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Cobalt sulfide counter electrode using hydrothermal method for quantum dot-sensitized solar cells

Dinah Punnoose [a], Hee-Je Kim [a,*], S. Srinivasa Rao [a], CH.S.S. Pavan Kumar [b]

[a] Department of Electrical and Computer Engineering, Pusan National University, Gumjeong-Gu, Jangjeong-Dong, Busan 609-735, South Korea
[b] Department of Physics, Pusan National University, Gumjeong-Gu, Jangjeong-Dong, Busan 609-735, South Korea

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ABSTRACT

Chalcogenides are potential alternatives to platinum (Pt) based counter electrode (CE). This study reports cobalt sulfide (CoS_2) thin films as robust, high-performance, economical, earth-abundant CE for quantum dot-sensitized solar cells (QDSSCs). CoS_2 thin film has been deposited on a fluorine-doped tin oxide substrate by a hydro thermal method using 3-mercapto propionic acid and used as an efficient CE for polysulfide redox reactions in quantum dot-sensitized solar cells (QDSSCs). CdS/CdSe-sensitized QDSSCs exploiting CoS_2 CE improved short-circuit photocurrent density and fill factor. We attained 2.27% solar light-to-electricity conversion efficiency, a value higher than reaped with Pt CE (1.73%). Electrochemical measurements testified that CoS_2 reveals high electro-catalytic activity towards polysulfide reduction, thus accelerating QDSSCs performance. CoS_2 also showed stability at a working state for over 10 h, resulting in highly reproducible performance, which is a serious challenge for solar cell.

1. Introduction

Quantum dot sensitized solar cells (QDSSCs), in which semiconductor quantum dots (QDs) of narrow band gap function as a photosensitizer, have of late attracted mounting interests as an alternative to the conventional dye-sensitized solar cell (DSSC), due to their tunable band gap, large light absorption coefficient and high stability [1–7]. In addition, QDs are easy to synthesize and, since their size is restricted to a few nanometers, they can effortlessly be accommodated within the mesoporous structure of nano crystalline oxide semiconductors, which is usually large by magnitude of one order [8]. Successive ionic layer adsorption and reaction (SILAR) [9] and chemical bath deposition (CBD) [10] are frequently used methods for growing semiconductor QDs directly onto a mesoscopic oxide film. The most prominent QDs are metal sulfides and selenides. Preceding research reports show that a combination of QDs leads to higher efficiencies than pure materials [11,12–15]. CdS, CdSe, PbS, PbSe and Sb_2S_3 are frequently used as sensitizers in QDSSCs. Inorganic semiconductor sensitizers, typically referred to as quantum dot (QD) sensitizers, have lately studied with great interest and surpass their dye homologs.

The QDs, upon photo excitation in QDSSCs the electrons are injected from CdSe and CdS QDs into TiO_2 and then to the FTO (fluorine doped tin oxide) substrate, on the other hand holes oxidize the polysulfide electrolyte. Electrons in the FTO move towards the cathode through an external circuit and takes part in a reduction reaction at the CE/electrolyte interface. As a result, an ideal CE (counter electrode) should possess high electro-catalytic activity for the reduction of charge carriers in the electrolyte, along with high conductivity. However, the power conversion efficiency of QDSSCs is still far below the theoretical value of 44% and much lower than the 12% value of DSSCs. The crucial factor for improving the power conversion efficiency (PCE) of QDSSCs has not been found yet. The low efficiency of QDSSCs could be ascribed to the improper assembly of QDs on a mesoporous TiO_2 film, which is used to obtain a well-covered monolayer without cluster formation or aggregation [16]. Low efficiency is also caused by a low open circuit voltage (V_{OC}) and fill-factor (FF), which could be ascribed to a fast recombination at the TiO_2/QD/electrolyte interface and high charge transfer resistance at the interface of the CE and the electrolyte [17–19]. Charge transfer to the oxidized redox polysulfide species on the surface of the CE is considered to be a major hurdle in obtaining high FF and power conversion efficiency (η).

In order to increase the efficiency of the QDSSCs, it is necessary to search for the novel electro catalytic counter electrode materials. Pt is widely used as CE in DSSC and shows high electro catalytic activity in the reduction of iodide/triiodide (I^-/I_3) electrolyte [20]. However, Pt shows very low electro catalytic activity for the

* Corresponding author.
E-mail address: heeje@pusan.ac.kr (H.-J. Kim).

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reduction of polysulfide electrolyte used in QDSSC which results in very low FF and power conversion efficiency [21,22]. Because, the sulfur containing compounds adsorbs onto the surface of Pt leading to low electro catalytic activity and conductivity of the CE; moreover, Pt is an expensive material [23,24]. Several studies have been reported as alternative CEs for polysulfide electrolyte such as CuS, CoS, NiS and PbS [25,26]. Many CEs have been reported to enhance the efficiency and fill factor (FF) of solar cells, such as CoS, Cu_2S, NiS, FeS, and Au [13,26–30]. *Yang* et al. reported the photovoltaic properties of CoS, CuS, and NiS CEs, and established that cobalt sulfide (CoS) is superior to the other two, in the order of CoS > CuS > NiS [31]. Further investigation shows that Cu_2S electrode has inferior long-term stability when compared to CoS electrode. Also, Cu_2S is not stable since the Cu substrate continually reacts with the polysulfide electrolyte and thereby reducing the stability in QDSSCs [31–33]. CoS is also less susceptible to poisoning by the sulfide/polysulfide electrolyte, furthermore, CoS exhibits excellent stability in polysulfide electrolyte, resulting in extremely reproducible performance [34].

Cobalt sulfide has received increasing attention owing to its variety of specialized applications such as super capacitors [35], photo electrochemical hydrogen generation from water [36], solar cells [37]. Yujie Sun et al. reported that a cobalt sulfide (CoS) film on conductive substrates is revealed to perform as an efficient and robust catalyst for electrochemical and photo electro-chemical hydrogen generation from neutral pH water. Wei Chen et al. reported a facile one-step electro deposition method is developed to prepare ternary nickel, cobalt sulfide interconnected nano sheet arrays on conductive carbon substrates as electrodes for super capacitors, resulting in exceptional energy storage performance. However, to the best of our knowledge, reports in using CoS_2 CE electrodes in QDSSCs with polysulfide electrolyte are inadequate. In previous studies, we synthesized cobalt sulfide CEs that showed excellent electro-catalytic activity and good electrical properties DSSCs [37]. In another study, a CoS/NiS composite CE showed greater electro-catalytic activity and improved photovoltaic performance compared to CoS_2, NiS, and Pt CEs for the polysulfide electrolyte used in QDSSCs [38]. Our previous work on CoS_2 CEs was done using chemical bath deposition (CBD) at low temperature (<100 °C) with different morphologies. However, there is no report on using a hydrothermally prepared CoS_2 CE in QDSSCs.

In the present work, we investigated CoS_2 CEs due to their low cost, high electro-catalytic effect toward polysulfide reaction, and superior chemical activity [39]. We deposited CoS_2 thin film by a hydro thermal method because this process is high-temperature and allows exact control over the size, shape dissemination, and crystallinity of metal oxide nanoparticles or nanostructures. These characteristics can be reformed by changing certain experimental parameters, including deposition time, deposition temperature, solvent type and composition of elements. By combining the optimized titanium dioxide (TiO_2)-QDs as a working electrode with the CoS_2 CE, a power conversion efficiency of 2.27% was observed. The present work, opts for the employment of CoS_2 as efficient CE based on the deposition time. The deposition time of the CoS_2 CE during hydrothermal method was varied in order to improve the efficiency and to replace the Pt CE.

2. Experimental

2.1. Fabrication of CEs

All chemicals used for the fabrication of CoS_2 thin film were purchased from Sigma–Aldrich and used without further purification. Prior to deposition, FTO substrates were cleaned ultrasonically with acetone, ethanol and distilled (DI) water each for 10 min. CoS_2 CEs were fabricated using 0.1 M of $CoCl_2{\cdot}6H_2O$, 0.4 M of 3-mercaptopropionic acid (3-MPA) and 0.8 M of thiourea using ethyl glycol as a solvent by hydro thermal method which is maintained at deposition temperatures of 100 °C, 120 °C, 150 °C for 2 h. No visible coating was observed at 100 and 120 °C, semi transparency coated film was observed for 150 °C and this optimized deposition temperature was fixed for 5 h, 10 h and 15 h. The autoclave was cooled to room temperature naturally and the deposited CoS_2 thin films were rinsed with ethanol and DI water. 5 h, 10 h and 15 h coated substrates was densely coated and kept nearly opaque and named as CoS_2-5 h, CoS_2-10 h, CoS_2-15 h respectively.

To fabricate the Pt electrode, the cleaned FTO glass substrate was coated with a Pt paste (Pt-catalyst T/SP, Solaronix) in the active area of ~0.7 cm^2 using the doctor blade method and sintered at 450 °C in the air for 10 min.

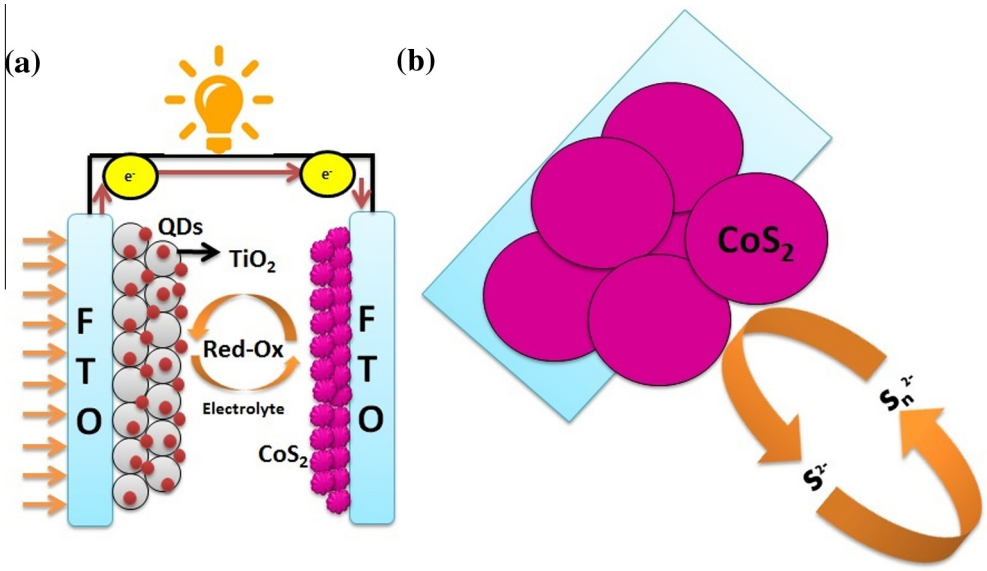

Fig. 1. (a) A representational structure of the TiO_2/QDs/CoS_2 QDSSC (b) its details.