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Copper selenide as a new counter electrode for zinc oxide nanorod based quantum dot solar cells

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ABSTRACT

This work investigates the improvement in efficiency of quantum dot sensitized solar cells (QDSSCs) using copper selenide (Cu_2Se) as a new counter electrode. Cu_2Se counter-based QDSSC exhibits power conversion efficiency (η) of 2.28%, which is higher than the 1.17% efficiency of copper sulfide (CuS) counter electrode. Electrochemical impedance spectroscopy results show that by the changing counter electrode from CuS to Cu_2Se, the charge transfer resistance at the counter electrode/electrolyte interfaces is reduced and, consequently, causes current density rise from 6.02 mA/cm^2 to 11.26 mA/cm^2. Also, open circuit voltage decay and dark current density–voltage results show that the lifetime of electron in the Cu_2Se counter-based QDSSC is higher than that of QDSSC with CuS counter electrode. Therefore, Cu_2Se counter electrode can be regarded as a promising alternative to the noble CuS counter electrode in QDSSCs.

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1. Introduction

Recently, numerous works have been carried out on quantum dot sensitized solar cells (QDSSCs), as cells founded on the semiconductor photoanode, typically TiO_2 or ZnO decorated by QD sensitizers [1–3]. Compared to TiO_2, ZnO has a higher electronic mobility and diffusion coefficient which facilitates the easier transportation of the electrons into the ZnO conduction band (CB) [4]. Furthermore, ZnO has several advantages over TiO_2 such as higher thermal stability, easier growth, and lower synthesis cost, making a proper alternative for TiO_2 [5]. In addition, the fabricated ZnO/Cu_2O solar cells based on Cu_2O films show effective rectifying behavior [6,7]. Since the efficiency of the solar cells is governed by the characteristics of both the photoelectrode and counter electrode, development of a highly efficient electrocatalyst for the counter electrode is extremely important. For counter electrode of QDSSCs, researchers suggest metal free materials for replacing Pt as electrocatalysts. Among the materials, Cu_2S and CuS are found to be as efficient and cost-effective catalysts which are frequently reported in the top category of QDSSCs. However, due to its electrocatalyst activity, CuS is not efficient as counter electrode for reducing polysulfide electrolyte. We reported in our previous work [8] that probability of the electron returning back from polysulfide redox level to CuS valance band is also high which is resulted in increasing recombination rate in the polysulfide/counter electrode interface of QDSSC and the decreasing rate of electrocatalyst activity. It is reported that metal selenides could also be appealing as a novel electrocatalyst for polysulfide reduction in QDSSCs [9]. These materials have high potentials in reduction of polysulfide as compared to CuS [10]. Particularly, Cu_2Se has an excellent electron transport, which makes it efficient for counter electrode in QDSSCs [11]. Thus, in the present study, Cu_2Se counter electrode is used to improve the electron transport and stability of the counter electrode. In this regard, Cu_2Se counter electrode is fabricated using the successive ion layer adsorption and reaction (SILAR) technique, which is further used for synthesis of the QDs in the solar cell. This counter electrode shows satisfactory electrocatalyst activity toward the polysulfide electrolyte.

2. Experimental works

Cu_2Se counter electrode was prepared by SILAR method. For this work, first Se^{2-} solution was prepared using the procedure mentioned in Ref. [12]. To prepare Se^{2-}, SeO_2 was reduced by $NaBH_4$ in ethanol under N_2 atmosphere as follows:

$$SeO_2 + 2NaBH_4 + 6C_2H_5OH \rightarrow Se^{2-} + 2Na^+ + 2B(OC2H5)_3 + 5H_2 + 2H_2O$$

Once $NaBH_4$ was added to an ethanol solution of SeO_2 under N_2 atmosphere, a gradual color change from deep red to transparent was observed, indicating the reduction of SeO_2 to Se^{2-}. Next, Fluorine tin oxide (FTO) substrates were dipped into an aqueous

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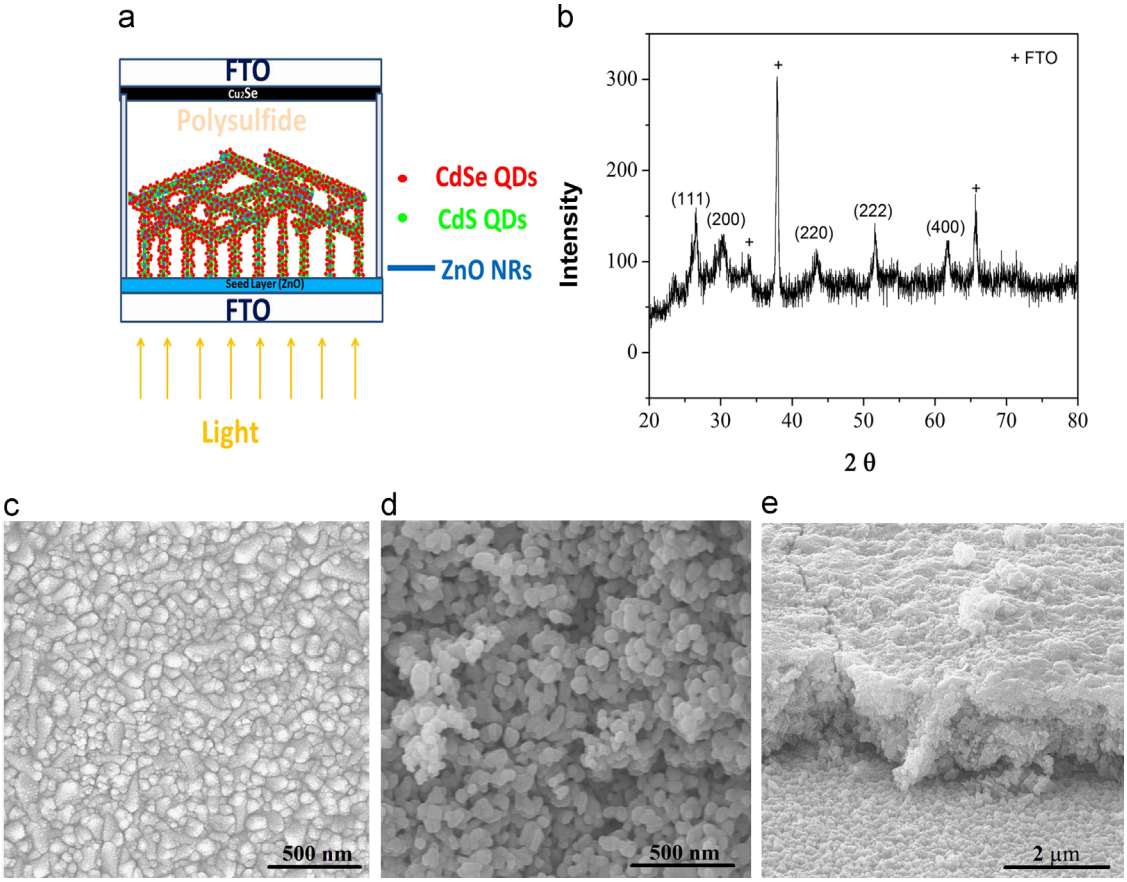

Fig. 1. (a) Schematic of quantum dot sensitized solar cell with Cu_2Se counter electrode. (b) The XRD pattern of Cu_2Se counter electrode. SEM image of: (c) a bare FTO; (d and e) Cu_2Se (five cycles) on the FTO.

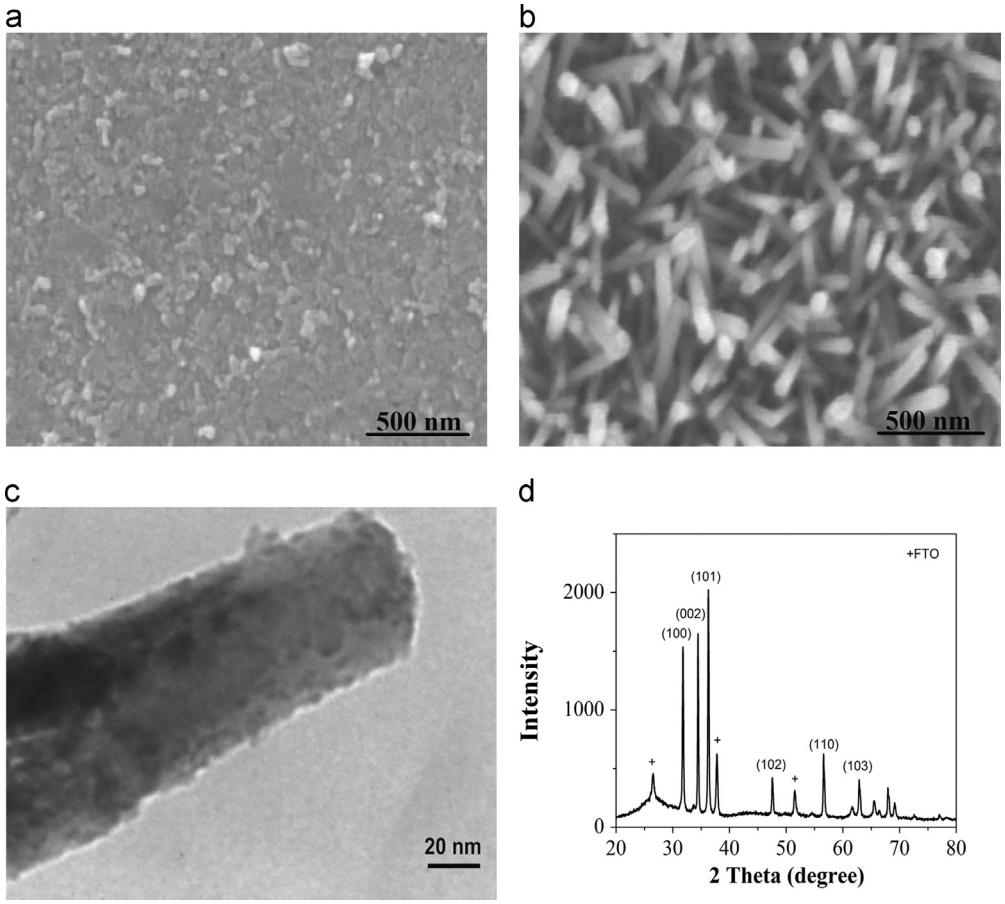

Fig. 2. SEM image of: (a) the ZnO seed layer on the FTO substrate; and (b) ZnO NRs arrays grown on ZnO seed. (c) TEM image of ZnO NRs/CdS/CdSe. (d) The XRD pattern of ZnO NRs.

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