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Facile fabrication of highly efficient carbon nanotube thin film replacing CuS counter electrode with enhanced photovoltaic performance in quantum dot-sensitized solar cells

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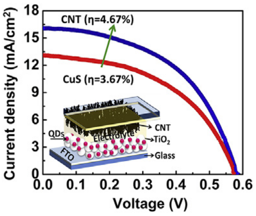
HIGHLIGHTS

- Facile fabrication of CNT electrode and used as highly efficient CE for QDSSC.
- CNT exhibits excellent electrocatalytic activity than CuS and Pt for S^{2-}/S_n^{2-} redox couple.
- The η of QDSSC with CNT CE (4.67%) is higher than CuS (3.67%) and Pt (1.56%).
- The CNT CE shows excellent stability in photoelectric performance.

GRAPHICAL ABSTRACT



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ABSTRACT

An ideal counter electrode (CE), with high electrocatalytic activity, high performance stability, cost-efficient and applicable fabrication simplicity, is necessary to give full play to the advantages of quantum dot-sensitized solar cells (QDSSCs). Herein, we report a facile one-step preparation for carbon nanotubes (CNTs) have been explored as an electrocatalyst and low-cost alternative to platinum (Pt) and cuprous sulfide (CuS) CEs for polysulfide reduction in QDSSCs. QDSSC using this newly prepared CNT as a CE achieves a higher power conversion efficiency of 4.67% than those with a CuS (3.67%) or Pt CE (1.56%). Besides, a preliminary stability test reveals that the new CNT CE exhibits good stability. The results of Tafel polarization and electrochemical impedance spectroscopy measurements revealed that the CNTs had higher electrocatalytic activity for the polysulfide redox reaction and a smaller charge transfer resistance (8.61 Ω) at the CE/electrolyte interface than the CuS (21.87 Ω) and Pt (54.99 Ω) CEs. These results indicate that the CNT CE has superior electrocatalytic activity and can potentially replace CuS and Pt as CEs in QDSSCs. The preparation method of the CNT CE is simple and shows much promise as an efficient, stable, cost-effective and environmentally friendly CE for QDSSCs.

1. Introduction

The rapid increase in the global population, increasing energy demands, and concerns over global warming have led to intensive research on solar cells over the last several decades. Of the various types of solar cells, quantum dots-sensitized solar cells (QDSSCs) are under intense investigation as third-generation solar cells. The structure and the working principle of QDSSCs are similar to those of dye-sensitized solar cells (DSSCs), except QDs replace the organic dyes [1–3]. Compared with organometallic or pure organic dyes, QDs have distinct advantages, such as a high extinction coefficient

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[4], large intrinsic dipole moments [5], the possibility of exploiting multiple exciton generation [6], an adjustable band gap that can tailor optical absorption over a wide wavelength range [7], and facile fabrication processes [8]. Based on these advantages, QDSSCs have been considered to be a promising type of third-generation solar cell. However, despite considerable progress that has been made in recent years and the many advantages, QDSSC performance is still poorer than that of DSSCs and PSCs due to the charge recombination at the QD/electrolyte interface and TiO_2/electrolyte interface and the poor catalytic activity of the counter electrodes (CEs) [2,9,10].

Apart from optimization of the QD photoanodes, more electrocatalytic catalysts as CEs are essential to efficiently reduce S_n^{2-} to S^{2-} for boosting the photovoltaic performance of QDSSCs [11]. In general, the role of the CE in a QDSSC is to collect electrons that flow from an external circuit and to regenerate hole scavengers by catalyzing the reduction of oxidized species in the electrolyte. Platinum (Pt) is a noble metal and is considered to be the best CE material because of its high catalytic activity toward reducing I_3^- ions in DSSCs [12]. In QDSSCs, to minimize the photocorrosion of CdS, CdSe, and CdS/CdSe photoanodes, the I^-/I_3^- redox couple is replaced by the polysulfide redox couple ($S^{2-}/S_n{}^{2-}$). However, the Pt CE has been problematic for catalyzing the polysulfide redox couple since the adsorption of S^{2-} onto the Pt surface can decrease the surface activity of the catalyst. Recently, efforts have been devoted to examining new CE materials for QDSSCs, but they are restricted by the arduous preparation of carbonaceous materials and metal chalcogenides [13–18].

Among the metal sulfides, the Cu_xS CE is most preferred since it not only yields high efficiency [19] but also shows the highest electrocatalytic activity toward reduction of polysulfide species in QDSSCs [20,21]. However, it has been reported that Cu_2S CEs can poison the photoanode, and the brass substrate is continuously corroded by the polysulfide electrolyte, leading to mechanical instability of the electrode and leakage of the electrolyte solution [22]. Development of a new CE is required for further enhancing the power conversion efficiency and stability with a cost-effective and facile process and to render QDSSCs commercially viable.

Carbon nanotubes (CNTs) have attracted much attention due to their characteristics of a highly specific surface, rapid electron transfer, high stability, and excellent electrical and electrocatalytic properties [23,24]. In QDSSCs, CNTs can be used as conducting scaffolds to capture and transfer electrons from the QDs or TiO_2 film to the electrode surface [25,26]. Similarly, CNTs can be used as a CE in DSSCs to reduce the charge transfer resistance at the interface of CE/electrolyte to improve performance and enable long-term stability [27]. Recently, Zeng et al. applied MWCNT films as a CE for a QDSSC by a spraying method [28]. The device exhibited an efficiency of 2.39%, which was increased to 4.60% by the composite MWCNT:CZTSe CE. The blending ratio of MWCNTs and CZTSe in the composite MWCNT:CZTSe CEs plays a critical role in increasing catalytic reaction towards the polysulfide electrolyte and optimizing the solar cells performance. Most of the previous approaches focused on fabrication of composite CNT CEs for improving the solar cell performance. However, to the best of our knowledge, there is no report on the detailed electrocatalytic performance of CNTs as a CE in QDSSCs.

A novel CNT CE has been applied to fabricate CdS/CdSe/ZnS sensitized solar cells. QDSSCs were also prepared using CuS and Pt CEs for comparison. The CNT-based CEs were prepared on FTO glass substrate using CNT paste and the doctor blade method. The as-prepared CE shows good conductivity for fast electron transfer pathways as well as high catalytic activity with large surface area that promote electron exchange at the catalyst–electrolyte interface. Under AM 1.5G simulated solar irradiation (100 mW cm^{-2}), the highly efficient CNT thin film achieved a power conversion efficiency of 4.67% versus 3.67% and 1.56% for the CuS CE and Pt CE, respectively. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were employed to compare the catalytic properties of various CEs. Notably, QDSSC devices with the CNT CE exhibited excellent photovoltaic performance and stability in sulfide/polysulfide electrolyte.

2. Experimental section

2.1. Preparation of CNTs, CuS, and Pt CE

The CNT film was prepared by the doctor blade technique on well-cleaned FTO glass substrates with a sheet resistance of 7 Ω cm^{-2} (Hartford Glass). Prior to fabrication, FTO substrates were cleaned ultrasonically with acetone, ethanol, and distilled water for 10 min each. To prepare a viscous CNT paste, 0.05 g of MWCNTs (purchased from Carbon Nano-Material Technology Co., Ltd.; type: multiwall; diameter: ~20 nm; length: ~5 μm) were placed in a pestle and mortar and smashed softly with 2 mL of ethanol for 10 min. Finally, we added 1 mL of a surfactant (Triton X-100) and 0.5 mL of nitric acid to the mixture and ground it for 10 min. The obtained paste was spread over the FTO substrate by the doctor blade method and heated at 150 °C for 20 min. The as-prepared thin film is the CNT electrode.

All the precursors used for the synthesis were analytical grade and purchased from Sigma-Aldrich. The synthesis was carried out without further purification. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and thioacetamide (C_2H_5NS) were used as sources of copper and sulfur, respectively. The substrate was then immersed vertically against walls into a 25-mL aqueous solution containing cationic and anionic precursors of 0.1 M $CuSO_4 \cdot 5H_2O$ and 1.0 M C_2H_5NS. After adding 0.7 M of acetic acid (CH_3COOH) in drops, the reaction mixture was stirred vigorously for 30 min. The deposition was carried out at a constant temperature of 65 °C for 60 min in a hot air oven. After the deposition, we removed the samples from the oven, rinsed them with water and ethanol, and dried them with a drier. The as-prepared CuS electrode had an active area of ~0.7 cm^2. To fabricate the Pt electrode, the ultrasonically cleaned FTO glass substrate was coated with Pt paste (Pt-catalyst T/SP, Solaronix) using the doctor blade method and annealed at 450 °C in air for 10 min.

2.2. Preparation of CdS/CdSe/ZnS photoanode

The photoanode was synthesized according to the literature with some minor modifications [29]. Commercially available anatase TiO_2 nanoparticle paste (Ti-Nanoxide HT/SP, Solaronix) with 20-nm particle size was directly screen-printed on FTO (0.27 cm^2 active area) by the doctor blade method, followed by annealing at 450 °C for 30 min. The thickness was 7.5 μm after solvent evaporation. The successive ionic layer adsorption and reaction (SILAR) method was used to deposit CdS and CdSe QDs on the TiO_2. The TiO_2 was successively immersed for 5 min each in aqueous solutions of 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ and 0.1 M Na_2S to deposit CdS QDs. This two-step process was repeated up to 5 times. The electrodes were first dipped into an aqueous solution of 0.1 M $Cd(CH_3COO)_2 \cdot 2H_2O$ for 5 min at room temperature and then into a Na_2SeSO_3 solution for 5 min at 50 °C. In eight cycles, the CdSe layer was sequentially deposited on the as-prepared TiO_2/CdS. To cover the ZnS passivation layer, the electrode was dipped alternately into aqueous solutions of 0.1 M $Zn(CH_3COO)_2$ and 0.1 M Na_2S for 2 min each, and the procedure was repeated for two cycles.