Synthesis Techniques and Characterization of Nanostructured Organic-Inorganic Hybrid Systems

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◆ This project is developing novel synthetic methodologies to synthesize and characterize nanostructured organic-inorganic semiconductor hybrid thin films. ◆

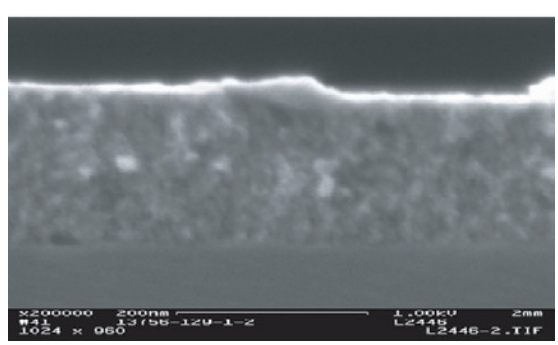
Solar cells based on nanostructured organic-inorganic systems (NOIS) films have demonstrated direct solar-to-electrical conversion efficiencies of greater than 11%. The solar flux at the earth's surface is 100 to 1000 W/m^2 depending on atmospheric conditions, representing a power density of 12 to 120 W/m^2 available essentially free of cost and waste by-products. The synthesis of Grätzel solar cells is a low-energy and nonpolluting process. The efficiency is apparently limited by the achievable porosity in the TiO_2 electrode (made by sintering random nanoparticles), the efficiency of solar absorption of the organic dye, and carrier diffusion through the liquid redox-couple electrolyte used in conventional Grätzel cells. In other words, the efficiency of this class of device is limited by our ability to control the nanostructure and chemistry of an oxide electrode and by our understanding of charge injection and transport processes at NOIS interfaces.

The desirable photovoltaic and semiconductor properties of titania have been recognized for many years. Sintered titania powder was used as the foundation upon which the Grätzel photovoltaic cell was designed and built. A great deal of effort has been put forth recently in the synthesis of nanostructured titania. One of the principal stumbling blocks in these efforts results from the highly crystalline nature of titania and the low crystallization temperature. Commonly, when the template is removed via calcination, these nanocrytallites sinter, merge, and densify, driven by the large thermodynamic reward of crystallization, resulting in significant loss of both surface area and pore structure.

This project has demonstrated the ability to generate photocurrent from novel, nanostructured titania thin films. These films have been made using surfactant templating and spin-casting methods. The initially deposited spin-cast thin films have a lamellar structure, with alternating layers of titania and surfactant bilayers. Calcination of the as-spun film above approximately 300°C results in a random "wormhole" structure in which the film is partially densified, losing some surface area but maintaining a nanoporous structure. The surface area of the titania film varies with surfactant/Ti stoichiometry but generally is in the range of 200 m^2/g. Scanning electron microscopy analysis of the calcined film revealed that it is striated but crack-free and composed of anatase. Photoconductivity studies with the templated titania thin films confirmed that photocurrent was indeed generated.

We improved this system by making the conducting oxide itself the high surface-area, rigidly open pore structure. To maintain the desired band-gap in the system, this nanoporous substrate must be coated with a thin layer of the appropriate semiconductor, which will in turn be decorated with the dye senstizer. This nanostructural hierarchy retains the desirable features of high surface area and open pores structure to maximize the photovoltaic performance of the system and minimizes the conduction path and number of interfaces between the point of charge injection and the conducting sub-phase.

In FY 2002, this project explored the use of surfactant templated nanoporous indium tin oxide (ITO), which could subsequently be coated with a thin film of TiO_2. This was accomplished by two parallel pathways – synthesis of ITO nanorods subsequently coated with a sol-gel coating of titania, and mesoporous ITO in which the pores could be lined with a thin film of titania. The synthetic methodology created by these strategies provides access to novel nanoporous conducting oxide electrode materials, which are lined with a monolayer, bilayer, or explicitly controlled multilayer of a semiconducting oxide at the interface. This strategy will preserve the desired band-gap for photovoltaic applications, as well as optimizing the open pore structure and high surface area of the material. These hierarchically structured nanoporous hybrid materials will provide a significant leap in photovoltaic and artificial photosynthesis capabilities, as well as providing a powerful new foundation for sensing and detection applications.

Methods for the installation of thin layers of conducting and semiconducting oxides were developed using self-assembly of organotitananes and organostannanes. Control of film thickness at the angstrom level was obtained.

The ITO nanorods were grown in polycarbonate membranes with 50-, 100-, and 200-nm-diameter pores using sol electrophoresis at an applied potential of approximately 2.5 V/cm. The nanorods were dried at approximately 100°C in air and sintered at 600 to 650°C for 1 hour at a rate of 2°C/minute. Continuous improvement and optimization of the growth conditions by modifying the ITO sol, applied potential, and sintering temperature is the next step. It was found to be possible to attach these nanorods to glass surfaces using TiO_2 or ITO sols. Photoconductivity of dye-coated nanorods was demonstrated in this project.