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Facile electrodeposition of cobalt hydroxide on anodic TiO_2 nanotubes arrays for enhanced photoelectrochemical application

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ABSTRACT

In the present work, we report a facile synthesis procedure with electrodepositon to develop new noble-metal-free $Co(OH)_2$/TNTAs heterojunction for photoelectrochemical water splitting. The porous $Co(OH)_2$ nanoflake covered upon TNTAs can effectively increase the specific surface area for the light absorption and improve the contact between electrode and electrolyte during the process of photoelectric catalysis. With the addition of $Co(OH)_2$ layer, the photocurrent density of TNTAs photoanode increase from 0.1 to ~0.6 mA/cm^2. Due to the convenient redox transformation of different chemical states of cobalt, the heterostructured $Co(OH)_2$ on TNTAs can effectively accelerate the charge separation and transfer during photocatalytic reactions and reduce charge transfer layer resistance at electrode/electrolyte interfaces, leading to an enhanced photoelectric response.

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1. Introduction

Since the work by Fujishima and Honda in 1972 using rutile TiO_2 anode coupled with a platinum cathode for photoelectrochemical (PEC) water splitting, a massive efforts have been made to develop efficient PEC water-splitting systems [1], particularly TiO_2-based photoelectrode materials. TiO_2 nanotube arrays (TNTAs) are grown *in situ* on Ti substrates by electrochemical anodization process in fluorine-containing electrolytes, have sparkled ever-increasing interest and been widely explored for use in PEC water splitting [2–6]. However, there are two main disadvantages that limit the utilization efficiency of solar energy for TNTAs. One is its wide bandgap (Eg = 3.2 eV) which leads to the low effective absorption (only 5% of solar spectrum) in the visible light region. The other one is the easy recombination of photogenerated electro-hole pairs. TNTAs has been intentionally doped [7,8], chemically modified [9,10], dye-sensitization [11], precious metal decoration [12], or coupling with other semiconductors to form the heterojunction [13,14] to narrow the band gap to increase solar-energy utilization and thus improve the PEC activities of TiO_2.

To further widen the light absorption and improve the photoelectrochemical activity, an effective water oxidation cocatalysts (OEC) containing earth-abundant elements is required. And cobalt metal oxides, hydroxides $Co(OH)_2$ and sulfides CoS have recently received increasing attention and shown promising potential as co-catalysts on semiconductors for photocatlytic H_2 production [15–17]. For example, Zhou and co-authors [18] used $Co(OH)_2$ as OEC on CdS nanowires can not only effectively accelerate the charge separation and transfer during the photocatalytic reactions, but also effectively avoid light corrosion leading to a high stability for hydrogen production reaction. Thus, it is recommended to develop a novel heterojunction by constructing $Co(OH)_2$ with TNTAs for highly effectively solar-driven water oxidation, due to the enhancement of oxygen evolution activity on the surface of TNTAs with the synergistic effect of $Co(OH)_2$ [19]. Wender et al. [20] reported that $Co(OH)_2$ nanoparticles as co-catalysts on the Fe_2O_3 nanoring surface could effectively enhance hydrogen production. Until now, the cobalt-based compounds have not been grown on TNTAs via complete electrodeposition in photoelectrochemical water splitting.

In this work, $Co(OH)_2$ layer was electrodeposited to improve the photoelectrochemical performance of TNTAs. The $Co(OH)_2$ layer coated by electrodepositon uniformly extends throughout the whole TNTAs with high ratios, as confirmed by scanning electron microscopy (SEM) and energy dispersion mapping (EDX). X-ray

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diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) further verify the creation of $Co(OH)_2$/TNTAs junctions. The conformal coating not only enhances the visible light absorption but also creates the OEC/TNTAs heterojunction to improve the separation of the photogenerated electron-hole pairs. With good stability and low contact resistance at the interface, the $Co(OH)_2$/TNTAs show significantly enhanced PEC performance under visible light illumination with photocurrent density as high as 600 $\mu A/cm^2$, which is about 8 times higher than that of pristine TNTAs. Our analyses indicate that the enhanced PEC performance could be attributed to the synergy of Co-based OEC and an energy band diagram was also proposed to further understand the working mechanism of $Co(OH)_2$/TNTAs photoanode.

2. Experimental section

2.1. Chemicals

All the reagent used in this research are analytical grade, which was used without further purification. Ammonium fluoride (NH_4F), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and anhydrous ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation TNTAs and $Co(OH)_2$/TNTAs photoanode

The well-ordered TNTAs on Ti foils were synthesized *via* a modified two-step anodization method. In a typical synthesis procedure, Ti foil (99.9%) with a size of 1×4 cm was first cleaned with acetone, ethanol, and DI water sequentially under ultrasonication each for 10 min as working electrode while the high density graphite as the counter electrode. The electrolyte solution was prepared by dissolving 0.5 wt% NH_4F in 3.0 mL H_2O and 97.0 mL ethylene glycol. The cleaned Ti foil was then used as an anode for the first step anodization at 60 V for 30 min at room temperature. After that, the oxidization layer on Ti foil was removed by sequential ultrasonication in 1 mol/L HCl and DI water for 20 min. Subsequently, the polished Ti foil was used for second anodization at 60 V for 30 min. The obtained TiO_2 precursor was thoroughly rinsed with DI water, which was then annealed at 450 °C in air for 2 h and allowed to naturally cool to room temperature for preparing well-ordered TiO_2 NTAs.

$Co(OH)_2$ films were produced by eletrodeposition at room temperature from $Co(NO_3)_2$ aqueous solution. The concentration of $Co(NO_3)_2$ was 0.05 mol/L and 1:1 HNO_3 was used as a pH buffer to adjust pH value around 4. Electrodepositions were carried out potentio statically at −0.95 V (*vs.* Ag/AgCl) for 30 s, 60 s, 90 s, 120 s, and 150 s. In order to compare the different behavior for different cobalt hydroxides, the $Co(OH)_2$ films were transformed into CoOOH films via linear sweep from −0.2 to 0.5 V with the scan rate of 2 mV/s in sodium hydroxide aqueous solution as electrolyte. The oxidation of $Co(OH)_2$ to CoOOH is via the following:

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^- \quad (1)$$

2.3. Characherization

The crystal structure were carried out with X-ray diffraction (XRD) on a PANalytical X'Pert Powder diffractimeter with Cu K_α radiation ($\lambda = 1.54$ Å) at 40 kV and 40 mA. Diffraction angle (2-theta) ranged from 10° to 80°, and the scanning step was 0.02°. The morphology of the samples were characterized using the scanning electron microscopy (SEM, JEOL, JSM-6360LA, 20 kV) equipped with an energy dispersive spectrometer (EDS). The surface composition and elemental chemical state of the samples were examined by X-ray photoelectron spectrometer (XPS) using a K-Alpha 1063 (Thermo Fisher Scientific, UK) equipped with Al Kα monochromator X-ray source.

2.4. Electrochemical measurement procedure

The PEC properties of the fabricated samples were measured by electrochemical analyzer (CHI760E electrochemical workstation, Chenhua Instrument, Shanghai, China) with three electrode cell system in an aqueous solution of 0.1 M Na_2SO_4 as the electrolyte. The working electrode with an active area of 1.0 cm^2. Light was provided by a 300 W Xe arc lamp fitted with an AM 1.5 G filter, and the power density was adjusted to 100 mW/cm^2. Linear sweep voltammetry (LSV) curves were collected at a scan rate of 10 mV/s with or without illumination. The electrochemical impedance spectroscopies (EIS) of different photoelectrode were measured with a frequency range from 100 kHz to 0.01 Hz without bias applied at amplitude frequency 10 mV. The Mott-Schottky (MS) plots were obtained at 10 kHz frequency. Finally, the transient open circuit potentials (OCP) were also measured with the dark and light illumination.

3. Results and discussion

The SEM images from top views of TNTAs coated with $Co(OH)_2$ films prepared from 30 s, 60 s, 90 s and 150 s, respectively, were shown in Fig. 1a–d. Fig. 1e showed that the as-prepared TNTAs had the uniform morphology with the inner diameter distribution around 100 nm. With increase of deposition time, the coating of $Co(OH)_2$ films would get more uniform and compact. Then the heterostructured $Co(OH)_2$/TNTAs were porous nanoflakes layered upon TNTAs, providing a larger specific surface area for the light absorption and contact area between electrode and electrolyte during the process of photoelectric catalysis. In addition, the SEM-EDS mapping was carried out to investigate the elemental distribution of $Co(OH)_2$/TNTAs_90 s, shown in Fig. 1f, which is the local region of Fig. 1c, revealing that the heterostructured $Co(OH)_2$/TNTAs had uniform spatial distribution. The component of the $Co(OH)_2/TiO_2$ heterojunction was confirmed by EDS, shown in Fig. 2a, mainly including Ti, O and Co, where the Pt was from the sputtered Pt to enhance the conductivity of sample for SEM characterization. Furthermore, XRD was carried out to investigate the phase of as-deposited materials. As shown in Fig. 2b, the XRD indicated that the photoanode consisted of hexagonal structured $Co(OH)_2$ (JCPDF No. 45-0031) and tetragonal structured anatase TiO_2 (JCPDF No. 21-1272). The two distinct diffraction peaks at $2\theta = 25.3$ and 37.6° were related to (101) of TiO_2 and (101) of $Co(OH)_2$, respectively. This well illustrates the successful fabrication of layerd $Co(OH)_2$ nanoflakes on the surface of the TNTAs semiconductor.

The chemical composition and elemental valence of TNTAs and $Co(OH)_2$/TNTAs was investigated by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα X-ray radiation, which are calibrated with the C 1 s peak at 284.8 eV (Fig. 3a and b). Fine scan XPS spectra of Ti is shown in Fig. 3a, with two peaks of Ti 2p observed at binding energies of 459.4 and 465.1 eV, respectively, which are assigned to Ti $2p_{3/2}$ and Ti $2p_{1/2}$, consistent with the XPS of Ti^{4+} in anatase phase [21]. With the coating of $Co(OH)_2$, the binding energies of Ti 2p for $Co(OH)_2$/TNTAs are slightly move toward high binding energy (~0.1 eV), indicating that the introduction of $Co(OH)_2$ does not affect the elemental properties of TiO_2 nanotubes. The existence of $Co(OH)_2$ can be further confirmed by high-resolution XPS analysis of Co 2p, as shown in Fig. 3b. As shown, the Co spectrum can be deconvoluted into two pairs of individual peaks located at 781.4 and 797.1 eV, respectively, identified as the binding energies of Co^{2+} in $Co(OH)_2$ [22].

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