Electrochromism vs. the Bugs:

Developing WO_3 Thin Film Windows to Control Photoactive Biological Systems

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Electrochromism vs. the Bugs

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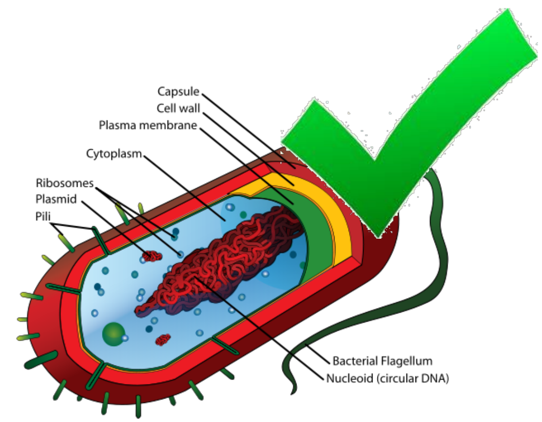
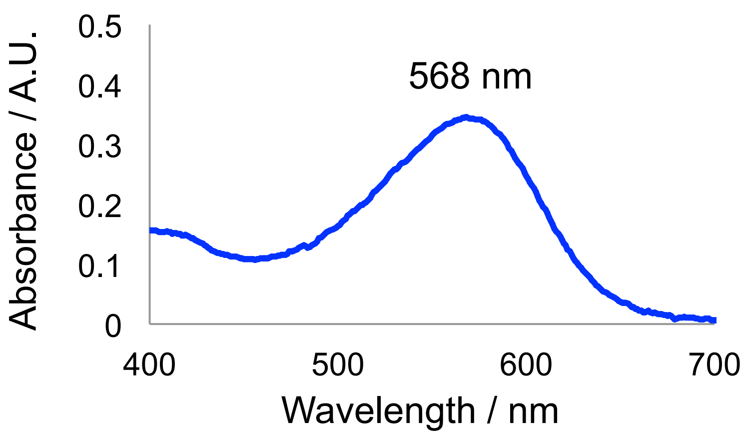
Goal: Control the response of a photoactive biological system

- Electrochromic materials allows an external stimulus (voltage) to control the amount of light delivered to the biological system.
- Direct integration of the electrochromic and biological systems
- Remote control of biological system

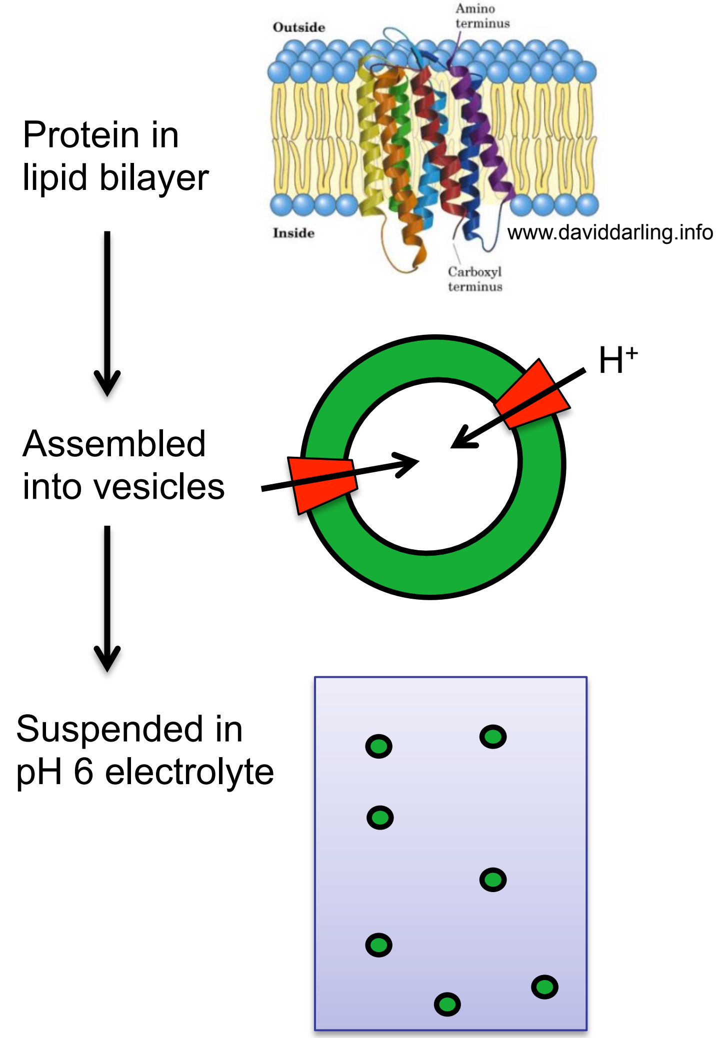


Bacteriorhodopsin

- Photoactive transmembrane biological proton pump from *Halobacterium salinarum*
- Absorbs visible light to pump protons
  - 1 proton/photon
- Stable over pH 3-10, up to 140 °C



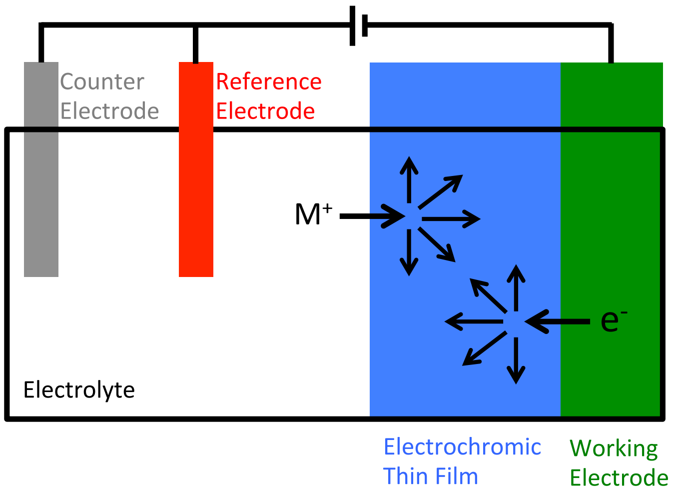
Optical absorbance of bacteriorhodopsin vesicle suspension



Electrochromics

- Injection of charge changes optical absorption of a thin film
- Evaluate electrochemically, optically
  - Liquid electrolyte or all solid state
- Consumer applications
  - Mirrors
  - Window coatings

www.Genetex.com

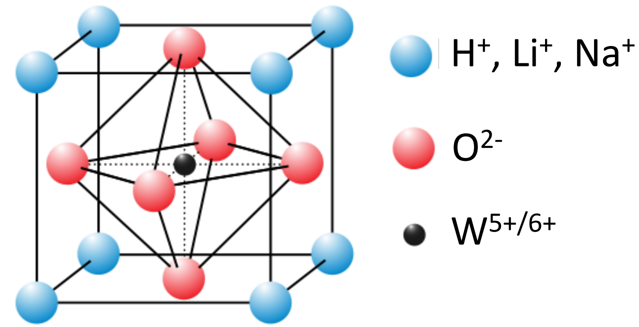


Electrochemical cell for testing electrochromic materials.

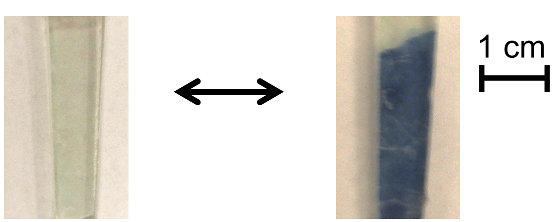
www.Boeing.com

WO_3

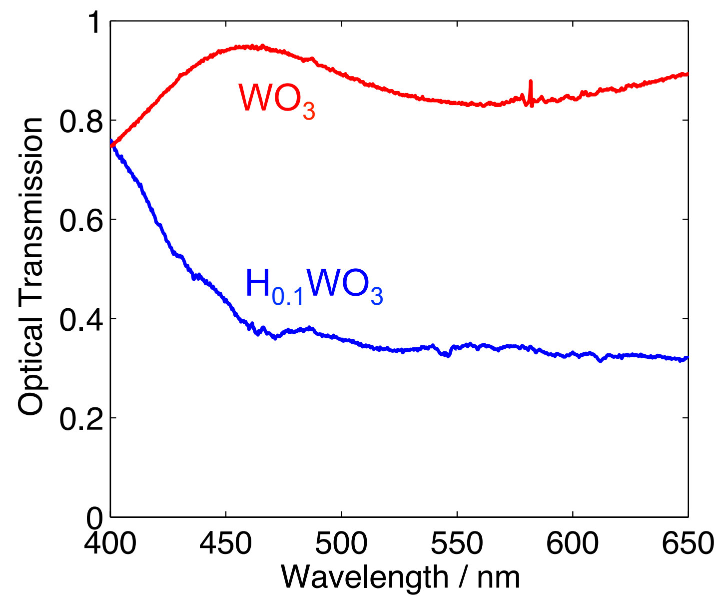
- Rhenium oxide crystal structure
  - monoclinic
  - pseudo-perovskite: empty A-site
- To decrease optical transmission
  - Insert H^+, Li^+, or Na^+ into A-site
  - Reduce W^{6+} to W^{5+}



$$WO_3 + xH^+ + xe^- \leftrightarrow H_xWO_3$$



500 nm WO_3 on FTO/glass



Sol-Gel Processing WO_3

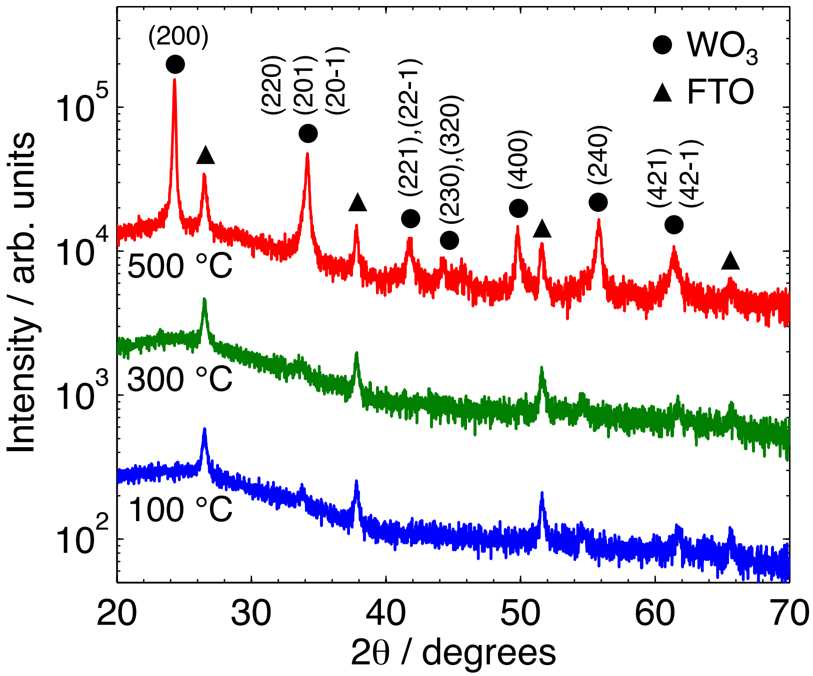
- Dissolve W powder in H_2O_2 at 0 °C for 2 hours
- Centrifuge 3000 rpm 15 minutes, remove precipitate
- Combine with equal volume glacial acetic acid
- Reflux overnight at 70 °C
- Remove solvents → acetylated peroxotungstic acid

- Dissolve 1.25 g acetylated peroxotungstic acid in 10 mL ethanol
- Spin coat onto Fluorine-doped SnO_2 on glass, 2000 rpm, 60 s
- Dry at 100 °C, 5 minutes
- Spin 4 layers
- Crystallize between 100-500 °C for 3 hours

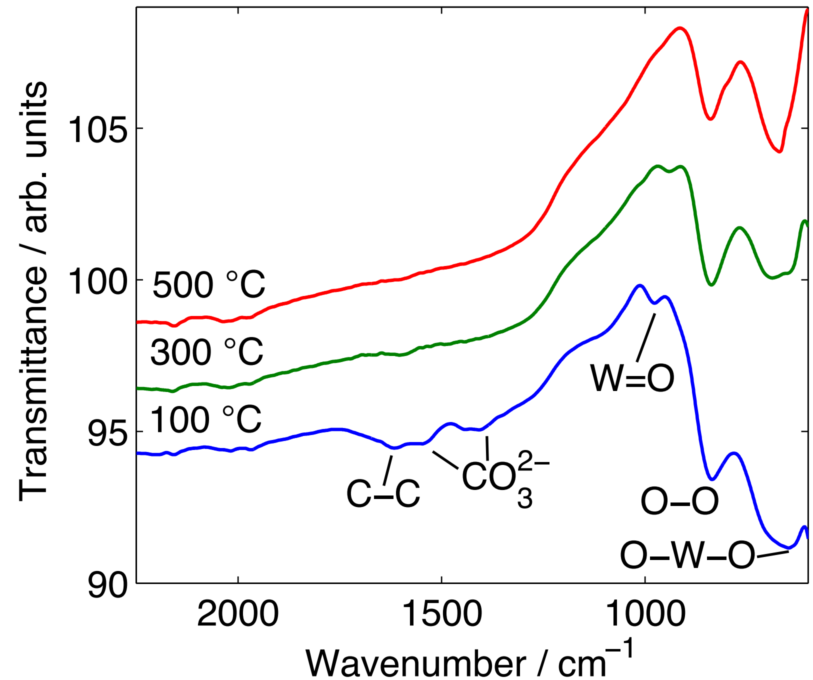
Adapted from
M. Deepa, A. Joshi, A. Srivastava, S. Shivaprasad, and S. Agnihotry, *J. Electrochem. Soc.*, **153**, C365 (2006).

Crystallization Temperature

X-ray Diffraction



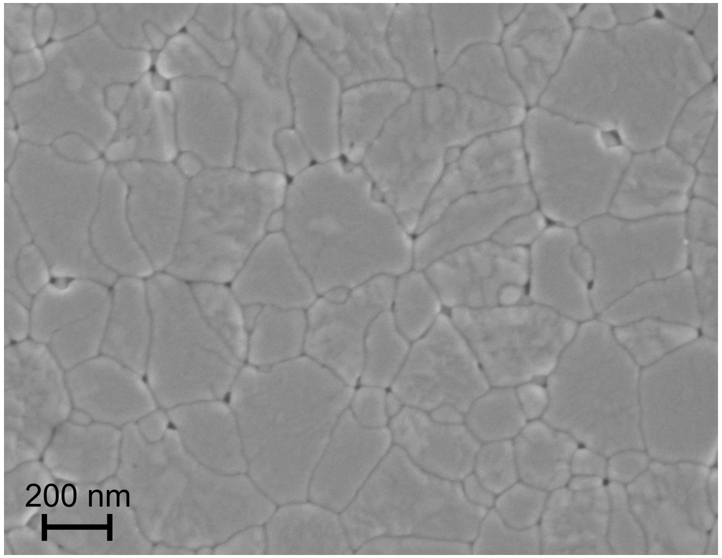
Infrared Spectroscopy

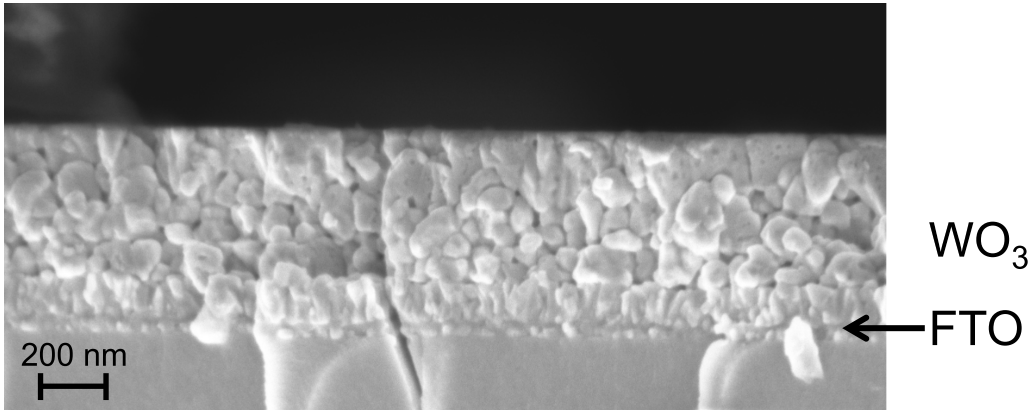


WO_3 is amorphous at 100, 300 °C,
(200)-oriented monoclinic WO_3 at 500 °C.

At 100 °C organics still remain in WO_3 film.

WO_3 Film Microstructure

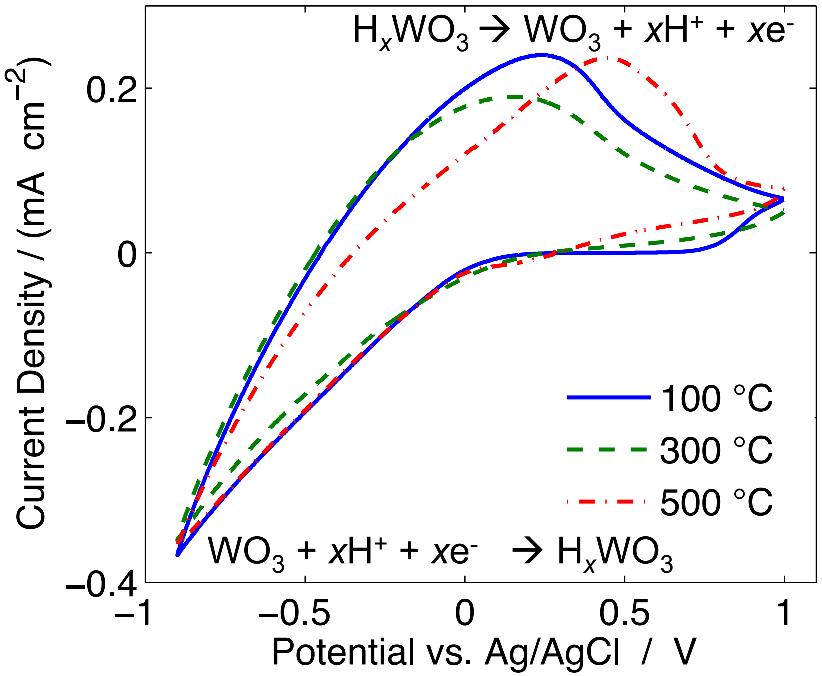




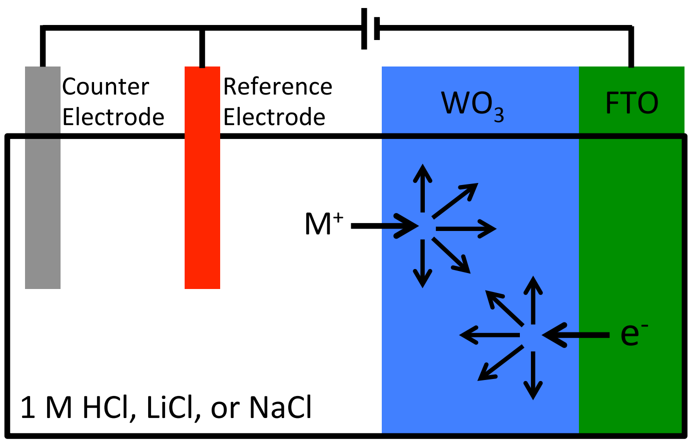
Films annealed at 500 °C exhibit slight porosity with grains ~100 nm in diameter.

Processing Temperature Effects

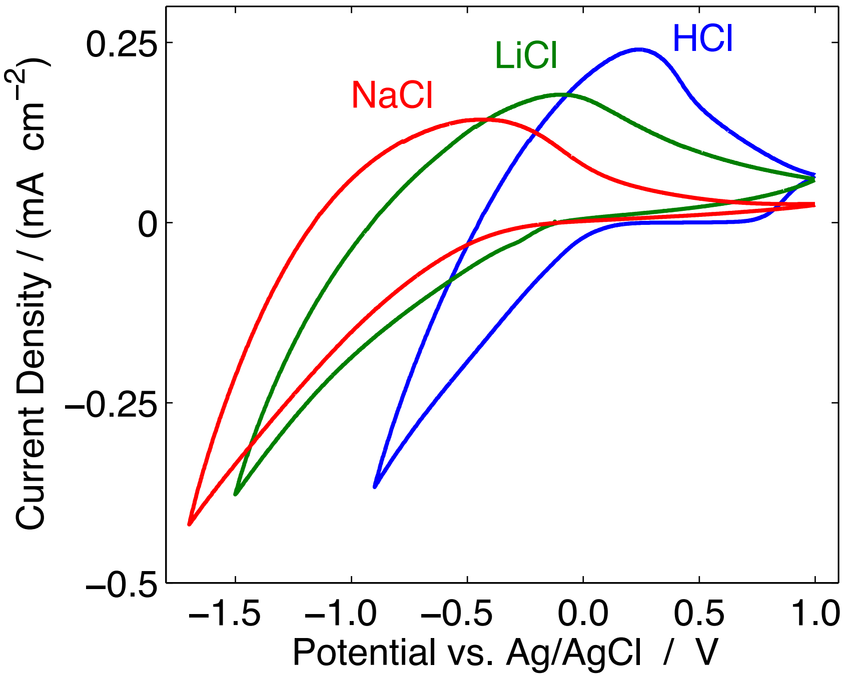
Cyclic Voltammetry



1 M HCl. 25 mV/s scan rate.



Effect of Electrolyte

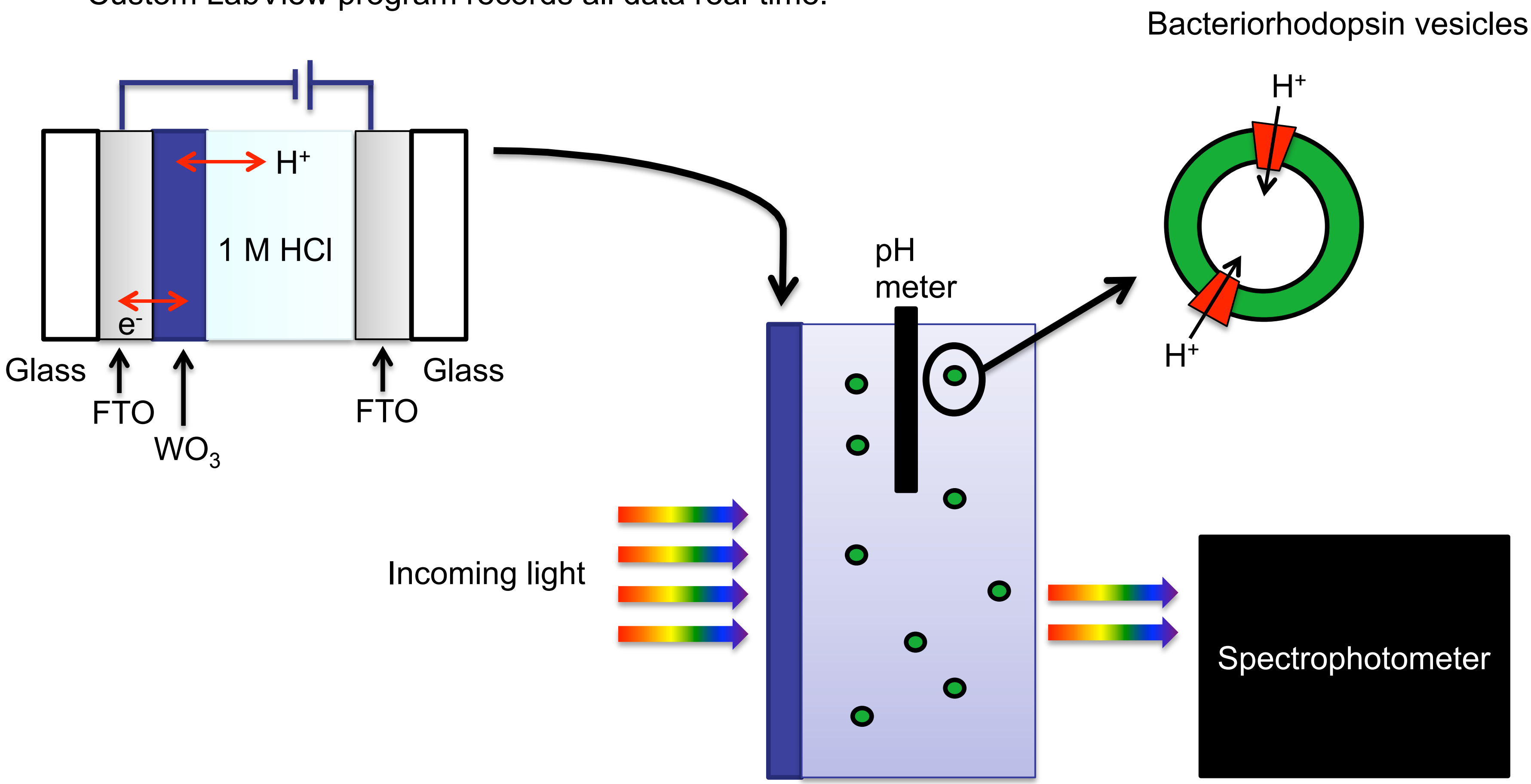


1 M salts. 25 mV/s. Films crystallized at 500 °C.

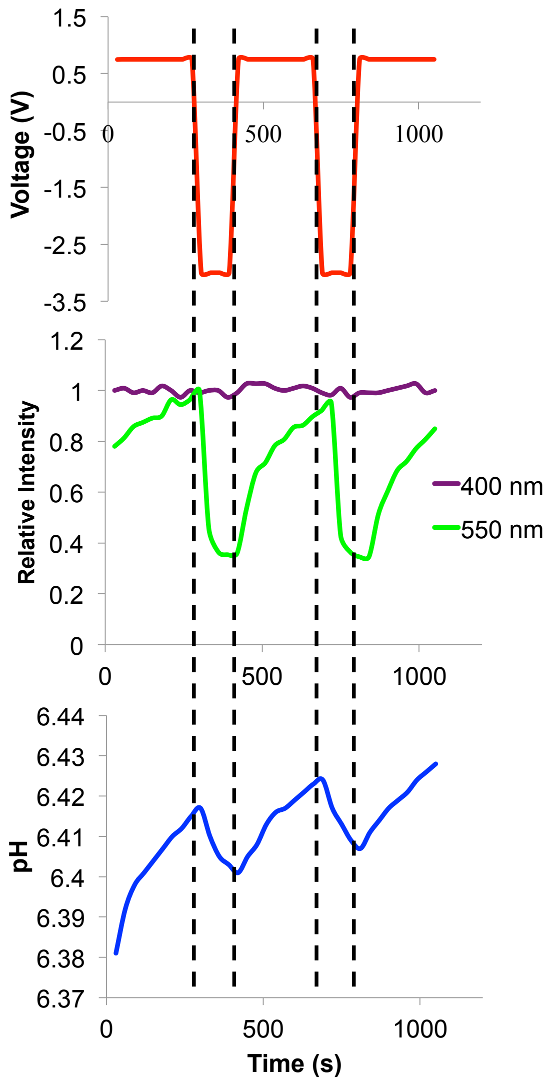
Larger ions require larger potentials to intercalate into WO_3 lattice.

Integrated Measurements

- Electrochromic window to modulate light incoming to bacteriorhodopsin vesicles
- Record pH and optical transmittance as a function of applied voltage.
- Custom LabView program records all data real-time.



Controlling the Biosystem



Modulate intensity of incoming light by applying a voltage across electrochromic WO_3 thin film.

Reversible pH changes correlate with voltage-induced changes in WO_3 optical absorbance.

<0.1 vol% vesicle loading

- in bulk solution $\Delta pH = 0.03$
- in vesicle $\Delta pH \sim 2$

Future Work

- Direct integration of WO_3 into biological environment
- Higher loading of “bugs” to realize greater pH change

Questions?

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