

Electrochemical Impacts of TiO_x Shells on Rutile TiO₂ Nanorods

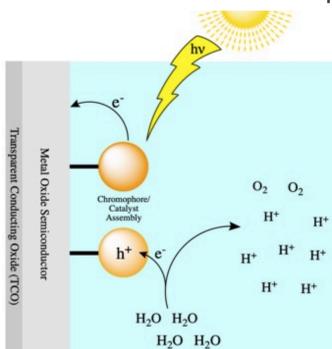
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I. Introduction and Background

Dye-sensitized photoelectrosynthesis cells (DSPECS) are devices that use sunlight to convert energy poor feedstocks like H₂O and CO₂ into energy rich molecules like H₂ and methanol. This conversion allows for solar energy to be converted into a storable form of energy. Energy conversion is accomplished using dye and catalyst molecular species attached to metal oxide photoanodes.

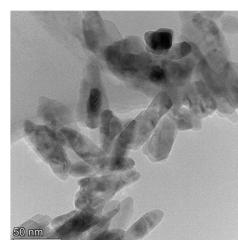


Schematic of DSPEC mechanism for water oxidation and CO₂ reduction.

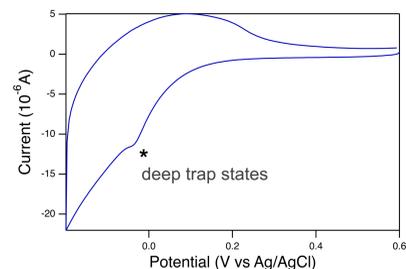
TiO₂ in the rutile morphology has been used for water oxidation processes and shows promise for uses in DSPECS. Rutile TiO₂ nanoparticles can be spread into thin films and used as photoanodes for DSPECS.

Often times, a metal oxide shell is deposited onto the photoanode material to improve the efficiency of DSPECS, yet little is known about why this change improves the performance of DSPECS.

The goal of this research is to understand how the addition of an ALD-deposited shell of TiO_x onto rutile TiO₂ changes the electronic structure and electron transfer kinetics of these materials.



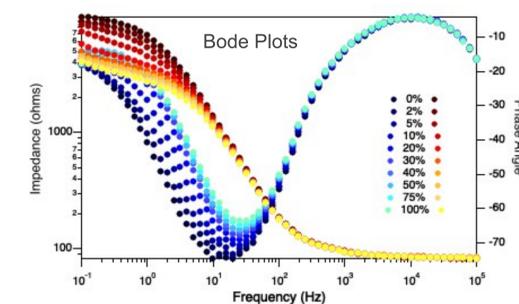
TEM Image of rutile TiO₂ nanorods on left and cyclic voltammogram of rutile TiO₂ on right.



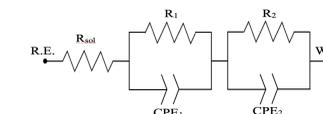
III. Photoelectrochemical Analysis

Photoelectrochemical Impedance Spectroscopy (PEIS)

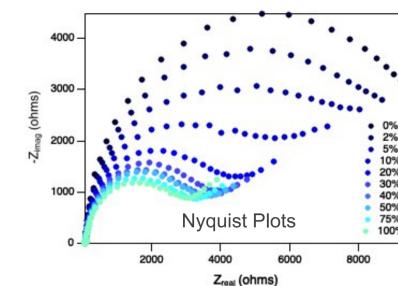
- PEIS is a perturbation technique that can be used to extract electrochemical information about materials exposed to light.
- Samples were dyed with [Ru(2-2'-bipyridine)2(4,4'-(PO₃H₂)₂-2,2'-bipyridine)]²⁺ and a 514 nm LED was the light source.
- The Bode and Nyquist plot (right) can be fit to combinations of circuit elements (shown below) to extract capacitance and resistance data about the electrochemical cell.
- From extracted resistance and capacitance data, the rates for back-electron transfer can be calculated for different metal oxides and core-shell materials.



Solvent: pH 4.7 Acetate Buffer, 3 mM Hydroquinone
10 mA AC Perturbation

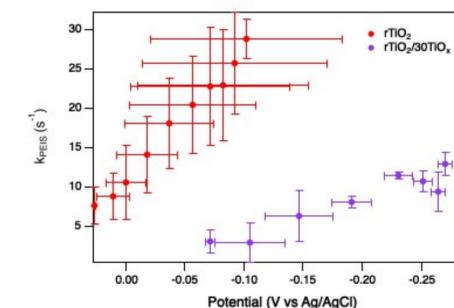


Representative circuit model used to fit PEIS data



Back-Electron Transfer is Slower in Core-Shell Materials

The graph on the left shows the rate constants for back-electron transfer for rutile TiO₂ nanoparticles in red and rTiO₂/30TiO_x core-shell nanoparticles in purple. The rate constants are lower for the core-shell material, indicating back-electron transfer is slower.

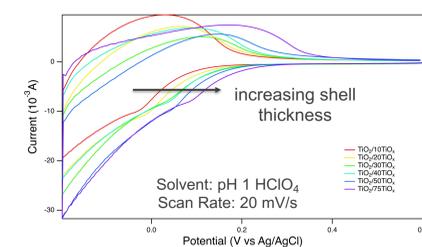


II. Sample Synthesis and Characterization

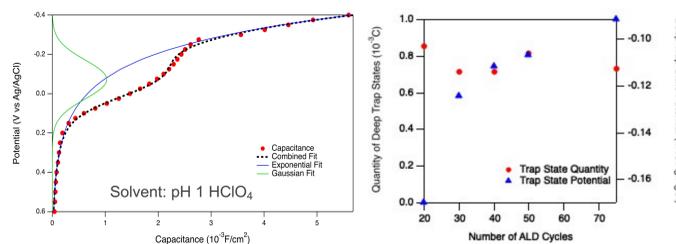
Synthesis of rutile TiO₂ with TiO_x Shells

- TiCl₄ + H₂O is added to water and stirred for several days to produce rutile TiO₂ nanorods.
- The nanorods are isolated and deposited onto FTO conductive substrates and then thermally treated to produce the thin film.
- Atomic Layer Deposition (ALD) is a gas-phase technique that allows atomically thin layers of a material to be deposited onto a substrate. ALD is used to produce the rTiO₂/TiO_x core-shell materials.

Electrochemistry Shows Shifting Trap States

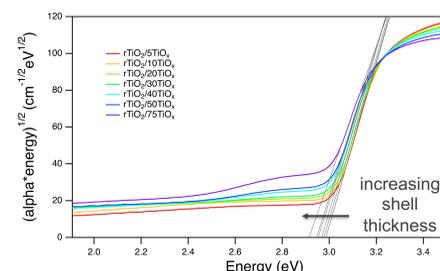


From cyclic voltammetry, one can see that the position of the deep trap states shifts to more positive potentials as shell thickness increases.

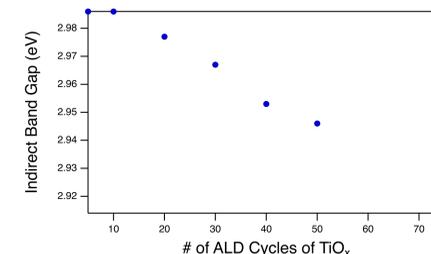


Chronoamperometry is used to quantify capacitance (left). Fitting to an exponential (blue) and a distribution of deep trap states (green) enables us to quantify the number of trap states (right) which is unchanged by shell thickness.

Band Gap Decreases with Shell Addition



Tauc plots, shown above, are constructed from diffuse reflectance spectroscopy. From this, the band gap can be extracted.



When band gap is plotted vs. shell thickness, we see that increasing the shell thickness decreases the band gap.

IV. Conclusions

- Understanding electrochemical changes brought on by deposition of shells onto rutile TiO₂ photoanodes can help us work towards improving DSPEC efficiency.
- I have confirmed the presence of a monoenergetic collection of deep trap states in rutile TiO₂ that shift to more positive potentials with increasing shell thickness.
- I have shown that the band gap also decreases with increasing shell thickness.
- From PEIS experiments, I have confirmed that the addition of TiO_x shells decreases the rate for back-electron transfer, suggesting improved photoanode efficiency.

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