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Cu-doped ZnO nanoporous film for improved performance of CdS/CdSe quantum dot-sensitized solar cells

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ABSTRACT

Copper (Cu) doped zinc oxide (ZnO) powders were synthesized by co-precipitation method with different at% (0 and 0.5 at%) of Cu dopant. Cu-doped ZnO nanoporous (NP) films were fabricated to enhance the performance of the ZnO based cadmium sulfide (CdS) and cadmium selenide (CdSe) quantum dot-sensitized solar cells (QDSSCs). The existence of Cu ions in the Cu-doped ZnO NP film was detected by X-ray fluorescence. The surface morphology, microstructure and crystal structure of Cu-doped ZnO NP films were analyzed by scanning electron microscopy, transmission electron microscopy and X-ray diffraction. The optical property of CdS/CdSe co-sensitized Cu-doped ZnO NP film was studied by UV–vis absorption spectroscopy. The photovoltaic performance and electrical property of Cu-doped ZnO CdS/CdSe QDSSCs were studied by current–voltage characteristic curves and electrochemical impedance spectroscopy under air mass 1.5 condition. As a result, short circuit current density and fill factor increased from 9.074 mA/cm^2 and 0.403 to 9.865 mA/cm^2 and 0.427 respectively, based on the enhanced absorbance and electron transport by Cu-doping. This led to the increasing light conversion efficiency from 2.27% to 2.61%.

1. Introduction

In recent years, quantum dot-sensitized solar cells (QDSSCs) have been considered as a promising approach of photovoltaic devices for the next generation renewable energy [1,2]. Compared to convention silicon solar cells, QDSSCs have attracted much attention because their absorption spectrum can be significantly extended toward infrared region by controlling their band gap [3,4]. Additionally, they have large intrinsic dipole moments, large extinction coefficient, multiple exciton generation effect and direct hot carrier transfer [5–12], which is expected to exceed the 'Shockley–Queisser efficiency limit' (~33%) [13]. Cadmium sulfide (CdS) and cadmium selenide (CdSe) quantum dots (QDs) are widely used as co-sensitizers of the QDSSCs [3,14–19] because of their superior light harvesting and facile charge injection [16,17]. Zinc oxide (ZnO) has many advantages in using CdS/CdSe QDSSCs due to its similar band gap (3.37 eV), higher electron mobility (115–155 cm^2/V·s), chemical stability and possibility of low temperature fabrication [3,16,20–26]. Li et al. reported the high light conversion efficiency of CdS/CdSe QDSSCs (4.463%) by using ZnO nanoparticle photoanodes [16]. However, the overall conversion efficiency of ZnO CdS/CdSe QDSSCs is still low compared to that of TiO_2 CdS/CdSe QDSSCs because its wide band gap narrows solar light response range [20]. Doping is one of the methods used to enhance optical and electrical properties of ZnO, such as absorbance and electron transport, by adjusting the band gap of ZnO [27]. Many studies have attempted to improve the properties of ZnO by doping with transition metals, such as aluminum [28,29], manganese [30,31], tin [32,33], indium [34], and copper (Cu) [20,27,35–37]. Among them, Cu is mostly a preferable dopant due to its abundance and low toxicity. In the fields of photovoltaic devices, light emitting diodes, photocatalyst and gas sensors, Cu-doped ZnO has shown outstanding improvement on electrical, optical, magnetic and photocatalytic performance [27,35,38–40]. Many kinds of doping methods have been widely used such as auto-combustion [41], ball-milling [42], co-precipitation [27,35], sol–gel process [38] and hydrothermal route [43]. Among these methods, co-precipitation is considered the suitable process due to its simplicity, inexpensiveness and low processing temperature condition. In addition, this method leads to good control of morphology, stoichiometry, uniformity and purity [35].

In this study, Cu-doped ZnO powders were synthesized by co-precipitation method with different at% of Cu dopant. Cu-doped ZnO nanoporous (NP) films were fabricated to enhance the performance of the ZnO CdS/CdSe QDSSCs. The surface morphologies, crystal structures, UV–vis absorption spectra, photovoltaic performance and internal resistances were studied to analyze the enhanced optical and electrical properties of the Cu-doped ZnO CdS/CdSe QDSSCs.

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2. Experimental details

2.1. Cu-doped ZnO powders synthesis

Cu-doped ZnO powders with different at% (0 and 0.5 at%) of Cu dopant were synthesized by the co-precipitation method. 0.5 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich) and 0.5 M oxalic acid ($H_2C_2O_4$, Sigma-Aldrich) aqueous solutions were prepared as starting precursors. 0 and 2.5 mM copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, Sigma-Aldrich) was added to the $Zn(NO_3)_2$ solution in accordance with the doping condition. $H_2C_2O_4$ solution was slowly poured into the precursors under vigorous stirring, leading to precipitated materials. The precipitated solutions were washed several times with distilled (DI) water by centrifuging to obtain neutral pure Cu-doped ZnO powders. The washed precipitates were dried at 90 °C for 12 h. Finally, Cu-doped ZnO powders were obtained by sintering dried precipitates at 450 °C for 3 h to remove residual compounds.

2.2. Cu-doped ZnO NP film formation

0.5 g of as-synthesized Cu-doped ZnO powders, 0.025 g of polyethylene glycol ($M_w = 20{,}000$, Junsei Chemical Co.), 0.3 ml of acetylacetone (Fluka) and 1 ml of 4-octylphenol polyethoxylate (Triton X-100, Bio Basic Co.) were added in 5 ml of ethanol to prepare the Cu-doped ZnO NP pastes. These mixtures were thoroughly grounded and blended in an aluminum mortar for 30 min by ball milling process. The mixed solutions were stirred at 60 °C for 1 h, leading to viscous pastes. Fluorine-doped tin oxide (FTO) glasses (7 Ω/sq, Hartford Glass Co. Inc.) were ultrasonically cleaned with acetone, ethanol and DI water. The Cu-doped ZnO NP pastes were deposited on the FTO glasses by doctor blade method with a 0.25 cm^2 active area. The Cu-doped ZnO NP films were formed by sintering at 400 °C for 30 min.

2.3. CdS and CdSe QD sensitization

To sensitize the CdS and CdSe QDs on the Cu-doped ZnO NP films sequentially, successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods were employed, respectively. For the CdS QD sensitization, the Cu-doped ZnO films were immersed in 25 mM cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$, Sigma-Aldrich) aqueous solution for 3 min, following brief rinsing with DI water and ethanol. The same process was carried out in 0.2 M sodium sulfide (Na_2S, Sigma-Aldrich) aqueous solution, following a nitrogen air stream. This procedure is called a one 'SILAR' cycle, and seven SILAR cycles were carried out.

To sensitize the CdSe QDs, 0.1 M selenium powder (Sigma-Aldrich) and 0.2 M sodium sulfite (Na_2SO_3, Sigma-Aldrich) aqueous solution were priorly refluxed at 120 °C for 2 h as a Na_2SeSO_3 solution. The precursor solution was completed by dissolving 25 mM $Cd(CH_3COO)_2$, 3 ml of ammonia (NH_4OH, Sigma-Aldrich) and 10 ml of Na_2SeSO_3 precursor solution in 20 ml of DI water. The CdSe QD sensitization was completed by immersing the CdS sensitized Cu-doped ZnO films in the precursor solution and heated at 90 °C for 45 min, following brief rinsing with DI water and ethanol. Finally, a zinc sulfide (ZnS) passivation layer was formed by two SILAR immersions in 0.2 M $Zn(NO_3)_2$ and 0.2 M Na_2S aqueous solutions.

2.4. QDSSC assembly

The CBD method was employed to fabricate copper sulfide (CuS) counter electrodes (CEs). A precursor solution was prepared by dissolving 1 M thioacetamide (C_2H_5NS, Sigma-Aldrich), 0.1 M $CuSO_4$ and 0.7 M acetic acid (CH_3COOH, Sigma-Aldrich) in DI water. Drilled FTO glasses were dipped in the purified precursor and heated at 60 °C for 30 min, following brief rinsing with DI water and ethanol. A polysulfide electrolyte was prepared by dissolving 2 M Na_2S, 2 M sulfur (Sigma-Aldrich) and 0.2 M potassium chloride (KCl, Sigma-Aldrich) in a mixture of methanol and DI water solution (the mixture ratio of 7:3). Finally, the Cu-doped ZnO CdS/CdSe QDSSCs were completed by assembling the photoanodes and CEs using a hot-melt sealing paper (SX 1170-60, Solaronix) and injecting electrolyte into the hole.

2.5. Measurements

The composition ratios of the Cu-doped ZnO NP films were measured by X-ray fluorescence (XRF, SEA1200VX, Seiko Instruments Inc.). The surface morphologies of the Cu-doped ZnO NP films were observed by scanning electron microscopy (SEM, S-4800, Hitachi). The microstructures of the Cu-doped ZnO nanoparticles were observed by transmission electron microscopy (TEM, JEM-2011, JEOL) operated at 200 kV. The crystal structures of the Cu-doped ZnO NP films were analyzed by X-ray diffraction (XRD, D8 Advance, Bruker Co.) patterns using a Cu K_α source. The absorption spectra of the CdS/CdSe co-sensitized Cu-doped ZnO films were measured by UV–vis spectrophotometry (Optizen 3220UV, Mecasys Co., Ltd.). The photovoltaic characteristics and internal resistances of the Cu-doped ZnO CdS/CdSe QDSSCs were measured under air mass 1.5 condition, corresponding to 1 sun (100 mW/cm^2) using a solar simulator (Model 10500, Abet Technologies). During measurements, all areas of QDSSCs except for the active area were covered with a black mask to avoid overestimation. The photovoltaic characteristics of the QDSSCs were characterized as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (*FF*) and light conversion efficiency (η). The internal resistances of the QDSSCs were characterized by electrochemical impedance spectroscopy (EIS, SP-150, BioLogic Science Instruments). The EIS spectra of the Nyquist diagram were measured with the frequency range from 10 mHz to 500 kHz at room temperature.

3. Results and discussions

Table 1 described the counts and the corresponding composition ratios of zinc (Zn) and Cu components obtained from the XRF analysis. From Table 1, the existence of the Cu component in the Cu-doped ZnO NP film was demonstrated. For the bare ZnO NP film, the counts of the Cu component were 0 (±9.8) cps. This corresponds to composition ratio 0 (±0.02) at%. The counts of the Zn component were 66,520 (±109.7) cps, corresponding to composition ratio 100 (±0.16) at%. On the other hand, the counts of the Cu component were 324 (±13.9) cps in the case of the 0.5 at% Cu-doped ZnO NP film. This corresponds to composition ratio 0.52 (±0.02) at%. The counts of the Zn components were 61,571 (±142.3) cps, which corresponds to composition ratio 99.48 (±0.22) at%. This confirms that the Cu-doped ZnO NP film was fabricated.

Fig. 1 shows the SEM images of the bare and 0.5 at% Cu-doped ZnO NP films. As shown in Fig. 1, the bare and 0.5 at% Cu-doped ZnO NP films were uniformly deposited on the FTO glasses with superior porosity. The diameter of the bare and 0.5 at% Cu-doped ZnO nanoparticles ranged from 70 to 90 nm. The diameter of the 0.5 at% Cu-doped ZnO nanoparticles was almost the same compared to that of the bare ZnO nanoparticles. This indicates that the morphology of ZnO NP films was not affected by the Cu-doping.

Table 1
Counts and corresponding composition ratios of Zn and Cu components in the bare and 0.5 at% Cu-doped ZnO nanoporous films obtained from XRF analysis.

Type	Counts (cps)		Composition ratio (at%)	
	Zn	Cu	Zn	Cu
Bare	66520 (±109.7)	0 (±9.8)	100 (±0.16)	0 (±0.02)
0.5 at% Cu-doped	61571 (±142.3)	324 (±13.9)	99.48 (±0.22)	0.52 (±0.02)