Synthesis and Characterization of Ordered Dye-Functionalized Oxide Nanostructures for Photoelectrochemical Applications

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Project Summary:

Nanostructures are advantageous in solar cell devices for highly-efficient conversion of light to electric power. In particular, dye-sensitized solar cells (DSSCs) using inexpensive porous nanocrystalline titania (TiO_2) film with an interconnected network of nanometer-sized crystals in conjunction with an efficient light-absorbing dye have achieved >10% conversion efficiency.

We are currently exploring the potential for utilizing ordered dye-functionalized oxide nanostructures, specifically TiO_2 and indium-tin-oxide (ITO) materials, in solar cell devices in an attempt to simplify the electron percolation pathways during the light conversion process in order to further improve the efficiency. To examine this potential, we have successfully synthesized TiO_2 and ITO nanorods with good uniformity using template-assisted sol electrophoresis, and have also managed to attach these nanorods onto conducting ITO glass using a layer of ITO sol. Figures 1a and 1b show the SEM images of grown TiO_2 and ITO nanorods attached to an ITO substrate. The nanorods are ~150nm in diameter for TiO_2 and ~140nm in diameter for ITO, and ~10μm in length for both materials. XRD analysis of the nanorods verified that TiO_2 maintained the anatase phase and also confirmed the cubic structure of ITO. Initial solar cell analysis found that electrodes consisting of these ordered nanorod structures exhibited an overall light conversion efficiency <0.1%, and observed to be highly unstable with very low short-circuit current and open-circuit voltage values.

Based on these initial findings, we directed our studies to electrodes with TiO_2 film prepared from the same TiO_2 sol used to form the TiO_2 nanorods in an effort to compare results and to determine the cause for the instability and reduced current and voltage values found for the electrodes with an ordered nanorod structure. Analysis of the TiO_2 film electrode yielded an overall light conversion efficiency of ~1%, which is ~10 times higher than the ordered nanorod electrode. However, it was found that prolonged air and light exposure reduced the performance of the solar cell. Figure 2a compares the initial I-V curve for the solar cell with the TiO_2 film immediately after dye immersion with the I-V curves obtained from the same electrode after exposure to air and light for various amounts of time. It can be seen that the I-V behavior eventually becomes unstable and the current begins to fluctuate after extended air and light exposure. This highly unstable behavior was comparable to the behavior found in our initial findings for the electrodes with an ordered nanorod structure. Figure 2b shows the decreasing trend in short-circuit current and open-circuit voltage for the TiO_2 film as the amount of air and light exposure increases. It can be seen that excess air and light exposure reduced the current and voltage values, thereby decreasing the efficiency by >50%, and eventually resulted in very poor performance. Further analysis also found that the amount of surface coverage has some influence on the performance of the solar cell and that the presence of visible surface defects reduces the effectiveness of the electrode during the light conversion process.

In general, our initial analysis of TiO_2 film electrodes indicated that dye oxidation and degradation, as well as surface defects, factor into the conversion efficiency and performance of the solar cell. The very low efficiency initially obtained for the ordered nanorod structure may have been influenced by the above-mentioned factors, as evidenced by the unstable I-V behavior in Figure 2. However, the random alignment of the nanorods seen in Figure 1, where a number of nanorods are sintered together and a few are free-standing, and the possibility of incomplete nanorod adhesion to the substrate surface, where minimal contact at the nanorod-substrate interface might have reduced electrical contact and limited the electron transport process, may

have also influenced the measurement. Further structural studies are currently underway to verify this, and methods to optimize the nanorod structure are being explored to further analyze the potential of these ordered nanostructures.

Publications and Presentations:

1) T.P. Chou, C.M. Chung, and G.Z. Cao, "Ordered Dye-Functionalized Titania Nanorods and Their Applications as Sensors," in Nanomaterials and Their Optical Applications, SPIE Proceedings 5224, eds. G.Z. Cao, Y.N. Xia, and P. Braun, 53-61 (2003).
2) "Ordered, Dye-Functionalized Titania Nanostructures for Photoelectrochemical Applications," T.P. Chou, S.J. Limmer, and G.Z. Cao, SPIE 48th Annual International Symposium in Optical Science and Technology, San Diego, CA, August 2003.

Funding that has resulted from this research:

"Highly Efficient Inexpensive Solar Cells Based on Ordered Nanostructures," still under review.
"Photoelectrochemical Cells Based on Nanofiber Films," still under review.

Figures:

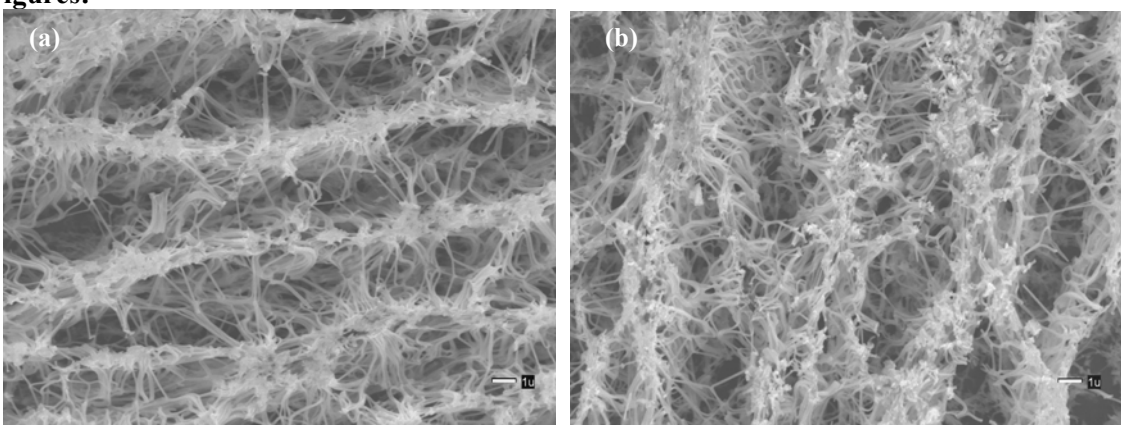

Figure 1. SEM images of an array of (a) TiO_2 nanorods and (b) ITO nanorods attached to an ITO substrate using ITO sol after sintering to 500ºC and 650ºC, respectively.

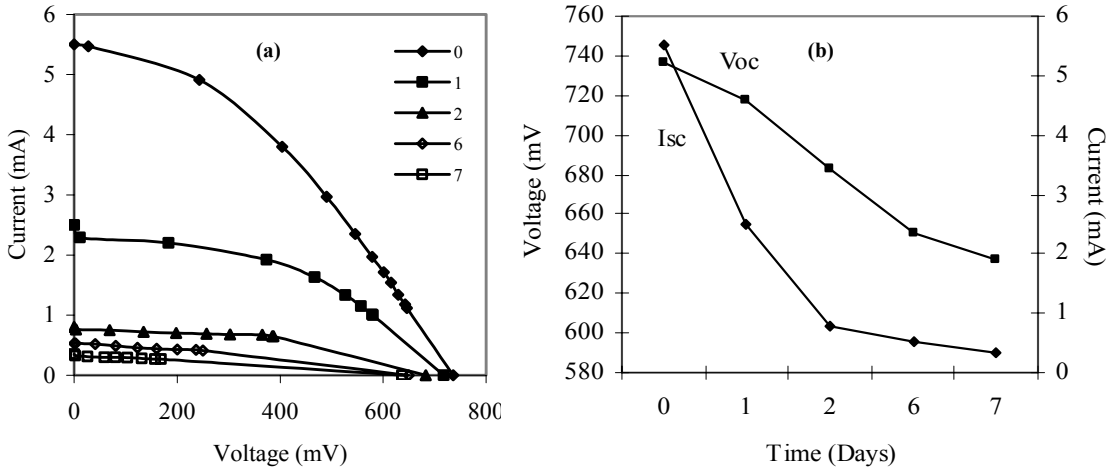

Figure 2. Plots showing (a) the current-voltage (I-V) curves of the solar cell with a 10μm-thick TiO_2 film electrode taken after 0, 1, 2, 6, and 7 days of air and light exposure to compare the effect of dye degradation by oxidation, and (b) the relative short-circuit current and open-circuit voltage trends resulting in decreased efficiency and reduced performance.