Materials Research Bulletin 100 (2018) 198–205

Contents lists available at ScienceDirect

Materials Research Bulletin

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

# Investigation of metal sulfide composites as counter electrodes for improved performance of quantum dot sensitized solar cells

Beilei Yuan[a], Lianfeng Duan[a,*], Qiqian Gao[a], Xueyu Zhang[a], Xuesong Li[a], Yue Yang[a], Li Chen[b], Wei Lü[a,*]

[a] Key Laboratory of Advanced Structural Materials, Ministry of Education, Changchun University of Technology, Changchun 130012, PR China
[b] School of Basic Sciences & Advanced Institute of Materials Science, Changchun University of Technology, Changchun 130012, PR China

ARTICLE INFO

*Keywords:*
Quantum dot-sensitized solar cell
CuS/CoS
Counter electrode
Open-circuit voltage
Power conversion efficiency

ABSTRACT

The electrochemical performance of counter electrodes (CEs) plays an important role for achieving high efficient quantum dot sensitized solar cells (QDSSCs). Considering the optical band gap energy of semiconductor materials and the $V_{oc}$ of the QDSSCs is determined by the energy difference between the quasi-Fermi levels ($_qE_f$) of the anode and cathode, so in this work, we synthesized the different metal sulfides and their composites including CuS/CoS, CuS/NiS, CuS, CoS and NiS by chemical bath deposition (CBD) method and used as CEs of QDSSCs. The effect of different CEs on performance of cells were investigated, and the best power conversion efficiency (η) of 5.22% was achieved by CuS/CoS CE, which is higher than that of CuS/NiS, CuS, CoS and NiS (η = 2.56%, 4.73%, 2.23% and 1.62%). The improved cell efficiency was attributed to the excellent electrical conductivity and catalytic activity of CuS and CoS, respectively. The result indicated that the combination of different metal sulfide composites could increase open-circuit voltage ($V_{oc}$) value without sacrificing the short-circuit current ($J_{sc}$), and leaving good perspectives for significantly higher solar cell performances.

## 1. Introduction

With the increasing problems of energy demands, global warming and emission of greenhouse gases, the development of renewable energy sources has been got much more attention [1–4]. Solar power is becoming a great choice to tackle the crisis and environmental problems. As one of the third generation solar cells, quantum dot-sensitized solar cells (QDSSCs) has attracted increasing attention, because of its relatively low cost, easy fabrication and high-efficiency energy conversion [5–7]. Basically, QDSSCs have similar structures with that of dye-sensitized solar cells (DSSCs). The semiconductor quantum dots (QDs) have presented the possibility of band gap tunability, high extinction coefficient, large intrinsic dipole moments, and potential processes of multiple exciton generation [8–13]. Furthermore, for the sensitizers of DSSCs, QDs also possess higher absorption coefficients [14], multiple exciton generation (MEG) [15], tunable bandgaps due to the quantum confinement effect [16], the possibility of hot electron injection [17], and easy fabrication processes [18]. Although the QDSSCs have been attracted great attention as the excellent properties for QDs, the highest power conversion efficiency of QDSSC is still lower than that of a DSSC in present study [19,20].

QDSSC is mainly composed of a transparent conductive glass, wide band gap oxide semiconductor thin films, quantum dots, electrolyte and counter electrode. The efficient charge transfers between sulfide sensitizers and the polysulfide redox couple generates a large short-circuit photocurrent ($J_{sc}$) in QDSSCs [21–27]. However, the large charge transfer resistance at the counter electrode results in a low fill factor (FF) and the small difference between the $TiO_2$ Fermi level and the $S^{2-}/S_n^{2-}$ redox level confines the open-circuit photovoltage ($V_{oc}$). A promising strategy to increase the $V_{oc}$ value without sacrificing the high $J_{sc}$ is to use a narrow band gap semiconductor as the counter electrode to provide an auxiliary tandem effect.

Actually, different kinds of CEs have been found for QDSSCs, such as carbon, carbon derivatives, noble metals and conducting polymers [28–31]. The commonly used noble metal CEs, such as Pt and Au, exhibit poor catalytic property toward polysulfide electrolyte because they usually passivated by sulfide compound absorbed on their surface and the Pt produces a large charge transfer resistance in the polysulfide electrolyte lead to low fill factor [32]. Apart from noble metal, the carbon and carbon derivatives, including activated carbon, mesocellular carbon foam, have no better catalytic activity and there is not enough contact with the base [33]. Conducting polymers have poor power conversion efficiency. So the correlational studies have been reported rarely in CEs for QDSSCs [34]. Therefore, the optimization and

* Corresponding authors.
*E-mail addresses:* duanlf@ccut.edu.cn (L. Duan), lw771119@hotmail.com (W. Lü).

https://doi.org/10.1016/j.materresbull.2017.12.021
Received 6 October 2017; Received in revised form 11 December 2017; Accepted 15 December 2017
Available online 20 December 2017
0025-5408/ © 2017 Elsevier Ltd. All rights reserved.

fabrication of CEs with high electrocatalytic activity and good stability are still very important for improving the performances of QDSSCs.

Recently, for improving electrocatalytic activity and low fill factor of the CE, metal sulfides have been got much attention due to its low cost, low resistance, good electrocatalytic activity and facile fabrication [5,35]. Furthermore, the metal sulfides would be good choice as CEs for covering related problems discussed above. Several works have reported the preparation and application of metal sulfides as CEs in QDSSCs. Lin et al. applied PbS thin films as CEs for QDSSCs by SILAR method and these exhibited the highest η of 4.7% [36]. Savariraj et al. prepared CuS thin films using a facile CBD method and got the highest η of 4.53% [37]. Yuan et al. reported that CoS thin films be synthesized and applied to the CEs of QDSSCs and achieved the highest η of 5.20% [38]. However, single metal sulfides as CE generally suffers poor electrical conductivity or catalytic activity. Therefore, we use metal sulfide composites as CEs of QDSSCs and these different metal sulfide composites may change the value of $V_{oc2}$ (the difference between the potential of redox/reduction of electrolyte and the Fermi level of CE), resulting in a noticeable change in the $V_{oc}$ of QDSSCs.

In this paper, inspired by above discussion, CuS/CoS, CuS/NiS, CuS, CoS and NiS thin films are deposited on fluorine doped tin oxide (FTO) glass substrates by chemical bath deposition (CBD), which are further used as CEs of QDSSCs, and the cell performances based on these CEs are systematically investigated. In Fig. 1, it has been described that the transport pathways of electrons and photoelectrical conversion configuration of a $TiO_2$/CdS/CdSe/ZnS for anode with the counter electrode of CuS/CoS for QDSSCs. The cell using CuS/CoS CE show a 5.22% power conversion efficiency (PCE) under one sun illumination, which is higher than that of CuS/NiS, CuS, CoS and NiS (η = 2.56%, 4.73%, 2.23% and 1.62%, respectively). The enhanced PCE of CuS/CoS CE is attributed to the combination of different metal sulfides, for that CuS shows the exceptional electrical conductivity and CoS shows the excellent catalytic activity. The result indicates that the combination of different metal sulfide composites could increase open-circuit voltage ($V_{oc}$) value without sacrificing the short-circuit current ($J_{sc}$), and leaving good perspectives for significantly higher solar cell performances.

## 2. Experimental details

### 2.1. Materials

FTO glasses were purchased from Zhuhai Kaivo Optoelec-tronic Technology Co., Ltd., cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), nickel sulfite hexahydrate ($NiSO_4{\cdot}6H_2O$), thioacetamide ($CH_3CSNH_2$) and sodium sulfite ($Na_2SO_3$) were supplied by Sigma-Aldrich. Acetic acid ($C_2H_4O_2$), cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$), L-cysteine ($C_3H_7NO_2S$), zinc acetate ($CH_3(COOH)_2Zn$) and potassium chloride (KCl) were bought from Aladdin. Sodium sulfide ($Na_2S{\cdot}9H_2O$), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$), selenium (Se), sodium hyposulfite ($Na_2S_2O_3$) and urea ($CH_4N_2O$) were purchased from Tianjin Guangfu Technology Development Co., Ltd. All chemicals were used without further purification.

### 2.2. Preparation of counter electrodes

The CBD method was used to deposit metal sulfide (CuS/CoS, CuS/NiS, CuS, CoS and NiS) to serve as CEs. For CuS CE, 1 M $Na_2S_2O_3$ aqueous solution and 1 M $CuSO_4$ aqueous solution were mixed with the volume ratio of 4:1, and the pH value was adjusted to 2 by Acetic acid. Then, the FTO glasses were immersed into as-prepared mixed solution and heated to 70 ℃ for 3 h. After cooling down to the room temperature, the substrates were washed with DI and then heated to 130 ℃ and kept for 30 min.

For NiS CE, a solution included 8 g $NiSO_4{\cdot}6H_2O$ and 2 g $C_3H_7NO_2S$ in 40 ml deionized water was prepared. The solution was stirred vigorously for 10 min to get a bottle-green solution. Under constant stirring, 4 g $CH_3CSNH_2$ and 12 g $C_2H_4O_2$ were added to the above solution and stirred ultrasonically for another 15 min. Then, the FTO substrates were put into the solution and kept at 90 ℃ for 120 min.

For CoS CE, a solution included 5 g $CoCl_2$ and 5 g $CH_3CSNH_2$ in 30 ml deionized water was prepared. The solution was stirred vigorously for 10 min to acquire a amaranth solution. Next, 12 g of $C_2H_4O_2$ was added to the above amaranth solution, and the reaction mixture was stirred vigorously for a further 15 min.

To prepare CuS/CoS and CuS/NiS CEs, 0.1 M $CuSO_4{\cdot}5H_2O$, 0.5 M $CH_4N_2O$ and 0.5 M $CH_3CSNH_2$ were dissolved in 30 ml deionized water, and the FTO glasses were immersed into as-prepared mixed solution and heated to 70 ℃ for 2 h. Then the as-prepared CuS substrates were put into a solution of containing 0.1 M $CoCl_2{\cdot}6H_2O$, 1 M $CH_4N_2O$, 0.5 M $CH_3CSNH_2$ and 0.6 M $C_2H_4O_2$ for further deposition of CoS. This film substrate named CuS/CoS. After cooling down to the room temperature, the substrates were washed with DI water and heated to 60 ℃ for 30 min. To deposit the CuS/NiS, the as-prepared CuS substrates were put into a solution that consisted of 0.1 M $NiSO_4{\cdot}6H_2O$, 1 M $CH_4N_2O$, 0.5 M $CH_3CSNH_2$ and 0.6 M $C_2H_4O_2$ and kept at 90℃ for 2 h.

### 2.3. Preparation of photoanode ($TiO_2$ /CdS/CdSe/ZnS)

$TiO_2$ films were made using the doctor-blade method by coating

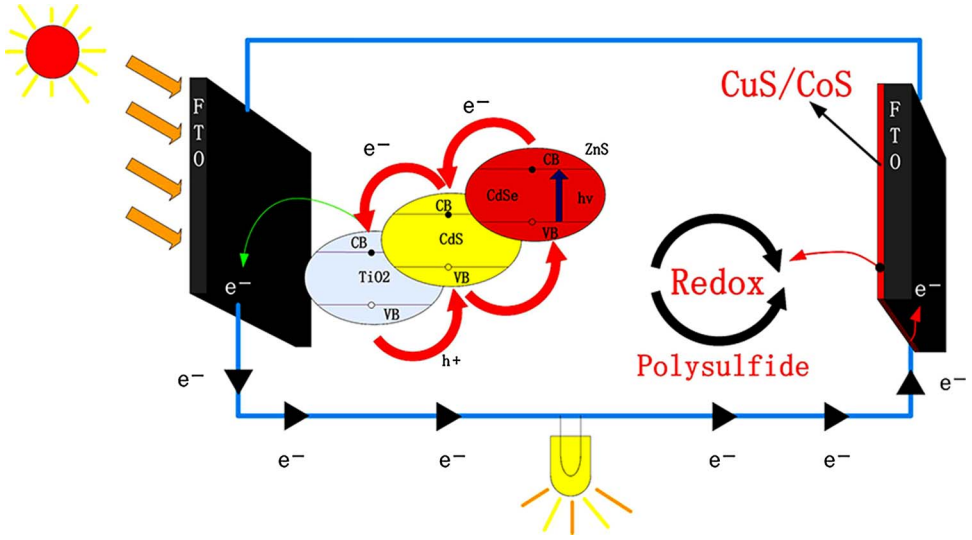


**Fig. 1.** Schematic structure of QDSSCs based CuS/CoS CE.

Download English Version:

https://daneshyari.com/en/article/7904926

Download Persian Version:

https://daneshyari.com/article/7904926

Daneshyari.com