The Next Generation of Dye-Sensitized Solar Cells

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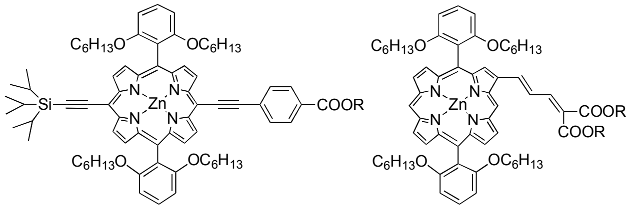
Abstract

Dye-sensitized solar cells (DSSCs) offer enormous promise as low-cost photovoltaic devices that can be manufactured in large area using environmentally benign materials, leaving a small carbon footprint integrated along their production path. We are working to boost the efficiency of DSSCs by radical redesign of the architecture of the DSSC dye and photoanode. Specifically, we are exploring the use of zinc porphyrins on zinc oxide nanotubes to change the paradigm of high-efficiency DSSCs. This work has the potential to advance DSSCs beyond the plateau efficiency where they have languished for the past fifteen years and move them into the realm of economic viability.

Duration

The proposed work will be undertaken during the ten-week summer research program in chemistry at Harvey Mudd College, 24 May 2010 – 30 July 2010. The bulk of the work will be done at Harvey Mudd College. There may be a two-day trip to Northwestern University and Argonne National Laboratory to do photoanode nanofabrication at some point during the summer.

Proposed Research



1 a) R=H
b) R=K

2 a) R=H
b) R=Li

Figure 1. *Zinc porphyrin dyes with tethers to the underlying photoanode in the* meso (**1**) *or β* (**2**) *positions.*

The overall efficiency of the best DSSCs has hovered about 10% for the past fifteen years. Improving the efficiency of these devices will require simultaneous changes in at least two, if not all three, of the critical components of the DSSC: dye, photoanode, and redox shuttle.[1] Towards this end, Prof. Joseph Hupp at Northwestern University is developing "super chromophores" which absorb a wider fraction of the solar irradiance with extinction coefficients (or *absorptivity*) orders of magnitude larger than those of the current generation of optimized ruthenium dye-based DSSCs. These two properties, fraction of the solar irradiance absorbed and dye extinction coefficient, are critical dye features largely controlling the photocurrent density and photovoltage in the working device. To first approximation, the product of photocurrent density and photovoltage determines the overall efficiency of the device. When rod-like porphyrin oligomer dyes are combined with alternate photoanodes to accommodate the structure

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[1] T.W. Hamann, R.A. Jensen, A.B.F. Martinson, H. Van Ryswyk, and J.T. Hupp, "Advancing beyond Current generation dye-sensitized solar cells." *Energy Env. Sci.* **2008**, *1*, 66-78.

and packing of dyes, the next generation of DSCCs should realize higher efficiencies due to photocurrent density and photovoltages enhancement.[1]

Zinc porphyrins, especially those with the tethering carboxylic acid in the β position (**2**, Figure 1), are an attractive template for these "super chromophores." Coupling zinc porphyrins through alkynyl groups in the *meso* position (**1**, Figure 1) allows for conjugated oligomers (molecular rods) with enhanced absorbance and significantly red-shifted absorption onset.

In collaboration with Prof. Hupp, we are exploring the architecture of porphyrin attachment and linkage on a range of potential semiconductor photoanodes with greatly differing architectures. Our present work concerns a battery of zinc porphyrins similar to those shown in Figure 1 attached to zinc oxide nanotube photoanodes (Figure 2). We find that a wide range of carboxylate-tethered porphyrins will attach to zinc oxide; however, only a small fraction of those dyes examined to date will successfully inject their photoexcited electron into the underlying semiconductor to create a photocurrent.[2] We have determined that the pKa (acidity) of the dye's tethering acid controls the success of injection. By changing both the electronic coupling of the porphyrin with the underlying zinc oxide conduction band and the pKa of the acid tether, we are determining the controlling factors in successful injection.

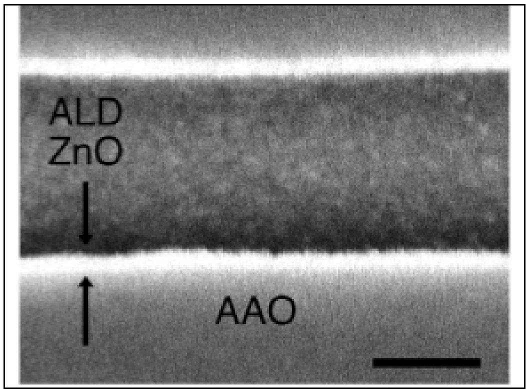

Figure 2. *Scanning electron micrograph of the longitudinal cross section of a zinc oxide (ZnO) nanotube grown by atomic layer deposition (ALD) within an anodized aluminum oxide (AAO) support. The nanotubes have an inside diameter of 200 nm and a length of 60 μm. The scale bar is 100 nm.*

EDUCATIONAL VALUE

Depending upon background and interests, undergraduate coworkers would be intimately involved in two parts of the project: 1) design, synthesis, and characterization of zinc porphyrin dyes; and 2) assembly and testing under simulated solar irradiance of zinc oxide nanotube-based DSSCs. Either part of the project would afford an undergraduate coworker an opportunity to conduct hands-on, cutting-edge materials science work with state-of-the-art instrumentation and materials while being immersed in a larger research group (3 undergraduate coworkers and one faculty member) studying electronic coupling and energy transfer in these devices and in model molecular systems. The undergraduate coworkers would be a member of a wider community of roughly 35 undergraduate coworkers from HMC and across the nation working in the Department of Chemistry at Harvey Mudd College this summer. As such, they would partake of all of the organized activities available with the HMC Chemistry Summer Research Program, including skill and career development activities.

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[2] R.A. Jensen, H. Van Ryswyk, C. She, J.M. Szarko, L.X. Chen, and J.T. Hupp, "Dye-sensitized solar cells: sensitizer-dependent injection into ZnO nanotube electrodes." *Langmuir ASAP* (web publication, awaiting print edition) DOI: 10.1021/la902991z

SIGNIFICANCE OF RESEARCH FOR ENVIRONMENTAL QUALITY

Dye-sensitized solar cells (DSSCs) have enormous potential as low cost photovoltaic devices capable of being deployed over large surface areas. The common name for these devices is “solar paint.” The current generation of Grätzel cells, the most advanced of these devices, are roughly 12% efficient, and Grätzel announced an 11+ % efficient porphyrin-based DSSC at the Fall 2009 Materials Research Society meeting in Boston. DSSC technology would become “disruptive” if it could attain 20% efficiency; at this level of performance these devices would revolutionize the way we produce electricity. One could begin to think about satisfying a majority of the world’s energy needs with these low cost, environmentally benign devices that boast low-carbon footprint production methods. The work described here has to do with the development and testing of critical ideas aimed at bridging basic and applied science in the nanofabrication at the heart of such devices.

FEASIBILITY

This project was initiated during a sabbatical leave at Northwestern University during 2007-2008. The output to date has included two publications (including an invited article in the inaugural issue of *Energy & Environmental Science*) and a range of oral paper and poster presentations. Eight undergraduate coworkers at HMC have or are currently researching portions of this project as their senior thesis in chemistry. All six members of the group last year participated in the inaugural Solar Fuels Gordon Research Conference, held in Ventura, where they presented a poster detailing their work. One student present a poster of her work at the national meeting of the American Chemical Society in Salt Lake City in March of 2009 and another will present at the spring 2010 meeting in San Francisco.

Our studies, while limited to the conceptual design and verification stage, are sufficiently advanced that we expect to publish additional results within the next year. The work described here would follow on, expanding the scope of our project, and serve to produce additional preliminary results which could be parlayed into external funding in the next NSF-Research at Undergraduate Institutions grant cycle.

BUDGET

2 Student stipends,[3] 10 weeks, standard HMC rate of $4,200 each	$8,400
Supplies (chemicals, AAO templates)	600
Faculty stipend	0
Total	9,000

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[3] The two HMC students to be supported by this stipend have not been selected at this time. They would be selected from the HMC students who apply in early February to the summer research program in chemistry at HMC. A number of students from majors outside of chemistry have expressed strong interest in this project and have been encouraged to apply to the program.