NANOSTRUCTURED MATERIALS FOR POWER AND ENERGY APPLICATIONS

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1 General Introduction

The development of low-cost, lightweight, and flexible energy harvesting and storage devices are an enabling technology for many different applications. The fabrication of highly efficient power conversion and energy storage devices with high power and energy density are highly dependent on the materials and device structures used to make up the active components. Some of the factors limiting the performance of organic and nanoparticle-hybrid devices include poor spectral response and restricted charge transport. These effects can result from poor light absorption, increased carrier recombination, low electronic charge carrier mobilities, relatively random thin film morphologies, and/or limited ionic intercalation and conduction pathways. Our efforts to address these issues for a variety of devices (including photovoltaics and battery electrode materials) include developing materials and fabrication methodologies that result in highly ordered structures to permit enhanced charge transport and developing unique device configurations to facilitate light absorption and charge transfer. This paper will provide an overview of current state-of-the-art for these devices, highlight current barriers to improved performance, and describe a number of specific approaches being investigated to address these issues.

2 Background

In recent years, polymer-based and dye-sensitized solar cells (DSSCs) have become a viable technology for the conversion of sunlight into electricity. The potential for high efficiency, low cost, and light-weight cells makes them a very promising system for many different solar power applications.[1-3] These devices are typically fabricated by using solution-based processing approaches that are scalable and amenable to low-cost manufacturing. Dye-sensitized solar cells are fabricated by first printing a mesoporous film of TiO_2 nanoparticles on a transparent conducting oxide substrate. After partial sintering, the highly porous TiO_2 film is light sensitized by immersing it in a dilute solution of a dye, typically a ruthenium bipyridyl complex, whereby a monolayer of dye becomes adsorbed to all of the internal surfaces of the film. The cell is completed by backfilling the pores with an electrolyte and attaching a counter-electrode. The device consists of a disordered but interconnected network of TiO_2. Efficient device operation depends critically upon charge transfer dynamics that occur at the internal, heterogeneous interfaces. The power conversion efficiency of current devices is primarily limited by two factors: Poor charge transport and limited spectral response. As shown in Figure 1, the former occurs in these devices due to a variety of factors including disordered film morphologies in the device active layer, which leads to tortuous pathways and restricted charge transport for the carriers, in addition to low intrinsic charge carrier mobilities of the materials used. The latter occurs because of relatively narrow absorption bands, as compared to the solar spectrum (also shown in the figure), and the need to maintain very thin films (again due to low carrier mobility) that do not absorb all of the light. By addressing these two limiting factors, devices with improved power conversion efficiencies will be developed.

The performance of electrochemical energy storage devices, on the other hand, is fundamentally limited by the materials used to make up the electrodes. Both the cathode and the anode are electrochemically active in batteries and the
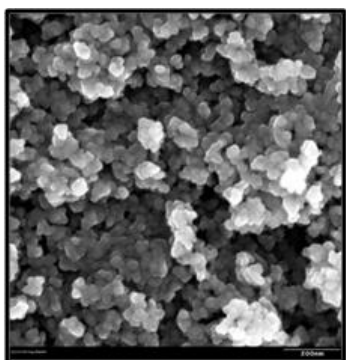
Disordered Device Morphologies
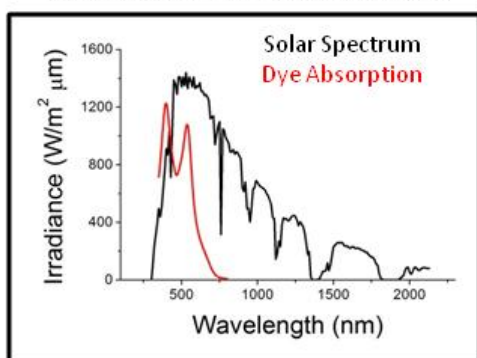
Narrow Absorbance Bands
compared to Solar Spectrum

Figure 1 – Factors leading to non-ideal
device performance characteristics.

maximum theoretical energy density is dictated by the specific capacities of the anode and cathode, and the electrochemical potential between them. The rate capability (i.e. power density) of the system, on the other hand, is much more dependent on kinetics rather than thermodynamics. Ion transport often limits the maximum rate at which devices can be charged and discharged which, in-turn, is limited by solid-state diffusion rates and the distances over which the ions must be transported. Consequently high rate capability systems require control over these transport processes.

A variety of different nanostructured electrode architectures are being developed and will be discussed. These include a nano-templating methodology based on porous anodic alumina in order to fabricate vertically aligned titania nanotubes of controllable shape and size and vertically aligned

carbon nanotubes for use as either intercalation (in batteries) or charge collecting (in solar cells) electrodes. In addition, efforts to understand and tune the device spectral response will be discussed. By utilizing an interfacial modification technique based on layer-by-layer deposition, nanoparticle surfaces have been functionalized with electronically active species and integrated into device structures. This technique is amenable to developing an 'energy cascade' device architecture commonly utilized in photosynthetic organisms. Finally, efforts focused on the development of nanostructured electrodes for high energy density and rate capability batteries will be described.

3 Dye-Sensitized Solar Cells

Titanium Dioxide (TiO_2) nanostructures continue to be an attractive option for use as working electrodes in photovoltaic devices. In addition to having favorable electronic properties, TiO_2 is readily available, relatively inexpensive, non-toxic, and can be adapted to suit a host of applications. Dye sensitized solar cells are based on a mesoporous TiO_2 film onto which light sensitizing dyes are adsorbed. The disordered morphologies that are obtained can lead to inefficient charge collection and limited device efficiencies. Facilitating this charge collection to the respective electrodes will be of critical importance to realize high efficiency devices. Of particular interest here is the ability to engineer TiO_2 nanostructures having dimensionalities that support enhanced charge transport, limit charge recombination, and possess relatively high surface areas. Vertically-aligned arrays of TiO_2 nanotubes are structures that conform to those criteria. We have developed a versatile approach for the fabrication of these arrays which is based on nanoscale templating in a porous anodic alumina membrane. This method affords a uniquely high degree of geometric control which permits a wide selection of achievable architectures. In other words, this method enables specific tailoring of the nanotubes in terms of their on-average spacing, diameter, wall thickness, and length.

Figure 2 shows a representative image of a TiO_2 nanotube array aligned on a substrate. The templating approach we have developed to fabricate such structures involves a modified sol-gel coating
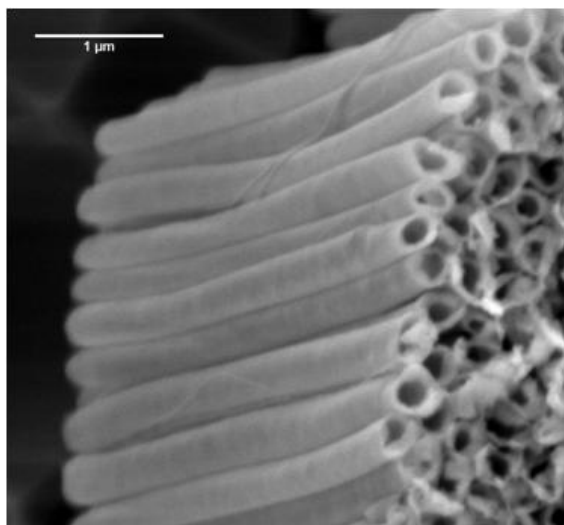
Figure 2 – Vertically aligned TiO$_2$ nanotube arrays

technique in which a titania precursor solution, titanium (IV) isopropoxide in ethanol, is infiltrated into a nanoporous alumina template of specific dimensions. These alumina templates are grown using a two-step anodization process whereby the anodizing conditions can be manipulated in order to obtain the desired template geometry (i.e. pore diameter, length, etc.). Following a post-anodization pore-widening step, the template is vacuum-infiltrated with the titania precursor solution and subsequently converted to crystalline TiO$_2$ through a series of heat treatment steps. The alumina template is selectively removed using a chemical etch, and a free-standing film of vertically-oriented TiO$_2$ nanotubes remains, as shown in the figure. The TiO$_2$ nanotube films can then be transferred to a desired substrate, commonly a glass slide coated with a transparent conducting oxide (TCO) film.

Such TiO$_2$ nanotube arrays have a geometry that is highly favorable for both enhanced charge transport and limited charge recombination. Indeed, when incorporated into active solar cell device architectures, power conversion efficiencies as high as 5.9% have been achieved with such nanotube arrays. Continuing challenges, however, center around the fact that these arrays have significantly lower internal surface areas than the mesoporous TiO$_2$ nanoparticle films discussed above. For instance, a typical 20 nm TiO$_2$ nanoparticle film possesses a measured specific surface area of 55 m^2/g. Typical template-fabricated TiO$_2$ nanotubes, on the other hand, have an *estimated* specific surface area of only 15 - 20 m^2/g. We have begun to address this issue by carrying out surface treatments of the nanotube arrays. Specifically, treating the films with a solution of TiCl$_4$ has the effect of 'decorating' the surface of the nanotubes with a dense layer of TiO$_2$ fibrils, thus increasing the specific surface area dramatically. An increase in specific surface area translates directly to an increase in dye loading, an increase in DSSC short-circuit current, and, ultimately, an increase in power conversion efficiency (PCE). An increase in device efficiency of about 1.5X, which is quite significant for active solar cell devices, was observed for 'best-performing' devices with and without this surface treatment. Once again, surface preparation conditions are observed to play a tremendous role in dictating device performance and we are developing the processing and fabrication approaches needed to modify and control this interfacial zone for improved nanotube-based solar cell devices.

4 Nanostructured Electrodes for Batteries

First generation Li-ion batteries are based on 2-dimensional planar designs containing electrodes (a LiCoO$_2$ cathode and graphite anode) with micron and millimeter sized particles and a non-aqueous liquid electrolyte trapped within millimeter sized pores of a polypropylene separator. These batteries are low power devices because of the low intrinsic diffusivity of Li ions through the solid state electrodes. However, by decreasing particle size and nanostructuring the electrodes, the rate of Li-ion insertion/removal can be increased because of the shorter Li-ion transport distances within the particles. Correspondingly, electron transport can also be enhanced because of shorter electron transport distances. The high surface area of nanoparticles also permits high contact area with the electrolyte and hence a higher lithium-ion flux across the interface compared to lower aspect ratio electrodes. Therefore, decreasing particle dimensions can increase the power density of Li ion batteries. Other advantages of utilizing nano-sized particles for the electrodes include the fact that they can undergo reactions that cannot take place in the
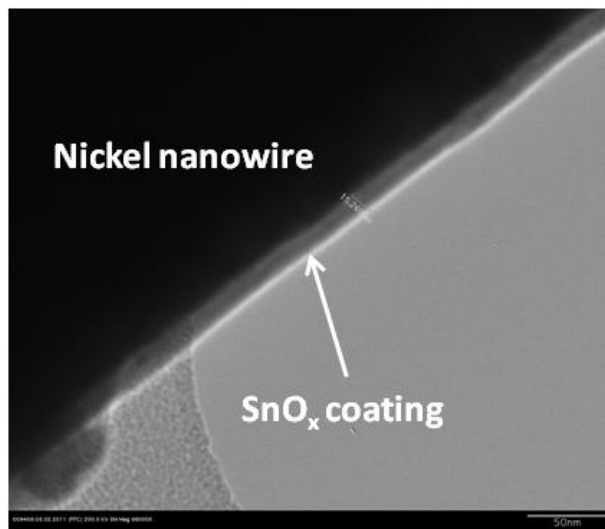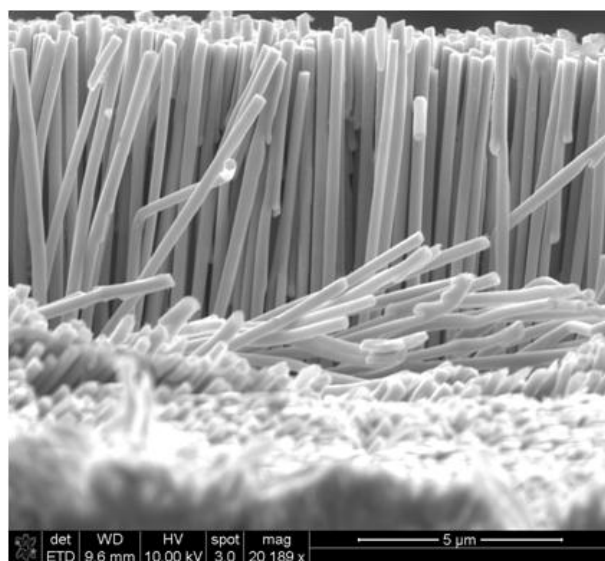
Figure 3 – Atomic layer deposition (ALD) of SnO$_x$ on nickel nanowire arrays.

bulk, or micron sized materials, and can mitigate the large volume expansions and contractions that take place in new, higher capacity, alloying-type electrodes.

Even though nanostructured electrodes can increase battery power density, the 2-D planar design fundamentally limits the amount of energy that can be stored and power that can be delivered per unit area, mass, and volume. However, 3-D battery architectures exploit the advantages of nano structuring, while decreasing the areal foot print of a

2-D design. Generally, a 3-D design consists of a 3-D matrix of the electrodes (periodic or aperiodic) in order to maximize the number of interfaces and thus interfacial reactions in the battery. The prime advantages one expects with the 3D architectures for energy storage in batteries, in addition to the small areal footprint, are the short transport lengths for ions in the solid-state electrode as well as between the anode and cathode. The 3D design minimizes both these distances and yields concomitant improvements in power density.

One strategy that is being employed is to conformally coat an anode (cathode) layer onto a nanoscale 3D architectured charge collecting array, followed by a solid electrolyte/separator, with the cathode (anode) filling the space in between the nanowires. Vertically aligned multiwall carbon nanotube arrays as well as metal nanowire arrays electrodeposited in nanoporous alumina templates are both being studied for this purpose. Atomic Layer Deposition (ALD) in particular represents a technique that is capable of such conformal deposition. ALD is a layer-by-layer vapor deposition methodology that affords extremely fine control over film thickness, composition and morphology. By sequential exposure of a surface to two separate precursor gases, a thin film is built up on the surface. Preliminary results on using atomic layer deposition as a means to uniformly and conformally coat both CNT arrays and nickel nanowire arrays with SnO$_x$ have already demonstrated promising results. SnO$_x$ is a material of much interest as an 'alloying anode' in next generation batteries. While the standard anode material, graphite, has a specific capacity of 372 mAh/g, SnO$_2$ has a reversible capacity of 781 mAh/g. Figure 3a shows that metal nanowires grown using electrochemical deposition into a nanoporous alumina template result in highly uniform structures. The template is selectively removed and the nanowires are subsequently coated with the active battery electrode material (SnO$_2$). Figure 3b shows that the use of ALD can create highly uniform SnO$_x$ coatings on the nickel nanowires.

By applying a similar process to carbon nanotube films, we have demonstrated reproducible electrochemical cycling of lithium ions into and out

of the SnO_x coating. While the magnitude of the area specific capacities were observed to be fairly high, the behavior was also observed to be highly dependent upon the specific surface treatment that the carbon nanotubes were subjected to prior to SnO_x deposition. In addition to their electrochemical characteristics, we are continuing to carry out detailed morphological analyses to more fully understand the effects of processing conditions on film deposition and device performance.

5 Conclusions

Aligned nanostructures are of continuing interest in a wide variety of energy harvesting and storage devices including next generation solar cells and batteries. We have developed a number of processing and fabrication approaches to create well controlled nanotube structures. These include templated growth and electrochemical deposition in nanoporous alumina membranes and atomic layer deposition onto ordered array structures. Performance characteristics of devices made from these structures show promising results and suggest that hybrid nanostructured devices offer a viable solution to reach improved performance.