Rutile TiO2 Nanowires as a Photoanode Material for Water Splitting Dye-Sensitized Photoelectrochemical Cells

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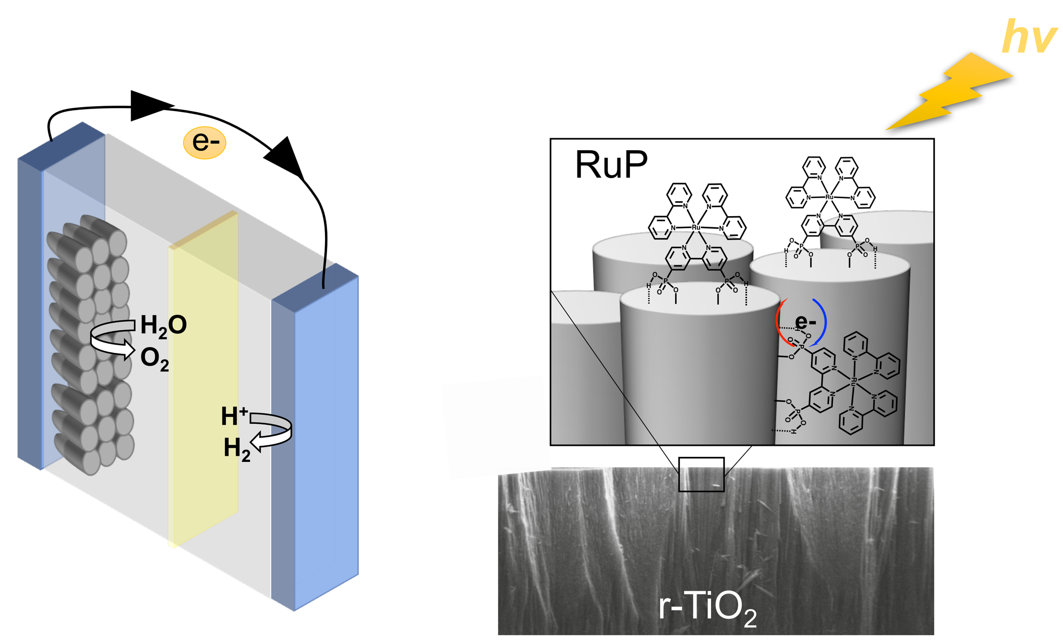
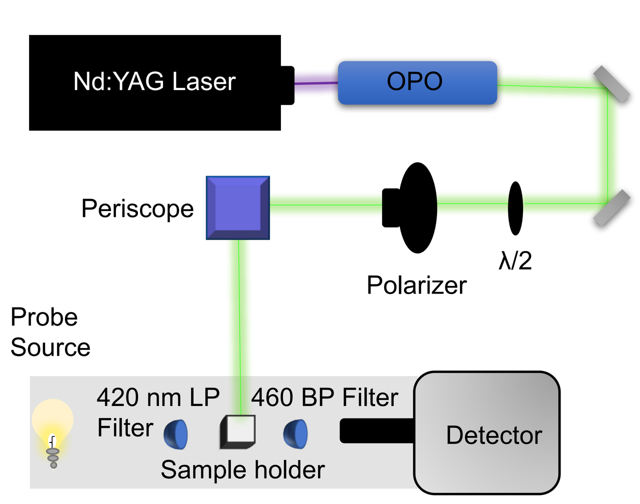
Background

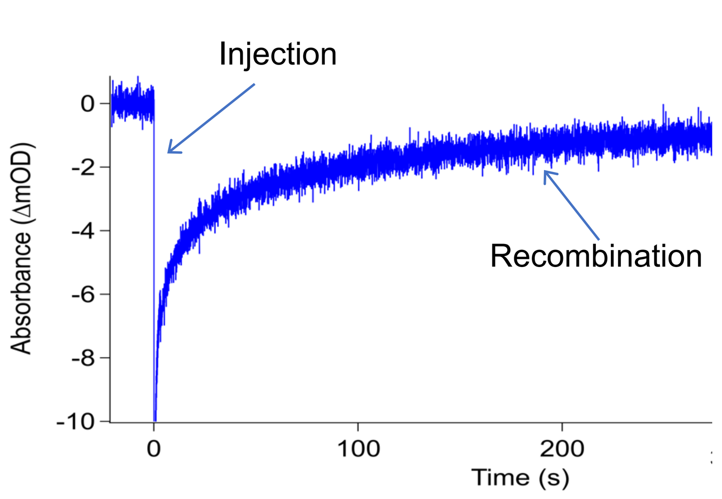
Water splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) convert solar energy into a chemical fuel by driving water oxidation at a photoanode comprised of a metal oxide sensitized with a light absorbing dye. Subsequent proton reduction at a cathode to produces H_2. Rutile TiO_2 (r-TiO_2) has been shown to be a promising photoanode material due to its lower recombination rates and increased dye stability relative to anatase TiO_2.[1] We explore r-TiO_2 grown in nanowire morphologies as a method of improving directional photoconductivity, decreasing recombination rates, and improving photoelectrochemical performance.



Transient Absorption

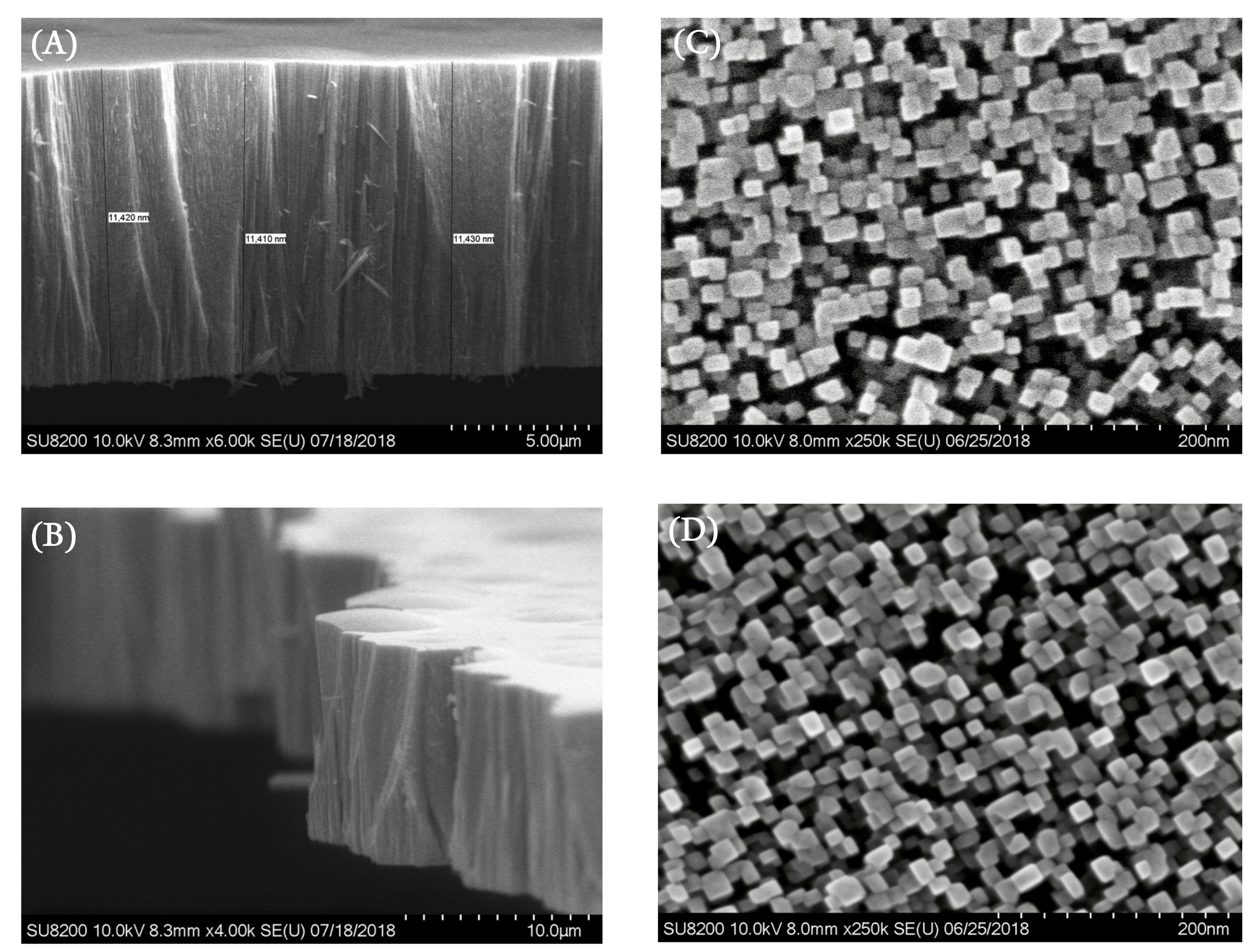
The nanosecond transient absorption (ns TA) spectrometer used was an Edinburgh Instruments LP920. A Quanta-Ray INDI laser and Spectra Physics BasiScan OPO was used as the excitation source for all transient absorption experiments. A schematic of the system is illustrated the right.





Recombination rates were measured with ns TA. A 7 ns, 532 nm pump pulse excites the dye. Injection occurs on the sub-ps to ps timescale, which is too fast to resolve with ns TA, while recombination ranges from ns to ms. Future applications include studying these systems with ultrafast TA to elucidate injection kinetics.

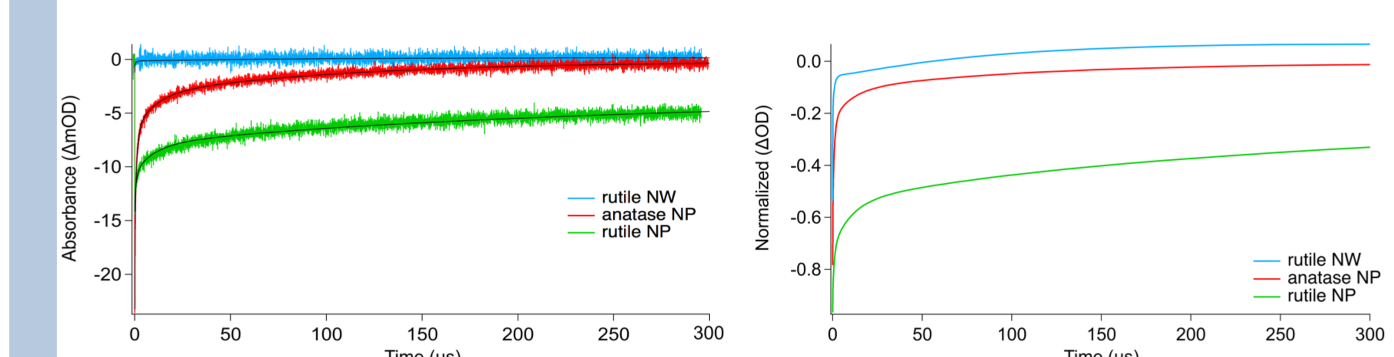
SEM Images



(A) Cross section of nanowires approximately 11.4 μm in length. (B) Zoomed out cross section. (C and D) Top view of nanowires.

Experimental Data

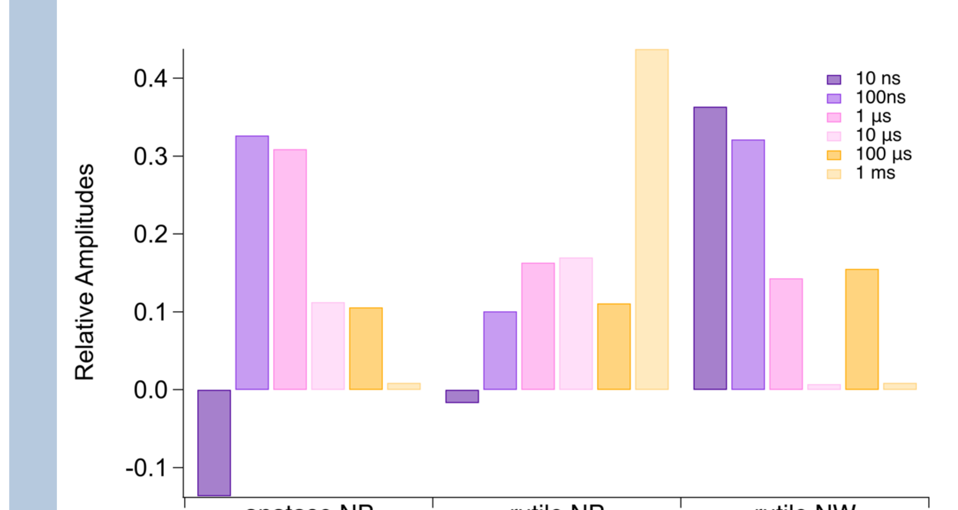
The rutile nanowire (NW) films were grown directly on FTO[1] while the rutile nanoparticles (NP) and anatase NP were doctor-bladed and annealed on FTO. The films were then sensitized with 4,4′-diphosphonato-2,2′-bipyridine)bis(2,2′-bipyridine)-ruthenium(II) bromide (**RuP**). The samples were excited at 532 nm and probed at 460 nm to track the ground state bleach of **RuP** which can be attributed to injection followed by recombination.



The decadic model was used to fit the data.[3] This model is a sum of exponentials with fixed time constants and a varying amplitude. For these fits, τ_n ranges from 10 ns to 1 ms.

$$y = \sum_0^n A_n * e^{\left(-\frac{t}{\tau_n}\right)} \qquad \ln\langle\tau\rangle = \sum_0^n A_n * \ln(\tau_n)$$

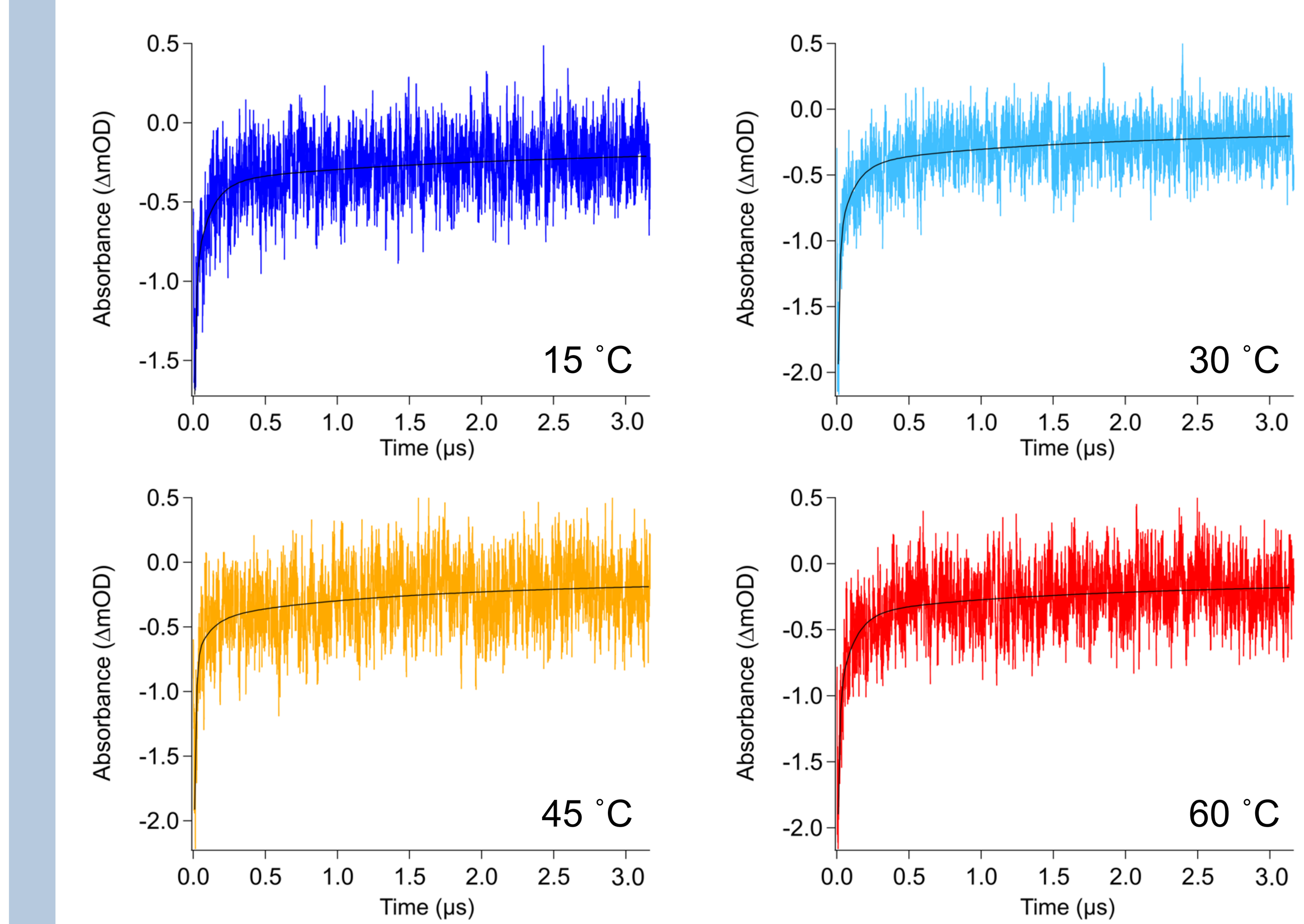
From this model, average lifetimes are determined from logarithmic weighting of the lifetimes (see above).



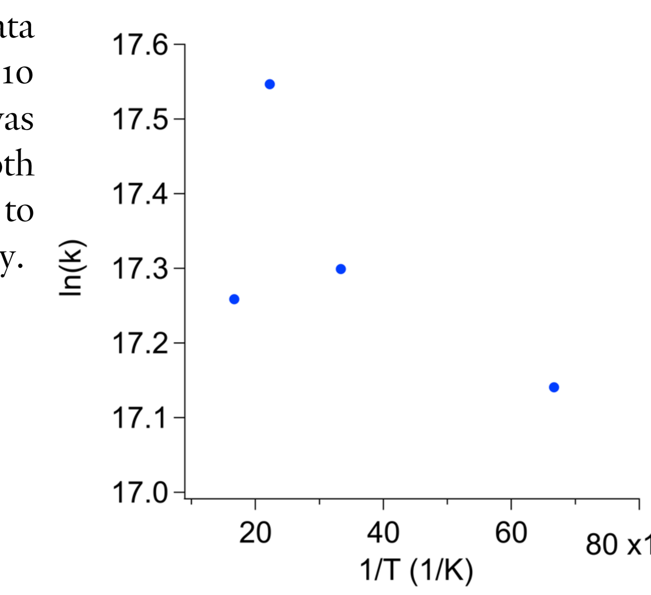
	Lifetimes (s)
Anatase NP	1.07×10^{-6}
Rutile NP	4.29×10^{-5}
Rutile NW	8.54×10^{-8}

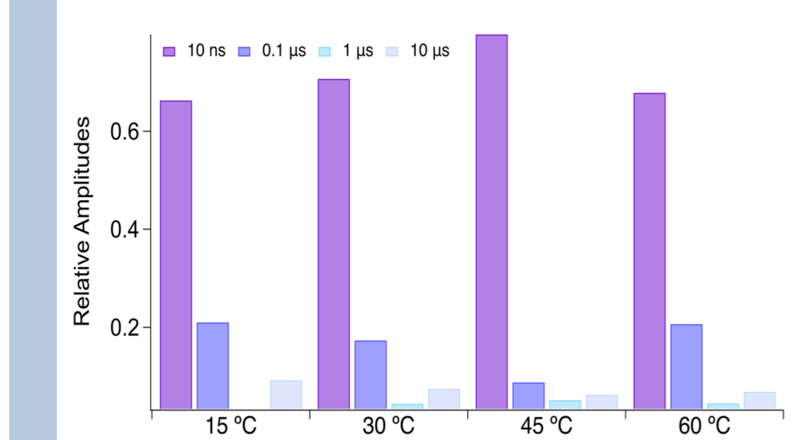
Temperature Controlled Experiments

Changes in rate of recombination were measured as a result of change in temperature.



The decadic model was used to fit the data with time constants ranging from 10 ns to 10 μs. A preliminary Arrhenius plot was constructed assuming the reaction is zeroth order. More measurements are required to obtain error bars and ensure reproducibility.





Temp (°C)	15	30	45	60
k (s^{-1})	17.14	17.29	17.55	17.26

Future Directions

- Grow nanowires on a substrate transparent to terahertz radiation to examine charge transfer directly in the nanowires and see processes such as injection and trapping.
- Utilize ultrafast transient absorption to better understand injection from the dye to the conduction band of the metal oxide.
- Determine second-order rate constants using potential controlled transient absorption measurements.
- Make an Arrhenius plot with second-order rate constants to determine the activation barrier for recombination.

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References:

[1] Swierk, J. R.; Regan, K. P.; Jiang, J. et al. *ACS Energy Letters,* **2016,** *1*, 603-606.

[2] Li, H.; Yu, Q.; Huang, Y. et al. *ACS Appl. Mater. Interfaces,* **2016,** *8*, 13384-13391.

[3] Zhang, Lei et al. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 18515-18527.