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Fabrication of CdS quantum dot sensitized solar cells using nitrogen functionalized CNTs/TiO_2 nanocomposites

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ABSTRACT

Effect of using nitrogen functionalized carbon nanotubes in photoanode materials of quantum dot sensitized solar cells (QDSSCs) was studied. Several SWCNT/TiO_2, MWCNT/TiO_2 and N-doped MWCNT/TiO_2 nanocomposites were prepared including different weight percents (0.25–0.40 wt%) of CNTs to TiO_2. The nanocomposites were applied as the photoanodes of QDSSCs. All photoanodes were fabricated by CdS and ZnS doping using successive ionic layer adsorption and reaction (SILAR) method. The measured optical band gaps of all photoanodes were approximately equal to 2.5 eV. The photoluminescence (PL) spectra of all photoanode nanocomposites illustrated four maxima at around 310, 365, 440 and 535 nm plus two shoulders near 285 and 720 nm which could be assigned to the emission bands of TiO_2, CdS and ZnS nanoparticles (NPs) as well as CNTs. The highest power conversion efficiency (η) was measured under one illumination of sun (AM 1.5, 100 mW/cm^2) for the 0.35% N-MWCNT loaded cell (1.78%) indicating 24.47% increase in the η value relative to that of the cell made up of bare TiO_2 (1.43%). The IPCE of 0.35% N-MWCNT was the greatest (~54% near 450 nm) among other cells containing 0.35% of SWCNT and MWCNT indicating it can convert the most incident light into electrical energy due to the most loading of CdS quantum dots on the N-MWCNT. The electrochemical impedance spectroscopy (EIS) evidenced that the R_s of the photoanode including 0.35%N-MWCNT (23.78 Ω) was smaller than that of the blank photoanode (32.28 Ω) and this was due to the increased charge transfer in the nanocomposite photoanode. Besides, a greater recombination resistance (R_2) was measured for the 0.35% N-MWCNT photoanode (494.2 Ω) compared with that of the bare TiO_2 photoelectrode (206.8 Ω).

1. Introduction

Quantum dot sensitized solar cells (QDSSCs) have gained considerable attention because they are promising toward the development of next generation solar cells. The multi-purpose properties of semiconductor quantum dots including tunability of the bandgap [1], high absorption coefficient, simple synthetic methods [2] and delivery of hot electrons make them attractive candidates for QDSSCs. The design of QDSSCs are similar to DSSCs which includes deposition of a narrow band gap semiconductor on a wide band gap semiconductor such as TiO_2 [3]. The power conversion efficiency (η) of QDSSCs can be improved by optimization of the fill factor (FF), the open circuit potential (V_{OC}) and the short-circuit current (J_{SC}). Improvement of short-circuit current can be accomplished by increasing the light harvesting ability through extending light absorption range and/or QD loading amount [4–9]. Also, facile electron transfer is beneficial to the elevation of electron density on the photoanode and therefore increasing the J_{sc} [10].

Carbon nanotubes with unique properties such as excellent charge transport capability, high surface area and existence of functional groups can be introduced as promising candidates for incorporation in both DSSCs and QDSSCs since they are beneficial to transport the electrons and boost the photocatalytic and photoelectric conversion efficiencies [11–22]. CNTs illustrate electron conductivity similar to that of metals. In a photovoltaic device, electron-hole pairs are generated, consequently CNT can conduct the electrons and collect them. Many studies exhibit that CNTs can significantly improve the short circuit current density and power conversion efficiency of QDSSCs [14]. Yu et al. fabricated DSSCs based on nanocomposites containing different percents of CNTs and TiO_2 hollow sphere nanoparticles and reported a conversion efficiency equal to 4.71% [23]. Sawatsuk et al. found almost 60% improvement in the efficiency of DSSCs using TiO_2/MWCNTs composite electrodes [24]. Golobostanfar et al. synthesized the MWCNT/TiO_2 nanocomposites by sol-gel method and examined their application in DSSCs and QDSCs and revealed that the conversion efficiencies of the cells were enhanced compared with the cells without

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MWCNT [16]. Moreover, Badawi et al. displayed 50% improvement in efficiency of CdSe QDSSCs using SWCNT/TiO_2 nanocomposite photoanodes [14].

It is clear that CNT has a hydrophobic surface, which tends to aggregate and precipitate in water and polar solvents in the absence of functional groups. Indeed, the hydrophobic CNT desires to aggregate; consequently functionalization can make the CNT hydrophilic. So far, many efforts have been made to prepare water-soluble CNTs. The presence of functional groups on CNT gives rise to cation-exchange property which can act also as anchoring agent for metal particles [25]. Furthermore, application of CNTs is appropriate to fabricate QDSSCs as they expose larger areas to solar radiation [13]. Since functionalized CNTs possess greater functional groups, more nanoparticles/quantum dots can be loaded on them [18]. The properties of CNTs can depend on the functional groups decorating their surfaces. Nitrogen doping could alter the electronic structures of carbon atoms, enhancing their chemical stability, surface polarity, electric conductivity and electron-donor characteristics [26,27]. The nitrogen doped carbon materials were used as counter electrodes in the DSSCs and as an anode materials in lithium-ion batteries. As a result, we applied the N-MWCNTs in the photoanode of our QDSSCs with the aim of increasing the efficiency of cells.

In the present work, functionalization of MWCNTs and SWCNTs were performed by acid treatment and nitrogen doping reactions. The CNTs/TiO_2 nanocomposites containing various weight percents of CNTs (0.25, 0.30, 0.35, and 0.40% of N-MWCNTs as well as 0.35% of MWCNTs and SWCNTs) were prepared and applied as photoanode pastes of QDSSCs. All photoanodes were fabricated by CdS and ZnS doping using successive ionic layer adsorption and reaction (SILAR) method and characterized by XRD, FE-SEM, EDS, UV–Vis and Raman techniques. The CuS counter electrodes were also produced using SILAR method. The photovoltaic performances of all QDSSCs were investigated by J–V and IPCE analyses and the results were compared with each other.

2. Experimental

2.1. Materials

The materials including cadmium nitrate tetrahydrate ($Cd(NO_3)_2{\cdot}4H_2O$), ethanol (EtOH), deionized water (DIW), sodium sulfide (Na_2S), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfur powder, zinc (II) acetate dihydrate, copper(II) nitrate trihydrate, cadmium(II) nitrate tetrahydrate, NaOH, ammonia (25% NH_3 in H_2O) were extra pure which were purchased from Sigma-Aldrich and Merck companies and used without further purification. The TiO_2 pastes (20 nm and 400 nm) were purchased from Sharif Solar Company (Sharif University of Technology, Tehran, Iran). The fluorine-doped SnO_2 (FTO, ~30 Ω/cm^2, 80% transmittance in the visible region) coated glass conductive substrates and Surlyn spacer were prepared from Solaronix Company. The single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) were also provided from Sigma-Aldrich Company.

2.2. CNT functionalization

For CNT functionalization, MWCNTs and SWCNTs were subjected to ultrasonic irradiation (Sono Swiss, model SW 12H with 50/60 Hz frequency, 1000 W power and 220–240 V voltage) in concentrated HNO_3 for 15 min. Then, the mixtures were refluxed at 90 °C for 6 h. Next, the oxidized CNTs were washed several times with deionized water and dried at 120 °C. In order to introduce N-containing functional groups, the oxidized MWCNTs were treated at 400 °C for 6 h in a flowing ammonia with a flow rate of 25 SCCM (10 vol% NH_3 in He). Finally, to neutralize the ammonia gas, it was important to use acetic acid solution [28].

2.3. Preparation of TiO_2/CNT nanocomposites

The TiO_2 paste (1 g) was dispersed in 10 mL ethanol, then CNTs (0.25, 0.30, 0.35, 0.40%wt of N-MWCNT, 0.35%wt of MWCNT and 0.35%wt of SWCNT) were added to the dispersed TiO_2 paste. CNTs were completely dispersed using ultrasonic irradiation. Then, ethanol was evaporated by a rotary instrument (Heidolph, Germany). The nanocomposite pastes were coated on transparent conducting FTO glass substrates (precleaned ultrasonically in DIW and EtOH) using the doctor blade technique. Afterward, the films were sintered at 450 °C for 30 min.

2.4. Fabrication of QDSSC electrodes

The photoanode electrodes were prepared by SILAR method in which the 0.1 M cadmium(II) nitrate tetrahydrate in ethanol was used as cation source and 0.1 M sodium sulfide in 1:1 methanol and water as anion source [29]. Each cycle of SILAR consists of successive immersion of the FTO glass electrode, precoated with active nanocomposite CNT/TiO_2 and scattering layer (400 nm TiO_2 paste), in metal ion and sulfide anion solutions for 1 min. Finally, all the working electrodes were coated with 3 cycles of ZnS (zinc(II) acetate dihydrate as Zn^{2+} cation source and sodium sulfide as S^{2-} anion source) in order to cover the CdS quantum dots and to suppress recombination in QDSSCs [30]. The CuS counter electrodes were prepared by 3 cycles of SILAR (each cycle was 30 s). A solution of 1 M sodium sulfide, 1 M sulfur and NaOH dissolved in water was used as the liquid electrolyte. The cells were assembled in sandwich type and sealed by Surlyn spacer. The electrolyte was injected into the cells by evacuation through a predrilled hole which was finally sealed. The active area of the photoanode was 0.25 cm^2.

2.5. Characterization

The UV–vis absorption spectra were obtained on a UV–visible spectrophotometer (Perkin Elmer Lambda 45). The photoluminescence spectra were recorded using Perkin Elmer LS55 instrument. The morphology of the CNTs and photoanodes were examined with a filed-emission scanning electron microscope (FE-SEM) (Sigma-Zeiss, Germany). The chemical composition of the N-MWCNT was examined using an energy dispersive X-ray spectrometer (EDS) analyzer (Oxford Instrument, England). The X-ray diffraction (XRD) patterns were recorded by a Philips analytical X-ray diffractometer (X'Pert MPD) with monochromated Cu-Kα (λ = 1.5406 Å) radiation. The photocurrent-voltage (J–V) characteristic curves were measured using an electerochemical analyzer potentiostat galvanostat (Palmsens) controlled by a computer. The sunlight was produced by a solar simulator at 100 mW/cm^2 (AM 1.5) intensity.

For each kind of QDSCs, three cells with the same CE and photoanode were prepared and evaluated. The need for meaningful performance comparison of different photovoltaic (PV) devices has given rise to efficiency measurements performance under standard solar spectral irradiation and test conditions. The photovoltaic conversion efficiency (η), which is determined from the current versus voltage (I–V) characteristics of an illuminated cell, is typically measured with respect to a standard solar spectrum at a given intensity (100 mW cm^{-2}). For a meaningful and accurate measurement of η, the irradiation is measured with a reference cell whose short-circuit current is calibrated with respect to a standard spectrum. The efficiency of a PV device is normally measured by a solar simulator using the reference cell method where the simulator intensity is adjusted so that the measured short-circuit current of the reference cell is equal to its calibrated value at the standard test intensity (100 mW cm^{-2}). Thus, in our case, the calibration is done with a calibration cell of Thorlabs Company. We put the reference cell in the device and set the certain current of this cell in 100 mW cm^{-2} and the I–V curves of our samples were measured in this