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Promising cobalt oxide and cobalt oxide/silver photocathodes for photoelectrochemical water splitting

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ABSTRACT

In this paper, novel promising photoelectrochemical electrodes of CoO nanowires and cocatalyst (Ag) modified CoO nanowires are prepared and studied in photoelectrochemical water splitting exhibiting an efficient photoelectrochemical activity for the first time. Detailed growth mechanisms for CoO nanowires and CoO/Ag nanowires are discussed. The effect of Ag is investigated. The enhanced absorption spectrum and photoelectrochemical performance are characterized. The photocurrent density of CoO/Ag nanowires reaches $-1.10\ mA\ cm^{-2}$ due to a high efficiency of light-harvesting, the high holes mobility via the direct pathways and increased interfacial electrons transfer of Ag nanoparticles. Such CoO-based catalysts may lead to effective photoelectrochemical activity and can be promising building blocks in photoelectrochemical water splitting systems.

1. Introduction

The increasing demand for energy has triggered huge efforts for energy stockpile and conversion from renewable energy sources [1]. Efficient hydrogen evolution from photoelectrochemical (PEC) water splitting is a promising route to realize the conversion from solar energy to the storable and clean energy [2]. A wide range of active semiconductor metal oxides photoelectrodes notably include TiO_2 [3–5], ZnO [6,7], WO_3 [8,9], Fe_2O_3 [10], Cu_2O [11] with various film morphologies have been investigated for PEC water splitting. However, despite progress in the past decade, these metal oxides photoelectrodes do not present good activity [12] and the water-splitting devices, which can harvest visible light usually exhibit a low efficiency of solar-to-hydrogen [13].

Cobalt oxide (CoO) is a wide band ($Eg > 2.6$ eV) material [14,15], known as a promising transition metal oxide, attract extensive interest due to their high electroactivity and easy processing [16–20]. Owning to their attracting optical and electrical properties, p-CoO semiconductors with various morphologies, such as nanoparticles [21], nanobelt [22], nanowire [23], nanorod [24], etc. have been applied in electronic and opoelectronic devices. Bao et al. have reported that the CoO with nanoparticles morphology can decompose water under the visible-light illumination without adding any co-catalysts or sacrificial reagents and carry out water splitting with a efficiency of about 5% [15]. The research firstly demonstated CoO nanoparticles photocatalyst show a high photocatalytic activity. In particular, compared with nanoparticles, one-dimensional (1D) CoO nanostructure, crystallizing in rock salt structure, can offer a direct pathway without any crystal boundary resistance, and shorten the ion diffusion length, which facilitate to increase the rate property [25]. Besides, 1D nanostructure can provide high surface area, enlarge the electrolyte-electrode contact region. Hence, 1D CoO nanostructure has been extensively investigated for other fields owing to their potential applications based on electric and catalytic properties [26] such as lithium-ion batteries [27], haemoglobin biosensors [28] and supercapacitors [29]. For instance, Zhou et al. have developed a supercapacitor electrode consist of CoO nanowire (NW) arrays that grown on 3D nickel foam with polypyrrole and achieved outstanding pseudocapacitive performance [16]. A p-type semiconductor was served as a photocathode and evolved hydrogen between the semiconductor and electrolytes. In addition, the hydrogen evolution was occurred when the conduction band gap edge was more negative compared with the hydrogen generation potential. However, there are few reports about the application of CoO NWs as photocathodes for photoelectrochemical (PEC) water splitting as far. Therefore, this work will develop CoO NWs structure grown directly on indium tin oxide (ITO) transparent conductive glass as the photocathode studied in PEC water splitting for the first time.

In addition, in order to broaden the absorption spectrum and improve photoelectrochemical performance of the metal oxide, significant effort has been made. Doping with metals/nonmetallic ele-

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ments, such as Fe [30], N [31–33] and S [34], meanwhile, sensitizing with quantum dots also have been extensively applied in overcome the drawback of visible light response of metal oxide [35,36]. Recently, cocatalyst modification has been viewed as an effective strategy to improve the photocatalytic performance [37–39]. In particular the cocatalysts with noble metals have attracted a great deal of attention, such as Pt [40], Au [41], Ag [42]. The noble metals usually served as reduction active sites, which is facilitate to capture photo-induced electrons from the semiconductor and then to reduce H_2O effectively [42], resulting in an efficient separation of photogenerated charges and enhanced photoelectrochemical activity. In the photoreaction process, silver served as noble metal can avoid corrosion and interact with sun light in the region of visible and infrared. However, as far as we know, there is no report on the fabrication of CoO-based one-dimensional nanoarrays modified with noble metal served as cocatalyst. In this paper, CoO NWs with diameter of 20–40 nm, and length more than 3 μm have been successfully synthesized by a simple hydrothermal method. Then, Ag nanoparticles were deposited onto the CoO NWs via hydrothermal method to obtain CoO/Ag NWs. The CoO/Ag NWs were utilized as the photocathode of PEC water splitting cells, which show promising photoelectrochemical properties, particularly exhibiting a high photocurrent, and the photocurrent density is up to $-1.10\ mA\ cm^{-2}$. The improved photocatalytic performance in PEC water splitting was achieved due to a high light-harvesting efficiency, the high holes mobility via the direct pathways and increased interfacial electrons transfer due to use of Ag particles, enhancing the charge separation efficiently and inhibit the recombination of photo-induced electron-hole pairs.

2. Experimental section

2.1. Synthesis of CoO NWs

CoO NWs were synthesized on ITO by a simple and versatile hydrothermal method. In detail, 110 mg cobalt nitrate hexahydrate and 100 mg urea were dissolved in 12 mL of deionized water. Then, the obtained homogeneous solution was further transferred into Teflon-lined stainless steel autoclave of 20 mL volume. And the autoclave was maintained at 100 °C for 6 h. finally, the autoclave cooled down to room temperature. The NW sample was collected and rinsed with distilled water and then annealed at 430 °C in N_2 gas for 3 h.

2.2. Synthesis of CoO/Ag NWs

Ag nanoparticles were synthesized uniformly on the surface of CoO NWs by hydrothermal process. CoO/Ag NWs were synthesized through hydrothermal reaction. 9 mg silver nitrate and 10 mg sodium citrate were dissolved in 50 mL deionized water, and the ITO glass coated with CoO NWs was immersed in the mixture solution at 90 °C for 3 h. Afterwards, the obtained CoO/Ag NWs were rinsed with deionized water and dried in ambient air.

2.3. Characterization

The crystal structure of the as-prepared samples was tested by a Rigaku D/max-2500 with a Cu Kα radiation (λ=0.154059 nm). The morphologies of the products were examined under the equipment of PHILIPS XL-30 scanning electron microscope and HITACHI H-7650 transmission electron microscopy operated at an accelerated voltage of 100 kV. The optical absorbance property of photocathode was studied by DU-8B UV–Vis double-beam spectrophotometer. Photoelectrochemical measurement was performed by electrochemical workstation (LK2005A, Tianjin, China) with a three-electrode configuration. The CoO-based structures saturated Ag/AgCl and a platinum foil as working photoelectrode, reference electrode and counter electrode, respectively. The whole PEC water splitting process was conducted in NaOH electrolyte solution (1 mol/L). The electrode with samples was illuminated under a xenon lamp ($100\ mW\ cm^{-2}$). Photocurrent density-time curves were conducted under irradiation with the 60 s light on/off cycles condition of CoO-based structures.

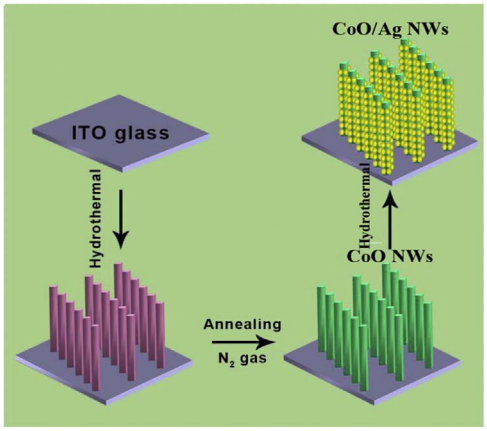

Fig. 1. Synthetic procedure of CoO/Ag NWs.

3. Results and discussion

Fig. 1 shows an illustrative synthetic procedure of CoO/Ag NWs. The preparation process involves two steps: (i) preparation of CoO NWs; (ii) preparation of CoO/Ag NWs. At first, CoO NWs were synthesized on ITO in a hydrothermal reaction after annealing in N_2 gas as shown in Fig. 1. Secondly, Ag nanoparticles were synthesized uniformly on the surface of CoO NWs by hydrothermal process.

The structural and photoelectrochemical characterization of CoO NWs were investigated. Fig. 2(a) shows the XRD patterns of the CoO NWs grown on ITO substrate. As seen in Fig. 1(a), all diffraction peaks of ITO substrate agree well with In_2O_3 (JCPDS file No.65-3170). In addition to the diffraction peaks of ITO, the XRD pattern of CoO NWs shows new diffraction peaks centered at 36.62°, 42.36°, 61.86°, which correspond to (101), (110), (112) planes of CoO (JCPDS file No.65-5474), suggesting successful coating of CoO on ITO substrate.

Fig. 2(b) and (d) show the low magnification SEM image of CoO NWs, which reveals that CoO NWs have been synthesized on the ITO glass substrate. Fig. 1(c) indicates that CoO NWs are smooth and exhibit a diameter of approximately 70 nm. Detailed microstructure information of CoO NWs was further studied through TEM and HRTEM. A TEM image of the CoO NW is shown in Fig. 2(f). It reveals that the CoO NWs present a uniform diameter of 70 nm approximately and the surface of the CoO NWs is smooth. The HRTEM image in Fig. 2(e) shows one distinct set of the fringes spacing, and the crystal lattice fringe space is 0.2132 nm, corresponding to the (110) lattice spacing of CoO [43].

The CoO NWs photocathode was performed under on/off cycle irradiation to determine the PEC performance and stability of CoO NWs, which is shown in Fig. 3(a). It can be observed that the maximum photocurrent of CoO NWs is $-0.18\ mA\ cm^{-2}$ at -0.40 V bias. A constant photocurrent with minimal decay is achieved in light on/off cycles, revealing that the current density-time patterns are reproducible for these photocathodes of CoO NWs. The crystal structure and morphology were presented in Fig. 3(b) and (c). Interestingly, there were no apparent change in the XRD pattern and SEM image before and after the PEC reaction, which confirmed that the surface of CoO NWs have not been reacted physical or chemical process.

The structural and photoelectrochemical characterization of CoO/Ag NWs were investigated. Fig. 4 exhibits the XRD patterns of the CoO/Ag NWs. As shown in Fig. 4, corresponding to the diffraction peaks of the ITO and CoO NWs in curve (i), the diffraction peaks in curve (ii) with 2θ value around 35.12°, 44.30°, 64.44° and 77.40° can