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Investigation on novel CuS/NiS composite counter electrode for hindering charge recombination in quantum dot sensitized solar cells

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ABSTRACT

To make quantum dot-sensitized solar cells (QDSSCs) more attractive, it is necessary for the power conversion efficiency (PCE) to be comparable to those of other emerging solar cells. Currently, copper sulfide (CuS) and nickel sulfide (NiS) are commonly used counter electrodes (CEs) in high-efficiency QDSSCs because of their low toxicity, environmental compatibility, and superior electrocatalytic activity in the presence of polysulfide electrolyte. For the first time, novel CuS/NiS electrodes were prepared by facile chemical bath deposition method. This article describes the effect of NiS layer on CuS film for preventing the recombination process to enhance the performance of QDSSCs. Under one sun illumination, the CE with the optimized CuS/NiS composite film exhibits higher short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and PCE of 12.47 mA cm^{-2}, 0.599 V, and 4.19%, respectively. These values are much higher than those of bare CuS (2.73%), NiS (1.82%), and Pt CEs (1.16%). This enhancement is mainly attributed to the improved surface morphology, higher sulfur atomic percentage with Cu vacancies, rapid electron transport, and lower electron recombination rate for the polysulfide electrolyte. Characterization with, cyclic voltammetry, and Tafel polarization was performed to study the reasons for efficient CE performance.

1. Introduction

In modern society it is possible to observe an everlasting permeation of electron devices and appliances and depletion of fossil fuels force exploration of alternative clean regeneration energy. According to the Koomey's law that the computing efficiency doubles every 1.57 years, encroaching the surge performance of rechargeable energy sources, which is essentially stable. Many researchers see the dye-sensitized solar cells (DSSCs) as one of the ways to deal with the modern requirements of energy and it is extensively considered as a renewable energy technology to harness electricity from solar energy. It is considered as an alternative to conventional solid-state solar cells due to its environmental friendliness, low cost, easy fabrication, and acceptable power conversion efficiency (PCE) [1–3]. In general, a typical DSSC is composed of a dye-sensitized nanocrystalline semiconductor as a photoanode, a redox electrolyte consisting of the I^-/I_3^- redox couple, and a counter electrode (CE) [4]. The bifunctional CE collects electrons from the external circuit and reduces the tri-iodide (I_3^-) ions generated after dye regeneration. To improve conversion efficiency, the CE material should have excellent electrocatalytic properties [5,6]. The conventional platinum (Pt) is deposited on transparent conductive oxide (TCO) substrate due to its superior electrocatalytic activity and electrochemical stability for the I^-/I_3^- redox couple [7–9].

In addition to DSSCs, several approaches have been developed for solar cells such as quantum-dot-sensitized solar cells (QDSSCs), organic solar cells, amorphous, nanocrystalline Si and now perovskite-based meso-super structured solar cells; [10]. However, the perovskite solar cells fabrication procedures make use of high-temperature and/or vacuum based processing and high cost precursor materials limit the commercial success of certain systems [11]. In particular, the QDSSCs promises to deliver one of the lowest cost technologies and greater conversion efficiency that are capable of converting sunlight to electricity. Conversely, QDSSCs shows partial efficiency because of the poor electro-catalytic activity among the electrolyte and the CE compared to challenging systems, for example DSSCs, thin-film-based solar cells, and also perovskite solar cells. The outstanding characteristics of QDs include tunable light-harvesting range, cost-effectiveness, high absorption coefficient, large intrinsic dipole moment, and generation of multiple electron carriers under high energy excitation [12]. Due to the above advantages, the QDSSC is perceived as one of the promising candidates in low-cost third generation solar cells. QDSSCs borrow the concept of DSSCs with the exception that dye molecules replace the inorganic QD absorbers. A typical configuration of QDSSC devices includes a photoanode based on a mesoporous metal oxide (mainly TiO_2) loaded with a sensitizer (mainly CdS, CdSe, SnS, Sb_2S_3 or PbS), an electrolyte

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(the optimal electrolyte for QDSSCs is a polysulfide redox couple (S_n^{2-}/S^{2-})), and a CE.

However, jin wang et al. fabricated with Mn doped QDs on TiO_2 film electrode at room temperature and achieved PCE and FF of 9.40% and 0.655 but the reported PCE of QDSSCs is still far below their theoretical value of 44% and that of DSSCs (12–13%) [13–15]. One of the possible reasons being the narrow absorption range of the quantum dots, especially in the case of CdS QDs, as well as charge recombination at the QD/electrolyte interface [16]. Other possible reasons include inferior optoelectronic properties of QD sensitizers and electron loss occurring through charge recombination at the interface of the counter electrode and electrolyte, which results in a drastic decrement in the short circuit current and open-circuit photo voltage [17–20]. To exploit the potential of QDSSCs and increase the efficiencies, a novel electrocatalytic material for use in CEs is essential.

Pt CEs is suitable electro-catalyst when iodide/triiodide redox electrolyte is used in DSSCs. It exhibits tremendous electrocatalytic activity and low charge transfer resistance (R_{CE}) at the interface of the CE and the electrolyte [21]. However, Pt CEs are unsuitable with the polysulfide electrolyte in QDSSCs because sulfur-containing compounds (S^{2-} or thiol) are preferentially adsorbed and lead to photo corrosion of the QDs. This decreases the surface activity, conversion efficiency, and short lifetimes of the QDSSCs [22]. Recently, various non-Pt-based materials have been reported as CEs to improve the electrocatalytic activity and performance of QDSSCs, such as CoS, NiS, CuS, PbS, hollow carbon, conducting polymer, and carbon-based materials (nanotubes, graphene, and carbon black). Among them, metal sulfide electrodes exhibit higher conversion efficiency (CuS > CoS > NiS), low charge transfer resistance, and superior catalytic activity, but shorter lifetimes because of sulfur corrosion for the redox reaction of polysulfide electrolyte [22–24].

While there are many alternatives, CuS and NiS are the most desired since they are not only cost-effective but also produce high PCE, superior photo and electrocatalytic properties, and conductivity. Even though CuS and NiS are p-type semiconductors, they show mixed ionic and electronic conduction due to the presence of Cu or Ni vacancies. The vacancies contribute to increasing the free holes in the material, which act as electron acceptors that exhibit excessive conductivity. Moreover, Cu_2S and Ni_3S_2 are unstable phases due to the formation of Cu and Ni vacancies, even in thermodynamic equilibrium with bulk copper or nickel metal [25].

Our previous studies have shown that CuS and NiS electrodes can act as the most effective catalytic materials, respectively showing conversion efficiencies of 1.72% and 2.61% in QDSSCs, which are higher than that of cells based on Pt (0.82%) [26,27]. But CuS electrodes show less stability than Pt-based cells because Cu substrate continually reacts with polysulfide electrolyte, which can contaminate the electrolyte and the photoanode [22]. The lower PCE of CuS and NiS CEs are due to the higher charge recombination at the interfaces of photoanode and CE. A promising strategy to reduce charge recombination at the CE/electrolyte interface is to modify the intrinsic properties of CE material is to fabricate composite electrode or metal ion dopants such as Co, Ni and Mn. The composite layer creates new electronic states in the host material, thus alters the recombination dynamics and charge separation. Zusing and co-workers pioneered the concept of CuS/CoS onto fluorine-doped tin oxide glass substrate and pushed the PCE of QDSSCs beyond 4% for the first time. Since then, comprehensive efforts have been paid on the composite material used as a CE in QDSSCs for improving the performance of QDSSCs. To overcome this problem, we fabricated a hybrid CE with a composite of copper sulfide/nickel sulfide (CuS/NiS CE) using a simple chemical bath deposition (CBD) method. The CBD method is the most simple, convenient, and common method for fabricating CEs for large-scale production. Both the photo-electrochemical performance and the catalytic properties of the CuS/NiS CE were much higher than that of bare CuS, NiS, and Pt-based cells. By combining the optimized TiO_2-QD photo electrode and the CuS/NiS CE with polysulfide electrolyte, a power conversion efficiency of 4.19% was achieved under 1 sun illumination, which is attractive for use in QDSSCs.

2. Experimental section

2.1. Materials

For the preparation of the CE and photoanodes, all materials were bought from Sigma-Aldrich and used without further purification. Copper sulfate pentahydrate [$CuSO_4 \cdot 5H_2O$], sodium thiosulfate [$Na_2S_2O_3$], urea [CH_4N_2O], nickel sulfate hexahydrate [$NiSO_4 \cdot 6H_2O$], thioacetamide [CH_3CSNH_2], acetic acid, cadmium acetate dehydrate [$Cd(CH_3COO)_2 \cdot 2H_2O$], sodium sulfide [$Na_2S$], sodium sulfite [$Na_2SO_3$], zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], sulfur [S], selenium powder [99.99%], potassium chloride [KCl], Pt, and TiO_2 paste [Ti-nanoxide HT/SP] were used without further purification.

2.2. Fabrication of TiO_2/CdS/CdSe/ZnS photoanodes

Ultrasonically cleaned FTO substrate was used to prepare the photoanodes and CEs. The commercial TiO_2 paste with 20-nm particle size was coated on a FTO substrate by the doctor blade method (with an active area of 0.27 cm^2). The coated substrate was gradually annealed at 450 °C for 30 min. The total thickness of the TiO_2 film was 7 μm after evaporation of the solvent. Thereafter, the TiO_2 electrodes were sensitized with CdS and CdSe QDs by successive ion layer absorption and reaction (SILAR) technique.

In this method, TiO_2 photoanodes were immersed in an aqueous solution of 0.1 M $Cd(NO_3)_2$ for 5 min, rinsed with DI water and ethanol for 1 min, dipped into an aqueous solution of 0.1 M Na_2S for 5 min, rinsed again with DI water and ethanol, and dried with a drier. The process was repeated for 5 cycles and conducted at room temperature. For the deposition of CdSe, the prepared TiO_2/CdS electrodes were dipped in a aqueous cationic precursor solution of 0.1 M $Cd(NO_3)_2$ for 5 min to allow Cd^{2+} ions to adsorb onto the TiO_2/CdS and then dipped into the aqueous anionic precursor solution of Na_2SeSO_3 for 5 min, where the pre-adsorbed Cd^{2+} ions react with Se^{2-} to form the desired CdSe. This process was conducted at 50 °C and repeated for 8 SILAR cycles. Finally, the TiO_2/CdS/CdSe electrodes were dipped into an aqueous solution containing 0.1 M $Zn(NO_3)_2$ for 5 min and then dipped in a solution of 0.2 M Na_2S for 5 min to form the desired ZnS. The film was rinsed with DI water and ethanol and dried with a drier. The two-step process comprises one SILAR cycle and was repeated two times.

2.3. Preparation of CuS, NiS, CuS/NiS and Pt counter electrodes

For the preparation of CEs, we used the CBD method, which is a simple and convenient method for the deposition of metal sulfide thin films for large-scale production. Prior to the metal sulfide deposition (CuS, NiS, and CuS/NiS), FTO substrates were cleaned with acetone, ethanol, and DI water and dried with hair drier. For the preparation of CuS electrodes, FTO substrates were horizontally dipped into a solution of $CuSO_4 \cdot 5H_2O$ (0.1 M), CH_4N_2O (0.4 M), and thioacetamide (0.4 M), kept in a hot air oven at 65 °C for 2 h, and then cleaned with DI water and ethanol. To fabricate NiS electrodes, FTO substrates were horizontally dipped into a solution containing cationic and anionic precursors of nickel sulfate hexahydrate (0.1 M) and thioacetamide (0.4 M), which act as sources of Ni^{2+} and S^{2-}, respectively. CH_4N_2O (0.8 M) and acetic acid (0.6 M) were used as strong reagents. The prepared solution with FTO substrates was kept in a hot air oven at 90 °C for 90 min.

The CuS/NiS counter electrodes were fabricated through deposition of NiS nanoparticles on the surface of CuS. The as-prepared CuS electrodes were placed horizontally in the aforementioned NiS solution at 90 °C for 90 min. For comparison, the cleaned FTO substrate was coated with commercial Pt paste (Solaronix, Pt catalyst T/SP) by the doctor-