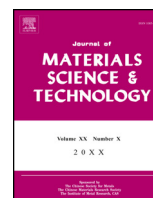




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Ternary non-noble metal zinc-nickel-cobalt carbonate hydroxide cocatalysts toward highly efficient photoelectrochemical water splitting

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ABSTRACT

TiO₂ photoanodes have aroused intensive research interest in photoelectrochemical (PEC) water splitting. However, they still suffer from poor electron-hole separation and sluggish oxygen evolution dynamics, leading to the low photoconversion efficiency and limiting commercial application. Here, we designed and fabricated novel ternary non-noble metal carbonate hydroxide (ZNC-CH) nanosheet cocatalysts and integrated them with TiO₂ nanorod arrays as highly efficient photoanodes of PEC cells. Compared with the pristine TiO₂, the photocurrent of photoanode with the optimal amount of ZNC-CH represents 3.2 times enhancement, and the onset potential is shifted toward the negative potential direction of 62 mV. The remarkable enhancement is attributed to the suppressed carrier recombination and enhanced charge transfer efficiency at the interface of TiO₂, ZNC-CH and electrolyte, which is closely related to the zinc elements modulated intrinsic activity of catalysts. Our results demonstrate that the introduction of multimetallic ZNC-CH cocatalysts onto photoanodes is a promising strategy to improve the PEC efficiency.

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1. Introduction

To meet the increasing global energy demand and reduce the harmful greenhouse-gas emission from burning of fossil fuels, worldwide researchers have focused on the development of effective approaches to generate clean and sustainable energy. Solar-driven water splitting is one of the most promising methods by efficiently and economically converting solar energy into storable and clean chemical fuel (hydrogen), which can be achieved using a photoelectrochemical (PEC) cell [1–3]. Over the past few decades, various metal oxide semiconductors have been studied as photoanodes in PEC applications, such as TiO₂ [4], ZnO [5,6], Fe₂O₃ [7,8], WO₃ [9,10], and BiVO₄ [11], etc. Among them, TiO₂ has attracted intensive research interest due to its biological and chemical inertness, cost effectiveness, abundance, and high resistance to chemical and photo corrosion. However, their limited efficiencies suffer from some inherent limitations, including large band gap, low electron mobility, and short hole diffusion length, hindering

its practical applications. To address these problems, considerable strategies have been demonstrated to be effective [12–14]. For example, different heteroatoms were doped to reduce the band gap of TiO₂ for extending the light absorption range from ultraviolet to visible light [15,16]. Low-dimensional TiO₂ nanostructures were used to shorten carrier diffusion length so as to lower the recombination of electron-hole pairs [17]. Heterojunction composites with staggered band alignment were constructed to increase the separation efficiency of carriers by integrating TiO₂ with other energy level matching semiconductors [18,19].

The great progress has been made in previous investigation, but the solar-to-chemical energy conversion efficiency of TiO₂ still remains undesired owing to a critical bottleneck of sluggish oxygen evolution dynamics related with the complex four electron reaction. The integration of cocatalysts with TiO₂ is very promising for enhancing the PEC activity because cocatalysts facilitate the oxygen evolution reaction (OER) by accelerating charge transfer process and reducing the overpotential of water oxidation [20,21]. Currently, precious metals and their alloys have been found to have excellent performance as cocatalysts. However, the scarce resources and high cost strongly restrict their large-scale applications. Earth abundant transition metal (Zn, Co, Ni, etc.) based

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materials, such as oxides, nitrides, and hydroxides [22–26], have been proved to be the most promising alternatives to enhance PEC performance owing to their high catalytic activity, chemical stability, and low toxicity. Compared to the single-component one, multimetallic materials from the combination of multiple transition metal cations with stoichiometric or even non-stoichiometric compositions are expected to offer the pronounced synergistic effect on OER [27,28]. This effect is attributed to the fact that multimetallic materials have higher electrochemically catalytic activities and stronger electronic conductivity due to the presence of multiple valences of the cations with more complex electronic structure [29–31]. For example, we demonstrated the fabrication of Ni-Mo oxides for improved properties as OER cocatalysts of Si nanowires [29]. The loading of ZnFe- and CoNi- layered double hydroxides (LDHs) nanosheets on TiO₂ nanoarrays led to enhanced PEC photocurrent [30,31]. Differently, the cobalt carbonate hydroxide (CCH) received less attention, while some results have shown the high catalytic activity. For example, Sun et al. fabricated a Cu(OH)₂@CCH core-shell heterostructure nanowire array on copper foam as a robust OER catalyst, exhibiting high OER catalytic activity with overpotentials of only 220 mV to achieve 100 mA cm⁻² in 30 wt% KOH [32]. Hu et al. designed Mn doped CCH nanosheets on Ni foams as highly efficient bifunctional electrocatalysts for water electrolysis [33].

Although CCHs have been demonstrated as highly efficient electrocatalysts, to the best of our knowledge, no attempts are made to synthesize and integrate multimetallic CH with photoanodes for improving PEC efficiency, probably owing to the incompatible semiconductor/cocatalyst interface. In this paper, we firstly report the successful synthesis of ternary non-noble metal Zn-Ni-Co carbonate hydroxide (denoted as ZNC-CH) nanosheets/TiO₂ nanorod arrays by a combination of hydrothermal process and water-bath reaction. The structures, morphologies and chemical compositions of ZNC-CH decorated TiO₂ photoanodes are characterized systematically, and the effect of deposited ZNC-CH amount (reaction time) on PEC properties are investigated. The results show that the TiO₂ photoanode with the optimum ZNC-CH reaction time has the highest photocurrent value of 1.16 mA cm⁻² at 1.23 V vs. RHE, which is 3.2 times higher than that of the pristine TiO₂. The onset potential is obviously shifted toward the negative potential direction from 690 to 620 mV. The results suggest that multimetallic carbonate hydroxides are promising cocatalysts to promote the PEC performance.

2. Experimental section

2.1. Synthesis of TiO₂ and ZNC-CH/TiO₂ nanorod arrays

TiO₂ nanorod arrays were synthesized by a hydrothermal process. In short, 0.269 g of anhydrous citric acid and 1 mL tetrabutyl titanate were dissolved in a mixed solvent consisting of 30 mL of concentrated hydrochloric acid (36%–38% by weight) and 30 mL of deionized water. The mixture was stirred for 15 min and then transferred to a Teflon-lined stainless steel autoclave. A cleaned FTO substrate was placed into the solution with the conductive side downward. The sealed autoclave was heated at 150 °C for 6 h. After the autoclave was cooled down to room temperature, the FTO substrate was taken out and rinsed with deionized water and ethanol, and then dried at 60 °C for 2 h. Finally, the sample was annealed at 500 °C for 2 h with a heating rate of 2 °C min⁻¹.

ZNC-CH nanosheets were grown on the surface of TiO₂ nanorod arrays via a water-bath reaction method. Firstly, 0.429 g of anhydrous zinc acetate, 1.99 g of Nickel (II) acetate tetrahydrate, 4.98 g of cobalt acetate tetrahydrate and 13.82 g of urea were dissolved in 200 mL of deionized water. The mixture was stirred for 20 min and

then transferred to a capped bottle. Afterward, the aforementioned FTO substrate was put into the solution with the as-grown TiO₂ nanorod arrays side downward. After the reaction at 90 °C for different reaction time (5, 10, 20, and 30 min), the sample was rinsed with deionized water and dried at 60 °C for 1 h in air.

2.2. Material characterization

Morphology of the as-fabricated samples was characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010, Hitachi Ltd, Tokyo, Japan) combined with energy dispersive X-ray spectroscopy (EDX). The microstructure was analyzed by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (FEI Tecnai G20 F20 S-TWIN TMP, FEI, Hillsboro, OR, USA). Elemental mapping was conducted under the TEM with an annular dark-field (ADF) detector. The phase was determined under an X-ray diffractometer (XRD, D/MAX-III-B-40KV, Cu K α radiation, λ = 0.15418 nm). The absorption and reflectance spectra were acquired through a UV-vis spectrophotometer (UV-3600, Shimadzu, Japan). The elemental chemical state was measured by X-ray photon spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA). The atomic ratio of metal elements was confirmed by inductively coupled plasma mass spectrometry (ICP-MS, OPTIMA 8000, PerkinElmer Inc, USA). Fourier transform infrared (FTIR) spectra were obtained under a Fourier transform infrared spectrometer (SENSOR 27, Bruker Optics, Germany).

2.3. PEC measurements

PEC measurements were performed in a 0.25 M Na₂SO₄ aqueous solution with an electrochemical workstation (PGSTAT 302N, Autolab, Switzerland) using a three-electrode configuration, in which the as-fabricated samples were used as the working electrode, a Pt mesh as counter electrode and a saturated Ag/AgCl electrode as reference electrode, respectively. Nitrogen (N₂) was used to remove the dissolved oxygen for keeping a N₂-saturated condition in the electrolyte. The photocurrent density-potential (*J*-*V*) and -time (*J*-*t*) curves with light on/off cycle measurements were conducted under AM 1.5G illumination (100 mW cm⁻²) provided by a solar light simulator (Newport 94043A, USA). The measured potential versus Ag/AgCl was converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation [34].

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}}$$

where E_{RHE} is the converted potential versus RHE, $E^{\circ}_{\text{Ag/AgCl}} = 0.1976$ V at 25 °C and $E_{\text{Ag/AgCl}}$ is the experimentally measured potential versus the Ag/AgCl reference. Incident-photon-to-current efficiency (IPCE) measurements were performed using a sunlight simulator (Newport 67001, USA) with a monochromator (Newport 74125, USA) and a Si detector (Newport 77330, USA). The electrochemical impedance spectra (EIS) were obtained by the same workstation under light illumination in the frequency range from 100 mHz to 100 kHz at a potential of 1.23 V versus RHE, and the AC amplitude was 7 mV.

3. Result and discussion

The typical SEM image of pristine TiO₂ nanorod arrays is displayed in Fig. 1(a), showing that dense and vertically quasi-aligned nanorods were grown on the FTO substrate with an average diameter of 100 nm and a length of several micrometers. TiO₂ nanorods are tetragonal in shape with smooth side facets and roughed square top facets. ZNC-CH nanosheets were deposited onto the

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