measurements were carried out. It was found that the atomically distributed Co^{2+} in Co-MOF possessed excellent hole storage capability and charge transfer efficiency, as evidenced by the high surface capacitance and extremely low surface charge transfer resistance.

1. Introduction

Solar energy conversion using a photo-electrochemical (PEC) water splitting system has been considered as a viable strategy to solve the global energy problems (Hisatomi et al., 2014; Jiang, et al., 2017). As the most important component in a PEC system, semiconductor photoelectrodes have attracted significant attention (Kment et al., 2017; Wheeler et al., 2012). Extensive studies on hematite (α-Fe_2O_3) has been carried out for water oxidation due to its low toxicity, abundance, appropriate band edge position, and high chemical stability (de Carvalho and Souza, 2014; Sivula et al., 2011).

Theoretically, the solar-to-hydrogen efficiency (STH) of α-Fe_2O_3 is predicted to be 16.8% under AM 1.5G irradiation (Chen, 2013). However, it is difficult to achieve this value due to several inherent deficiencies of α-Fe_2O_3 (de Carvalho and Souza, 2014; Sivula et al., 2011). One of the major problems preventing its practical application is the sluggish water oxidation kinetics at the interface between semiconductor and electrolyte. Normally, in order to produce the photocurrent, a large applied potential is required. So, it is necessary to explore highly efficient catalysts to reduce the applied potential. Noble metal oxides of ruthenium/iridium are the most active oxygen evolution catalysts owing to their low overpotential and large current density (Lee et al., 2012). Tilley et al. (2010) prepared a hematite nanostructure using a particle-assisted deposition technique. It was demonstrated that modification of the hematite with IrO_2 nanoparticles led to a higher photocurrent density from 3.45 to 3.75 mA cm^{-2}@ 1.23 V_{RHE} and a cathodic shift of 200 mV in the current onset potential (V_{onset}) (Tilley et al., 2010). However, they suffer from high cost and poor durability, which hinders their application. To solve this problem, many studies have been carried out to develop highly efficient and low-cost oxygen evolution reaction (OER) catalysts involving transition metal compounds (Zhong et al., 2011; Zhong and Gamelin, 2010; Xu et al., 2016; Chen et al., 2017; Malara et al., 2015). In particular, cobalt-based materials such as CoO_x or cobalt phosphate catalysts "Co-Pi" can be promising alternatives to noble metal oxides (Zhong et al., 2011; Zhong and Gamelin, 2010; Du et al., 2017; Li et al., 2016). In particular, Co-Pi on 1D α-Fe_2O_3 nanostructures improves the overall photocurrent density and shifts V_{onset} to more cathodic values, due to the bridging effect of phosphate ions that facilitate hole injection from hematite to Co ions (Klahr et al., 2012). An improvement in the photocurrent density from 2.1 to 2.8 mA cm^{-2} at 1.23 V vs. RHE, corresponding to a 33% improvement, was achieved over mesostructured hematite, which was fabricated using the atmospheric-pressure chemical vapor deposition (APCVD) method followed by surface modification via photo-

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electrodeposition of Co–Pi (Zhong et al., 2011).

It is well known that the catalytic process only occurs on the surface of catalysts: therefore, it is essential to downsize Co-based species to expose more catalytic active sites (Qiao et al., 2011). Thus, a Co-based metal–organic framework (MOF) in which Co centers separated by organic linkers are atomically distributed seems to be an ideal candidate for applications of our interest. For instance, a cobalt-containing catalyst (Co-ZIF-9) worked effectively for the electrochemical OER. It was found that Co-ZIF-9 can activate the water molecule effectively with lower activation barriers through binding the OH- group to the atomically distributed metal sites (Wang et al., 2014). This process leads to the elimination of a proton, which will be accepted by the nearby benzimidazolate linkers (Wang et al., 2014). Recently, another Co-based MOF, zeolitic imidazolate frameworks-67 (ZIF-67), has also been studied intensively for its electrocatalytic activity toward the OER. Intrinsically, ZIF-67 showed poor catalytic activity for the OER (Dou et al., 2017). It is mainly because that Co^{2+} in the bulk of ZIF-67 are closely coordinated to four imidazole linkers; which may probably hamper the adsorption of O species on the active metal sites (Saracco et al., 2014). However, some successful attempts have been made to improve its performance. For example, coordinatively unsaturated metal sites (CUMS) were produced by etching some of the ligands using dielectric barrier discharge plasma technology. The CUMSs in ZIF-67 were considered to be the active catalytic centers for the OER (Tao, et al., 2017). In another study, active atomic-scale CoO_x species were obtained when O_2 plasma was used, which acted as active sites catalyzing the OER (Dou et al., 2017).

In spite of a number of studies on Co-based MOFs as electro-catalysts having been conducted, research on the catalytic effect of ZIF-67 as a co-catalyst for PEC water splitting have been rare, although it may provide attractive possibilities. In this study, we endeavoured to improve the PEC performance of hematite photoanodes by in situ growth of Co-MOFs through a simple and facile ion-exchanging method. $Co(NO_3)_2$ and 2-methylimidazole were used as precursors for the in situ growth of Co-MOF. Co^{2+} nodes were linked through N atoms by 2-methylimidazole groups. When Co^{2+} interacts with 2-methylimidazolate, the N atom with strong electronegativity can act as an electron sink, which renders Co in a higher valence state (Liu et al., 2016). The Co ions with highly positive charges will interact with oxygen, which is beneficial for reversible chemisorption of O species such as OH and OOH and acting as OER-active centers. The atomically distributed Co^{2+} on the surface of hematite is expected to store the photo-generated holes effectively and transfer them to the electrolyte efficiently.

2. Experimental section

2.1. Material preparation

(a) Synthesis of bare hematite films

Pristine α-Fe_2O_3 films on conductive glass substrate were fabricated based on a facile hydrothermal method. In a typical process, a clean FTO ($F:SnO_2$) glass was placed into a 10-mL beaker, which contained 4 mL of solution of 0.0972 g $FeCl_3 \cdot 6H_2O$ (0.09 M) and 0.034 g $NaNO_3$ (0.1 M) at pH 1, adjusted by HCl. Next, the above beaker was carefully placed into the 100-mL Teflon-lined autoclave and kept in an oven at 95 °C for 4 h. After cooling to room temperature, a uniform yellowish layer of FeOOH was formed on the FTO substrate. The resultant samples were rinsed with distilled water for several times and blow-dried with nitrogen. Then, the FeOOH film was annealed at 550 °C for 2 h and at 750 °C for 15 min in air, followed by natural cooling to room temperature to produce a bare hematite film.

(b) Preparation of Co-modified hematite photoanodes

To prepare Co-modified hematite films, a series of bare hematite films were first prepared for further modification. In a typical synthesis, 58 mg of $Co(NO_3) \cdot 6H_2O$ (0.1 M) was dissolved in 2 mL of deionized water. The as-synthesized bare hematite films were spin-coated with 100 μL of the as-prepared $Co(NO_3) \cdot 6H_2O$ aqueous solution at 1200 rpm for 12 s. Then, the surface-treated samples were subjected to heating at 70 °C for 20 min. The resultant samples were referred to as Fe_2O_3@0.1Co.

(c) Preparation of MIm (2-methylimidazole)-modified hematite photoanodes

For MIm-modified hematite photoanodes, the as-synthesized bare hematite films were immersed into 4 mL of a 2-methylimidazole aqueous solution (0.8 M) for 20 min and washed with distilled water. Then, the surface-treated samples were subjected to heating at 70 °C for 20 min. The resultant samples were referred to as Fe_2O_3@0.8 MIm.

(d) Preparation of Co-MOF-modified hematite photoanodes

To prepare in situ Co-MOF-modified hematite photoanodes, the Co-modified hematite films (such as Fe_2O_3@0.1Co) were immersed into 4 mL of a 2-methylimidazole aqueous solution (0.8 M) for 20 min and washed with distilled water. Then, the surface-treated samples were subjected to heating at 70 °C on a hot plate for 20 min. The resulting samples were referred to as Fe_2O_3@0.1Co@0.8MIm, where "0.1Co" and "0.8MIm" refer to the 0.1 M $Co(NO_3) \cdot 6H_2O$ and 0.8 M MIm precursor solutions, respectively. Varying concentrations of $Co(NO_3)_2$ (0.05 M, 0.1 M, and 0.2 M) and 2-methylimidazole (0.4 M, 0.8 M, and1.6 M) were used, and the as-prepared samples were referred to as Fe_2O_3@0.05Co@0.4MIm, Fe_2O_3@0.1Co@0.8MIm, Fe_2O_3@0.2Co@1.6MIm, Fe_2O_3@0.3Co@2.4MIm, Fe_2O_3@0.05Co@0.8MIm, Fe_2O_3@0.2Co@0.8MIm, Fe_2O_3@0.1Co@0.4MIm and Fe_2O_3@0.1Co@1.6MIm, respectively.

2.2. Material characterization

The crystal structures of the samples were characterized by X-ray powder diffractometer (Rigaku D/MAX-2500) using Cu Kα radiation (λ = 0.154 18 nm) operating at 30KV and 20 mA. Scanning electron microscopy (SEM) was carried out on a scanning electron microscope (JEOL/JSM7500) to characterize the surface morphology and elemental analysis. Transmission electron microscope (JEOL 2100F) with electron energy loss spectroscopy was employed to characterize the surface characteristics and micro-structure of the samples. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB-250XI spectrometer (Thermo Fisher Scientific, USA) with monochromated Al Kalph (150 W) as the X-ray source for excitation. The optical properties of the samples were characterized by a UV–visible spectrophotometer (Shimadzu, UV-2600), with $BaSO_4$ as a reference.

2.3. Photoelectrochemical measurements

The photoelectrochemical experiments were conducted using a Zennium electrochemical workstation (ZAHNER, Germany) in a three-electrode system with the as-prepared sample as the working electrode, Ag/AgCl electrode as the reference electrode and coiled platinum wire (1 cm^2 in area) as the counter electrode in a 1.0 M NaOH electrolytic solution (pH 13.6). A 300-W xenon lamp solar simulator was used as the light source. The light power density at test point was adjusted to be 100 mW cm^{-2} with a power meter. The electrochemical impedance spectroscopy (EIS) was carried out under light irradiation with a 0.05 V bias against a reference electrode of Ag/AgCl in an aqueous solution containing 0.5 M KCl, 0.01 M $K_3[Fe(CN)_6]$, and 0.01 M $K_4[Fe(CN)_6]$ using the same three-electrode system. Mott–Schottky (M − S) measurements were performed with a potential frequency of 1 kHz under dark condition. Incident photon conversion efficiency (IPCE)