Designed Nanostructured Materials for Energy Conversion and Storage Devices

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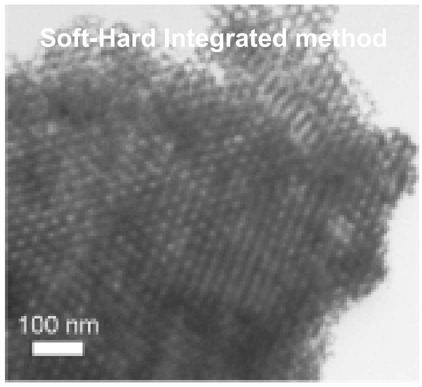
POSTECH

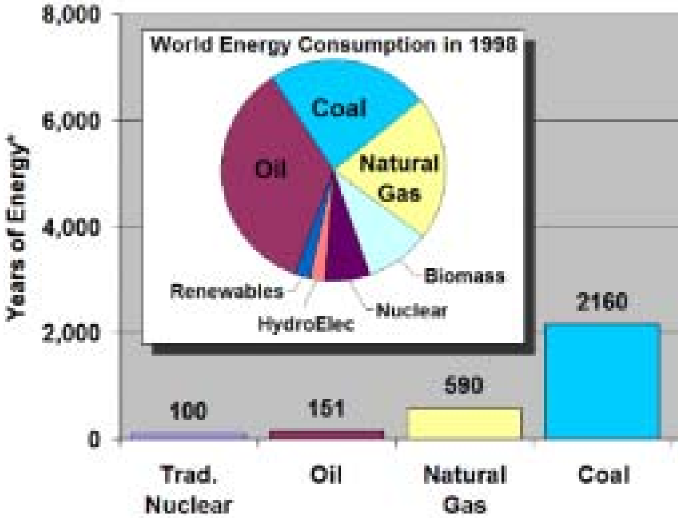
Outline

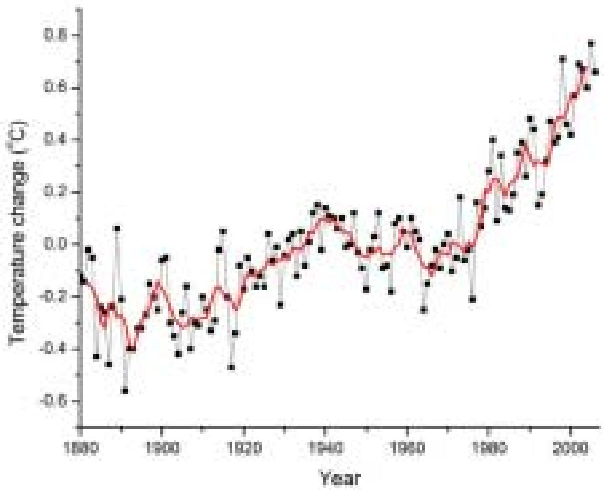
- Motivation
- Soft-Hard Integrated Assembly
- Fuel Cells
- Solar Cell
- Lithium ion battery



Motivation

Energy and Environmental Concerns





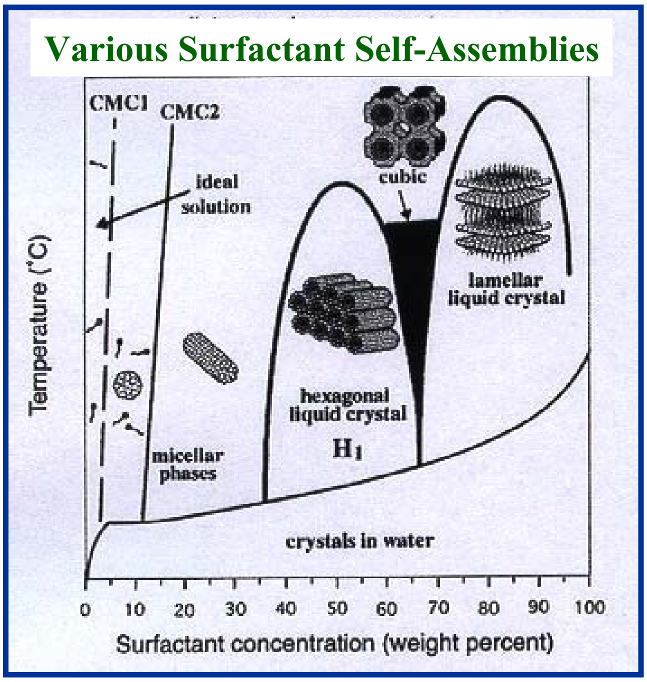
Alternative Energy Sources needed

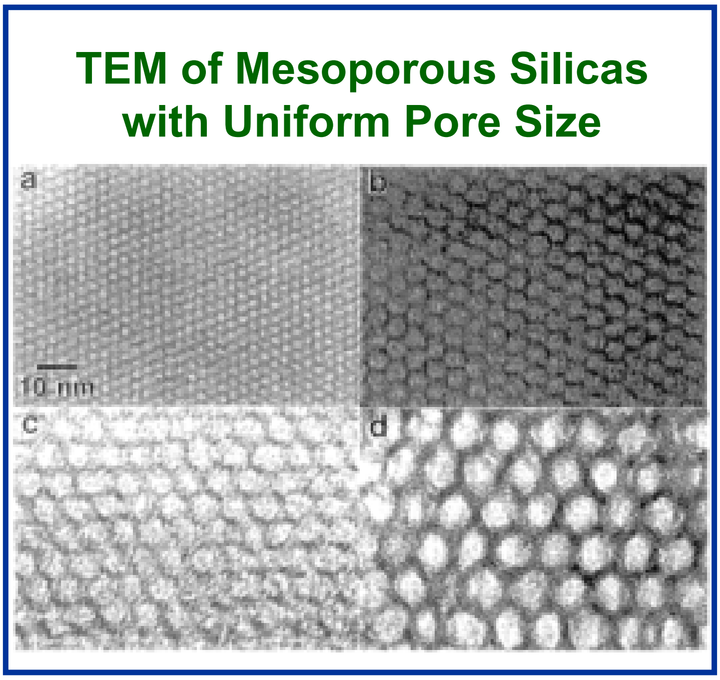
Better Energy Conversion & Storage Devices

Lewis, Nathan. Forum: Scientific Challenges in Sustainable Energy Technology. Palo Alto Research Center, Palo Alto, California, 10 Feb. 2005.

GISS Surface Temperature Analysis.
http://data.giss.nasa.gov/gistemp/graphs/

Synthesis of Mesoporous Silica Materials
using Surfactant-Self-Assembly as Template
Soft-template method





Kresge et al. *Nature* **1992**, 359, 710.

Toward Ordered Mesoporous Crystalline Transition Metal Oxides

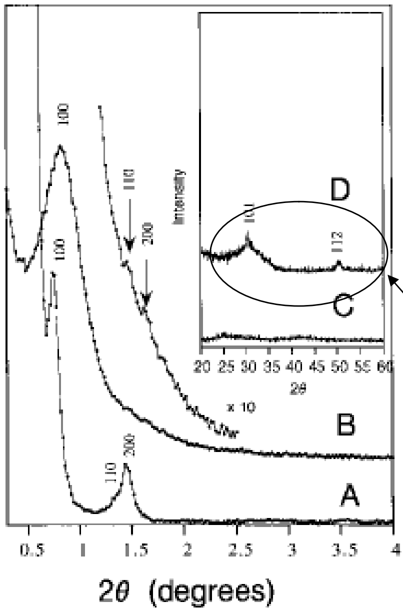
- **Non-siliceous mesoporous metal oxides (TiO_2, Nb_2O_5….)**
  :Important for electrode materials and catalysis

- **Many Research Groups have pursued after discovery of MCM-41**
  :Limited Success (Through Soft-Template Method)

- **Structure collapse occurs during the crystallization of the walls and removal of soft-template**

- **Very recently, hard template was employed to make crystalline mesoporous metal oxides**

Soft-template method



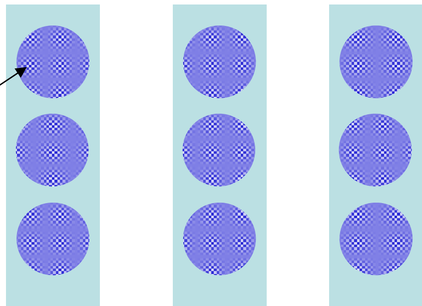
Stucky et al Nature 1998

♦ Not easy to preserve the porous strcutre after heat-treatment

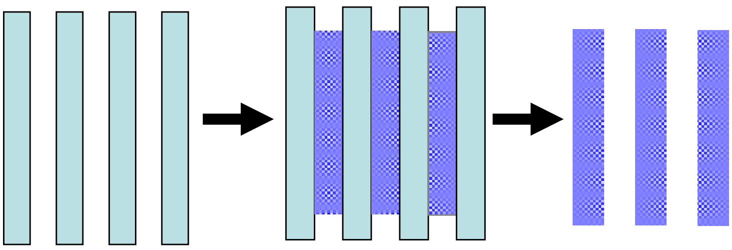
♦ Maximum heating temperature: 400 °C for 30 min⇒Low-crystallinity

Low-crystallinity

crystals



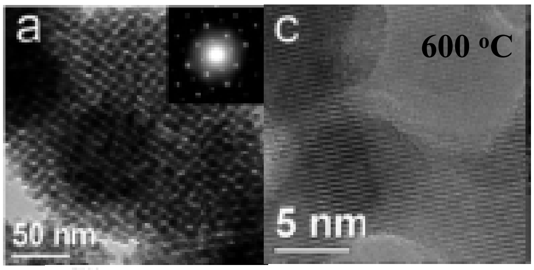
Hard template method

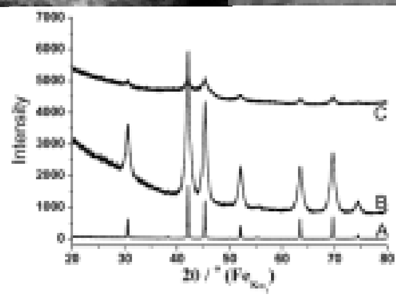


Mesoporous silica

Mesoporous silica /Metal oxide

Metal Oxide





♦ Fully crystalline

♦ Tedious synthetic step

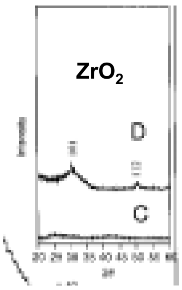
Bruce et al JACS 2006

Soft Template

- MCM-41 type synthesis

• Advantage: Simple Synthetic Method

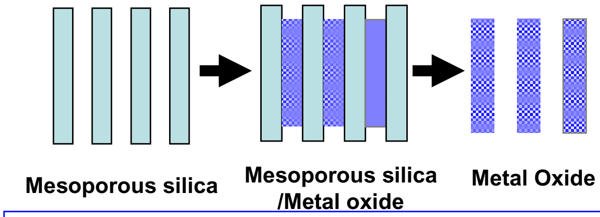
- **Disadvantage: Low-crystallinity**



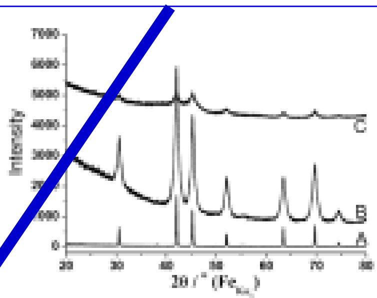
Stucky et al *Nature* 1998, 396, 152

Hard template

- **Recently developed technique to make crystalline mesoporous metal oxides**



• Advantage: Fully Crystalline Materials



P. G. Bruce et al. *J. Am. Chem. Soc.* 2006, 128, 5468

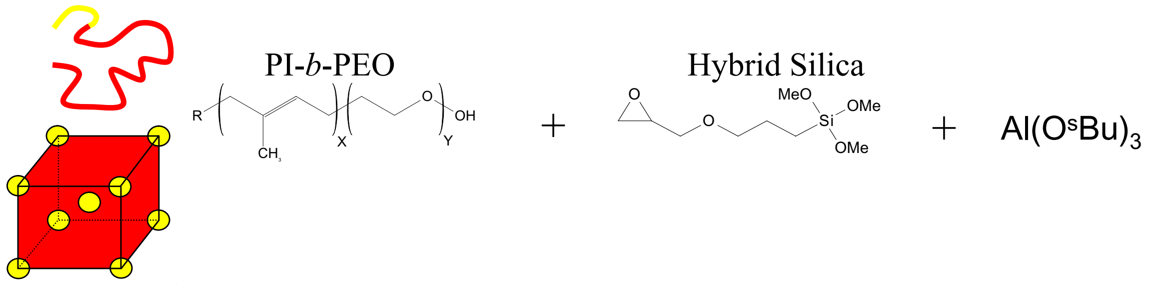
- **Disadvantage: Very tedious Multi-Step Method**

We need a new efficient way

PI-*b*-PEO synthesis

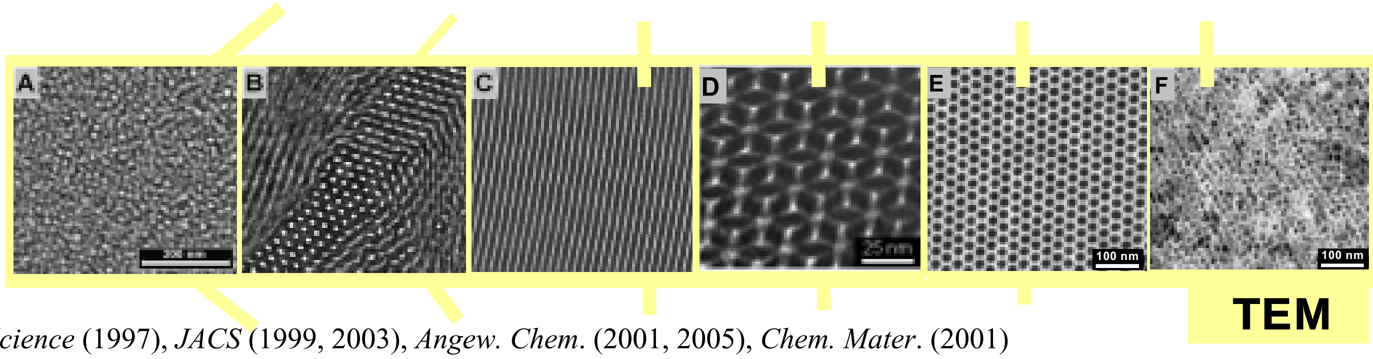
Wiesner Research Group: Route to Mesoporous Materials

Polymers as structure-directing agents for inorganics



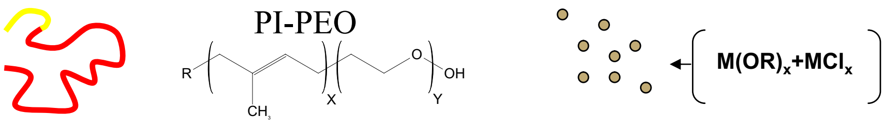
Goes into PEO only

Increasing the amount of inorganic material



Science (1997), *JACS* (1999, 2003), *Angew. Chem.* (2001, 2005), *Chem. Mater.* (2001)

Soft and Hard Integrated Assembly (SHIA) Method



Mn~27,220, PEO~ 16.7wt%

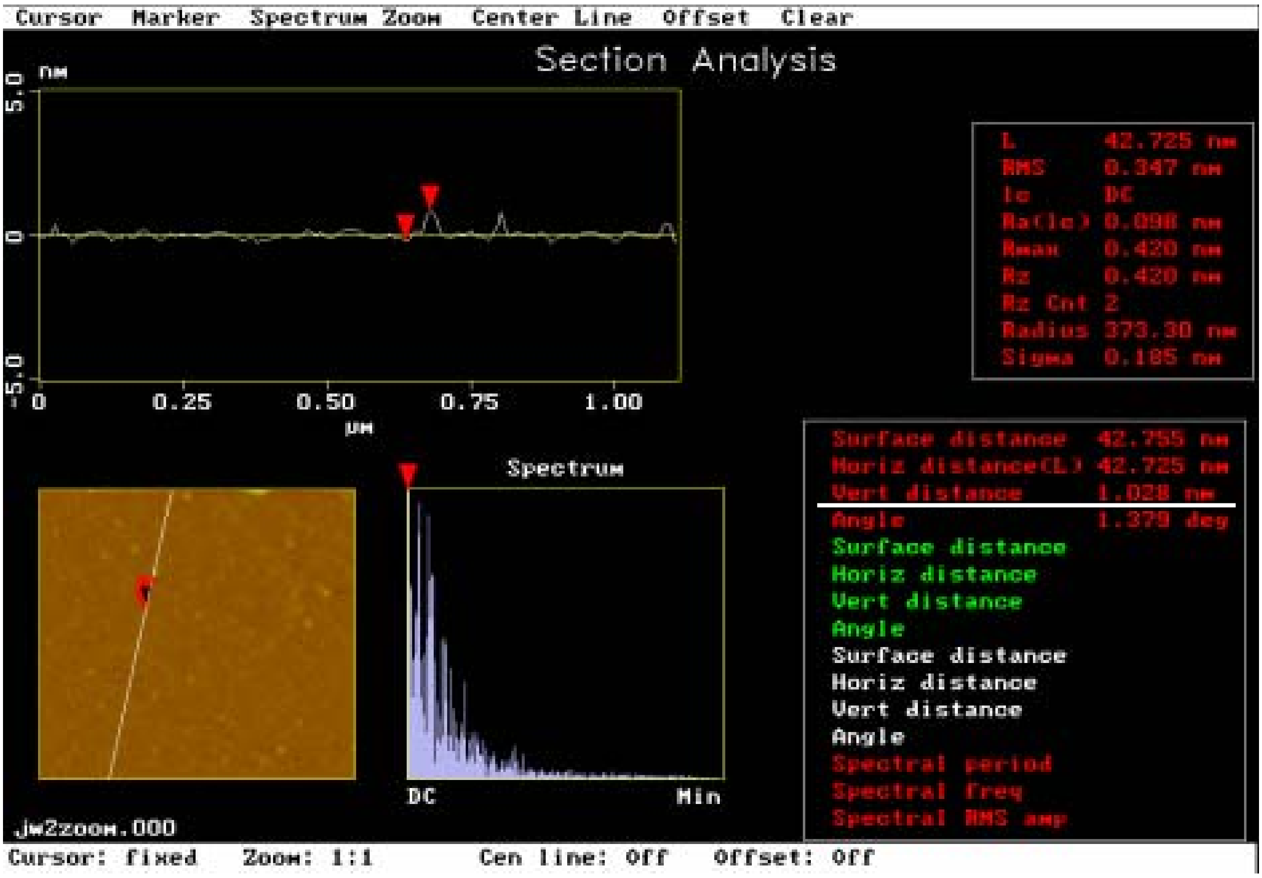
Metal Oxide Nanoparticles

Hexagonally arranged polymer-metal oxide hybrid

Highly crystalline mesoporous me tal oxide with carbon

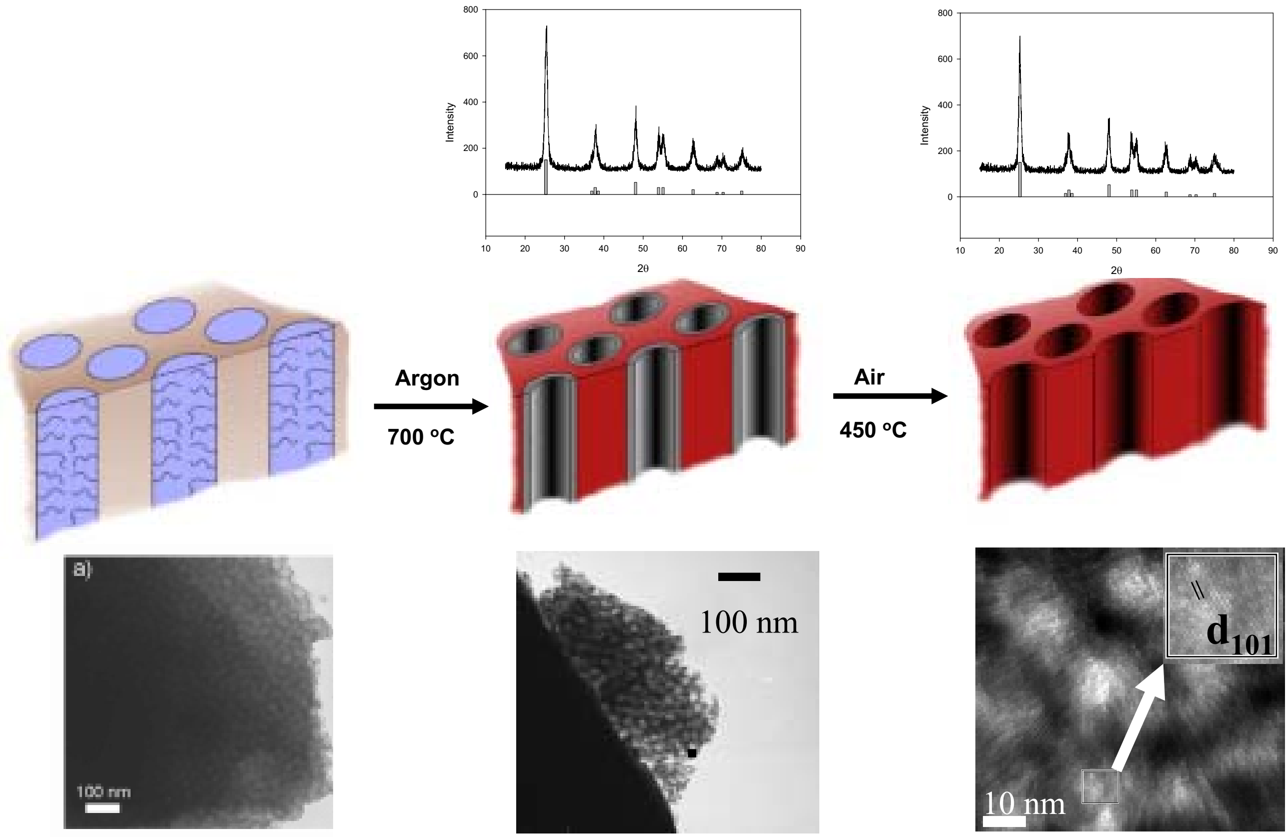
Fully crystalline meso-porous metal oxide

J. Lee et al 2007 *Nature Materials* revised version

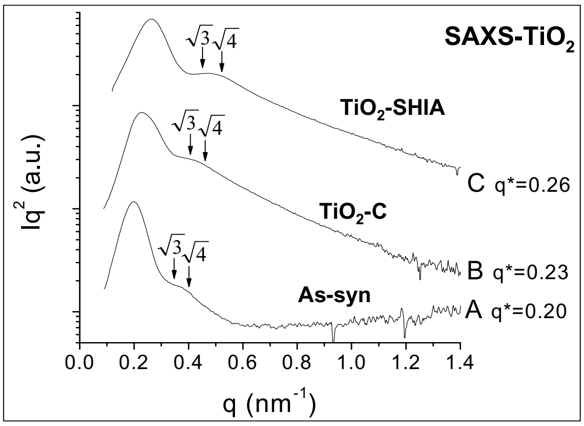


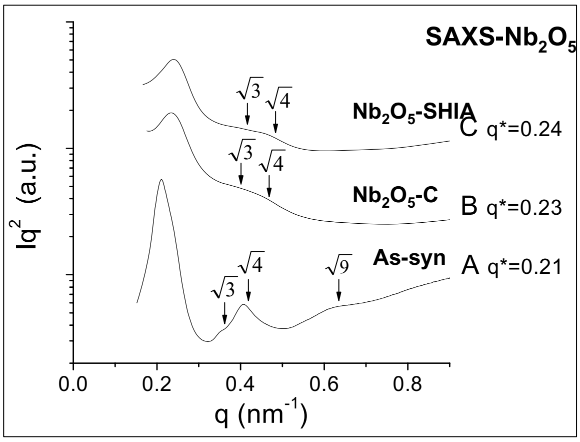
1h 30 min

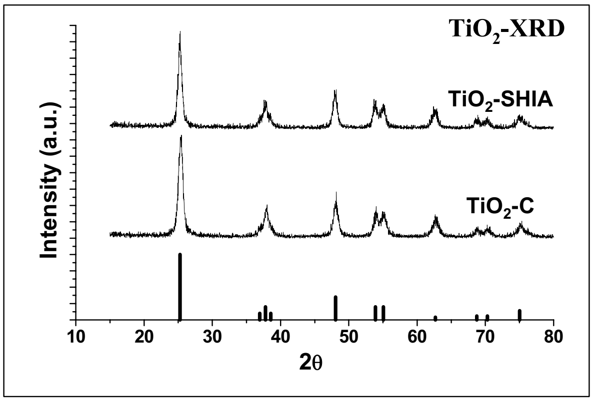
Example: Mesoporous Anatase TiO_2

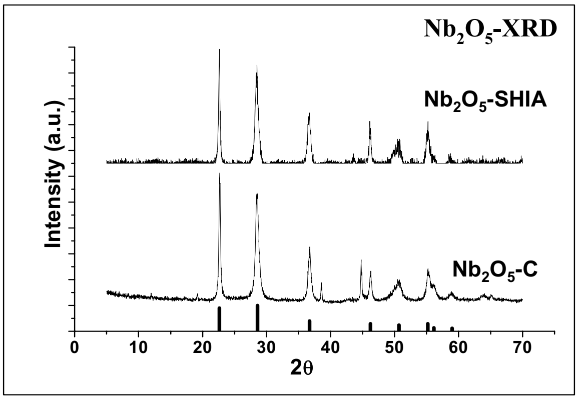


J. Lee et al 2007 *Nature Materials* revised version



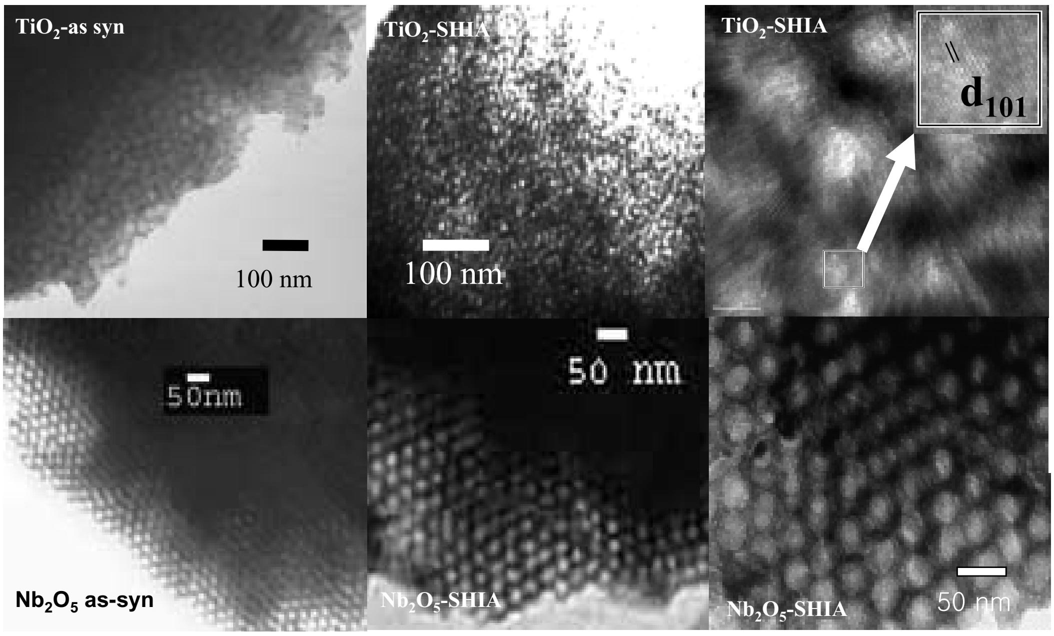




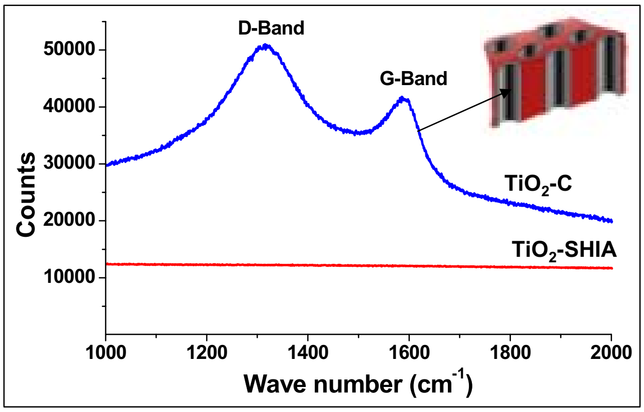


J. Lee et al 2007 *Nature Materials* revised version

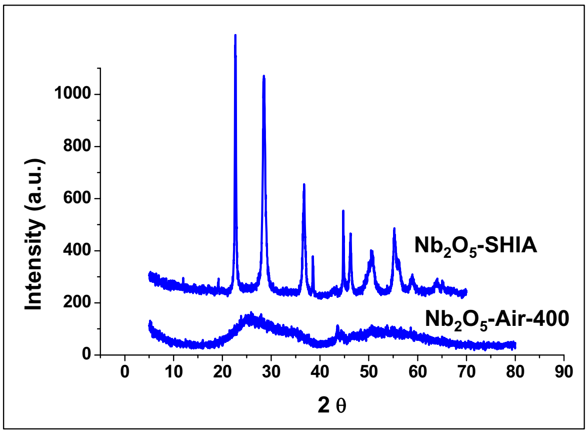
TEM images of Fully Crystalline Mesoporous Transition Metal Oxides



Raman Spectroscopy

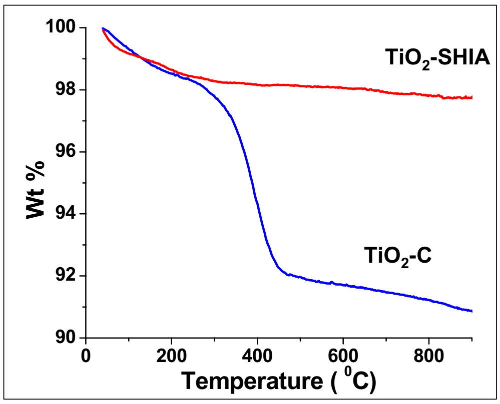


X-ray Diffraction



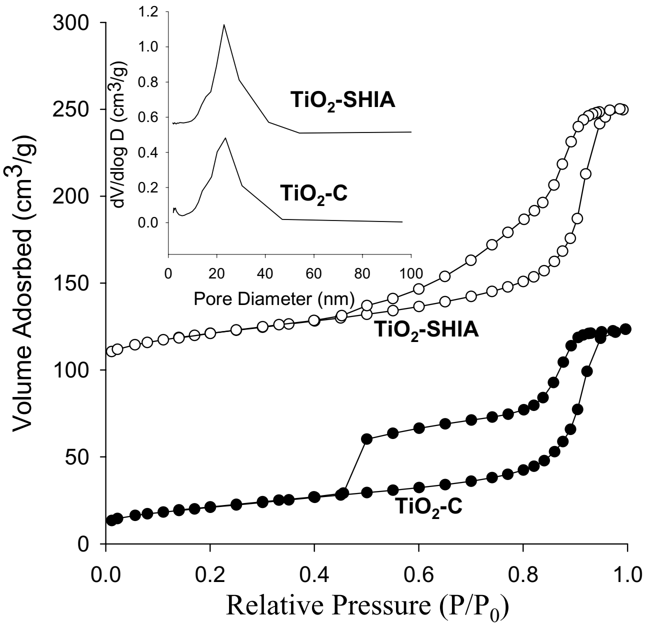
The Mesoporous Nb_2O_5 via conventional way has nearly amorphous walls

Thermogravimetric Analysis

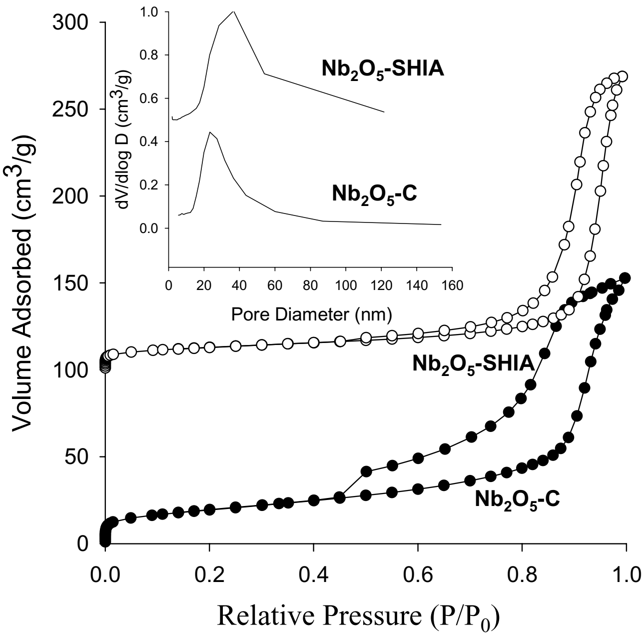


Nitrogen Sorption Experiment

BET surface area of TiO_2 SHIA: 89 m^2/g

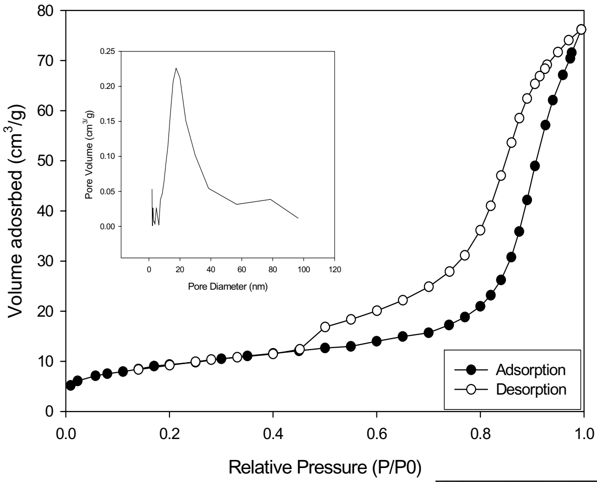


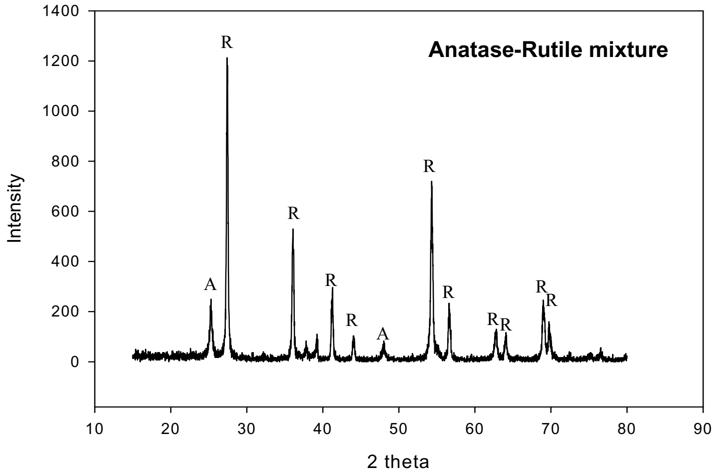
BET surface area of Nb_2O_5 SHIA: 54 m^2/g

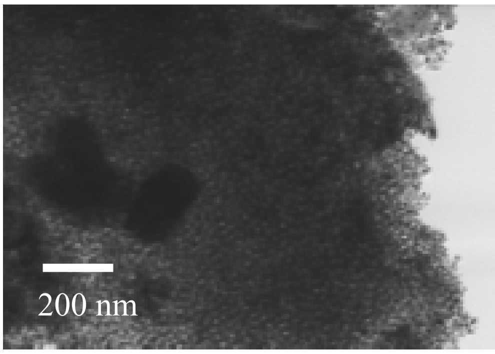


The normally heat-treated sample under air at 700 °C
: BET surface area ~0.2 m^2/g

The mesopores was preserved even after heat-treatment at *1000 °C!!!*

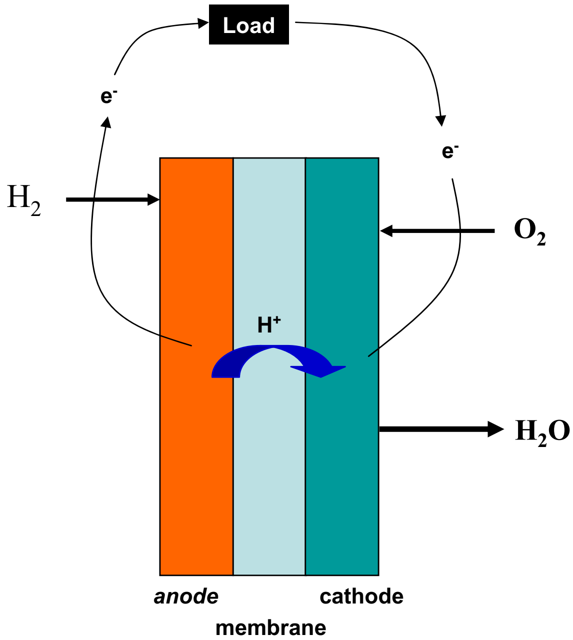






Fuel Cells

Fuel Cell Basics

Anode: $H_2 \longrightarrow 2H^+ + 2e^-$

Cathode: $O_2 + 2e^- + 2H^+ \longrightarrow H_2O$

Direct energy conversion device of fuel to electricity

Here: electrode materials only

Issues with Current Electrode Materials

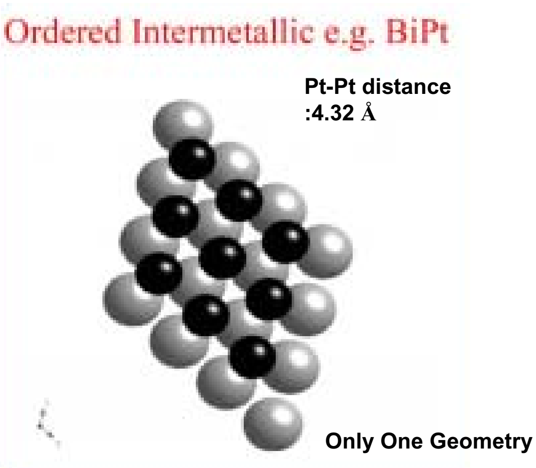
- ◆ Carbon: Corrosion
- ◆ Complicated synthetic method
- ◆ PtRu Alloy: Poisoning & low mass activity

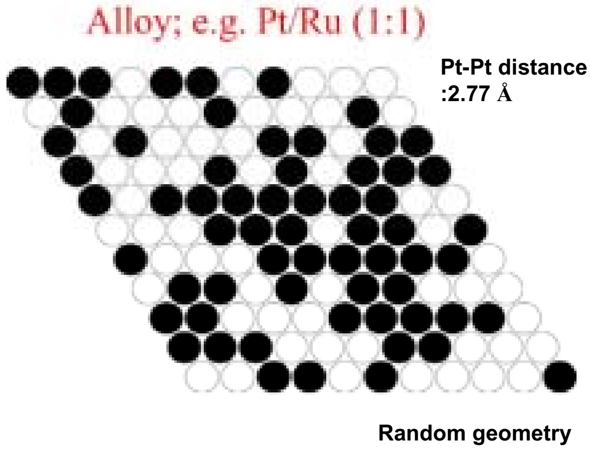
Solution

Intermetallic Nanoparticles on Mesoporous Metal Oxides

cfci cornell fuel cell institute

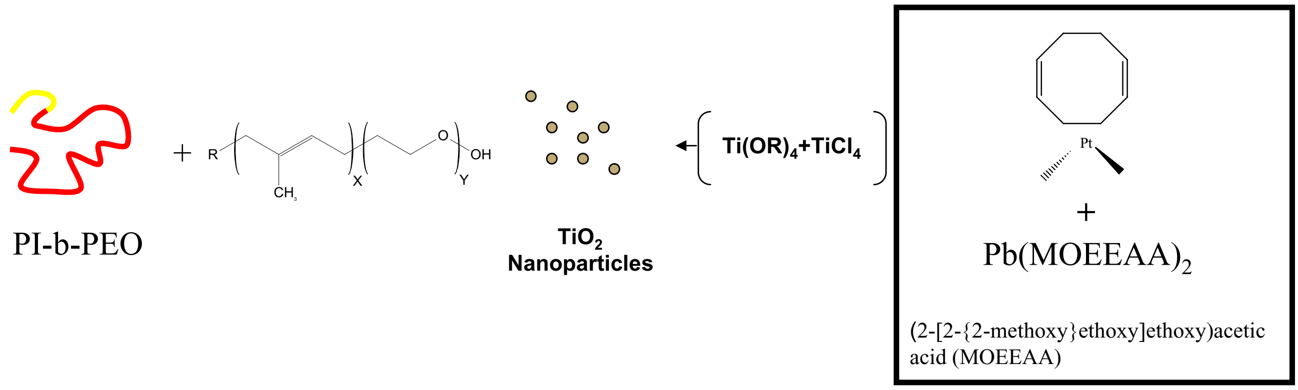
Claim to fame: Intermetallic catalyst



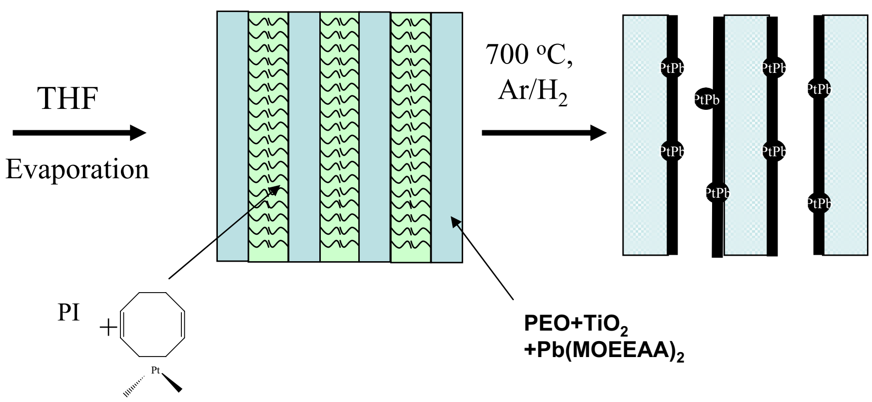


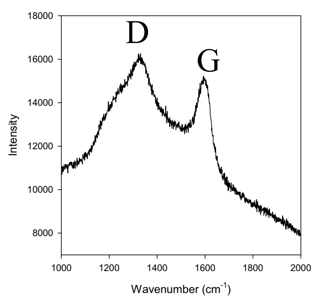
The long Pt-Pt distance in intermetallic compounds precludes the adsorption of CO

Integrating intermetallic catalyst in mesoporous TiO_2



Metal Precursor

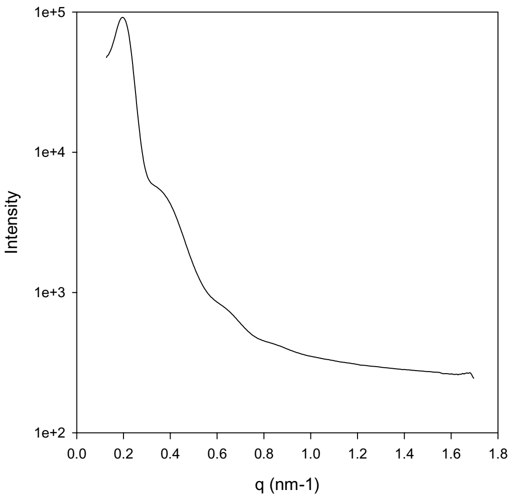


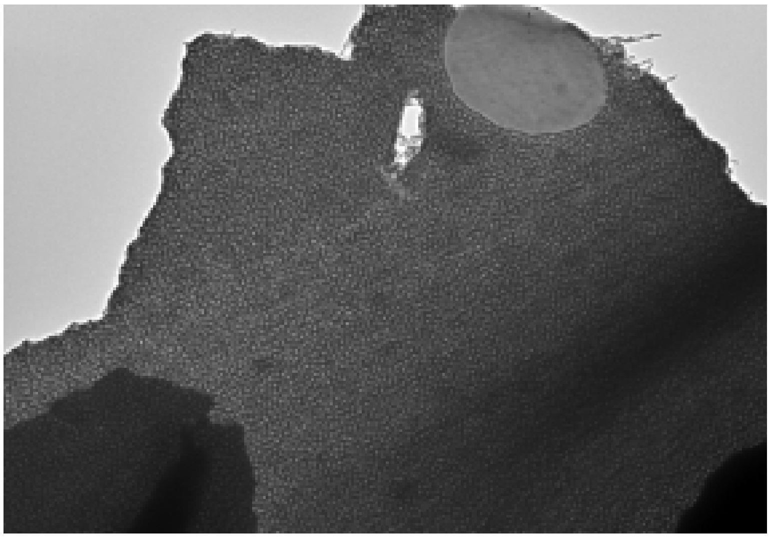


Presence of carbon

J. Lee et al **2007, to be submitted**

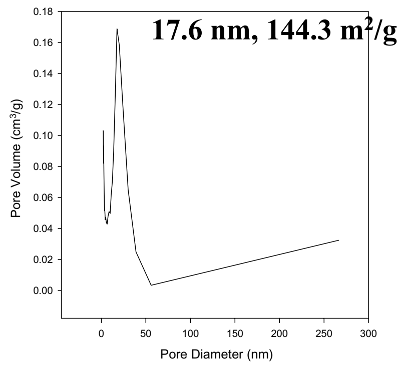
Small-Angle X-ray scattering of As-syn material



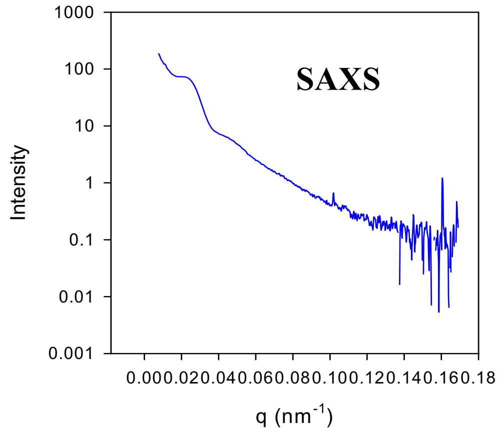


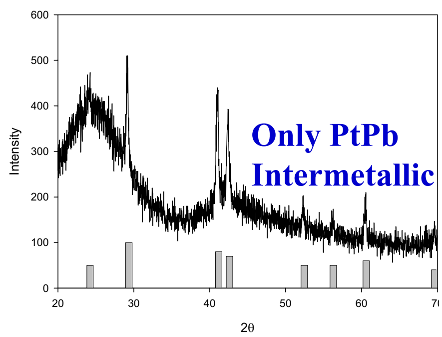
Short-range ordered hexagonal

Nanoparticles dispersed in Uniform Large Mesoporous TiO_2

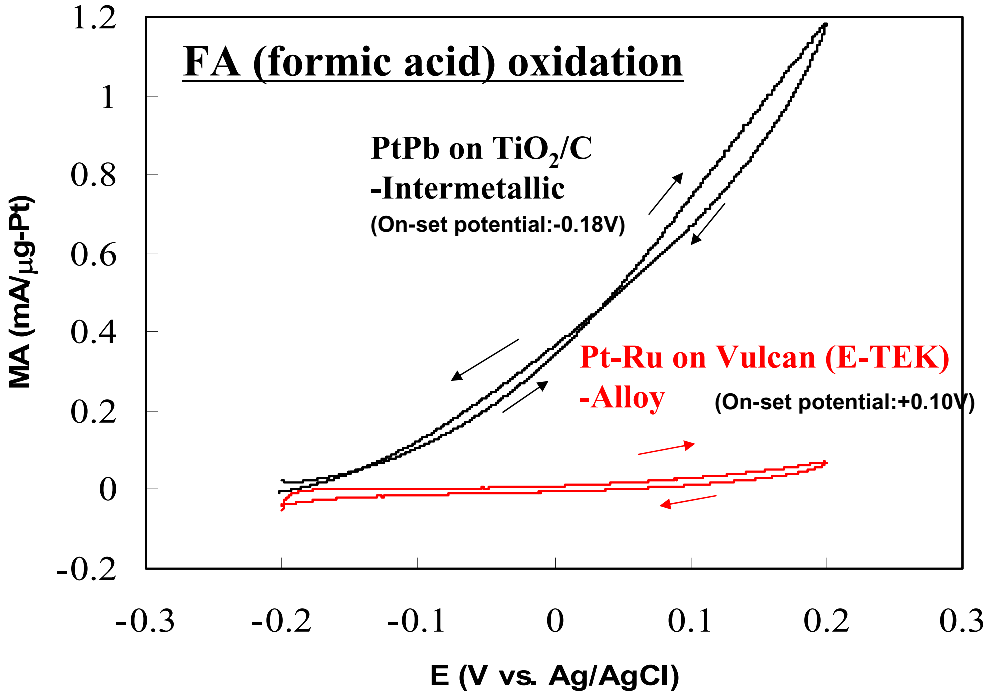


Carbon/silica matrix



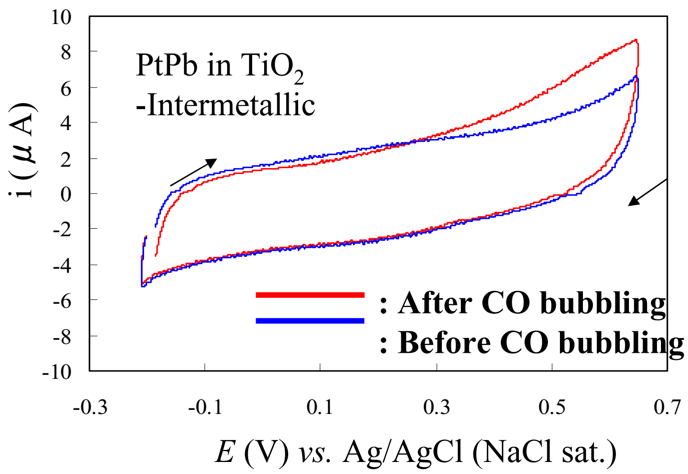


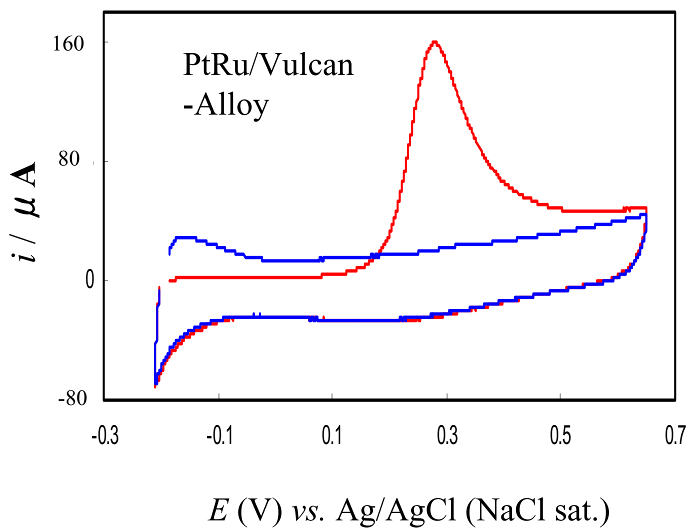
Electrochemical testing of novel materials



A high mass activity
Much lower onset potential

CO stripping oxidation

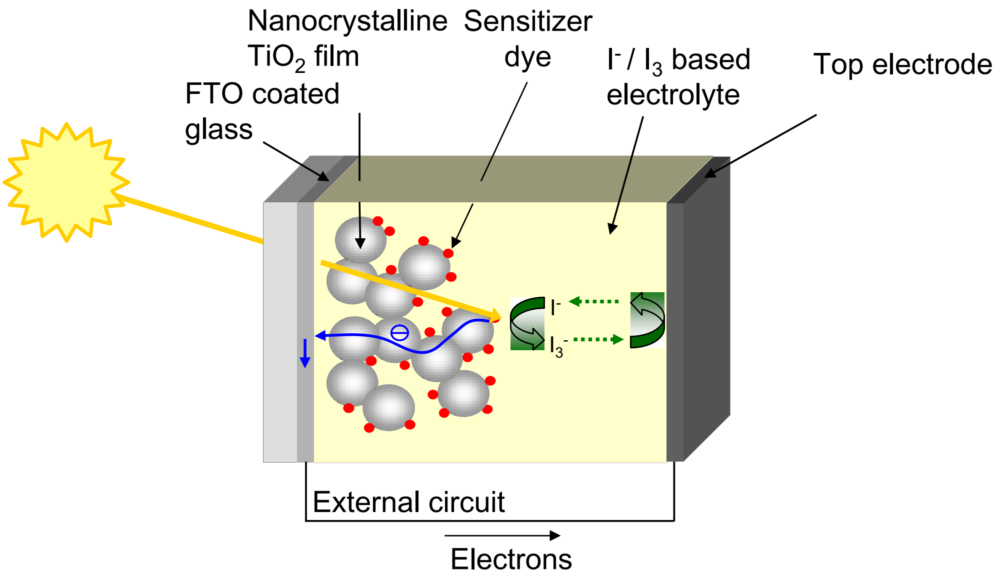




Much less CO poisoning

Photovoltaics

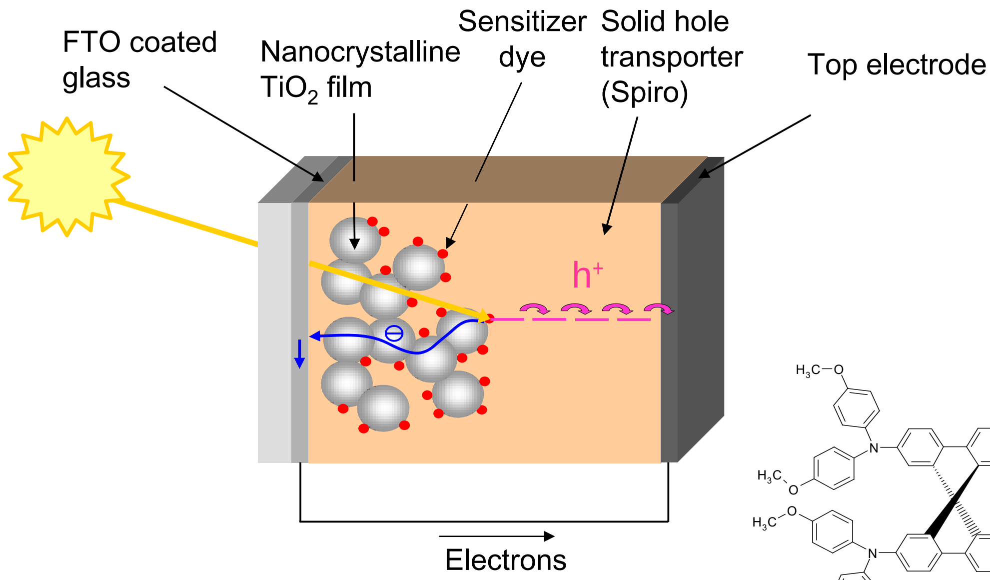
Dye-sensitized solar cells

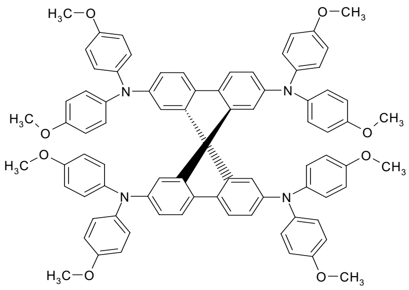


Current performance: η=11%

O'Regan, B. & Grätzel, M. - *Nature 353*, 737-740 (**1991**)

Solid state dye-sensitized solar cell





Spiro-MeOTAD

2,2,7,7-tetrakis-(*N,N*-di-*p*-methnanoparoxyphenylamine)-9,9-*spiro*bifluorene

Current performance: η=4%

Bach, U. et al. – *Nature 395*, 583-585, (**1998**)

Collaboration with Cavendish Laboratory, University of Cambridge, UK

Cornell University USA

Prof. Ulrich Wiesner

Prof. Ulrich Steiner

OE Group-Cambridge

Prof. Sir Richard Friend

CCMR

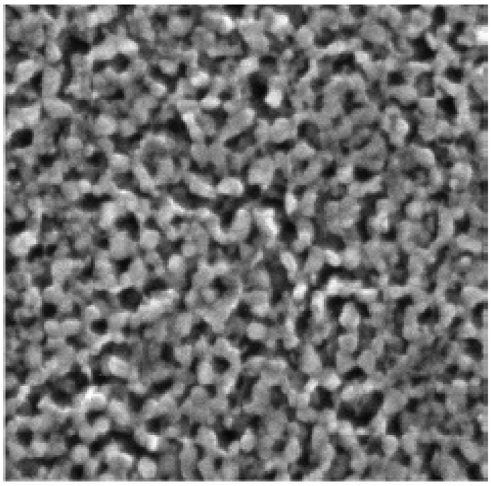
Financial Support

PolyFilm EU-RTN

Nanoscience Centre

Problem with Previous TiO_2

◆ **Heat-treatment at low temperature: amorphous region still present**

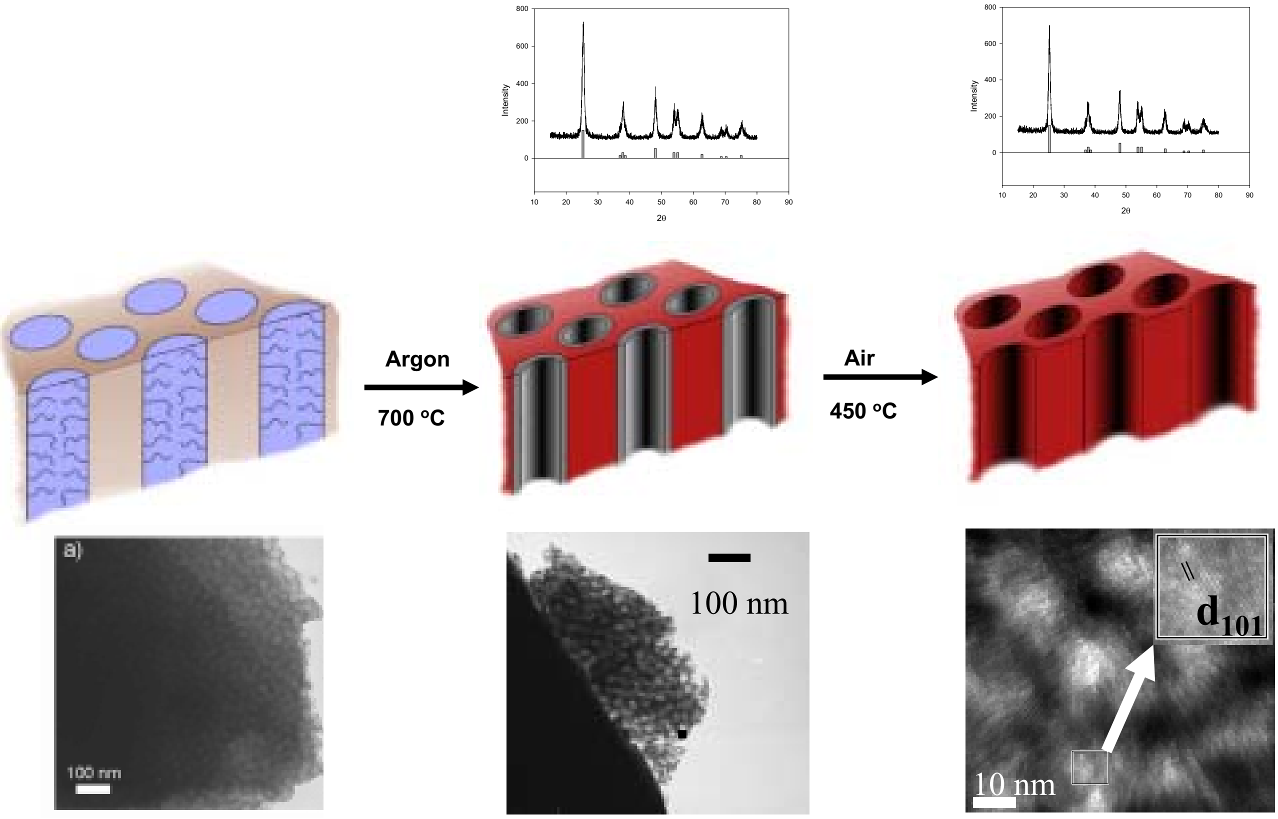


350 °C~450 °C for 30 minutes

Soft-template

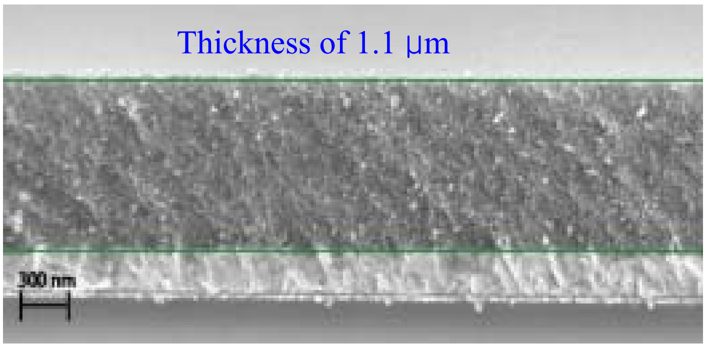
Nano Lett **2005, *5*, 1791**

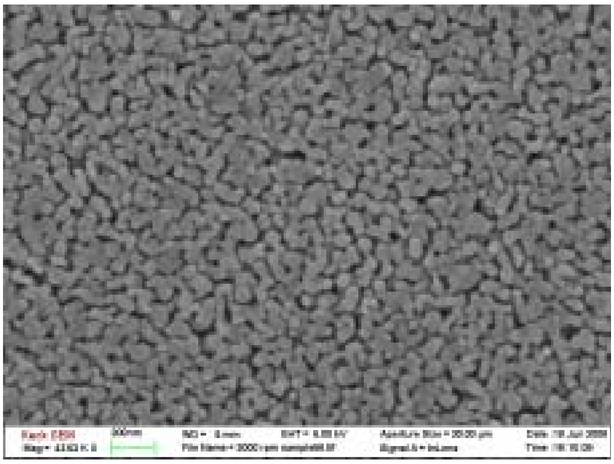
Recap Mesoporous TiO_2



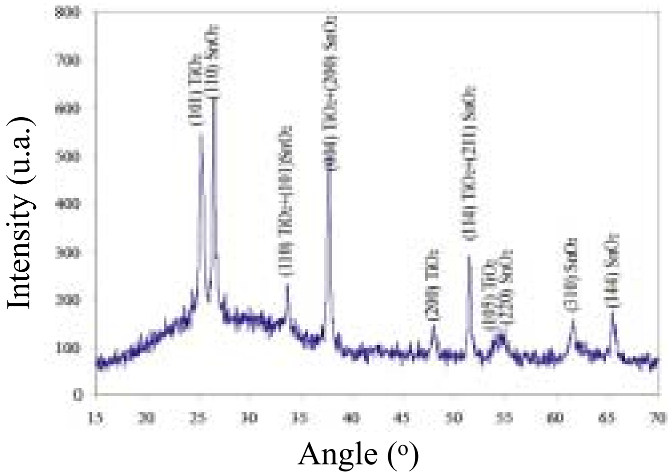
J. Lee et al 2007 *Nature Materials* revised

Cross-section of mesoporous TiO_2



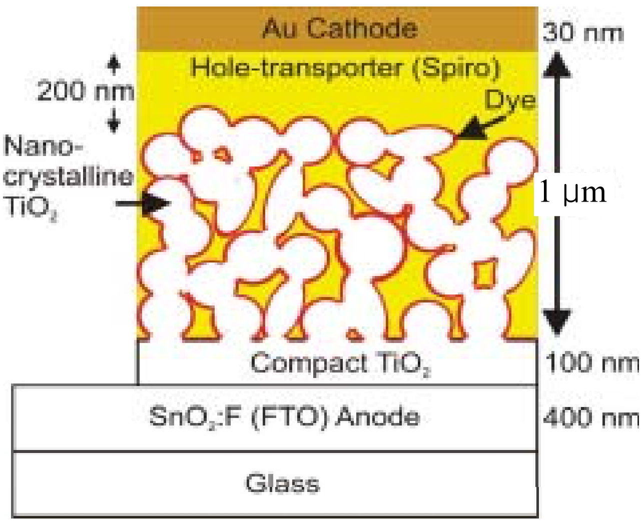


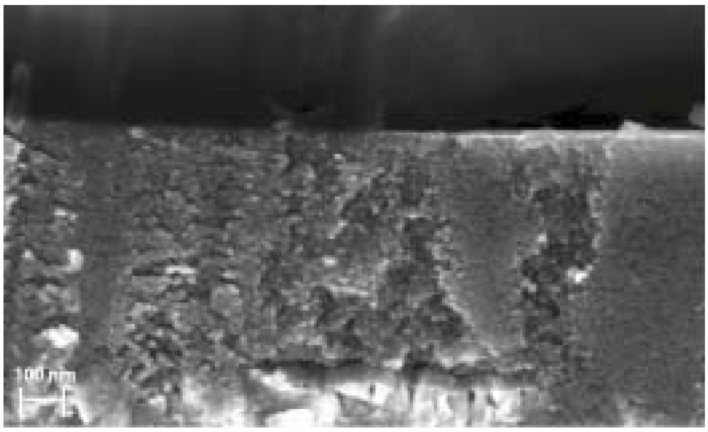
X-ray of mesoporous TiO_2



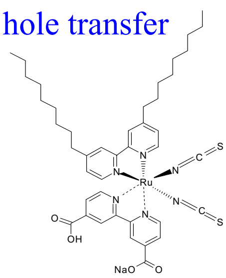
Highly Crystalline Anatase

Dye sensitized solar-cell

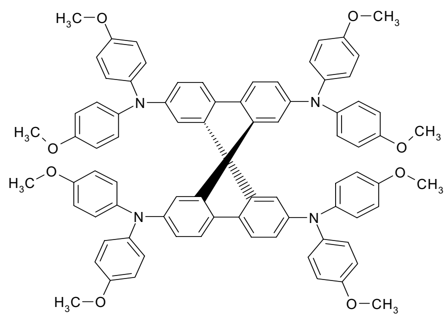




❖ Light absorption in dye, electron transfer to TiO_2, hole transfer to Spiro-MeOTAD.

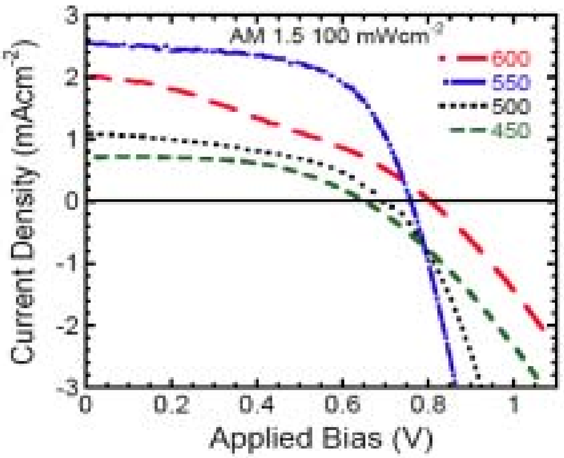


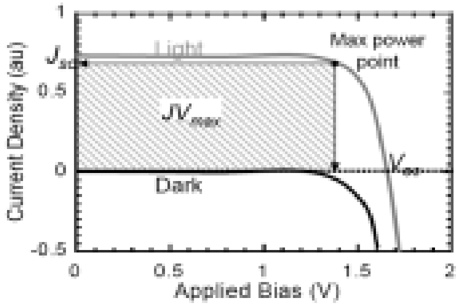
Dye Z907



Spiro-MeOTAD

Device results





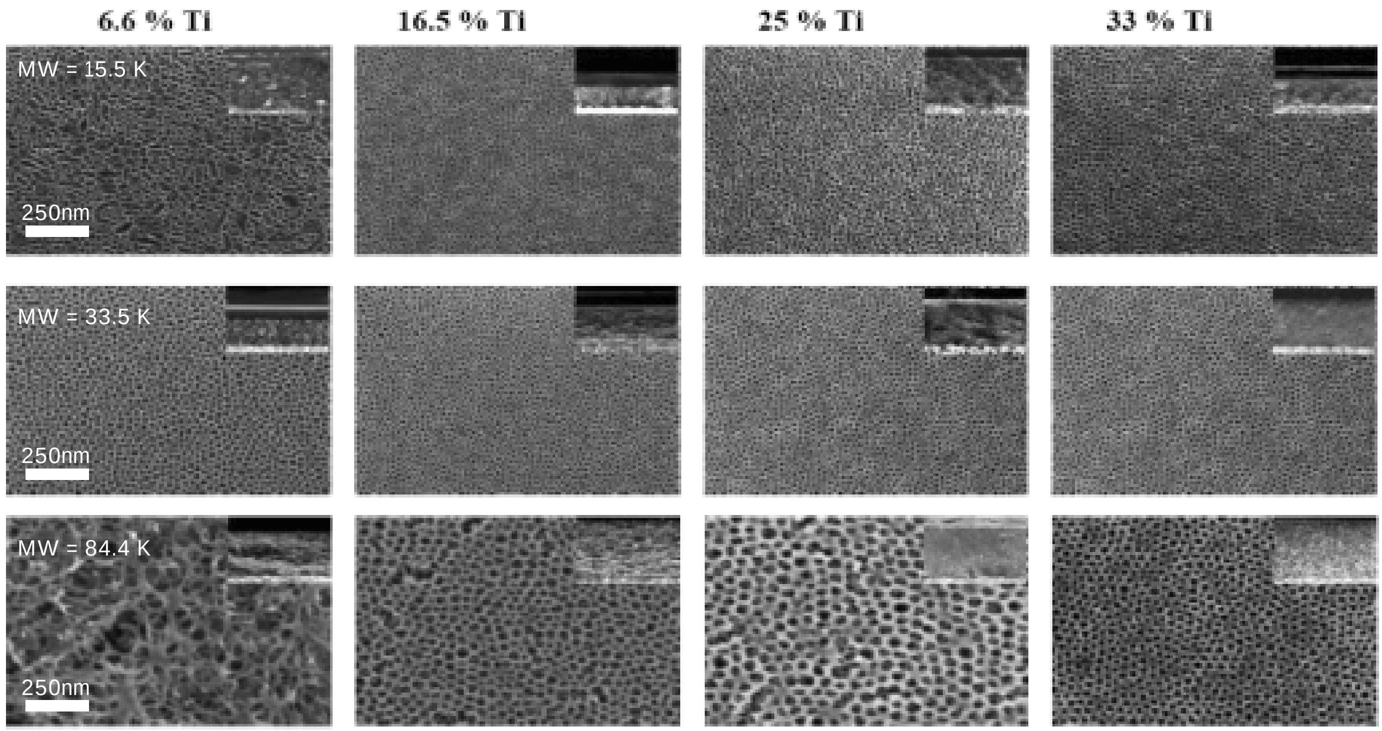
Performance parameters

J-V data as a function of temperature annealing

	600°C	550°C	500°C	450°C
J_{sc} ($mAcm^2$)	2.0	2.54	1.09	0.71
V_{oc} (V)	0.81	0.76	0.70	0.65
η (%)	0.56	1.17	0.35	0.25
FF	0.35	0.61	0.46	0.54

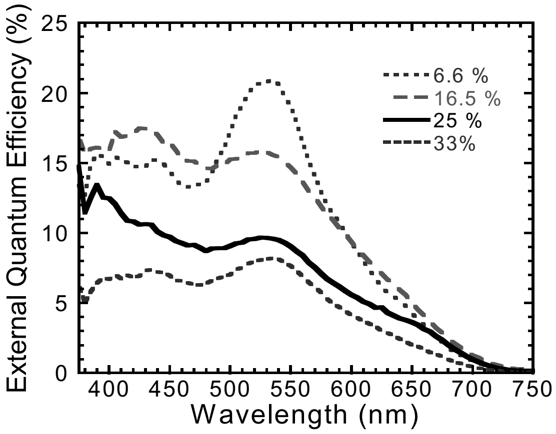
As the temperature increased, the amorphous regions were converted to crystalline materials

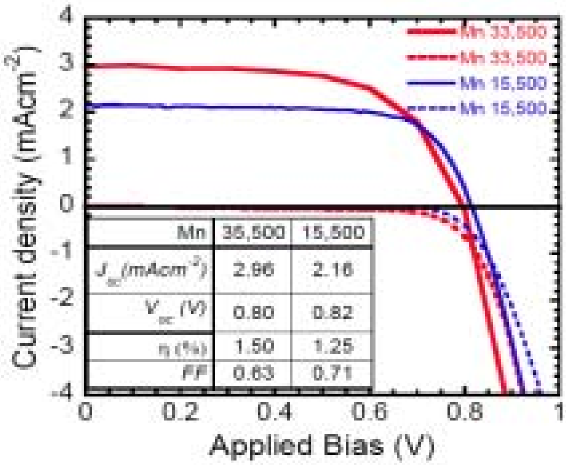
Composition Variations



Results

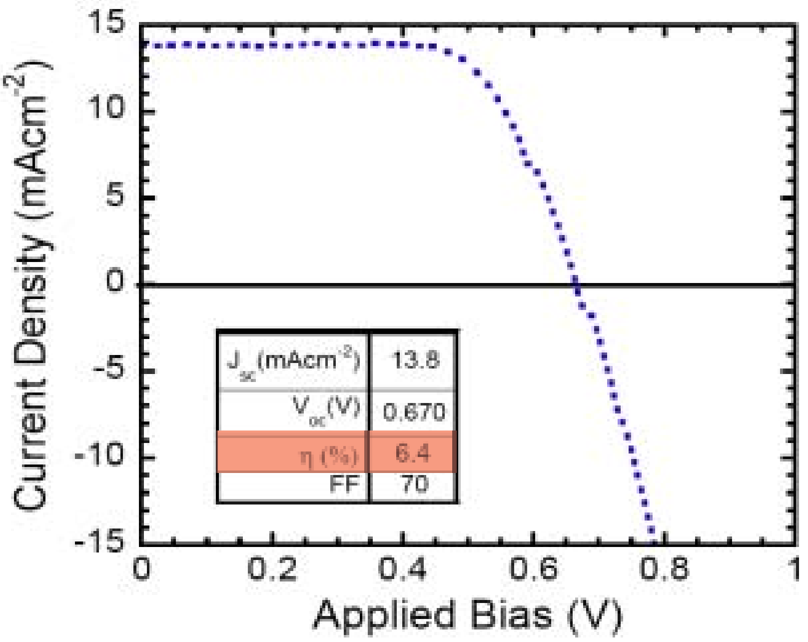
16.5 % Titania, varying molecular weights





Another approach: Patent application being written

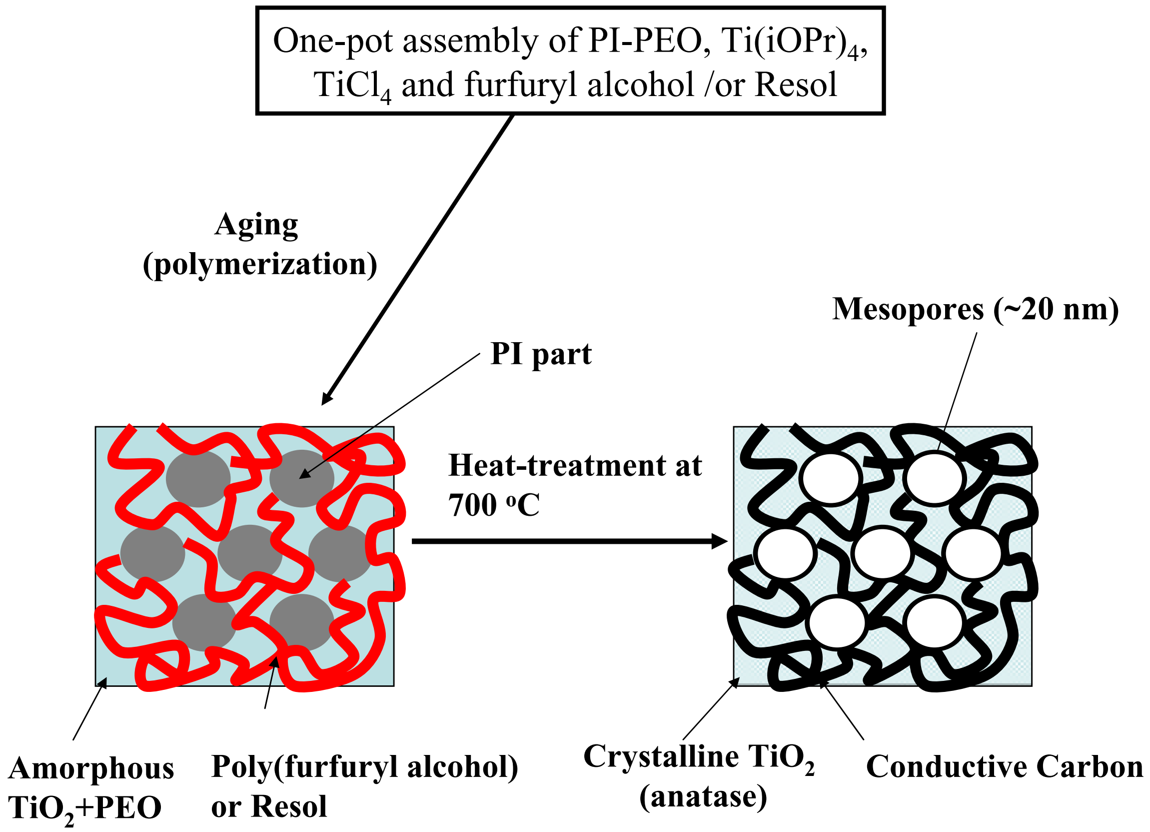
Performance under simulated sun light

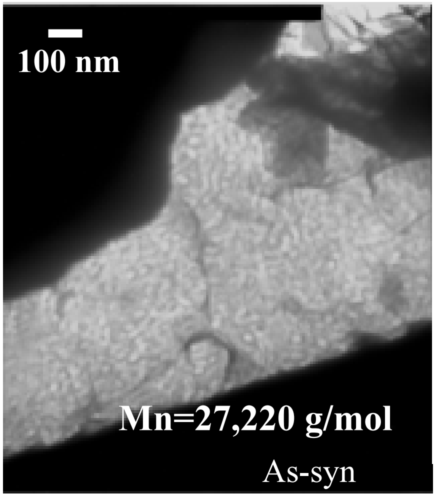


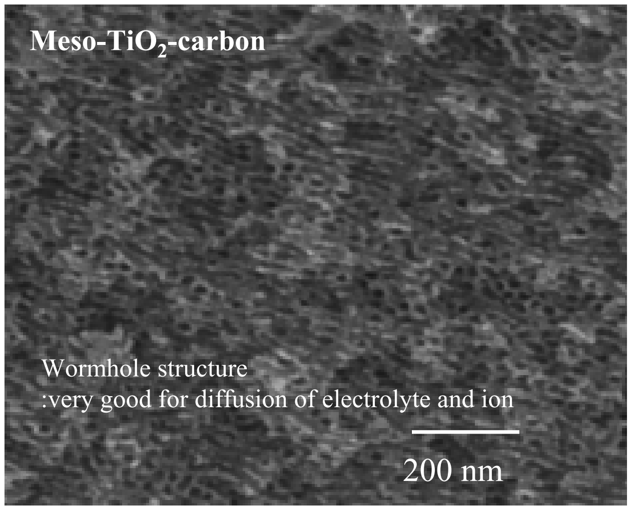
Liquid electrolyte
- 3.5 μm

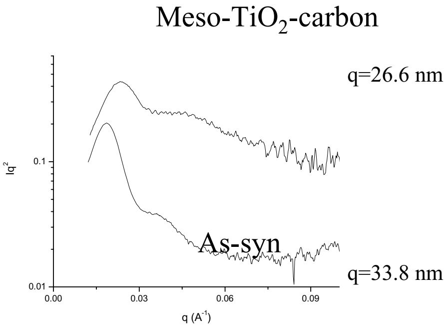
VERY EXCITING !!

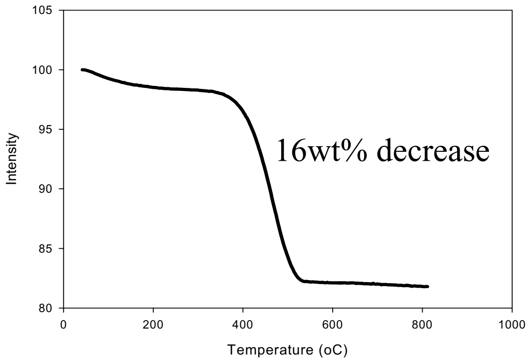
Facile synthesis of well-organized crystalline TiO_2/carbon composites for use as anode in Lithium ion batteries

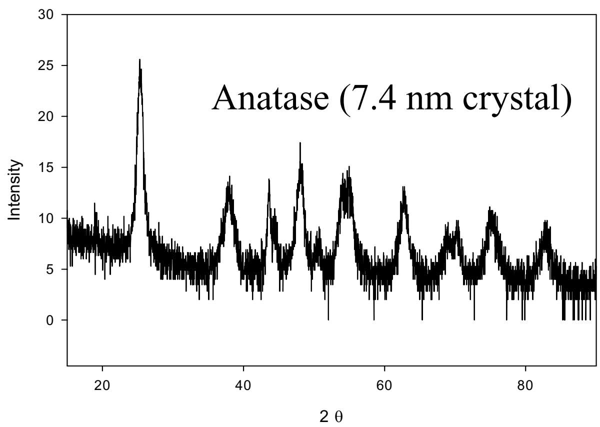


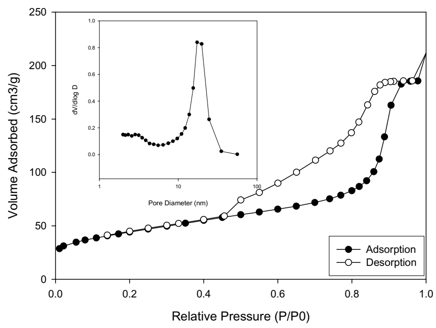






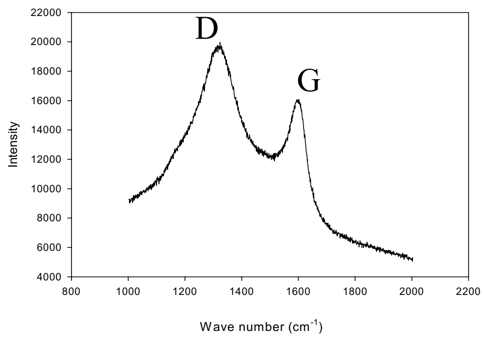


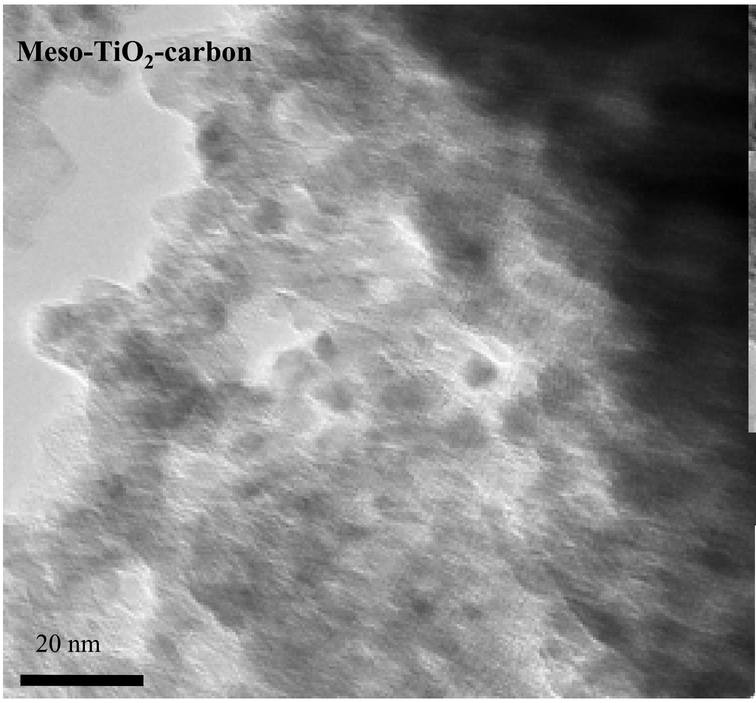


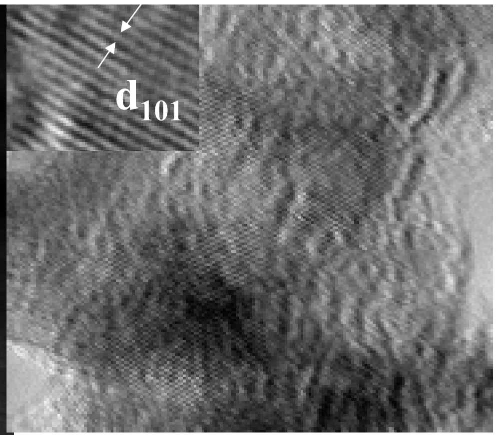


154 m²/g, 0.3 cm³/g

9.4x10⁻³ S/cm



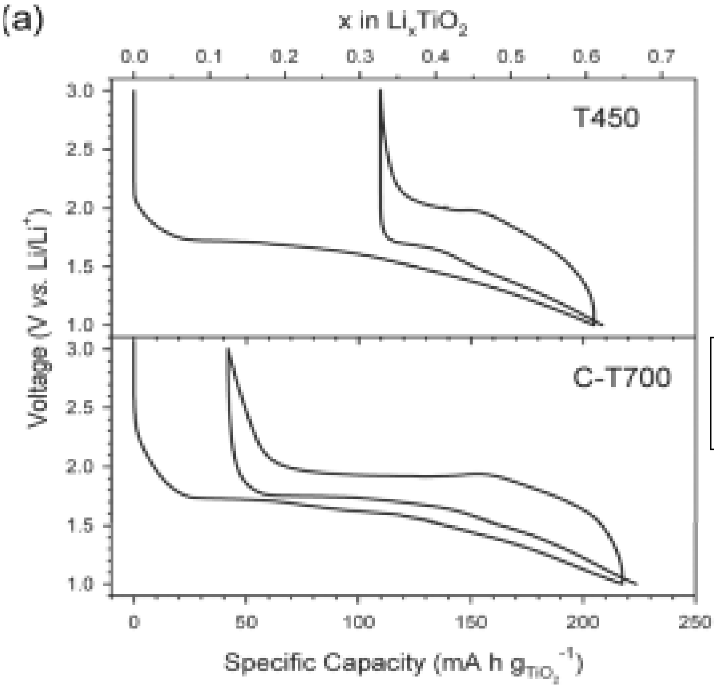




Shows crystalline wall

Wall is composed of TiO_2 nanoparticles

Electrode was made without adding conducting carbon



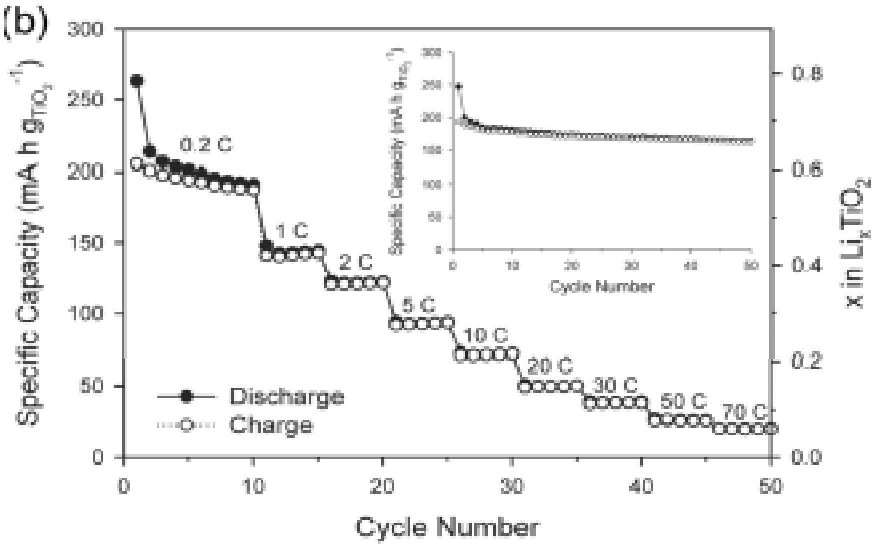
Insertion capacity

0.65 Li/Ti for C-T700 and **0.60** Li/Ti for T450

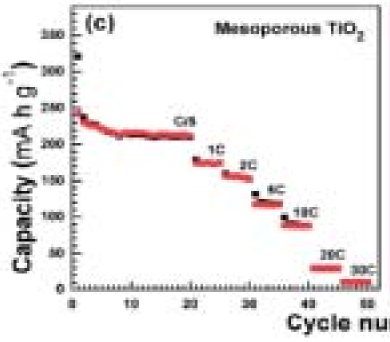
Desertion capacity

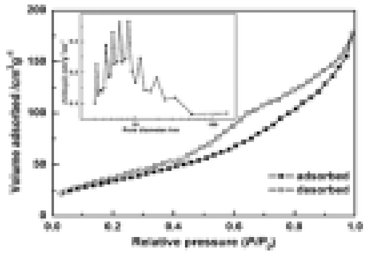
0.55 Li/Ti for C-T700 and **0.30** Li/Ti for T450

Added small amount of conducting agent (to obtain best result)



From MPI,
Chem.Commun, 2006, 2783

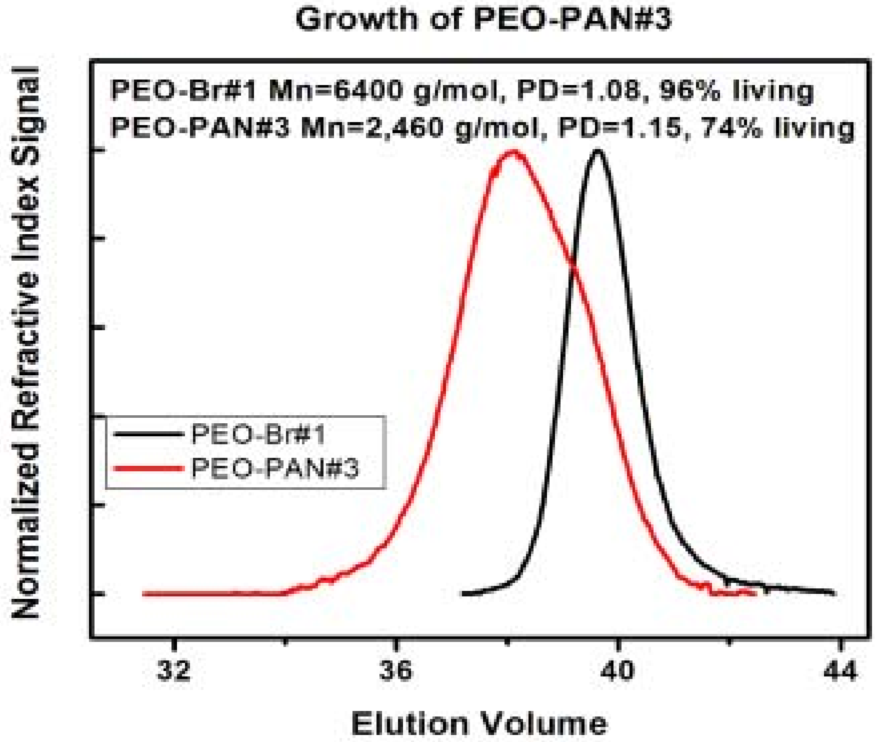




One of best electrode materials
:Excellent Cyclability and High Rate Capability

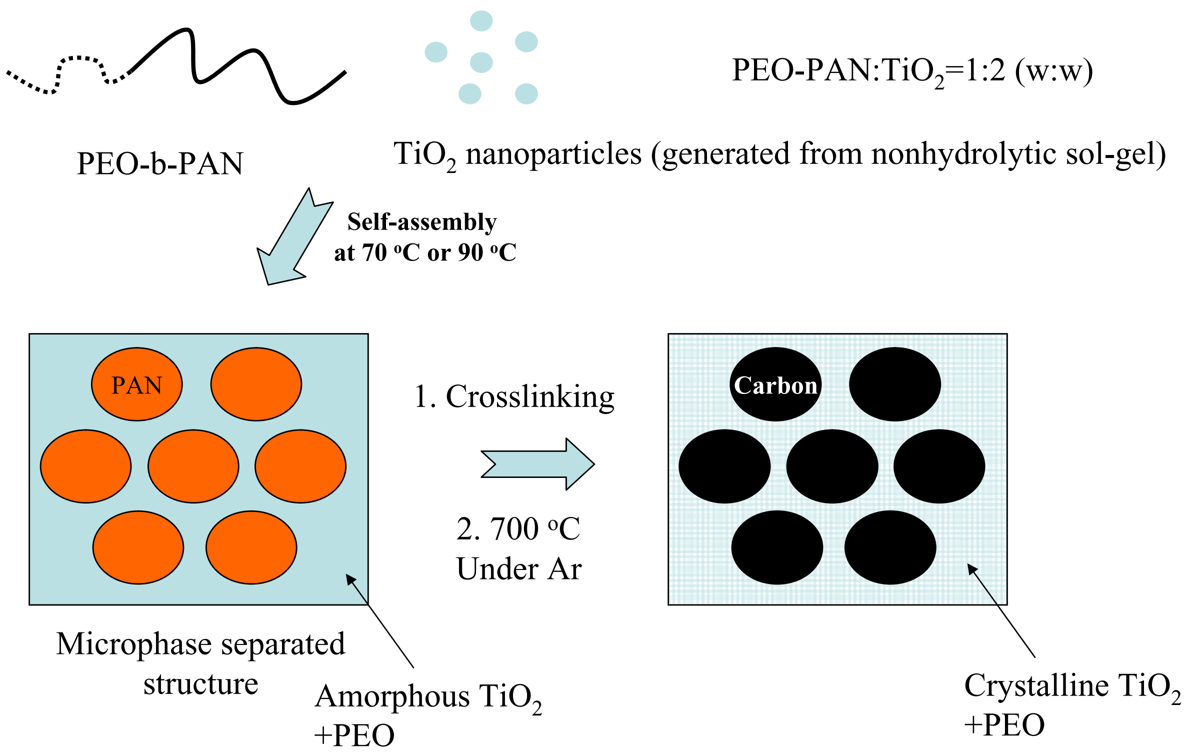
0.75 Li/Ti for insertion and 0.60 Li/Ti for de-insertion

Nano-structured graphitic carbon/titanium dioxide composite by microphase separation of PEO-PAN and titanium dioxide sol toward functional electrode material



PEO: Anionic polymerization **PAN: ATRP**

Schematic representation



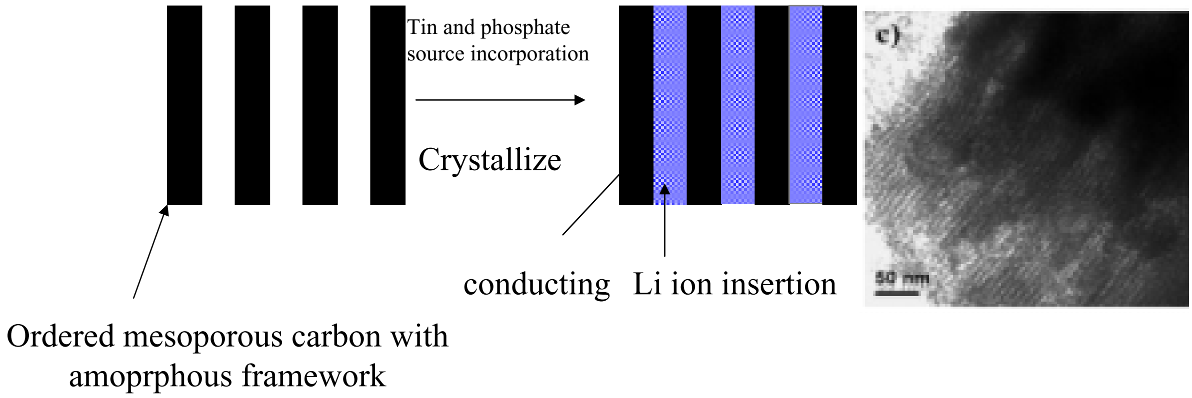
Background

- Transition metal oxide/carbon composite materials have been synthesized to use as electrode materials

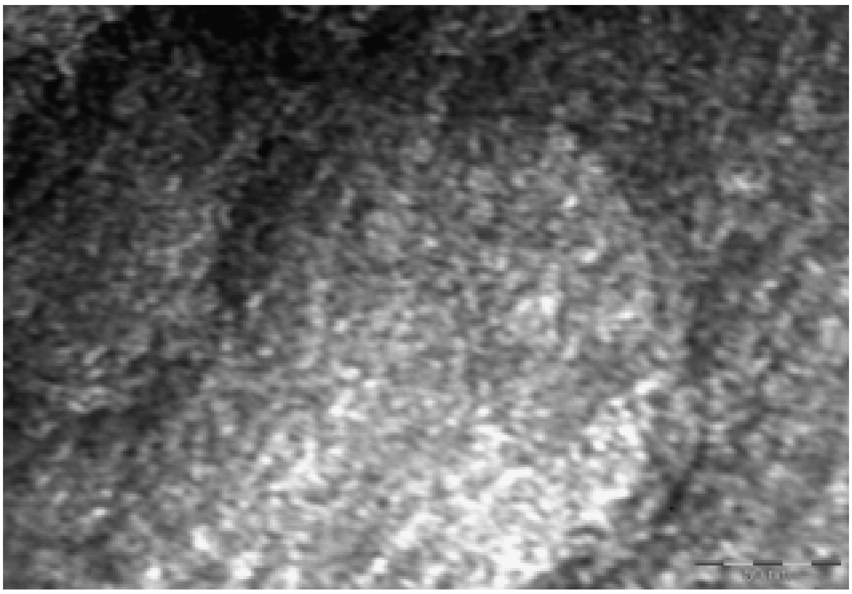
- Typical method to make carbon/transition metal oxide composite
⇒Loading of transition metal oxide in carbon materials

- To make homogeneously mixed nanocomposite of carbon and metal oxide, ordered mesoporous carbon was used

Zhao et al, Adv. Mater. 2004, 16, 1432

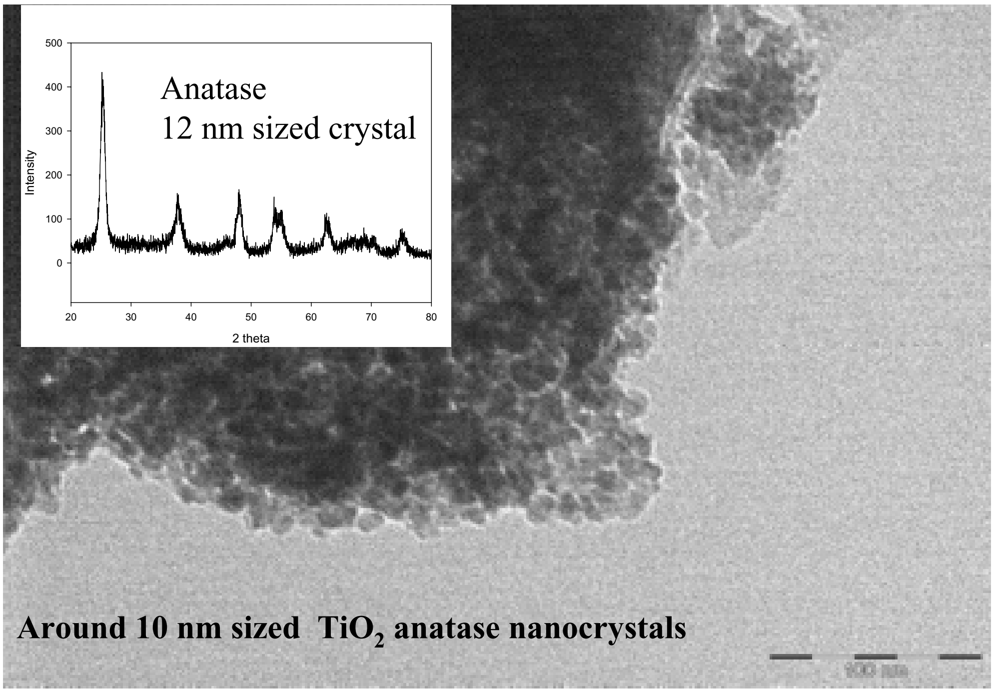


TEM of microphase separated As-syn composite

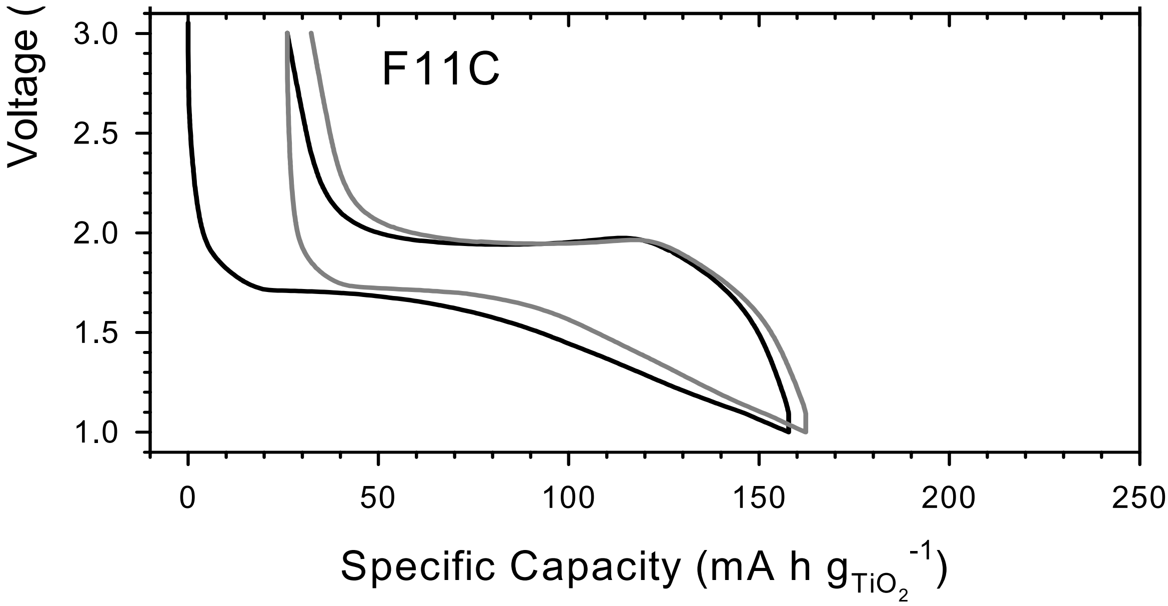


The dark part is titanium oxide part

TEM image of carbon/crystalline TiO_2 samples

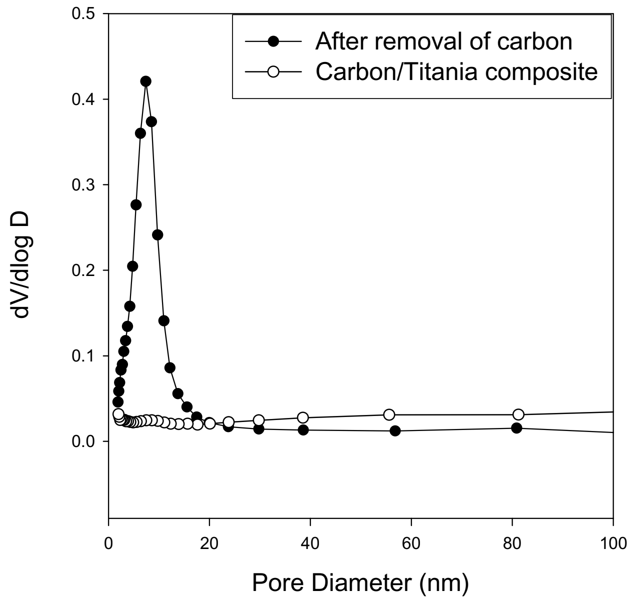


Carbon content ~10 wt% from TGA under air



Carbon/Titania composite, but, mesopores are needed to improve performance

After removal of carbon



Pore size distribution

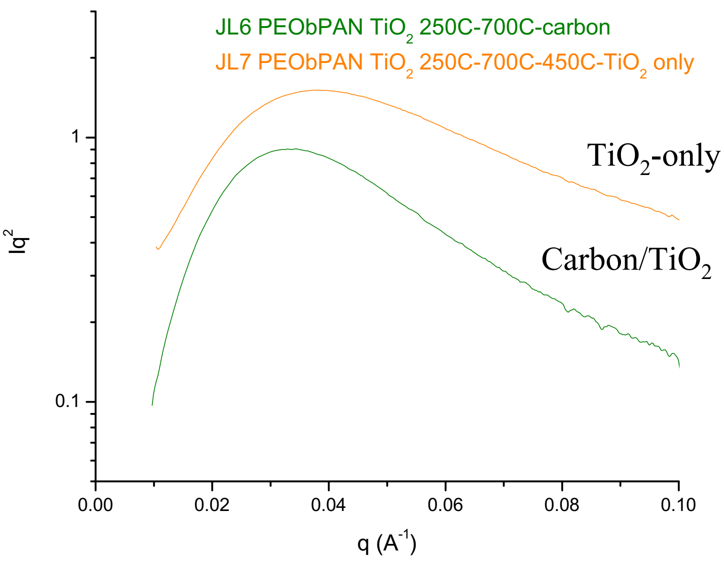
7.4 nm sized pores are generated by removal of carbon

Evidence of microphase seperation

	BET surface area (m^2/g)
Carbon/TiO2	52
TiO2	115

PEO-b-PAN
:a structure-directing agent for *fully crystalline* mesoporous transition metal oxides

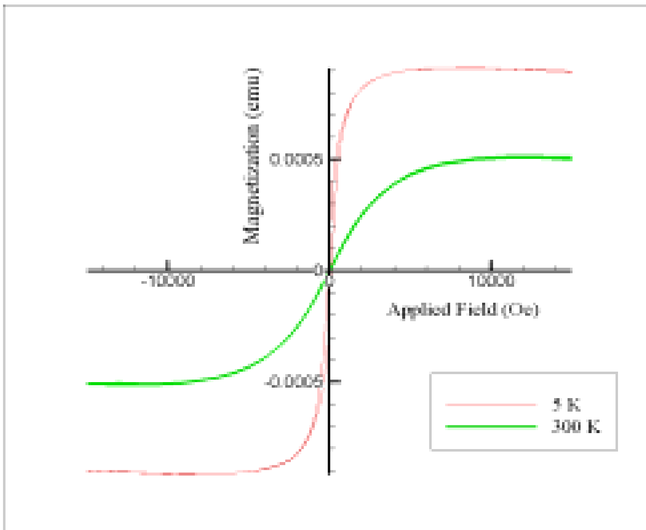
SAXS

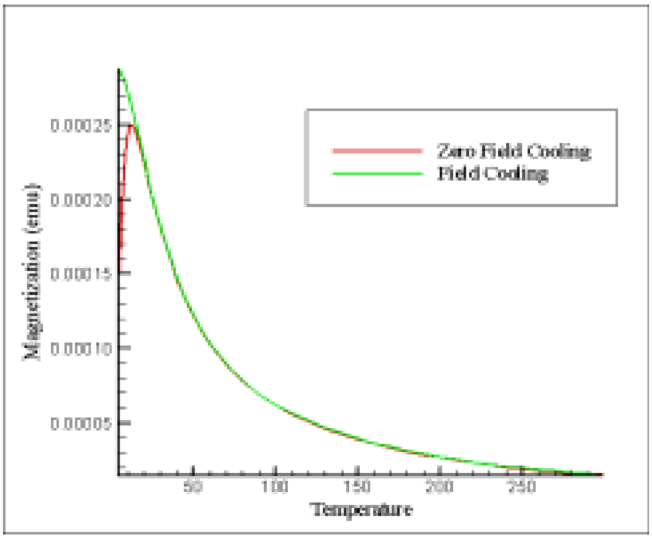


Broad Pattern

Magnetic Properties

- SQUID (Superconducting quantum interference device) data





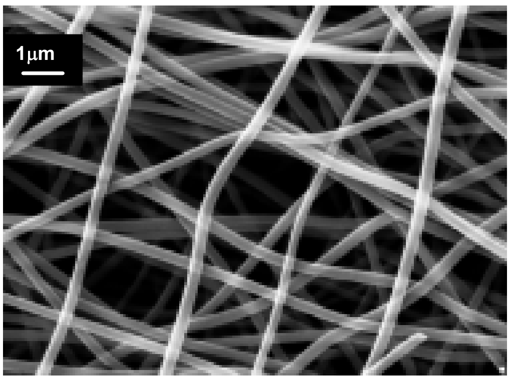
10 wt% Magnetite NP (4nm)/IS53-143, annealed at 180°C for 48 hrs

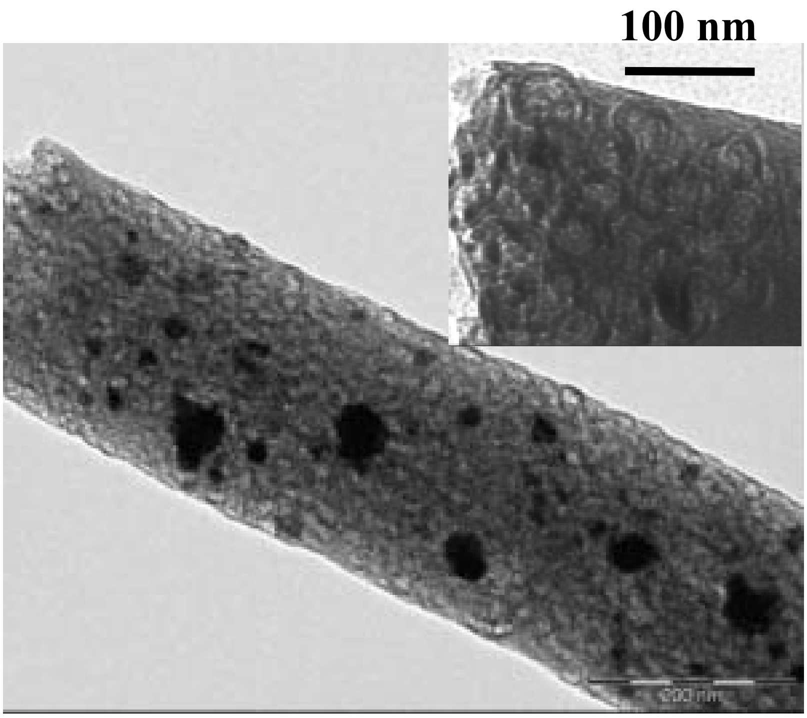
Blocking temperature=13 K

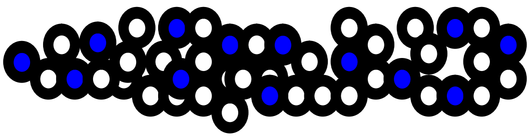
$$\tau_m = \tau_o \exp(\frac{KV}{k_B T_B})$$

Magnetite/PSPI Nanofibers exhibit superparamagnetic properties.

Hierarchical carbon nanofiber

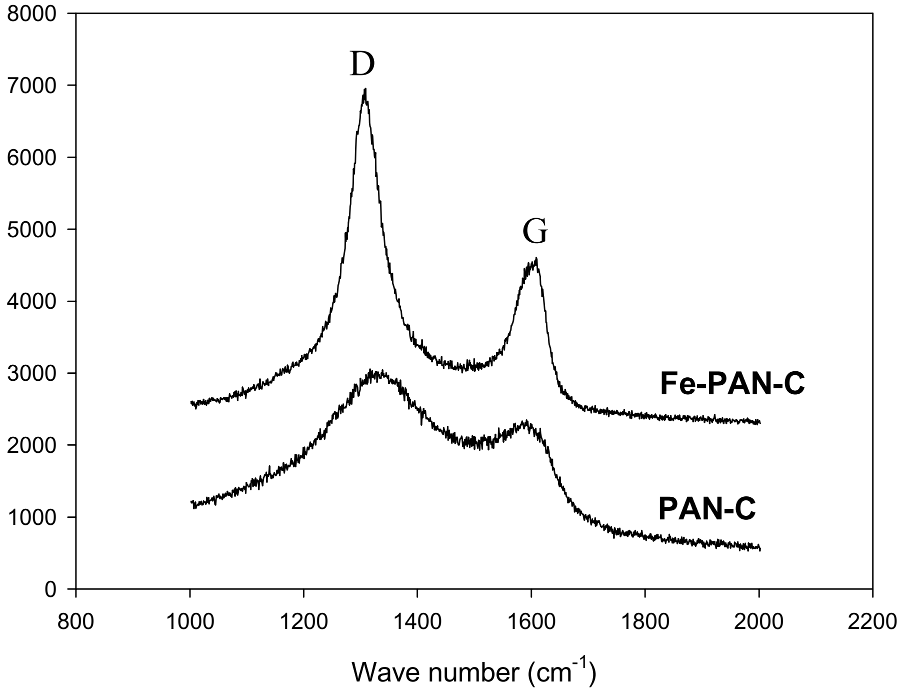






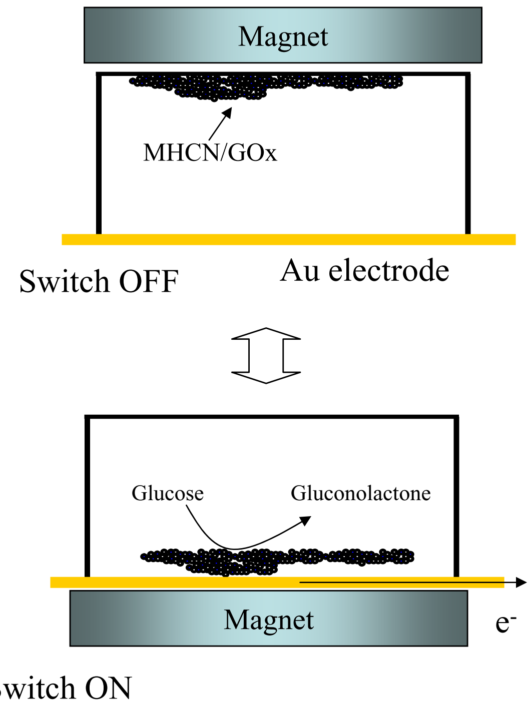
Hollow graphite is known to be good electrode material

Raman Spectroscopy



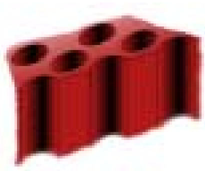
More Graphitic

Magnetically Separable Electrode Materials

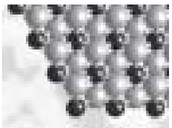


Summary

- **Highly crystalline mesoporous TiO_2 materials were successfully used as anode materials for high efficiency solid-state photovoltaics**



- **Intermetallic nanoparticles on mesoporous metal oxide were highly active fuel cell catalysts**



- **High efficiency solar cell electrode was fabircated using soft-hard integrated self-assembly**