Band edge engineering of composite photoanodes for 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 3037, Storrs, CT 06269, USA*
[b] *Center for Clean Energy Engineering, University of Connecticut, 44 Weaver Rd, Storrs, CT 06269, USA*

A B S T R A C T

As dye-sensitized solar cells (DSSCs) transition from iodide/triiodide-based electrolytes to organometallic complex redox couples with higher rates of recombination with electrons in the semiconductor, there is a need for semiconductor nanostructures that can rapidly transport electrons out of the device while maintaining high surface areas for the semiconductor/dye/electrolyte interface. A previously reported composite, with TiO_2 nanoparticles coating ZnO nanorods, met these criteria but suffered from a barrier to electron transfer from the TiO_2 to the ZnO. Here, the band edge positions of the TiO_2 and ZnO have been shifted by doping with Zr^{4+} and Co^{2+}, respectively, to arrive at the desired energetic alignment. The materials were characterized using diffuse-reflectance spectroscopy and a three-electrode measurement of the open circuit photovoltage under bandgap excitation (OCV). The OCV measurement indicated that the doping moved the conduction band minimum of ZnO to a more positive potential than that of the TiO_2, enabling electron transfer from dye-sensitized TiO_2 nanoparticles to the underlying ZnO nanorods for efficient charge collection. However, DSSC devices fabricated with the composite nanostructures did not show improved performance. This paper details a methodology for producing and measuring band-edge shifts along with the benefits and limitations thereof.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

One-dimensional nanostructured metal oxides are promising materials for applications such as dye sensitized solar cells [1,2] (DSSCs) and water splitting [3] where rapid electron transport and high interfacial area are needed. This becomes especially important as DSSCs move away from iodide/triiodide-based electrolytes and toward redox couples, such as cobalt(II/III) [4] or ferrocene/ferrocenium (Fc/Fc⁺), [5] that have faster rates of recombination with electrons in the photoanode, necessitating fast electron transport out of the photoanode for efficient charge collection. ZnO has been found particularly useful in DSSCs [1,6–9] since it can be grown in 1-D morphologies using facile methods and has other favorable material properties such as a high electron mobility and appropriate band edge positions.

The major drawbacks of ZnO nanorods in DSSCs, as compared to the standard TiO_2 nanoparticle film [10], are a reduced surface area and reactions with carboxylic dyes resulting in partial dissolution of the surface. Some ZnO–TiO_2 and ZnO–ZnO composite nanostructures have been proposed to address one or both of these

problems [11–15], but in our own composite of ZnO nanorods coated with TiO_2 nanoaparticles, we reported evidence of an energy barrier preventing electron injection from TiO_2 nanoparticles to ZnO nanorods, hindering charge collection [16]. For an efficient core-shell photoanode, the conduction band minimum (CBM) potential of the shell material must be more negative than that of the core material (but more positive than the dye LUMO level). Achieving this condition requires raising the CBM energy of the TiO_2 and/or lowering the CBM energy of the ZnO, as depicted in Fig. 1.

A number of transition metal dopants have been incorporated into metal oxide semiconductors to change their optical and photoelectrochemical properties [17–20]. In particular, previous reports have shown that Co^{2+} can substitute for Zn^{2+} atoms in ZnO, causing the lattice cell to contract due to the slightly smaller Shannon crystal radius of Co^{2+} (0.72 Å) compared to Zn^{2+} (0.74 Å) in the wurtzite structure, resulting in a smaller bandgap [21–23]. In TiO_2, there are multiple reports that Zr^{4+} substitution of some Ti^{4+} atoms results in an increased bandgap [24–27]. If the O 2p orbitals remain largely unchanged, keeping the valence band maximum (VBM) potential constant, the altered bandgap corresponds mainly to a CBM shift.

We have doped the ZnO with cobalt to lower its CBM energy and doped TiO_2 with zirconium to raise its CBM energy. In this report

---

Fig. 1. Schematic of band edge engineering to overcome barrier to electron transfer from TiO_2 to ZnO.

we will discuss the effect of doping on those band potentials and on performance of the DSSCs in two different electrolytes: one containing the standard iodide/triiodide couple and one with the fast recombining Fc/Fc^+ couple.

2. Experimental

2.1. Reagents and Materials

All chemicals were purchased from Sigma-Aldrich and were ACS grade or better, except where noted. N719 dye was purchased from Dyesol (Australia). Fluorine-doped tin oxide glass (FTO, sheet resistance $8\,\Omega\,/\square$) was purchased from Hartford Glass Co (USA).

2.2. Electrode Fabrication

ZnO nanorods were synthesized by a two-step chemical bath deposition (CBD) technique, then coated with TiO_2 nanoparticles by electrostatic layer-by-layer deposition, as previously reported [28]. The ethanolic ZnO seed layer precursor solution was modified by the addition of $0.6\,M\,H_2O$ to increase the spacing between the nanorods [29]. Doping ZnO with Co^{2+} and TiO_2 with Zr^{4+} was achieved by substituting 10 mol% of the zinc nitrate with cobalt(II) nitrate and 5 or 10 mol% of titanium tetraisopropoxide with zirconium tetraisopropoxide, respectively.

2.3. Surface/Structure Characterization

Scanning electron microscopy (SEM) of the nanomaterials on FTO glass was performed using an FEI Quanta FEG250 SEM in high vacuum mode. Elemental analysis of the doped and undoped ZnO and TiO_2 was made using the EDX attached to the SEM. The ZnO nanorods and TiO_2 nanoparticles were additionally characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154178$ nm) at a scanning rate of $0.04°\,s^{-1}$ in the 2θ range from $10°$ to $90°$.

2.4. Optical Characterization

The UV–vis spectra of doped and undoped TiO_2 and ZnO were obtained by using Cary 50 UV–vis spectrophotometer. The diffuse reflectance spectra were obtained using a Shimadzu 2450 UV–vis spectrophotometer with an ISR-240A integrating sphere attachment with barium sulfate as the standard.

2.5. Photoelectrochemical Characterization

Illuminated open circuit photovoltage (OCV) was measured to find the flat band potential of each semiconductor in solution. A

ZnO nanorod array or TiO_2 nanoparticle film on FTO glass was immersed in a three-electrode electrochemical cell and served as the working electrode, along with a Ag/AgCl reference electrode and Pt wire counter electrode. The electrolyte was aqueous 0.1 M $LiClO_4$ basified to pH 11 with NaOH. The working electrode was illuminated from the back (non-conducting) side with a 300-W Xe arc lamp (Oriel). The cell open-circuit voltage was monitored as a shutter kept the sample dark for 30 s, then illuminated for 60 s, then dark for 60 s. To avoid reaction of photogenerated electrons with dissolved oxygen in the electrolyte, the solution was purged with nitrogen gas for 10 minutes before measurement. According to data from the manufacturer, the lamp outputs about 100 mW in the spectral region between the bandgap edge of ZnO (370 nm) and the cutoff of FTO transmission (350 nm); this is the power available for bandgap excitation of ZnO, with somewhat more available for TiO_2 (with a bandgap edge of 385 nm). Focused onto a 1 cm^2 area, for either semiconductor this was judged to be more than enough UV intensity to achieve a saturation condition in which the bands flatten and the Fermi level (measured as the working electrode potential) is close to that of the conduction band edge potential [30].

2.6. 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 h 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.

2.7. Electrolyte Composition

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 in 3-methoxypropionitrile and was deoxygenated by bubbling nitrogen for 10 minutes prior to cell fabrication to minimize reaction of ferreocene with oxygen [5,31]. Additives such as 4-tert-butylpyridine were avoided to minimize complications arising from band-edge energy shifts.

2.8. Solar Cell Characterization

Current-voltage (J–V) measurements were made using a Keithley 2400 source/meter controlled by a PC, while irradiating at 1000 W/m^2 with AM 1.5G simulated sunlight produced by a solar simulator (Newport 91160). The DSSC photocurrent and photovoltage were measured with an active area of 1 cm^2.

2.9. Transient Measurements

Measurements of electron transport time were made using transient decay of photocurrent under square wave modulation of a white light LED as described previously except with a 40-Ω resistor [16]. Electron lifetime was measured in a similar way using the photovoltage transient at open circuit. At least 50 transients were averaged for noise reduction.