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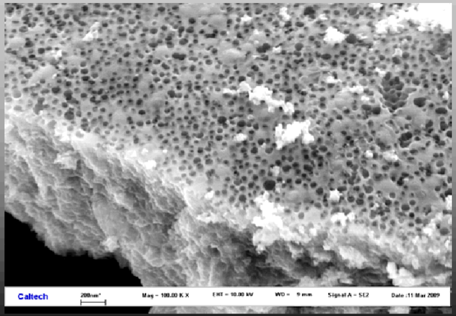

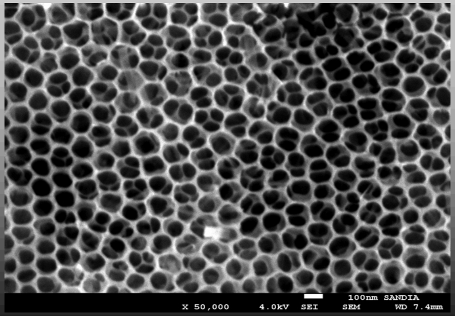

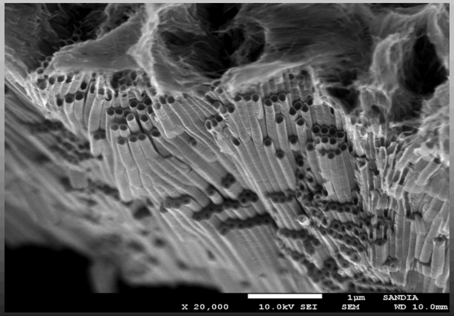

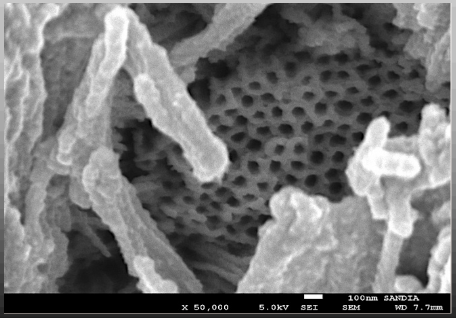

Composite WO_3/TiO_2 Nanotubes for Solar Photoconversion and Electrochromic Applications

Karla R. Reyes, and David B. Robinson

Materials Chemistry

Sandia National Laboratories, Livermore CA

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Solar Photo-conversion: Problems and Progress

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Problem: Low Efficiency

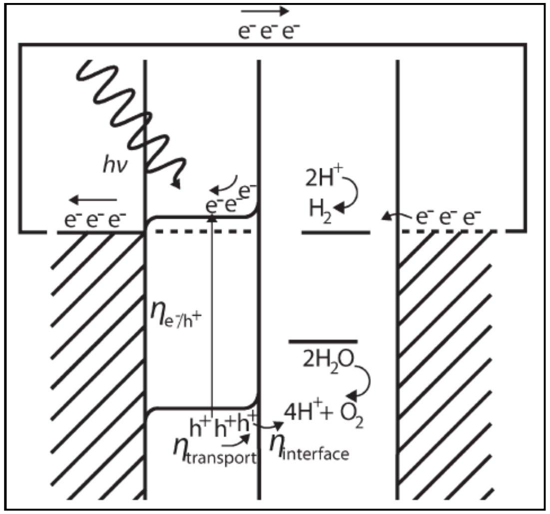
- The overall efficiency of the metal oxides is still too low for commercial use.
- There are three factors that are jeopardizing the incident photon to current efficiency (IPCE) of metal oxides:

$$\text{IPCE} = \eta_{e^-/h^+} \cdot \eta_{transport} \cdot \eta_{interface}$$

1) Poor absorption of solar light

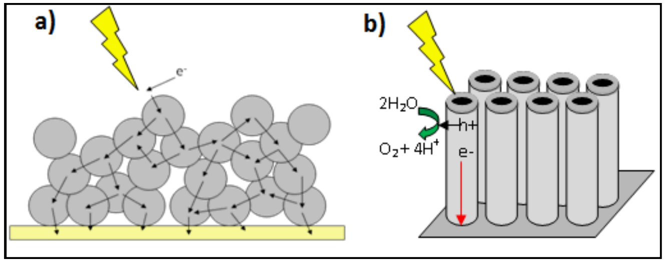
2) Poor charge-carrier transport

3) Poor interfacial charge transfer



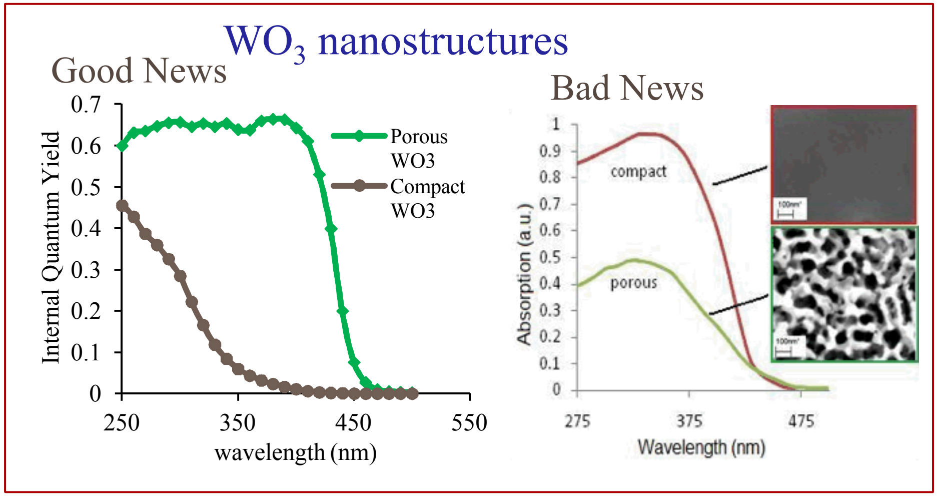
Progress: Improved Transport

- Nanostructured morphology improves e^-/h^+ transport, consequently reducing the e^-/h^+ recombination.



$IQY \approx \eta_{transport} \cdot \eta_{interface}$
improved transport

$Abs \approx \eta_{e^-/h^+}$
→ poor absorption



LABORATORY DIRECTED RESEARCH & DEVELOPMENT
Early Career Program

Sandia National Laboratories

New Approach- Manipulation of semiconductors to correct each of those limiting factors in comprehensive and synergistic approach.

Problem	Poor absorption	Poor transport	Poor transfer
Process	$\eta_{e-/h+}$	$\eta_{transport}$	$\eta_{interface}$
Proposed Solution	Composite materials (WO_3/TiO_2) with long absorption pathway	Organized nanostructures (TiO_2 nanotubes)	Add organic pollutants with a fast oxidation rate

Research Goals-

Develop composite WO_3/TiO_2 materials with long absorption pathways using TiO_2 nanotubes as a "skeleton" AND use these materials in a photo-electrochemical cell for wastewater treatment with simultaneous H_2 production.

Milestones-

1. Development of a new composites WO_3/TiO_2 nanostructures.
2. Characterization of new composite materials.
3. Performance analysis for photoelectrochemical water splitting and simultaneous photodegradation of organic pollutants.

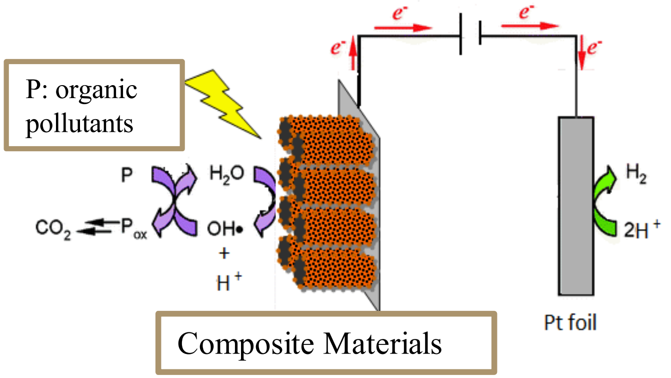
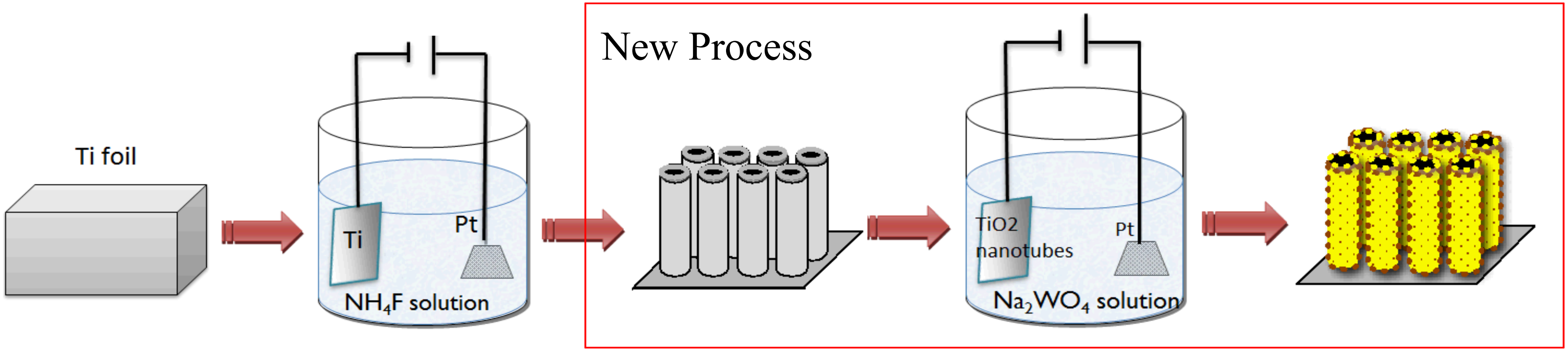


Diagram of the combined waste treatment and energy harvesting photo-electrochemical device

Solar Energy + **Wastewater**	=	**Clean Energy** + **Clean Water**

Synthesis of Composite Materials

TiO_2 nanotubes	WO_3 electrodeposition



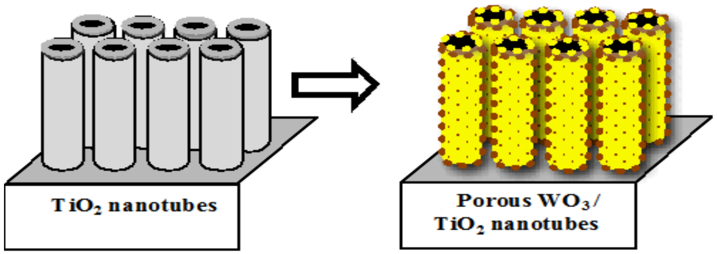
Experimental conditions
- 0.3 % NH_4F in 95:5 ethylene glycol/ water
- Potential: 50 V
- Time: 1 to 24 h

Experimental conditions
- 25 mM Na_2WO_4 and 25 mM H_2O_2 in water (pH=1.4)
- Potential: -0.437 V vs. Ag/AgCl
- Time: 5-15 min

- Several published papers about how the anodization parameters change the morphology of the nanotubes.
- Nanotubes from less than 1 μm to over 100 μm have been reported.

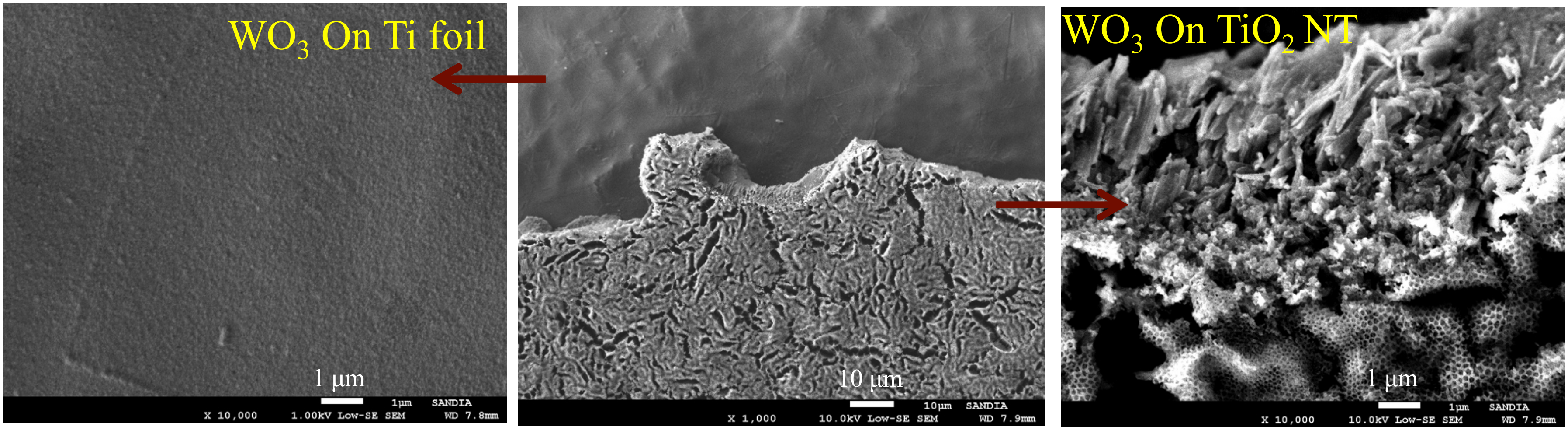
- Few published papers about WO_3 electrodeposition on flat surfaces (glass and Si wafer), but none on nanostructured substrates (TiO_2 nanotubes).

WO_3 Electrodeposition



WO_3 electrodeposition on a flat Ti foil produced a compact WO_3 layer

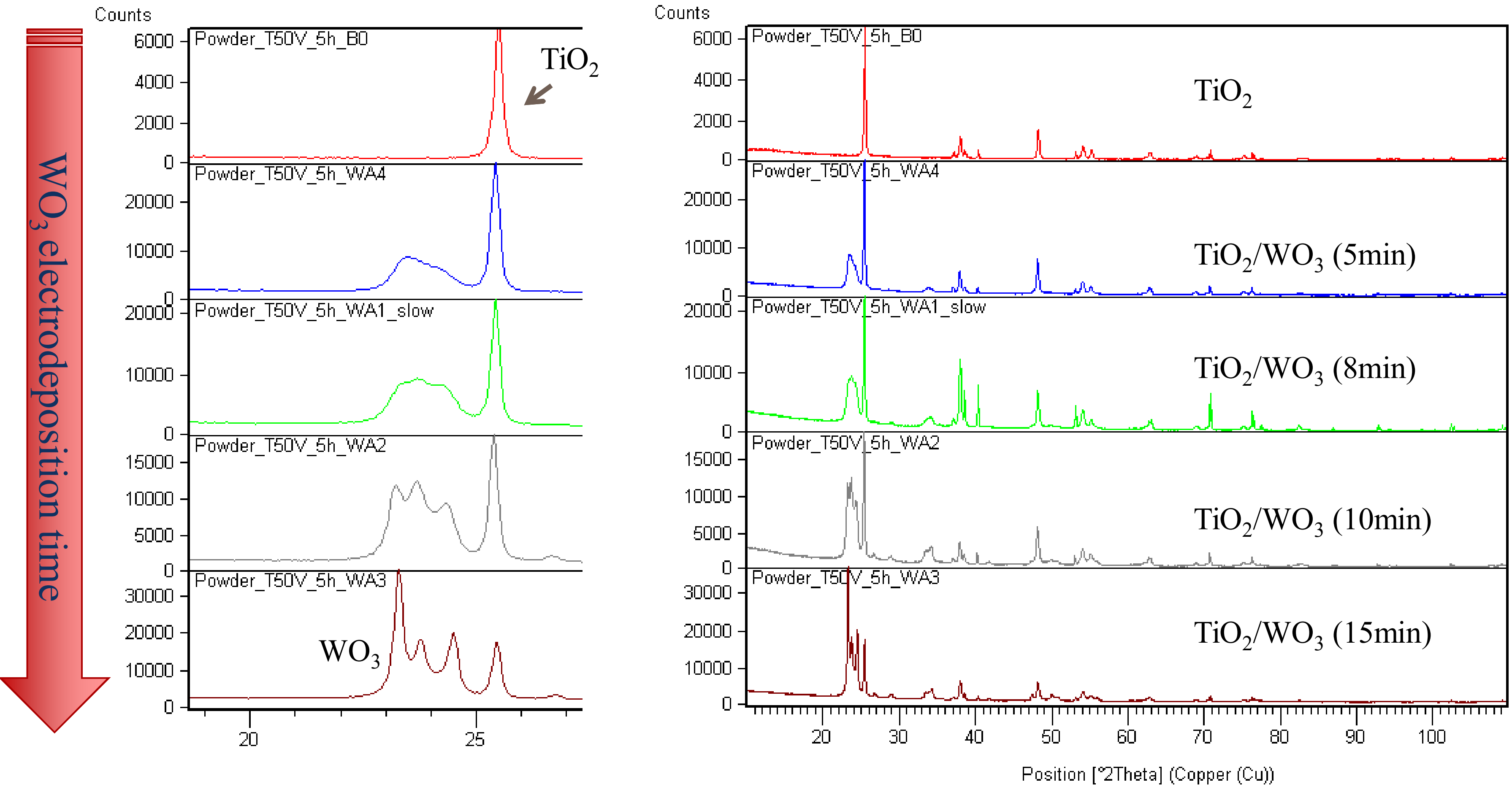
WO_3 electrodeposition on a TiO_2 nanotubes produced diverse WO_3 nanotructures.



TiO_2 nanotubes can be used as a template to create unique WO_3 nanostructures !

Different WO_3 Deposited Charge Density

- Electrodeposition time is proportional to WO_3 deposited charge density.
- XRD patterns show anatase TiO_2 and monoclinic WO_3 phases.



Morphology of Composite Materials

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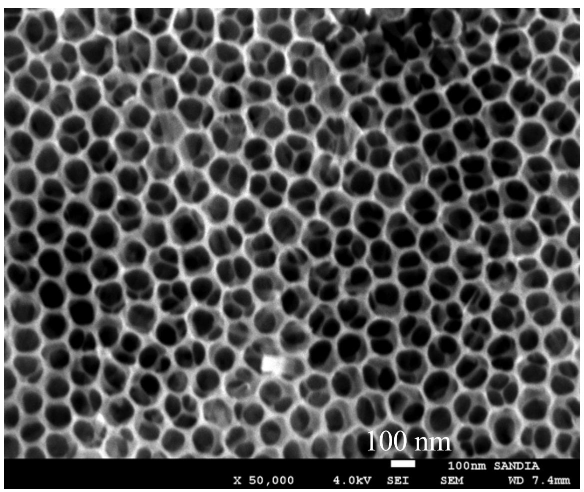
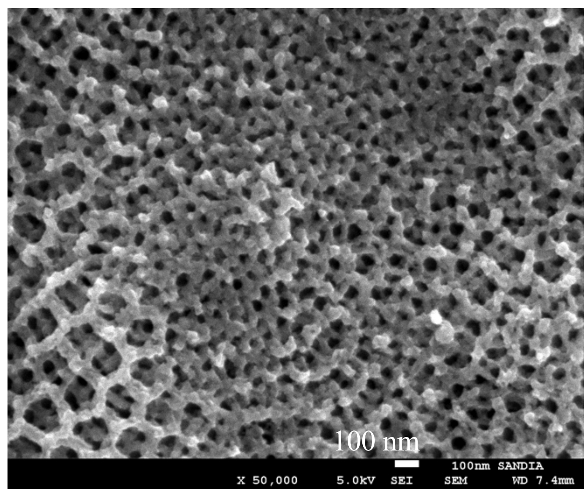
At low concentration, WO_3 particles were electrodeposited on the TiO_2 nanotube walls.

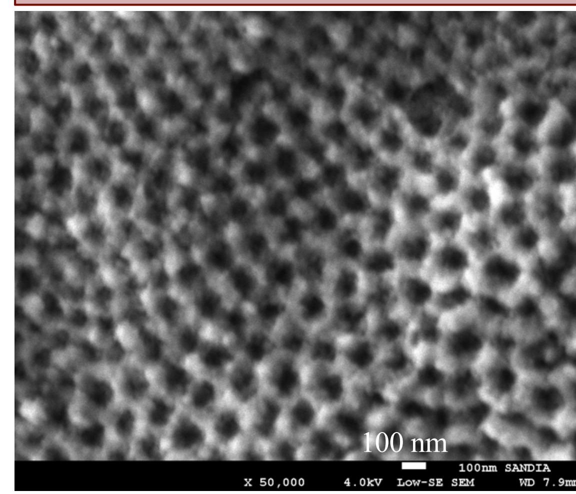
TiO_2 nanotubes



TiO_2/WO_3 (5 min)



TiO_2/WO_3 (8 min)

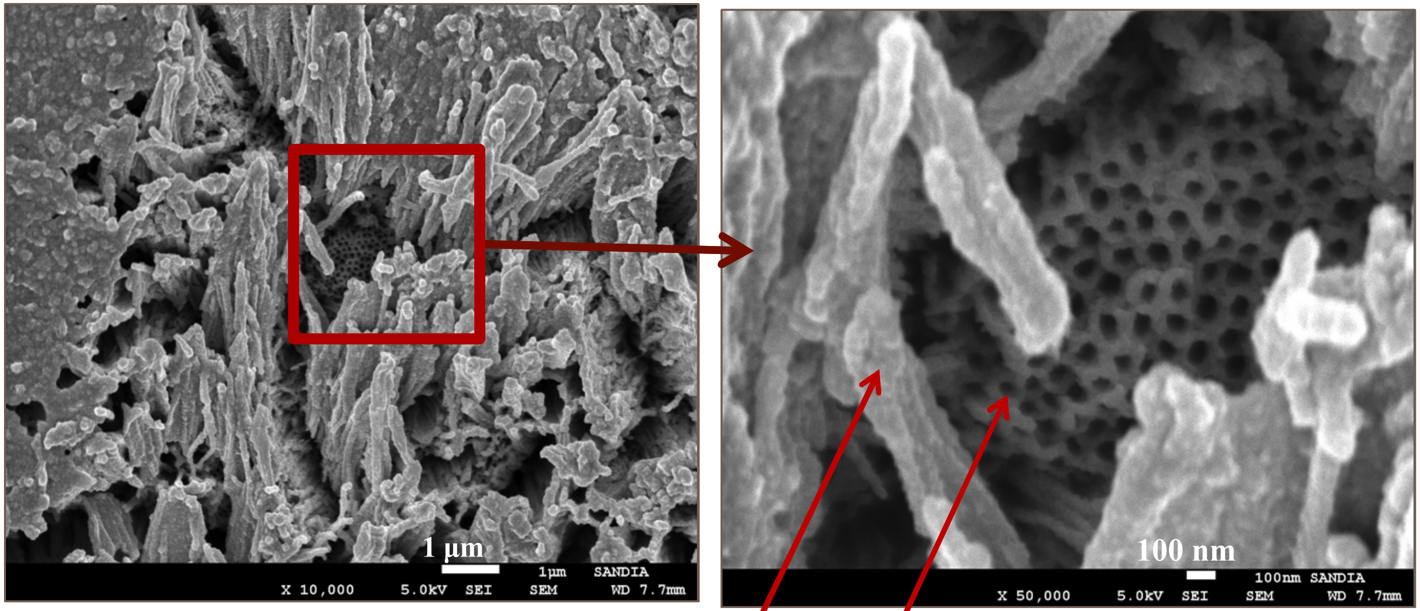


WO_3 electrodeposition time

Morphology of Composite Materials

WO_3 coral-like nanostructures were developed on top of the TiO_2 nanotubes.

TiO_2/WO_3 (10 min)



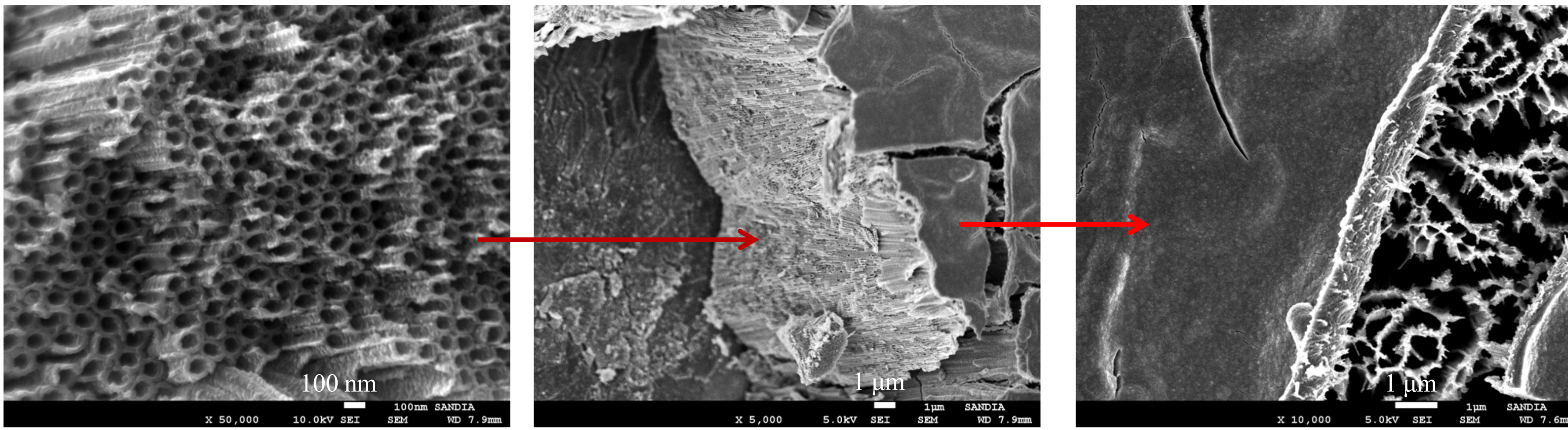
TiO_2 nanotubes

WO_3 coral-like structures

Morphology of Composite Materials

WO_3 compact layer was created on top of WO_3 nanostructures and TiO_2 nanotubes.

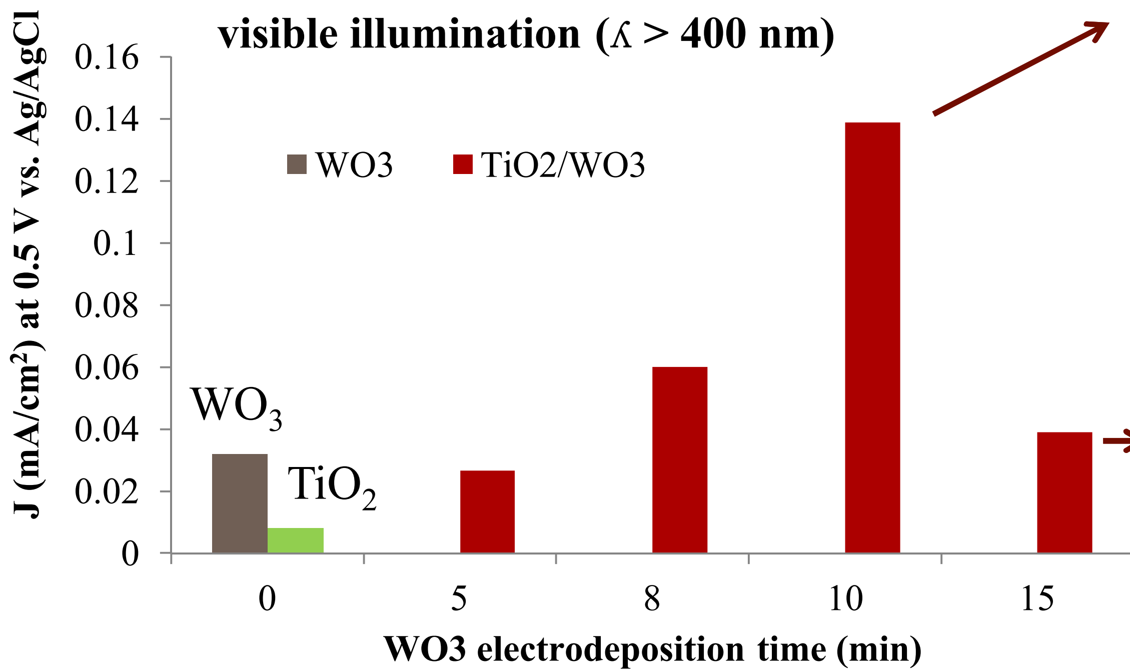
TiO_2/WO_3 (15 min)

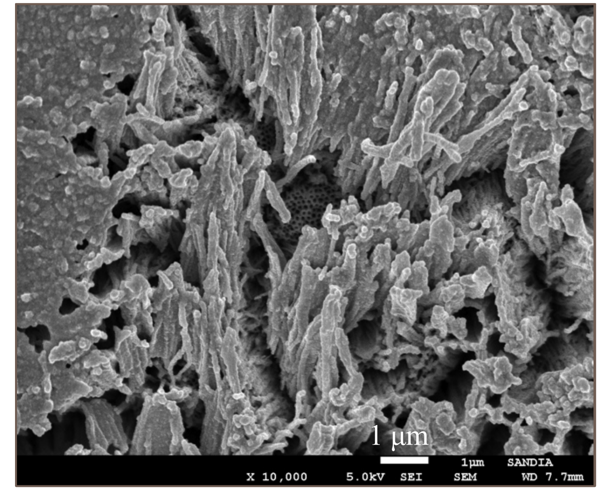


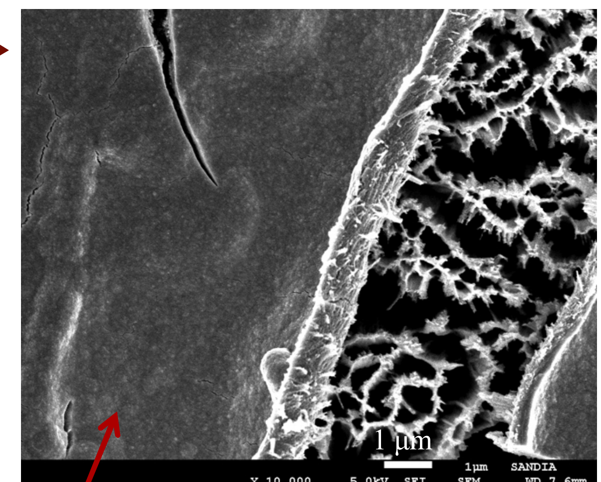
Edge View-
TiO_2 nanotubes

Top View-
WO_3 compact layer

Effect of the morphology





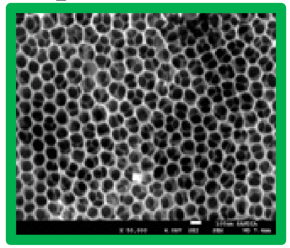


Photocurrent density was not proportionally dependent on WO_3 concentration, but depends on WO_3 nanostructures.

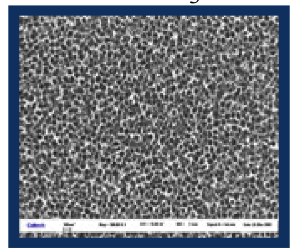
electron/hole recombination center

Optical and IPCE Results

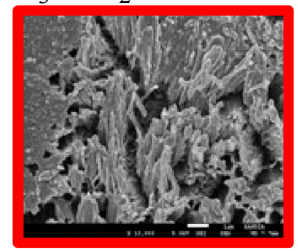
TiO_2 nanotubes

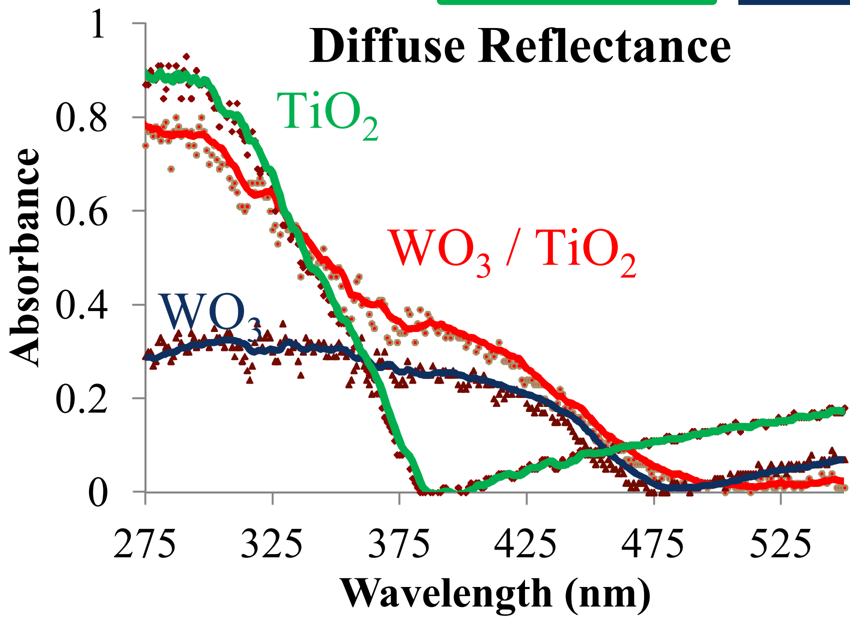


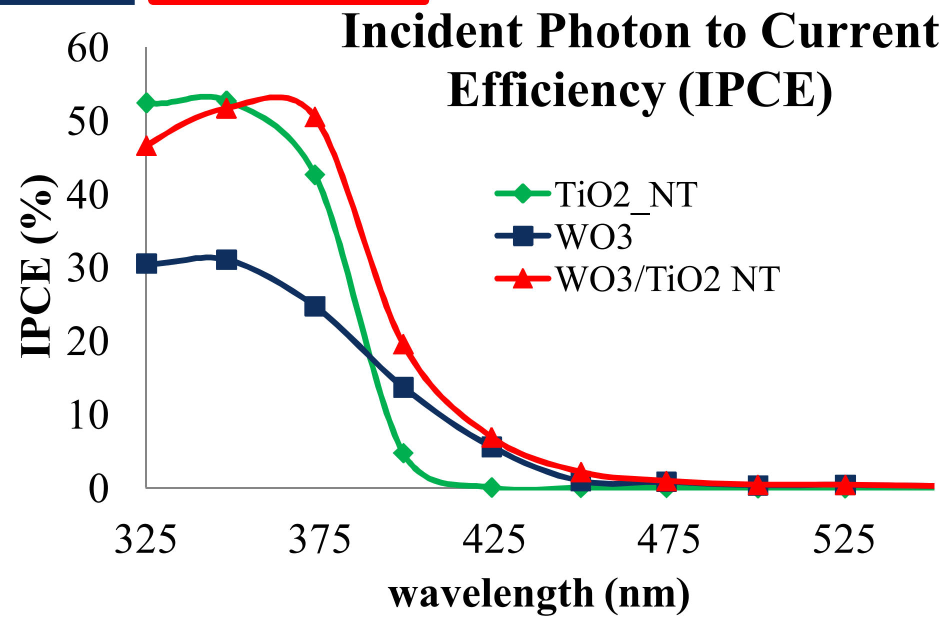
Porous WO_3



WO_3/TiO_2 nanotubes





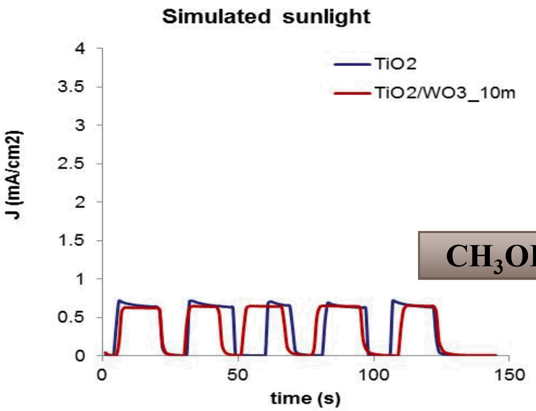


WO_3/TiO_2 nanotubes absorb almost all the UV light and extend the absorption up to the visible region.

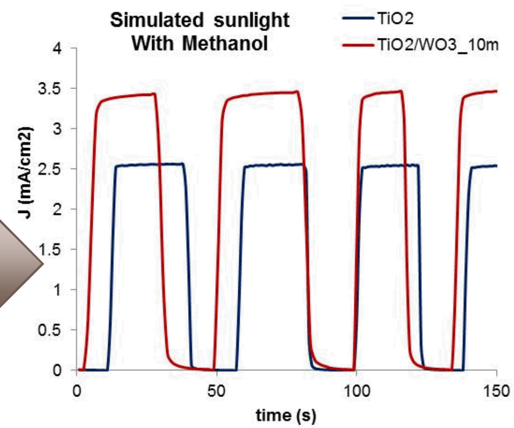
IPCE % increased from ~30% (WO_3) to ~50% (WO_3/TiO_2) in the UV range and extended up to the visible region.

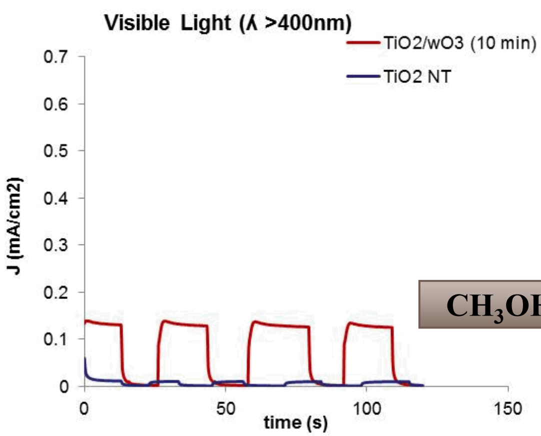
Composite nanostructures showed better sunlight absorption and higher photo-efficiency.

Nanostructures with Enhanced Photo-activity

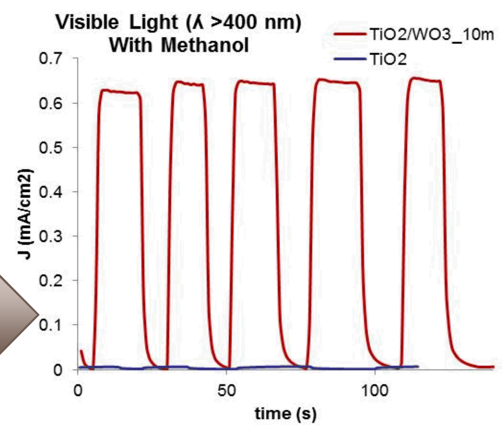


CH_3OH



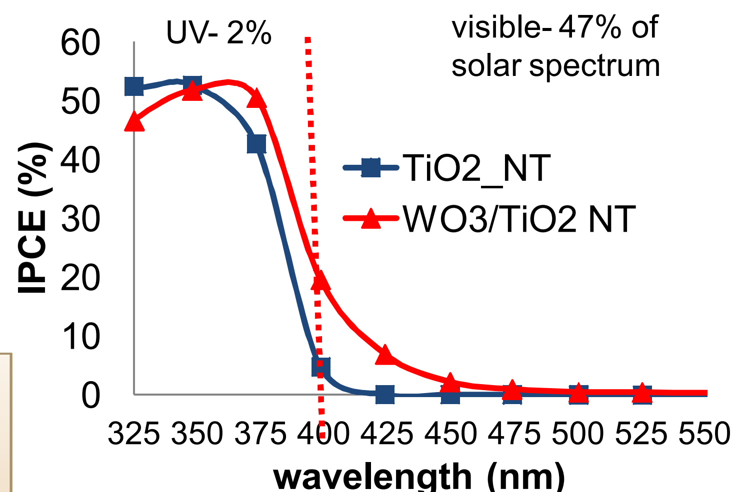


CH_3OH



- The role of sacrificial agents (Methanol) is to react irreversibly with the photogenerated holes, consequently reducing the rapid e^-/h^+ recombination.
  - TiO_2/WO_3 exhibited 6-fold larger photocurrent.
  - TiO_2 nanotubes exhibited 3.5-fold photocurrent.

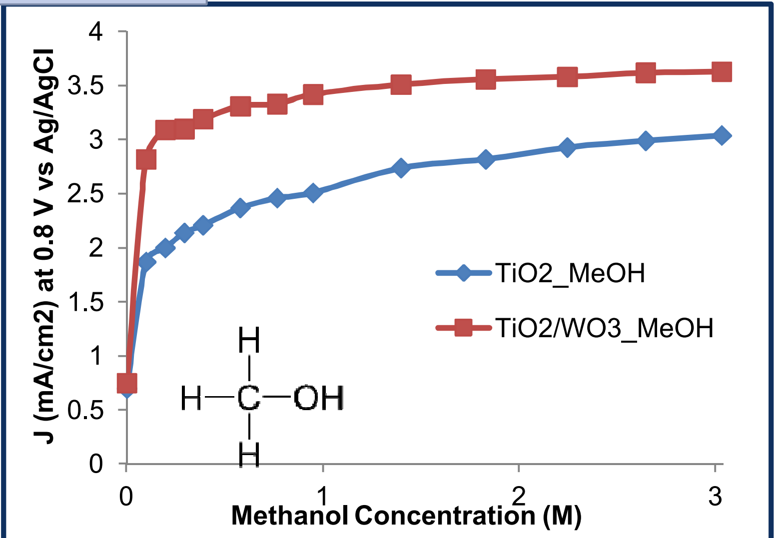
TiO_2/WO_3 in presence of methanol exhibited almost 1 mA/cm^2 higher currents. (Why?)



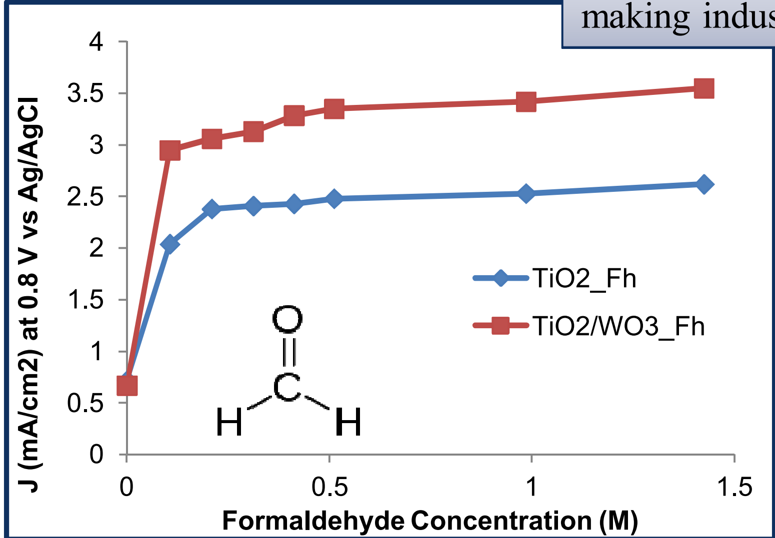
- Under visible illumination, TiO_2/WO_3 electrodes are almost 100 times better than bare TiO_2 nanotubes.
- A little improvement in the visible light absorption produces a big improvement in the photocurrent .

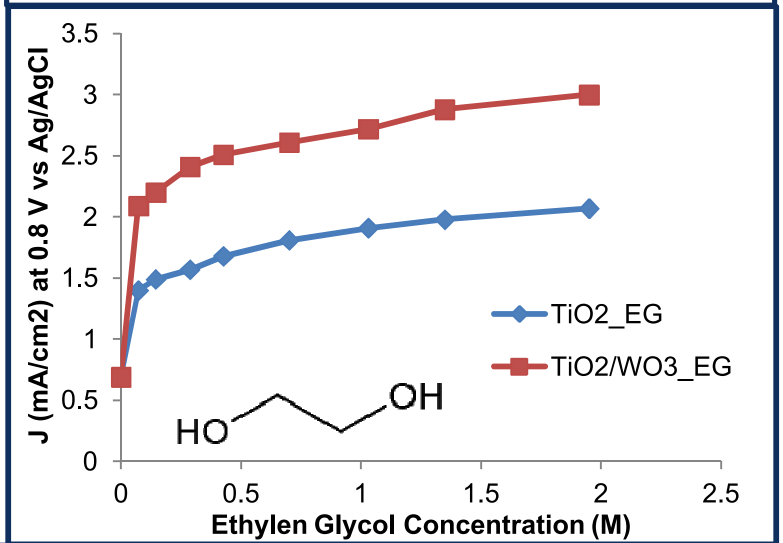
Photocurrent Improvement with organic pollutants

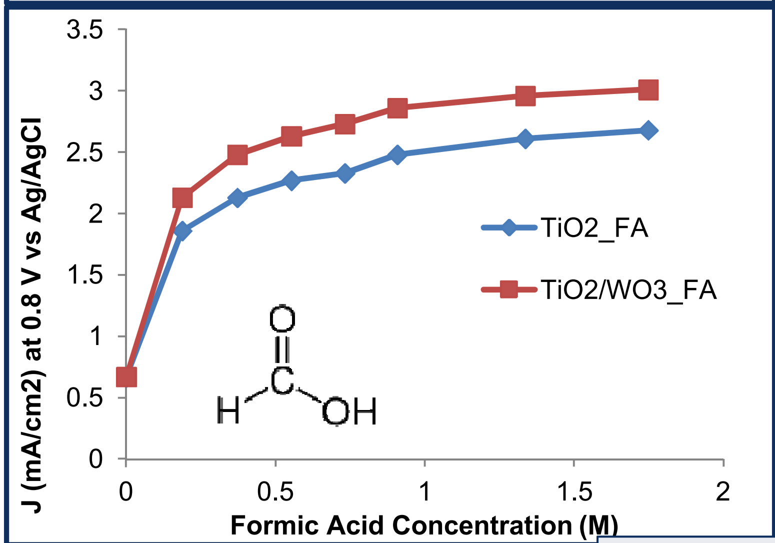
Proof of concept



Wood and cabinet making industry





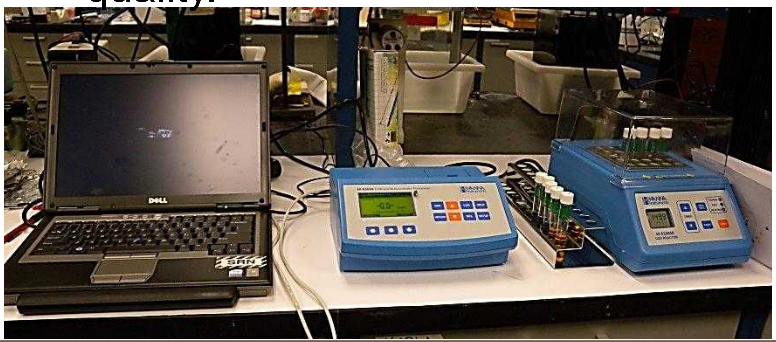


Deicing agent used in airport and roads

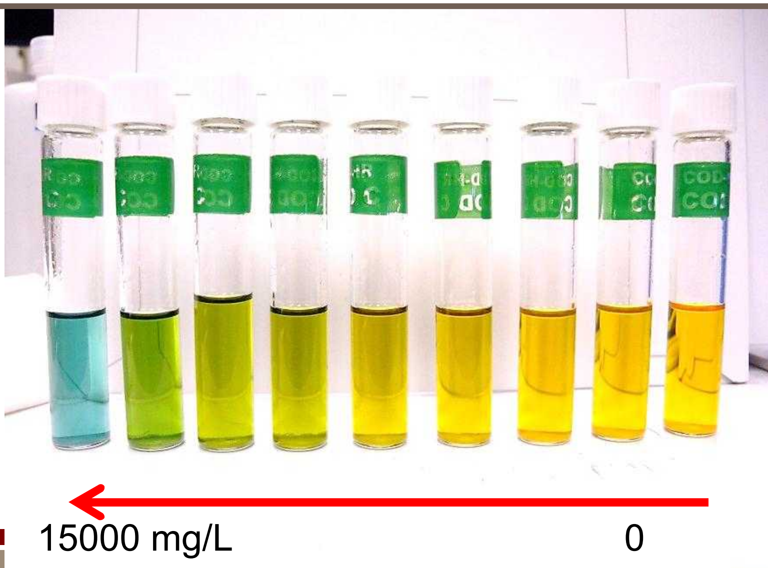
Wood, leather and fiberglass industry

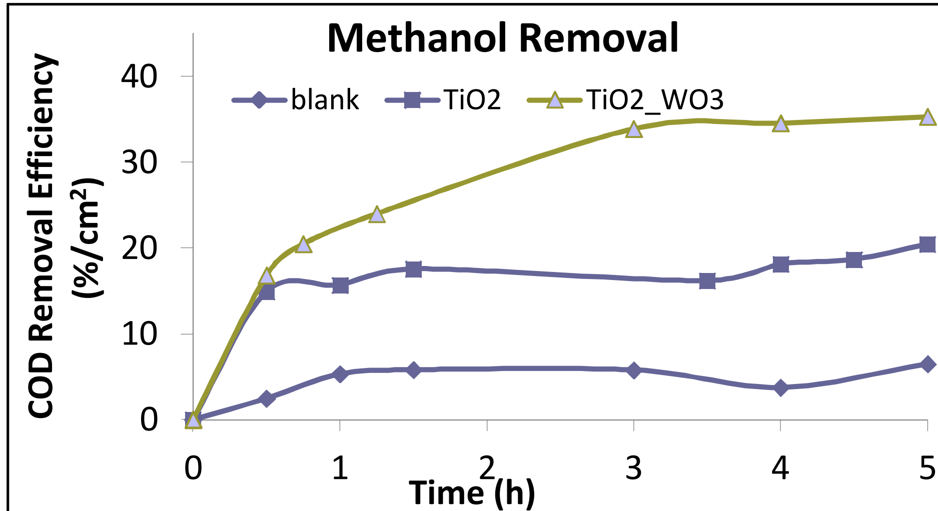
Photo-degradation of organic pollutants

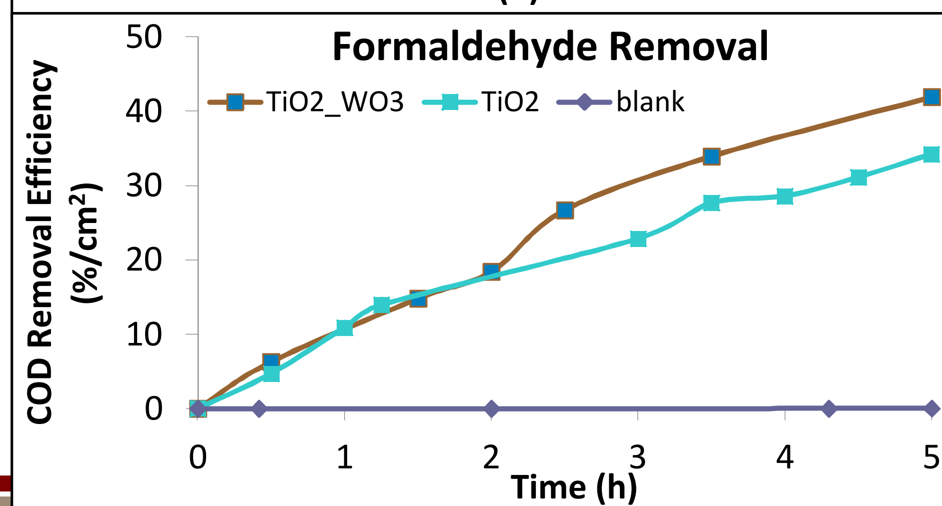
- Chemical Oxygen Demand (COD) is used to indirectly measure the amount of organic compounds in surface water and wastewater. COD is a useful measurement of water quality.



Oxidizable organic compounds reduce the dichromate ion (orange) to chromic ion (green).

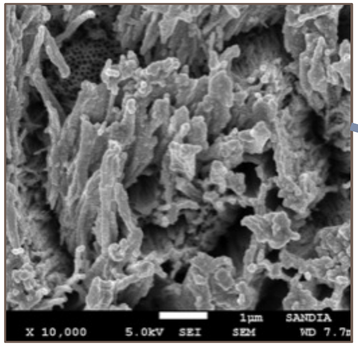






Significance of Results

- Composite Nanostructures
  - Unique structures
  - Reduce electron/hole recombination
  - Improve light absorption
  - Higher performance
- Proof of Concept-
  - a solar cell can be used for simultaneous wastewater treatment and water splitting.
- More Applications-
  - electrochromic cells like smart windows, Li batteries.
  - high-contrast displays, antiglare rearview mirrors.
  - CO_2 conversion to hydrocarbon fuel
  - water filtration



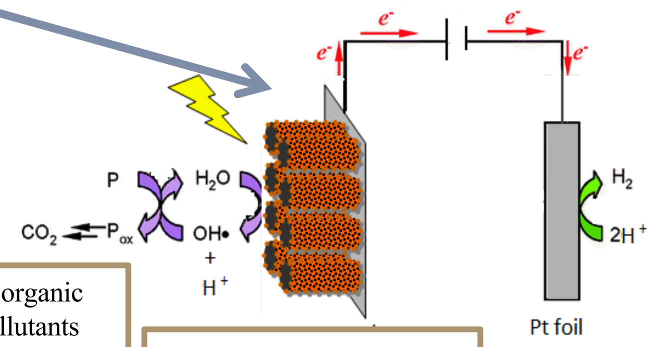
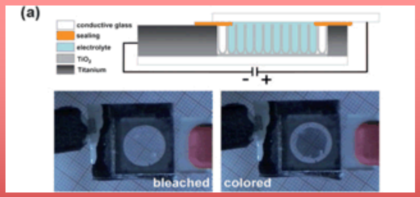
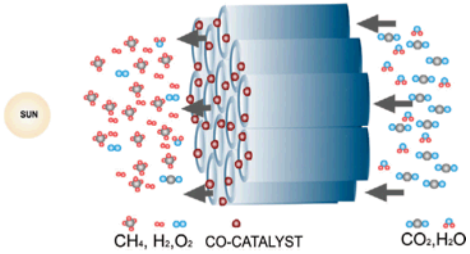


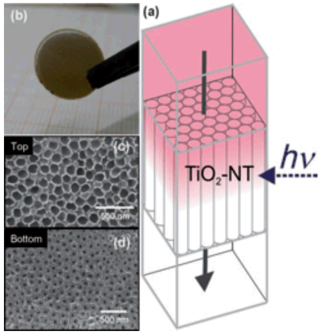
Diagram of the combined waste treatment and energy harvesting photo-electrochemical device



Electrochromic Devices
Schmuki et al. *Angew. Chem. Int. Ed. 2011, 50, 2904 – 2939*



Depiction of TiO_2 NT flow-through membrane, sensitized with appropriate catalysts, for photo catalytic conversion of CO_2 to hydrocarbon fuels.
Shankar et al. J. Phys. Chem. C, Vol. 113, No. 16, 2009

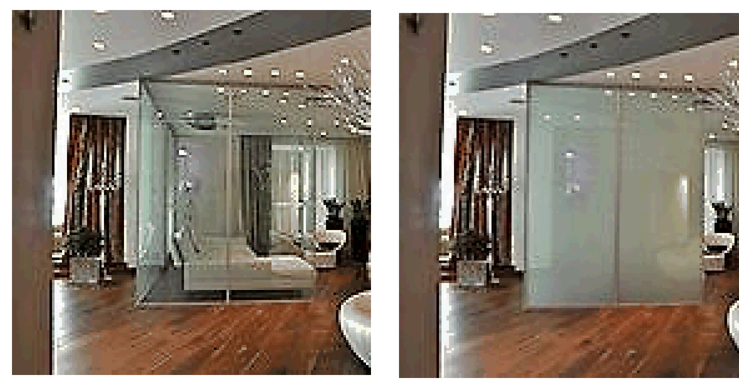


A TiO_2 NT membrane, lift-off, and bottom-opening processes for water filtration.
Schmuki et al. *Angew. Chem. Int. Ed. 2011, 50, 2904 – 2939*

Electrochromic Applications

- Electrochromic (EC) materials respond to an applied bias by reversible changing their spectral absorption properties via a redox reaction.
- EC materials are of particular interest for their use in smart glass (such as windows and display).
- Smart windows can control the amount of light and heat that passes through the window. Consequently, energy consumption can decrease by 30-40% for the building.
- Commercial smart windows still cost up to $1,000 per m^2 of glass due to the high cost of the manufacturing process (sputtering).
- Cheaper manufacturing process are needed to make the electrochromic devices a more attractive commercial option.
- Wet chemistry syntheses, such as electrodeposition, are good alternative because of the low cost and flexibility.

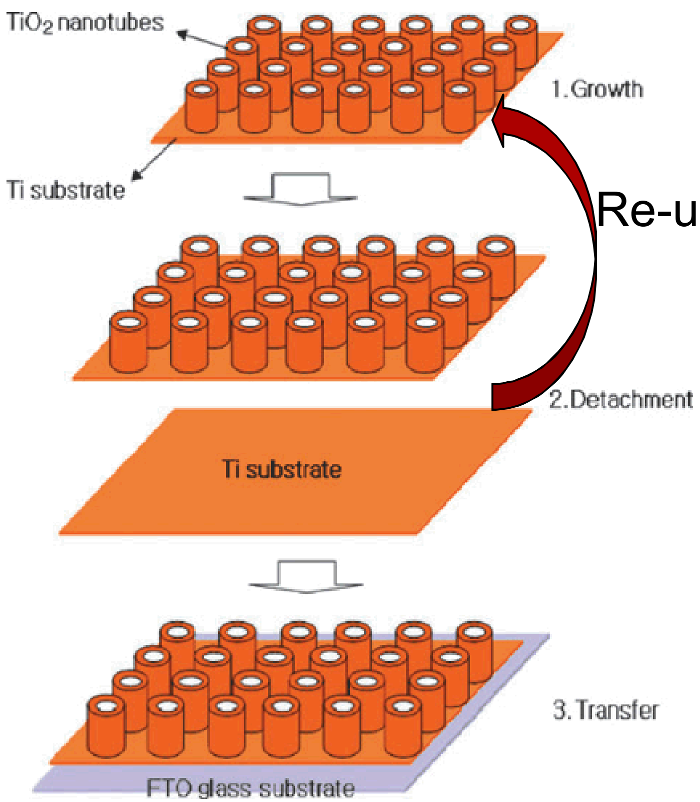
http://green.blogs.nytimes.com/2010/06/08/a-new-twist-on-the-smart-window/



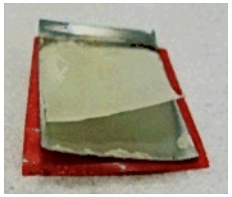
http://en.wikipedia.org/wiki/Smart_glass

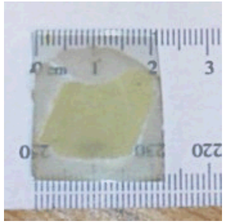
Detachment and Transfer

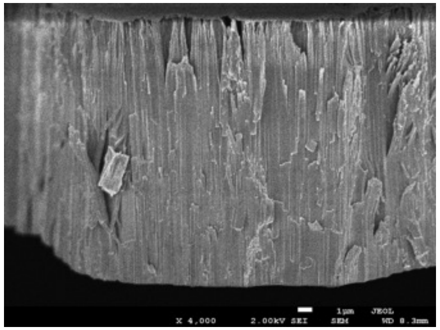
- Detachment- HF selectively dissolves amorphous TiO_2, but not anatase TiO_2.
  - TiO_2 NTs are annealed at 500°C for 2hr (anatase).
  - 0.5h anodization creates thin amorphous layer between TiO_2 NTs and Ti foil.
  - HF dissolves the amorphous layer.
- Transfer – Adhesion layer
  - It has to be conductive, but transparent.
  - P25 TiO_2 paste
- WO_3 electrodeposition



Re-use of Ti foil







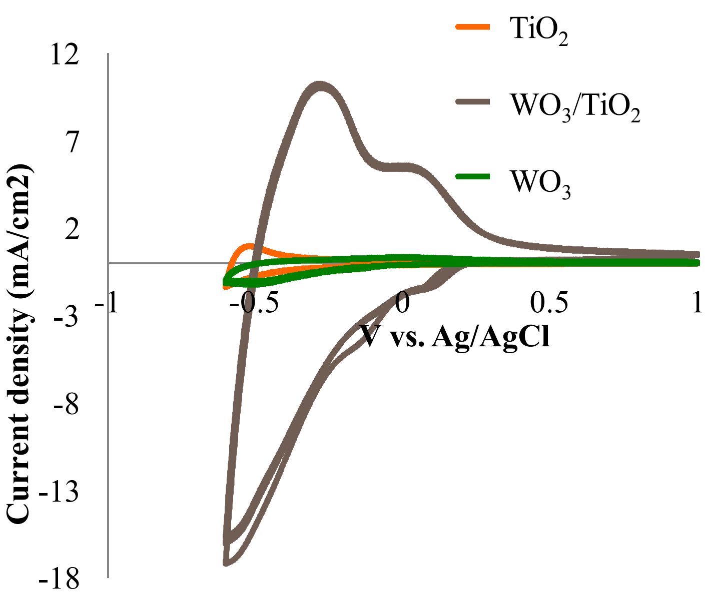
SEM images of the free-standing membrane showed good structural stability

Composite WO_3/TiO_2 nanostructures for high-electrochromic activity

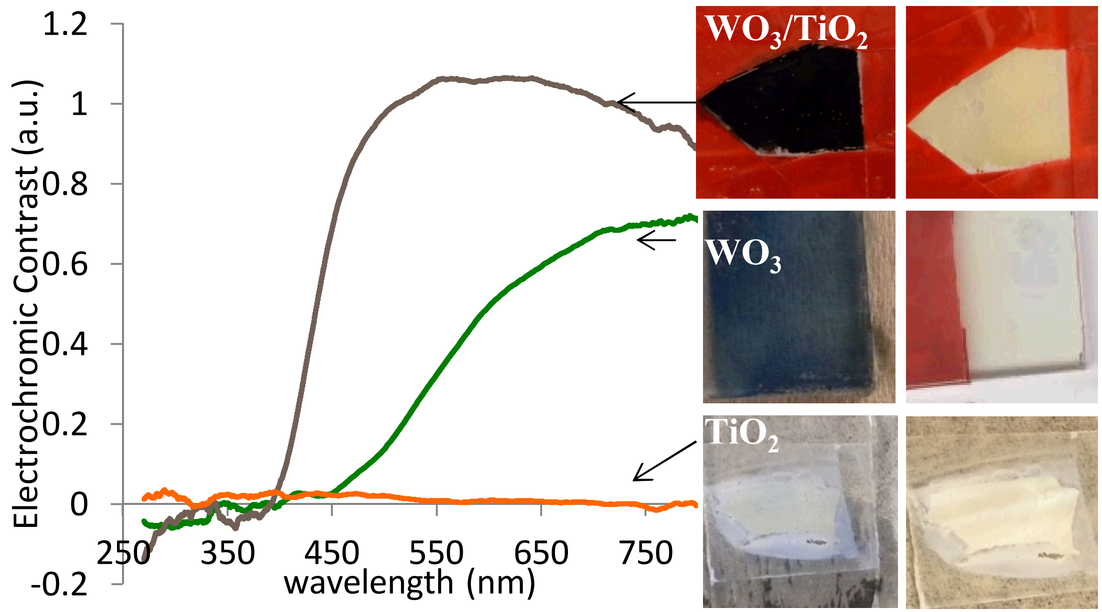
$WO_3 + H^+ + e^- \leftrightarrow HWO_3$
(W^{6+} bleached) (W^{5+} colored)

$TiO_2 + H^+ + e^- \leftrightarrow HTiO_2$
(T^{4+} bleached) (Ti^{3+} colored)

Cyclic Voltammetry



Electrochromic Contrast

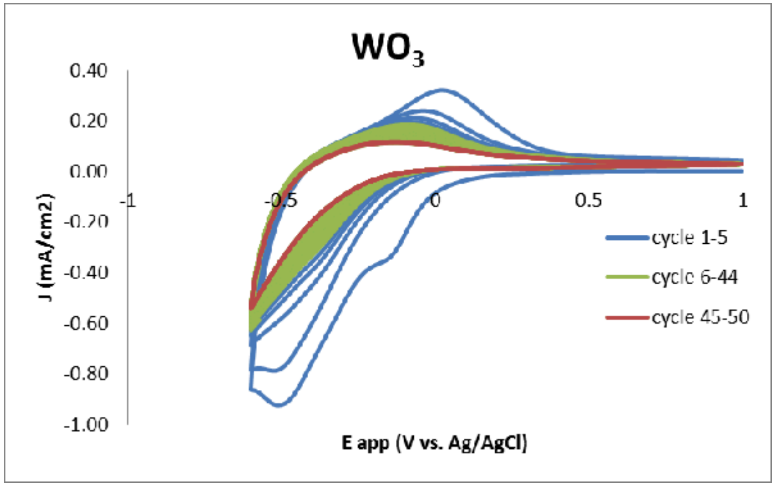


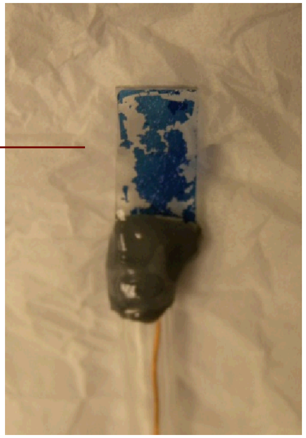
WO_3/TiO_2 nanotubes (NT) showed 10-fold increase in insertion capacity compared to TiO_2 NT and WO_3.

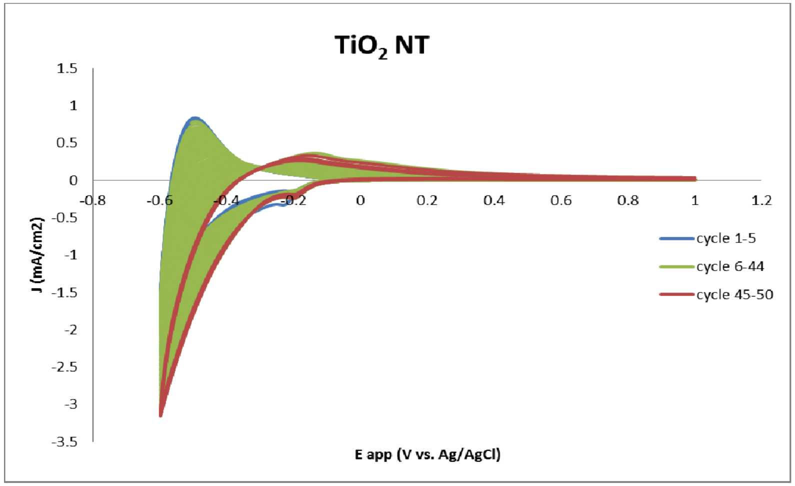
WO_3/TiO_2 nanotubes (NT) showed 10-fold increase in insertion capacity compared to TiO_2 NT and WO_3.

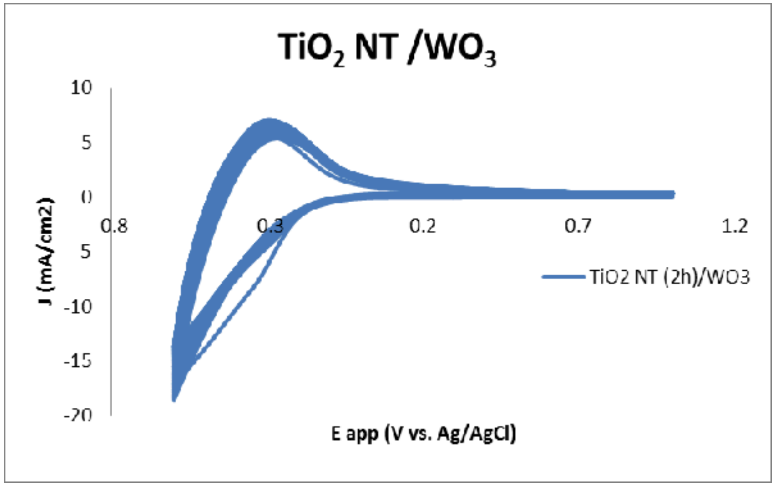
- The samples were placed into an electrochemical cell filled with 0.1 M $HClO_4$.
- Pt gauze and Ag/AgCl electrode were used as counter and reference electrode, respectively.
- A SP-200 Bio-logic Potentiostat was used to scan voltage from +1.0 to -0.6 V vs. Ag/AgCl.

Stability: 50 cycles

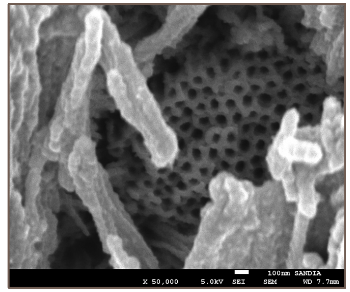








Summary



Composite Nanostructures

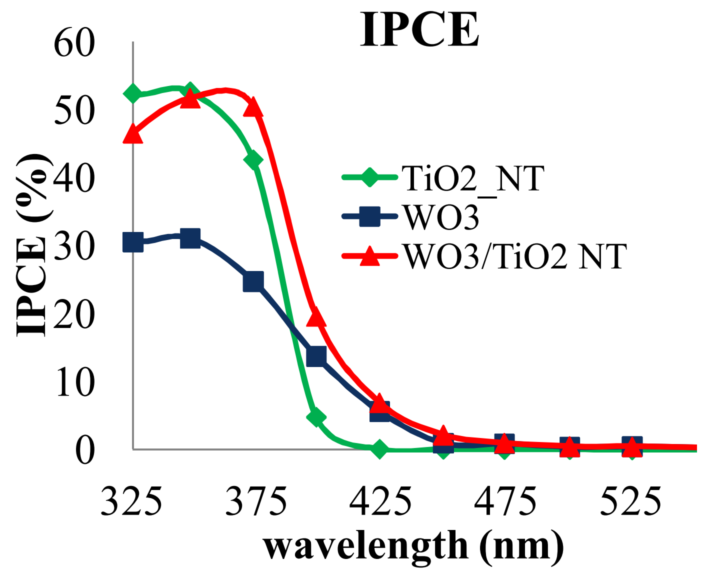
- reduce e^-/h^+ recombination → increase $\eta_{transport}$
- improve light absorption → increase $\eta_{e-/h+}$
- Higher efficiency → higher IPCE

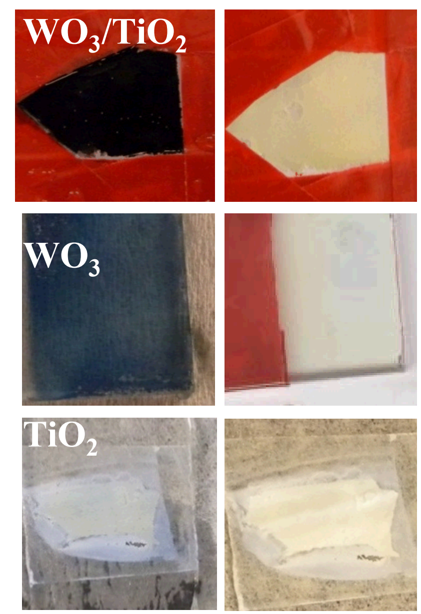
Proof of Concept-

- pollutants photodegradation increases the photocurrent densities → increase $\eta_{interface}$
- COD removal efficiency of ~40% (after 5h, 0.5 cm^2 electrode)

More Applications

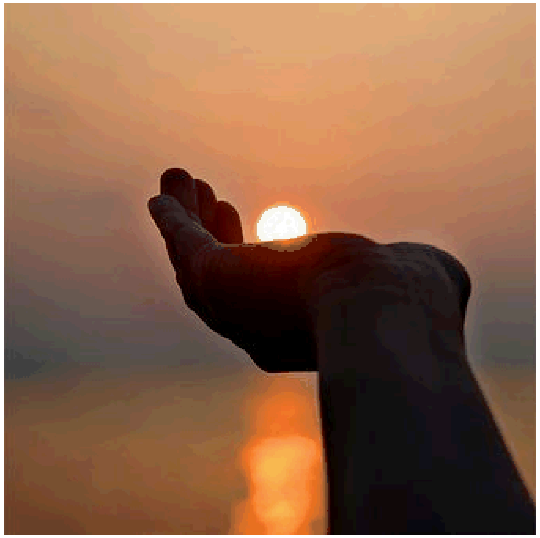
- electrochromic cells (such as smart windows and Li batteries).
- higher contrast, higher ion storage capacity, and better stability.





Acknowledgements

- Mentor- *Dave Robinson*
- Summer Intern – *Zach Stephens*
- Manager- *Adam Rowen*
- Plating lab setup- *Todd Barnett*
- IPCE setup- *Brian Patterson and Paul Schrader*
- XRD- *Vitalie Stavila*
- SEM/EDS- *Jeff Chames*
- Safety- *Steve Orth*
- Funding: *Early Career LDRD*
- Org. 8223- Materials Chemistry

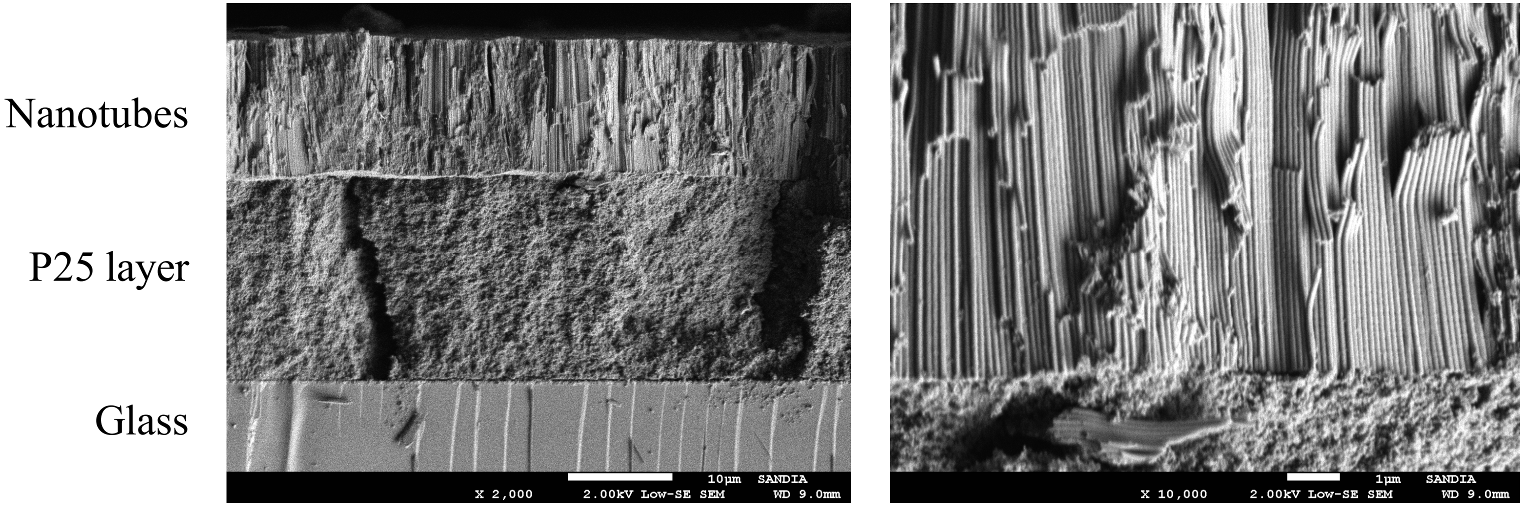


Muchas gracias !

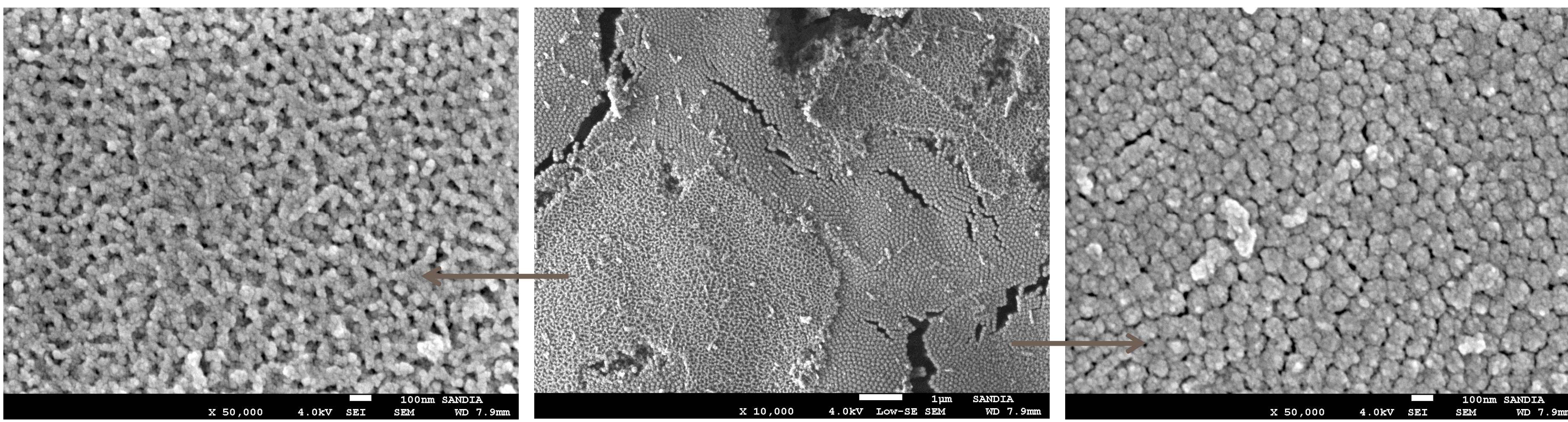
EXTRA SLIDES

Morphology

Sandia National Laboratories



SEM cross sectional images of TNTs membrane (H5) on P25 layer/FTO glass. Anodization time was 2h and the estimated thickness of the TiO_2 NT was 12.8 µm.



SEM plain view images of WO_3/TiO_2 on P25 layer/FTO glass. WO_3 coral-like nanostructures can be seen on the surface.