Transparent TiO_2 nanotube/nanowire arrays on TCO coated glass substrates: Synthesis and application to solar energy conversion

Craig A. Grimes

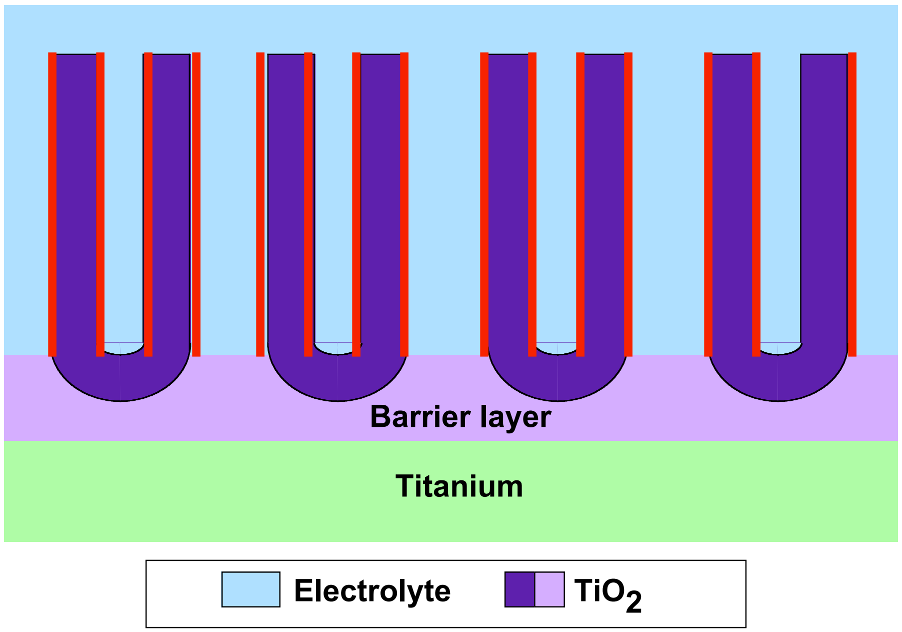
Department of Electrical Engineering
Center for Solar Nanomaterials

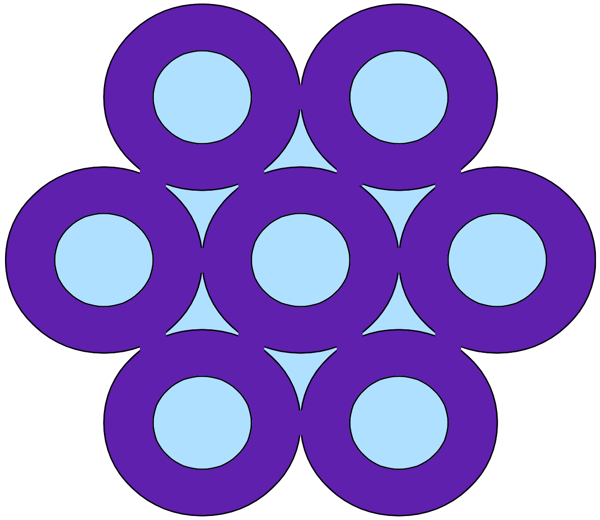
PENNSTATE
1855

Support through DoE Basic Energy Sciences

Nanotube Array Architecture

Offers exciting potential for broad-spectrum energy absorption with minimal charge recombination.

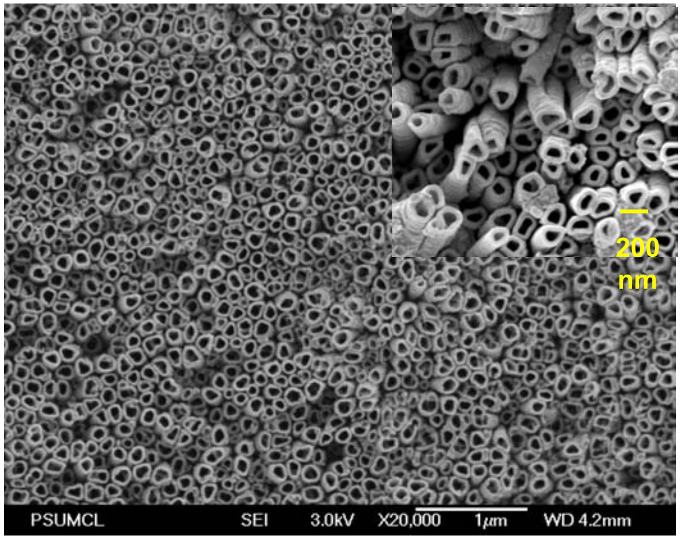


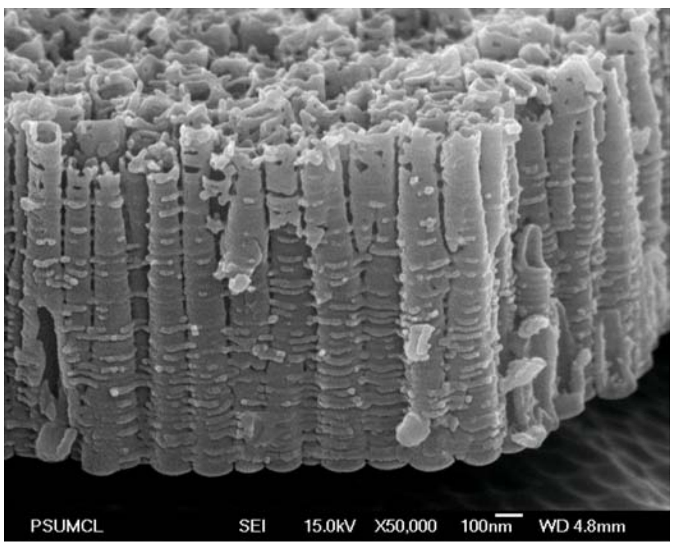


Surface area = 1000 to 3000 times that of flat surface

Vertically oriented titania nanotube arrays

Unique self-assembled nano-architecture

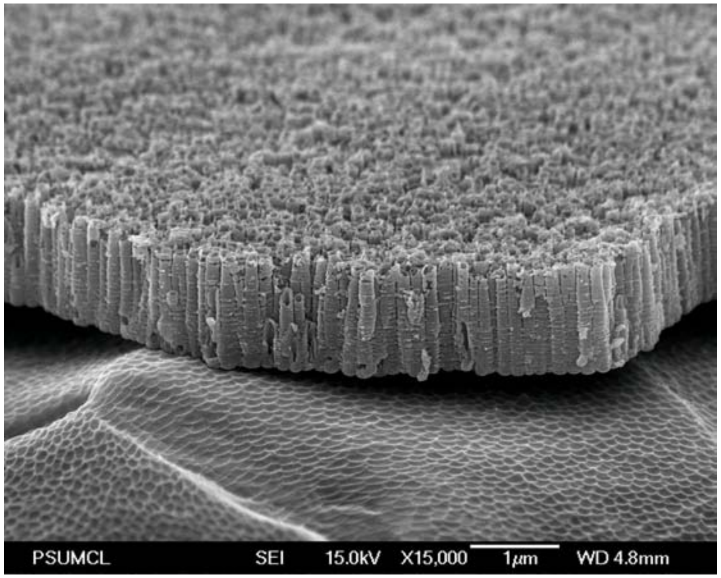


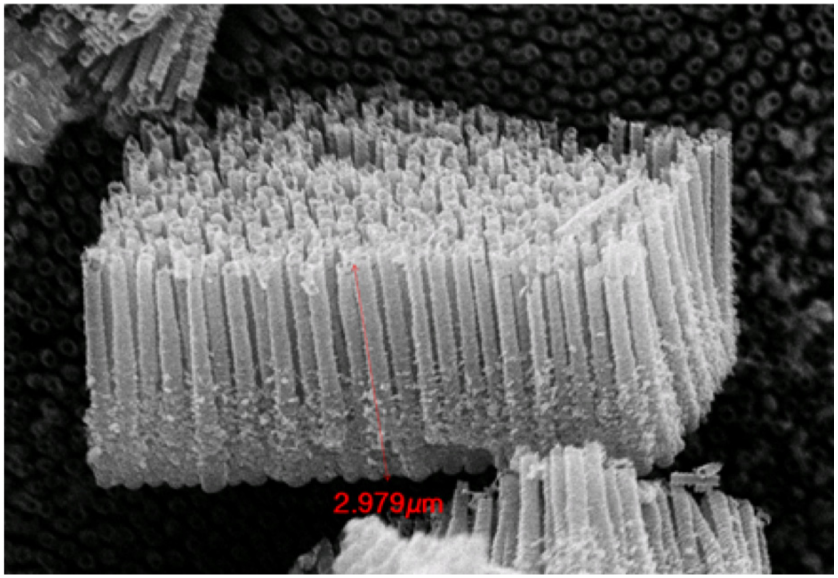


- Indigenously developed*
- Precise control of tube dimensions
- Pore size: 12 - 180 nm
- Length: 120 nm- 1000 μm
- Wall thickness: 4 nm - porous
- Tube spacing, lots to none

Nano Letters 2005, 2006, 2007, 2008
J. Materials Research 2001, 2003, 2004, 2005
J. Physical Chemistry B & C 2006, 2007
J. Materials Chemistry 2007, 2008

Titania nanotube array architecture

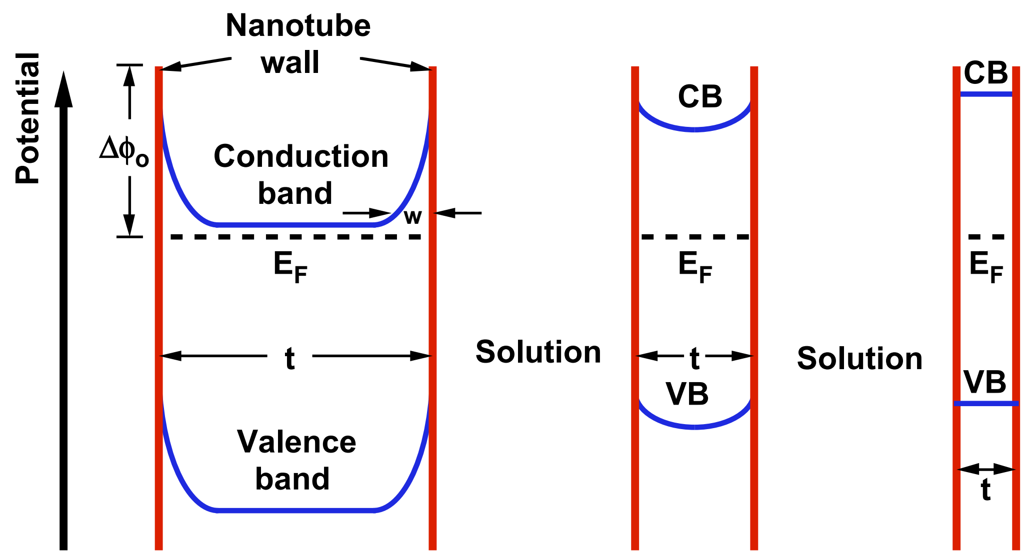




* Vertically oriented, immobilized, ordered structures
* Reduced light reflection and improved absorption
* Ohmic contact to under-layer
* Manipulation of properties using a variety of techniques

Effect of Nanotube Wall Thickness

$$\Delta\phi_0 = \frac{kT(t/2)^2}{6eL_D}$$



Space Charge Layer

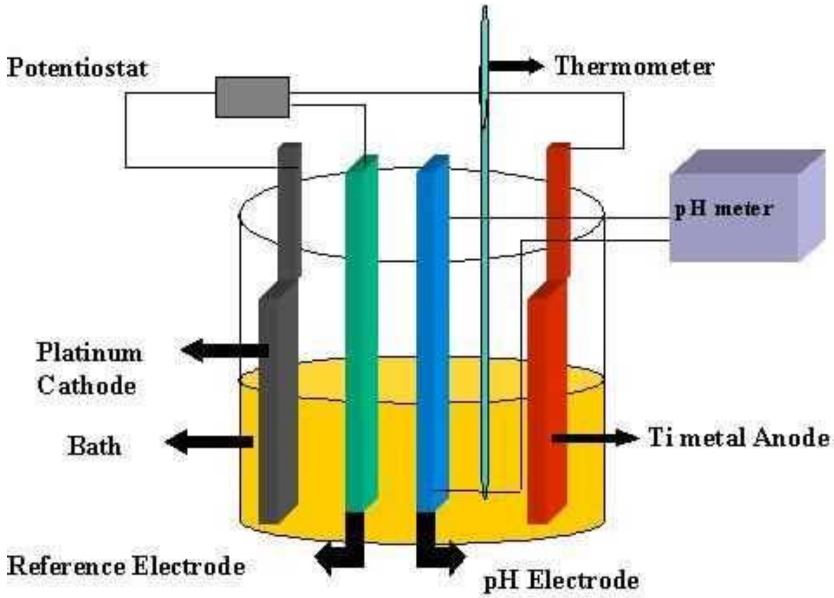
$$L = L_D \left[2eV_s / kT\right]^{1/2}$$

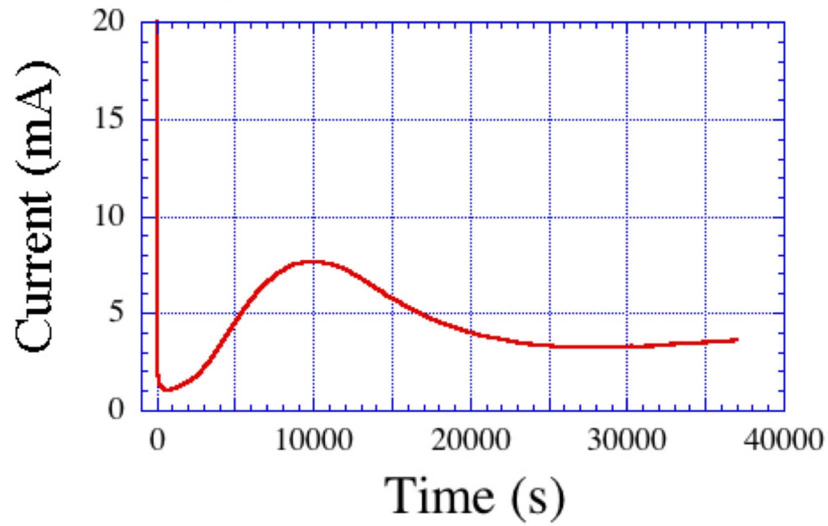
Debye Length

$$L_D = \left[\varepsilon_0 \varepsilon kT / 2e^2 N_D\right]^{1/2}$$
$$\approx 7\ nm$$

Tailor architecture to control charge transport

Nanotube Array Fabrication





Electrolyte: Water or polar organics typically with F^-

Potential: 3V to 90V

Features of significance: Porosity, Length, Crystallinity and Wall thickness

Transparent TiO_2 Nanotube Array Films

Fabrication

Ti film deposition (Sputtering, 500°C)

↓

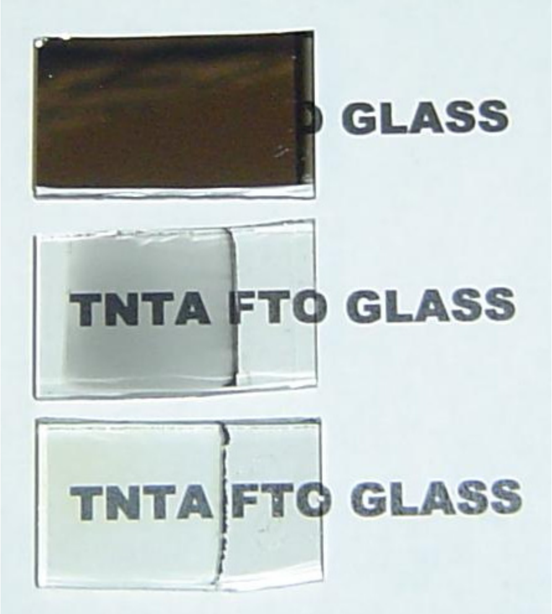
Anodization

↓

Heat treatment

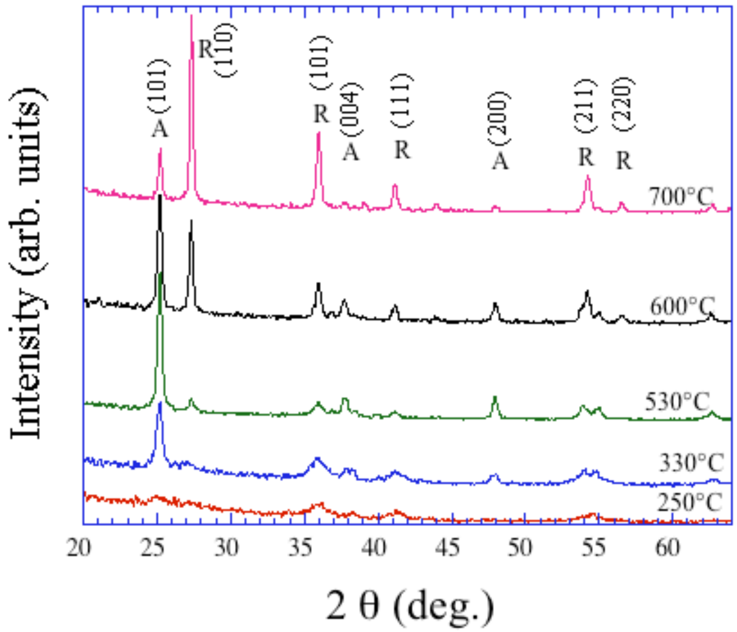
↓

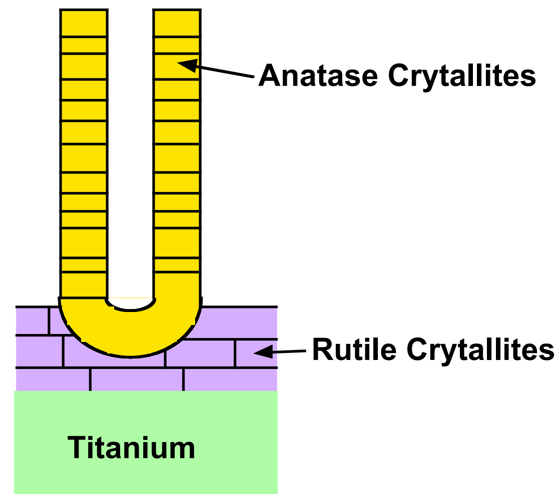
Transparent nanotube film



G. K. Mor, O. K. Varghese, M. Paulose, C. A. Grimes,
Transparent Highly-ordered TiO_2 Nanotube-arrays via Anodization of Ti Thin Films,
Adv. Func. Mater. 15 (2005) 1291-1296

Titania nanotube: Structural

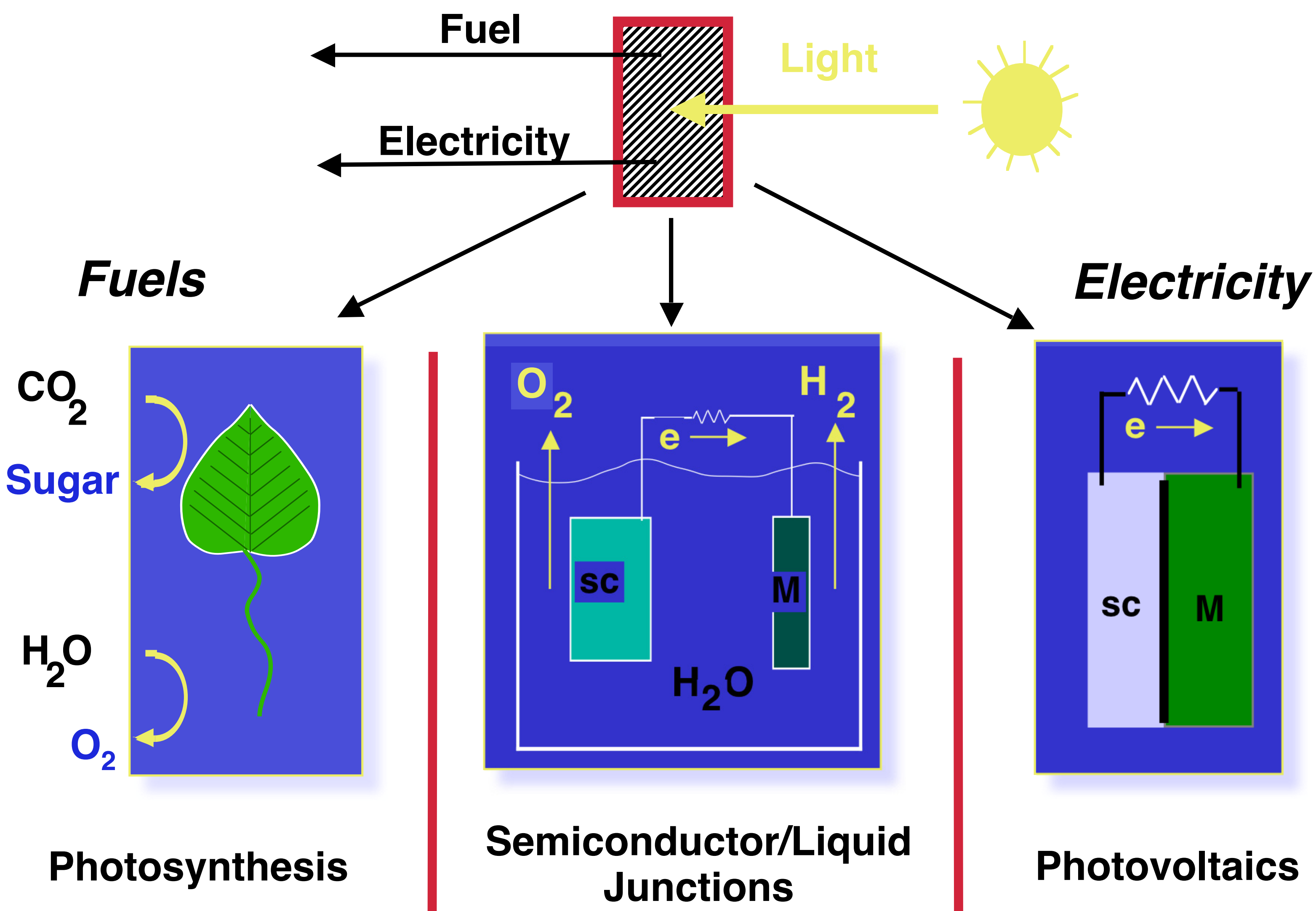




- **Constraints imposed by the wall make anatase crystallites reside on the tubes and rutile on the base.**
- **Appear as stacked anatase column on a rutile foundation.**

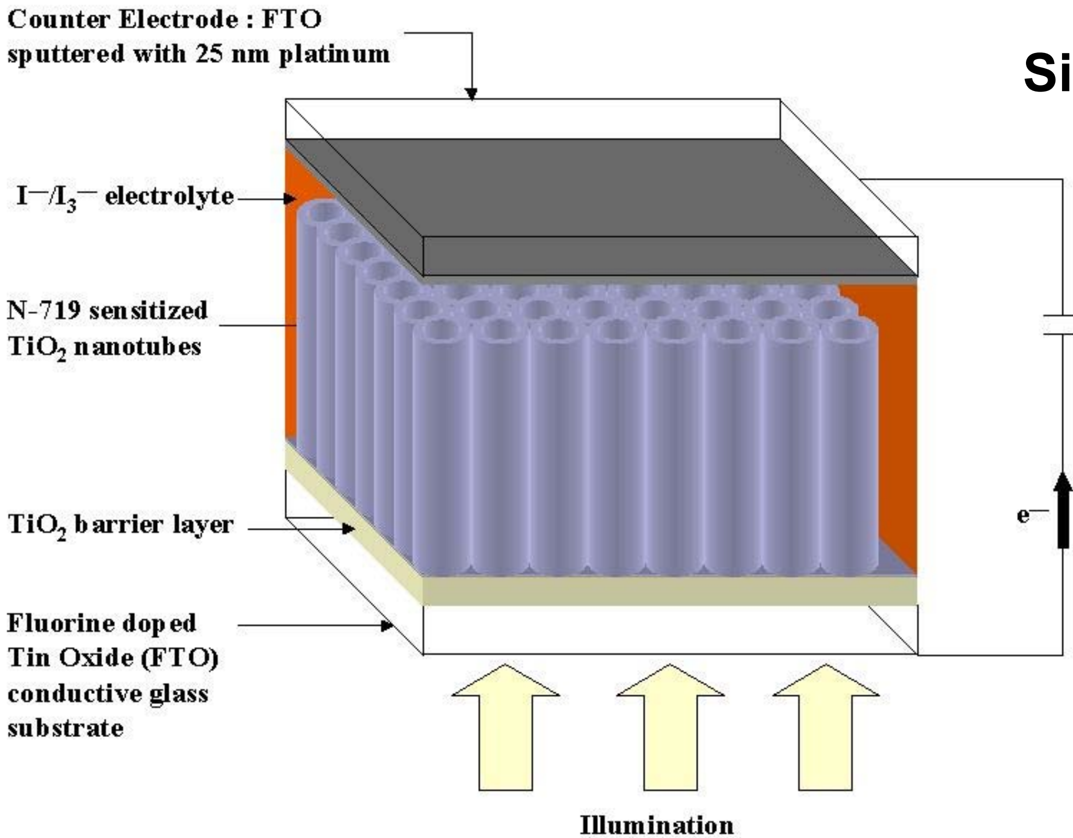
O. K. Varghese, …C. A.Grimes, J. Mater. Res. 18 (2003) 156-165

Energy Conversion Strategies



Slide courtesy of Prof. Nate Lewis

Transparent Highly Ordered Nanotube Array Films Used in Dye Solar Cells

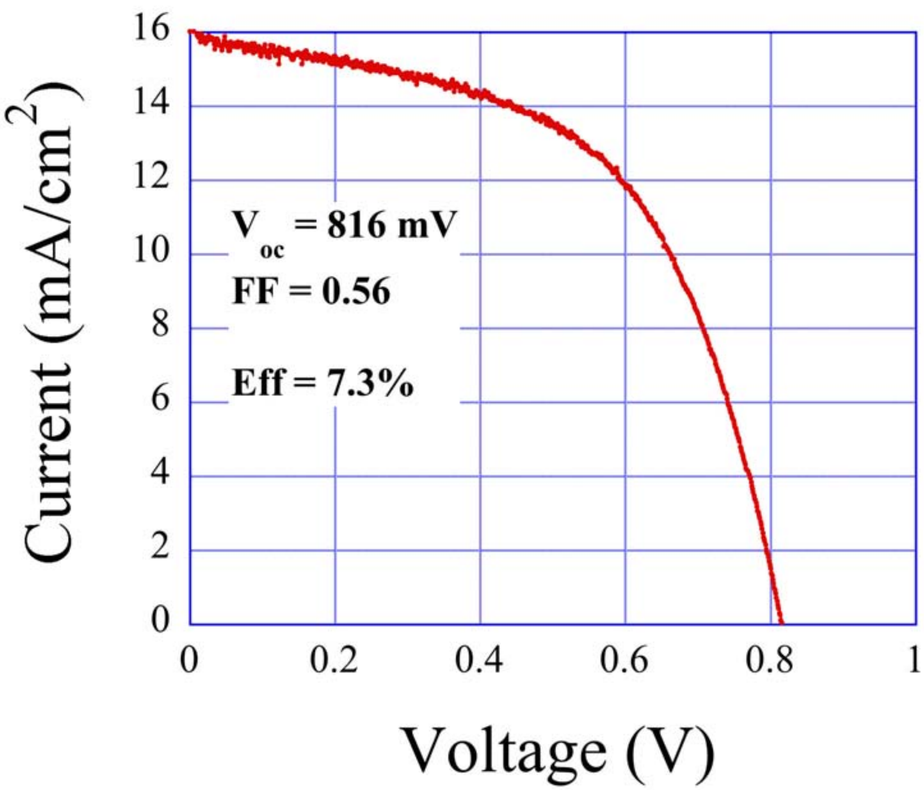


Significant Fab. Variables

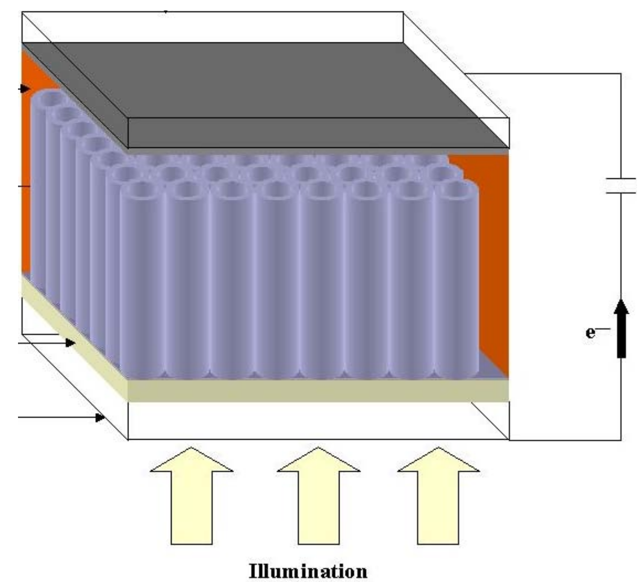
- Porosity
- Length
- Wall thickness
- dye
- x-tal vs ohmic
  - resistivity
  - adhesion

Device orientation critical

Transparent Highly Ordered Nanotube Array Films Used in Dye Solar Cells

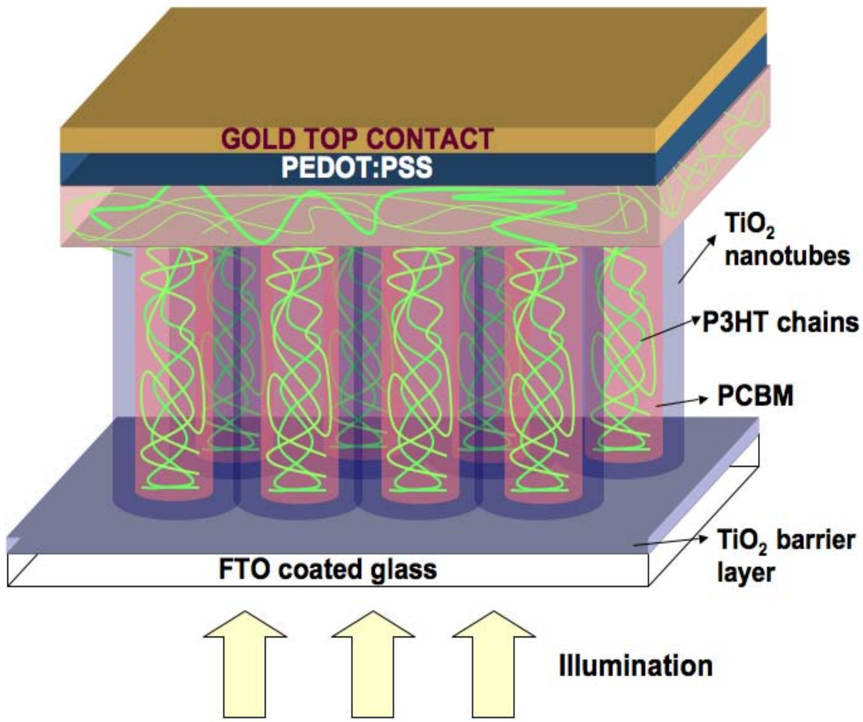


7.8 μm thick film



G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, and C. A. Grimes,
Use of Highly-Ordered TiO_2 Nanotube-Arrays in Dye-Sensitized Solar Cells.
Nano Letters 6 (2006) 215-218.

Solid state double heterojunction device



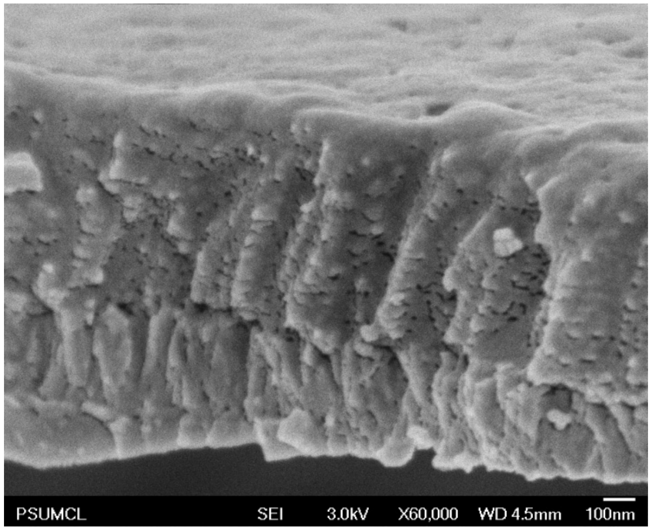
PEDOT:PSS

P3HT+PCBM-C71

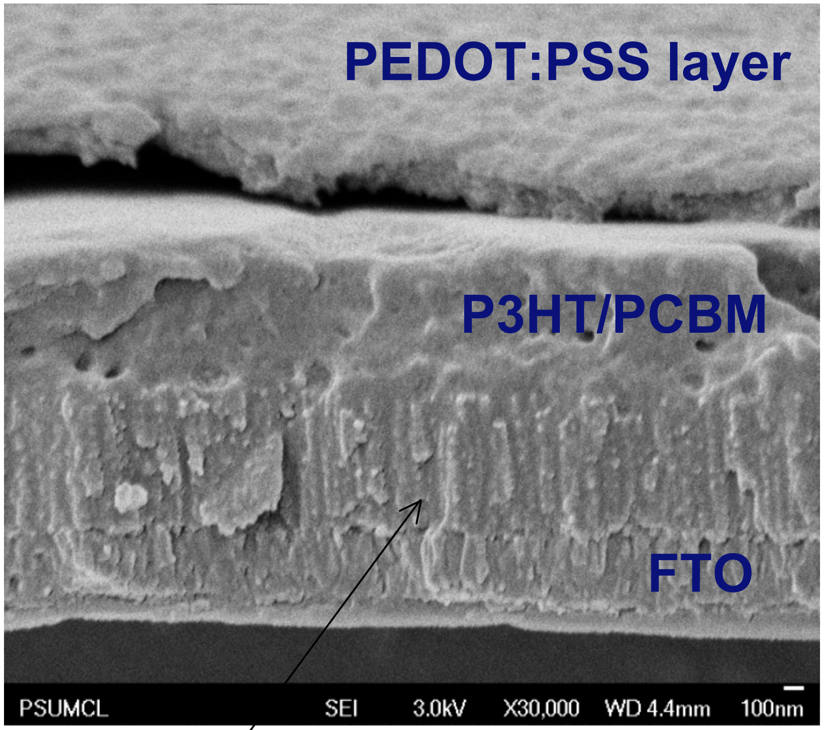
• Blend of regioregular poly(3-hexylthiophene) and a methanofullerene (Phenyl C71-butyic acid methyl ester) **P3HT(p-type)+PCBM-C71(n-type)**

• poly(3,4-ethylenedioxythiophene)+poly(styrenesulfonate) used as hole collector material **PEDOT:PSS**

Polymer filled TiO_2 nanotubes

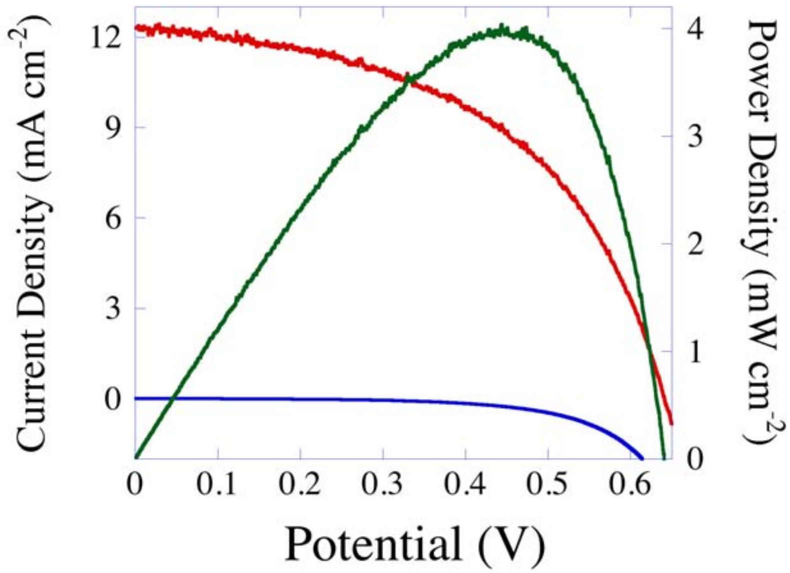


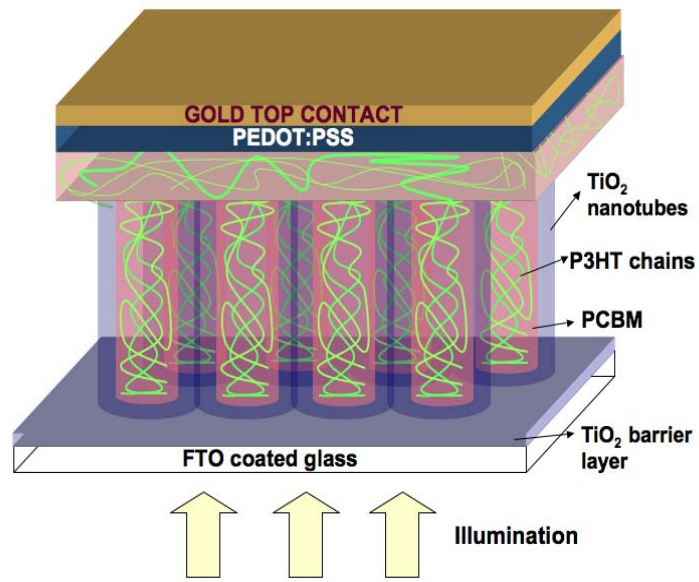
P3HT/PCBM + TiO_2 NTs



P3HT/PCBM filled TiO_2 NTs

4.1% Efficiency under AM 1.5: Good adhesion, less than optimal x-tal



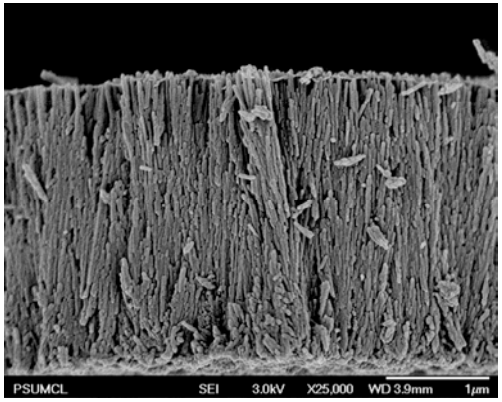


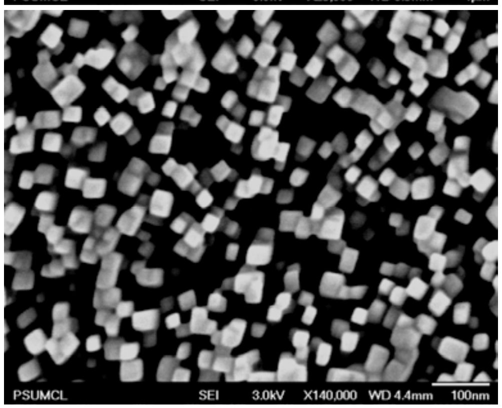
I_{sc} = 12.43 mA/cm^2, V_{oc} = 0.641, FF = 0.511

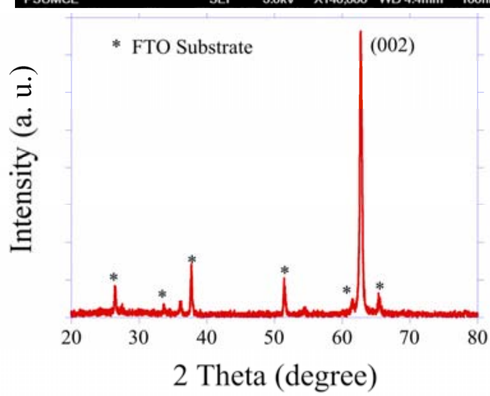
G. K. Mor, K. Shankar, M. Paulose, O. K. Varghese, C. A. Grimes,
High Efficiency Double Heterojunction Polymer Photovoltaic Cells using Highly Ordered TiO_2 Nanotube Arrays.
App. Phys. Lett. 91 (2007) 152111

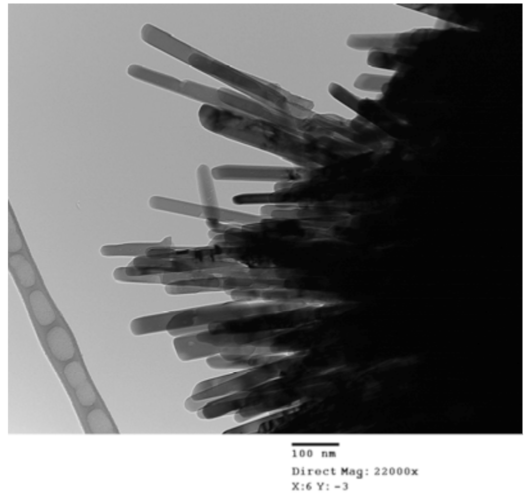
Single Crystal TiO_2 Nanowire Arrays on FTO Coated Glass

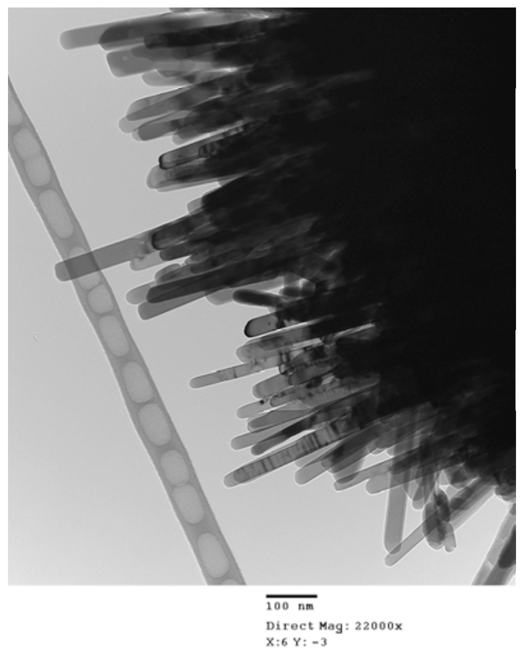
Single Crystal TiO_2 Nanowire Arrays on FTO Coated Glass

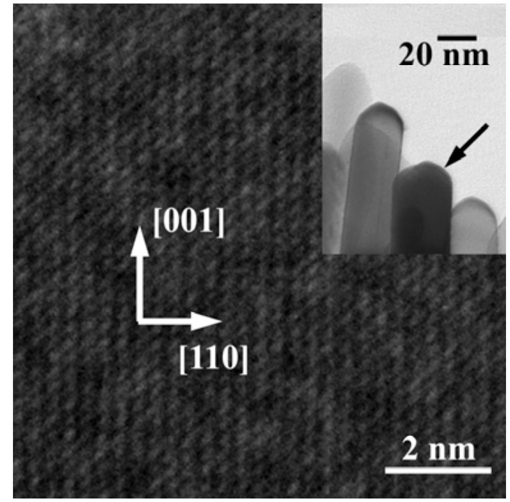


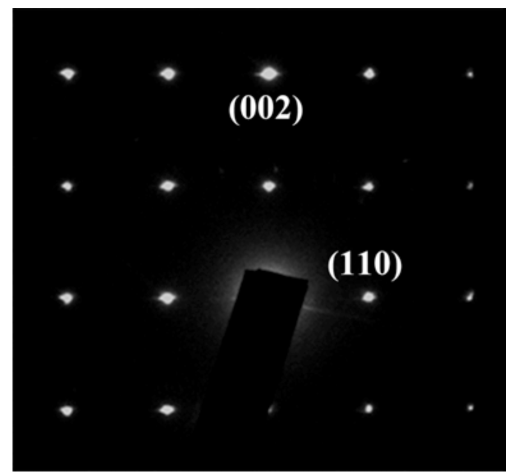




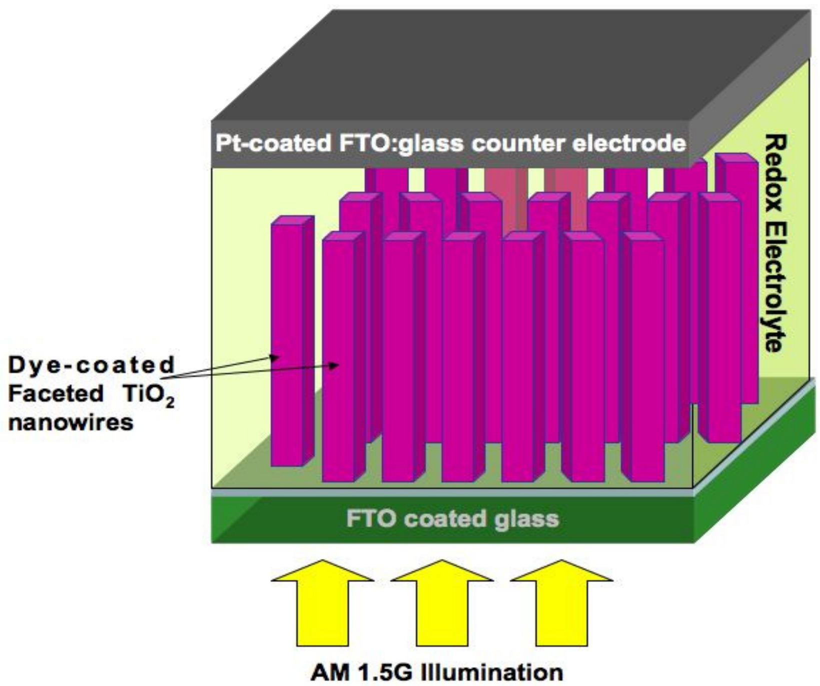


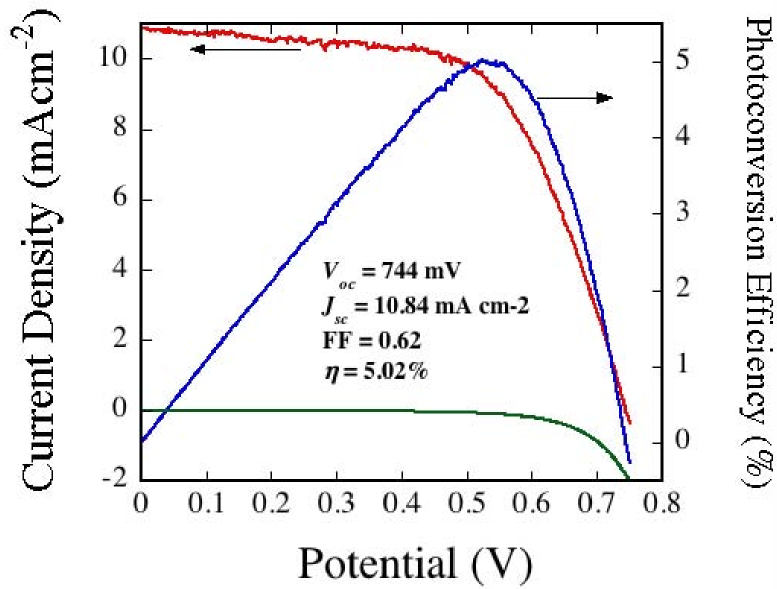






Single Crystal TiO_2 Nanowire Arrays on FTO Coated Glass

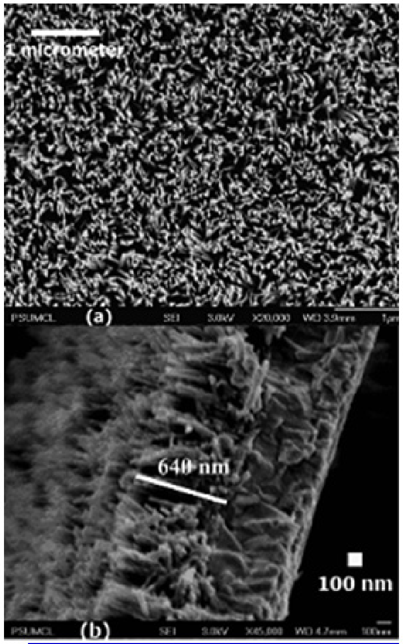


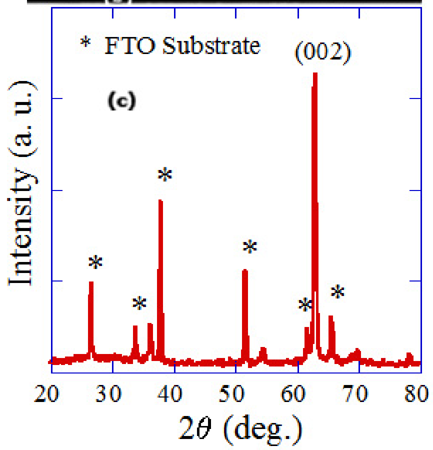


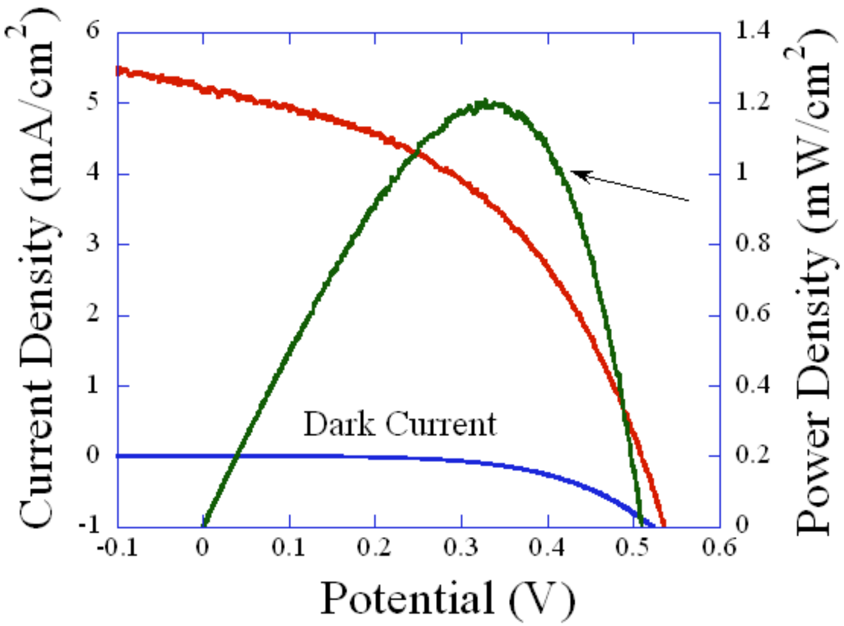
2.0 μm long
AM 1.5 illumination (100 mW/cm²)

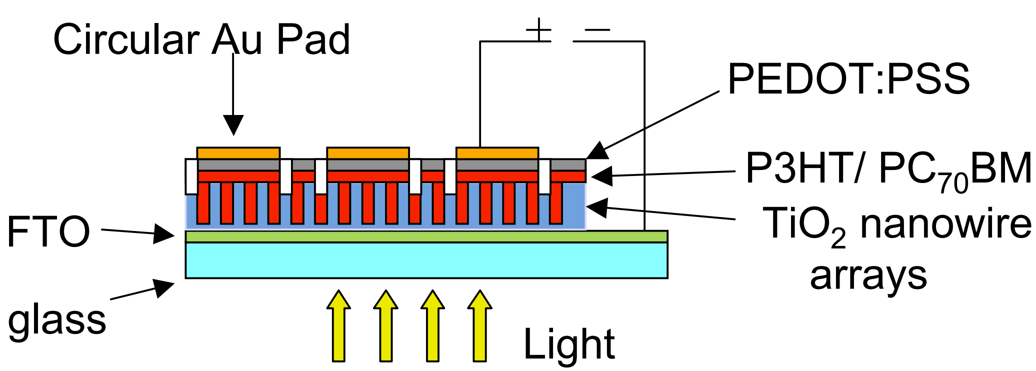
But, low fill factor indicates some damage to FTO substrate…

P3HT/PCBM Heterojuctions using Rutile TiO_2 Nanowire Arrays (≈ 800 nm)









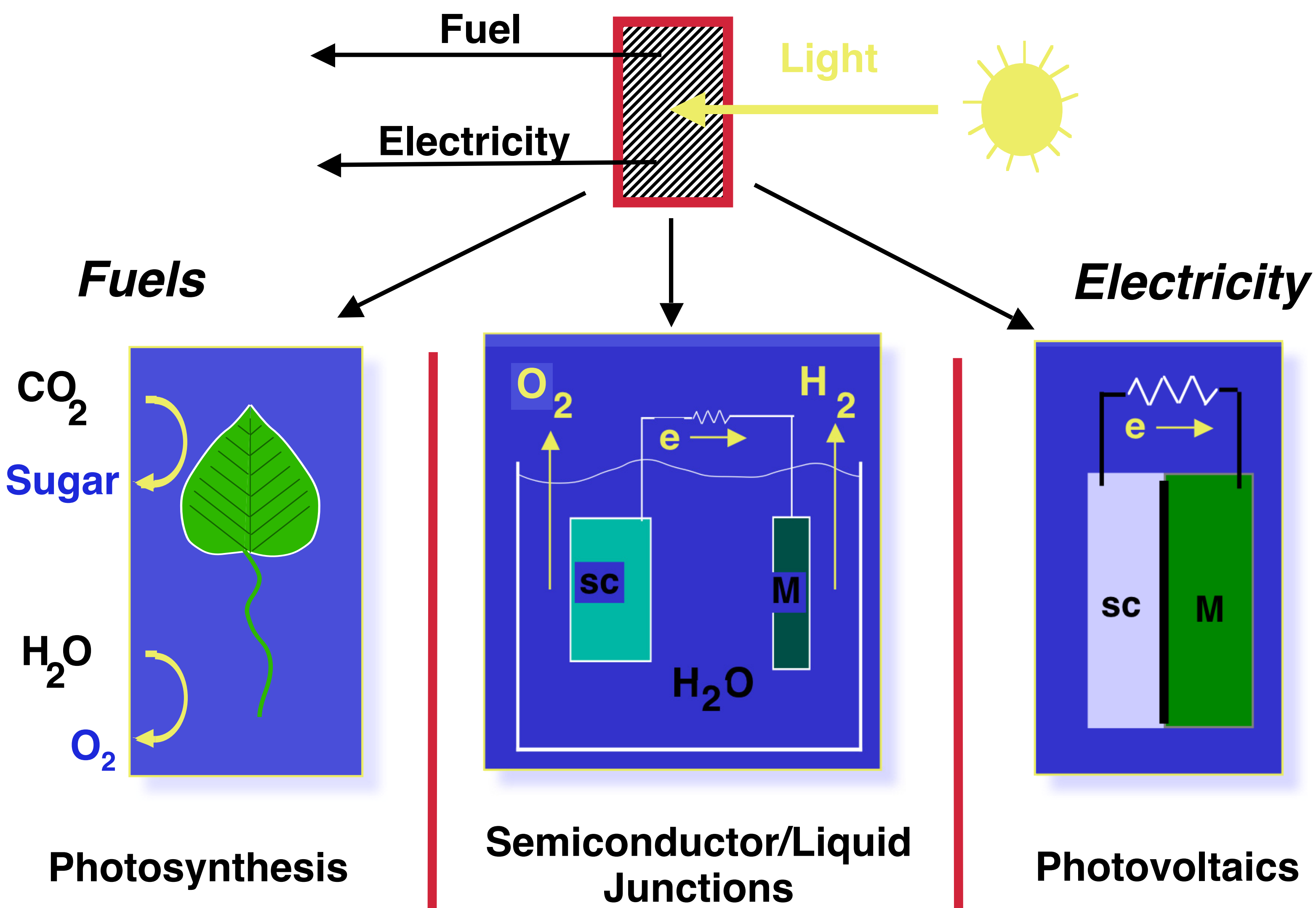
Summary: Solar Cells

- Nanotube/wire arrays unique material architecture

  Device limitations coupled with those of FTO coating

- Nanotube DSSC with 7.3% efficiency (≈ 7.8 μm long)
- Nanowire DSSC with 5.5% efficiency (≈ 2 μm long)
- Solid state organic-inorganic solar cell at 4.1%
- Continue to pursue device structures, compositions, assembly, and dye architectures.

Energy Conversion Strategies



Slide courtesy of Prof. Nate Lewis

How to put the H_2 in the H_2 Economy?

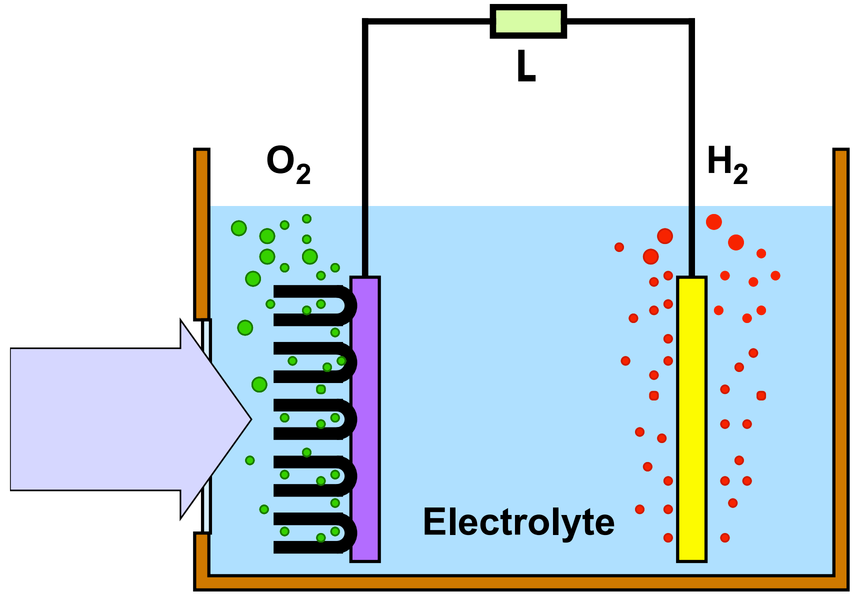
Today

- **≈ 96% from fossil fuel**

1 kg of H_2 via steam-methane reforming (SMR) yields 10.66 kg of CO_2

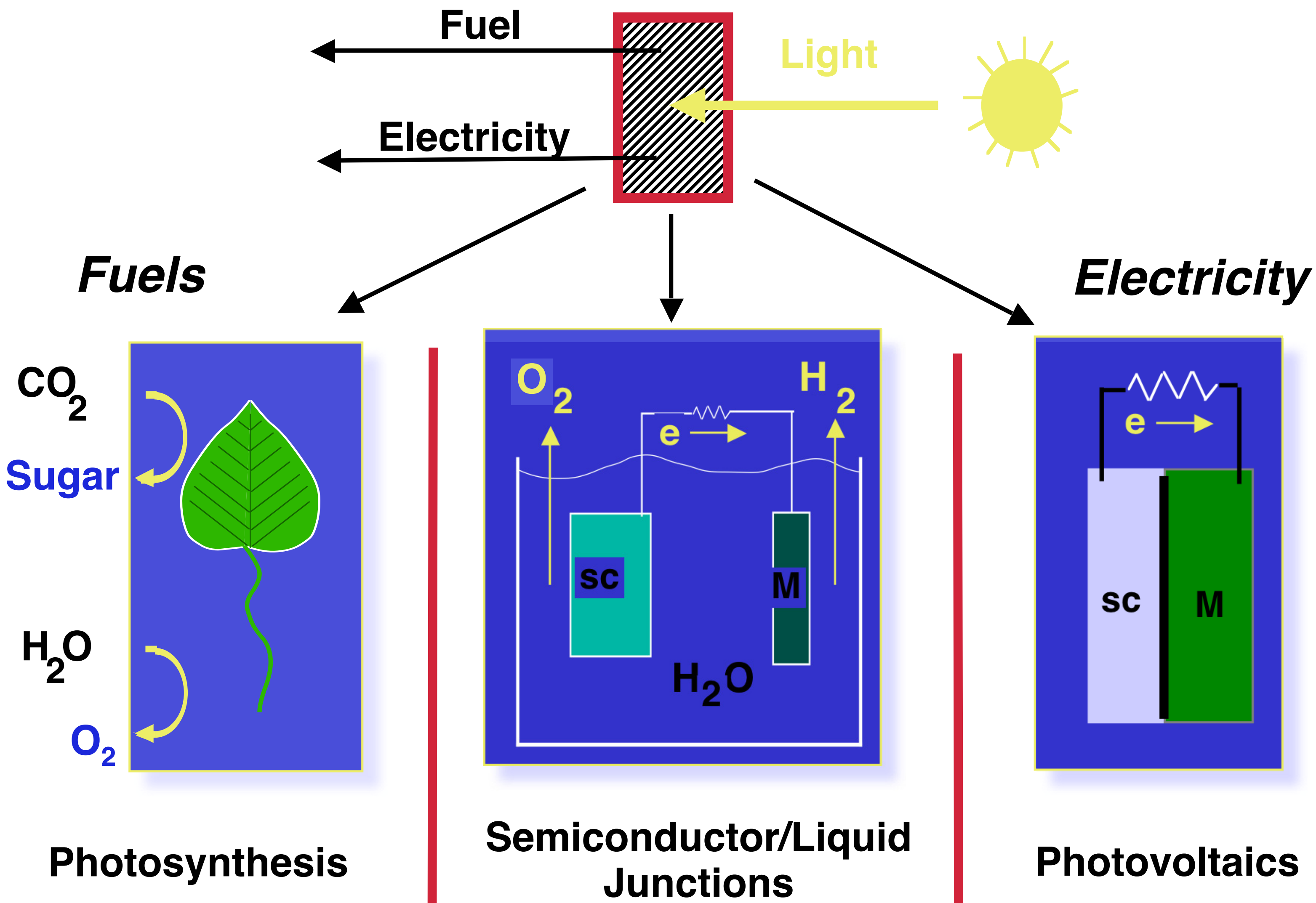
- **≈ 4% from water electrolysis**

Solar Water Splitting



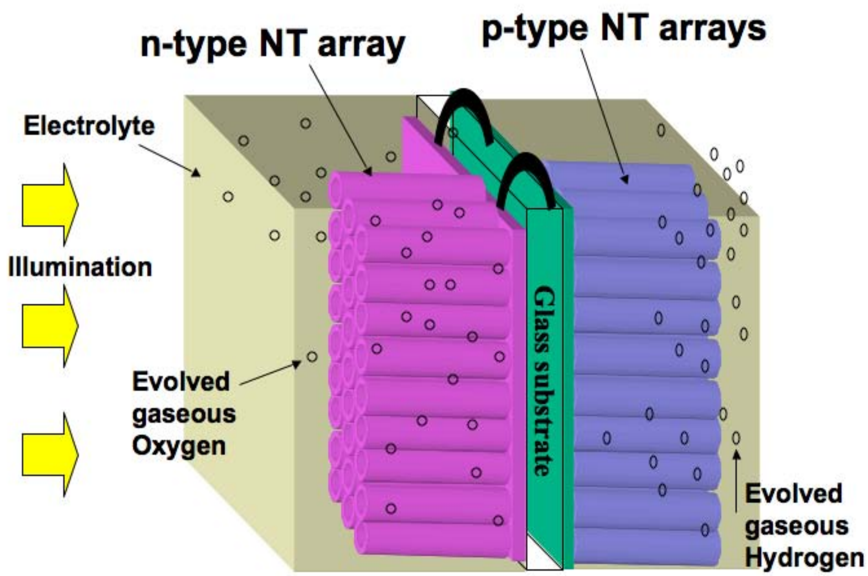
$$2H_2O + Light \rightarrow 2H_2 + O_2$$

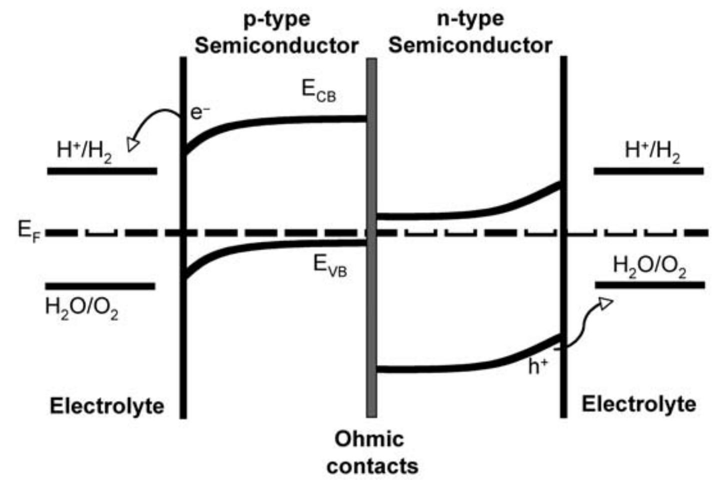
Energy Conversion Strategies



Slide courtesy of Prof. Nate Lewis

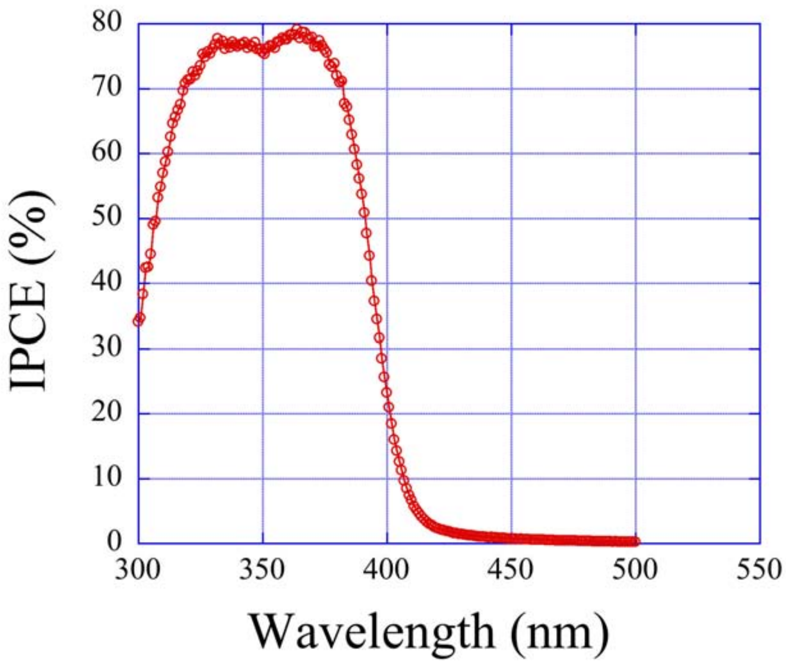
Our Interest: Photoelectrochemical Diodes





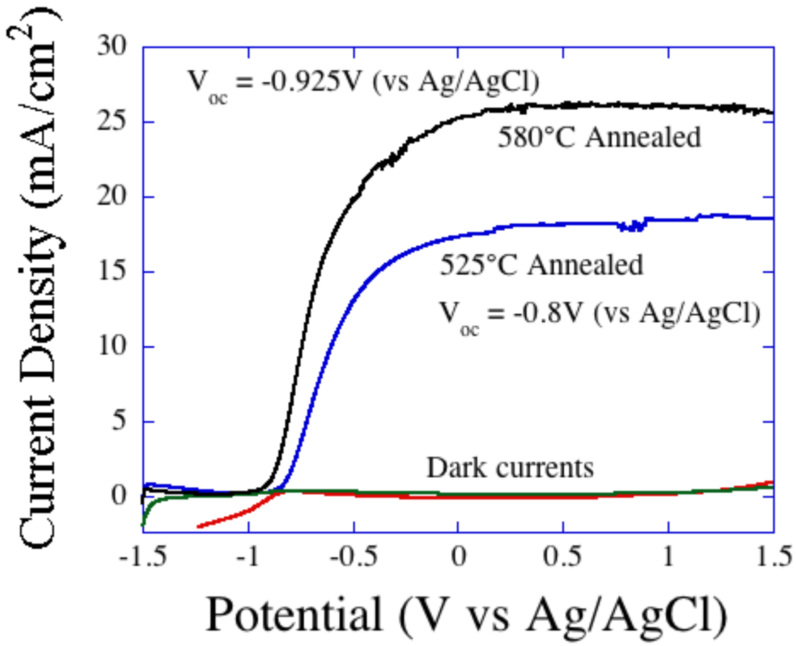
- To date no photocorrosion stable p-type semiconductors
- Need to generate > 1.23 eV with appropriate band levels
- Overall current determined by side generating less current

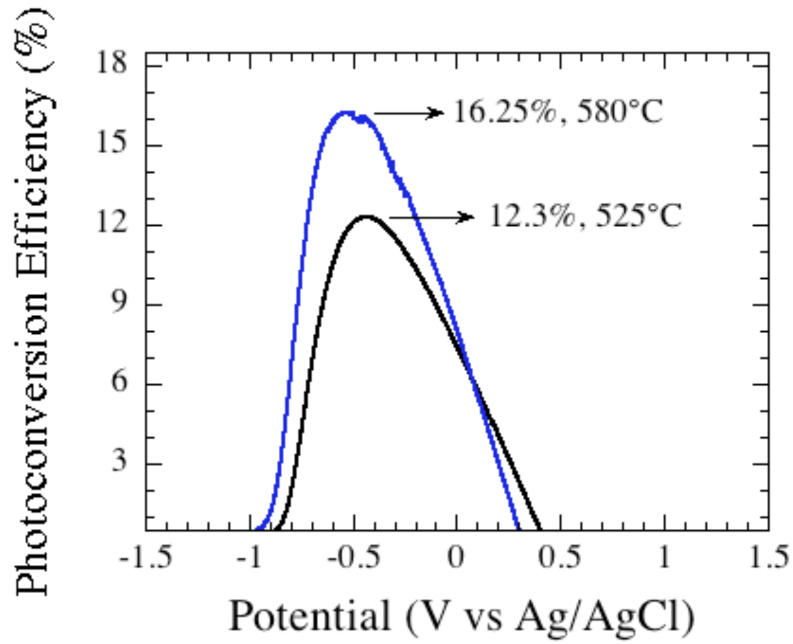
Photochemical Properties of TiO_2 NTA's: Quantum Efficiency



Device quality films quantum efficiency ≈ 80%

Photochemical Properties





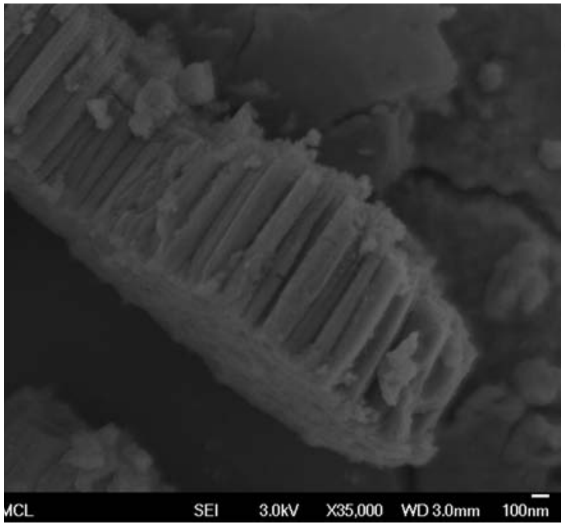
40 µm long, 205 nm outer diameter

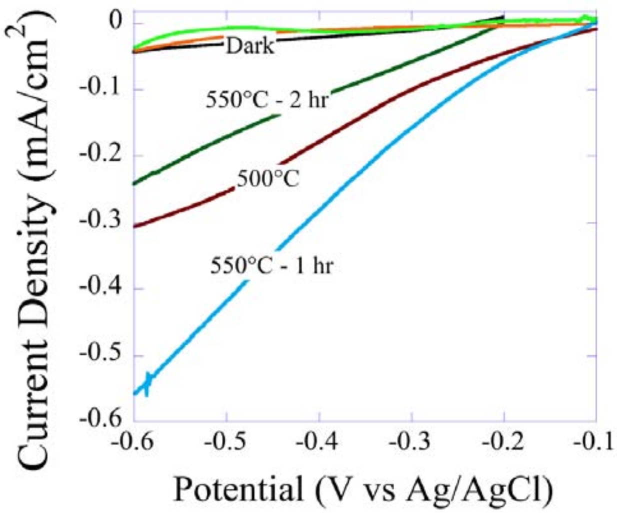
320 nm - 400 nm band illumination

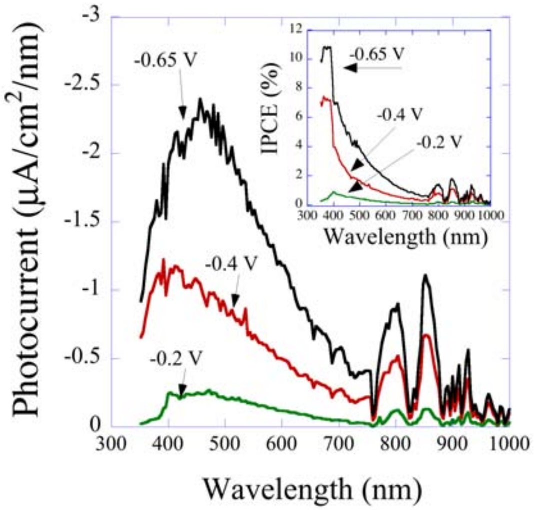
1 M KOH

M. Paulose, K. Shankar,…, C. A. Grimes, *J. Phys. Chem. B* 110 (2006) 16179-16184

Copper-rich CuTiO Nanotube Arrays



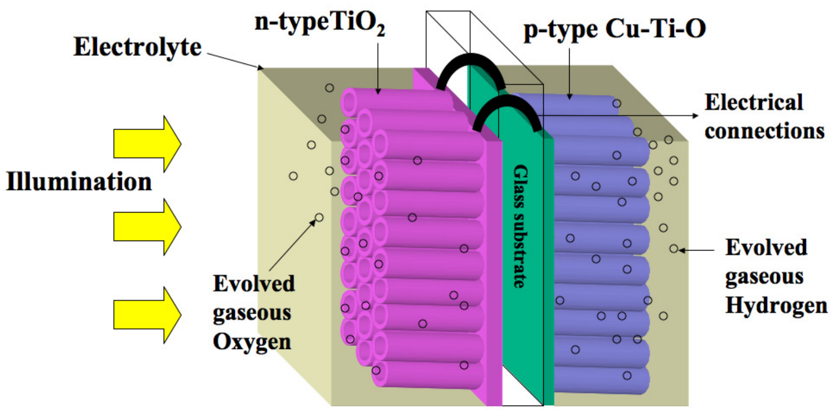




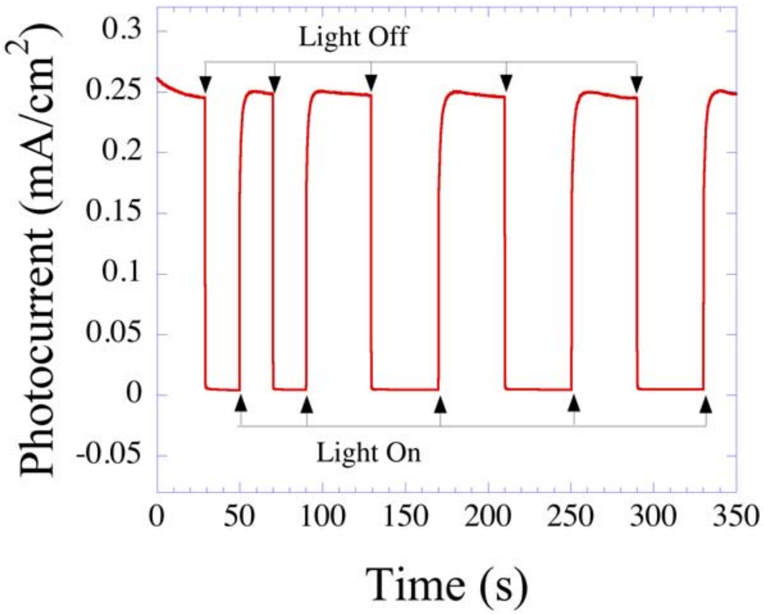
Nanotube arrays formed from 74:26 Cu:Ti metal film

- **Unable to achieve desired crystallization due to FTO temperature limitations**

Photoelectrochemical Diode Operation



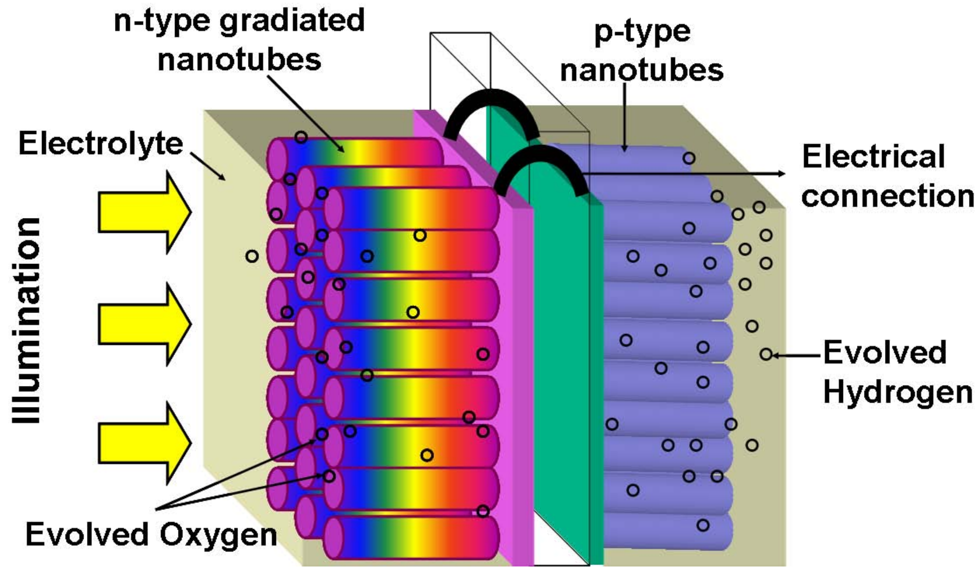
TiO_2 in 1 M KOH: Cu-Ti-O in Na_2HPO_4



Photoconversion Efficiency: (1.23 eV *I)/0.1 = 0.30%

G. K. Mor, O. K. Varghese, R. H.T. Wilke, S. Sharma, K. Shankar, T. J. Latempa, K.-S. Choi, C. A. Grimes
p-Type Cu-Ti-O Nanotube Arrays and their use in Self-Biased Heterojunction Photoelectrochemical Diodes for Solar Hydrogen Generation, Nano Letters 8 (2008) 1906 - 1911

The Future (?): Efficient, visible-light responsive PEC diodes made from plentiful materials



- **Seek to synthesize multi-bandgap materials ("rainbow") to enhance light harvesting in visible range.**

- **Seek to control parasitic recombination losses in naturally abundant Cu_2O and Fe_2O_3 moving photoconversion efficiencies from 0.3% to > 30% under visible light spectral photoresponse ?**

Summary

• Vertically oriented TiO_2 (and ternary oxide) nanotube/nanowire arrays:

Unique, easily synthesized material architecture for conversion of sunlight to electricity or hydrogen.

• Transparent substrate critical to device success- to date the inherent temperature limitations of ITO/FTO coatings directly impact device efficiencies.

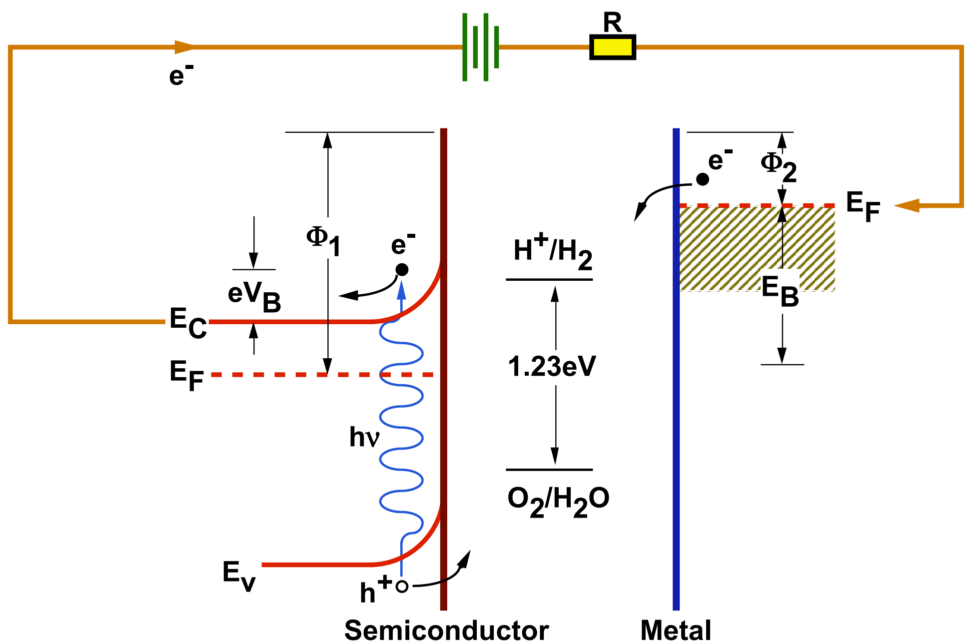
Thank-you For Your Time & Interest

Questions or Comments

Email: cgrimes@engr.psu.edu

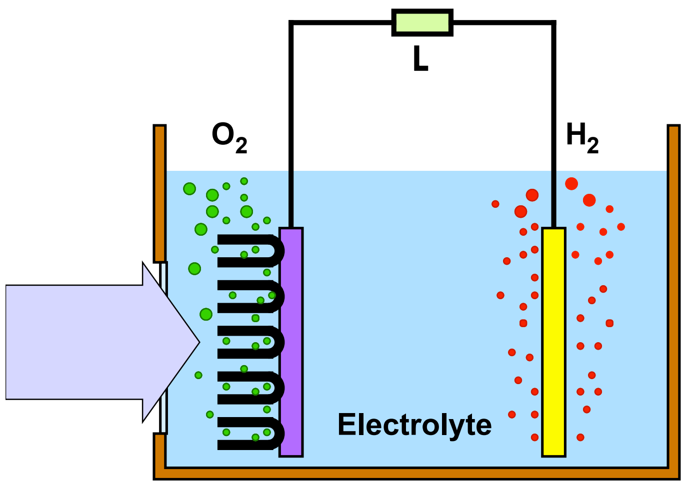
Semiconductor Photoelectrodes: Criteria

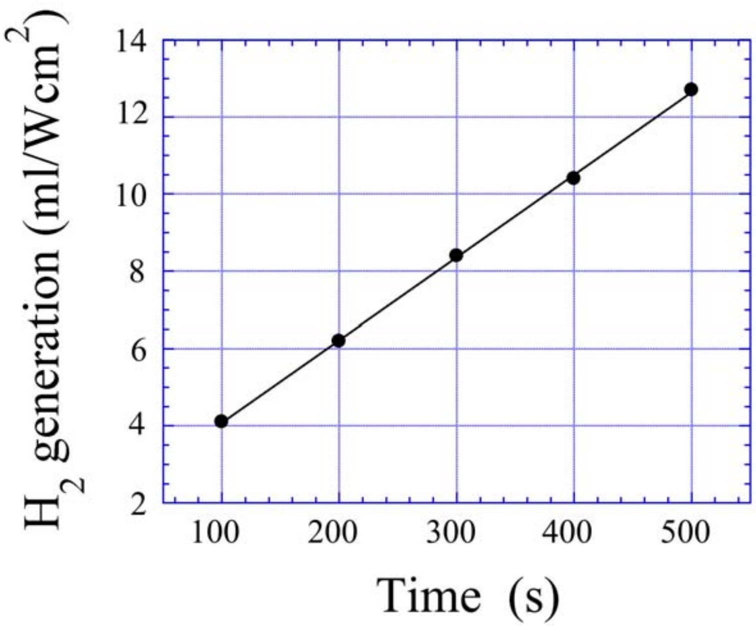
- band gap greater than 1.23 eV but low enough to absorb visible light
- band edge bracketing
- high stability
- fast charge transfer
- low cost



Material properties & architecture critical to success

TiO_2 Nanotube-arrays: H2 Generation via Water Photoelectrolysis





H_2 generated using a 6 µm nanotube array
600°C annealed; 100 mW/cm^2 UV,

generation rate = 80 mL/W•hr•cm^2
= 80 L/hr for a m^2 sample*

➢ **Our aim: Develop optimum and plentiful material nanoarchitectures for highly efficient water splitting**