Electrochemical and Optical Studies of Electronic and Photovoltaic Properties of Metal Oxide and Sulfide Semiconductor Nanomaterials

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In a continuing effort to develop photovoltaic devices based on nanocrystalline metal oxides, we have characterized poly(3-undecyl-2,2'-bithiophene) in TiO_2 solar cells both electrochemically and optically. An onset oxidation potential of the polythiophene was found to be 0.8V (vs. Ag|AgCl|sat KCl), which yielded a HOMO at 1.0 V vs. NHE. A bandgap of 2.04 eV was determined and yielded a LUMO of -1.04 V vs. NHE making electron injection to TiO_2 possible upon light absorption. Three different TiO_2 layers were tested to determine the dependence of TiO_2 morphology on photovoltaic performance. Titania film morphology plays an important role in photovoltaic performance with polythiophene as sensitizer and hole conductor. Short circuit current density in nanocrystalline cells (233.6 $\mu A/cm^2$) were over twice that of flat titania cells (89.8 $\mu A/cm^2$). The best photocurrent (448 $\mu A/cm^2$) was from the TiF_4-TiO_2 based cells when using the polymer. We propose that pore filling is easier in the TiF_4-TiO_2 due to larger pore sizes. These observations suggest that the relative size of the sensitizer molecule and the pores of nanocrystalline films may be a critical factor to consider in photovoltaic devices based on nanoporous materials. Photocurrent enhancement was observed in flat titania cells over time under illumination possibly due to both an annealing process between the titania and polymer and a possible increase of polymer photoconductivity.

In another effort, we have studied the electronic conductivity of semiconductor nanoparticle monolayers of PbS and CdTe voltammetrically using interdigitated arrays (IDA) electrodes at the air-water interfaces. The bandgap determined from electrochemical measurements is in good agreement with that of optical measurement. The bandgap can be manipulated by changing the interparticle distance, decreasing with decreasing interparticle separation. There is also indication of trap states in the I-V response that correlates with evidence of traps states in optical studies. The location of the trap states at positive potential suggests that the trap states are hole traps, instead of electron traps. Such distinction is otherwise difficult make optically. The effect of light on the electronic conductivity has also been studied and found to be significant. These results demonstrated the power of electrochemical techniques in probing elec tronic structures of semiconductor nanomateria