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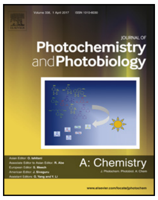

Improved photovoltaic performance of quantum dot-sensitized solar cells based on highly electrocatalytic Ca-doped CuS counter electrodes

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ABSTRACT

Herein we report the fabrication of highly efficient Ca-doped CuS counter electrodes (CEs) in order to modify the photovoltaic characteristics of quantum dot-sensitized solar cells (QDSSCs). CuS CEs with different degrees of Ca doping are deposited on fluorine-doped tin oxide (FTO) coated glass surfaces *via* the widely adopted chemical bath deposition (CBD) method and used directly as CEs for TiO_2/CdS/CdSe/ZnS photoelectrode based QDSSCs. The results indicate that the QDSSCs incorporating 20% Ca-doped CuS CEs exhibit an excellent conversion efficiency (η) of 4.92%, short circuit current density (J_{sc}) of 15.47 mA cm^{-2}, open circuit photovoltage (V_{oc}) of 0.611 V, and fill factor (FF) of 0.521 under illumination of one sun (AM 1.5, 100 mW cm^{-2}). These values are significantly higher than those obtained for QDSSCs incorporating bare CuS CEs (η = 3.51%, J_{sc} = 12.03 mA cm^{-2}, V_{oc} = 0.596 V, FF = 0.490) under similar conditions. The improved surface morphology of Ca-doped CuS materials offers more active sites for the catalytic reactions and an improved pathway for fast charge transport and a lower electron recombination rate for the electrolyte redox couple. The film thickness, elemental composition, crystallographic phase, surface topography, and chemical bond configurations of Ca-doped CuS CEs were characterized by scanning electron microscopy, inductively coupled plasma – atomic emission spectrometry, energy dispersive X-ray analysis, X-ray diffraction, atomic force microscopy, and X-ray photoelectron spectroscopy analysis. More importantly, impedance spectroscopy analysis and Tafel polarization curves indicate that Ca-doping on CuS CEs reduces charge transfer resistance and leads to high and consistent catalytic activity for the reduction of polysulfide electrolyte. This study demonstrates that an appropriate amount of Ca-doping of CuS CEs is an effective method of enhancing the performance of QDSSCs.

1. Introduction

The demand for energy is expected to rise considerably in the coming years as a result of rapid population growth and economic development. Solar energy is one of the most reliable and promising renewable energy sources for handling long-term issues in the energy crisis. Solar energy will play an essential role in global energy production. Therefore, in order to deal with the increasing energy demand, it is necessary to develop environment-friendly alternative energy resources to achieve sustainable global energy development. Currently, the ideal method for the direct transformation of solar energy into electrical energy employs various types of solar cell devices. Quantum dot-sensitized solar cells (QDSSCs) belong to the new-generation photovoltaic devices and have attracted considerable research interest due to their many unique properties, including a wider range of band gap tunability [1], high absorption coefficient [2], solution processability [3], possibility of the formation of multiple electron carriers under high energy excitation [4], large intrinsic dipole moments [5], and direct hot carrier transfer [6]. The device architecture and cell mechanisms of QDSSCs appear to be similar to those of conventional dye-sensitized solar cells (DSSCs) [7,8]. The only difference involves the replacement of organometallic dye molecules with inorganic quantum dots (QDs) as light sensitizers. However, despite the aforementioned advantages, the photovoltaic power conversion efficiency (PCE) of QDSSCs are still significantly lower than those obtained from of DSSCs due to the electron-hole recombination process which occurs at the counter electrode/electrolyte

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interface, the high charge transfer resistance at the photoelectrode/electrolyte interface, and the low coverage of QDs on the active layer [9–12].

In addition to the development of the photoelectrodes, modification and optimization of the counter electrode (CE) materials can significantly enhance the photovoltaic performance of the QDSSCs [13]. CEs in QDSSCs provide an uninterrupted path for the transfer of electrons from the external circuit to the electrolyte and are responsible for the catalytic reduction of redox active electrolytes at the CE/electrolyte interface [14]. An ideal CE exhibits long-term chemical stability and superior conductivity [15–17]. In this respect, highly effective CEs are required for the reduction of S_n^{2-} to nS^{2-} and to thereby improve the performance parameters of the QDSSCs, such as conversion efficiency, fill factor, photocurrent density, and open circuit voltage.

Recently, researchers have developed a large number of CE materials for QDSSCs, including different types of carbonaceous organic materials (mesoporous carbon, nanotubes, and carbon black) [18–20], conductive polymers [21], graphene oxide composites [22], metal nitrides [23], carbides [24], and sulfides [25,26]. Among the available metal sulfide CE materials, copper sulfide (Cu_xS) has been considered the most attractive for incorporation into highly efficient QDSSCs due to its high electronic conductivity, superior electrocatalytic activity towards the reduction of polysulfide electrolyte, and high energy conversion efficiency [27–29]. Furthermore, copper sulfide has a wide variety of applications, such as in molecular imaging [30], photocatalysis [31], rechargeable Li-ion batteries [32,33], biological sensors [34], and microwave shielding coatings [35]. In addition, it is a promising p-type inorganic semiconductor and provides exceptional physical, chemical, optical, and structural properties in photovoltaic applications [36]. CuS CEs suitable for QDSSCs can be fabricated via a number of techniques, such as the hydrothermal method [37], proximal adsorption [38], successive ionic layer adsorption and reaction (SILAR) [39], electrodeposition [40], chemical bath deposition (CBD) [41], and alternating current etching [42]. Among the fabrication techniques, CBD is one of the most widely used and straightforward methods for preparing CuS CEs for efficient QDSSCs. CBD is a convenient method for depositing strongly adhering CuS thin films on high surface area fluorine-doped tin oxide (FTO) substrates at relatively low operating temperatures.

A promising strategy for altering the catalytic activity and electrical conductivity of the metal sulfide CEs is to incorporate alkaline earth metal ion dopants onto the surface of host materials. Furthermore, alkaline earth metal ion substitution favors the forward transfer of electrons at the CE/electrolyte interface. This enhances the photovoltage and energy conversion efficiency of the cell devices. Recently, extensive efforts have been made to develop Ca-doped metal sulfide CEs in order to modify the photoelectrochemical properties of QDSSCs [43,44]. It has been reported that calcium ion dopant plays an essential role in the reduction of electrical resistance and is responsible for the structural transformation of solution-processed thin films [45]. Based on these experimental findings, it may be expected that the introduction of Ca-dopant into CuS CEs would improve the photovoltaic performance of resulting QDSSCs.

Herein we report on the preparation of high-quality Ca-doped CuS thin films on conducting FTO glass plates *via* a simple and effective CBD method, for application as CEs in QDSSCs. A similar observation has also been reported by Dehghani *et al.* using metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) doped graphene sheet/CuS nanocomposite thin films as the CEs in QDSSCs via successive ionic layer adsorption and reaction (SILAR) method, in which a CE with graphene sheet supporting material showed a PCE of 2.73% [46]. Therefore, an extension to that research, a systematic study was undertaken on the effect of Ca-doping on CuS thin films by chemical bath deposition (CBD) method. Afterwards, different structural and electrochemical studies were carried out for bare CuS and Ca-doped CuS CEs. The results obtained by the experiments indicate that Ca-doped CuS CEs prepared by CBD method can effectively reduce the charge transfer resistance at the CE/electrolyte interface and improve the power conversion efficiency of QDSSCs near 5%. The firm deposition of Ca-doped CuS thin films on FTO substrates indicates that the doping with Ca can provide CuS CEs with enhanced catalytic activity and electrical conductivity. After the deposition of Ca-doped CuS particles on FTO substrate, the surface area increases dramatically, thereby providing sufficient active sites for electrocatalytic reaction and accelerating ion diffusion. These results confirm that Ca dopant in CuS CEs provides improved short-circuit current density, photovoltage, fill factor, and consequently improves the conversion efficiency of QDSSCs. The cell based on 20% Ca-doped CuS CE delivered a PCE of 4.92% (with $J_{sc} = 15.47\ mA\ cm^{-2}$, $V_{oc} = 0.611\ V$, FF = 0.521), which can be compared to that of undoped CuS CEs ($\eta = 3.51\%$, $J_{sc} = 12.03\ mA\ cm^{-2}$, $V_{oc} = 0.596\ V$, FF = 0.490).

2. Materials and methods

2.1. Chemicals

Cadmium acetate dihydrate [$Cd(CH_3COO)_2 \cdot 2H_2O$], calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], copper (II) nitrate [$Cu(NO_3)_2$], thioacetamide (C_2H_5NS), sulfur (S), sodium sulfide (Na_2S), and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich. Titanium dioxide (TiO_2) paste (Ti-Nanoxide HT/SP) was purchased from Solaronix, Switzerland. All chemicals were used as received without further purification.

2.2. Synthesis of CuS and Ca-doped CuS counter electrodes

We have implemented a widely used and simple chemical bath deposition (CBD) technique to prepare the CuS and CuS CEs at various concentrations of Ca-doping. For the Ca-doped CuS thin films, $Cu(NO_3)_2$ and C_2H_5NS aqueous solutions were used. These served as Cu^{2+} and S^{2-} sources, respectively while $Ca(NO_3)_2 \cdot 4H_2O$ was used as the doping material. The aqueous CuS solution was prepared by mixing 0.1 M $Cu(NO_3)_2$ with 0.8 M C_2H_5NS in a beaker during magnetic stirring. Subsequently, to add calcium metal ions, different molar percentages of $Ca(NO_3)_2 \cdot 4H_2O$ (10 mM, 20 mM, and 30 mM) is added and stirred briskly to react for approximately 50 min. FTO (2.2 mm thickness, sheet resistance 13 Ωsq^{-2}, Sigma-Aldrich) glass substrates were used for the preparation of photoanodes and counter electrodes. Prior to deposition, FTO conductive glass plates were cleaned using acetone and ethanol solution for 20 min in a sonicator, followed by distilled water for 15 min. The clean FTO glass substrates were subsequently vertically immersed in the growth solution and sintered at 80 °C for 70 min. After deposition, all Ca-doped CuS CEs were thoroughly rinsed several times with distilled water and ethanol to remove any chemical impurities from the surface and subsequently dried with a dryer. For the optimization of CEs, we adopted the same method used by H.J. Kim *et al.* [47]. The temperature range mentioned in their study was relevant for Ca-doped CuS thin film formation but not the time. Unfortunately, at a deposition time of 120 min, CuS thin film begins to peel off from the FTO substrate and couldn't observe any morphological changes. In order to investigate the film growth mechanism, the samples were deposited consistently at different deposition times below 120 min. After the completion of deposition, thin film peel-off was observed at the time more than 70 min. So further experiments were done with Ca-CuS CEs using deposition time of 70 min at 80 °C. The CuS CEs obtained after the incorporation of selected calcium molar