II.K.24 Highly Ordered Nanotube Arrays and their Use in Water Photoelectrolysis

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Objectives

We seek to both discover and develop highly efficient, easily fabricated materials for the solar generation of hydrogen by water photoelectrolysis. Building upon our earlier work in the development of highly ordered TiO$_2$ nanotube arrays we seek to modify synthesis techniques to achieve in-situ low temperature crystallization, and control the bandgap response of the nanotube arrays to enhance their visible spectrum properties, while maintaining their excellent charge transfer behavior, by in-situ doping of the titania during synthesis through cation incorporation from the anodization electrolyte. Further, we seek to extend our nanotube array architecture, an architecture that appears ideal for water photoelectrolysis, to visible light responding n and p-type ternary oxide nanotube arrays for use in achieving efficient photoelectrochemical diodes.

Technical Barriers

Currently the TiO$_2$ and ternary oxide nanotube arrays are amorphous when synthesized, requiring a high temperature annealing step for crystallization. Achieving as-synthesized crystallized nanotube arrays requires modification of the anodization electrolyte, control of bath temperature, and control of the anodization current. Synthesis of both p and n-type Cu-Ti-O nanotube arrays for use in achieving high efficiency photocorrosion stable photoelectrochemical diodes requires refinement of synthesis techniques to enhance tube structure, control of charge transfer properties, and composition.

Abstract

We seek to both discover and develop highly efficient, easily fabricated materials for the solar generation of hydrogen by water photoelectrolysis. To this end we are building upon, and extending, our knowledge base on the synthesis and application of TiO$_2$ nanotube arrays, a material architecture that appears ideal for water photoelectrolysis. To date we have optimized, refined, and greatly extended synthesis techniques suitable for achieving highly ordered TiO$_2$ nanotube arrays of given length, wall thickness, pore diameter, and tube-to-tube spacing for use in water photoelectrolysis. We are now building upon this knowledge base to achieve visible light responsive, photocorrosion stable n-type and p-type ternary oxide nanotube arrays for use in achieving efficient photoelectrochemical diodes.

Progress Report

TiO$_2$ Nanotube Array Synthesis

It is well established that the properties of the TiO$_2$ nanotube arrays are dependent upon their specific architecture, including nanotube array length, wall thickness, pore diameter, and tube-to-tube spacing. Hence it was with great excitement that in the summer of 2006 we determined fabrication routes by which self-aligned highly-ordered TiO$_2$ nanotube arrays up to 134 µm in length could be achieved by potentiostatic anodization of Ti foil, representing a factor of x20 increase of the previous length record. Depending upon the anodization voltage the inner pore diameters of the resulting nanotube arrays ranged from 10 nm to 150 nm. The very long nanotube-arrays were achieved in fluoride ion containing baths in combination with a variety of non-aqueous organic polar electrolytes including dimethyl sulfoxide, formamide, ethylene glycol, and N-methylformamide. In initial measurements, 45 µm long nanotube-array samples, 550°C annealed, under bandgap (320 nm – 400 nm) illumination showed a water photoelectrolysis photoconversion efficiency of 16.25% [1,2].

With an eye towards in-situ doping of the TiO$_2$ nanotube arrays during their electrochemical synthesis, thereby shifting their bandgap while maintaining their outstanding charge transfer properties, we investigated the effect of five different cationic species on the formation of TiO$_2$ nanotube arrays by potentiostatic anodization of titanium in formamide-water mixtures containing fluoride ions [3]. We find the cation choice to be a key parameter influencing both the nanotube growth rate and resulting nanotube length, with the length and aspect ratio of the nanotubes increasing with increasing cation size. Under similar conditions, electrolytes containing the tetrabutylammonium cation resulted in the longest nanotubes (~94 µm), while the shortest nanotubes (~3 µm) were obtained when H' ions were the sole cationic species in the anodization electrolyte.
We attribute this difference in nanotube growth to the inhibitory effect of the quaternary ammonium ions that restrict the thickness of the interfacial (barrier) oxide layer; a thinner interfacial oxide layer facilitates ionic transport thus enhancing the nanotube growth. In a saturated solution of NaF in formamide nanotubes with a pore diameter of 12 nm were obtained, while a formamide Bu₄NF solution resulted in nanotubes of 5 nm wall thickness; both values are the smallest reported values for anodically formed TiO₂ nanotube arrays. The wall thickness is such we believe we are near a regime where quantum effects might soon be seen, e.g. generation of multiple excitons from a single photon. We are now able to fabricate nanotube arrays of up to 1 mm length [4,5], and synthesize nanotube arrays in fluorine free electrolytes [6].

Since the high temperature annealing step that is currently required for crystallization results in an unwanted increase in the series resistance due thermal oxidation of the underlying metal substrate a significant effort of ours in the past year, 2007, has been towards developing a technique to crystallize the TiO₂ nanotube array during synthesis. To date we have been able to achieve direct synthesis of partially crystalline nanotube arrays, as reported in [7]. We continue to try and optimize synthesis conditions to achieve fully crystalline nanotube arrays directly from the beaker.

Nitrogen Doping of TiO₂ Nanotube Arrays

We have and continue to investigate electrochemical methods to introduce anionic dopants into TiO₂ [8] N-doped thin films with chemical composition TiO₂−x Nₓ, up to x = 0.23, were fabricated by anodic oxidation of Ti films in electrolyte solutions containing ammonium ions, nitrate ions and fluoride ions enabling simultaneous nanostructuring and doping of the growing anodic oxide. Analysis by X-ray photoelectron spectroscopy (XPS) indicates that nitrogen atoms substitute for oxygen sites within the TiO₂. For nitrogen doped films UV-vis spectroscopy indicates a shift in the primary absorption threshold as well as significant optical absorption in the visible wavelength range from 400 to 530 nm. The concentration of the incorporated anionic dopants, and the morphology of the doped thin film are strong functions of electrolyte chemistry and anodization time. Longer anodization periods resulted in a well-developed nanotube-array structure but smaller amounts of incorporated nitrogen. XPS depth profiling reveals the nitrogen doping to be inhomogeneous, with maximum nitrogen incorporation occurring near the oxide-electrolyte interface at the surface of the anodized film.

FDTD Modeling of Light Absorption by TiO₂ Nanotube Arrays

On an ongoing basis we couple our experimental results with numerical simulation of light propagation through the highly-ordered TiO₂ nanotube-arrays using the electromagnetic computational technique Finite-Difference Time-Domain (FDTD) [9,10]. Our objective is to determine an optimal architecture for water photoelectrolysis [9]. We have determined the absorbance and transmittance spectra in the wavelength range 300 nm – 700 nm as a function of nanotube-array dimensions including length, pore size, barrier layer thickness, and surface roughness. We have also investigated the light absorption properties when the nanotube arrays are coated with N719 dye, as relevant for use in dye sensitized solar cells [10]. A significant increase in the light absorption by the nanotubes was observed for increasing nanotube length, smaller pore sizes, and increased surface roughness. Our efforts demonstrate FDTD to be a broadly applicable simulation technique capable of guiding design of an optimal architecture for light harvesting and subsequent transfer of the photogenerated charge.

Ternary Oxide Nanotube Arrays

n-type Ti-Fe-O Nanotube Arrays [11]

In 2007 we reported the synthesis, characterization and application to water photoelectrolysis of Ti-Fe-O nanotube arrays [11]. The underlying premise of the work is to combine the light absorbing properties of hematite (2.2 eV bandgap) with the outstanding charge transfer properties of TiO₂ in the nanotube array architecture (which appears to be the ideal architecture for water photoelectrolysis). Since the minority carrier diffusion length in iron oxide is small, ≈4 nm, critical to achieving high photoconversion efficiencies in the Fe-Ti-O nanotubes was the premise that we needed to, and could, control the wall thickness down to a comparable length scale, as we have been able to do in TiO₂. However for the work reported in [11] we were initially unable to control the wall thickness, in all cases achieving a wall thickness of approximately 23 nm. Starting from thin films of variable Fe:Ti content, made by sputter co-deposition onto FTO coated glass substrates, Fe-Ti-O nanotube arrays were synthesized using an ethylene glycol electrolyte and then characterized. Although the films were poorly crystallized, with a maximum length of ≈1 µm, and had wall thicknesses of ≈23 nm we still obtained over 2.0 mA/cm² under AM 1.5 illumination (second best photocurrent value ever reported from an iron oxide system). We believe this is a very important starting point of work we continue to pursue, as discussed in the next section.

p-type & n-type Cu-Ti-O Nanotube Arrays [12]

Copper and titanium remain relatively plentiful in the earth’s crust, hence their use for large-scale solar energy conversion technologies is of significant interest. We have fabricated vertically oriented p-type Cu-Ti-O...
nanotube array films by anodization of copper rich (60% to 74%) Ti metal films, and n-type Cu-Ti-O nanotube array films by anodization of copper poor (24% to 11%) metal films, co-sputtered onto fluorine doped tin oxide (FTO) coated glass [12]. p-type Cu-Ti-O nanotube array films 1 µm thick exhibit external quantum efficiencies up to 11%, with a spectral photoresponse indicating that the complete visible spectrum, 380 nm to 950 nm, contributes significantly to the photocurrent generation. Water-splitting photoelectrochemical pn-junction diodes have been fabricated using p-type Cu-Ti-O nanotube array films in combination with n-type TiO$_2$ nanotube array films, since to date the n-type Cu-Ti-O nanotube array films suffer from tube clogging due to unwanted precipitate falling from solution during synthesis that in turn degrades their photoelectrochemical properties. With the glass substrates oriented back-to-back, light is incident upon the UV absorbing n-TiO$_2$ side, with the visible light passing to the p-Cu-Ti-O side. In a manner analogous to photosynthesis, photocatalytic reactions are powered only by the incident light to generate fuel with oxygen evolved from the n-TiO$_2$ side of the diode and hydrogen from the p-Cu-Ti-O side.

Figure 1 presents a schematic illustration of the n-TiO$_2$:p-Cu-Ti-O photoelectrochemical diode, with light incident upon the TiO$_2$ film. Narrow bandgap semiconductor materials (0.8 – 2.4 eV) typically suffer UV induced photocorrosion, which is minimized by the design of Figure 1 in which the TiO$_2$ layer will absorb the high-energy UV photons, in turn generating oxygen. The photoresponse of a n-TiO$_2$:p-Cu-Ti-O coupled system, see Figure 1, under global AM 1.5 illumination is shown in Figure 2. The n-TiO$_2$ nanotube array film was made by sputtering a Ti film upon a FTO coated glass substrate, then performing an anodization to achieve a titania nanotube array structure approximately 600 nm long, 30 nm pore size, with wall thickness of about 7 nm; the initially amorphous sample was oxygen annealed at 450°C for one hour for crystallization. The p-Cu-Ti-O sample is that resulting from anodization of a 74:26 Cu-Ti metal film, 550°C vacuum annealed for 1 hr, nanotube array length 1 µm, pore size ≈65 nm, wall thickness ≈35 nm. The films, atop FTO coated glass substrates, were mounted by use of epoxy into a glass sheet that allowed separate collection of the evolved gases. The TiO$_2$ nanotube array side of the diode was kept in 1M KOH, and the Cu-Ti-O side is kept in 0.1M Na$_2$HPO$_4$ with a salt bridge linking the two solutions. Keeping the Cu-Ti-O side in KOH solution resulted in significantly greater photocurrents, ≈20x, however the performance decayed with time as the CuO turned into copper. The AM 1.5 illumination was incident upon the TiO$_2$ side of the diode, which absorbs UV while passing visible light to the Cu-Ti-O side, thus minimizing any UV-assisted photocorrosion of the low bandgap material. A photocurrent density of approximately 0.25 mA/cm$^2$ is achieved. The photoconversion efficiency, calculated using $(1.23 * I)/0.1$, where I is the photocurrent density in A/cm$^2$ and 0.1 W/cm$^2$ is the power density of the incident light (1 sun), is 0.30%. Measured over a four-hour test the hydrogen generation rate of a 1 cm$^2$ sample is approximately 92 µL/hr, or 0.92 L/hr for a 1 m$^2$ sample. A sustained hydrogen to oxygen evolution rate of 2:1 was confirmed through use of a gas chromatograph, with no evidence of film photocorrosion.
Water Photoelectrolysis: General Considerations

It rapidly becomes clear reading the photoelectrolysis literature that quoted efficiency values are in many cases meaningless, with wildly disparate and non-comparable techniques used for calculating photoconversion efficiencies. As a consequence we were motivated to consider the subject, and compare for the same TiO$_2$ nanotube array sample the effect of the various photoconversion efficiency calculation techniques. A resulting treatise on the subject, with comparative measurements, is included in our recent book on the subject of water photoelectrolysis [13] as well as a separate article [14]. An invited review paper offered the opportunity to summarize key issues surrounding the fabrication, properties, and application to water photoelectrolysis of TiO$_2$ nanotube arrays [15].

Future Directions

We intend to continue with our efforts in both electrochemical and plasma-anneal doping of the TiO$_2$ nanotube arrays. Our objective here is to maintain the remarkable charge transfer properties demonstrated by the TiO$_2$ nanotubes while shifting the band gap towards the visible spectrum. In other work, we will continue to explore the synthesis and application of ternary oxide nanotube arrays for use in water photoelectrolysis. We have achieved Cu-Ti-O nanotube arrays that, depending upon the relative Ti-Cu amount, are n-type (Ti rich), or p-type (Cu rich). The Ti addition to the copper oxide makes it stable to photocorrosion. We will continue our efforts towards the synthesis of photocorrosion-stable self-biased n-type Ti-Cu-O / p-type Cu-Ti-O photochemical diodes for efficient visible light water splitting.

Finally, in an effort parallel to our water photoelectrolysis work, as time allows we are investigating the use of the ternary oxide nanotube arrays to the visible light photoconversion of CO$_2$ to methane.

References


Publications (including patents) acknowledging the grant or contract


In Review


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