

Photovoltaic Devices Based on Nanoparticles and Nanowires

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The amount of energy incident onto Earth from our sun is so large that covering only 0.1% of the earth's surface with solar cells that are 10% efficient could generate enough power to meet the current demands of the world's population.^{1,2} However, harnessing this energy with inexpensive materials and low cost manufacturing technologies remains an important challenge. While steady progress has been made in solar cells based on the p-n junction diode, the cost of producing electricity from sunlight is still 4-5 times more expensive than competitive technologies. Furthermore, it is projected that solar cells based on conventional technologies will not be competitive with energy derived from other sources until 2030.¹ New developments in solar-to-electric conversion methods are needed and would impact everyone's lives. This project is about a high-risk but potentially high-reward approach to solar-to-electric energy conversion.

The objective of this research project is to establish the fundamental principles that will enable the assembly of quantum-dot sensitized solar cells (QDSSC) based on ensembles of nanometer size heterointerfaces between two semiconducting nanostructured materials. An example of the proposed QDSSCs that make use of nanowires (e.g., ZnO) and nanoparticles (e.g., CdSe) is shown in Fig. 1. In this design, nanoparticles with dimensions (~3-5 nm) smaller than the length (~10 μ m), diameter (~10-100 nm) and spacing (~10-100 nm) of the nanowires are attached to the periphery of the wires through a linker molecule to form many nanometer sized heterojunctions. We are using bifunctional molecules of the form X-R-Y for linking nanoparticles to nanowires surfaces. The X and Y groups have specific affinities for surfaces of nanoparticles and nanowires, respectively, while R is the molecular backbone, perhaps conjugated for efficient charge transport. The general strategy is to form molecular monolayers on nanoparticles first and then attach the functionalized particles to nanowire surfaces. A thin layer of liquid electrolyte containing a redox couple or a hole conductor (such as a hole conducting polymer) is sandwiched between this photoelectrode and a counter electrode to form the QDSSC. The device configuration depicted in Fig. 1, can separate the positive and negative photogenerated carriers into different regions of the solar cell using the following mechanism.

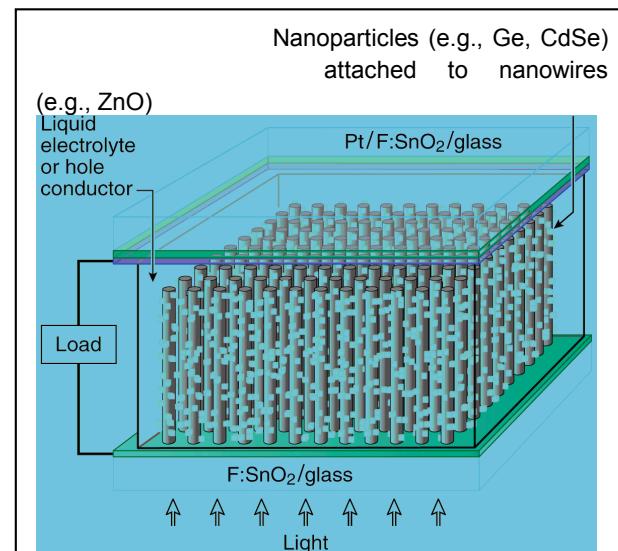


FIGURE 1. Schematic of a solar cell based on an ensemble of nanometer scale heterojunctions between nanoparticles (e.g., CdSe) and wide band gap semiconductor nanowires (e.g., ZnO).

After incident photons are absorbed by the QDs, photoexcited electron-hole pairs are confined within the nanocrystal. The X and Y groups have specific affinities for surfaces of nanoparticles and nanowires, respectively, while R is the molecular backbone, perhaps conjugated for efficient charge transport. The general strategy is to form molecular monolayers on nanoparticles first and then attach the functionalized particles to nanowire surfaces. A thin layer of liquid electrolyte containing a redox couple or a hole conductor (such as a hole conducting polymer) is sandwiched between this photoelectrode and a counter electrode to form the QDSSC. The device configuration depicted in Fig. 1, can separate the positive and negative photogenerated carriers into different regions of the solar cell using the following mechanism.

If they are not separated quickly they will simply recombine. However, wide band gap semiconductors such as ZnO forms a type-II heterojunction with semiconductors such as CdSe. Consequently, once photoexcited, an electron in the QD will lie above the conduction band edge

of the ZnO. Thus, the electron can decrease its energy by transferring into the ZnO. The time scale for this process can be, very fast, subnanoseconds. After the electron is injected into the ZnO, the positively-charged QD can be neutralized either by hole injection into a hole conductor or through an electrochemical reaction with a redox couple in an electrolyte. For our initial cells we are using an electrolyte containing the triiodide/iodide (I_3^-/I^-) redox couple in acetonitrile to neutralize the positively-charged QDs. However, we are planning to investigate other possibilities including a glassy film of nanoparticles as well as hole conducting polymers.

FIGURE 2. (a) Cross sectional scanning electron micrograph of ZnO nanowires. (b) High resolution transmission electron micrograph (HRTEM) of a CdSe quantum dots capped with MPA (c) Bright-field TEM of a ZnO nanowire decorated with CdSe QDs (d) HRTEM of CdSe QDs attached to a ZnO nanowire. (We are collaborating with Prof. C. Barry Carter and his group in HRTEM characterization.)

device, and (iii) characterization of the solar cell, its components and the heterointerfaces, with particular emphasis on the interfacial electronic structure and electron transfer. Specifically, our team is focusing on heterojunctions between wide band gap semiconducting nanowires, such as ZnO and TiO₂, and nanoparticles of semiconductors with band gaps energies covering the solar spectrum (e.g., CdSe, Ge and PbSe.)

There are four specific research aims and our current and future research activities revolve around these aims. These are

- 1) synthesis of semiconductor nanoparticles and nanowires from solution phase and from the gas phase by plasma assisted deposition;
- 2) surface functionalization of nanoparticles for their assembly onto semiconductor nanowires and for the rational control of stability and electron transport rates;
- 3) characterization of interfacial electronic structure in molecule-semiconductor and semiconductor-molecule-semiconductor heterojunctions;
- 4) designing, building, characterizing and testing model solar cells based on these nanoparticle-nanowire or nanoparticle-molecule-nanowire junctions.

During the first year, we have successfully assembled the first quantum-dot sensitized solar cell of the type shown in Fig. 1 using ZnO nanowires [Fig. 2(a)] and CdSe quantum dots [Fig. 2(b)] and demonstrated a clear photovoltaic effect and electron transfer from the quantum dots to the ZnO nanowires. ZnO nanowires were grown on transparent conducting oxide

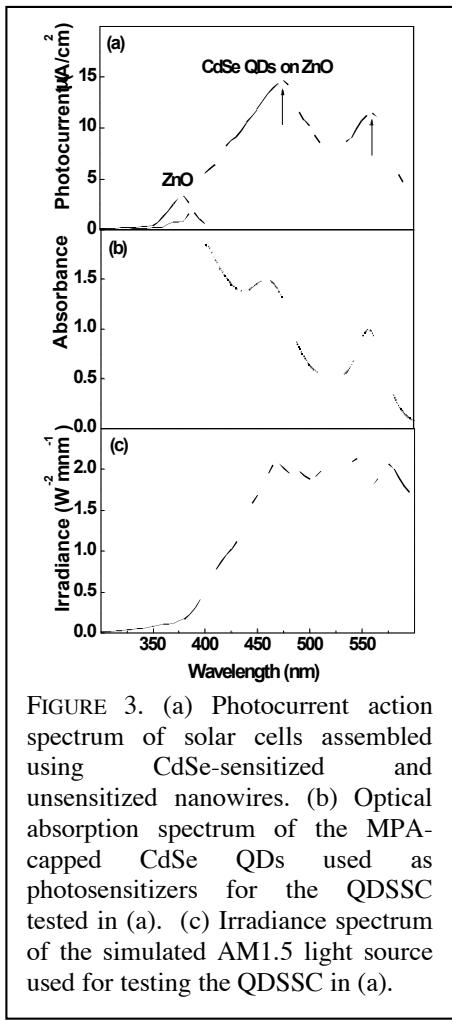


FIGURE 3. (a) Photocurrent action spectrum of solar cells assembled using CdSe-sensitized and unsensitized nanowires. (b) Optical absorption spectrum of the MPA-capped CdSe QDs used as photosensitizers for the QDSSC tested in (a). (c) Irradiance spectrum of the simulated AM1.5 light source used for testing the QDSSC in (a).

electrons to the ZnO nanowires.

We are extending the above approach to Ge nanoparticles grown using a gas plasma and starting time-resolved two-photon photoemission spectroscopy to investigate the rate of electron transfer between the QDs and ZnO. In addition, we are exploring alternative solar cell architectures where the electrolyte is replaced with a hole conducting polymer or a glassy film of nanoparticles.

A number of graduate students are working on various aspects of this project. Three are supported by NIRT while others are supported by other individual fellowships. We have initiated a number of outreach activities including a partnership with the Minnesota Science Museum where the project is featured as a part of their “Science Buzz” exhibit. Part of this exhibit is an interactive web page where our group members answer questions from the general public on nanotechnology and its role in solar cell technologies.

References

- [1] For further information about this project email aydil@umn.edu.
- [2] United States Department of Energy Report on the Basic Energy Sciences Workshop on Solar Energy Utilization by N. S. Lewis et al. (2005); http://www.er.doe.gov/bes/reports/files/SEU_rpt.pdf .
- [3] J. B. Baxter, A. M. Walker, K. van Ommering, and E. S. Aydil, *Nanotechnology* **17**, S304 (2006).

substrates in aqueous solutions of methenamine and zinc nitrate.³ CdSe nanocrystals were synthesized from CdO tri-*n*-octylphosphine selenide (TOPSe). After synthesis, the surfaces of the particles are covered with several different hydrophobic ligands, including tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylphosphine selenide (TOPSe), and hexadecylamine (HDA). We then exchanged these ligands with mercaptopropionic acid (MPA, HS-CH₂CH₂-COOH); MPA is a short bifunctional molecule with groups that bind to both CdSe (-SH) and ZnO (-COOH). Indeed, when nanowires were immersed in colloidal solutions of MPA capped CdSe Qds, the QDs were attached to the nanowires as shown in Figs. 2(c) and 2(d). Solar cells assembled from the nanowires in Figs. 2(c) and 2(d) exhibited the photovoltaic effect and clear evidence for electron injection into the nanowires from excited CdSe QDs. For example, Fig. 3(a) shows the photocurrent action spectrum of a typical QDSSC and an unsensitized nanowire solar cell for comparison. The unsensitized solar cell generates very little photocurrent for wavelengths longer than 400 nm, which are below the band gap of ZnO. In contrast, the QDSSC shows a much larger photocurrent between 400 and 600 nm, where the CdSe QDs absorb. In fact, the shape of the photocurrent spectrum resembles that of the QD optical absorption spectrum, shown in Fig. 3(b). Thus, we conclude that the additional photocurrent generated in the visible region of the spectrum is due to electron-hole pairs photoexcited in the QDs followed by injection of