Surface Chemistry and Nanotechnology: An Approach to Green Energy

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Once upon a time….

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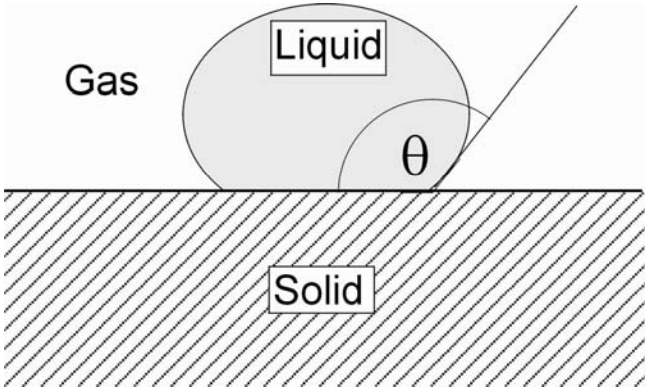
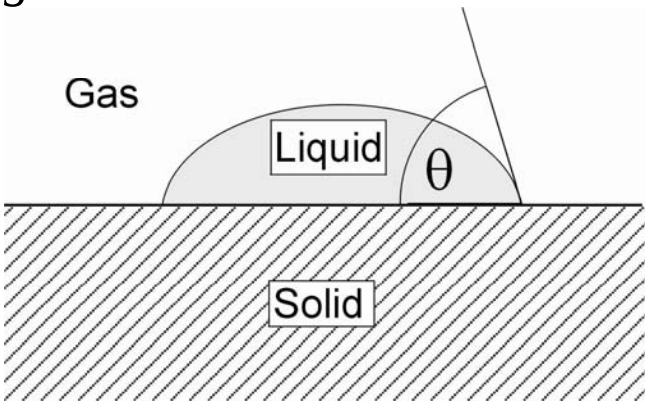
Institute for Micromanufacturing

Template Wetting Nanofabrication

- Many ways to make nanostructured materials
  - Layer by layer assembly
  - Self assembled monolayers
  - Nanolithography
  - Etc.
- Templating methods
  - Start with a template with nanopores
    - Nuclear track etched polymers
    - Porous alumina
    - Porous silicon
  - Coat walls of pores in template
    - Surface preparation (typically with organosilane chemistry)
    - Electroplating
    - Vapor deposition
    - **Wetting**



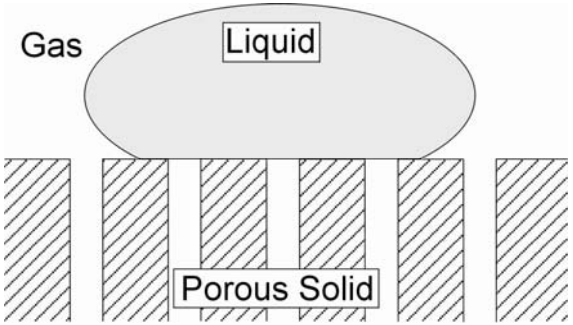
Nonwetting: contact angle is greater than 90°



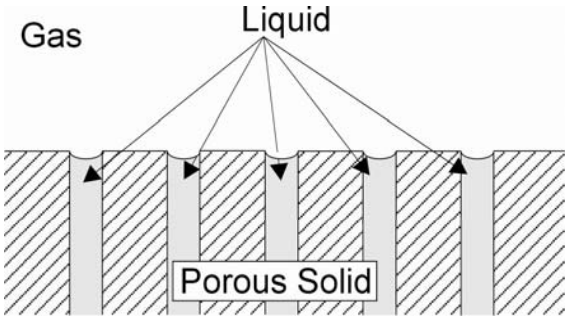
Partial wetting: contact angle is less than 90°

Template Wetting Nanofabrication

- Wetting of porous materials
  - For *sufficiently small pores*, nonwetting liquids will not readily penetrate
  - Want wetting behavior
    - Liquid readily penetrates into pores
    - Small contact angle
    - Note – can also measure contact angle in a capillary tube
- The template wetting process
  - Preparation of wetting solution
    - Contains precursor to nanotube/nanowire material
    - If necessary, add wetting agent
    - Resulting solution must "wet" surface of template



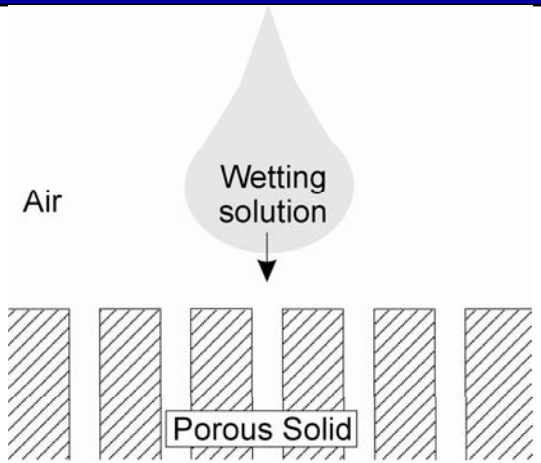
Nonwetting: Contact angle is greater than 90° and liquid is excluded from pores



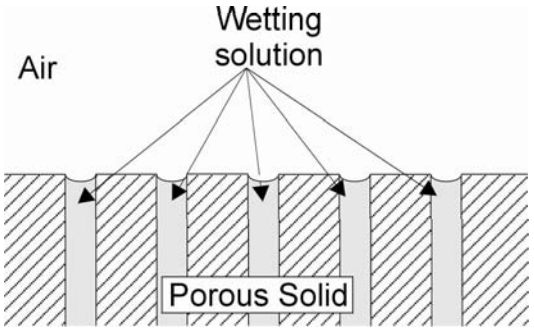
Wetting: Contact angle is less than 90° and liquid wets the porous solid

Template Wetting Nanofabrication

- Pipette solution onto template
  - How much and what concentration?
    - Depends on desired structure – nanowire, nanotube with a particular wall thickness
  - If solution is designed correctly, it will wet the template – filling the pores



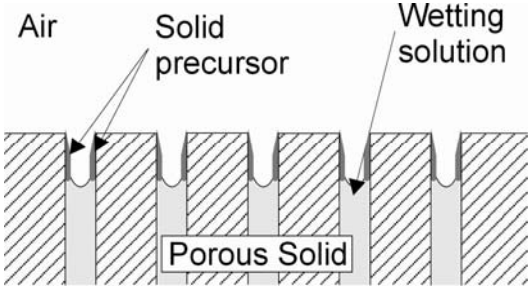
The wetting solution is applied to the template.



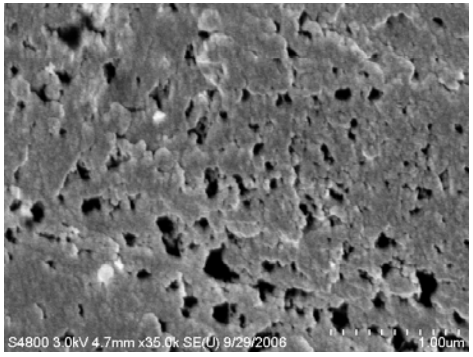
The solution wets the solid surface resulting in liquid filled pores.

Template Wetting Nanofabrication

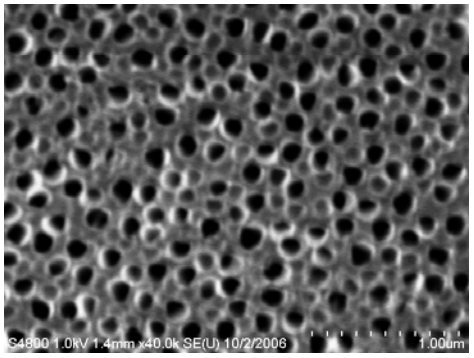
- Evaporation of solvent
  - Precursor material left behind on pore walls
  - Result is nanotubes or nanowires of precursor material
  - Some excess may be on top
    - Can physically scrape off or for a bit cleaner surface, RIE etch



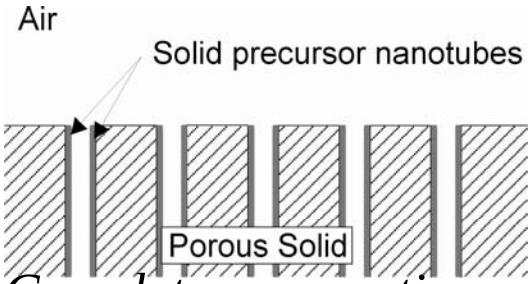
As the solvent evaporates, the nanotube precursor material deposits on pore wall surfaces.



SEM of porous alumina with excess Pt(acac)



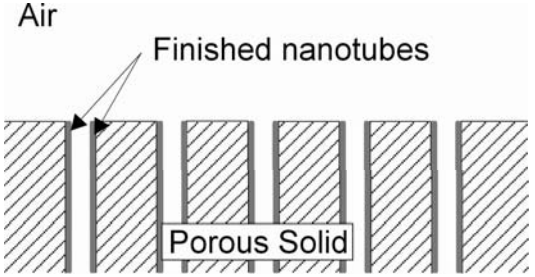
SEM of porous alumina with excess ZrOH removed by sputtering



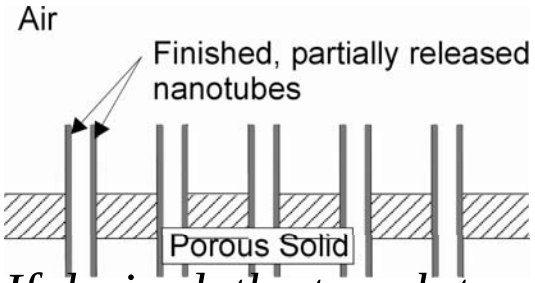
Complete evaporation of solvent leaves behind solid precursor nanotubes.

Template Wetting Nanofabrication

  - Post-treatment to convert nanotube precursor to desired material
    - Heat treatment
    - Oxidize/reduce precursor
    - Sintering
    - Calcination
    - Etc.
  - If desired, etch all or part of template away (dilute KOH)
- Advantages of template wetting
  - Wide array of materials possible
    - Many polymers
    - Metals
    - Ceramics
    - In general – anything you could synthesize in solution
  - ***Fast and simple processing***
  - Nanotubes/nanowires aligned in template
- Disadvantages of template wetting
  - Nanotubes/nanowires aligned in template
  - May require wetting agent
  - Not well established theory for design of new materials/structures

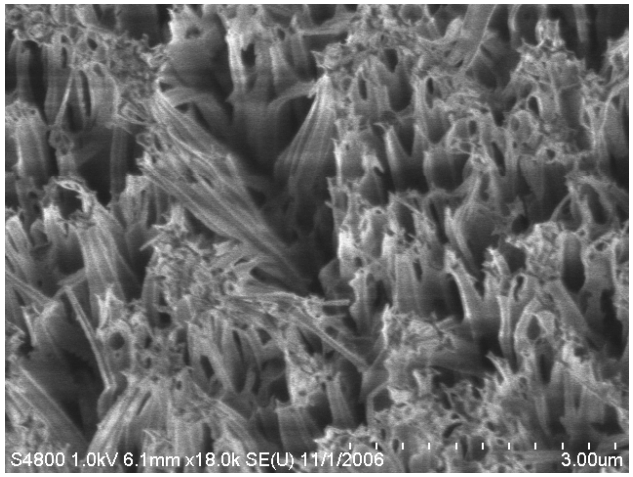


Post-treatment performed to yield the nanotubes of desired material.



If desired, the template can be selectively etched to release the nanotubes.

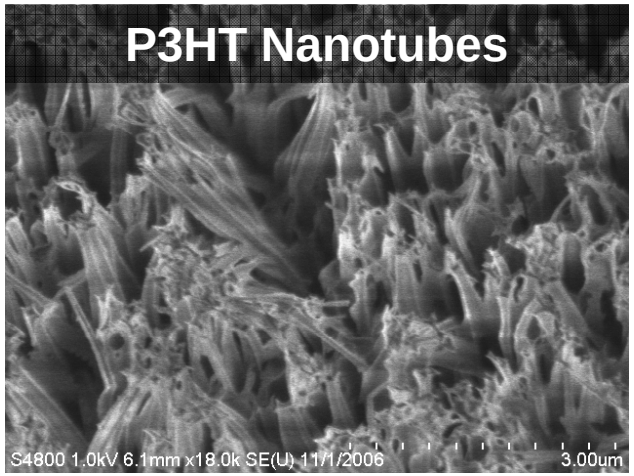
Brainstorming: What could we do with this?

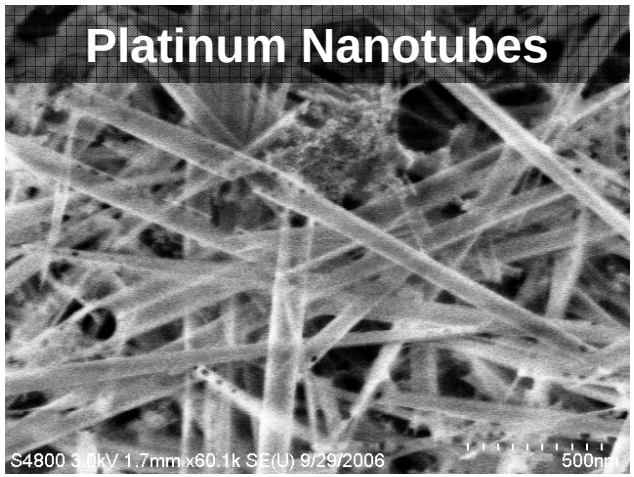


- Arrays of nanotube/wires - can be aligned vertically
- Could remove them from the template completely
- Lots of surface area
- Limited number of template materials
  - Alumina
  - Silicon
  - Polycarbonate
  - Titanium
  - Maybe some others
- Nearly limitless possibilities on nanotube/wire material

Applications of Nanostructures from Template Wetting

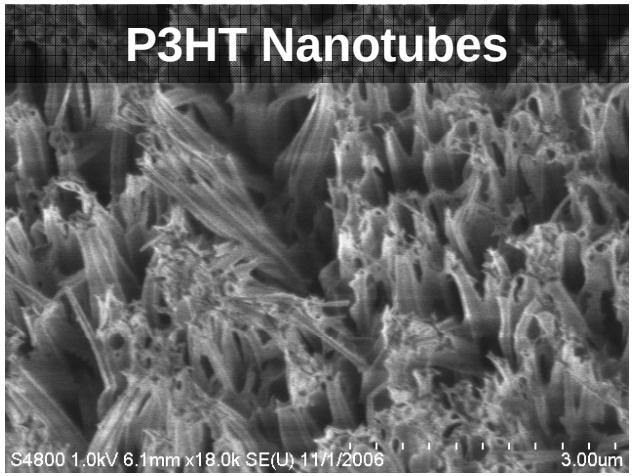
- Ceramics:
  - Sulfated zirconia (superacid)
    - Proton exchange membrane for fuel cells
    - Acid catalysis
- Metals:
  - Platinum, Palladium
    - Fuel cell catalysis
  - Gold
    - Conductive electrodes for enzyme immobilization (bio fuel cells!)
    - Surface enhanced Raman Spectroscopy
- Piezoelectrics
  - (Lead zirconium titanate or PZT, PVDF, ZnO)
    - Piezoelectric MEMS devices (microphones, vibration sensors, energy scavenging)
- Polymers:
  - Conductive and semiconducting polymers (polythiophenes, polypyrroles, etc.)
    - Electrochemical Supercapacitors
    - Photovoltaics, LEDs, and photodiodes
    - Sensors
- Hydrogen Storage

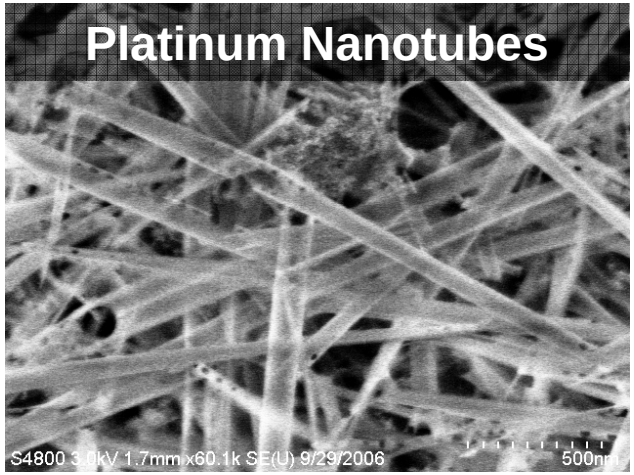




Applications of Nanostructures from Template Wetting

- Ceramics:
  - Sulfated zirconia (superacid)
    - Proton exchange membrane for **fuel cells**
    - Acid catalysis
- Metals:
  - Platinum, Palladium
    - **Fuel cell** catalysis
  - Gold
    - Conductive electrodes for enzyme immobilization (**bio fuel cells!)**
    - Surface enhanced Raman Spectroscopy
- Piezoelectrics
  - (Lead zirconium titanate or PZT, PVDF, ZnO)
    - Piezoelectric MEMS devices (microphones, vibration sensors, **energy scavenging**)
- Polymers:
  - Conductive and semiconducting polymers (polythiophenes, polypyrroles, etc.)
    - **Electrochemical Supercapacitors**
    - Photovoltaics, LEDs, and photodiodes
    - Sensors
- **Hydrogen Storage**



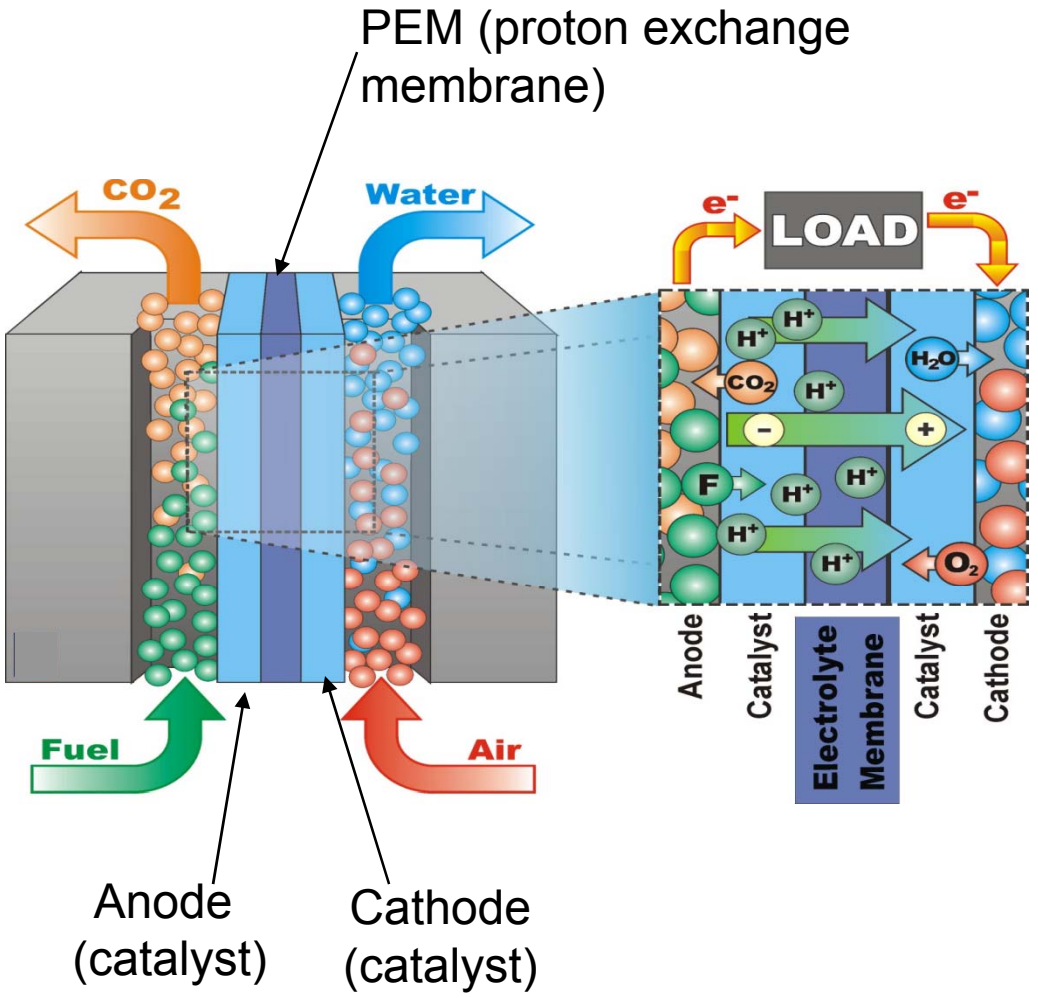


What is a fuel cell?

- Simple definition – a device which converts chemical energy to electrical energy
- Must supply fuel and oxidant to the cell (a battery contains these as part of the device)
- Two “half cell reactions” are involved at an anode and cathode respectively
- Wide variety of different types of fuel cells
  - Lets look at one type, the Hydrogen PEM fuel cell
    - Proton Exchange Membrane
    - Proton Electrolyte Membrane
    - Polymer Electrolyte Membrane

Operation of PEM Fuel Cells

- Hydrogen PEMFC
  - Hydrogen and oxygen separated by electrolyte membrane
  - Anode reaction:
    $2H_2 \rightarrow 4H^+ + 4e^-$
  - Cathode reaction:
    $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$
  - Protons pass through electrolyte membrane
  - Electrons go through circuit to power some load
- Other types of fuel cells have different:
  - Fuels
  - Mobile ions (not necessarily H^+)
  - Kinds of electrolyte

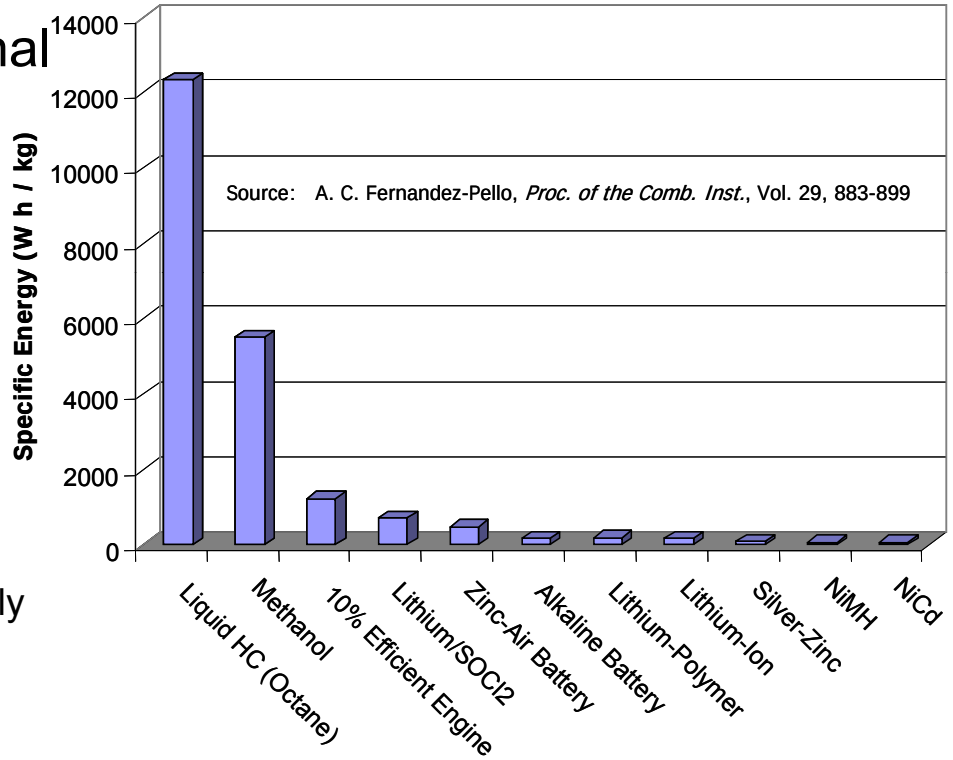


Different types of Fuel cells

Fuel cell type	Mobile ion	Operating temp.	Applications
Alkaline (AFC)	OH^-	50-200°C	Space program
Proton Exchange Membrane (PEMFC)	H^+	30-100°C	Vehicles and mobile power
Direct methanol (DMFC) and other liquid fuels	H^+	20-90°C	Portable electronics
Phosphoric acid (PAFC)	H^+	~220°C	~200 kW CHP systems
Molten carbonate (MCFC)	CO_3^{2-}	~650°C	Medium to large scale CHP (MW capacity)
Solid oxide (SOFC)	O^{2-}	500-1000°C	All size CHP systems (2kW to multi-MW capacity)
Enzymatic bio-fuel cells	H^+	20-40°C	Bio-implants and energy scavenging

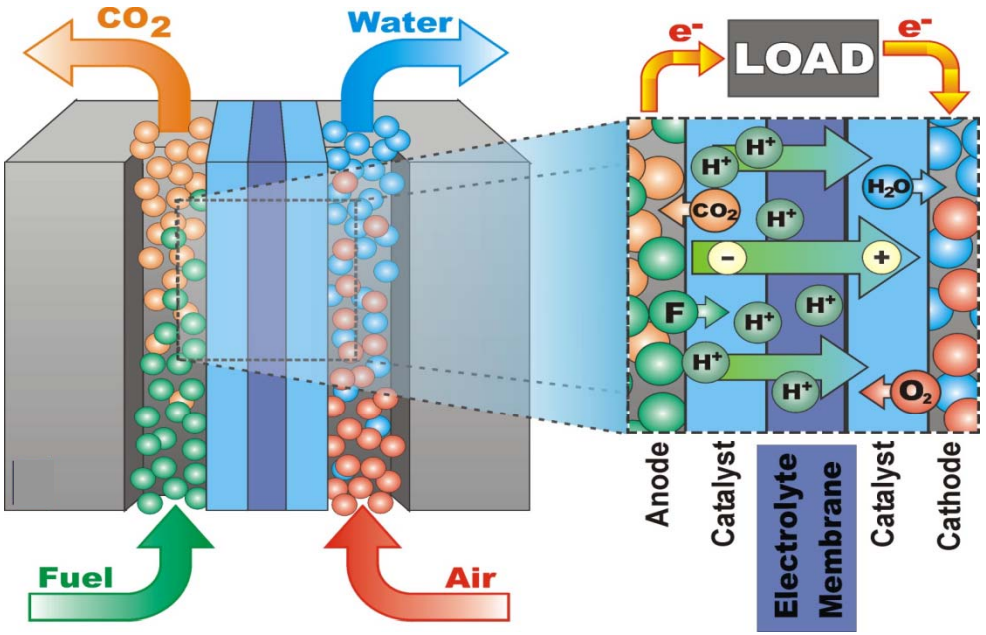
Why all the excitement?

- Environmentally friendly
  - No or minimal emissions
- Much more efficient than conventional combustion engines
  - Not Carnot limited!
  - 80-90% efficiency not unreasonable
- High energy density
  - Battery replacement
    - Batteries
      - Major fraction of weight of portable electronics
      - Frequent replacement/recharging required
      - Disposal not environmentally friendly
      - Technology has not fundamentally changed in over 100 years
    - Fuel cells
      - Higher theoretical energy density
      - Potentially viable portable power source
      - Costs are nearly competitive with batteries now!



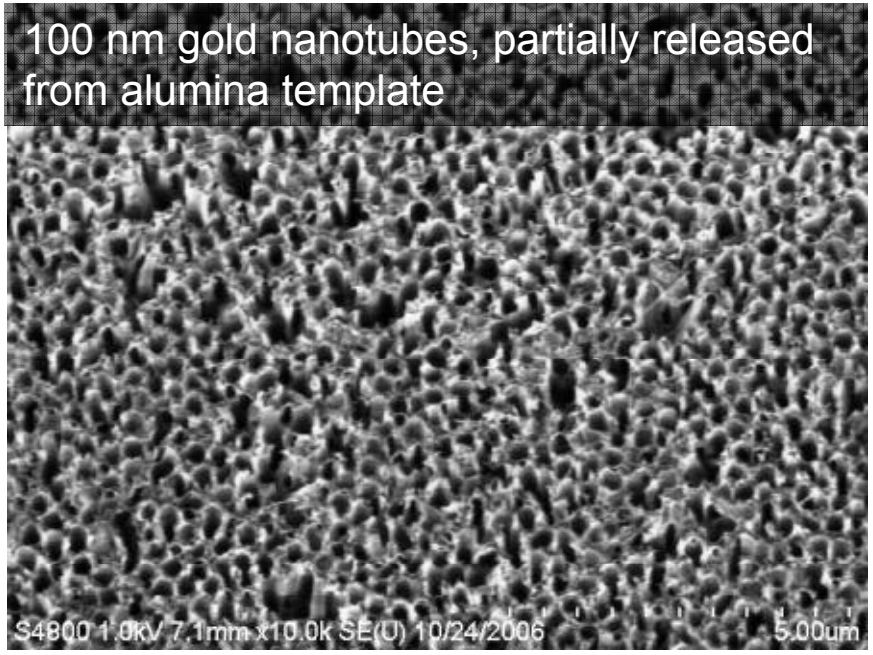
So what's the problem?

- Challenges
  - Catalysis
    - Required to get significant reaction rates
    - Expensive (typically Pt based)
  - Choice of fuel
    - Hydrogen
      - Difficult and dangerous to store
      - Reforming of hydrocarbon fuels
      - Hydride storage materials
    - Methanol
      - Crossover
      - Catalyst poisoning
    - Formic acid
      - Cheap and safe
      - Higher theoretical OCP than MeOH
      - Corrosive
  - Membrane material
    - Nafion – current standard
  - Design issues
    - Current collection
    - Fuel transport to catalyst
    - Proton transport to membrane
    - Waste removal



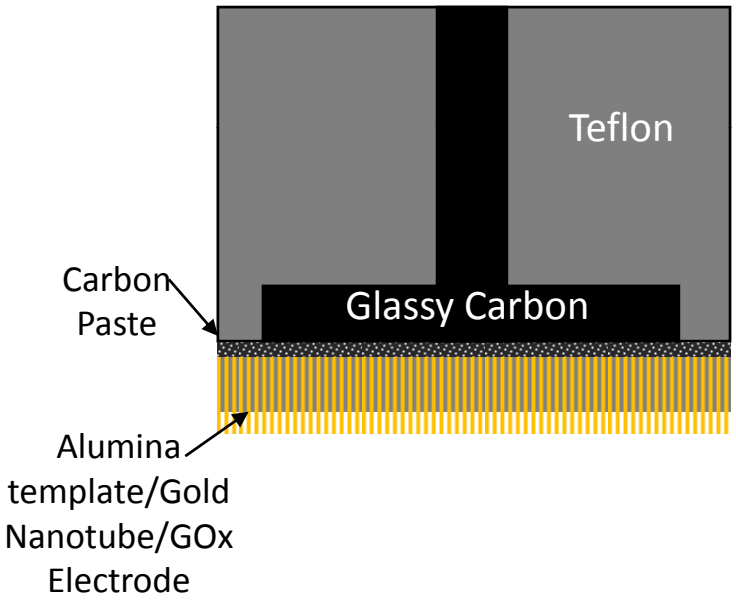
Gold Nanotubes via Template Wetting

- Enzymatic bio-fuel cells
  - Major challenges
    - Immobilization of enzymes
    - Efficiency in collecting electrons
    - Enzyme stability and lifetime
- Gold nanotubes and nanowires
  - High surface area, conductive substrate for enzyme immobilization
  - Use gold chloride solution as precursor



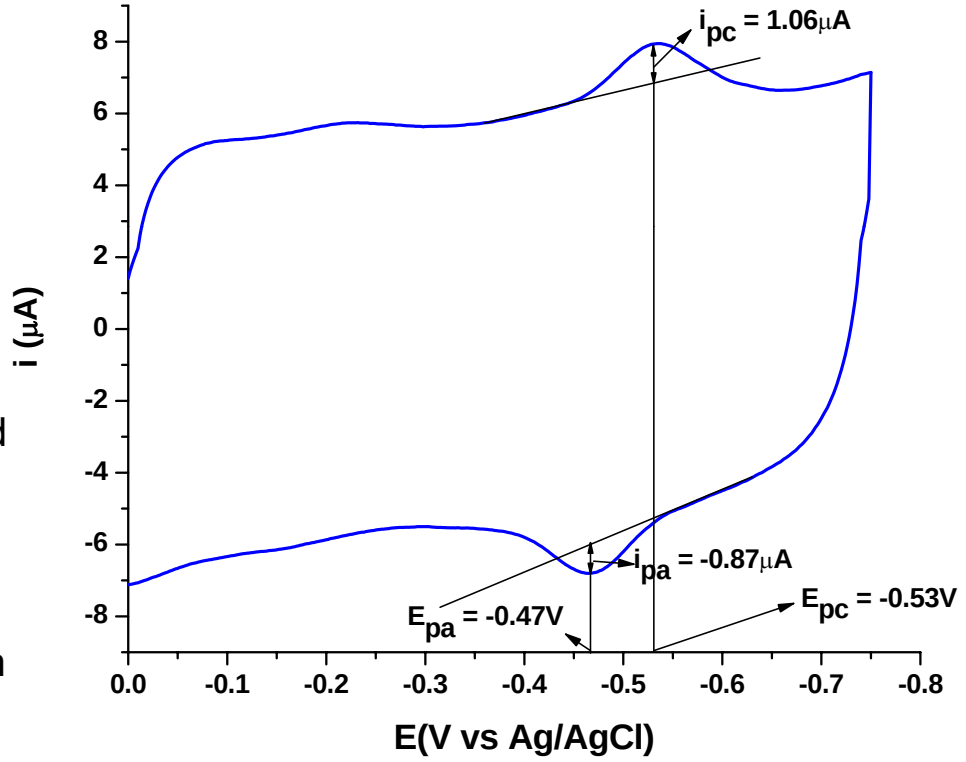
Gold Nanotubes Electrode Preparation and Testing

- Electrode preparation
  - Template wetting with gold chloride solution
  - Annealed in air at 200°C
  - Excess gold on top surface removed via RIE etching in helium plasma
  - 60 second etch in dilute KOH(aq) to partially release nanotubes
  - Soaked overnight in 5 mg/1mL glucose oxidise – phosphate buffer solution
  - Graphite paste used to attach backside of template to glassy carbon electrode for electrochemical testing



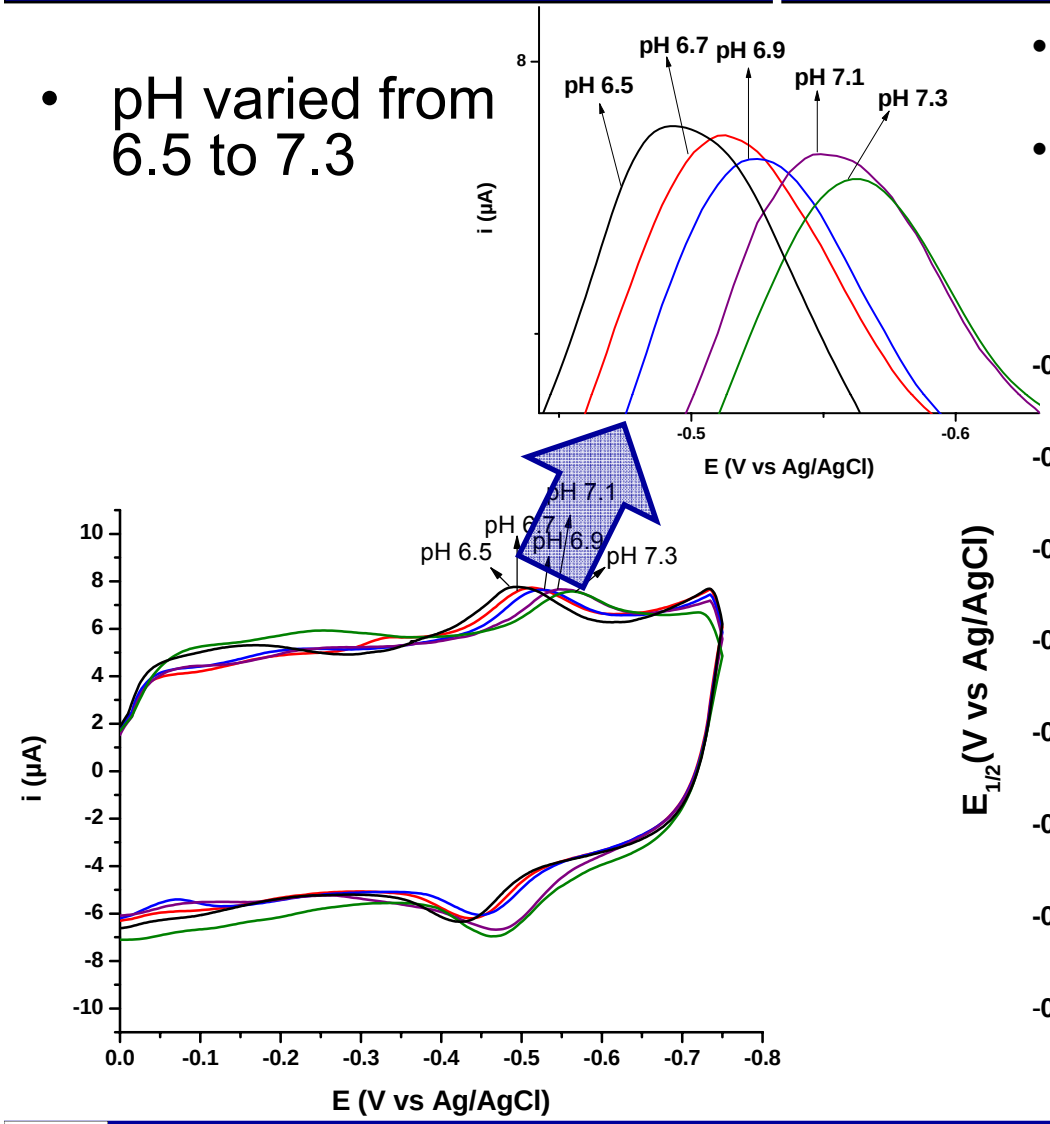
Cyclic Voltammetry – GOx/Gold Nanotube: Electron Transfer Rate Coefficient

- CV plot in 0.1 M PBS, pH 7.1, scan rate of 60 mV/s, 5 mM glucose
  - Electron transfer rate coefficient
    - $k = \frac{mnF\nu}{RT}$
    - Where *n* is number of electrons transferred (2), *v* is the scan rate, *F* is Faraday's constant, *T* is temperature (298K), *R* is the gas constant, m and are constants obtained from literature (0.192 and 0.5)
  - From literature
    - k=0.026 s^{-1} for GOx physisorbed on flat gold surface
    - k=1.53 s^{-1} for GOx physisorbed on carbon nanotubes
  - For GOx physisorbed on gold nanotubes
    - k=0.90 s^{-1}

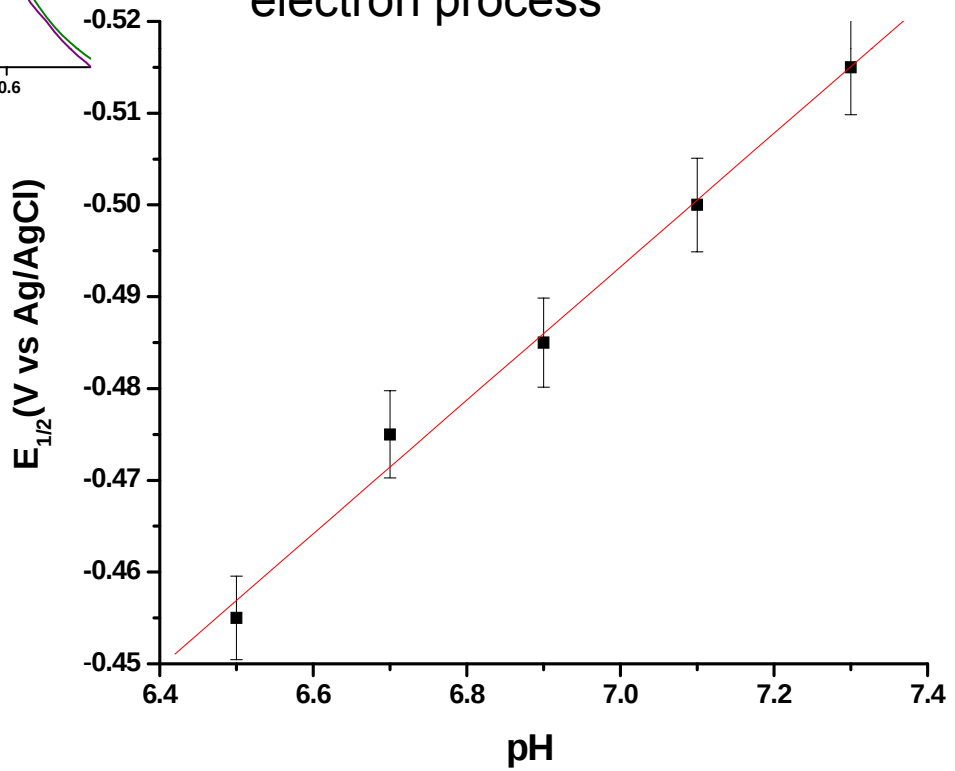


Cyclic Voltammetry – GOx/Gold Nanotube: pH Effect

- pH varied from 6.5 to 7.3

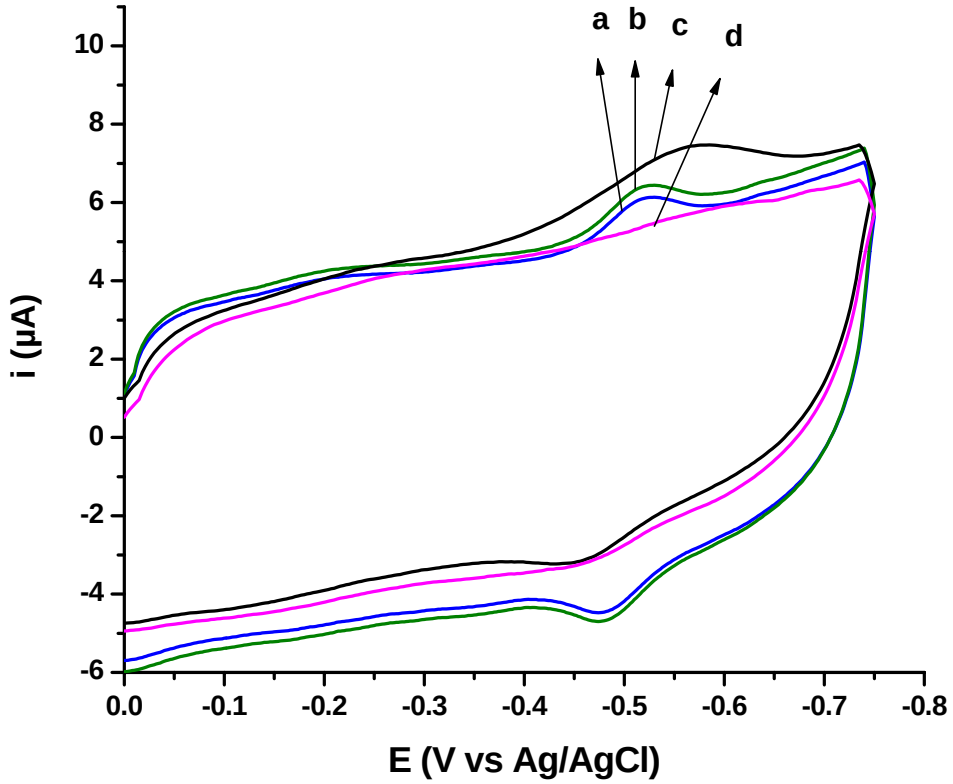


- Conformal changes in Gox cause negative shift in peak potential
- Slope of plot of midpoint potential vs. pH
  - -58.82 mV/pH, consistent with prediction for 2 proton/ 2 electron process



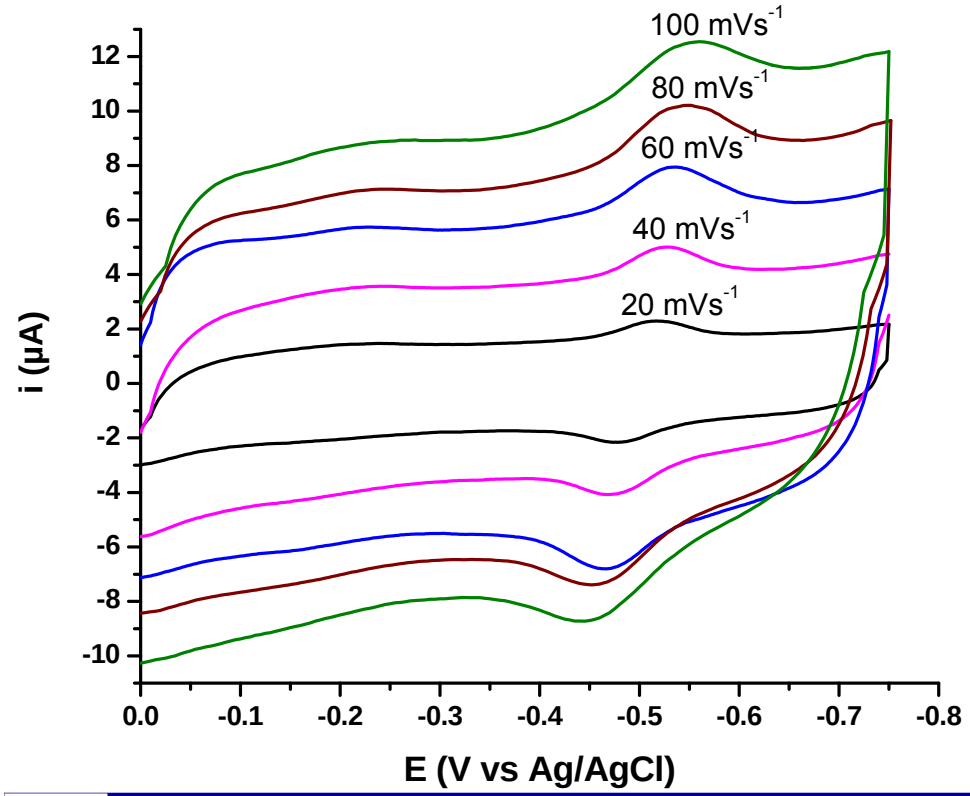
Cyclic Voltammetry – GOx/Gold Nanotube: GOx or FAD Activity?

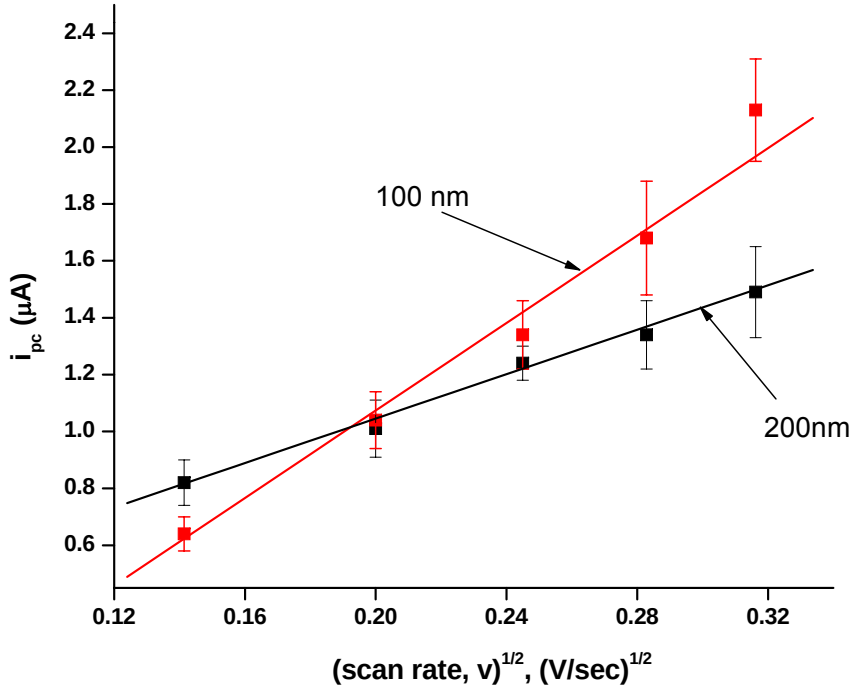
- Active FAD center of GOx enzyme could adsorb and show activity
- Guanidine hydrochloride (GHCl)
  - Strips FAD from enzyme
  - Does not strip free FAD from surface
- Cyclic voltammograms
  - a) before soaking over in PBS
  - b) before soaking in GHCl
  - c) after soaking in PBS overnight
  - d) after soaking in GHCl overnight.



Cyclic Voltammetry – GOx/Gold Nanotube: Scan Rate

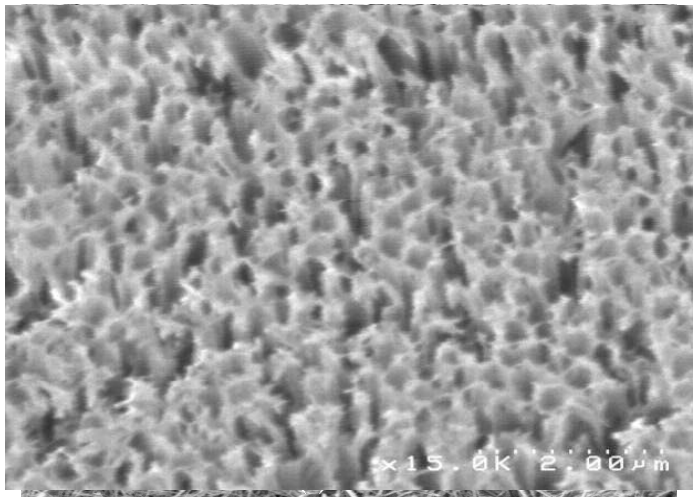
- Linear relationship between square root of scan rate and peak current
- Slope is a function of gold nanotube diameter
  - Greater for 100 nm gold nanotube



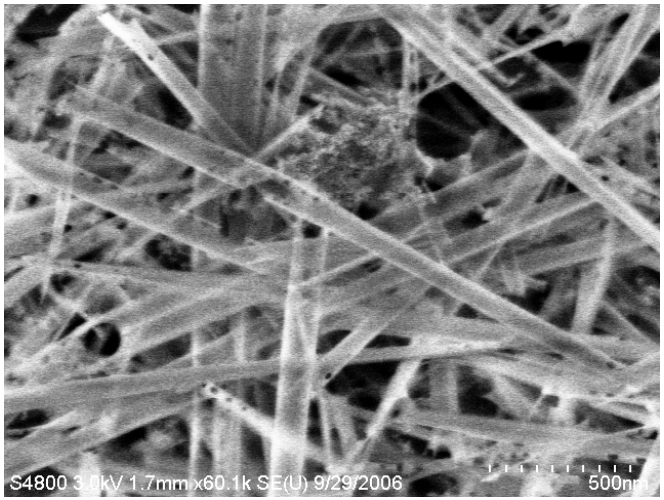


Other Fuel Cell Related Work with Template Wetting Nanofabrication

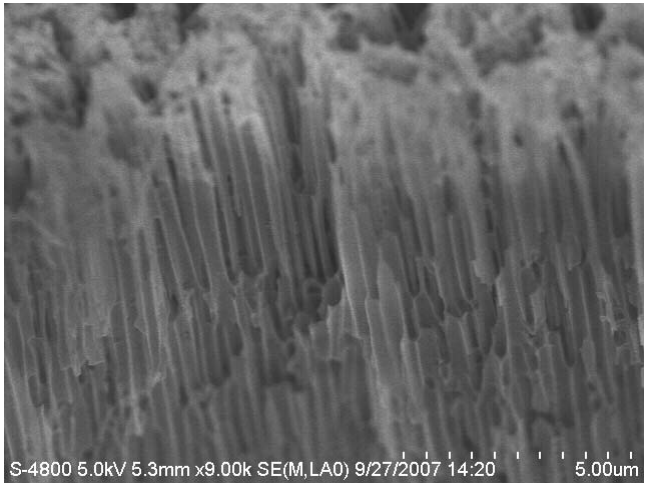
- Fuel cell catalysis
  - SEM photos
    - Platinum nanotubes from Pt(acac) solution after release from template
  - For catalysis
    - High surface area
    - Tubes may reduce mass transfer resistance in thicker catalyst layers (tubes ~60 μm long)
    - Potential for bimetallics, alloys
- Fuel cell membranes
  - Porous alumina template (20 nm) coated with sulfated zirconia
  - Greater proton conductivity than Nafion
  - Better crossover for formic acid



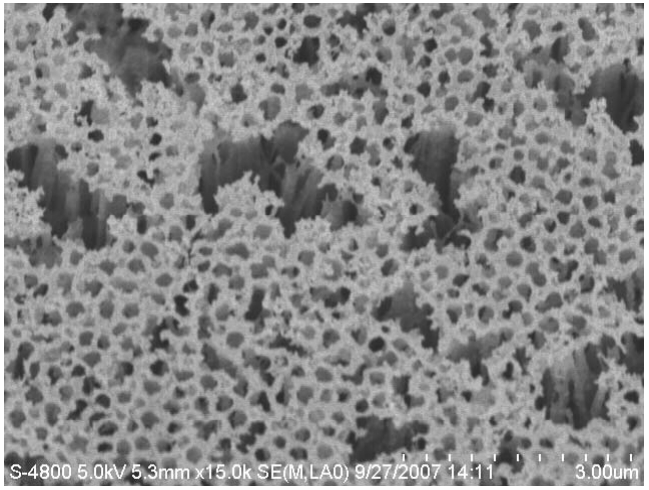
Platinum Nanotubes

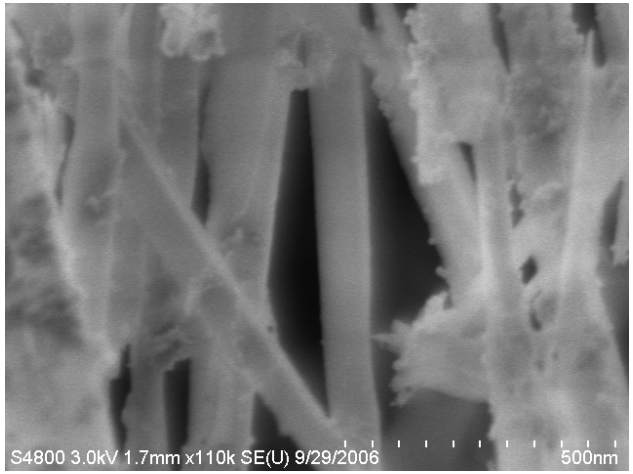


SEM Images of Pt Nanotubes



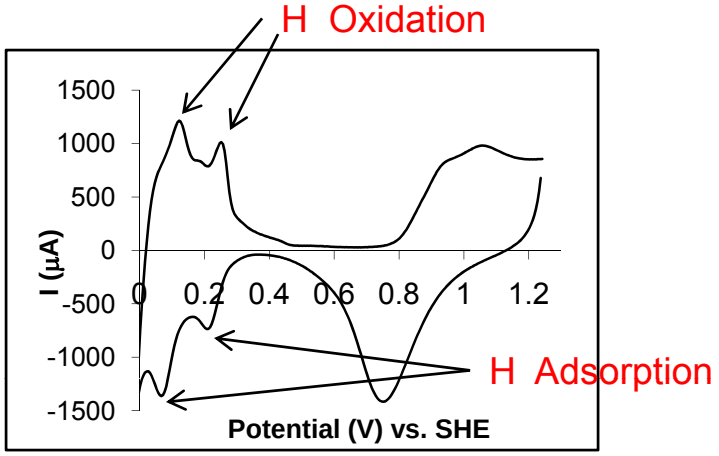
- High Yield of Pt Nanotubes
- Nanotube Diameter ≈ Template Pore Diameter
- Tubes extend all the way through template – 60 μm thick catalyst layer
- Tube walls are very thin, ~ 5 nm





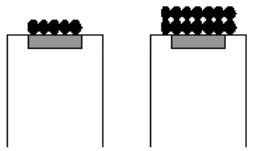
Catalytic Surface Area Measurement

- Hydrogen adsorption method
  - CV in 0.5M H_2SO_4 (aq)
  - Integrating current-time curve for hydrogen peaks
  - 210 μC/cm^2 to adsorb monolayer of H on Pt surface



Catalyst	Loading (mg/cm^2)	A_{real} (an) (m^2/g)	A_{Real} (ca) (m^2/g)
Pt Black (10 wt% Nafion)	10.0	2.93	2.70
Pt Black (10 wt% Nafion)	1.0	33.76	31.02
100 nm Pt Nanotubes	1.12	5.87	6.21
200 nm Pt Nanotubes	1.12	5.15	5.84

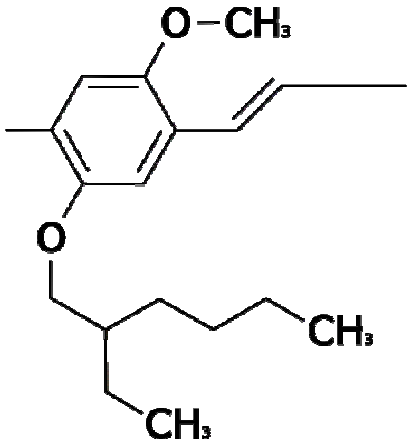
- Agreement with manufacturers values for low level of Pt black loading
- Active surface area of Pt Black reduced significantly as loading increases
  - Stacking effect of catalyst particles which can block active sites



- A_{real} for Pt nanotube samples are ~2 times greater than higher loading Pt black

Semiconducting Polymers

- What are they?
  - Conjugated backbone
    - Conduction via π-orbital overlap
    - Optically active
      - Solar cells, photodiodes, LEDs
- Why are these materials of interest?
  - Application
    - Single nanotube LEDs, Solar Cells, Photodetectors
    - Catalysis
    - Electrochemical Supercapacitors
  - Benefits
    - Low Cost
    - Ease of Processing
  - Drawbacks
    - Short carrier diffusion lengths
- Research needs
  - Improved device efficiencies
  - Improved understanding of conduction mechanisms

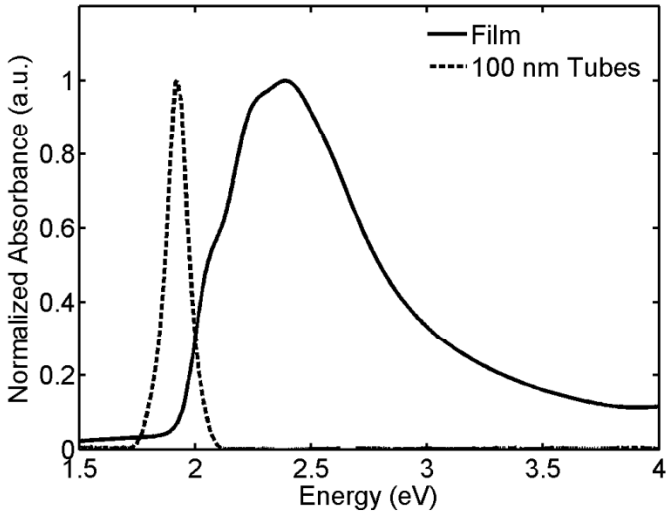


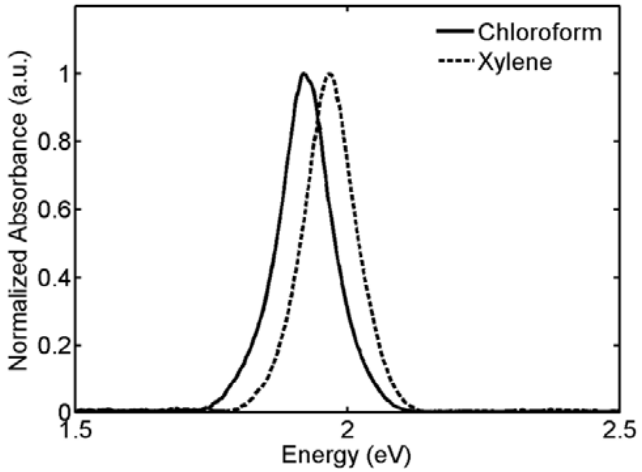
MEH-PPV

Goal: make nanotubes and nanowires of electronic polymers

P3HT Nanotubes

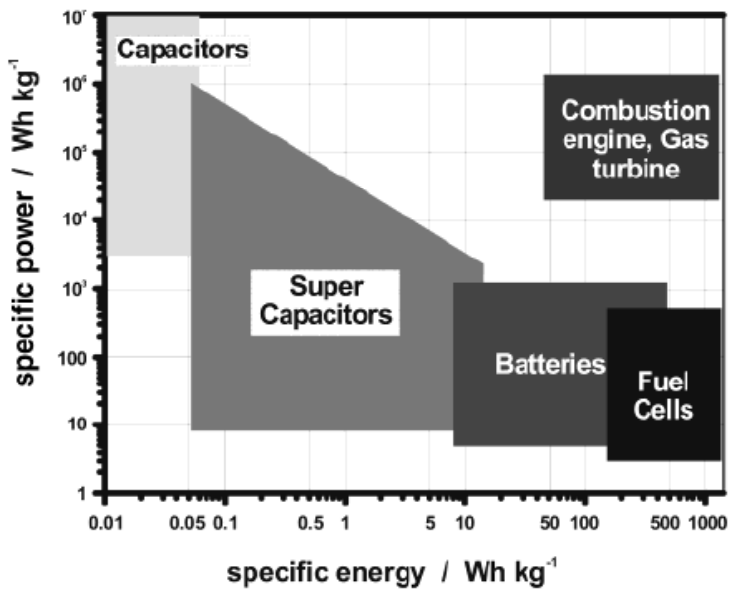
- UV-vis spectroscopy results
  - Thin film vs. nanotubes
    - Much narrower absorption band
    - Shift in absorption energy
    - Increased polymer chain alignment in nanotubes
  - Nanotubes made with chloroform vs. xylene
    - Not much difference
    - Slight shift in absorptoin energy

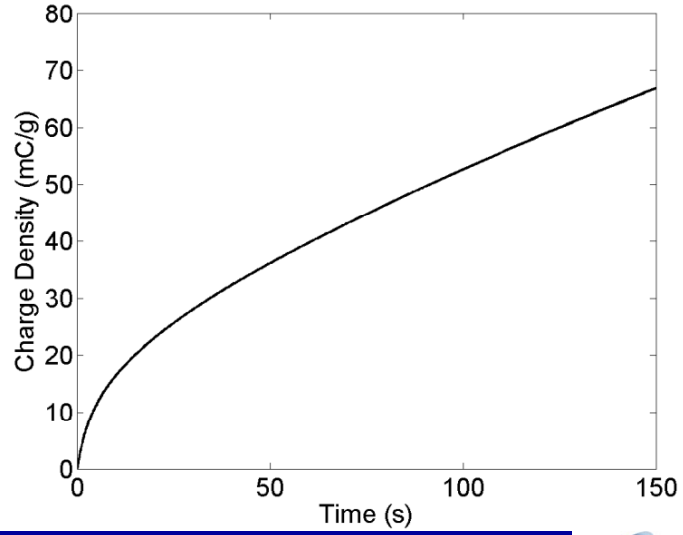




Nanostructured Supercapacitors

- **Low energy density** compared to other power sources but **high power density**
- Rapid recharge/discharge rates
- Supercapacitors using our process
  - Formed via successive template wetting procedures
  - Very high surface area = large capacitance
    - Theoretically on order of 100 F/g (400 J/g)
    - Potential power source for small sensors, other devices
- Prototype device
  - Gold electrodes, polystyrene dielectric
  - Purely electrostatic
  - Achieved ~7 F/g active material
  - Performance limited by high internal resistance

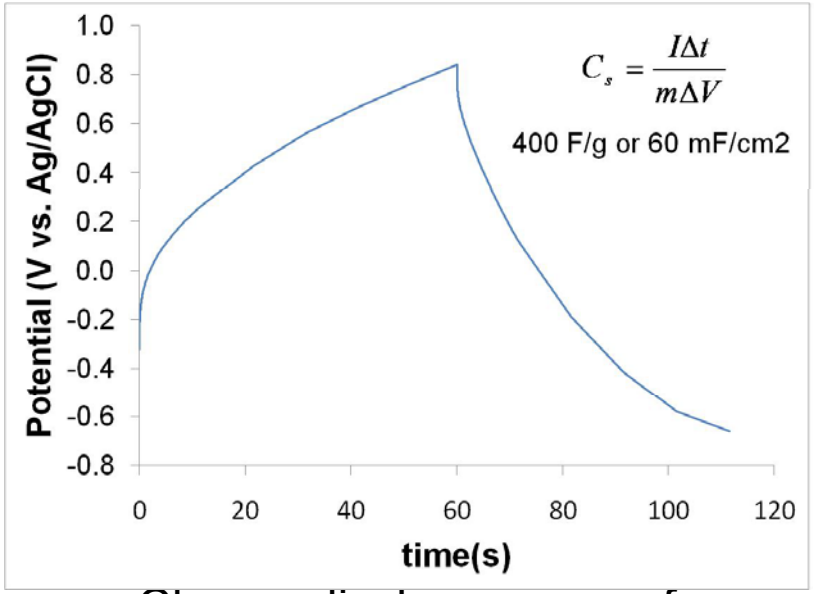




Results and Future Work: Nanostructured Supercapacitors

- Electrochemical supercapacitors
  - Store charge within electrode material
  - Best reported performance with RuO_2
    - Too expensive for most applications
  - Conjugated polymers show great promise
- Polythiophenes
  - Both n and p type doping can be achieved
  - P3HT (poly-3-hexylthiophene)
  - Achieved over 400F/g active material!

- Future plans
  - Working on electrolyte fabrication/characterization
  - Full device fabrication



Charge-discharge curve for P3HT Electrode

Conclusions

- Template wetting
  - Promising nanofabrication technology
  - Wide array of materials
- Green Energy Applications
  - Fuel cells
    - Enzymatic biofuel cells
    - Fuel cell catalysis
    - Fuel cell membranes
  - Electrochemical supercapacitors

Questions?