Facile Synthesis of $\text{Zn}_{1-x}\text{Co}_x\text{O}/\text{ZnO}$ Core/Shell Nanostructures and Their Application to Dye-Sensitized Solar Cells

Venkata Manthina^{a,b}, Alexander G. Agrios^{a,b}

^a Department of Civil & Environmental Engineering, University of Connecticut, 261 Glenbrook Rd Unit 2037, Storrs, CT 06269, USA

^b Center for Clean Energy Engineering, University of Connecticut, 44 Weaver Rd, Storrs, CT 06269-5233, USA

Abstract

Heterostructures consisting of Co-doped ZnO nanorod cores encased in an undoped ZnO shell were successfully synthesized to serve as photoanodes for dye-sensitized solar cells (DSSCs) by a two-step chemical bath deposition (CBD) technique. This yields a highly favorable structure in which electrons injected from the dye into the ZnO then step down in energy into the Co-doped core, where the electron is transported to the collector while the ZnO shell acts as a barrier to recombination with the electrolyte. Incorporation of the core/shell structures into DSSCs resulted in large improvements in photocurrent and photovoltage in comparison to pure ZnO nanorod-based DSSCs. SEM and XRD characterization indicate incorporation of the Co^{2+} into the ZnO matrix, without separation of the Co into other phases, providing no energy barriers. In addition, the ability of these heterostructures to reduce recombination rates in redox couples with fast recombination rates was probed by comparing DSSC device performance in both iodide/triiodide-based and ferrocene/ferrocenium-based electrolytes.

Keywords: core-shell nanocomposites, Co doped ZnO, band edge, dye sensitized solar cells, ferrocene/ferrocenium electrolyte, photoanode

1. Introduction

Dye sensitized solar cells (DSSCs) [1, 2] are low-cost alternatives to silicon photovoltaics. The conventional DSSC consists of two sandwiched pieces of conducting glass, one of them coated with mesoporous layer of nanoparticulate TiO_2 with a self-assembled monolayer of chemisorbed dye molecules, filled with an electrolyte for dye regeneration. The dye is a transition metal complex or organic chromophore that harvests sunlight by absorbing strongly in visible region of the solar spectrum. The principal photovoltaic losses in the DSSCs are due to incomplete light harvesting, recombination of the photoinjected electrons with the electrolyte[3] and the overpotential required for dye regeneration.

ZnO , TiO_2 and SnO_2 nanoparticles are commonly used photoanode materials in DSSCs [4-8], while platinum and carbon based materials are used as the counter electrode [9, 10]. In a 10 μm thick nanoparticulate film an electron visits about 10^6 nanoparticles on average before reaching the FTO surface[11]. This long walk gives ample opportunity for the electron to recombine with the dissolved redox species, decreasing the efficiency of the DSSC. One dimensional ZnO nanorods are promising alternative to nanoparticulate film due to fast electron transport and decreased recombination[12]. ZnO/TiO_2 core/shell nanostructures have been synthesized for fast electron transport and high surface area, but there exists an energy barrier between the ZnO and TiO_2 . [13] Chemical bath deposition (CBD) is frequently used for the synthesis of ZnO nanorods[14-18] due to its low cost, low temperature[19], ease of doping[20], environmental friendliness, and suitability for large area applications.

We previously reported cobalt doped ZnO nanostructures synthesized by chemical bath deposition and applied in DSSCs as the photoanode[21]. Doping ZnO with Co^{2+} has been shown to reduce its bandgap, and our photoelectrochemical characterization indicated a 0.1 V positive

shift in the conduction band edge potential of the Co-doped ZnO compared to pure ZnO. We also found that the cobalt doped ZnO nanorods reduced the transport time, which agrees with literature reports that cobalt-doped ZnO nanorods have a higher electron mobility of $75 \text{ cm}^2/\text{V-s}$ when compared to $8.85 \text{ cm}^2/\text{V-s}$ for ZnO[22, 23]. In order to improve the efficiency of the CoZnO based DSSCs we added a protective layer of ZnO on the Co-doped ZnO to improve the stability of the nanorods and form an energetically favorable heterostructure (shown in Figure 1).

In this report, the morphology evolution of the ZnO coated on the ZnCoO nanorod and its effect on the performance of the DSSCs were followed by varying the reaction time during the shell deposition by CBD. The optimum thickness of the shell was evaluated based on the photocurrent density. The results show that the compact ZnO shell can effectively relay photogenerated electrons from the excited dye molecules to the conduction band of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$, suppressing recombination of the injected electrons with the redox couple in the electrolyte. The effect of the ZnO shell deposition time on the performance of the CoZnO nanorods was also studied.

Incorporation of the core/shell nanostructures into the DSSCs resulted in large improvements in photocurrent and photovoltage in comparison to the pure ZnO nanorod-based DSSCs. In addition, device performance of DSSCs based on these films has been compared using a standard iodide/triiodide electrolyte versus ferrocene/ferrocenium as a model alternative redox couple with fast recombination kinetics, to probe the potential for heterostructures of this type to cope with such redox couples by reducing recombination rates.

Figure 1. Schematic of Core-shell (CS) nanostructures.

2. Experimental

2.1 Reagents and Materials

Zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), cobalt nitrate hexahydrate, polyethyleneimine and ethanol were purchased from Sigma-Aldrich (USA) and were ACS grade. N719 was purchased from Dyesol (Australia). SnO_2 : F glass (FTO, transmission > 80% in the visible spectrum; sheet resistance $8 \Omega / \square$) was purchased from Hartford Tec Glass (USA).

2.2 ZnO Core-Shell synthesis

First ZnO seeds were prepared, the formation of ZnO seeds began with the dissolution of 5 mM zinc acetate dihydrate in ethanol by stirring for 3 hours at room temperature[24]. Deionized water is added to the seed solution for increasing the size of the ZnO seeds as described in our previous reports[14]. The ZnO seeds were deposited on a precleaned FTO substrate using drop coating technique followed by sintering in air at 350°C for 30 minutes. ZnO nanorods were

grown from the ZnO seeds by chemical bath deposition. Undoped ZnO nanorods were grown by placing seeded FTO substrates in an aqueous solution of 50 mM zinc nitrate hexahydrate, 50mM hexamethylenetetramine and 6mM polyethyleneimine in a 100-ml glass bottle at 90°C for 24 hours. The precursor solution was stirred for at least 30 minutes. Cobalt-doped zinc oxide ($\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$) nanorods were made in the same way but using 45 mM zinc nitrate hexahydrate and 5 mM cobalt nitrate hexahydrate, with other components unchanged.

ZnO shell is grown on $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods by chemical bath deposition. FTO substrates with $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods were placed in an aqueous solution of 50 mM zinc nitrate hexahydrate and hexamethylenetetramine and 6mM polyethyleneimine in a 100-mL glass bottle at 90°C for 3 hours.

All the samples were rinsed in ethanol after the deposition and sintered at 500°C for 1 hour to remove any organics deposited during the chemical bath deposition process.

2.3 Solar Cell Assembly

After sintering, films were allowed to cool to 100°C then immediately immersed in 0.3 mM N719 in ethanol. After 12 hours they were removed and rinsed in acetonitrile and dried in air.

Each sensitized electrode was sealed against a counter electrode on a hot plate at 120°C using a hot-melt plastic frame (Solaronix, Meltonix 1170, 25 μm thick), applying light pressure with a glass rod. The assembled cell was filled with electrolyte through two holes in the counter electrode. The holes were then sealed using hot-melt plastic and a thin glass cover slide. The exposed conducting glass leads of each electrode were coated with copper tape (3M) for improved electrical conductivity. Minimal electrolyte recipes were used to exclude complications due to interactions with the various additives that are commonly used. Iodide/triiodide (I^-/I_3^-) electrolyte was prepared with 0.5 M tetrabutylammonium iodide and 0.05

M iodine (I_2) in 3-methoxypropionitrile. The ferrocene/ferrocenium (Fc/Fc^+) electrolyte contained 0.1 M ferrocene and 0.05 M ferrocenium hexafluorophosphate (Aldrich) in 3-methoxypropionitrile. The Fc/Fc^+ electrolyte was prepared fresh and deoxygenated by bubbling nitrogen 10 minutes prior to cell fabrication to minimize reaction of ferrocene with oxygen. In general, up to 3 devices were fabricated for each experimental variable change in order to make the deviation statistics.

2.4 Solar Cell Characterization

Current–voltage (J – V) measurements were made using Keithley 2400 source/meter controlled by a PC, while irradiating at 100 mW/cm^2 (1 sun) with AM 1.5G simulated sunlight produced by a solar simulator (Newport 91160), calibrated against a silicon reference cell with KG5 filter (PV Measurements, Inc., Boulder, CO). The DSSC active area was 1 cm^2 . Measurements of electron transport time and lifetime were made using transient decay of square wave modulation of the white light LED as described previously[13]. Briefly National instruments components in a PXIe chassis high-resolution analog voltage output and digitized input was used to apply square wave modulation to the white LED light which was illuminated on the DSSC. The modulating frequency is maintained from 0 to 100 kHz. At least 50 transients were averaged to reduce the noise in measurements. The photovoltage decay follows a pseudo single exponential decay. The recombination rate constant is extracted from the slope of the semi-logarithmic plot. As the recombination reaction follows first order reaction the electron lifetime is given by $K_{\text{rec}} = 1/\tau_n$ where K_{rec} is the recombination is rate constant and τ_n is the electron lifetime The experiments were also performed in short circuit condition monitoring the photocurrent decay and the time constant extracted is the electron transport time (τ_r).

2.5 Materials Characterization

The morphology of CoZnO nanorods was investigated by scanning electron microscopy (FEI Quanta FEG250 SEM in High vacuum mode) attached with Energy dispersive X-ray spectroscopy (EDS). Crystal phase was characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 0.154178$ nm) at a scanning rate of $0.04^\circ \text{ s}^{-1}$ in the 2θ range from 10° to 90° . The thickness of the shell was analysed by measuring the change in the diameter of the nanorods after the deposition of the shell using SEM.

3. Results and discussion

3.1 $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods

The cobalt doped ZnO nanorods (shown in Figure 2) were previously reported to have an average diameter of 1100 nm and length of 6 μm , with no extraneous peaks visible by XRD, and EDS analysis indicating 8 at% substitution of Zn by Co[21]. The average diameter of the ZnO nanorods synthesized was 800-900 nm and length of 5 μm .

Figure 2. SEM image of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods (a) Top view and (b) Cross-section.

Core-shell (CS) nanostructures of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ -ZnO have been synthesized to reduce the recombination and take advantage of the fast electron transport of the cobalt doped ZnO. For an ideal core-shell nanostructure to block recombination, the conduction band edge of the shell material should have potential a more negative than that of the core material, and more positive than the LUMO of the dye to allow efficient electron injection. Complete coverage of the shells is needed for reducing recombination. Figure 3 shows the evolution of the ZnO shell grown on $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods over 3 hours of deposition. Initial growth of ZnO coats the tip and edges. After 3 hours, uniform coverage of the nanorod by ZnO is obtained. The thickness of the shell deposited after 3 hours of deposition was 50 nm analyzed using SEM.

Figure 3. Cobalt doped ZnO nanorods after (a) 1 h and (b) 3 h of ZnO shell growth.

Figure 4. Normalized XRD pattern of cobalt doped ZnO nanorods and pure ZnO nanorods. Peaks are indexed to the ZnO wurtzite structure; peaks assigned to FTO are marked 'F'.

Figure 4 shows the XRD pattern of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods and ZnO nanorods. The peaks of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods are indexed as hexagonal wurtzite ZnO structure with no other phase. The strong peak at (002) indicates the nanorods are oriented perpendicular to the FTO substrate surface, which indicates the nanorods grow preferentially along the *c*-axis. Sharp XRD peaks indicates high degree of crystallization which is expected from the hexagonal shape of the nanorods shown in Figure 2. No shift in the (002) peak of the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods was observed indicating that there is no distortion of the ZnO lattice. The intensity of the (002) peak increased after doping the ZnO nanorods with cobalt, due to increase in crystallite size[25]. The diameter of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods is larger than that of ZnO, which implies that the radial growth rate on the (002) plane is enhanced by the Co doping[26], which is consistent with SEM images showing the larger average diameter of $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ nanorods.

3.2 Kinetic Measurements

Time constants for electron transport (τ_{tr}) and electron lifetime (τ_n) were measured based on photocurrent and photovoltage transients, respectively, for complete solar cell devices subjected to LED illumination with a square-wave intensity modulation. Values of τ_n , which are characteristic times for the recombination of electrons in the semiconductor with the dissolved redox couple in the electrolyte, are shown in Figure 5 a. For voltages above 0.5 V, which includes what would be the operating range of a DSSC device based on these materials, the electron lifetime pure ZnO nanorods is improved by doping with Co, and there is an additional slight improvement of τ_n after chemical bath deposition of the ZnO shell.

Figure 5. Time constants for DSSC devices in I^-/I_3^- electrolyte comparing three nanostructures: (a) electron lifetime versus open circuit photovoltage, and (b) electron transport time versus short-circuit current

Time constants for electron transport are shown in Figure 5b. The electron transport occurs in the core of the ZnO nanorods.[27, 28] Given that τ_{tr} can typically span multiple orders of magnitude, the values shown here are quite close between samples and over the range of light intensities (and therefore J_{sc}) that were measured. This may indicate that the measurement is limited by the RC time constant of the nanorods, obscuring any real differences between them[13].

3.3 Device Performance

In Figure 6, DSSC devices made from different nanomaterials are compared under standard AM1.5 1 sun illumination. In I^-/I_3^- electrolyte (Figure 6a), where recombination rates overall are relatively low, the differences in short-circuit current (J_{sc}) are attributable to the differences in surface area between the different nanorods, and the different dye loadings that would result. Specifically, the $Zn_{0.9}Co_{0.1}O$ rods are wider (1100nm) and longer (6 μm) than the ZnO rods (diameter of 900nm and length 5 μm),[21] and adding a ZnO shell to the $Zn_{0.9}Co_{0.1}O$ rods will

make them slightly larger. The low photocurrents observed compared to typical TiO_2 nanoparticle-based DSSCs are due to two factors: (1) slower electron injection[5] into ZnO due to its relatively high dielectric constant[29] and (2) lower roughness factor (ratio of total surface area to projected surface area) for the nanorods by more than an order of magnitude. The decreased open-circuit voltage (V_{OC}) after cobalt doping can be ascribed to the positive shift in the conduction band edge[21].

Figure 6. I-V Measurements Core-Shell nanostructures with ZnO shell in (a) I^-/I_3^- electrolyte (b) Fc/Fc^+ electrolyte.

The differences in performance become more drastic when comparing the same nanomaterials in the extreme conditions of a Fc/Fc^+ electrolyte (Figure 6b), where the high semiconductor–electrolyte recombination rates dominate overall losses and exaggerate the performance effects of recombination differences between different materials. Particularly notable is the 35% increase in J_{SC} when $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ rods are coated with the ZnO shell. As will be discussed more below, we attribute this effect to the lowered conduction band edge in $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ compared to ZnO, which causes most electron transport to occur through the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ core, while the ZnO acts as an insulating shell between the core and the electrolyte (see Figure 7). Therefore the improved photocurrent is due less to inherent differences in recombination rates and more to the structure’s tendency to separate the electrolyte from the region of high electron density in the semiconductor. This structural effect is less important at open circuit, where at steady-state all injected electrons must recombine, and none are extracted through the doped core. Therefore the difference in V_{OC} between the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$ rods and the $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}/\text{ZnO}$ core/shell nanorods is small. The much lower V_{OC} for the pure ZnO nanorods is in spite of that material’s more negative conduction band and can only be explained by a significantly higher rate of electron recombination with the Fc/Fc^+ electrolyte than either of the other materials. This illustrates how the small difference in recombination rates (measured in Γ/I_3^- , in Figure 5a) has an exaggerated effect in Fc/Fc^+ that overwhelms the difference in conduction band energy level.

Figure 7. Band diagram of the core-shell nanostructures

3.4 Effect of ZnO Shell Thickness

The thickness of the ZnO shell was varied from 50 to 200 nm by changing the shell growth time from 3 hrs to 6 hrs for analyzing the ideal shell thickness. In I^-/I_3^- electrolyte (Figure 8a), CS structures with 50 nm thickness performed better than those with 100 nm, whereas CS structures with 100 nm thick shells performed better in Fc/Fc^+ electrolyte (Figure 8b). In Fc/Fc^+ , with fast recombination, complete coverage of the core is critical, as exposed $\text{Co}_{0.1}\text{Zn}_{0.9}\text{O}$ results in rapid recombination and a decreased photocurrent. The reason for the poor performance of the 200 nm thickness ZnO shell DSSC in both I^-/I_3^- and Fc/Fc^+ electrolyte is the longer distance the electrons have to travel before recombining with the electrolyte. An optimized ZnO shell thickness can enhance efficiency by providing an effective balance between injection and recombination. The

shell must provide coverage of the core and separation between the core and the electrolyte while being thin enough that injected charges transfer rapidly to the core.

Figure 8. . Effect of ZnO shell thickness on the performance of the core-shell DSSC in (a) I-/I₃⁻ and (b) Fc/Fc⁺ electrolyte. Numbers in parentheses are the time of ZnO shell deposition in hours.

4. Conclusions

Core-shell nanostructures of cobalt-doped ZnO with a ZnO shell were synthesized using low temperature chemical bath deposition. Co-doped ZnO nanorods have a more positive conduction band edge potential and longer electron lifetimes under working conditions than pure ZnO nanorods. The core-shell structure allows electrons to travel through the Co-doped core while the ZnO shell insulates the core from the electrolyte. In DSSC devices with a fast recombining Fc/Fc⁺ electrolyte, this core-shell structure results in higher open-circuit voltage and much higher open-circuit current than either pure ZnO nanorods or Co-doped ZnO nanorods without the shell. The low cost, green, simple and single pot chemical bath deposition of the CS nanostructures is an added advantage of the present approach, which points to ways to improve DSSC performance when using electrolytes with faster recombination than I⁻/I₃⁻.

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