Fuel generation and CO_2 recycling through solar photo-catalysis using nanostructured metal oxides

Workshop on Materials Challenges in Devices for Fuel Solar Production and Employment, Trieste, Italy, May 19-23, 2014

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News Headlines in May 1st Week, 2014

CBS NEWS: **First time in 800,000 years: April's CO2 levels above 400 ppm**

USA Today: **Carbon dioxide in atmosphere at record level**

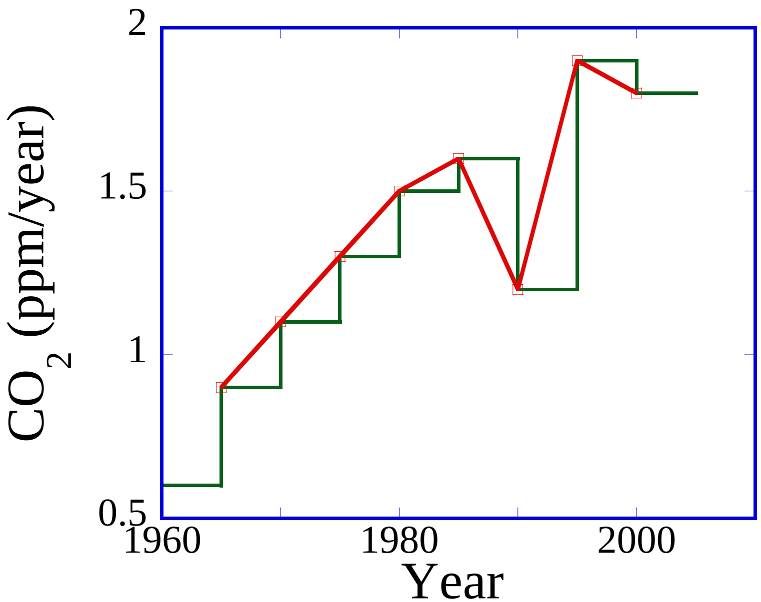
BBC: **Carbon dioxide passes symbolic mark**

National Geographic: **Climate Milestone: Earth's CO2 Level Passes 400 ppm**

So what?

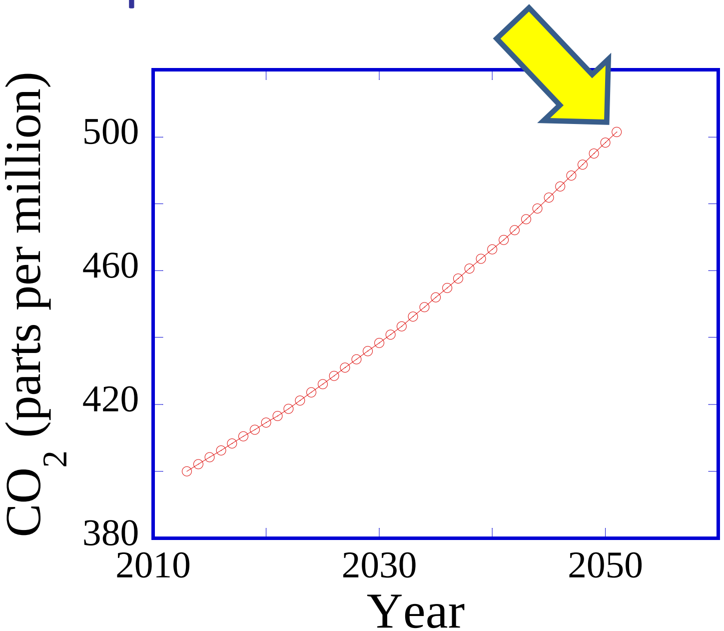
CO_2 Levels: Past, Present, Future

- CO_2 concentration was at the present level about 2.7 million years ago in the mid-pliocene period (sediment core data)
- Level never exceeded 280 pars per million (ppm) in the human history till eighteenth century.



http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ ar4_wg1_full_report.pdf

Temperature increase ~ 1.4 °C



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Correlation Between CO_2 Level and Temp. Rise

- CO_2 accounts for more than 60% of radiative forcing (~1.9 W/m^2 in 2012)
- For 100 years till 1997, global average temperature increased by about 0.74 °C
- A temperature rise of 2°C is expected when the concentration reaches 550 ppm
- > ~550 ppm when sustained are considered high enough to bring catastrophic modifications to the global environment

Where is this CO_2 coming from?

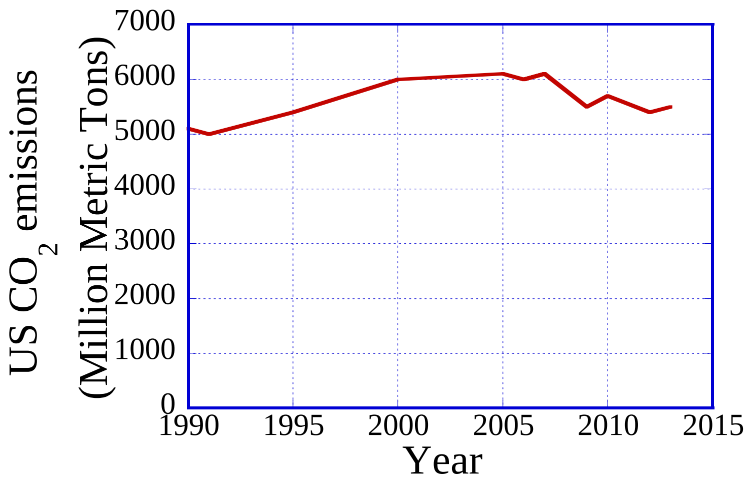
- The CO_2 in the atmosphere is primarily anthropogenic

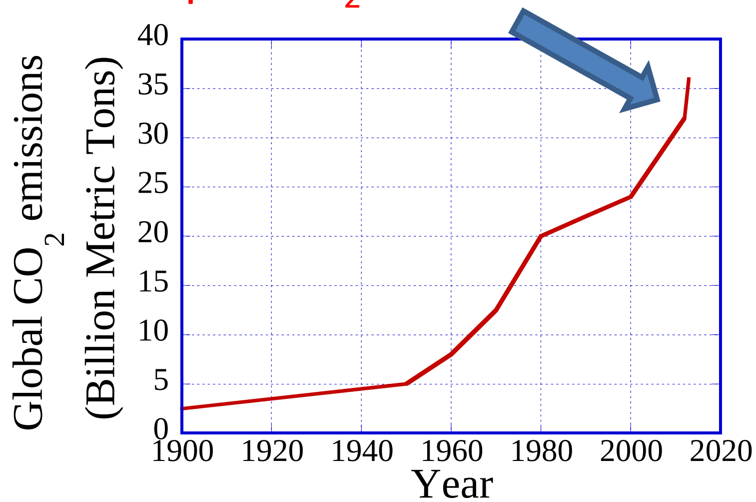
1 liter   2.3 kg

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

- Burning isooctane would produce CO_2 almost three times its mass

Per capita CO_2 emission ~4.7 metric tons





http://www.epa.gov/

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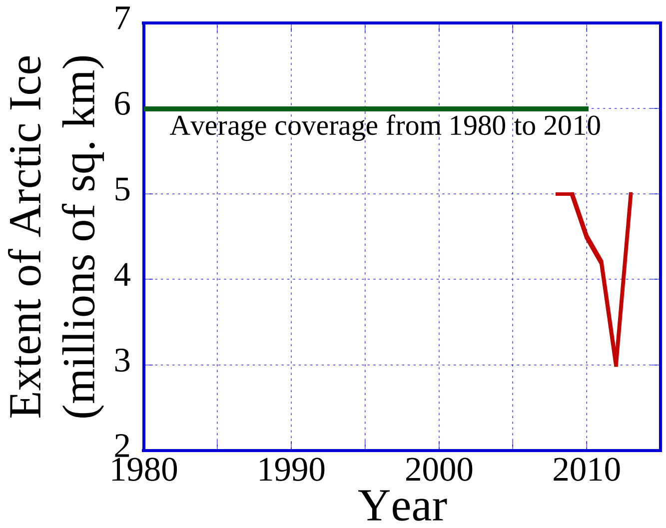
What is CO_2 doing to the environment?

- About 55% of CO_2 is absorbed by land and ocean
- CO_2 uptake by ocean alone is presently ~25%
- CO_2 dissolution is increasing the acidity of ocean water
- pH reduction will have adverse effects on marine ecosystem and environment

  e.g. calcium carbonate dissolution



http://nsidc.org/arcticseaicenews/2013

The Other Side of the Coin

- Population is increasing
- Energy need is increasing
- Limited fossil fuel inventory

A paradigm shift is required

Options for sustainability:

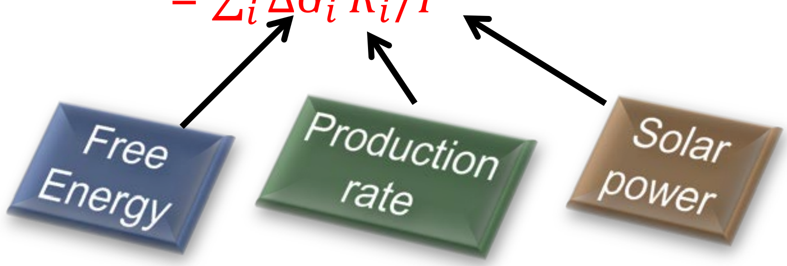
1. Carbon free energy
2. CO_2 recycling

Solar Conversion of CO_2 to Hydrocarbon Fuels

- Unabated production and use of hydrocarbon (non-fossil) fuels without relying on the availability of fossil fuels
- Recycling of CO_2 that provides an everlasting solution for atmospheric CO_2 accumulation due to hydrocarbon fuel burning and related environmental damage

*Efficiency = Energy output from fuels/ Solar energy input

$$= \sum_i \Delta G_i \, R_i / P$$



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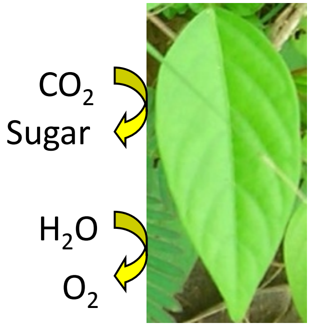
Ways for Solar CO_2 Conversion: Biofuels

- Indirect conversion of solar energy to chemical energy
- Plants use solar energy to convert carbon dioxide into carbon compounds
- Using biochemical processes the biomass is converted into fuels



Photosynthesis

Biofuels

Biogas

- anaerobic decomposition of organic matter
- product consists of 50 – 80% methane and rest CO_2

Bioethanol

- conventionally produced from sugary biomass
- sugarcane molasses or enzymatically hydrolyzed starch are subjected to fermentation with yeast

$$C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_6O$$

- Lignocellulosic approach is promising

Biodiesel

- Crude vegetable oil or edible crop oil is subjected to a transesterification or esterification process

Limitations: The overall efficiency is < 1% and it could cause food vs fuel problem and affect biodiversity

Ways for Solar CO_2 Conversion: Thermochemical

Syngas produced from CO_2 and H_2O on a catalyst surface heated to very high temperatures using concentrated sunlight, is converted into hydrocarbon fuels using standard processes such as Fischer Tropsch

- Requires ~ 1500 °C
- Indirect conversion
- Efficiency of syngas production can be 18 – 20

Ways for Solar CO_2 Conversion: Tech. Combination

Example: Audi's plant in Germany uses Sabatier process to combine hydrogen from solar/wind powered electrolyzers and CO_2 from a nearby biogas plant to generate 'e-gas'

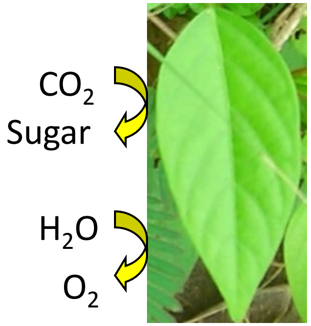
- Involvement of multiple technologies limits the overall efficiency maximum to about 8%

Ways for Solar CO_2 Conversion: Photocatalytic

Direct conversion of CO_2 and H_2O to hydrocarbons possible through solar photocatalytic process

- Hydrocarbons are produced from CO_2 and H_2O directly on a semiconductor surface by the charge carriers generated in the material by sunlight
- The process takes place at or near room temperature
- The efficiency, in principle, can be as high as ~17%
- Simple and inexpensive technology

$$CO_2 + 2H_2O \Leftrightarrow CH_4 + 2O_2$$

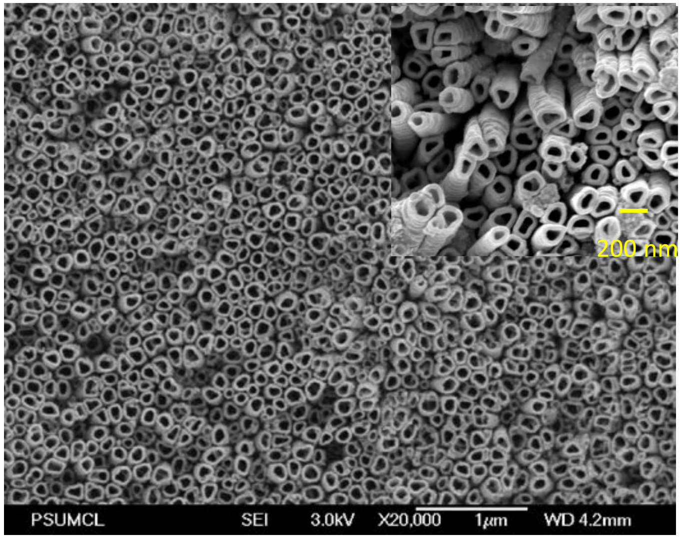


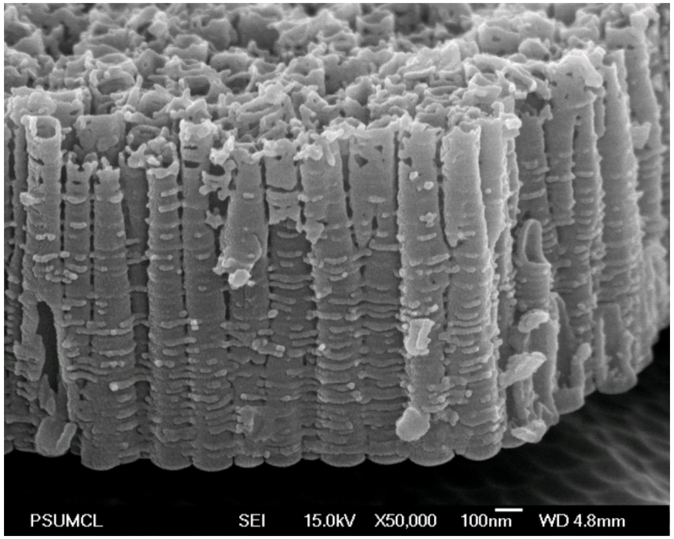
Photosynthesis

Material Requirements

- Stable
- Absorb visible light from solar spectrum
- Band gap > 1.33 eV
- Appropriate positioning of conduction and valence bands

Vertically Oriented Titania Nanotube Arrays

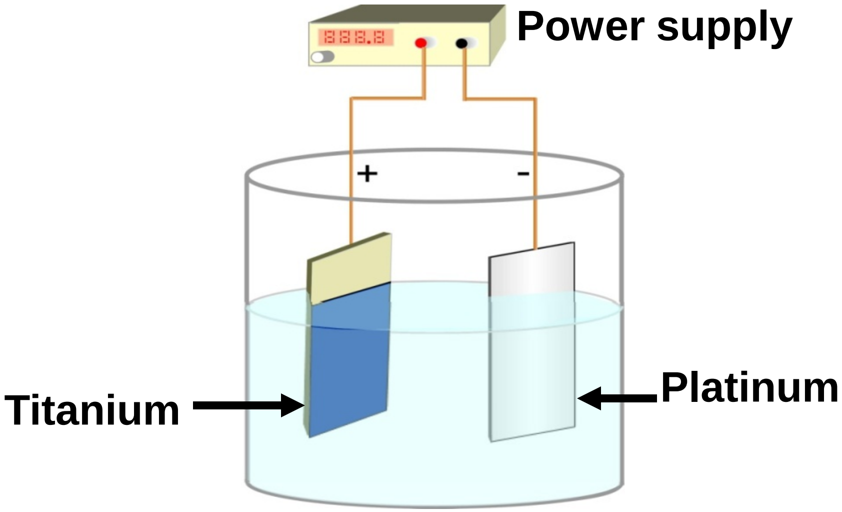


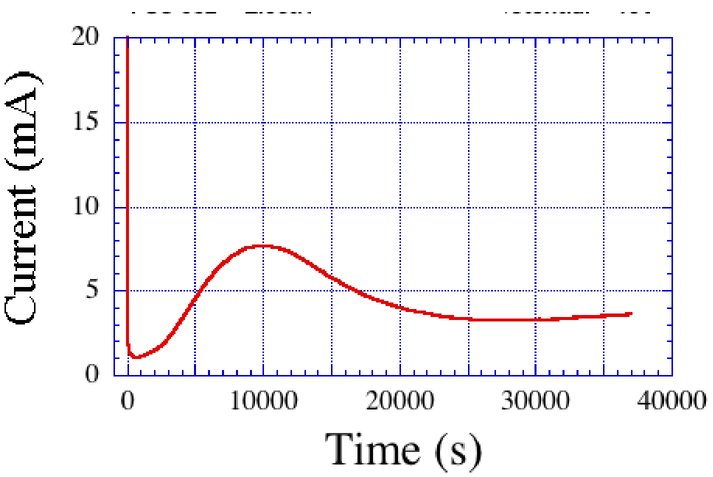


- Unique self-assembled nano-architecture*
- Precise control of tube dimensions
- Pore size: 20 - 260 nm
- Length: 120 nm- 1000 μm
- Wall thickness: 7 nm - porous
- Tube spacing, lots to none

*Gong *et al. J. Materials Research* 16 (2001) 3331-3334
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

Nanotube Array Fabrication



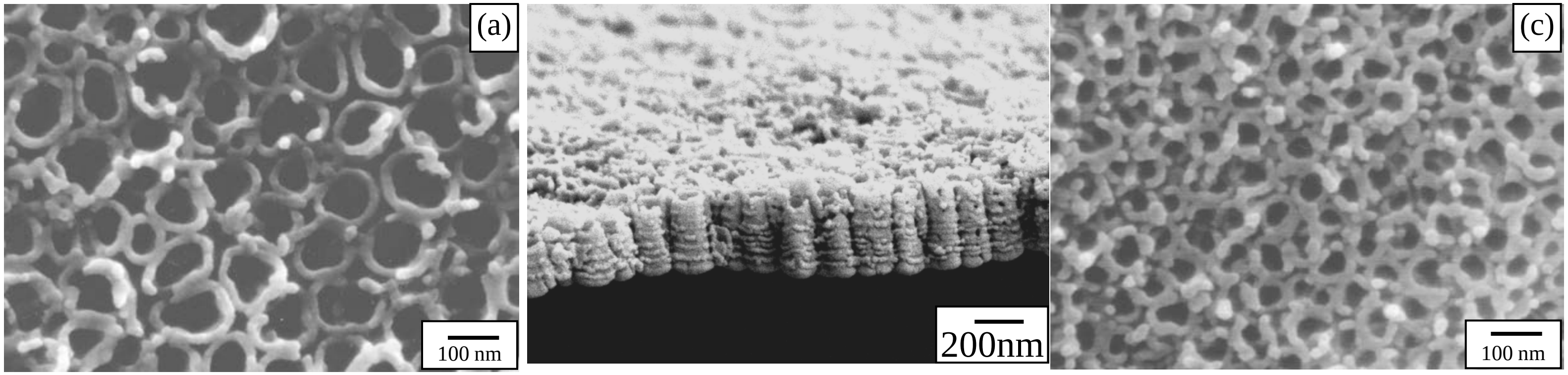


Electrolyte: Fluorine containing aqueous or organic solution (e.g. HF in water or NH_4F in ethylene glycol)

Voltage: 3- 120 V

Duration: Minutes to days

Titania Nanotube Arrays: The 1st Generation



Electrolyte:	**Water and HF**
Potential:	**8V to 23V**
Length:	**<500nm**
Pore size:	**22nm to 90nm**
Wall thickness:	**13 to 35 nm**

- Nano-porous titania was formed on Ti using aqueous HF by Zwilling et al [*Surf. Interface Anal. (1999)*]
- Titania nanotube array was developed by Gong et al [*J. Materials Research (2001)*]

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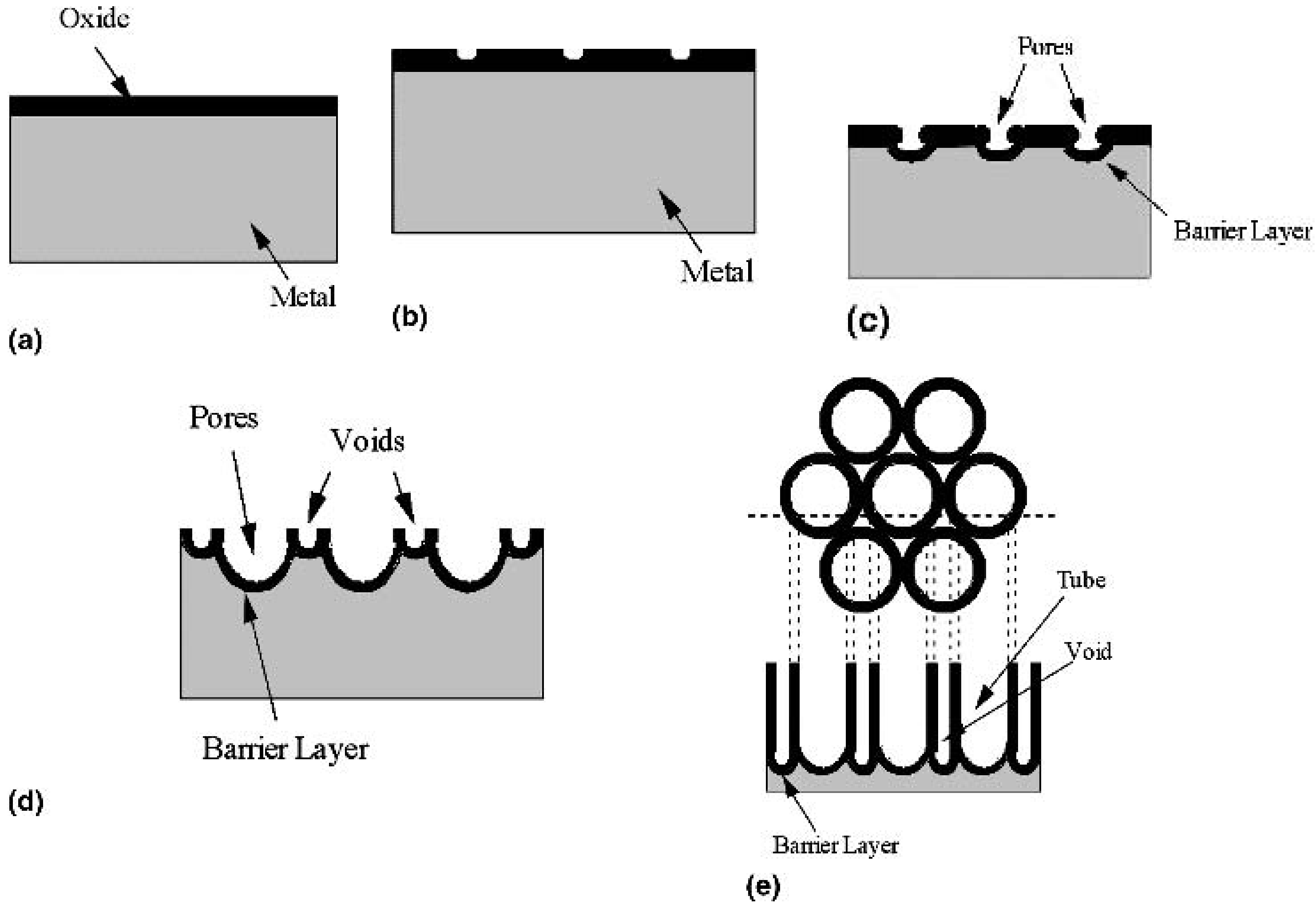
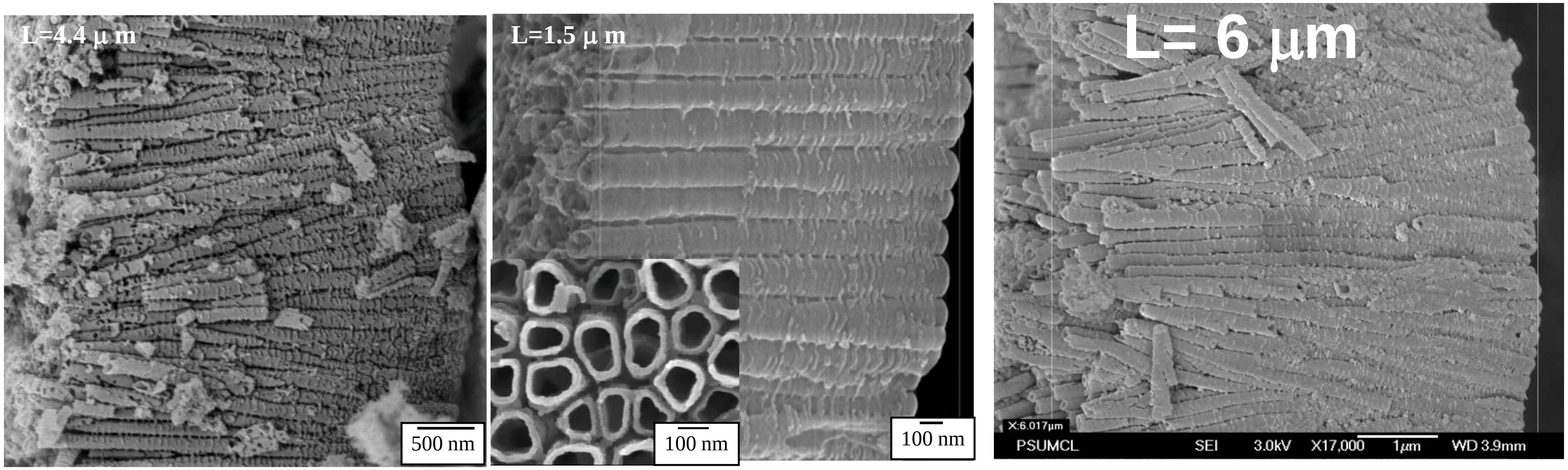
Growth Mechanism



Mor *et al.*, J Materials Research 18 (2003) 2588-2593

Titania Nanotube Arrays: The 2nd Generation



Electrolyte: Potassium fluoride, Sodium hydrogen sulfate, Trisodium citrate, Sodium hydroxide, water

Potential: 10V to 25V; **PH:** 3 - 5

Length: < 6.3 μm

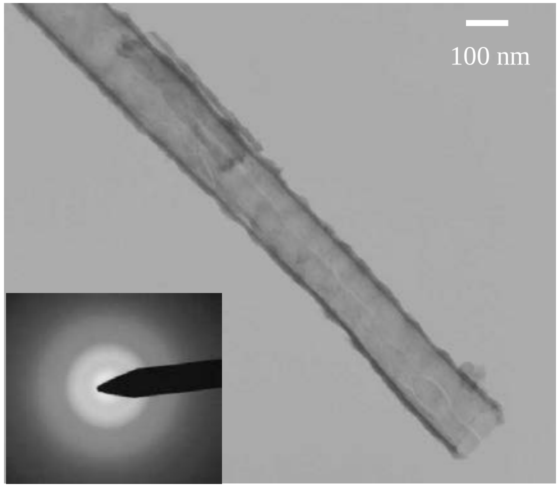
Pore size: < 120 nm

Wall thickness: 10-25 nm

Q. Cai, M. Paulose, O.K. Varghese, C.A. Grimes, J Materials Research (2005)

O.K. Varghese, M. Paulose, K. Shankar, G.K. Mor, C.A. Grimes, J Nanoscience and Nanotechnology (2005)

Titania Nanotube Arrays: The 3rd Generation



Electrolyte: NH_4F/HF, water (<4%) and Polar organics like ethylene glycol, formamide, n-methyl formamide, dimethyl sulfoxide, diethylene glycol

Potential: < 120 V

Length: Up to about 1000 μm

Pore size: < 400 nm

Wall thickness: 4 to 25nm

M. Paulose *et al.* *J. Phys. Chem. B* 110 (2006) 16179-16184

H.E. Prakasham *et al*. J. Phys. Chem. C (2007)

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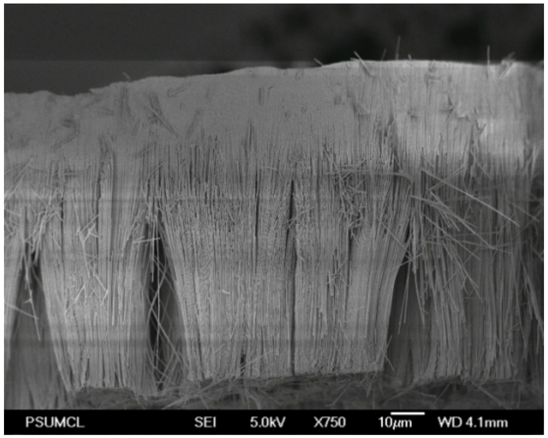
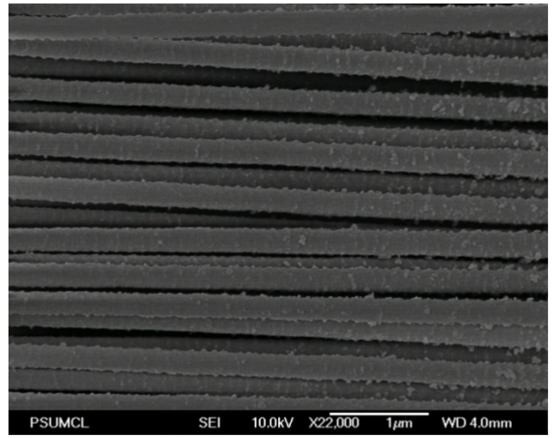
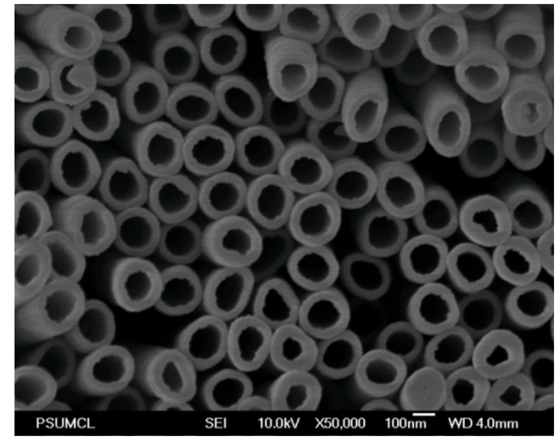
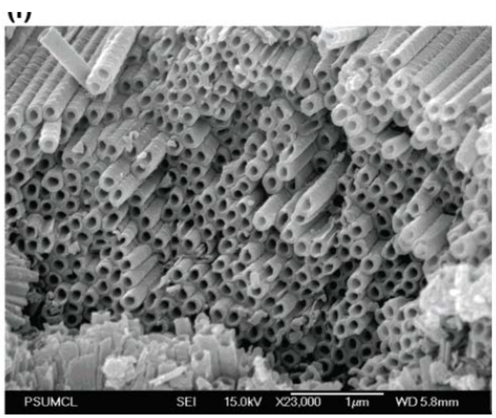
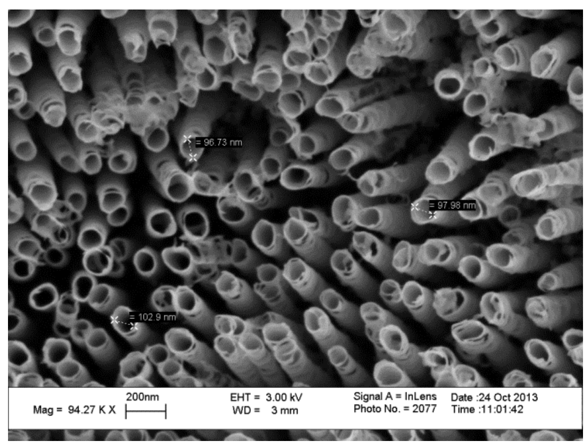
Titania Nanotube Arrays: The 3rd Generation

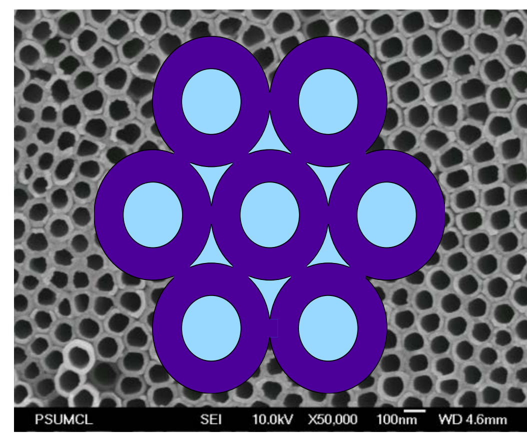




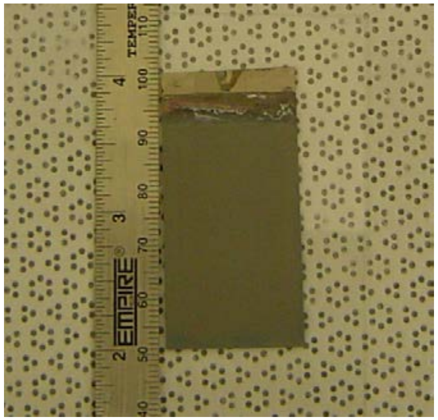


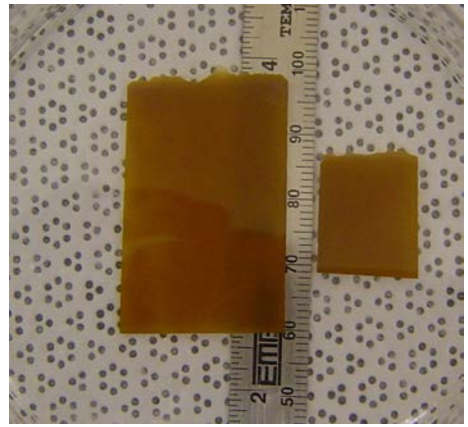


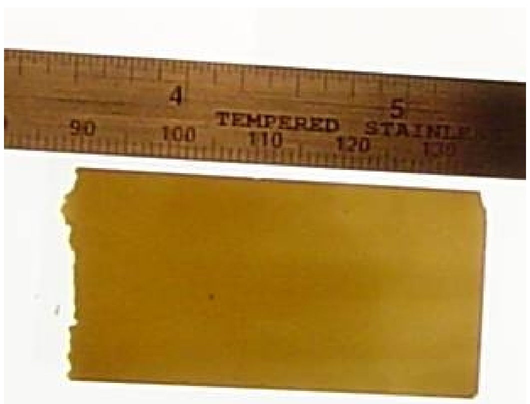




TNT Array Self Standing Membranes/pipes



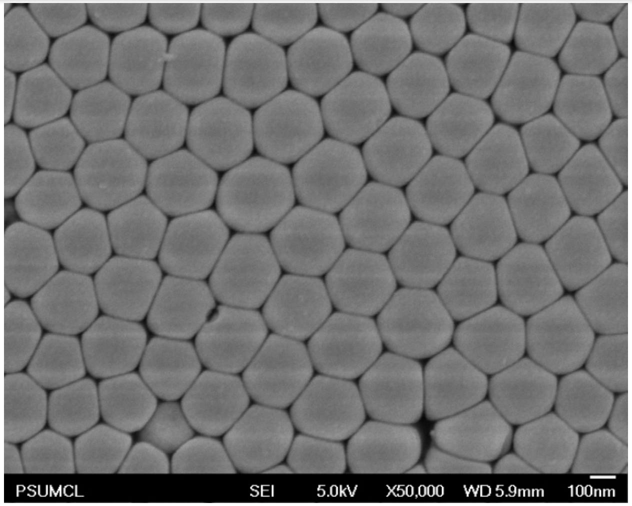


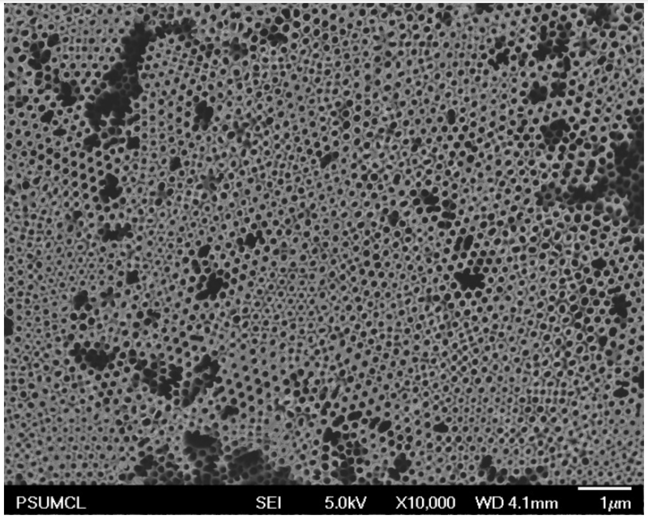


Self-standing membrane (amorphous)

Self-standing membrane (Crystalline); 130 μm thick

Flow-through Membranes

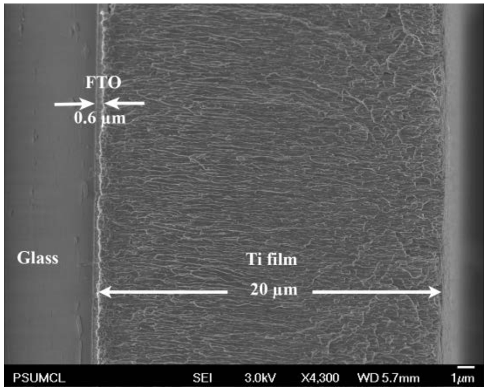


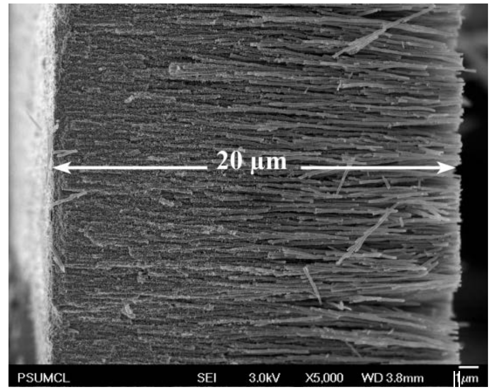


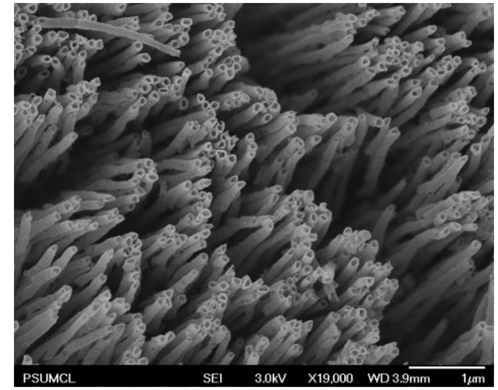
- **Flow through membrane by opening the pore bottom**

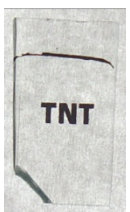
M. Paulose, …., O.K. Varghese,…, J. Physical Chemistry C 111 (2007) 14992-14997

High Thickness Transparent Titania Nanotube Array Films

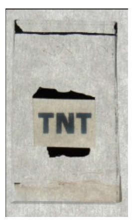




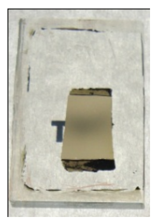




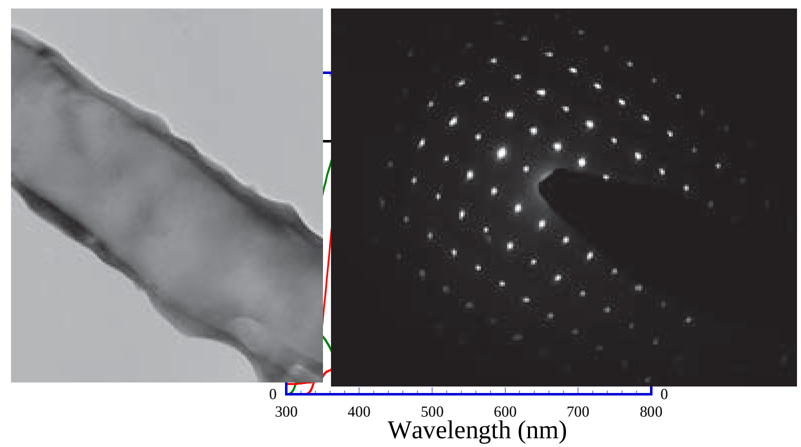
0.7 µm



4 µm



20 µm



- Exhibit antireflection behavior
- Only anatase phase

O. K. Varghese, M. Paulose, C. A. Grimes, *Nature Nanotechnology* (2009)

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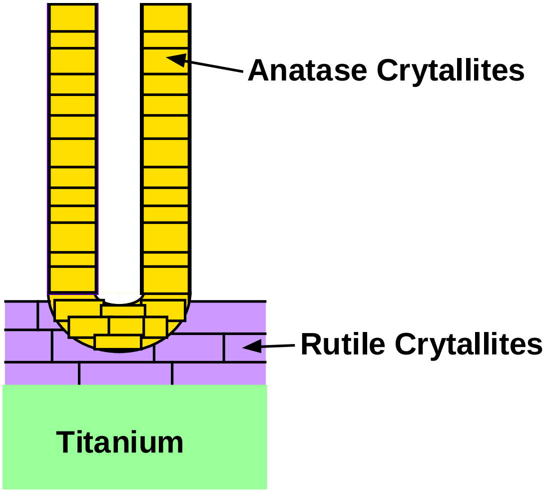
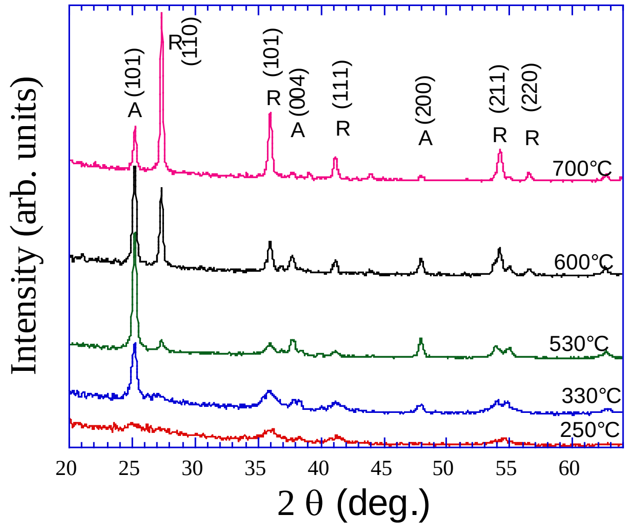
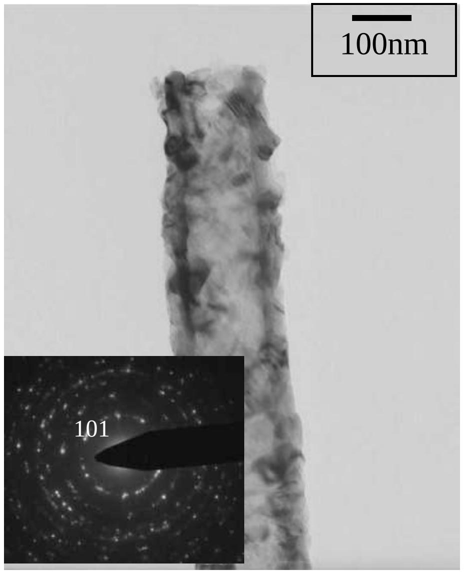
From Useless to Most Useful

As fabricated NTs are amorphous and hence poor electron transport



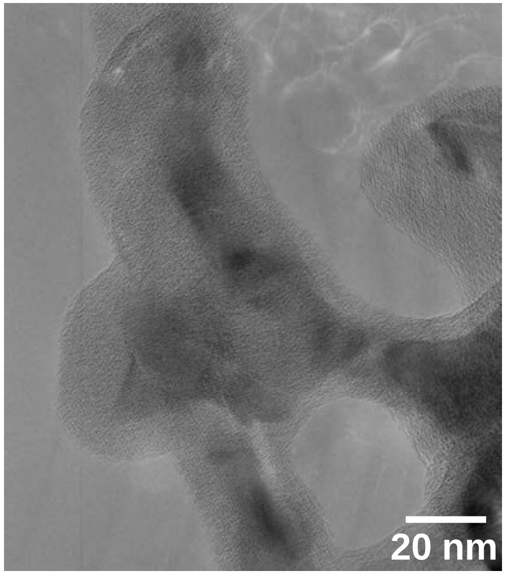


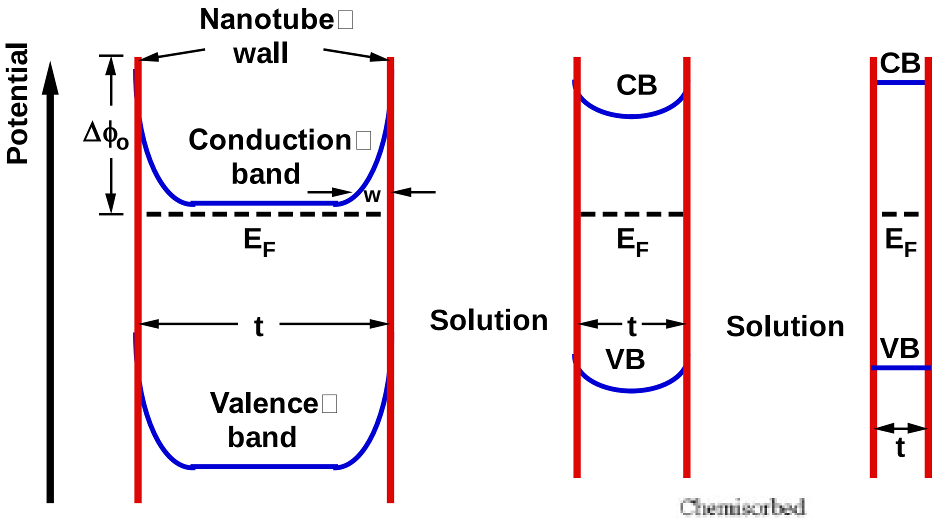


- Heat treated NTs consist of anatase crystallites in walls
- Rutile is formed in the base layer when the support metal oxidizes

O.K. Varghese *et al.,* J Materials Research 18 (2003) 156-165

Carrier Transfer and NT Wall Thickness

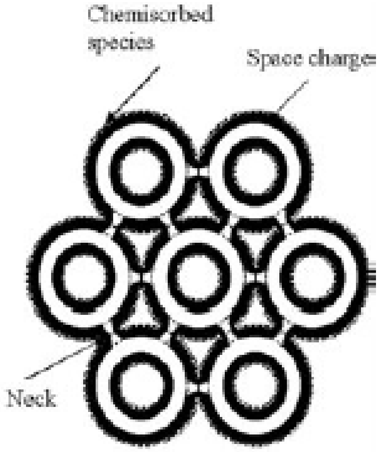




Space Charge Layer

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

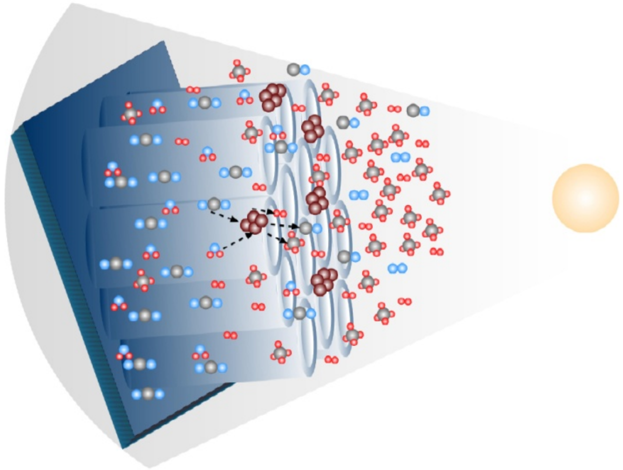
Debye Length $$L_D = \left[\varepsilon_0 \varepsilon kT / e^2 N_D\right]^{1/2} \approx 7\ nm$$

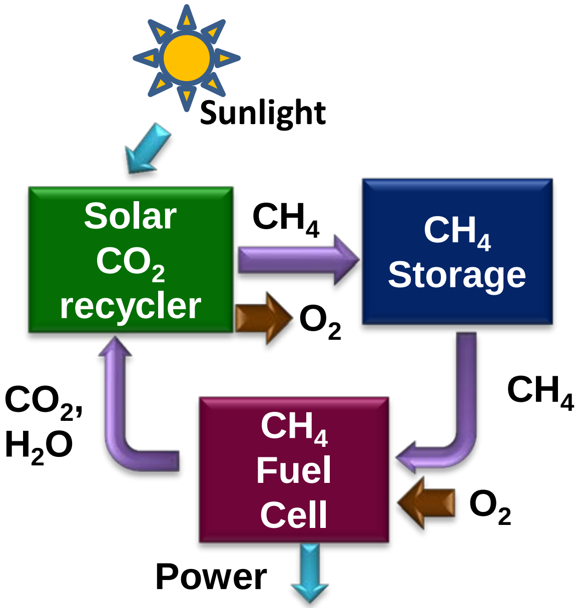


Electron Diffusion length ≈ 100 μm

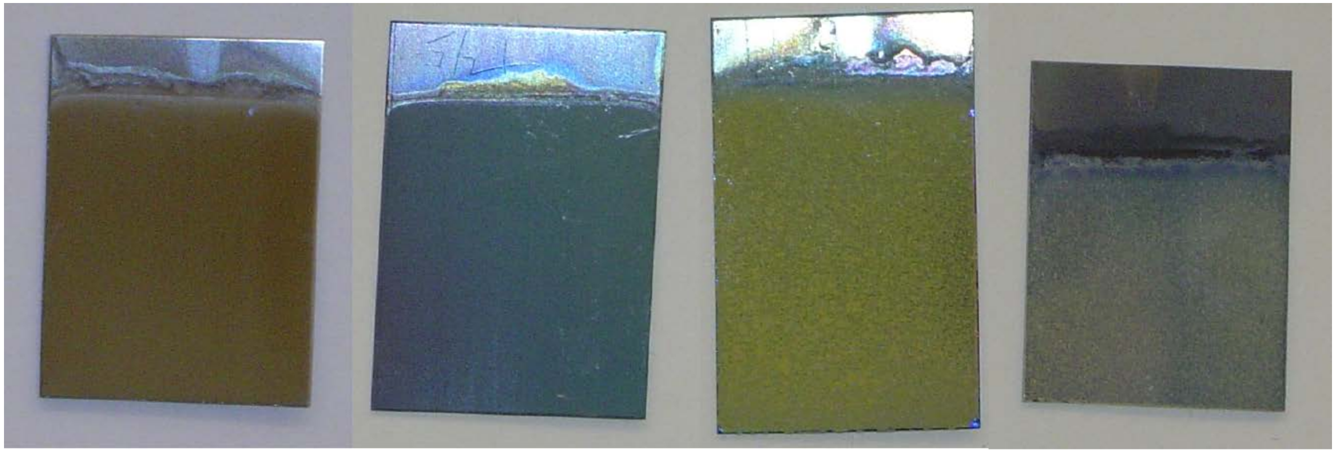
Hole Diffusion length for TiO_2 : 1 to 10 nm

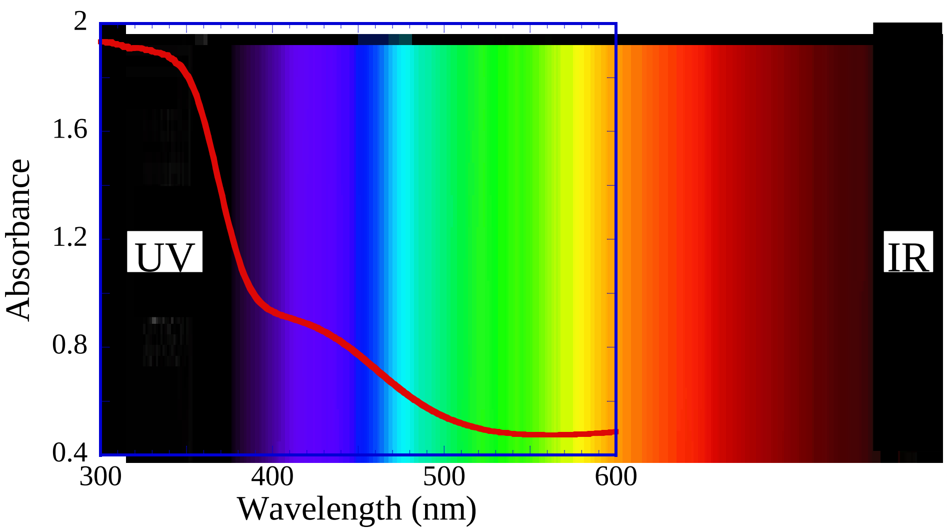
Photocatalytic Conversion of Humid CO_2 to Hydrocarbons Using Titania Nanotube Arrays

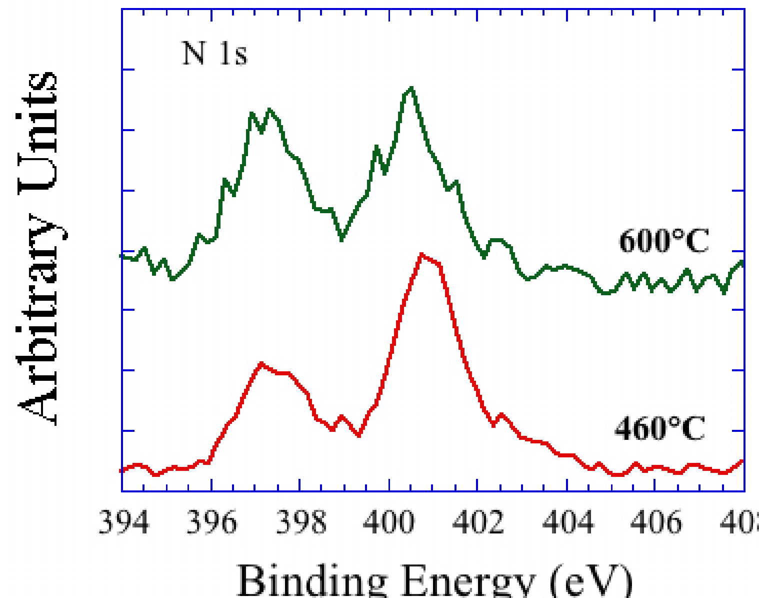




Enhanced Light Absorption Through Nitrogen Doping



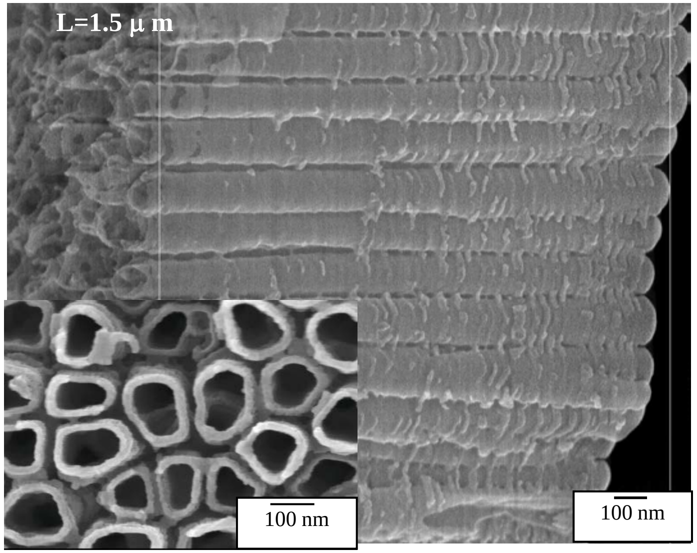


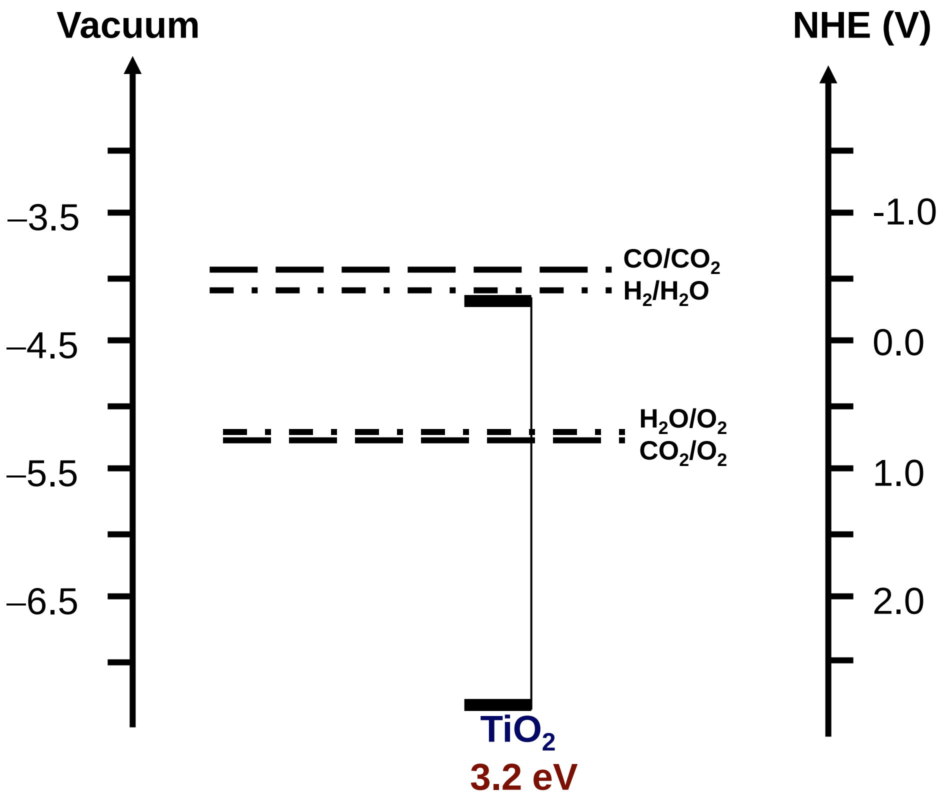


O.K. Varghese *et al.*, Nano Letters, 9 (2009) 731-737

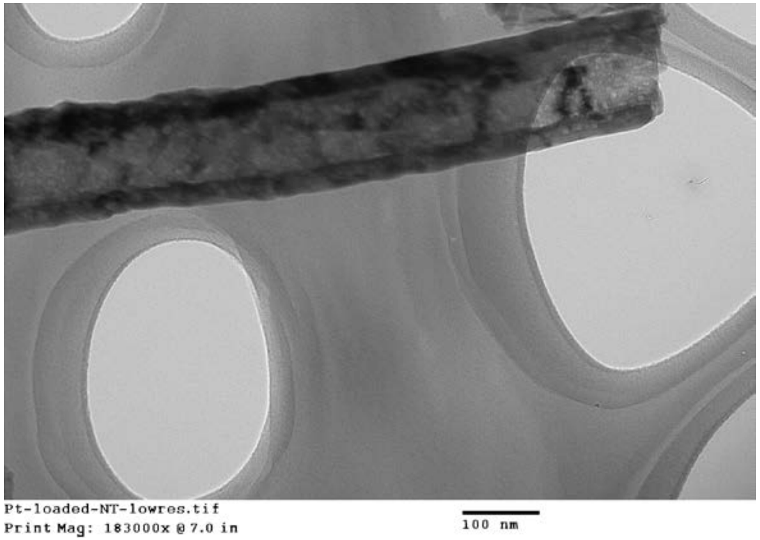
Enhanced Carrier Transfer

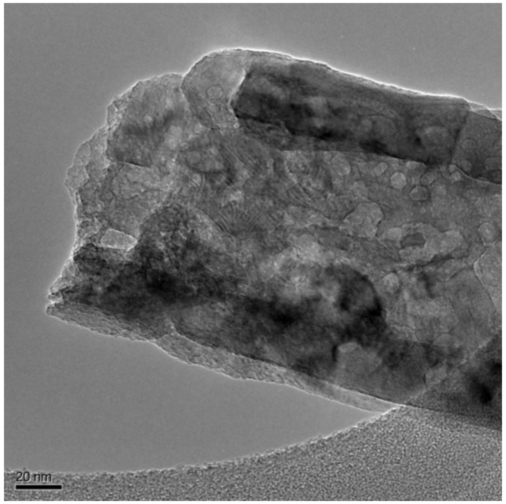
- Need a co-catalyst for the effective conversion of CO_2

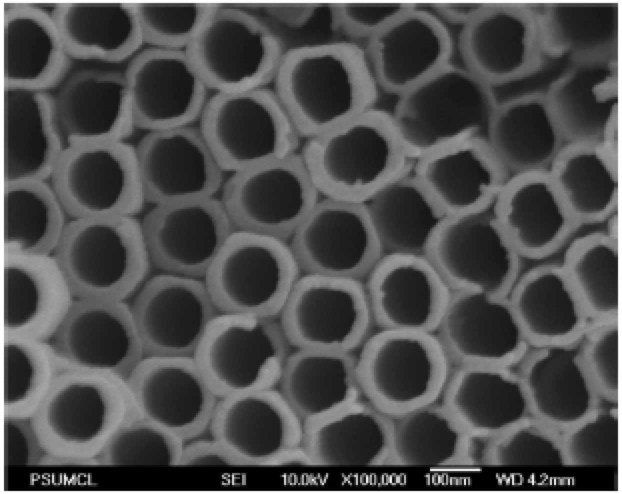




Platinum Loading



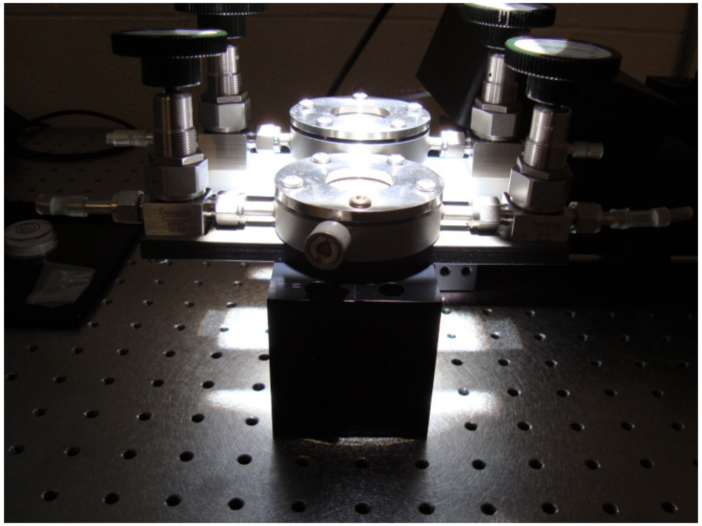




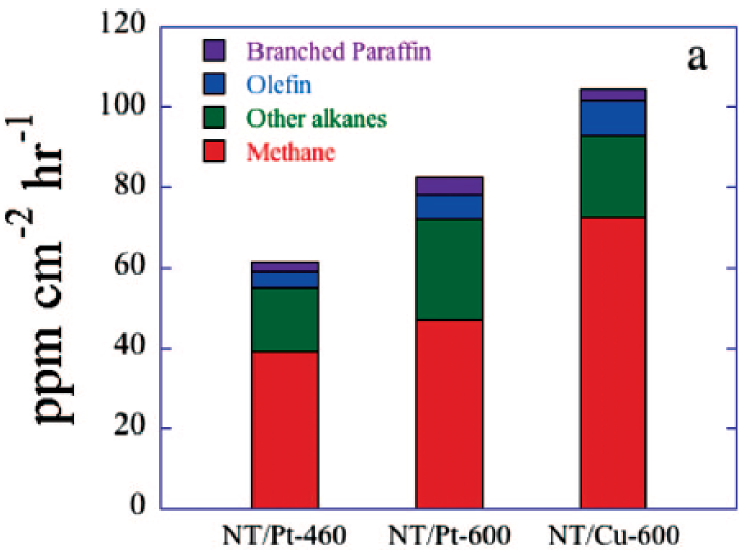
- **No pore clogging**
- **Co-catalyst island spread ~ 40nm**

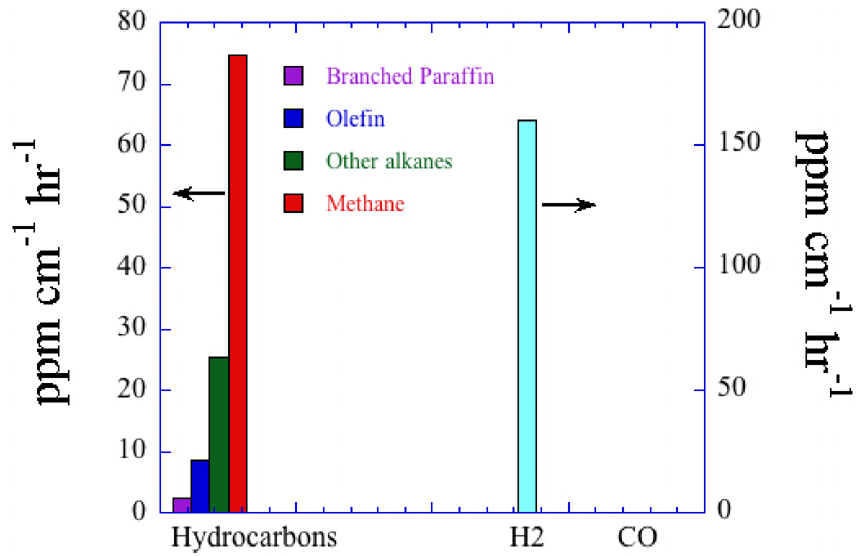
Test Conditions

- **Either under sunlight or class A solar simulator**
- **Exposure time 2.5 to 3.5 hours (sunlight power density 102 to 75 mW/cm^2, simulator at 100 mW/cm^2)**
- **Chamber volumes 7.5 cm^3 and 8.6 cm^3**



Solar Fuel Generation





600°C annealed, sensitized with both Pt (≈ 52% surface area) and Cu (≈ 48% surface area) nanoparticles

Hydrocarbons: 111 ppm/cm^2•h, or 0.83 μl/cm^2•h, or 160 μl/g•h

Using solar spectrum energy levels of 100 mW/cm^2, ≈ 20x better than previous record set under UV light

O.K. Varghese *et al*, Nano Letters, 9 **(2009) 731-737**

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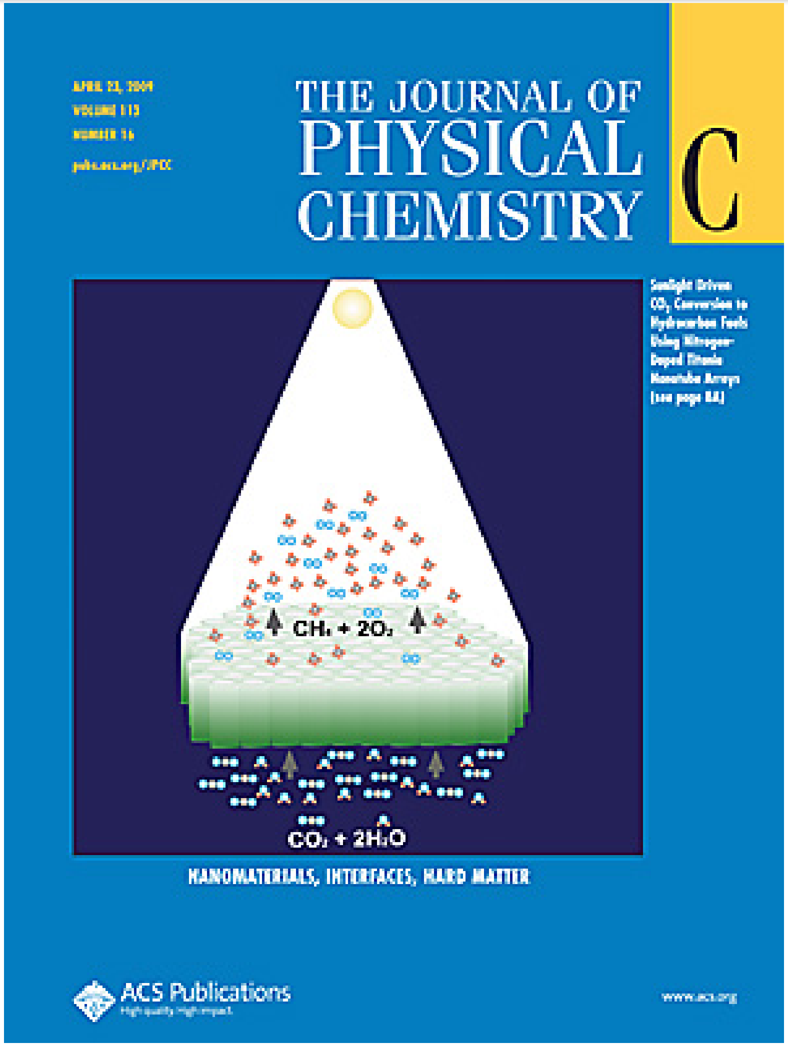
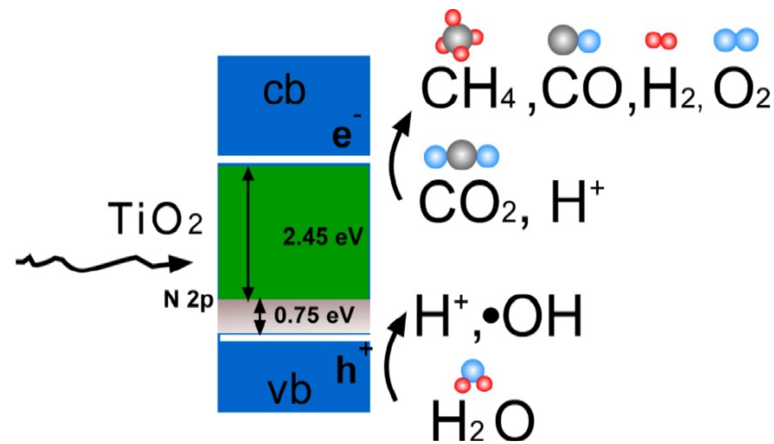
Possible Methane Formation Route





$$H_2O + h^+ \longrightarrow \bullet OH + H^+$$
$$H^+ + e^- \longrightarrow H^\bullet$$
$$H^\bullet + H^\bullet \longrightarrow H_2$$
$$2CO_2 + 4e^- \longrightarrow 2CO + O_2$$
$$CO + 6e^- + 6\,H^+ \longrightarrow CH_4 + H_2O$$

S. Rani,….,O.K. Varghese,….., Physical Chemistry Chemical Physics 12 (2010) 2780-2800

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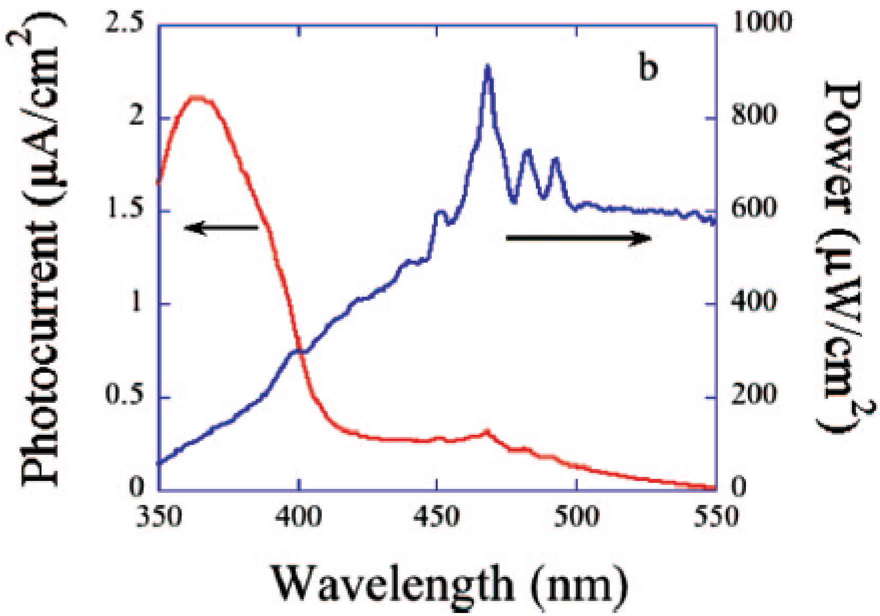
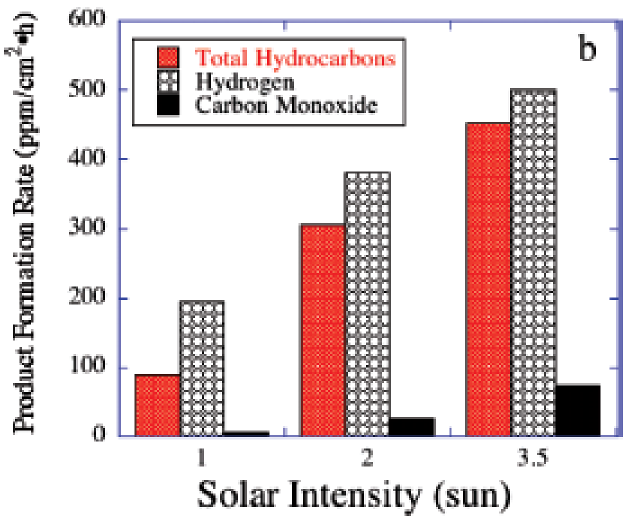
Low Efficiency Problem



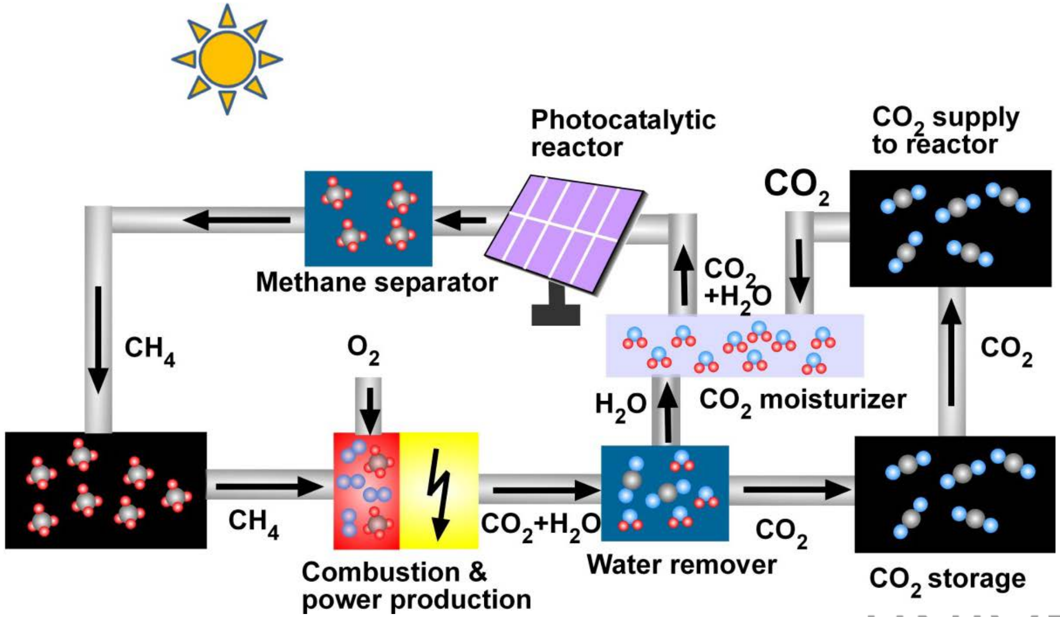


O.K. Varghese *et al*, Nano Letters, 9 **(2009) 731-737**

S.C. Roy et al, ACS Nano, 4 (2010) 1259 - 1278

Technology Prospects

- Present efficiency is < 0.1%
- If efficiency becomes ~ 10%, 1000 cubic ft methane can be generated from 3000 sq. ft in 8 hours (sunny day) converting 45 kg of CO_2
- The material cost for a 3000 sq. ft unit <$500 and payback time is around 50 days



A simplified scheme showing operation of a natural gas power plant in association with a photocatalytic reactor.

Varghese, Nanomaterials & Energy 2 (2013) 244

Summary

- CO_2 recycling using solar energy is one of the most promising ways to address present fuel and CO_2 related problems
- Direct Conversion of solar energy to hydrocarbon fuels is possible through solar photocatalytic route
- Energy conversion efficiency is very low
- Nanomaterials can change the scenario