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Research Paper

Optimization of performance and stability of quantum dot sensitized solar cells by manipulating the electrical properties of different metal sulfide counter electrodes

Arumukham Manjceevan, Jayasundera Bandara*

National Institute of Fundamental Studies, Hantana Road, Kandy, CP 20000, Sri Lanka

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ABSTRACT

Fabrication of low cost and high catalytic active counter electrode (CE) for quantum dot sensitized solar cells is one of the dynamic ways to enhance the performance of quantum dot solar cell. In this investigation, different CE materials such as copper sulfide (Cu_2S), cobalt sulfide (CoS) and nickel sulfide (NiS) were deposited on fluorine doped tinoxide (FTO) glass and brass plate by single step electrophoretic deposition technique and solar cell performance and stability of three different CEs were tested. Electrochemical deposition parameters were optimized for the optimization of CEs performance. Electrical properties of Cu_2S, CoS and NiS CEs were investigated by electrochemical impedance spectroscopy and electrical properties were compared with the observed solar cell performances and stability. Of the tested CEs materials, enhanced solar cell performance was observed with Cu_2S CE than the CoS or NiS CEs while brass substrae was found to be a better substrate than FTO for these CE materials. The optimized Cu_2S/brass plate CE showed current density of (Jsc) 17.9 mA.cm^{-2}, open circuit voltage of (Voc) 494.5 mV, fill factor of (FF) 59.0% and efficiency of 5.2% with the solar cell fabricated with PbS/CdS q-dot anode. While Cu_2S/FTO glass plate CE showed Jsc of 16.1 mA.cm^{-2}, Voc of 489.4 mV, FF of 52.9% and efficiency of 4.2% of with the same q-dot anode. A higher electrocatalytic activity together with the lower charge transfer resistance (Rct) and good inter-connected Cu_2S particles on brass electrodes were found to be the major CE properties that decides the performance of CE.

1. Introduction

Quantum dot sensitized solar cells (QDSCs) are promising next generation solar cells due to their characteristic features like tunable band gaps, multiple electron/hole generation and simple fabrication procedures [1,2]. Quantum dot (Q-dot) sensitized solar cells typically have similar configuration as in the dye sensitized solar cells (DSSCs) in which q-dots act as sensitizers in QDSCs [3]. Despite QDSCs have similar configuration to that of DSSCs, the highest reported efficiencies for CdSeTe [4], CdS/CdSe [5] and PbS/CdS [6] QDSCs are 8.0, 7.1 and 5.7% respectively. Hence, the power conversion efficiencies of QDSCs are still far below than the power conversion efficiencies of DSSC with porphyrin sensitizer 13% [7] as well as perovskite materials 15% [8].

The inferior solar cell efficiencies of QDSCs could be mainly attributed to; (a) rapid electron loss due to recombination of excited electron in TiO_2 and/or in q-dots with electrolyte [4,9,10] and (b) energy loss in between counter electrode and electrolyte interface [11,12]. Therefore, in order to enhance the performance of QDSCs, research has been focused mainly on minimizing of charge recombination in TiO_2 interface as well as minimizing energy loss between the counter electrode and the electrolyte interface. Hence, the optimization of CE is an imperative to improve the performance of QDSSCs. Counter electrodes such as CoS/FTO[1,13], NiS/FTO [14], Cu_2Se/FTO [15] and Ni_2Se/FTO [15], Pt/FTO [16–18], Cu_2S/FTO [1,16,17,19–21], PbS/FTO[22], $Cu_2ZnSnSe_4$ [23] and NiS [1,14] have been investigated as possible alternative counter electrodes to optimize the performance of QDSCs. Previous study revealed that the energy loss between the counter electrode-electrolyte interface is one of the major reasons that contributes to poor fill factor and low efficiency of QDSSCs [11,12]. Hence, good catalytic activity of CE for the reduction of oxidized redox species of the electrolyte is an important parameter for better performance QDSSCs solar cell.

In the case of DSSCs, the platinum CE exhibits unchallenged catalytic activity with I_3^-/I^- redox couple electrolyte. However, Pt

* Corresponding author.
E-mail addresses: bandaraj@ifs.ac.lk, jayasundera@yahoo.com (J. Bandara).

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shows poor CE properties with polysulfide electrolytes due to strong chemisorption of electrolyte on Pt CE [3,24] resulting in poor solar cell efficiency in q-dot sensitized solar cell. On the other hand, polysulfide electrolyte with metal sulfides CE exhibits more desired properties than I_3^-/I^- redox couple due to photocorrosion of metal sulfides by I_3^-/I^- species causing in rapid deterioration of solar cell performance[12].It is known that the CE properties such as resistance to photocorrosion, reduced charge transfer resistance and high catalytic activity are the desired properties of a CE of a QDSC [12,14,19,25]. Owing to their high conductivity, good catalytic activity and more importantly due to less charge transfer resistance properties, CoS and Cu_2S materials on FTO are considered to be the good CEs for QDSCs [11,12]. However, the stability is the major concern of CoS and Cu_2S counter electrodes due to corrosion of these materials and hence stability of CE is one of the major bottlenecks in Q-dot solar cell research [12]. Finding of stable alternative CE materials and substrates for q-dot solar cell is imperative for further improvement of the q-dot solar cell performance as well as for long term stability of q-dot solar cells. The main objective of this report is to investigate different CE materials and substrates as possible CEs for q-dot solar cells. In this investigation, different metal sulphides such as CoS, NiS and Cu_2S were deposited on different substrates such as FTO and brass. The CE properties of CoS, NiS and Cu_2S on FTO and brass substrates were investigated against the PbS/CdS sensitized photoanode on FTO. The performances and stability of PbS/CdS QDSCs with different counter electrodes were correlated to surface, electro-catalytic properties as well as electronic properties of such counter electrodes for the first time.

2. Experimental Section

2.1. Preparation of Cu_2S, CoS and NiS counter electrodes

FTO glass (Soloronix: sheet resistance 15 $\Omega.cm^{-2}$: thickness 2 mm) and brass plate (0.65 $\Omega.cm^{-2}$: thickness 1.24 mm) were ultrasonically cleaned in the detergent and washed in cold deionized water, hot deionized water and ethanol sequentially and finally dried off by using hot plate. Different sulfide materials on CE electrodes were electrodeposited either on top of FTO or brass conducting surfaces by single step electrodeposition method with the three electrode system using Pt, Ag/AgCl and FTO glass (or brass plate) as counter, reference and working electrodes respectively. For the deposition of Cu_2S, an electrolyte consisting of 40 ml of 0.05 M $CuSO_4.5H_2O_{(aq)}$ and 0.15 M $Na_2S_2O_3.5H_2O_{(aq)}$ in the 150 ml beaker was employed and electrodeposition of was performed at −1.1 V for four minutes. After deposition of Cu_2S, the electrode was dried off by using air blower, washed by deionized water and again dried off consecutively. Finally, the Cu_2S deposited CE was treated with 0.1 M $Na_2S_{(aq)}$ and 0.1 M S for one minute and rinsed with deionized water and ethanol. In a similar manner, for the preparation of CoS CEs on either on FTO or brass, CoS was electrodeposited by using electrolytes containing of 0.05 M $CoSO_4.5H_2O_{(aq)}$ and 0.15 M $Na_2S_2O_3.5H_2O_{(aq)}$at −1.1 V for four minutes. For the electrodepositon of NiS either on FTO or brass, 0.05 M $NiSO_4$, 0.15 M $Na_2S_2O_3.5H_2O_{(aq)}$electrolyte was employed at the electrodepositon was carried out at −0.85 V for four minutes. The CEs fabricated with Cu_2S, CoS and NiS on FTO glass and brass plate were denote as A, B, C, D, E and F respectively while platinum counter electrode is denote as G.

2.2. Fabrication of solar cell device

For the fabrication of solar cell, as a first step, a compact TiO_2 layer was deposited on FTO. To fabricate a compact TiO_2 layer on bare FTO, 20 μl of a mixture containing of Titaniumisopropoxide (0.177 ml, 97%, Fluka), diethanolamine (0.1 ml, 99%, Fluka) in butan-1-ol (1.822 ml, 99%, AnalaR) were spin coated at 5000 rpm and dried at 130 °C for five minutes. The coating and drying process were repeated for three times and finally sintered at 500 °C for 45 minutes. On top of the compact TiO_2 layer, a 15 μm TiO_2 mesoporous layer was fabricated by doctor blade method using Dyesol TiO_2 paste (DSL 18-NRT, 20 nm average particle size) and TiO_2 paste prepared by modified Pichini methods. The modified Pichini based sol-gel preparation methods 1 (TiO_2Pichini1) and 2 (TiO_2Pichini2) have been detailed in our previous publication [6]. In the fabrication of TiO_2 mesoporous layer following steps were taken; (a) Dysol paste was doctor bladed with two scotch tape thickness and sintered at 500 °C for 30 minutes, (b) on top of the Dyesol TiO_2 layer, a layer of TiO_2Pichini1 was doctor bladed with two scotch tape thickness [26] and sintered at 450 °C for 30 minutes with 3 °C/minutes ramping of temperature, (c) finally, TiO_2Pichini2 was doctor bladed with two scotch tape thickness and sintered.

The SILAR method (successive ion layer adsorption and reaction) was employed to deposit Q-dots on mesoporous TiO_2photoanode. As reported in our earlier work [6], PbS, CdS, ZnS were coated on TiO_2photoanode by SILAR method. In brief, the bare TiO_2photoanode was immersed in a solution containing 3-mercaptoproponic acid (0.015 M) and 0.02 M $Na_2S_{(aq)}$ solution for 1.5 minutes followed by immersing into the 0.02 M $Pb(Ac)_{2(aq)}$ solution for 1.5 minutes. Extra $Pb(Ac)_2$ was removed by washing with methanol. To convert adsorbed Pb into PbS, Pb adsorbed TiO_2photoanodefilm was again immersed into a solution containing 0.015 M 3-mercaptoproponic acid and 0.02 M $Na_2S_{(aq)}$. The whole process is labeled as one cycle of PbS deposition. Likewise, for CdS and ZnS deposition, the above process was repeated using either 0.05 M $Cd(Ac)_{2(aq)}$or 0.05 M $Zn(Ac)_{2(aq)}$ as cationic species and mercaptoproponic acid mixed 0.05 M $Na_2S_{(aq)}$ as anionic solutions respectively. In a typical photoanode fabrication, one cycle of PbS was deposited first on TiO_2 and three cycles of CdS were deposited on the PbS layer by SILAR deposition method and finally deposition was completed with two cycles of ZnS deposition. Finally, the q-dot sensitized photoanode and the counter electrode were sandwiched by placing a parafilm spacer in between photoanode and the CE. A liquid electrolyte was prepared with 2 M Na_2S, 2 M S and 0.2 M KCl in water: methanol mixture of 3: 7 ratio and the assembled solar cell was filled with 20 μl of electrolyte.

2.3. Characterization

Fabricated CE materials were characterized by using x-ray diffraction (XRD) measurements, UV-visible spectroscopic measurements, Scanning Electron Microscopy (SEM) analysis, cyclic voltammetry analysis, electrochemical impedance analysis (EIS) and Tafel polarization measurements. The XRD measurements were performed by using powder diffraction (Siemens D5000 X-ray diffractometer with Cu Kα radiation operating at 40 KV, scanning from $2\theta = 20$ to 80°). Morphology of the counter electrodes were observed by Carl Zeiss EVO LS 15 scanning electron microscope. Photovoltaic performance (current-voltage curve) were measured using Keithley 2400 source meter under illumination using a solar simulator at AM1.5G (Newport AAA solar simulator at 100 mW/cm^2). The intensity of solar simulator was calibrated with standard Si-reference cell. Active area of photo-voltaic cell was 0.159 cm^2. External quantum efficiency (EQE) was measured as the function of wavelength from 300 nm to 1100 nm using Bentham PVE300 unit with a TMc300 monochromator based IPCE with the Xenon arc lamp. The EIS measurements were performed under dark conditions by using Zahner Zannium universal electrochemical work station equipped with a frequency