TIGP-Nano

Nano-Science and Technology for Solar Cells and Solar Fuels

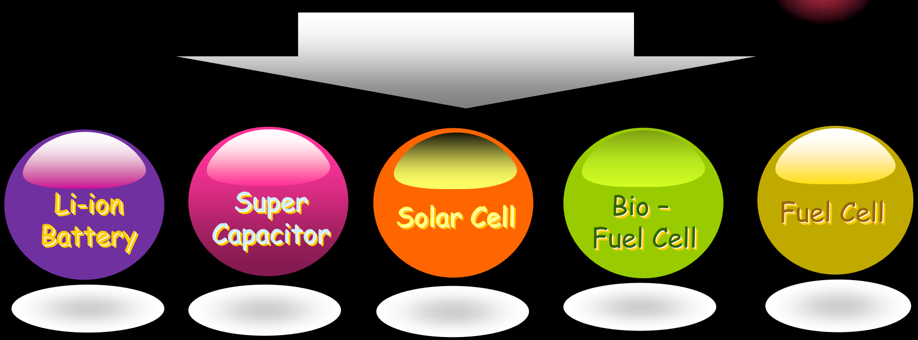
- Are we ready for the "powered-by-sun" era?
- Can "nano" help in time?

Li-Chyong Chen
Center for Condensed Matter Sciences
National Taiwan University

Tackle the Next Generation Energy Challenges

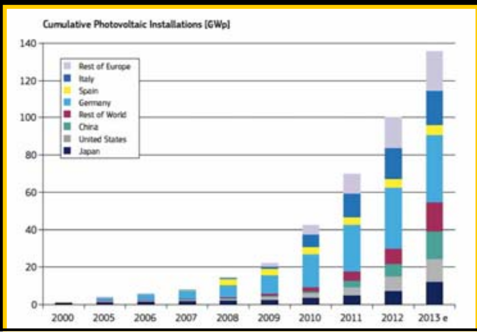
Green & Miniaturized Products

Nano-materials for Energy Applications

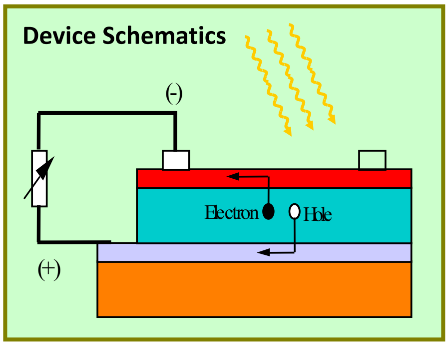


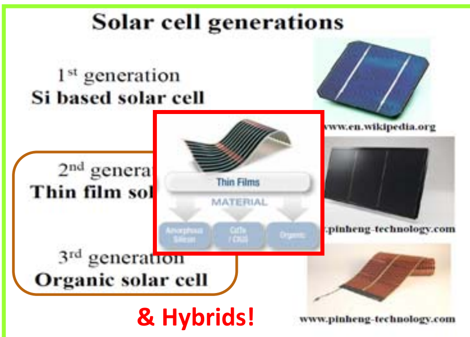
Photovoltaic (PV) History

- 1839 Photovoltage Discovered in Electrode/Electrolyte System (Antoine-César BECKEREL)
- 1876 Photovoltage Observed in Solid Se
- 1954 First Practical Solar Cell (c-Si; efficiency = 6%) at Bell Lab
- 1963 Sharp Produced First Commercial Si Modules
- 1978 : World Production of 1MWp
- 1985: Si Solar Cell > 20% under Standard Sunlight (UNSW)
- 2014: World Production of 100 GWp Total .3 Terawatts
- 2014: 25% on Large Area Solar Cell (Sunpower)



Research Opportunities of Nano in Photovoltaic

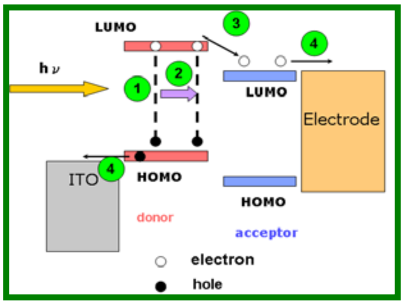




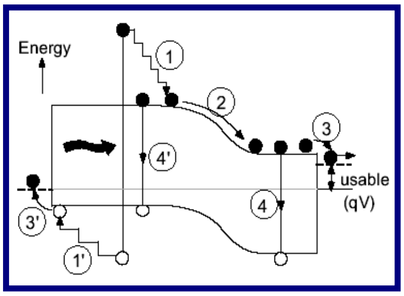
Photovoltaic Processes and Losses

Light Absorbance
Charge Carrier Generation (1)
Exciton Diffusion (2)
Charge Carrier Separation and Transport (3)
Extraction/Injection of Carriers through Contacts (4)

1 : Thermalization loss
2 & 3 : Junction & contact voltage loss
4 : Recombination loss

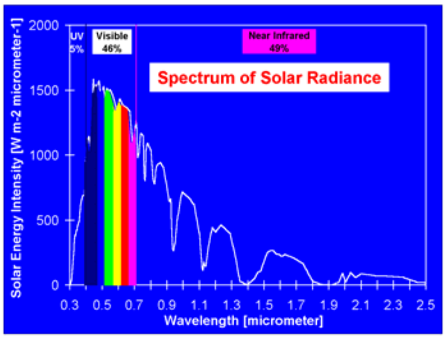


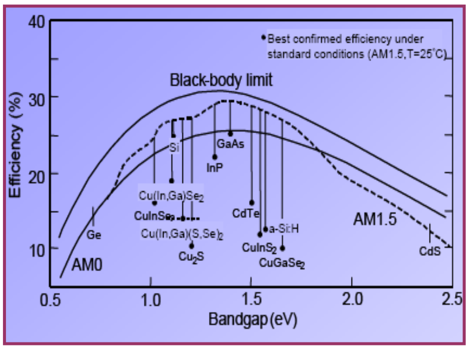
Organic



Semiconductor

Solar Spectrum and Solar Cell





Shockley-Queisser Limit in Single p-n Junction

Modern technology: Tandem cell & Concentrator

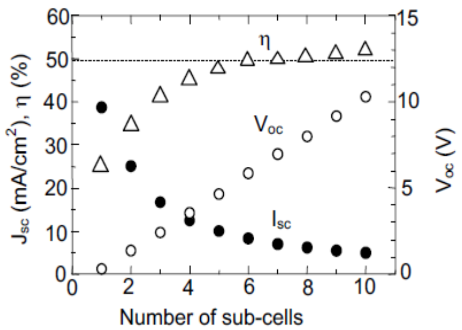
Four-junction device with bandgaps
1.8 eV/1.4 eV/1.0 eV/0.7 eV
Theoretical efficiency > 52%

Choice of materials dictated by
efficiency, materials availability,
ease of manufacturing,
module reliability,
market acceptance, etc.

InGaN and InAlN-based Solar Cells

Band-gap of InGa(Al)N can be adjusted from 0.7 to 2.5 eV by changing only the composition.

➡ Current matching will be easily achieved using InGa(Al)N system
(A current generated in each sub-cell is assumed to be the same)



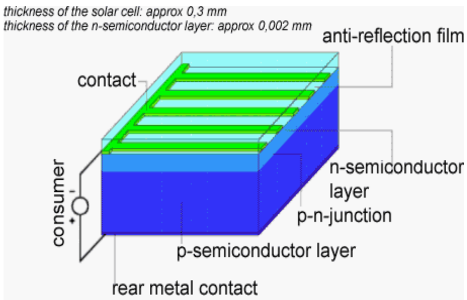
Performance for multi-junction tandem cells with a different number of sub-cells

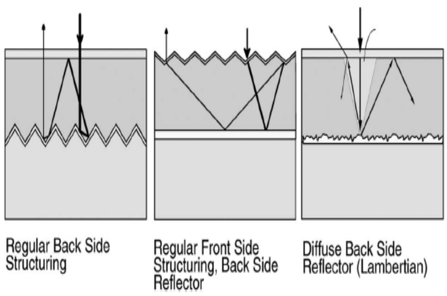
Theoretical Efficiency > 50% !!!

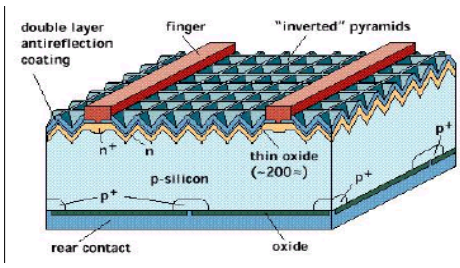
Real-world Challenge:
Material Growth
(Phase Separation)
➡ Reducing V_{oc} &
Increasing Recombination

A. Yamamoto et al., Phys. Status Solidi C 7, 1309 (2010).

Silicon Solar Cells with Antireflection







24.7% laboratory cell (FZ)

16-22% production cells

13-17% commercial modules

25-year warranties

Adolf Goetzberger et al.,*"Photovoltaic Materials, History, Status and Outlook,"* *Materials Science and Engineering R* 40 (2003) 1–46

Merits of Nanowires/Nanorods in High-efficiency Solar Cells and Solar Hydrogen/Fuels

Si, GaN or InGaN, etc. Nanowires/Nanorods

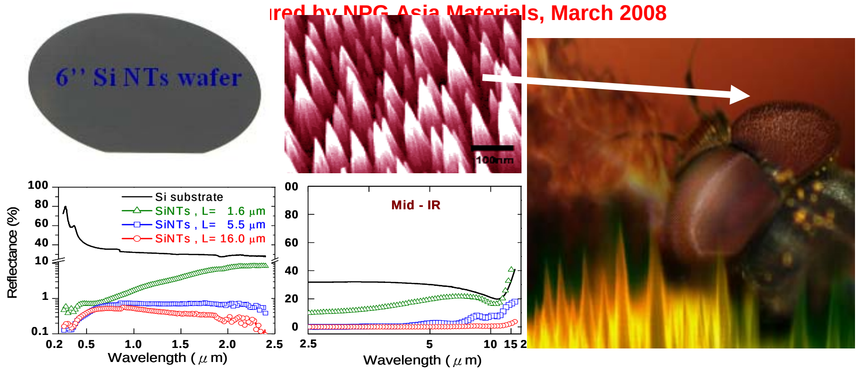
- Larger surface area/more junctions
- Enhanced light harvesting
- Directional carrier transport
- More efficient carrier separation
- Longer carrier lifetime
- Higher photon conversion gain

A Man-made Moth Eye

Broadband and Quasi-omni-directional Anti-reflection Properties with Biomimetic Silicon Nanostructure

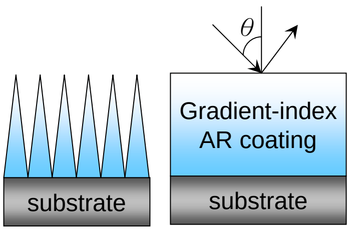
(NTU) Y. F. Huang, et al., Nature Nanotechnology 2, 770-774 (2007) & US Patent 2005

red by NPG Asia Materials, March 2008



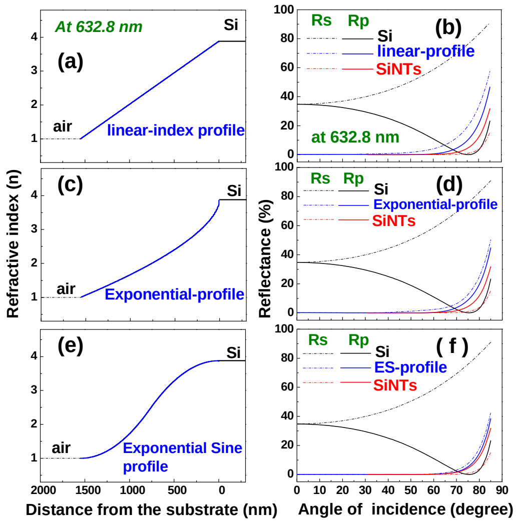
Many plants and animals have tiny surface structures that absorb certain wavelengths of light. These naturally formed nanostructures provide the colors in butterfly wings, camouflage for cicadas and enable moths to capture as much light as possible when flying at night.
Now, we have created nanostructure surfaces which mimic moth eye and surpass its function in anti-reflection in that they absorb almost all incident light.

Optical Modeling and Simulation
(gradient layer between air and substrate)



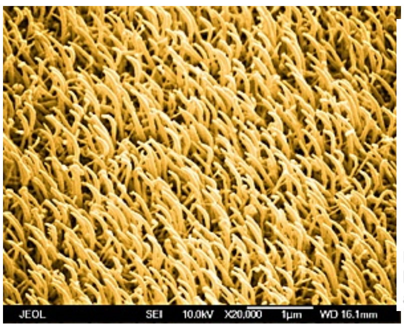
Gradient-index profile:
1. Linear
2. Exponential
3. Exponential-sine

Nature Nanotechnology 2, 770-774 (2007)



Solar cells: Column capture

A layer of nano-sized columns improves the light absorption efficiency of solar panels.



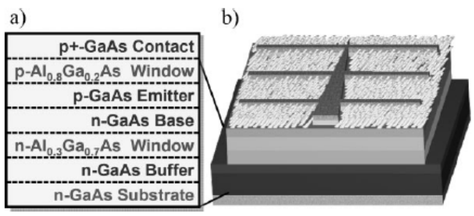


Figure 1. a) Epitaxial structure of a single-junction GaAs solar cell. b) Schematic of a GaAs solar cell fabricated employing ITO nanocolumns as the conductive AR coating.

(NCTU) P. C. Yu, *et al*., "Efficiency enhancement of GaAs photovoltaics employing antireflective indium tin oxide nanocolumns." *Adv. Mater.* 21 (2009).

When Si Solar Cells Go Nano

JOURNAL OF APPLIED PHYSICS **97**, 114302 (2005)

Comparison of the device physics principles of planar and radial *p-n* junction nanorod solar cells

Brendan M. Kayes and Harry A. Atwater[a)]
Thomas J. Watson, Sr. Laboratories of Applied Physics, California Institute of Technology, MC 128-95, Pasadena, California 91125

Nathan S. Lewis[b)]
Arthur Amos Noyes Laboratories of Chemical Physics, California Institute of Technology, MC 127-72, Pasadena, California 91125

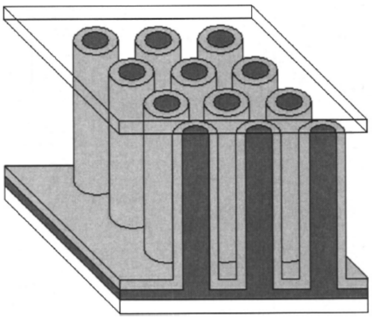
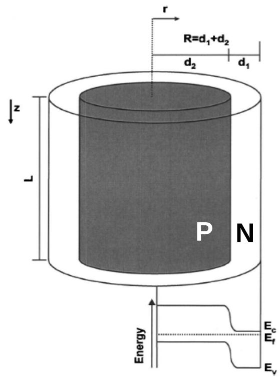
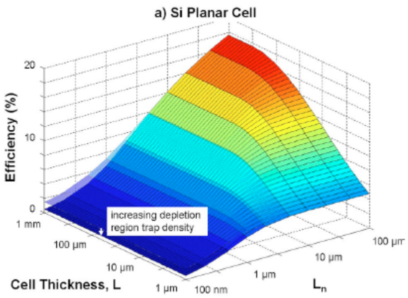


FIG. 3. Schematic cross-section of the radial *p-n* junction nanorod cell. Light is incident on the top surface. The light grey area is *n* type, the dark grey area *p* type.



Planar vs Nanorod Si



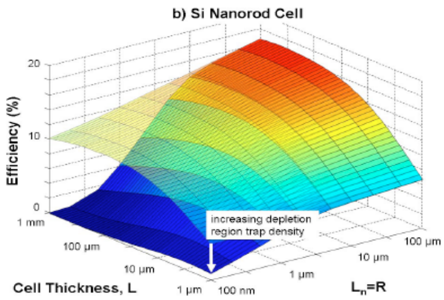


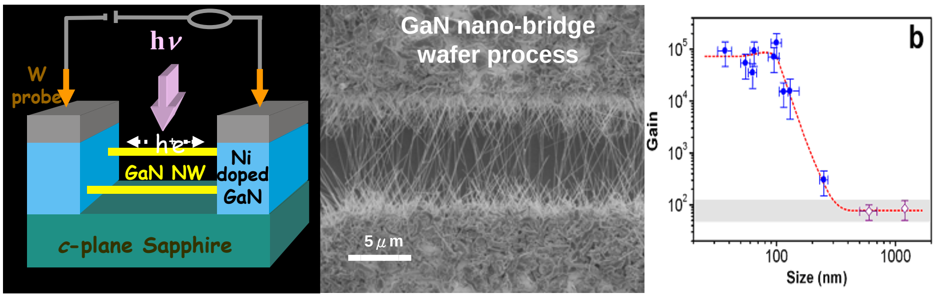
FIG. 8. (Color online) Efficiency vs cell thickness L and minority-electron diffusion length L_n for (a) a conventional planar *p-n* junction silicon cell and (b) a radial *p-n* junction nanorod silicon cell. In both cases the top surface shown in the plot has a depletion-region trap density fixed at 10^{14} cm^{-3}, so that $\tau_{n0}, \tau_{p0} = 1$ μs, while the bottom surface has a depletion-region trap density equal to the trap density in the quasineutral region, at each value of L_n. In the radial *p-n* junction nanorod case, the cell radius R is set equal to L_n, a condition that was found to be near optimal.

Harry Atwater, et al., JAP 2005

Building a Nano-scale Bridge On-chip

On-chip Fabrication of Well Aligned and Contact Barrier-Free GaN Nanobridge Devices with Ultrahigh Photocurrent Responsivity

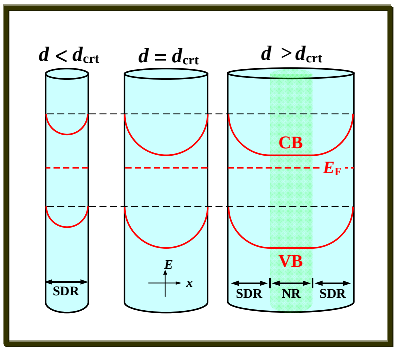
(NTU) *R. S. Chen, et al., Small 4, 925-929 (2008)*

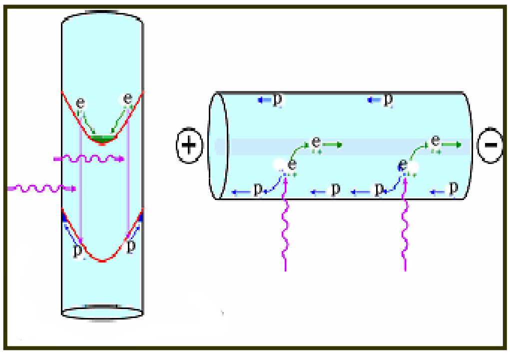


- Nanowire: Naturally formed core-shell structure, 1D electron gas-like property
- On-chip process for building GaN nanobridge devices, which provide a large surface area, short transport path, and high responsivity for next-generation sensors and detectors

What happens in nanowires as the wire diameter goes smaller and smaller?

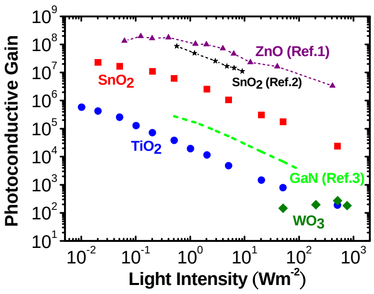
Surface Band-bending Effects & Carrier Separation

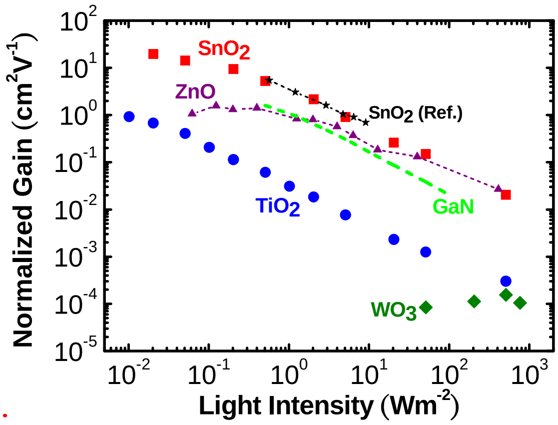




Comparison of Normalized Gain in Different Nanowires

$$\Gamma_n = \tau_{life} \times \mu \times \eta$$

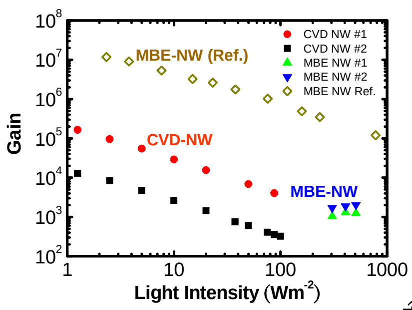




Material matters for sure.

SnO_2 > ZnO/GaN > TiO_2 >> WO_3

Ref. 1. C. Soci *et al*, *Nano Lett.* **7**, 1003 (2007); Ref. 2. L. Hu *et al*, *Small* **7**, 1012 (2011);
Ref. 3. R. S. Chen *et al*, *Appl. Phys. Lett.* **2012**, *101*, 113109.

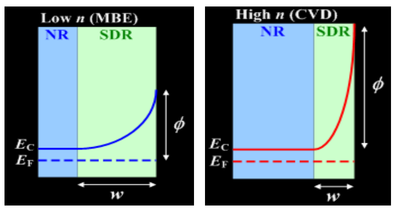


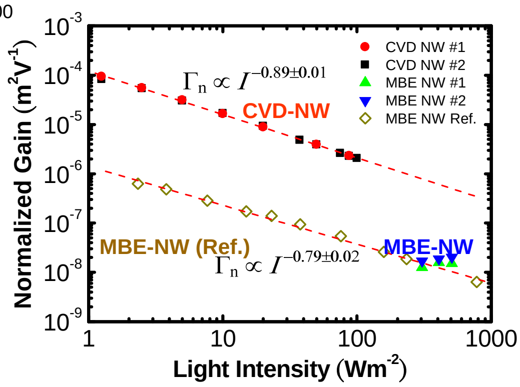
Sample No.	*d* (nm)	*l* (μm)	*V* (V)	Remark
CVD-NW #1	60±10	16.9	0.5	this work
CVD-NW #2	130±15	11.3	0.02	this work
MBE-NW #1	82±12	1.1	0.1	this work
MBE-NW #2	110±30	1.0	0.1	this work
MBE-NW Ref	65±15	0.4	3.0	Ref. 2

$$\Gamma_n = \eta \times \tau_{life} \times \mu = \eta \times \frac{\Gamma}{(\frac{V}{l^2})}$$

$$\Gamma = \tau_{life} \times \mu \times \frac{V}{l^2}$$

Growth condition matters too!





RS Chen, et al., *Appl. Phys. Lett.* *101*, 113109 (2012).

Next-Generation PV: Organic or Hybrid

Advantages

Processed easily over large area

- Spin-coating
- Doctor blade technique (wet-processing)
- Evaporation through a mask (dry-processing)
- Screen-printing

Low cost

Light weight

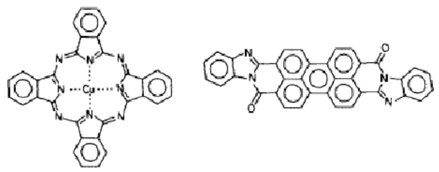
Flexible and transparent

Band gap tunable by chemically incorporating different groups

Technical Challenges:
poor efficiency, stability, life time issue

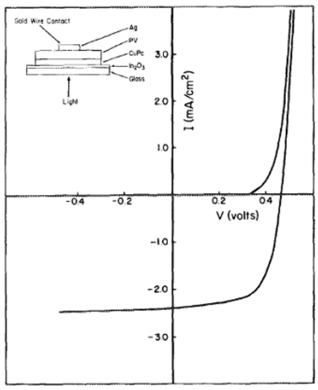
First Demonstration of OSC

The first breakthrough of organic based solar cell



CuPc PV

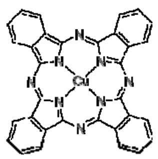
Tang's group in 1986.
Deposit CuPc and PV thin film in sequence by thermal evaporation under high vacuum.
The power conversion efficiency reaches 1%



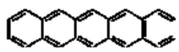
Under 75 mW/cm² illumination
Active area: 0.1 cm²

C. W. Tang, Appl. Phys. Lett. **48**, 183 (1986)

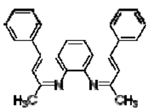
Active Materials



copper phthalocyanine (CuPc)

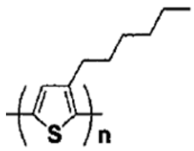


pentacene

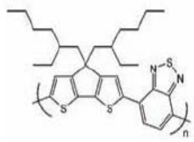


bathocuproine (BCP)

small molecular materials

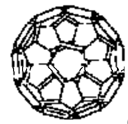


P3HT

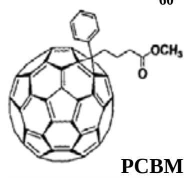


PCPDTBT

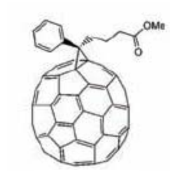
polymer materials



C_{60}



PCBM



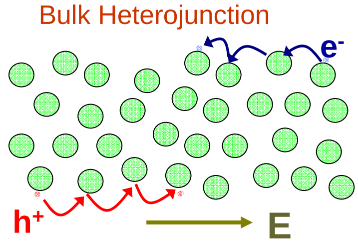
$PC_{70}BM$

fullerene system

Material Issue in Organic Solar Cells

Hopping Model

Bulk Heterojunction



Hole mobility		Electron mobility	
P3HT	1.5×10^{-4}	PCBM	10^{-3}
CuPc	10^{-4}	a-Si-H	10^{-1}~10^{-2}
ZnPc	10^{-6}	C60	0.5
MEH-PPV	~10^{-6}	ZnO	20
Pentacene	5	GaN	440

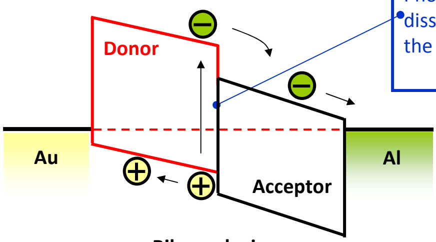
Unit: $cm^2\ V^{-1}s^{-1}$

Mobility in OSC:
several orders slower than semiconductor!

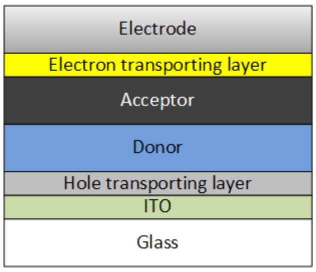
Technical Challenge in OSC (I)

- **Planer Heterojunction OSC**
  – Formed between a homogeneous donor layer and a homogenous acceptor layer
  – Charge collection efficiency (η_{CC}) will be relatively large
  – The exciton diffusion efficiency (η_{ED}) might be a bottleneck

Photogenerated excitons can only be dissociated at the D-A interface and thus the device is exciton diffusion limited.



Bilayer device

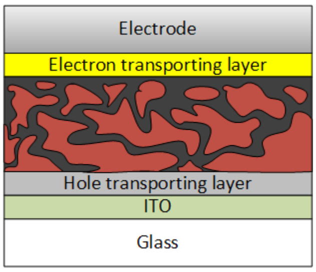


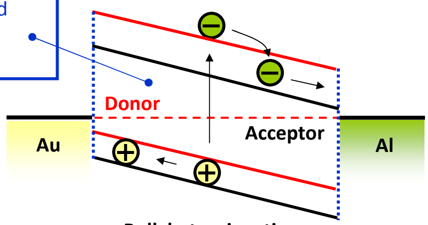
The bilayer structure usually use in the small molecular OSC system with the thermal evaporation fabrications.

Technical Challenge in OSC (II)

- **Mixed HJ (Blending, BHJ) OSC**
  – Usually used in polymer based organic solar cell employs the solution process
  – The η_{ED} approaches to unity in the mixed HJ generally
  – Charge collection efficiency (η_{CC}) in mixed HJ OSC often plays the role of the bottleneck

The donor is blended with the acceptor. Thus, photogenerated excitons can be dissociated into charges immediately.



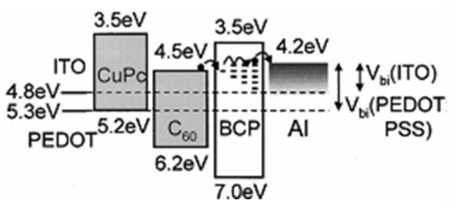


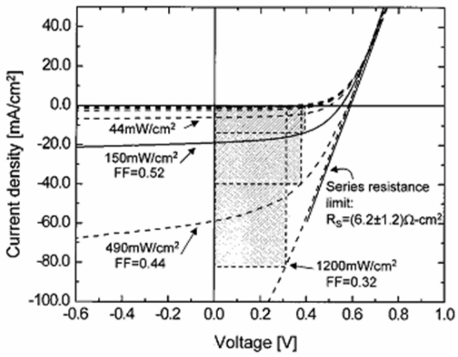
Bulk heterojunction

The polymer OSC system usually use the BHJ structure with the spin coating process.

Evolution of OSC (I)

Using BCP as the exciton blocking layer



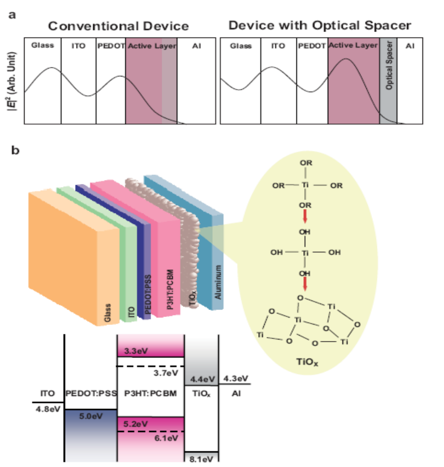


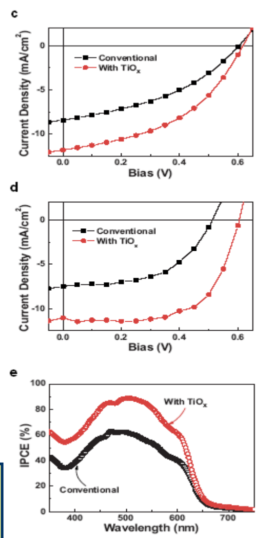
Under 150 mW/cm² illumination
Active area: 0.0079 cm²

Introducing C60 and BCP as the acceptor and exciton blocking layer respectively. The power conversion efficiency reaches 3%

P. Peumans and S. R. Forrest, Appl. Phys. Lett. **79**, 126 (2001)

Evolution of OSC (II)

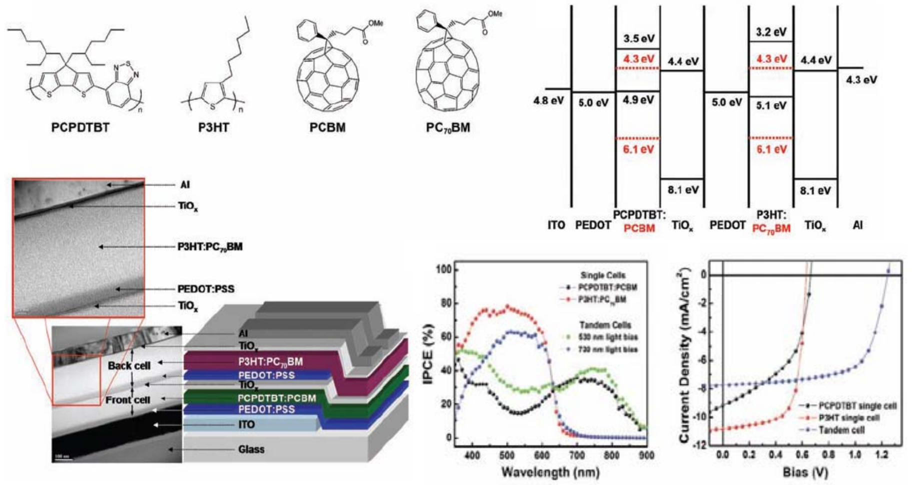




TiOx with high electron mobility acts as the hole blocking layer and the optical spacer.
The power conversion reach 5 %

J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. Ma, X. Gong, and A. J. Heeger, Adv. Mater. **18**, 572 (2006)

Evolution of OSC (III)

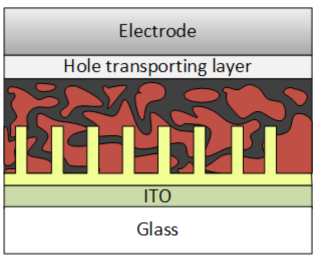


The tandem device introduce the optical spacer and the low band gap material.
The power conversion efficiency reach 7%, which is one of the highest value of the record of efficiency in OSC.

J. Y. Kim. K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, and A. J. Heeger, Science 317, 222 (2007)

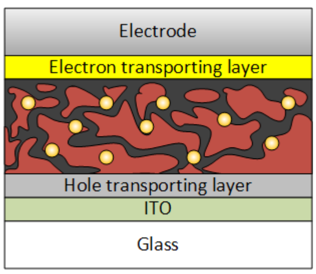
Organic/Inorganic Hybrids

with 1-D nanostructure



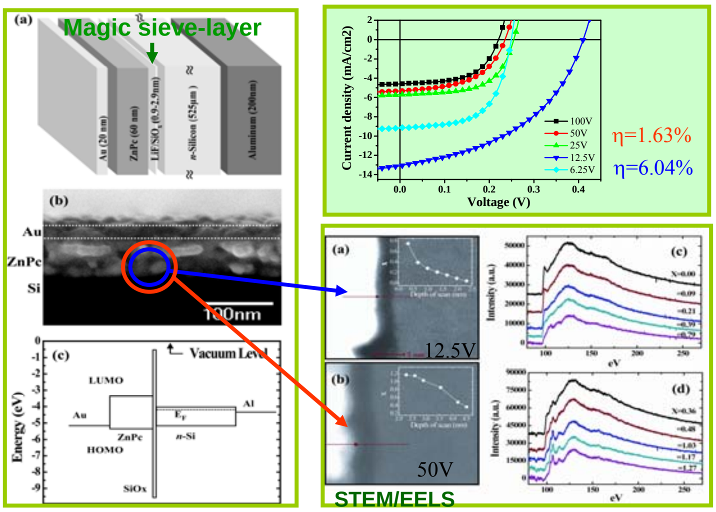
➡To increase the interfacial area
➡To enhance exciton dissociation and/or charge collection

with nanoparticle



➡To enhance light harvesting

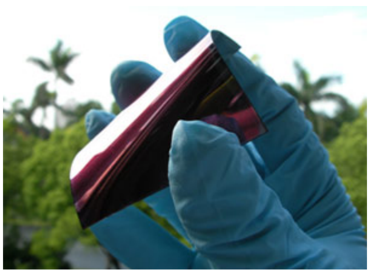
Hybrids: Interfacial control is critical

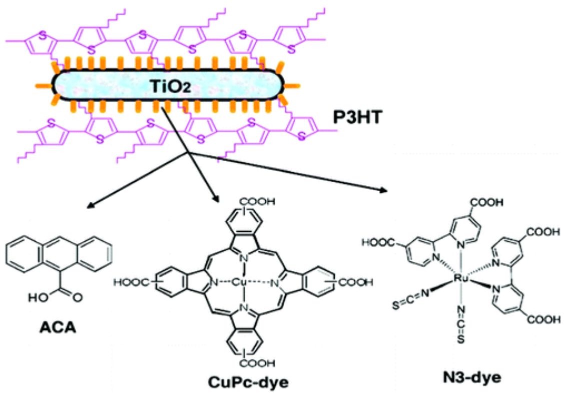


Enhanced Charge Separation by Sieve-layer Mediation in High Efficiency Inorganic-organic Solar Cell

Chen et al., Advanced Materials 21, 759-763 (2009) & US Patent pending

Hybrid TiO_2/P3HT Solar Cell:
Cheaper and Greener

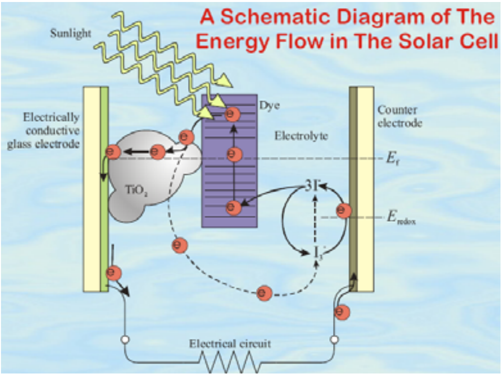


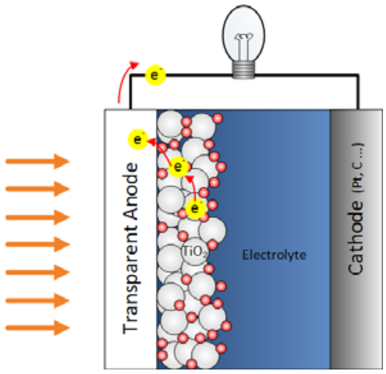


Interface modification:
- Wettability
- Interface band-structure
- Carrier separation/transport

C. W. Chen et al.,
J. Am. Chem. Soc. 131, 3644 (2009).

Dye Sensitized Solar Cell





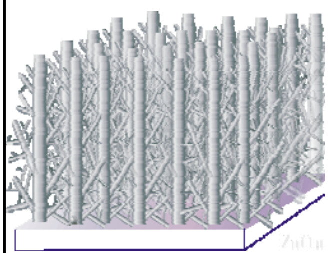
Advantages
- Most efficient 3rd generation solar tech.
- Work in low-light conditions
- Flexible

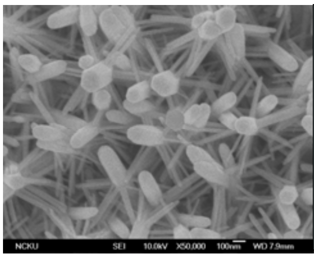
Drawback
- Temperature stability problems
- Encapsulation issue

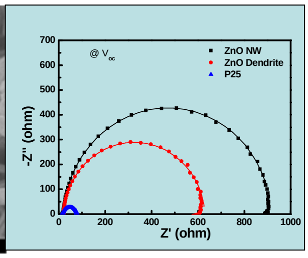
Dye + light → Dye*
Dye* + TiO_2 → $e^-(TiO_2)$ + Dye^+
e^- (TiO_2) + C.E. → TiO_2 + e^-(C.E.) + energy
½ I_3^- + e^- (C.E.) → 3/2 I^- + C.E
C.E. is the counter electrode
Dye* indicates an excited state of the dye

Michael Graetzel, Ecole Polytechnique Federale de Lausanne, Switzerland

ZnO Nanodendrites for DSSC



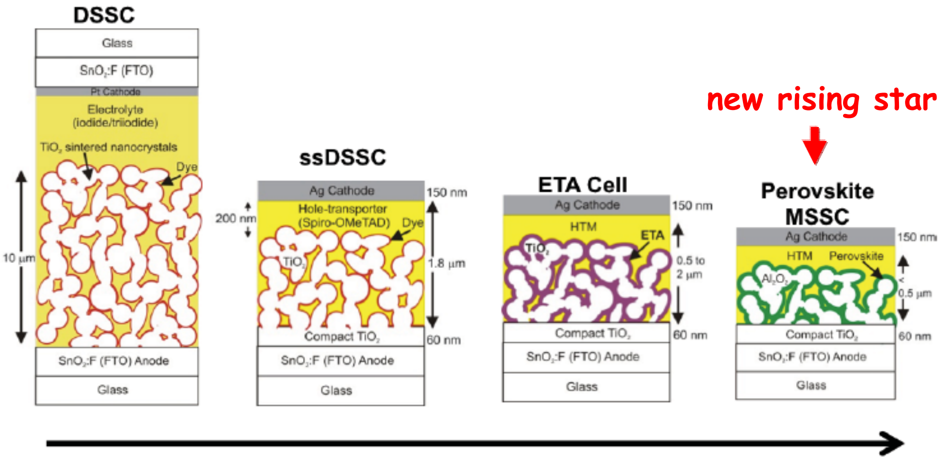




	Eff.(%)	J_{sc}(mA)	V_{oc}(V)	F.F.	$K_{eff}(s^{-1})$	τ_{eff}(s)	$R_k(\Omega)$	$R_w(\Omega)$	$D_{eff}(cm^2/s)$
ZnO NW	0.45	1.93	0.49	0.48	3.02	0.33	873	0.33	7.6x10^{-4}
ZnO ND	0.62	2.12	0.54	0.54	4.57	0.22	608	0.53	6.5*10^{-4}
P25	3.6	9.37	0.58	0.66	9.33	0.11	54	0.60	7.6*10^{-5}

Unique growth of 1-D structure plus the in-house developed **EIS** analysis to enhance the surface area and transport for next generation solar cells.
-J. J. Wu, et al., ChemPhysChem, (2009) Vol. 10. p.2698-2702

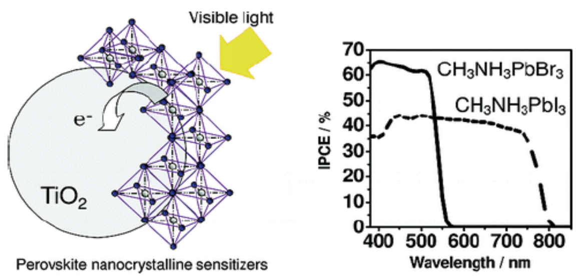
Technology Development

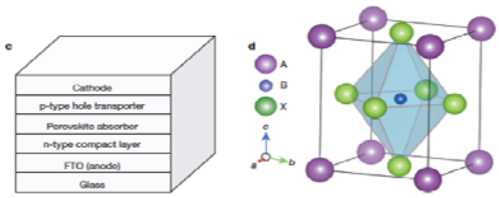


Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

Akihiro Kojima,† Kenjiro Teshima,‡ Yasuo Shirai,§ and Tsutomu Miyasaka*,†,‡,||

J. AM. CHEM. SOC. 2009, *131*, 6050–6051





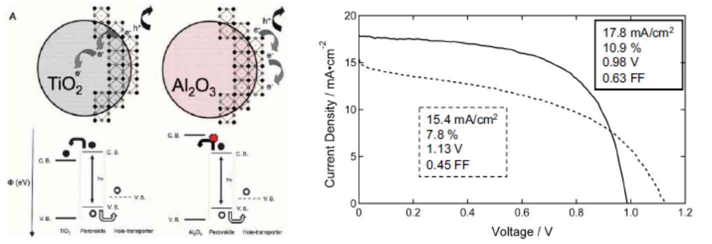
X = Cl^-, Br^-, I^-
B = Pb, Sn, Ge ...
A = ORGANIC ($CH_3NH_3^+$)

ABX_3

Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites

Michael M. Lee,[1] Joël Teuscher,[1] Tsutomu Miyasaka,[2] Takurou N. Murakami,[2,3] Henry J. Snaith[1*]

SCIENCE VOL 338 2 NOVEMBER 2012 643



Extremely hot competition!

OPEN

Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%

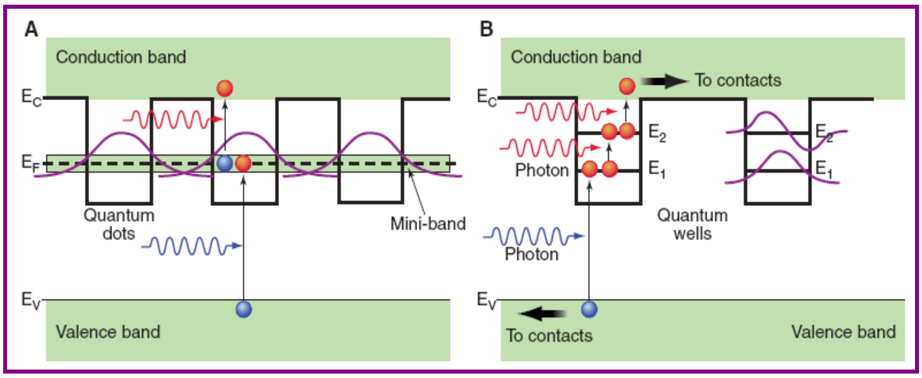
SUBJECT AREAS:
NANOPHOTONICS
OPTICAL MATERIALS AND DEVICES
INORGANIC CHEMISTRY
APPLIED PHYSICS

Received
5 July 2012
Accepted
6 August 2012
Published
21 August 2012

Hui-Seon Kim[1], Chang-Ryul Lee[1], Jeong-Hyeok Im[1], Ki-Beom Lee[1], Thomas Moehl[2], Arianna Marchioro[2], Soo-Jin Moon[2], Robin Humphry-Baker[2], Jun-Ho Yum[2], Jacques E. Moser[2], Michael Grätzel[2] & Nam-Gyu Park[1]

[1]School of Chemical Engineering and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea, [2]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

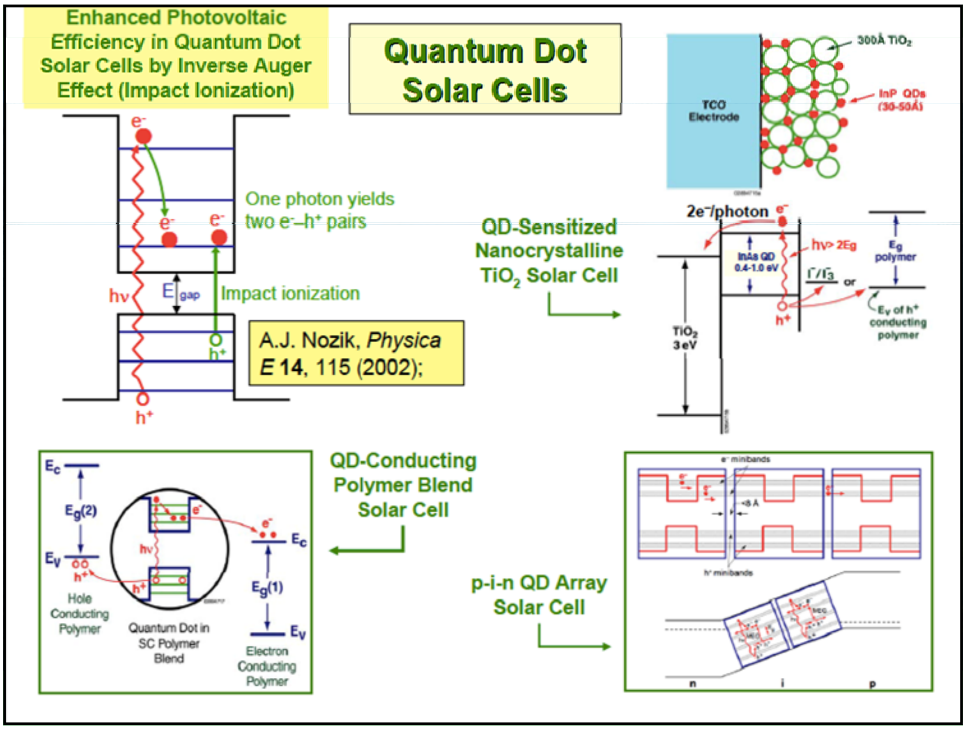
Quantum-dot Photovoltaic Device



Possible methods of circumventing the 31% efficiency limit for thermalized carriers in a single–bandgap absorption threshold solar quantum conversion system.

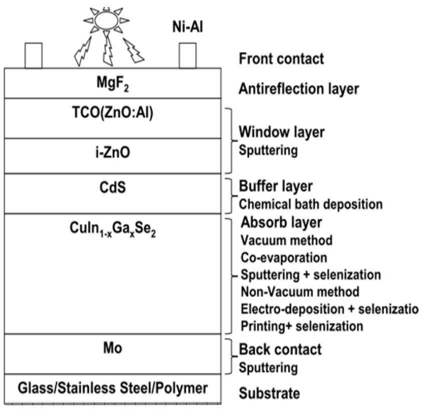
(A) Intermediate-band solar cell
(B) quantum-well solar cell

N. S. Lewis, Science **315**, 798 (2007)



Alternative Thin Film SCs

●Copper Indium Gallium Diselenide (CIGS) Solar Cells



Device structure

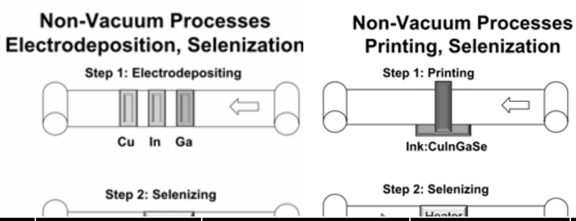
Advantages

- High cell efficiency (19.2%) and module efficiency (13.4%).
- The band-gap can be determined by the In/Ga ratio
- Can be deposited on flexible substrates
- Comparatively long lifetime

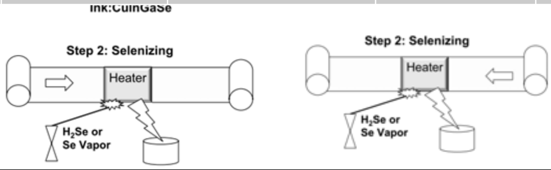
Disadvantages

- Limited availability of indium
- Toxicity of CdS n-type buffer layer

Manufacture of CIGS solar cell

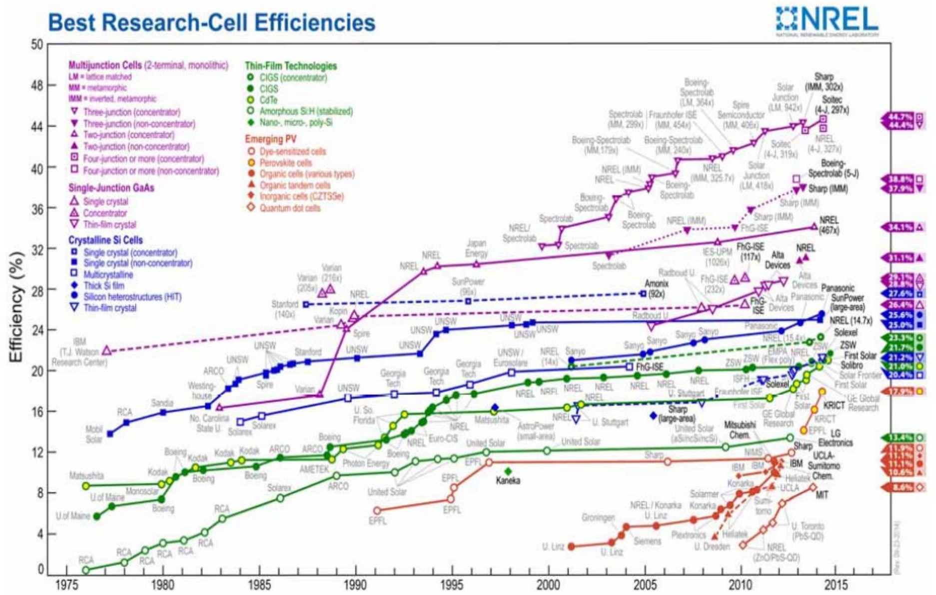


	Sputtering Selenization	Co-evaporation	Printing Selenization	Electrodeposition Selenization
Process control	Easy	Hard	Easy	Easy
Efficiency	Moderate	High	Low	Low
Material utilization	×	Modest	High	High
Hazardous H_2Se	✓	×	✓	✓
Production rates	Low	Low	High	High



PV Technology Status

Categories of solar cells			Efficiency
Si-based	Crystalline	Single crystalline	12-20%
		Poly crystalline	10-18%
	Amorphous	Si, SiGe, SiC	6-9%
Thin Film	Single crystalline	GaAs, InP	18-30%
	Poly crystalline	CdS, CdTe, Cu(In, Ga)Se_2	10-20%
New Concept	Nano & Organic	P3HT:PCBM, CuPC/C60, ZnO, TiO_2	≤9%



Solar-Fuel and Fuel-Cell

We seek as a "Holy Grail" a renewable energy source driven by solar energy that produce a clean and storable fuel….

- By Allen J. Bard and Marye Anne Fox, Acc. Chem. Res. 28 (1995) 141

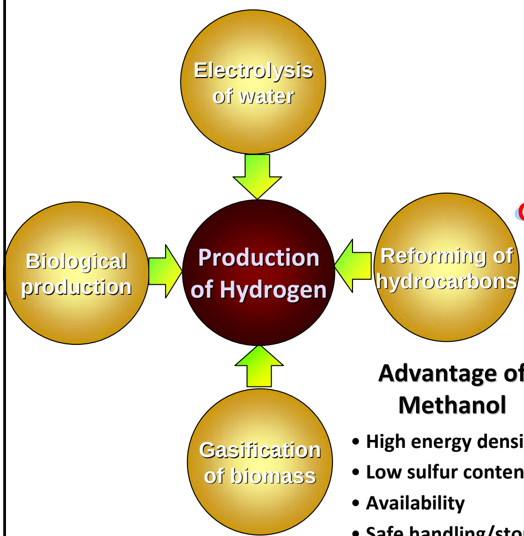
- Hydrogen, the purest and zero carbon emission
- Hydrocarbons with low carbon to hydrogen ratio

Outline

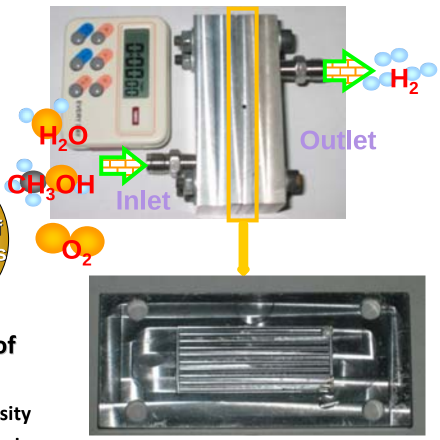
- Why hydrogen economy?
- What matters?
  - Choices of materials
  - Choice of fuels or electrolytes
  - Nano enhancement
  - Surface/Interface effect

  etc. ….
- Case studies
- ZnO-, GaN-nanorods based
- Graphene oxides and hybrids

Hydrogen (Energy) Age to Come



Micro-reformer



Advantage of Methanol

- High energy density
- Low sulfur content
- Availability
- Safe handling/storage
- Relatively low reforming temp
- Low CO formation

Challenge of Hydrogen Source

Liquid Fuel vs Hydrogen Bottles

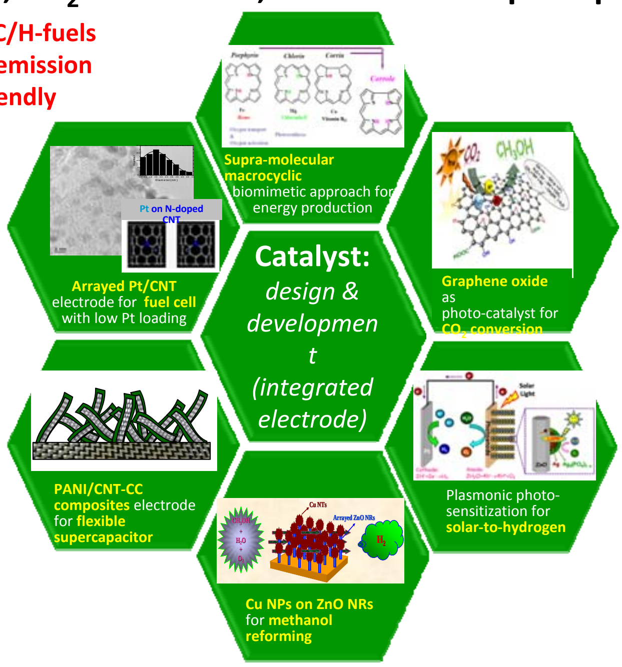
48 hours of operation at 5 KW is either：

or

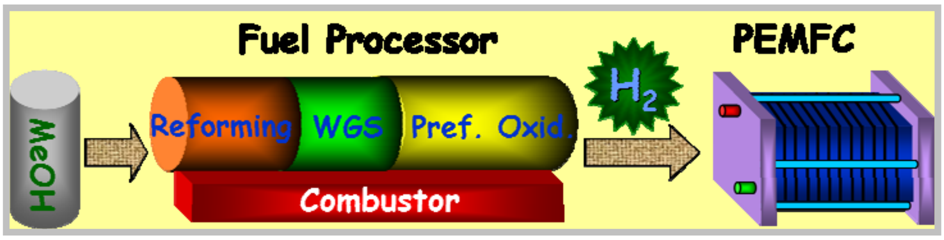
Fuel Processor with 55 Gallons of Methanol/Water Mixture

Fuel production, CO_2 conversion, fuel cell and supercapacitor

- **Hydrogen or low C/H-fuels**
- **Reducing carbon-emission**
- **Environmental friendly**
- **Earth-abundant**
- **Mobile**



Reformed Methanol Fuel Cell Systems



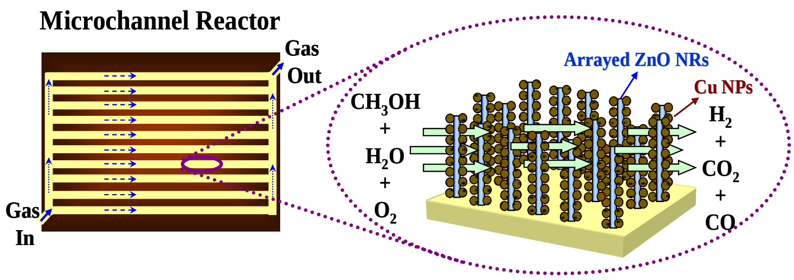
Reforming Reaction：

- **Steam Reforming of Methanol**
  $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ $\triangle H_0$ = +49.4 kJ/mol [Endothermic]
- **Partial Oxidation of Methanol**
  $CH_3OH + 1/2O_2 \rightarrow CO_2 + 2H_2$ $\triangle H_0$ = -192.2 kJ/mol [Exothermic]
- **Oxidative Steam Reforming of Methanol (Autothermal Reforming)**
  $CH_3OH + a\ O_2 + b\ H_2O \rightarrow CO_2 + (4a+3b)H_2$ $\triangle H_0$ ~ 0 kJ/mol

Next-generation High-efficiency Reformers for H-production with Low CO Emission

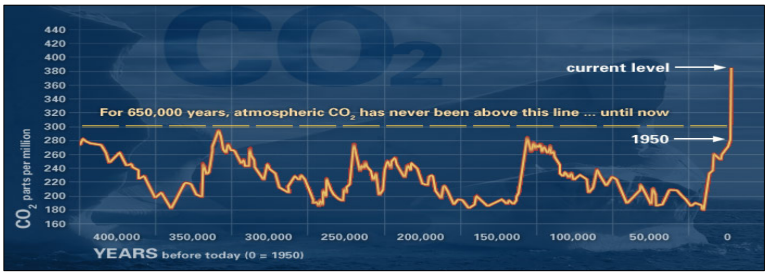
Nanostructured ZnO@Cu as Catalyst for Microreformers

Y. G. Lin, et al., Angew. Chem. Int. Ed. 48, 7586-7590 (2009)



Superb catalytic performance of the Cu NP-decorated ZnO NR nano-structures for methanol reforming in a microreformer has been reported. The breakthrough can be to the larger surface area and enhanced dispersion of fine Cu NPs, formation of microstrain, the modification of electronic structure of Cu species, and the existence of strong metal-support interaction effect. These results present new opportunities in the development of highly active and selective NR@NP nanoarchitectures for a wide range of catalytic reaction systems.

Global Climatic Changes by CO_2 Emission



→ Prevent further increase in atmospheric CO_2 concentrations!

http://www.way2science.com/index.php/global-warming

Towards a Total Solution for Energy:
Clean and Sustainable

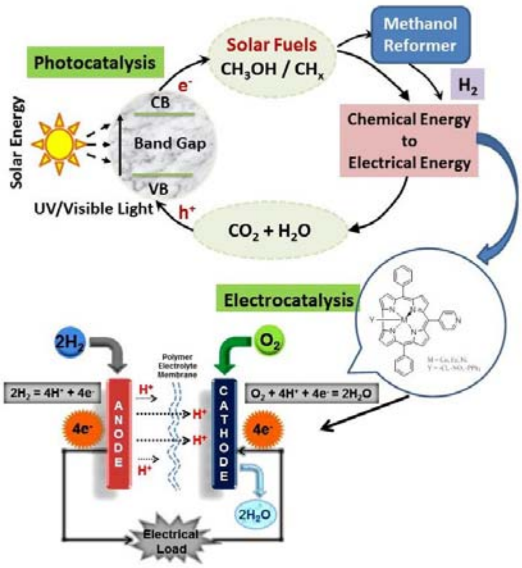


Photo-voltaic *vs.*

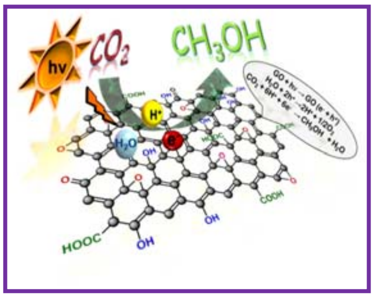
Photo-catalysis

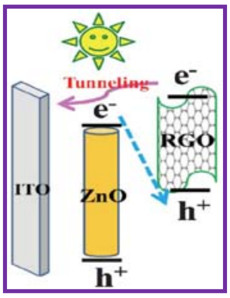
Issues:
- No sun no power in PV
- Storage technologies
- Cost

etc.

Case Study on Photo-catalyst

Graphene Oxides and their Hybrids for Solar H_2/Fuels and CO_2 Conversion Applications



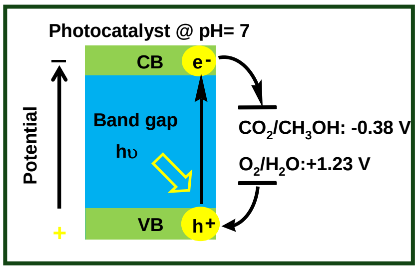


CO_2 Conversion

Photosynthesis

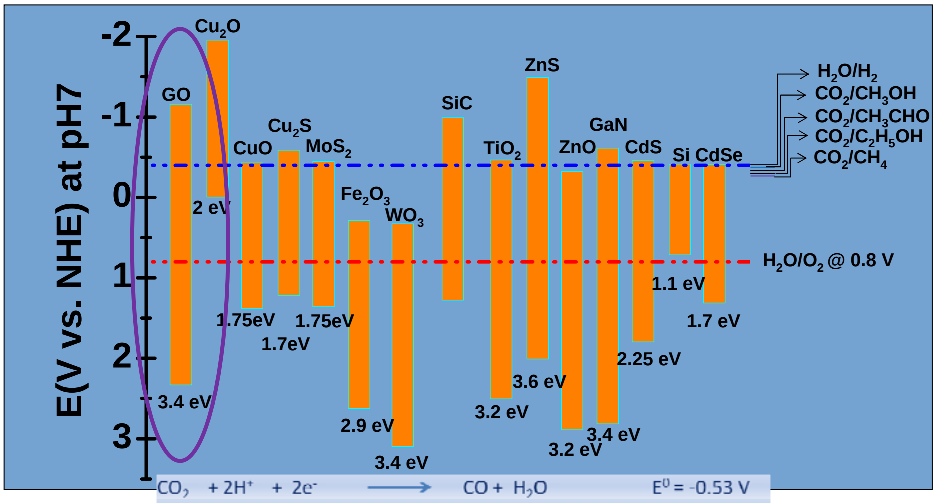
Trapping and subsequent photoinduced conversion to a value added product without using additional power sources!

Artificial Photosynthesis



- Low-cost, earth-abundant materials
- High solar-to-fuel efficiency
- Product selectivity

Band-edge Position of Selective Materials



$CO_2 + 2H^+ + 2e^-$	→ $CO + H_2O$	$E^0 = -0.53$ V
$CO_2 + 2H^+ + 2e^-$	→ HCO_2H	$E^0 = -0.61$ V
$CO_2 + 4H^+ + 4e^-$	→ $HCHO + H_2O$	$E^0 = -0.48$ V
$CO_2 + 6H^+ + 6e$	→ $CH_3OH + H_2O$	$E^0 = -0.38$ V
$CO_2 + 8H^+ + 8e$	→ $CH_4 + H_2O$	$E^0 = -0.24$ V
$CO_2 + e^-$	→ $CO_2^{\bullet -}$	$E^0 = -1.90$ V

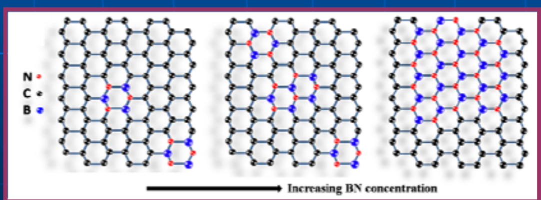
On-going graphene research activities at CCMS

Amazing graphene:

a fruitful research field with enormous technology implications

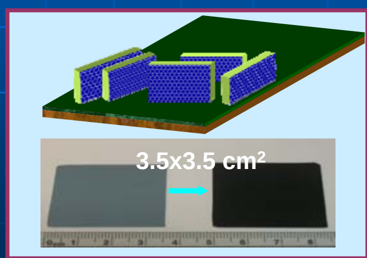
- **Gap opening by *in-situ* BN co-doping using CVD**
- **Graphene plasmonics and devices based on graphene w/wo BN (w/AFRL)**
- **Aligned few-layered graphene array**
- **Functional graphene and hybrids for supercapacitor and sensor**

Many more to explore…



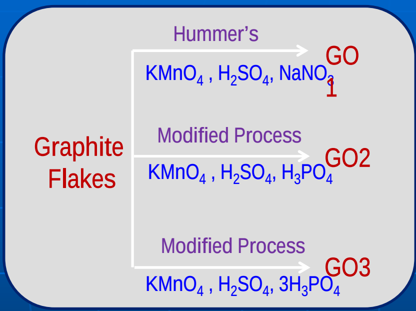
Homogeneous ternary graphene with 600 meV gap!

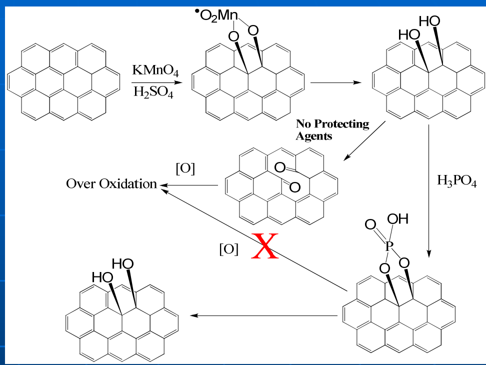
ACS Nano 7 (2013) 1333



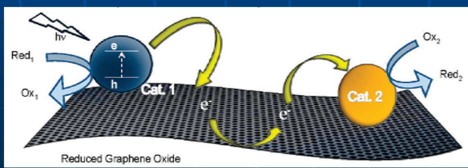
Carbon 49 (2011) 4911
US Patent (2012) 0156424 A1

Graphene Oxides by Hummer's Method & Modified Process





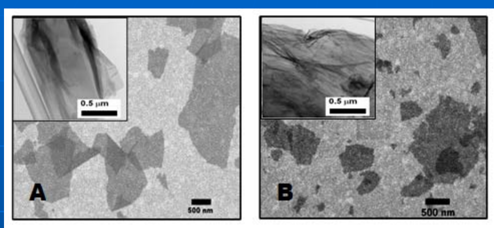
GO basal plane protection by H_3PO_4



Electronic structure depends on the stoichiometric C-to-O atomic ratio

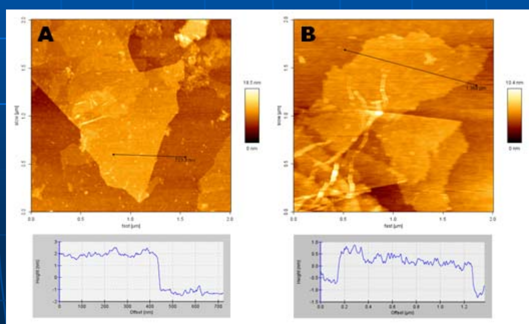
Nanoscale 5 (2013) 262 & Higginbotham *et al*. ACS Nano 4 (2010)

Morphology: SEM and AFM



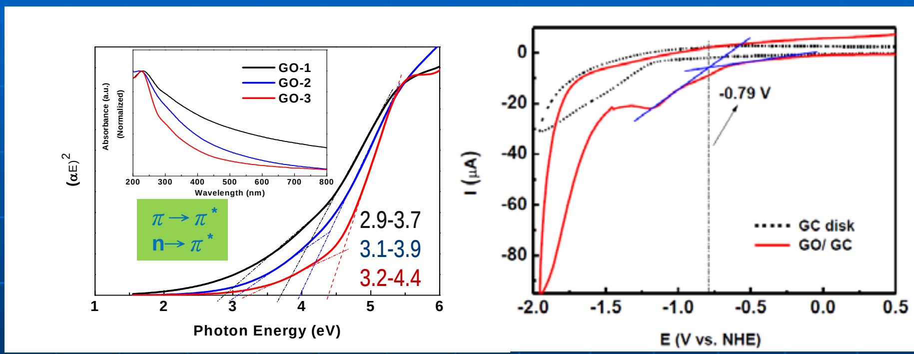
Wrinkled paper like morphology from phenolic and epoxy functional groups on the basal plane

Lateral dimensions of several micrometers and a thickness of 1-3 nm



Nanoscale, 2013, 5, 262–268

Band Gap and Conduction Band Position of Graphene Oxides

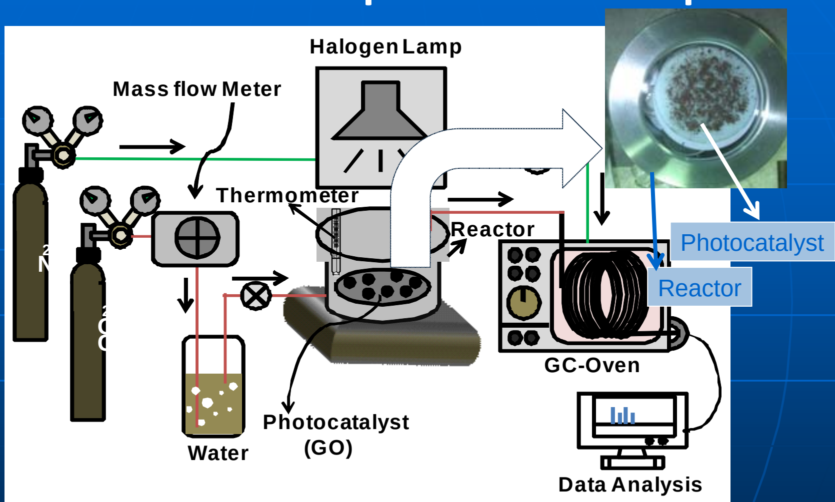


Intrinsic Semiconductor-like Absorption

CE: Pt , RE: Ag/AgCl
WE: GC
Electrolyte :0.1 M TBAP + AcCN (Sat. N_2)
Scan Rate : 100 mV s^{-1}

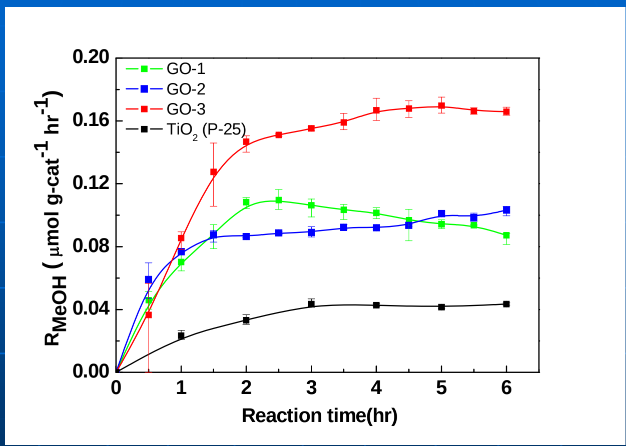
Nanoscale, 2013, 5, 262–268

Solar-to-Fuel Experimental Setup



Before reaction:
1.Purging N_2 for 1h, and then CO_2 for 1h.
2.Exp. conditions:
Flow rate: 4 ml/min(Continuous flow reaction)
Light source: ELH, Reaction temperature: 30 ℃

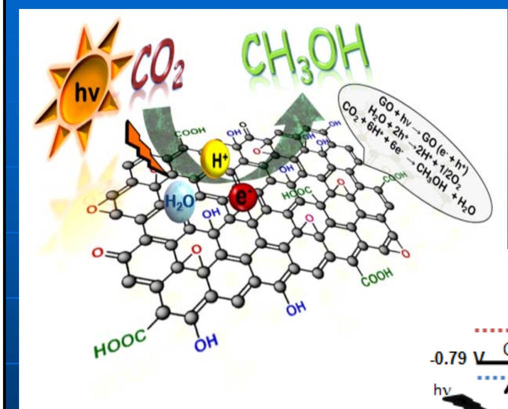
CO_2 to Methanol Conversion



Methanol formation rate of GO: 6 times higher than TiO_2

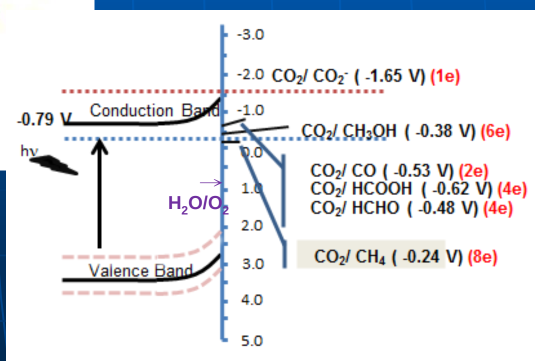
Nanoscale, 2013, 5, 262–268

CO_2 Reduction on GO



It's real and more effective than TiO_2 but …

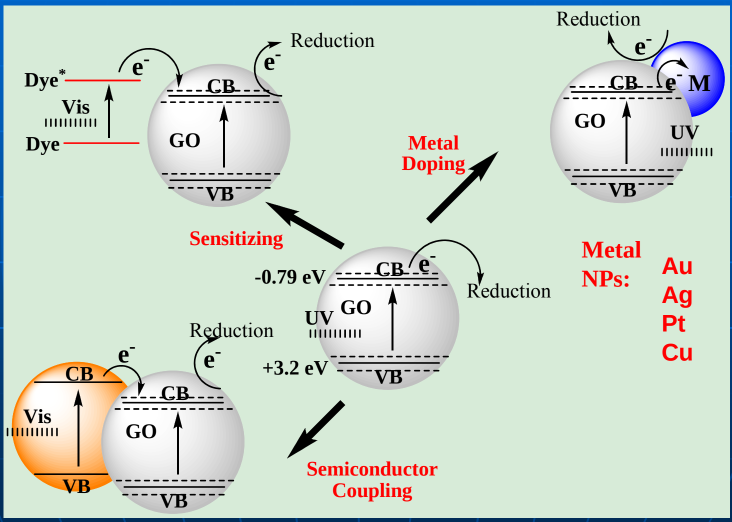
still lots of rooms to improve!



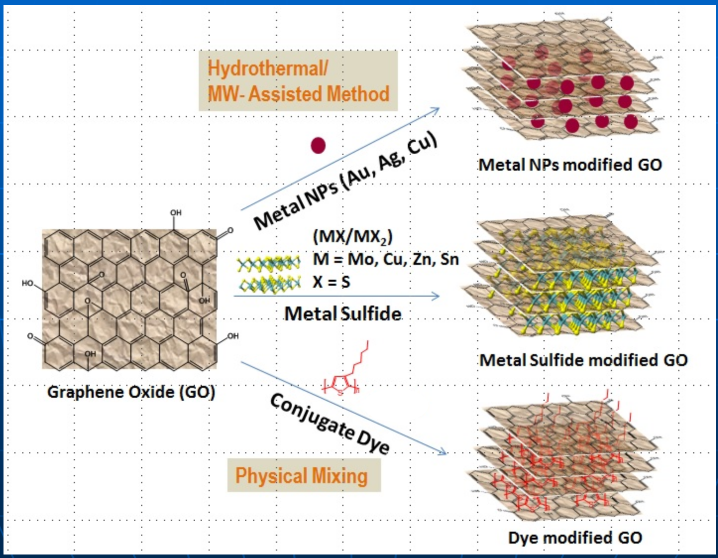
- **Higher production rate**
- **Higher stability**
- **Product selectivity**

etc.

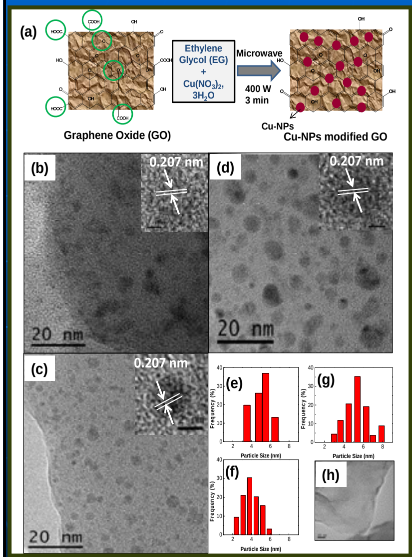
Sensitizers and co-catalysts

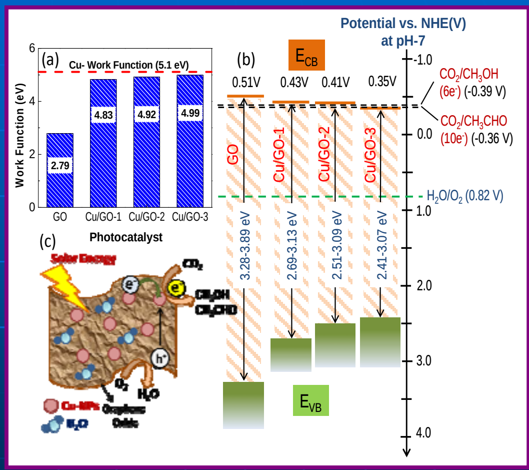


GO-based hybrids with metal NP, metal sulfide/oxide and molecular dye



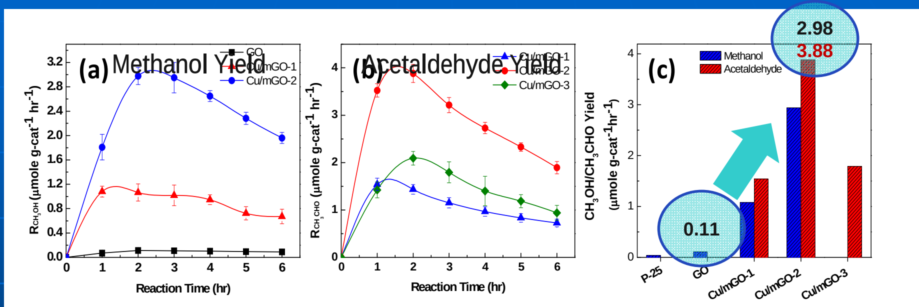
Highly Efficient Visible Light Photocatalytic Reduction of CO_2 to Hydrocarbon Fuels by Cu-NPs Decorated Graphene Oxide





Indrajit Shown, et al.,
Nano Lett. 14, 6097 (2014)

Photocatalytic CO_2 Reduction on Cu/GOs

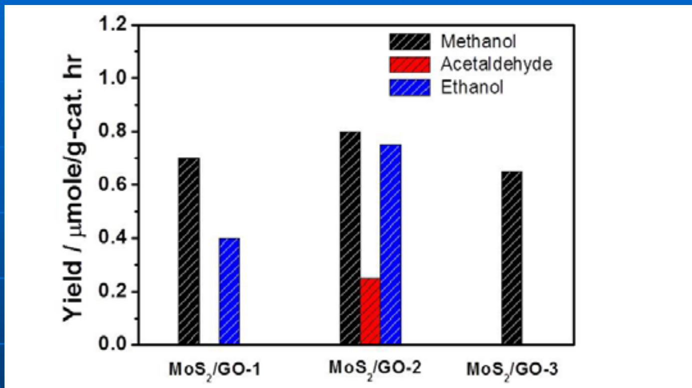


$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O \qquad -0.39$$

$$2CO_2 + 10H^+ + 10e^- \longrightarrow CH_3CHO + 3H_2O \qquad -0.36$$

- Methanol formation rate more than 25 times higher than GO
- Solar to fuel (methanol+acetaldehyde) yield increased 60 times

Solar Fuel Production Rate of MoS_2/GOs



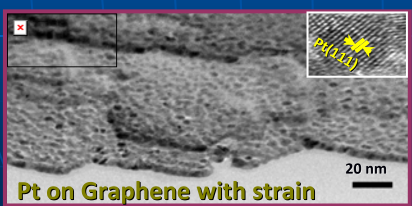
$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$ -0.39

$2CO_2 + 10H^+ + 10e^- \longrightarrow CH_3CHO + 3H_2O$ -0.36

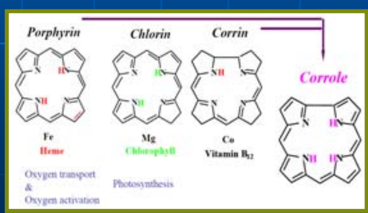
$2CO_2 + 12H^+ + 12e^- \longrightarrow C_2H_5OH + 3H_2O$ -0.33

Case Study on Electro-catalyst

CNTs/Graphene & Macro-cyclic Compounds as Electro-catalysts for Fuel Cells

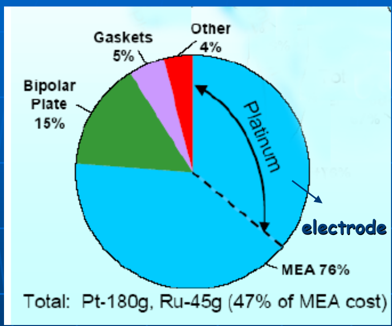


Pt on Graphene with strain



Cost Issue for Electro-catalyst

Cost of Fuel Cells (PEMFCs)



~ 50 millions cars in 2010 = 90,000 tons
Total Pt in the world ~ 28,000t!

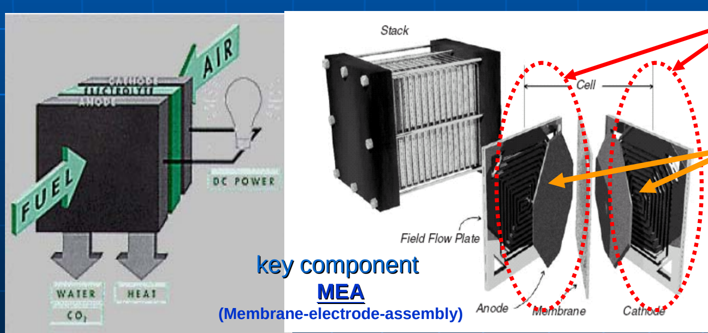
H. Gasteiger et al. Appl. Catal. B: Environ. 56 (2005) 9
X. Yu, Journal of Power Sources 172 (2007) 133

R & D goals
- Improving Efficiency in the Usage of Pt & Ru
- Searching for Non-precious Metal Catalysts

Why CNTs or Graphene?

➢ **Green and miniaturized products:**
- power for portable electronics

➢ **Integrated material / device design**
- enhanced electrochemical properties
- novel micro energy devices

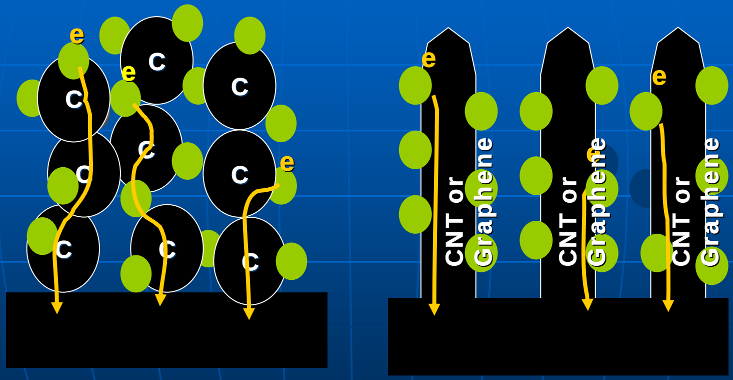


Chip Process?

CNTs or Graphene?

Carrier Pathways

Bumpy Road | **Expressway**

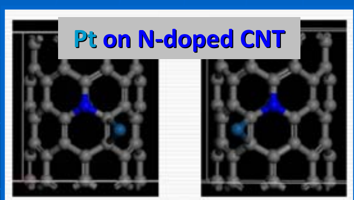


Convention al process

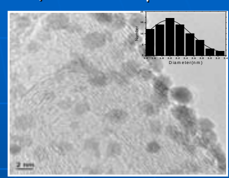
New approach: Direct growth

Hybrids Pt on Graphene or Carbon Nanotube

(I) Chemical Effect: accepter versus donor



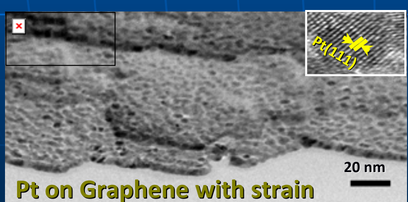
Pt/Ru on N-doped CNT



Only 1/10 of precious metal is needed.

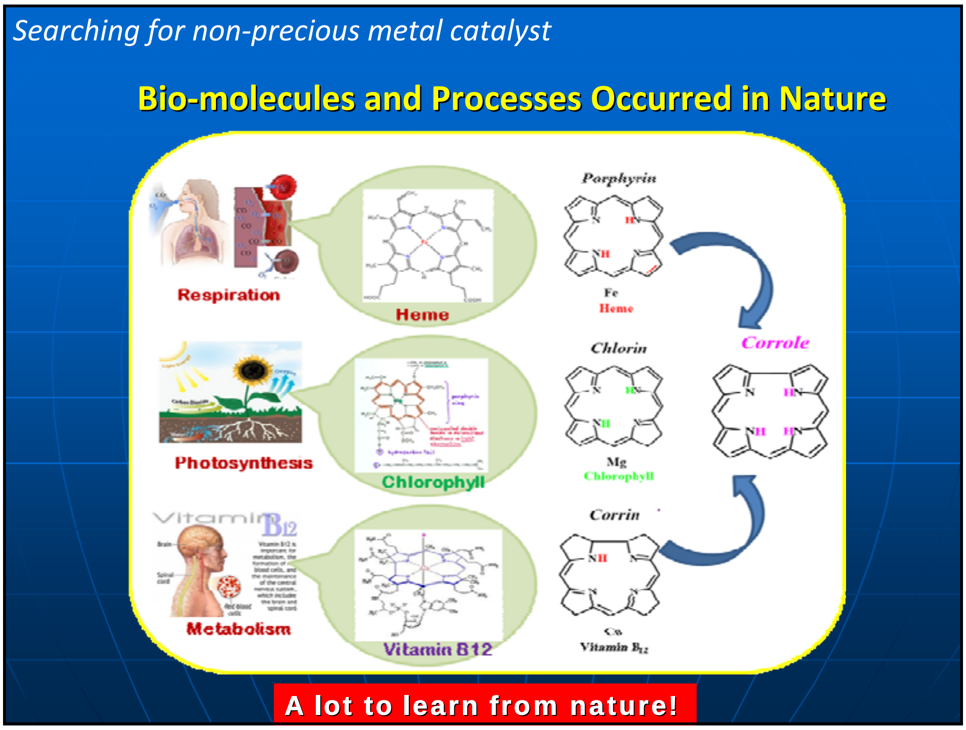
N-doping in CNT affects nucleation, growth and diffusion of Pt.
→ Better dispersion, activity and stability in fuel cells

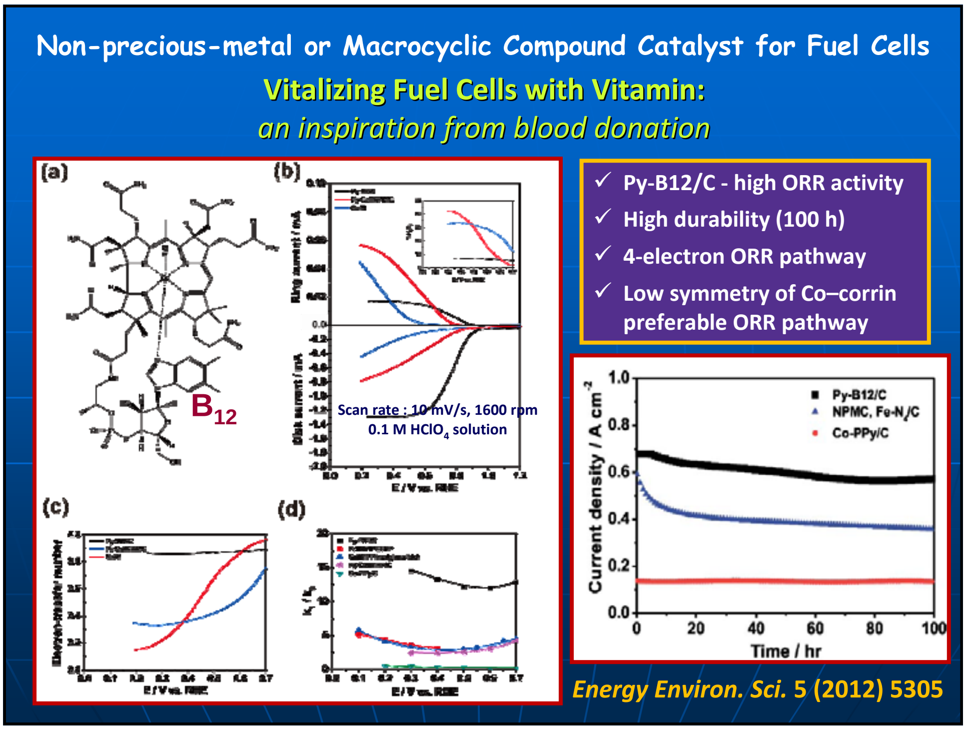
(II) Strain Effect: inward versus outward charge transfer



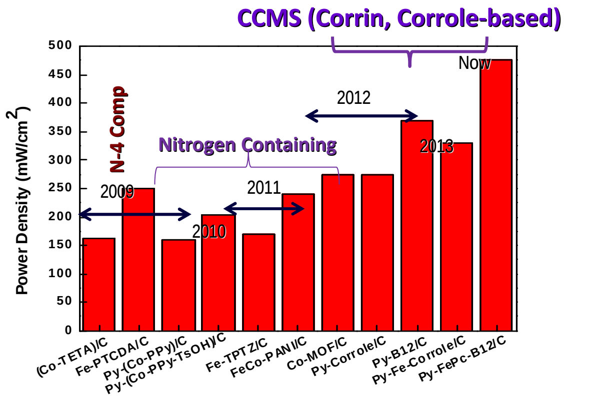
- Manipulation on the charge transfer of graphene has been demonstrated at CCMS.
  - Enhanced oxidation/reduction in H-based energy production/storage *via* EC route
  - Effective sensing of molecular/bio-events
- Surface modifications and layered hybrids with novel properties can be explored jointly

Large-scale , wafer-based processes of both graphene and CNTs are established at


Searching for non-precious metal catalyst
Bio-molecules and Processes Occurred in Nature
Respiration
Heme
Porphyrin
Fe
Heme
Corrole
Photosynthesis
Chlorophyll
Chlorin
Mg
Chlorophyll
Vitamin B12
Metabolism
Vitamin B12
Corrin
Co
Vitamin B12
A lot to learn from nature!


Non-precious-metal or Macrocyclic Compound Catalyst for Fuel Cells
Vitalizing Fuel Cells with Vitamin:
an inspiration from blood donation
(a)
B12
(b)
Scan rate : 10 mV/s, 1600 rpm
0.1 M HClO4 solution
E / V vs. RHE
(c)
(d)
✓ Py-B12/C - high ORR activity
✓ High durability (100 h)
✓ 4-electron ORR pathway
✓ Low symmetry of Co–corrin preferable ORR pathway
Py-B12/C
NPMC, Fe-N/C
Co-PPy/C
Current density / A cm-2
Time / hr
Energy Environ. Sci. 5 (2012) 5305

Power Density Comparison for Selected N_4-macrocyclics



J. Zhang et al., Electrochimica Acta 52 4532, 2009; J. P. Dodelet et al., Science 324 71, 2009 ; Z. F. Ma et al., Electrochem. Comm., 11, 206, 2009; C. Y. Wang et al., J. Am. Chem. Soc. 132, 1754, 2010; P. Zelenay et al., Science 332 443, 2011; J. J. Zhang et al., Electrochimica Acta 56 4744, 2011; D. J. Liu et al., Chem. Sci 3 3200, 2012; S. T. Chang et al. Energy Environ. Sci, 5, 5305, 2012; H. C. Huang et al. Adv. Funct. Mater., 22, 3500, 2012; H. C. Huang et al. J. Mater. Chem A., 1, 14692, 2013;

The original paper on B12 (Energy and Environmental Sci. 2012 has been highlighted by *Materials Today, Chemistry and Industry, Chemistry World, etc.*

Status and Expectation

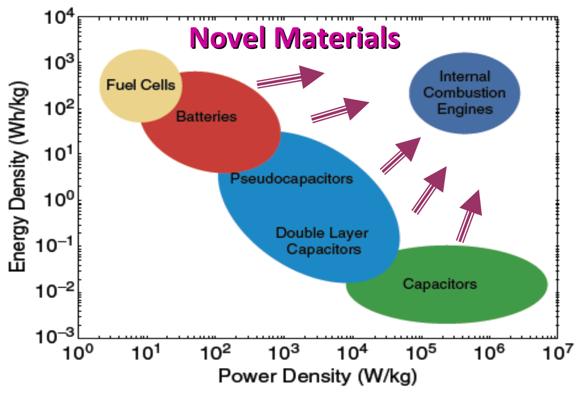


Figure 2. Comparison of the power density and energy density for batteries, capacitors, and fuel cells. (Energy is the capacity to do work; power is the rate at which work is done.)

Realization of Micro-Energy Device:

Nano-materials, Interface Physics and Chemistry

Outlook of Nano-Energy:

Resource-Conscious R & D
Environment-Health-Safety Awareness

- Hybrids, integrated device design
- Interface controlling/enabling
- IC-compatible, on-chip process
- Adding value to traditional/matured industry
- Next-generation electronic, optoelectronic, spintronic, energy, *etc.*, devices operating at RT (or practical T) & lower power/cost

Better Life and Better Earth
Creativity is the only Limit!

☆ Thank You

Embracing Diversity: Interdisciplinary, Cross-institution and International

~ 40+ Postdocs/RA/Students from 8 Departs/Institutes