Electrochimica Acta 127 (2014) 180–185

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

A new *in-situ* preparation method to CuS electrodes for CdS/CdSe co-sensitized solar cells

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ARTICLE INFO

Article history:
Received 19 December 2013
Received in revised form 28 January 2014
Accepted 4 February 2014
Available online 16 February 2014

Keywords:
Semiconductor-sensitized solar cell
counter electrode
copper sulphide
$TiCl_4$ treatment
in-situ preparation

ABSTRACT

A new *in-situ* preparation method to CuS electrodes has been developed by the combination of $TICl_4$ treatment and chemical bath deposition (CBD). It is found that $TiCl_4$ pre-treatment toward the substrates and post-treatment toward the CuS films are the key to high quality CuS films. Two kinds of CuS electrodes are obtained on Ti sheet and fluoride-doped SnO_2 conductive glass (FTO), respectively. I-E polarization analysis and electrochemical impedance spectra reveal that this kind of CuS electrodes exhibits good interfacial electron transfer property and electrocatalytic activity. Up to 4.59% of light-to-electricity conversion efficiency has been achieved for CdS/CdSe -sensitized solar cells with our as-prepared CuS counter electrodes.

1. Introduction

Semiconductor-sensitized solar cells (SSCs) have been researched worldwide since the semiconductors as sensitizers exhibit some superior advantages to organic light absorbers (ruthenium-polypyridine complexes or organic dyes), such as high extinction coefficients, controllable band gaps by particle sizes and low cost, *etc* [1–3]. Various inorganic semiconductor materials have been used in SSCs, including CdS [4], CdSe [5], CdTe [6], PbS [7], $CuInS_2$ [8], InP [9], and Sb_2S_3 [10] and so on. Recently, new perovskite-sensitized solar cells have brought an amazing efficiency higher than 15% [11]. To quantum dot-based solar cells (QDSCs), its highest efficiency can only reach around 6% [12]. Therefore, more efforts are still needed to improve the cell performance [13,14].

As an indispensible part of QDSCs, the counter electrode (CE) is in charge of catalyzing the reduction of the redox shuttle (S_x^{2-}/S^{2-}) in the electrolyte by electrons from external circuit and keeping the cell running [15]. Therefore, the primary requirement of CEs is high electrocatalytic activity, good stability and low cost. Currently, two main types of CE materials (carbon-based CEs and metal sulfide-based CEs) have been commonly used. Carbon materials can provide high surface area, three-dimensional interconnected pore structure and relatively good catalytic activity, and are thus regarded as appropriate CE materials for QDSCs, including active carbon/carbon black, orderly carbon ball and porous carbon nanorods, mesocellular carbon foams, nitrogen-doped hollow carbon nanoparticles, RGO (reduced graphene oxide) and so on [16–20]. The highest efficiency of QDSCs with carbon counter electrodes was 4.81% [16]. Besides, conducting polymer materials, such as polythiophene and polypyrrole were also used in QDSCs [21].

In fact, metal sulfide electrodes are also good choice for the QDSCs. *In-situ* prepared Cu_2S electrode on brass sheet is the most widely counter electrode, however, this electrode suffers from continuous corrosion of the polysulfide electrolyte, eventually leading to the mechanical instability and sealing problems [22,23]. Other metal sulfide electrodes, such as PbS [24], CoS [25], Co_3S_4 [26], have been developed. Meanwhile, some composite electrodes including CuS/CoS [27], Cu_2S/carbon [28], Cu_2SnS_3 [29], Cu_2ZnSnS_4 [30], $CuInS_2$/carbon [31], were also investigated. Typically, Cu_2S/RGO composite electrode for Mn-doped CdS/CdSe sensitized solar cells can present 5.4% efficiency [32]. However, appropriate counter electrodes are still lacking to meet all the requirements of QDSCs.

Among these metal sulfides, CuS electrodes can provide relatively higher conductivity and electrocatalytic activity toward polysulfide electrolytes and exhibit potential application in QDSCs [8,33,34]. Hydrothermal method has been adopted to prepare $Cu_{1.8}S$/CuS electrode on FTO and CuS nanomaterials which was subsequently used for CuS CEs for the QDSCs [8,35]. In this respect, a new *in-situ* preparation method with the combination of $TiCl_4$

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http://dx.doi.org/10.1016/j.electacta.2014.02.020
0013-4686/

treatment and chemical bath deposition method (CBD) has been developed to afford CuS electrodes on different conductive substrates (FTO conductive glass and Ti sheet). It is found that $TiCl_4$ pre-treatment toward the substrate and post-treatment toward the CuS film are the key to increasing the stability of CuS films. Further I-E polarization analysis and electrochemical impedance spectra reveal that CuS electrodes exhibit good conductivity and low charge transfer resistance as well as good electrocatalytic activity toward the polysulfide electrolyte. Up to 4.59% has been achieved for the CdS/CdSe co-sensitized solar cells with CuS electrodes.

2. Experimental

2.1. Materials

$CuSO_4{\cdot}5H_2O$, $Na_2S_2O_3{\cdot}5H_2O$, glacial acetic acid, $CdCl_2{\cdot}2.5H_2O$, NH_4Cl, $CdSO_4{\cdot}8/3H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$, $Cd(CH_3COO)_2$, $Na_2S{\cdot}9H_2O$, Na_2SO_3, thiourea, $Cu(CH_3COO)_2{\cdot}H_2O$, titanium(IV) isopropoxide, and ammonia were from Sinopharm Chemical Reagent Co. Ltd. Sodium nitrilotriacetate (NTA) and selenium powder were purchased from Alfa Aesar Chemicals. All the chemicals were directly used without further purification, and all the solutions for the electrolyte and CdS/CdSe deposition were prepared by using Milli-Q high-purity water (Millipore Model RG). Na_2SeSO_3 was synthesized by heating selenium powder (26 mM) and Na_2SO_3 aqueous solution (67 mM) at 70 °C for 3 h [36]. The electrode substrates were fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness: 2.2 mm, sheet resistance: 14 $\Omega{\cdot}square^{-1}$) and Ti sheet (thickness: 0.2 mm). Before use, FTO glass and Ti sheets were first washed with mild detergent, rinsed with distilled water for several times and subsequently with ethanol in an ultrasonic bath, and finally dried under air stream.

2.2. Preparation of CuS-based counter electrodes

FTO glass and Ti sheet as conductive substrates were first pre-treated with 0.03 M $TiCl_4$ aqueous solution at 70 °C for 30 min, subsequently rinsed with water for several times and dried under air stream. Then, the above-substrates were immersed into 100 mL mixed solution of 0.05 M $CuSO_4$, 0.2 M $Na_2S_2O_3$, 0.2 mL glacial acetic acid [37]. The above solution was heated to 70 °C and kept at this temperature for 4 hr. After cooling down to the room temperature, the substrates were taken out, rinsed with distilled water and dried in air. Finally, the as-prepared CuS films on the substrates were further treated with 0.03 M $TiCl_4$ solution again, rinsed with water and dried in air.

2.3. Fabrication of CdS/CdSe QDSCs

A double layer TiO_2 photoanode was prepared on FTO substrate by doctor blading technique, consisting of a 7 μm-thickness transparent layer with 20 nm anatase TiO_2 particles and a 3 μm-thickness light-scattering layer with the mixture of 300 nm rutile TiO_2 particles and 20 nm anatase TiO_2 particles [38].

CdS/CdSe co-sensitized photoanode was fabricated by chemical bath deposition (CBD) technique [39]. Briefly, CdS QDs were deposited onto TiO_2 porous films in the aqueous solution of 20 mM $CdCl_2$, 66 mM NH_4Cl, 140 mM thiourea, and 230 mM ammonia for 50 min at 10 °C. Subsequently, CdSe QDs were deposited onto CdS decorated TiO_2 films by immersing into the mixed solution of 80 mM Na_2SeSO_3, 80 mM $CdSO_4$, and 160 mM NTA. Here, a dual treatment with CdS and subsequent ZnS toward CdS/CdSe coated TiO_2 films was adopted by SILAR method (successive ionic layer adsorption and reaction) according to the literature [40]. Briefly, the CdS/CdSe coated TiO_2 film was alternatively dipping the film into 0.1 M $Cd(CH_3COO)_2$ (or $Zn(CH_3COO)_2$) and 0.1 M Na_2S solutions for 1 min twice. Finally, the CdS/CdSe-decorated TiO_2 film, polysulfide electrolyte (1 M Na_2S and 1 M S) and CuS counter electrode were assembled into a sandwich-type cell.

2.4. Characterization

The surface morphologies of the CuS electrodes were obtained by using a scanning electron microscope (SEM, FEIXL30S-FEG). The film thickness was determined by a surface profiler (KLA-Tencor, P-6). X-ray diffraction pattern (XRD) was carried out on M18X-AHF, MAC Science with Cu K_α radiation source. I-E polarization analysis was recorded by using a three-electrode system on ZAHNER IM6e electrochemical workstation with a scanning rate of 5 $mV{\cdot}s^{-1}$ in the potential ranging from -0.3 to 0.3 V at 20 °C. In this three-electrode system, as-prepared CuS electrode is the working electrode, a Pt electrode with the area of 0.09 cm^2 as the counter electrode and a Pt wire as the pseudo-reference electrode which potential is that of the polysulfide electrolyte, and 1 M polysulfide solution as the electrolyte [31]. The cells were illuminated under 100 $mW{\cdot}cm^{-2}$ (AM 1.5) by an Oriel solar simulator 91192, and the *J-V* characteristics of the cells were recorded on Princeton Applied Research, Model 263A. For *J-V* characteristics, a mask with a window of 0.15 cm^2 was clipped on the TiO_2 side to define the active area of the cell. Electrochemical impedance spectra (EIS) of the symmetric thin layer cells were performed on ZAHNER IM6e electrochemical workstation in the frequency ranging from 0.1 to 10^6 Hz with a perturbation amplitude of 10 mV. The obtained impedance spectra were fitted with *Zview* software based on appropriate equivalent circuit.

3. Results and discussion

As we know, the quality of counter electrode is of great concern for highly efficient QDSCs, including chemical stability, mechanical stability and catalytic activity toward the polysulfide electrolyte. Amongst, mechanical stability is the primary requirement for the CuS electrodes. Fig. 1(a)-(d) show the photos of CuS films after 4 hr deposition on the substrates with or without $TiCl_4$ pre-treatment, respectively. We can see that, when the FTO glass is pre-treated by $TiCl_4$, a homogeneous CuS film can be achieved in comparison with the untreated FTO glass. When this method is further employed to the Ti sheet for the CuS film, more homogeneous film will be obtained in comparison to the untreated Ti sheet. Moreover, it is found that the CuS film is more easily deposited on the surface of Ti sheet than that on FTO glass if the two substrates are not treated by $TiCl_4$. In fact, there is a very thin TiO_2 layer on the surface of purchased Ti sheet, which can increase the surface roughness of Ti sheet itself. It is thus reasonable that, $TiCl_4$ pre-treatment will increase the surface roughness of the substrates, which is beneficial to the physical contact between CuS nanoparticles and the substrate to afford an even film. Further $TiCl_4$ post-treatment toward the CuS film will improve the interfacial contact between the CuS nanoparticles to increase the stability of the films in the polysulfide electrolyte. As shown in Fig. 1(e)-(f), the CuS films without $TiCl_4$ post-treatment are found to easily peel off after the I-V test, in comparable to CuS films with twice $TiCl_4$ treatment. Besides, the as-prepared CuS films cannot be scratched off, indicating the film surface is mechanically robust (good adherence to the substrate) [41].

Here, relatively thicker CuS films with longer deposition time (over 4 hr) are not given because the films are easily peeled off from the substrates when they are in contact with the polysulfide electrolyte [35]. Therefore, the CuS films for the following discussion are all based on the 4 hr deposition.

Fig. 2a and b show the SEM images of as-prepared CuS films on FTO glass and Ti sheet, respectively. We can see that CuS films on