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Synthesis of $CuInS_2$ nanowire arrays via solution transformation of Cu_2S self-template for enhanced photoelectrochemical performance

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ABSTRACT

A novel universal solution method has been proposed to prepare $CuInS_2$ nanowire arrays (NWAs) using Cu_2S NWAs as the template. The screw-like $CuInS_2$ nanowires are constructed by many stacked nanoplates oriented along the direction of [221], and show diameters of 400–700 nm and lengths of several micrometres. Experimental results suggest that relatively higher In^{3+} concentration is beneficial to the insertion of In^{3+} into Cu_2S to form $CuInS_2$ with conserving the nanowire morphology. A novel exchange-erosion formation mechanism is proposed to illustrate the formation of the screw-like $CuInS_2$ NWAs. The photoelectrochemical (PEC) performance has been investigated using the $CuInS_2$ NWAs as photocathodes, and they exhibit double-increased photocurrent (0.3 mA cm^{-2} at −0.1 V *vs.* RHE) compared to the pristine Cu_2S NWAs, which can be ascribed to the enhanced light absorption and increased contact area for fast interfacial photocarrier separation and PEC reactions. The photocurrent has been further increased to 0.71 mA cm^{-2} *via* decorating CdS quantum dots on the surfaces of $CuInS_2$ nanowires. It is believed that this facile method can be generalized to prepare other copper chalcopyrite-based NWAs for highly efficient PEC water splitting.

1. Introduction

Solar-driven photoelectrochemical (PEC) water splitting has attracted considerable attention as an efficient way to produce carbon-free fuels from solar energy [1,2]. Since the pioneering work by Fujishima and Honda in the early 1970s [3], various semiconductors have been intensively studied as photoelectrodes for efficient solar-to-hydrogen conversion in the past forty years [4–7]. In terms of hydrogen generation, *p*-type semiconductors are advantageous over *n*-type ones because the photo-generated electrons can be directly injected into the electrolyte on semiconductors and thus directly reduce water to hydrogen at the semiconductor/water interface without potential energy loss [8]. However, the number of inherent *p*-type semiconductors is relatively small.

Due to their high absorption coefficients, relatively high carrier mobility, tunable band gap values, and suitable band alignment for water reduction, copper-based chalcopyrite *p*-type semiconductors such as $CuInSe_2$, $CuGaSe_2$, $CuInS_2$, $CuGaS_2$, and their mixed crystals have received great attentions as photocathodes for PEC water splitting [9–13]. Especially, $CuInS_2$ is a semiconductor with a direct band gap of ~1.5 eV, allowing it utilize sunlight efficiently and without requiring a highly toxic Se source [14,15]. Additionally, the $CuInS_2$-based solar cells show a high theoretical solar energy conversion efficiency of ~25% [16], and the highest efficiency has been reported to be 11.4% [17]. The specific properties of $CuInS_2$ demonstrate that this semiconductor is attractive as an efficient photocathode for hydrogen production by PEC water reduction. Among various routes to prepare $CuInS_2$ photocathodes for efficient PEC water reduction, non-vacuum methods have attracted much attention owing to their low-cost fabrication processes [15,18]. However, the corresponding $CuInS_2$ photocathodes have shown relatively low PEC performance [19].

To realize highly efficient PEC cells, a nanostructured photoelectrode possesses favourable intrinsic characteristics of large specific surface area, direct electron transport pathway, and enhanced light absorption ability [20–24]. Luo *et al.* [25] developed a low-cost solution method to fabricate nanostructured $CuInS_2$ electrodes by solvothermal treatment of electrochemically deposited Cu_2O films, which showed excellent PEC water splitting ability after coating with CdS, Al-doped ZnO and TiO_2 overlayers. Domen et al. [15] reported the preparation of porous $CuInS_2$ by sulfurization of electrodeposited metals, which also exhibited outstanding PEC performance after modification with CdS and TiO_2. In particular, one-dimensional (1D) nanostructures (*i.e.*, nanowires, nanorods,

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and nanotubes), especially vertically aligned ones, have been widely used to improve the PEC performance owing to the advantages of enhanced light trapping, short carrier diffusion length, and increased specific surface area compared with the bulk structures [26–29]. Therefore, 1D $CuInS_2$ nanoarrays are considered to eventually lead to the overall goal of high efficient and scalable PEC photocathodes.

Up to now, there are only a few reports on the synthesis of 1D $CuInS_2$ nanoarrays. Shi et al. [30] proposed a one-step solvothermal approach with porous alumina as the hard template for the fabrication of $CuInS_2$ nanowire arrays (NWAs). Wu et al. [31] demonstrated the synthesis of $CuInS_2$ nanotube arrays using a successive ionic layer absorption and reaction (SILAR) process with self-dissolved ZnO nanowire template. Sheng et al. [16] reported the preparation of $CuInS_2$ nanorod arrays *via* annealing Cu-In intermetallic compound precursor thin film under a H_2S and N_2 atmosphere. Nevertheless, it is challenging to fabricate high-quality $CuInS_2$ nanoarrays in large-scale by the above methods, and their PEC performance has not been investigated. Recently, Yang et al. [32] reported the fabrication of vertically aligned $CuInS_2$ nanorod arrays from an aqueous solution using anodic aluminum oxide (AAO) template-assisted growth and transfer. However, the fabrication procedures for both the $CuInS_2$ nanorod arrays and the corresponding photocathodes are very complicated, resulting in poor PEC performance (photocurrent density: $\sim$2 $\mu A/cm^2$ at 0.3 V *vs.* RHE). Although there are previous studies for the preparation of $CuInS_2$/$CuInSe_2$ nanomaterials (nanocrystals [33], nanoplates [34,35], nanospheres [36], nanowire bundles [37], etc.) using CuxS/CuSe as the self-sacrificial template [38], their powder-like morphologies have limited their applications especially for PEC water splitting as photoelectrodes.

Herein, we first report the fabrication of $CuInS_2$ NWAs by a novel self-sacrificial template-directed method using Cu_2S NWAs as the template through a solvothermal process. The template-mediated growth mechanism has been proposed according to the experimental results. The PEC performance of the $CuInS_2$ NWAs was investigated compared to the pristine Cu_2S NWAs. Moreover, CdS quantum dots (QDs) were subsequently decorated onto the $CuInS_2$ nanowires to further improve the PEC activity.

2. Experimental

2.1. Synthesis of $CuInS_2$ NWAs

The pristine Cu_2S NWAs were grown on Cu mesh *via* a gas-solid reaction method (see Scheme 1a) [39–41]. The volume ratio of H_2S and O_2 was 2:1, and the reaction temperature was set to be 30 °C. After 10 h reaction, the Cu surface became black and fluffy (Fig. S1), dense Cu_2S NWAs were grown on the surface. The $CuInS_2$ NWAs were synthesized *via* solution transformation of Cu_2S NWAs in an autoclave by a solvothermal reaction (Scheme 1b–d). Typically, a Cu_2S NWAs substrate (2 cm × 2 cm) was put into a Teflon autoclave angle against the vessel wall, facing down, and 10 mL ethylene glycol solution containing 0.15 M $InCl_3$ and 0.3 M thioacetamide was poured into the autoclave to immerse the substrate. The autoclave was then put into an oven heating at 200 °C for a certain reaction time and cooled down to room temperature naturally.

2.2. Decoration of CdS QDs onto $CuInS_2$ NWAs

A SILAR method was used to deposit CdS QDs onto the $CuInS_2$ NWAs [42]. As shown in Scheme 1e–f, the $CuInS_2$ NWAs were immersed into the following solutions in sequence: 0.1 M $Cd(NO_3)_2$ ethanol solution for 20 s, deionized water for 10 s, 0.1 M Na_2S aqueous solution for 20 s, and then ethanol for 10 s. The four-step process is called one SILAR cycle, and the thickness of the CdS layer can be controlled by the deposition cycle.

2.3. Characterization

The morphologies of the samples were characterized by a field emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra 55, Germany) operating at 20 kV. Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) operating at 200 kV was used to observe the microstructures of the samples. The crystalline structure was analysed by X-ray diffraction (XRD) using an advanced X-ray diffractometer (D8 ADVANCE, Bruker, Germany) in the diffraction angle range $2\theta = 20–80°$, with Cu Kα radiation ($\lambda = 0.154056$ nm) at voltage of 40 kV and a current of 40 mA. The Raman spectra were acquired by using a dispersive Raman microscope (Senterra R200-L, Bruker Optics, Germany), operated with a 532 nm laser. The X-ray photoelectron spectra (XPS) were acquired using a Japan Kratos Axis UltraDLD spectrometer with a monochromatic Al Kα source (1486.6 eV). The UV-vis-NIR absorption and diffuse reflectance spectra (DRS) were carried out using a UV-vis-NIR spectrophotometer (Lambda 950, PerkinElmer, USA). The photoluminescence (PL) spectra were obtained with a steady-state and time-resolved fluorescence spectrofluorometer (QM/TM/IM, PTI, USA).

2.4. PEC measurements

For easy measurement, the samples were fixed on glass slides by epoxy resin (see Scheme 1g), and an enamelled Cu wire was connected to the side part of the Cu substrate using conductive silver paint [43]. To prevent photocurrent leakage, the uncoated parts of the electrode were isolated with epoxy resin, and the exposed area for absorbing the light was $\sim$1.0 cm^2. A three-electrode PEC cell using a 200 mL aqueous solution of 1.0 M KCl (pH = 5.97) was used to carry out the current density measurements.

The sample as working electrode (WE), Pt mesh as counter electrode (CE), and Ag/AgCl (saturated KCl) as reference electrode (RE) were the three electrodes in the PEC cell. Illumination was provided by a solar simulator (CHF-XM500, Beijing Perfectlight) using a 500 W Xenon lamp and equipped with AM 1.5 G filter. Light power intensity was maintained at 100 mW cm^{-2} at the sample position. An electrochemical workstation (CHI 650E) was used to measure current-voltage characteristics of the photocathodes under chopped light irradiation (light on/off cycle: 10s), with a scan rate of 5 mV s^{-1}. The transient photocurrent densities were produced under chopped light irradiation (light on/off cycle: 10 s) at a fixed electrode potential of −0.55 V *vs.* Ag/AgCl (0 V *vs.* RHE).

The measured potentials *versus* the Ag/AgCl RE were converted to the RHE scale *via* the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + E_0 \quad (1)$$

where E_{RHE} is the converted potential *versus* RHE, $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/AgCl RE, and E_0 is the standard potential of Ag/AgCl (saturated KCl) at 25 °C (*i.e.*, 0.197).

The electrochemical impedance spectra (EIS) was carried out with a sinusoidal perturbation with 5 mV amplitude and frequencies ranging from 100 kHz to 0.1 Hz. The EIS measurement for the Mott-Schottky plot was performed at frequency of 1 kHz with AC amplitude of 10 mV and scan step of 1 mV.

The incident photon to current efficiency (IPCE) was carried out at 0 V *vs.* RHE under monochromatic irradiation from the Xenon lamp equipped with bandpass filters to show the spectral distribution of photocurrent generation. The IPCE is expressed as:

$$IPCE = (1240I)/(\lambda P_{light}) \quad (2)$$