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Full Length Article

Quantum dot sensitized solar cells fabricated by means of a novel inorganic spinel nanoparticle

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ABSTRACT

A novel inorganic spinel compound with formula $Zn_{0.5184}La_{0.7859}Ce_{0.3994}Al_{1.0026}O_4$ (ZLCA) was synthesized by the gel combustion method and its exact formula was approved by the XPS analysis. The TEM image exhibited that the ZLCA NPs were very fine, spherical and slightly agglomerated particles with their particle size changed in the range of ~5–20 nm. Then, several quantum dot-sensitized solar cells (QDSSCs) were fabricated using this new compound which was doped into the TiO_2 pastes of photoanodes and subsequently the CdS, CdS and ZnS layers were deposited on the ZLCA-doped TiO_2 layer by the SILAR and the CBD methods. Results indicated that the photovoltaic parameters of the optimized cell (η = 3.50%, J_{SC} = 11.690 $mA{\cdot}cm^{-2}$) were boosted compared with those of the reference cell which was free of ZLCA NPs (η = 2.14%, J_{SC} = 7.075 $mA{\cdot}cm^{-2}$) indicating rather high improvements of approximately 64 and 65% in the efficiency and short-circuit current density, respectively. The UV–Vis absorption spectra of all nanocomposite photoanodes revealed broad absorption bands between ~320 and 600 nm. The lowest intensity of the photoluminescence peak for the CdSe cell fabricated using 0.6%ZLCA suggested that it had the least charge recombination and the easiest electron transfer which was confirmed by the J-V and efficiency results. The Electrochemical impedance spectra (EIS) illustrated that the charge transfer resistances (R_{CT}) of cells were dropped by addition of the ZLCA into the TiO_2 compared with that of the cell made without using ZLCA NPs. The R_{CT} resistance was 1900 Ω for pure TiO_2 but it was decreased to 81.6 Ω in the optimized cell containing 0.6%wt of ZLCA. Thus, it could be decided that doping 0.6%wt ZLCA was appropriate to attain suitable photocurrent efficiency for the QDSSCs because it was used in a minimum quantity to accelerate the electron transport, decrease the recombination and increase the cell efficiency.

1. Introduction

The requirement to discover renewable energy sources is a necessary task in order to defeat the danger of global warming and emission of greenhouse gases [1–4]. The demand for clean, renewable and low-cost energy by the human society has encouraged the researches to find ways for developing the solar cells [5–7]. Inorganic semiconductors have been considered as ideal next-generation sensitizers because of their bandgap tunability by controlling the absorption coefficient and quantum-dot size. As well, quantum dots can produce more than two electrons from a single photon when be placed exposed to the sun radiation (multiple-carrier generation) [8].

The power conversion efficiency of QDSSCs is lower than that of dye sensitized solar cells (DSSCs) and this is predominantly as a result of the narrow adsorption range of QDs, weak electron collection by the TiO_2 from the QDs, charge recombination at the QD-electrolyte interface, recombination at the counter electrode-electrolyte interface and the difficulty in deposition of a satisfactory large number of QDs on a mesoporous TiO_2 matrix to acquire a well-covered monolayer without aggregation/cluster formation [9]. Another possible reason is the utilization of an instable electrolyte in which metal chalcogenide undergoes severe degradation [10].

Typically, the charge recombination takes place in the structure of solar cells at three possible interfaces including working electrode/electrolyte, quantum-dot-sensitizer/electrolyte, and transparent-conducting oxide/electrolyte [11,12]. Therefore, controlling these interfaces is the key issue for increasing charge collection efficiencies. Among different efforts to improve the photovoltaic properties, the control of interface for reducing the charge recombination and rising the light harvesting ability has proven to be the most impressive investigations [13–15]. In this

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regard, coupling TiO_2 with various semiconductors acting as the photosensitizers has attracted much attention in solar energy utilization [16–18].

It was found that introduction of Mn-ZnS and Mn-ZnSe shell structures in QDSSCs led to high cell performances of 5.17 and 5.67%, respectively, confirming the electron transport and recombination were considerably suppressed compared to those of QDSSCs fabricated using ZnS or Mn-ZnS in solar cells [9]. In another work, Ni^{2+}-doped CdS (CdNiS) QD layer was introduced to a TiO_2 surface in order to create intermediate energy levels in the QDs [10]. It was shown that the Ni^{2+} dopant improved the light absorption of the device, accelerated the electron injection kinetics, reduced the charge recombination and resulted in improved charge transfer and collection so that 15% CdNiS cell displayed the best photovoltaic performance with a power conversion efficiency (η) of 3.11% [10]. Recently, it was stablished that 10 molar% Mn-doped CdS QDSSCs gave $\eta = 2.85\%$ which was higher than the value obtained for bare CdS (2.11%) [19]. Also, the cell device based on the Mn-CdS electrode revealed superior stability in the sulfide/polysulfide electrolyte in a working state for over 10 h [19].

Since electrocatalytic activity and stability of counter electrodes (CEs) play a key factor on the performance of QDSSCs [20], a solution processed method was used to deposit metal sulfides (CoS, NiS, CuS and PbS) on vertically aligned ZnO nanorods as effective CEs in polysulfide electrolyte based QDSSCs [21]. It was indicated that the QDSSC based on ZnO/PbS CE produced $\eta = 4.76\%$ that was much higher than those of QDSSCs made using ZnO/CoS (2.75%), ZnO/NiS (3.12%), ZnO/CuS (4.10%) and Pt (1.54%) CEs [21]. In another investigation, carbon nanotubes were used as CE to fabricate a QDSSC which yielded a higher power conversion efficiency of 4.67% that was higher than those of QDSSCs made by means of CuS (3.67%) and Pt (1.56%) CEs [22]. Recently, combining a PbS nanoparticle catalyst with NiS nanoparticles gave CEs using a simple chemical bath deposition method that were used in CdS/CdSe/ZnS QDSSCs [23]. It was exhibited that the QDSSC obtained using the NiS/PbS CE afforded a higher $\eta = 4.52\%$ compared with that of the cell applying NiS (3.26%), PbS (3.06%) or Pt (1.29%) CEs. Besides, efficiency was not decreased over 10 h under room conditions [23].

Because the TiO_2 band gap is about 3.3 eV, it just can adsorb the light in the ultraviolet (UV) spectral range and this characteristic limits the photovoltaic parameters of quantum dot solar cells (QDSSCs) using TiO_2 photoanodes. Researchers attempt to increase the visible light harvesting capacity of TiO_2 using new inorganic semiconductors as dopants [24–26]. The metal ion doped QDSSCs improve the power conversion efficiency [26–28]. The electronic and photophysical properties of QDs can be modified by doping optically active transition metal ions. Dopants create trap states between the band gaps and control the transfer rates of charge carriers and their recombination in QDs [29–31].

In this work, a novel inorganic spinel semiconductor, i.e. $Zn_{0.5184}La_{0.7859}Ce_{0.3994}Al_{1.0026}O_4$ nanoparticles (ZLCA NPs), were synthesized using the gel combustion technique and doped in the TiO_2 films of QDSSCs photoanodes for achieving higher efficiencies. The ZLCA NPs were added in different amounts (0.2, 0.4, 0.6, 0.8, 1%wt) into the TiO_2 films in order to find the optimum dopant level providing the highest cell efficiency. The next layers which contained CdS, CdSe and ZnS QDs were deposited by successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods. The nanocomposite photoanodes were characterized by TEM, FE-SEM, XPS, UV–Vis, photoluminescence (PL) and electrochemical impedance spectroscopy (EIS) techniques. The current-voltage characteristics of the QDSSCs were evaluated by taking the J-V diagrams. The most appropriate photovoltaic conversion efficiencies were achieved equal to 2.53 and 3.50%, respectively, for the cells fabricated using the TiO_2 + 0.6%ZLCA/CdS/ZnS and TiO_2 + 0.6% ZLCA/CdS/CdSe/ZnS photoanodess indicating nearly 63 and 61% enhancement in the cells efficiencies relative to their related cells made without using the ZLCA NPs. In addition to the increased efficiency, the growing trend in the short-circuit currents were witnessed so that in the optimum cell, the short circuit current ($11.690\ mA{\cdot}cm^{-2}$) was improved by 65% compared with that of the cell without ZLCA NPs ($7.075\ mA{\cdot}cm^{-2}$) which is a significant increase.

2. Experimental

2.1. Materials

The commercially available cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), selenium, aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$), $La((NO_3)_3{\cdot}6H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, trisodium salt, glycerin ($C_3H_8O_3$), ethanol, methanol, acetic acid, sodium sulfide (Na_2S), sodium sulfite ($NaSO_3$), terpineol (anhydrous), ethyl cellulose, sulfur powder, titanium tetrachloride, and sodium hydroxide (NaOH) were obtained from Merck and Sigma-Aldrich companies. TiO_2 powder nanoparticles (P25, Degussa) were obtained from Degussa Company (Germany). The fluorine-doped tin oxide (FTO, $\sim$30 Ω/cm^2, 80% transmittance in the visible region) coated glass conductive substrates and Surlyn spacer were prepared from Solaronix Company.

2.2. Synthesis of $Zn_{0.5184}La_{0.7859}Ce_{0.3994}Al_{1.0026}O_4$ (ZLCA) nanoparticles

The gel combustion method was used for the synthesis of the ZLCA nanoparticles [32]. In brief, an aqueous solution containing $Zn(CH_3COO)_2{\cdot}2H_2O$, $La((NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and glycerine was prepared so that their corresponding molar ratios were 0.5:0.8:0.4:1:20, respectively. The solution was then stirred for 10 h at 80 °C until a gel was formed. After that, the gel was calcined at 700 °C for 8 h under ambient atmosphere in the furnace. A white product was obtained which had a puffy shape that was very easily powdered to ultrafine nanoparticles using a spatula.

2.3. Preparation of the TiO_2 pastes

The TiO_2 paste (that was prepared in our laboratory) was dispersed in ethanol. Then, desired amount of the ZLCA NPs (0.2, 0.4, 0.6, 0.8, 1%wt) was added to the dispersed TiO_2 paste. The mixture was completely homogenized using ultrasonic irradiation. Next, ethanol was evaporated by a rotary evaporator instrument (Heidolph, Germany) and finally a creamy colour paste was remained. The ZLCA-doped TiO_2 film was coated on a transparent conducting FTO glass substrate by the doctor blade technique. Afterward, the film was sintered at 500 °C for 30 min in the furnace.

2.4. Fabrication of QDSSCs

Photoanode and counter electrode FTO glasses were ultrasonically cleaned sequentially in deionized water (DI) and detergent, acetone, and ethanol, each for 15 min. The ZLCA-doped TiO_2 pastes were coated on the FTO glass by the doctor blade method, followed by sintering at 500 °C for 30 min in the furnace. The CdS, CdSe and ZnS QDs layers were deposited on the ZLCA-doped TiO_2 films by SILAR and chemical bath deposition (CBD) methods. For the growth of the first layer, the film was dipped in an ethanol solution containing 0.1 M $Cd(NO_3)_2$ for 1 min as the Cd^{2+} cation source, rinsed with ethanol and dried, after that it was dipped into the 0.5 M Na_2S