Chinese Chemical Letters xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Communication

Cobalt oxide and carbon modified hematite nanorod arrays for improved photoelectrochemical water splitting

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ARTICLE INFO

Article history:
Received 7 November 2017
Received in revised form 23 November 2017
Accepted 27 November 2017
Available online xxx

Keywords:
Hematite nanorods
Surface modification
Photoelectrochemical water splitting
Water oxidation
Electrochemical impedance spectroscopy

ABSTRACT

Given the proper band gap, low cost and good stability, hematite (α-Fe_2O_3) has been considered as a promising candidate for photoelectrochemical (PEC) water splitting, however suffers from the sluggish surface water oxidation reaction kinetics. In this study, a simple dip-coating process was used to modify the surface of α-Fe_2O_3 nanorod arrays with cobalt oxide (CoO_x) and carbon (C) for the improved PEC performance, with a photocurrent density at 1.6 V (*vs.* reversible hydrogen electrode, RHE) increased from 0.10 mA/cm^2 for the pristine α-Fe_2O_3 to 0.37 mA/cm^2 for the CoO_x/C modified α-Fe_2O_3 nanorods. As revealed by electrochemical analysis, thanks to the synergistic effect of CoO_x and C, the PEC enhancement could be attributed to the enhanced charge transfer ability, decreased surface charge recombination, and accelerated water oxidation reaction kinetics. This study serves as a good example for improving PEC water splitting performance via a simple method.

With the increasing global energy demand and environmental problems caused by fossil-fuel combustion, photoelectrochemical (PEC) water splitting has been attracting increasing attentions and considered as a promising route to convert solar energy to clean hydrogen energy [1]. Undoubtedly, in a PEC cell, semiconductor photoelectrodes are the essential components, which absorb solar light and where water redox reactions happen [2]. Since the pioneering study of PEC by Fujishima and Honda [3], booming researches have been conducted for semiconducting photoelectrode materials for solar water splitting, including oxides, sulfides, (oxy)nitrides, and silicon-based photoelectrodes [4–6]. Despite a successful development of PEC performance for these materials, there is not yet a single system that integrates high solar-to-hydrogen (STH) efficiency, durability, and low cost for practical solar-hydrogen production.

Hematite (α-Fe_2O_3), a n-type semiconductor with band gap of ~2.1 eV, appears a couple of advantages on PEC water splitting, such as excellent stability, good visible light absorption, non-toxicity, earth-abundant resource and low cost [4]. These merits of α-Fe_2O_3 make it a promising photoelectrode for PEC water splitting. However, as a photoanode, α-Fe_2O_3 still suffers from the low conductivity, high charge combination rate, short hole diffusion length, and sluggish surface water oxidation kinetics, which greatly limit its PEC performances [7]. In the past decades, several approaches have been implemented to improve PEC performance for water splitting over α-Fe_2O_3 [4,8] by (a) nanostructure design for efficient charge collection, (b) metal ion doping for improved electrical conductivity, (c) heterojunction for charge separation, and (d) surface modification for accelerated surface water oxidation reaction.

Since the aqueous solution growth successfully demonstrated by Vayssieres *et al.* [9], α-Fe_2O_3 nanorods with efficient charge transfer directed in the one-dimension pathway have been extensively investigated as a typical photoanode for further modifications. Started with α-Fe_2O_3 nanorods, a number of foreign elements (*e.g.*, Cr [10], Ta [11], Nb [12]) could be doped into the nanorods for improved charge transfer ability, different cocatalysts (*e.g.*, Co_3O_4 [13], Co-Pi [14]) and passivation layer (*e.g.*, Al_2O_3 [15], P [16]) have been deposited on the surface to accelerate surface water oxidation reaction and reduce surface charge recombination, which resulted in considerable PEC enhancement. In recent years, there have been more expectations to simultaneously improve the charge transfer ability and the surface reaction kinetics for further enhancement in PEC performances, and of course, significant advances have been achieved. For example, Shen *et al.* [17] obtained α-Fe_2O_3/$Ag_xFe_{2-x}O_3$ core/shell nanorod films *via* ultrasonication treatment of solution-based β-FeOOH nanorods in Ag precursor solution followed by high temperature annealing, which

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https://doi.org/10.1016/j.cclet.2017.11.037

Please cite this article in press as: M. Wang, et al., Cobalt oxide and carbon modified hematite nanorod arrays for improved photoelectrochemical water splitting, Chin. Chem. Lett. (2017), https://doi.org/10.1016/j.cclet.2017.11.037

achieved an improved incident photon-to-current efficiency (IPCE) from 2.2% to 8.4% at 400 nm due to increased carrier density and accelerated surface oxidation reaction kinetics. Gong *et al.* [18] reported a TiO_2/Ti:Fe_2O_3/FeOOH photoanode with an improved photocurrent of approximately 3.1 mA/cm^2 at 1.23 V (*vs.* reversible hydrogen electrode, RHE), in which the atomic layer deposition (ALD) grown TiO_2 interlayer suppressed charge recombination at the substrate/hematite interface, the doped Ti^{4+} increased the hematite bulk conductivity, and the loaded FeOOH served as an oxygen evolution reaction (OER) cocatalyst to accelerate water oxidation kinetics. Lee *et al.* [19] modified high-temperature annealed single-crystalline hematite photoanodes by platinum doping to improve the charge transfer characteristics in bulk and Co-Pi cocatalyst to enhance the OER on surface, resulting in a stable and excellent performance of 4.32 mA/cm^2 PEC water oxidation current at 1.23 V (*vs.* RHE) under simulated 1-sun irradiation.

Motivated by these advances, in this study α-Fe_2O_3 nanorods grown on a conductive substrate were modified with cobalt oxide (CoO_x) and carbon (C) by ultrasonic dipping in a cobalt nitrate/glucose aqueous solution. In comparison to the CoO_x or C singly modified counterpart, the CoO_x/C modified α-Fe_2O_3 nanorods showed further increased PEC activity for water splitting. It was evidenced that the improved carrier transfer ability both in the bulk and on the surface, was synergistically contributed by the coexistence of CoO_x and C on the surface, resulting in the facilitated charge transfer from the bulk to the surface reactions across the photoanode-electrolyte interface and thus the enhanced PEC performance. This study could be a good example of using a simple method to achieve a multi-functional modification for improved PEC performances.

The β-FeOOH films were synthesized through hydrothermal method at 100 °C and transferred to α-Fe_2O_3 films by annealing at 750 °C in air [20], which were finally modified by CoO_x and C. The morphology of CoO_x/C modified α-Fe_2O_3 is shown in Fig. 1a. It could be clearly observed that the nanorod arrays are perpendicular to the fluorine-doped tin oxide (FTO) substrate and have a diameter range from 50 nm to 70 nm, with an average length of about 600 nm as reported before [11]. It is evident that the modification process has no influence on surface morphology of α-Fe_2O_3, as shown in Fig. S1 in Supporting information. Considering the short hole diffusion length ($2-4$ nm) and low electrical conductivity of α-Fe_2O_3 [21,22], this nanorod-array configuration has been believed to improve the photo-induced charge carrier separation [23]. With the rhombohedral crystal structure, α-Fe_2O_3 has a high degree of anisotropy in the direction of charge carrier mobility, and the conductivity in the (001) basal planes (*e.g.*, in the [110] direction) has been measured up to 4 orders of magnitude higher than that in the perpendicular direction [4,24]. As evidenced by X-ray diffraction (XRD) patterns in Fig. 1b, α-Fe_2O_3 phase exits in all samples and no other phases can be identified, in addition to substrate phase (*i.e.*, FTO). Interestingly, the (110) peak intensity at 35.61° of α-Fe_2O_3 film is much higher than that of (104) peak at 33.15°, while the (110) peak has lower intensity in natural isotropic powder [24]. Transmission electron micro-scope (TEM) image in the inset of Fig. S1a clearly indicates the (001) basal planes vertical to (110) planes formed in [110] growth direction [25]. Together with Fig. 1a and b, it could be evidenced that there is a strong preferential orientation of [110] axis [26] and the relatively high-conductivity (001) planes are parallel to the nanorod lengthwise direction.

UV–visible and Raman spectra were used to explore the possible change in light absorption and structure of CoO_x/C modified α-Fe_2O_3 films, as induced by surface modification. As shown in Fig. 1c, in the region from 300 nm to 800 nm, both α-Fe_2O_3 and CoO_x/C modified α-Fe_2O_3 nanorod films exhibited almost the same optical absorption properties, with absorption onset at around 600 nm. Tauc plots [27] further confirmed that the pristine and CoO_x/C modified α-Fe_2O_3 nanorod films have very close band gaps of 2.08 eV (Fig. S3 in Supporting information), within the reported values ranging from 2.0 eV to 2.1 eV for α-Fe_2O_3 [28]. Raman spectra recorded from 100 cm^{-1} to 2000 cm^{-1} (Fig. S2 in Supporting information) demonstrated that there is no obvious difference in the crystal structure for all the nanorod films. All these observations indicated that the CoO_x/C modification has no obvious influence on optical property and crystal structure of α-Fe_2O_3 nanorods.

Given the ignorable difference among surface morphology, crystal structure and optical property, it then comes to be of great importance to figure out the valance states and distribution of CoO_x and C on α-Fe_2O_3. Fig. 1d plots the Co $2p_{3/2}$ binding energy spectra of CoO_x and C modified α-Fe_2O_3 nanorods (taking $Co_{0.02}$ and $Co_{0.02}G_{0.001}$ as examples) from 795 eV to 775 eV. Both profiles can be deconvoluted into three species, in which peaks in range of 790–785 eV represent shake up satellites and others can be

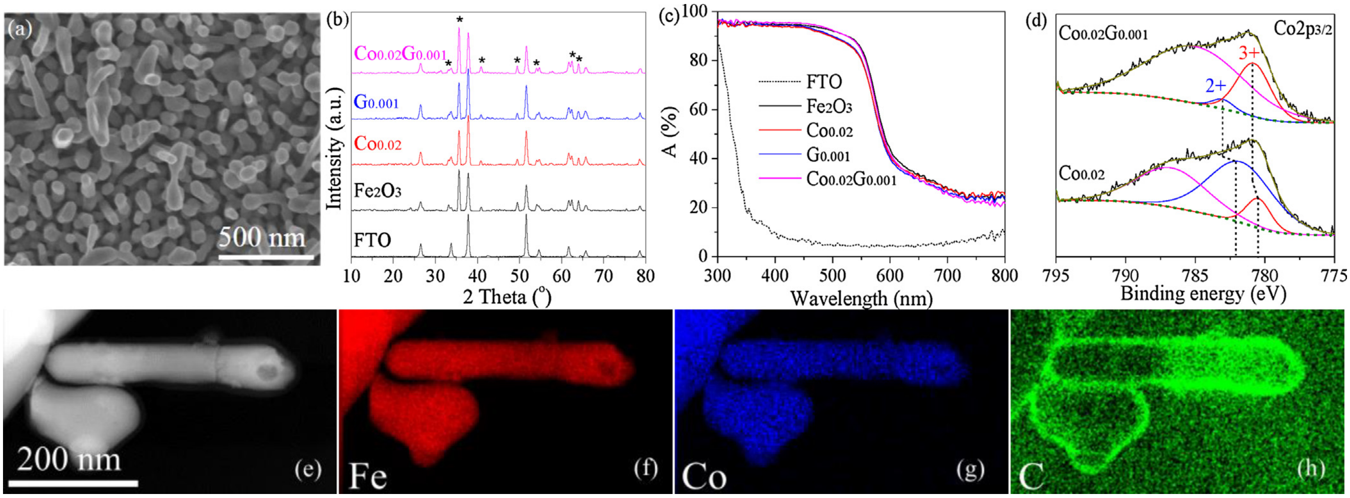

Fig. 1. (a) Scanning electron microscope (SEM) image of CoO_x/C modified α-Fe_2O_3 nanorods (taking $Co_{0.02}G_{0.001}$ as the example). (b) XRD patterns of CoO_x/C modified α-Fe_2O_3 nanorods, in which star represents XRD peaks of hematite as indexed by PDF card (#33-0664). (c) UV–vis absorption spectra of CoO_x/C modified α-Fe_2O_3 nanorods. (d) Co $2p_{3/2}$ binding energy spectra of $Co_{0.02}$ and $Co_{0.02}G_{0.001}$. (e) HAADF image of CoO_x/C modified α-Fe_2O_3 nanorods (taking $Co_{0.02}G_{0.001}$ as the example) and (f-h) element mappings of Fe, Co, C, respectively.

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