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A new probe into thin copper sulfide counter electrode with thickness below 100 nm for quantum dot-sensitized solar cells

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ABSTRACT

Currently, most of CuS counter electrodes (CEs) used in quantum dot-sensitized solar cells (QDSSCs) are provided with a thickness of hundreds of nanometers or even several microns. Considering the CE with low thickness having many advantages, thin CuS films with thickness ranging from 47 nm below to 115 nm have been synthetized in this paper via chemical bath deposition (CBD) method with different bath concentrations. A power conversion efficiency (PCE) of 3.25% has been achieved utilizing CuS thin films a thickness of only 64 nm as CEs in QDSSCs without any structural optimization, which is higher than the value of the cell employing CuS CE with thickness of 2.8 μm. Electrochemical impedance spectroscopy, Tafel polarization, and two-point current-voltage measurements are used to investigate the electrocatalytic and conductive performance of CuS CEs with different thickness. Owing to the highest electrocatalytic capacity and good conductivity of the 64 nm-thick CuS CE, QDSSC assembled with this CE has reached relatively high PCE under one sun illumination (100 mW cm^{-2}, AM 1.5). In addition, cyclic voltammetry measurements indicate that the thin CuS CE has a good stability against the polysulfide electrolyte.

1. Introduction

Counter electrode (CE) is a vital part of quantum dot-sensitized solar cells (QDSSCs) [1,2]. For the efficient and compatible electrolyte containing S_n^{2-}/S^{2-} redox couples adopted in QDSSC, Pt CE widely used in dye-sensitized solar cells (DSSCs) has encountered bottlenecks in QDSSC applications due to the chemisorption of the sulfur atoms on its surface [3,4]. Therefore, various alternative materials such as Au [5], carbon [6,7], polymer [8], Cu_xS ($x = 1-2$) [9–13], PbS [14], CoS [15], Cu_2ZnSnS_4 [16], and some composite materials [17,18] have been reported as potential CEs. Among which, copper sulfide (Cu_xS, $x = 1-2$) materials appear to be a category of very suitable candidates with low cost, nontoxicity, and superior catalytic activity toward S_n^{2-}/S^{2-} redox couples [19,20]. Moreover, it is reported that CuS CEs tend to own higher conductivity, catalytic performance and be more stable compared with Cu_2S, $Cu_{1.8}S$, $Cu_{1.75}S$ and $Cu_{1.12}S$ CEs in QDSSCs [21,22].

Extensive researches about CuS CEs are mainly concentrated on creating novel structures or ameliorating preparation method. In general, the thicknesses of CuS films by different synthesis routes are mostly reported to be hundreds of nanometers or even several microns, and the corresponding power conversion efficiencies (PCE) of QDSSCs range from 2% to 5%. The group of Meng synthesized the CuS films on fluorine-doped tin oxide (FTO) glass using the chemical bath deposition (CBD) method combined with $TiCl_4$ treatment, the assembled QDSSCs obtained a PCE of 4.02% with 900 nm-thick CuS CEs [23]. Zhao et al. had compared the CuS CEs prepared through hydrothermal method with different thickness from 100 nm to 2 μm [24], Among them, QDSSC with 1 μm-thick CuS CE got the highest PCE of 3.65%, while the PCE of QDSSC using 100 nm-thick CuS CE was 1.75%. Little attention has been devoted to the CuS CE with thickness below or around 100 nm. Nevertheless, CE with small thickness have many advantages, such as saving materials usage, avoiding hindering the charge transfer from being too thick [25], and strong

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attachment to the substrate and other materials. Previous research have revealed that Pt CEs with thickness of only 2 nm are sufficient to catalyze the electrolyte in DSSC [25]. Therefore, it is important to study whether CuS CEs with small thickness can also give a high catalytic performance towards the S_n^{2-}/S^{2-} electrolyte in QDSSCs.

In this paper, CBD method was used to grow CuS thin films due to its simplicity and good repeatability, different CuS thin films with thickness from 47 nm below to 115 nm were fabricated on FTO glass as CEs. The effects of bath concentration on the thickness, surface morphology, optics, and conductivity properties were studied in detail. The corresponding photovoltaic performance, electrochemical catalytic activity, and stability towards S_n^{2-}/S^{2-} redox couple of CuS CEs were investigated. Among them, QDSSCs assembled with 64 nm-thick CuS CEs acquired the highest PCE of 3.25%. To the best of our knowledge, it is the highest PCE of QDSSCs using such thin CuS CEs.

2. Experimental details

2.1. Preparation of copper sulfide thin films

The CuS thin films were prepared by CBD method on FTO (TEC-8, 8 Ω sq^{-1}, LOF) substrates. The FTO glasses were ultrasonically cleaned with distilled water, acetone, and ethanol then dried in N_2 atmosphere. The chemical bath used for synthesizing the CuS thin films was prepared as follows: an aqueous solution of 20 ml of 0.025 M of copper(II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) and a 20 ml of 0.05 M of sodium citrate ($C_6H_5Na_3O_7$) were mixed at first, the pH of the solution was adjusted to 1.5 with dilute sulfuric acid, then, 8 ml of 0.025 M of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) aqueous solution was added in the above solution, a clear solution was obtained. FTO substrates were dipped into the above solution, and heated to 75 °C for 60 min, the as-synthesized CuS film was labeled as CS 1. To investigate the effect of the precursor solution on synthesized films, CS 2, CS 2.5, CS 3, and CS 3.5 were prepared by multiplying the concentration of precursor solution components, respectively. The concentration parameters of bath solution are shown in Table 1. Relatively thick CuS films prepared by doctor blading (labeled as CS-DB) were used as reference, the slurry was prepared according to the previous report [26], specifically, two kinds of ethyl cellulose (EC) powders, i.e., EC (5–15 mPa s) and EC (30–60 mPa s) were dissolved in ethanol to obtain 10 wt% solutions, herein, they were labeled as M9 and M70, respectively. 0.5 g CuS powders scrapped from the as-prepared films were added into 2.5 g terpineol, 1.2 g M9, and 1.2 g M70, after stirring for 12 h, the prepared slurry was scraped on FTO substrate, then they were annealed at 370 °C in air for 30 min in tube furnace.

2.2. Preparation of CdS/CdSe co-sensitized TiO_2 films

TiO_2 nanoparticle films with optimized thickness of 10 μm fabricated via screen printing on FTO substrates were used as the photoanodes. The matrix of photoanode was prepared simply by the commercial TiO_2 nanoparticles (Degussa P25) without casting a scattering layer of large TiO_2 particles or any other TiO_2 structural optimization. The CdS and CdSe QDs were deposited onto TiO_2 photoanode in turn through successive ionic layer absorption and reaction (SILAR) processes according to our previous work [27,28]. in brief, 7 CdS cycles and 4 CdSe cycles were adopted to co-sensitize TiO_2 photoanode. After CdS/CdSe co-sensitization, the samples were coated with ZnS passivation layer via dipping alternately into 0.5 M $Zn(NO_3)_2$ ethanol solution and 0.2 M Na_2S methanol solution for 2 min each.

Table. 1
Concentration parameters of precursor solution, thickness, RMS parameters of CS 1, CS 2, CS 2.5, CS 3, and CS 3.5.

Sample name	$CuSO_4$ (M)	$Na_2S_2O_3$ (M)	Sodium citrate (M)	Thickness (nm)	RMS (nm)
CS 1	0.025	0.025	0.05	*	25.4
CS 2	0.05	0.05	0.1	47 ± 6	19.8
CS 2.5	0.0625	0.0625	0.125	64 ± 3	18.4
CS 3	0.075	0.075	0.15	92 ± 5	19.5
CS 3.5	0.0875	0.0875	0.175	115 ± 7	29.4

* thickness of CS 1 was too thin for step profiler to be measured.

2.3. QDSSCs assembly

The CdS/CdSe co-sensitized TiO_2 photoanode with an effective area of 0.25 cm^2 and different CEs (CS 1, CS 2, CS 2.5, CS 3, CS 3.5, CS-DB, and Pt) were separated by hot-melt Surlyn films then sealed through hot-pressing. Pt CEs were prepared via scraping H_2PtCl_6 solution onto FTO substrate and heated in air at 410 °C for 30 min [29]. The redox electrolyte consisting of 1 M Na_2S, 1 M S and 0.2 M KCl in water/methanol (3:7 by volume) was injected into the interspace between the photoanode and the CEs from the CEs side through a predrilled hole.

2.4. Measurements

The crystal structure of prepared films was examined by X-ray diffraction (XRD) using an X-ray diffractometer (Philips X'pert, Holland) with CuKa radiation (λ = 1.5418 Å). The surface morphology of the CuS films were characterized using a field-emission scanning electron microscope (FE-SEM; FEI Sirion-200, USA), the chemical composition of synthesized films were determined using the energy dispersive X-ray spectroscopy (EDX). Surface conditions and root mean square roughness of films were acquired using atomic force microscope (AFM, CSPM-5500, China), and the measured area is 16 μm × 16 μm. The thickness of the films was determined with a step profiler (XP-2, AMBIOS Technology Inc., USA). UV-visible absorption spectra were recorded by a double beam UV-visible spectrophotometer (U-3900H, Japan) in the wavelength range from 200 to 900 nm.

The photovoltaic performance of QDSSCs was measured with a Keithley 2420 digital source meter under irradiation of a solar simulator (Newport Oriel 94043A, USA, AM1.5, 100 mW cm^{-2}). The irradiation intensity was calibrated with standard crystalline silicon solar cell (Oriel, Newport, USA). For cell devices prepared under each condition, at least 4 cells were prepared and tested in parallel. The total active area of QDSSCs was 0.25 cm^2. The monochromatic incident photon-to-current conversion efficiency (IPCE) spectra were measured using 300 W Xe lamp light source with monochromatic light from 300 to 800 nm.

The current–voltage (*I–V*) measurements were conducted in dark, several gold electrodes with thickness of around 50 nm were evaporated on CuS films, and the measured sample area is 13 mm × 18 mm. Electrochemical impedance spectroscopy (EIS) was obtained by applying sinusoidal perturbations of ±5 mV over the bias 0.5 V at frequencies from 10^5 Hz to 0.1 Hz on the electrochemical workstation (CHI660A, CH Instruments, Inc. Austin, TX), using the symmetrical cells at room temperature in the dark. The composition of electrolyte used for EIS measurement was identical to that used in the cell devices. Tafel plots and cyclic voltammetry (CV) were also measured on the electrochemical work station using symmetrical cells, the scan rate of Tafel measurements was 10 mV s^{-1}, and the CV test was cycled 30 times from −0.65 V to 0.65 V with a scan rate of 0.1 V s^{-1}.