Growth Characterization of Dye-Functionalized Titania Nanostructures for Photoelectrochemical Applications

Tammy P. Chou[+], Steven J. Limmer[+], Guozhong Cao[+], and Glen E. Fryxell[*]

[+]Department of Materials Science and Engineering, University of Washington, Seattle, WA
[*]Pacific Northwest National Laboratory, Richland, WA

Project Summary:
Titanium oxide (TiO_2) nanostructures have great potential for investigating systems of alternative power supply to resolve current environmental and energy issues. A greater need for more efficient conversion of light to electrical power or chemical fuels in photoelectrochemical devices have initiated exploration of TiO_2 structures in the nanoscale. Although current dye-functionalized TiO_2 films have shown to impart a large effective surface area, efficient light absorption, and sufficient charge formation and diffusion, many limitations important for high efficiency light conversion have been encountered, restricting further exploration into other TiO_2 structures.

In this study, the synthesis and characterization of ordered TiO_2 nanostructures for use in photoelectrochemical devices is explored. In addition, the connectivity of the mesoporous TiO_2 structure through the development of ordered titania nanostructures (i.e., uniform nanorods and ordered mesoporous films) will also be investigated. The function of creating electron-hole pairs from visible light to produce electric power at the nanoscale is also examined to further improve light conversion and energy production. The synthesis of an array of ordered TiO_2 nanorods would reduce the random distribution of particles typically found in films, and would prevent the formation of randomly-oriented pore structures giving rise to non-uniformity.

The synthesis of ordered TiO_2 nanorods utilizes sol-gel electrophoretic deposition in a track-etched hydrophilic polycarbonate membrane or in an anodic alumina membrane with 200 nm diameter pores. TiO_2 nanorods with a uniform diameter and a smooth external surface along the entire length of the rods were formed. The XRD spectra of both sol-gel-derived TiO_2 powders and nanorods after firing clearly indicates that well-crystallized, more photochemically-active anatase phase was formed. TEM also indicated that the TiO_2 nanorods were fully dense and polycrystalline with an average grain size of approximately 10 nm in diameter after sintering. In addition, it is possible to obtain TiO_2 nanorods unidirectionally-aligned and perpendicularly-bonded to a substrate. Various methods of attachment were explored to obtain the most favorable growth formation of an array of TiO_2 nanorods on a substrate in order to achieve optimal organization, better alignment capabilities, adhesion control, and surface coverage. The organization of the TiO_2 nanostructure is important to ensure high overall surface area for efficient dye self-assembly since dye sensitization occurs along the external surface of dense rods, or along the interior surface of the pore channels of ordered mesoporous TiO_2 film.

Further work will focus on alignment and adhesion control of ordered TiO_2 nanorods on a substrate in order to optimize dye assembly onto these nanostructures for use in photoelectrochemical devices. Both liquid and solid electrolyte systems will be explored to obtain the most favorable configuration for high efficiency light conversion. In addition, the growth of indium-tin-oxide (ITO) nanorod arrays with unidirectional order would be further explored to function as individual transparent electrodes. A layer of dye-sensitized mesoporous TiO_2 film would be incorporated along the entire surface of these nanorods, allowing for greater surface coverage and accessible surface area. This large ITO-TiO_2 interface would lead to direct pathways between the ITO nanorods and the dye molecules associated with the mesoporous TiO_2 film for efficient photon absorption, and electron migration and redirection.

Publications, Presentations and Proposals:

1. "Functionalized, Hierarchically-Structured Mesoporous Silica by Sol Electrophoresis and Self-Assembly." Tammy P. Chou, Steven J. Limmer, and Guozhong Cao. SPIE 47th Annual Meeting: Optical Science and Technology in Seattle, Washington, July 2002.
2. "Nanorods of Various Oxides and Hierarchically-Structured Mesoporous Silica by Sol Electrophoresis." Tammy P. Chou, Steven J. Limmer, and Guozhong Cao. Gordon Research Conference: Solid State Studies in Ceramics in Meriden, New Hampshire, August 2002.
3. "Functionalized, Hierarchically-Structured Mesoporous Silica by Sol Electrophoresis and Self-Assembly." Tammy P. Chou, Steven J. Limmer, and Guozhong Cao. ACerS Regional Meeting in Seattle, Washington, October 2002.

Selected Figures:

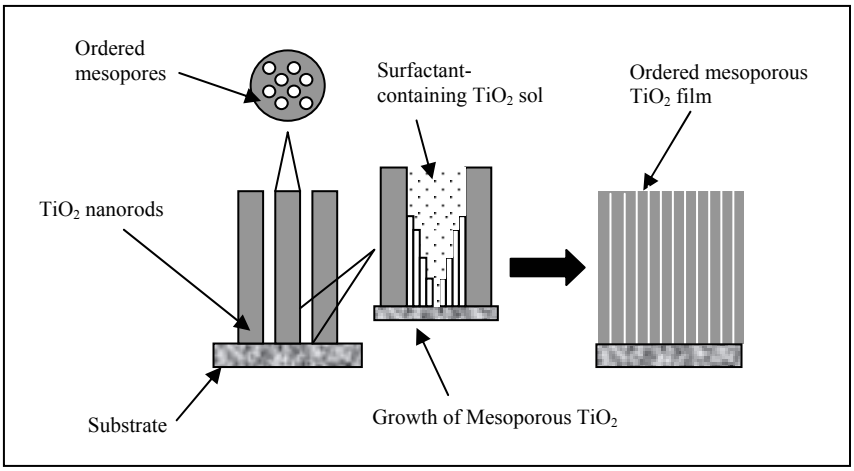

Figure 1. Schematic of the formation of ordered mesoporous TiO_2 film with all pores unidirectionally-aligned and perpendicular to the substrate by way of the initial growth of ordered TiO_2 nanorods and subsequent formation of TiO_2 film with ordered mesopores. Such TiO_2 film with ordered nanostructures would combine the high surface area of sol-gel-derived mesoporous films and the ordered nanostructure of nanorods, in which the mesoporous nanorods will serve as nuclei for continued formation of mesoporous film.

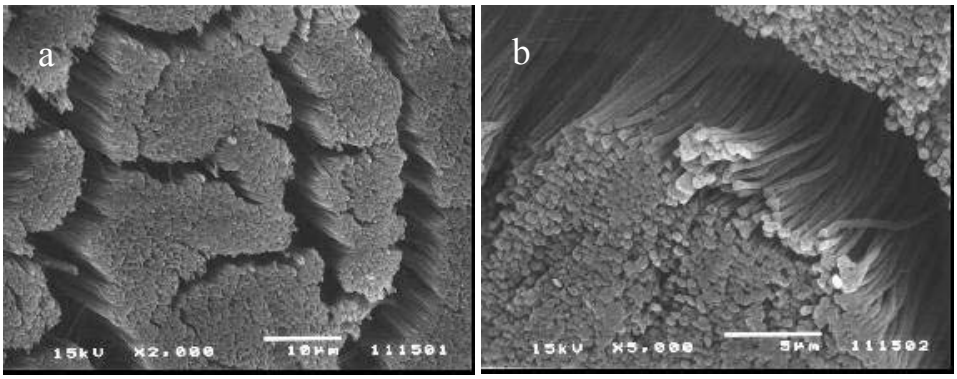

Figure 2. SEM images of a) an array of ordered TiO_2 nanorods grown by sol electrophoresis in a 200 nm alumina membrane, and b) dense, solid TiO_2 nanorods attached to glass by epoxy.