*22nd National NSF EPSCoR Conference*
*October 24-28, 2011*

The Coeur d'Alene

# Nanotechnology for Renewable Energy:
# Playing photons and electrons in low-dimensional carbon nanostructures

**Judy Wu**

**Department of Physics and Astronomy**

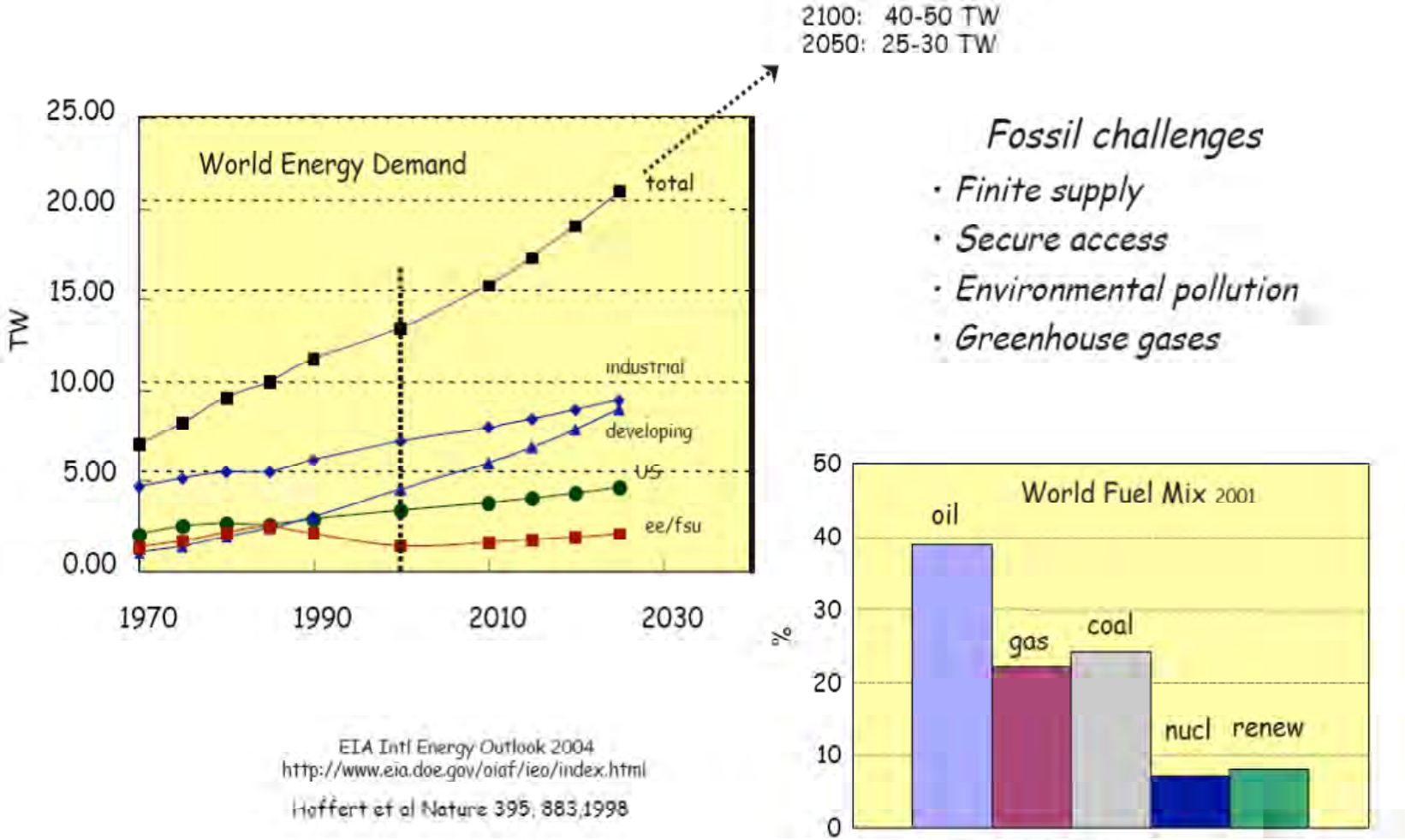
**University of Kansas**

# Outline

- Introduction
- NSF EPSCoR Kansas Nanotechnology for renewable energy team
- Carbon-based Nanostructured electrochemical photovoltaics
- Graphene photonic and plasmonic transparent conductors for thin film photovoltaics
- Summary and future work

# World Energy Demand and Fuel Mix

***Current and Projected to 2100***




**EIA-Energy Information Administration**

# Fossil Energy Resources are <u>Limited</u>

| Table III: World Energy Resources and Availability. | |
|---|---|
| **Resource** | **Energy Potential (TWy)** |
| Oil and gas (conventional) | 1,000 |
| Oil and gas (unconventional) | 2,000 |
| Coal | 5,000 |
| Methane clathrates | 20,000 |
| Oil shale | 30,000 |
| Uranium (conventional) | 370 |
| Uranium (breeder) | 7,400 |
| Sunlight on land | 30,000 per year |
| Wind | 2,000 per year |
| Fusion (if successful) | 250,000,000,000 |

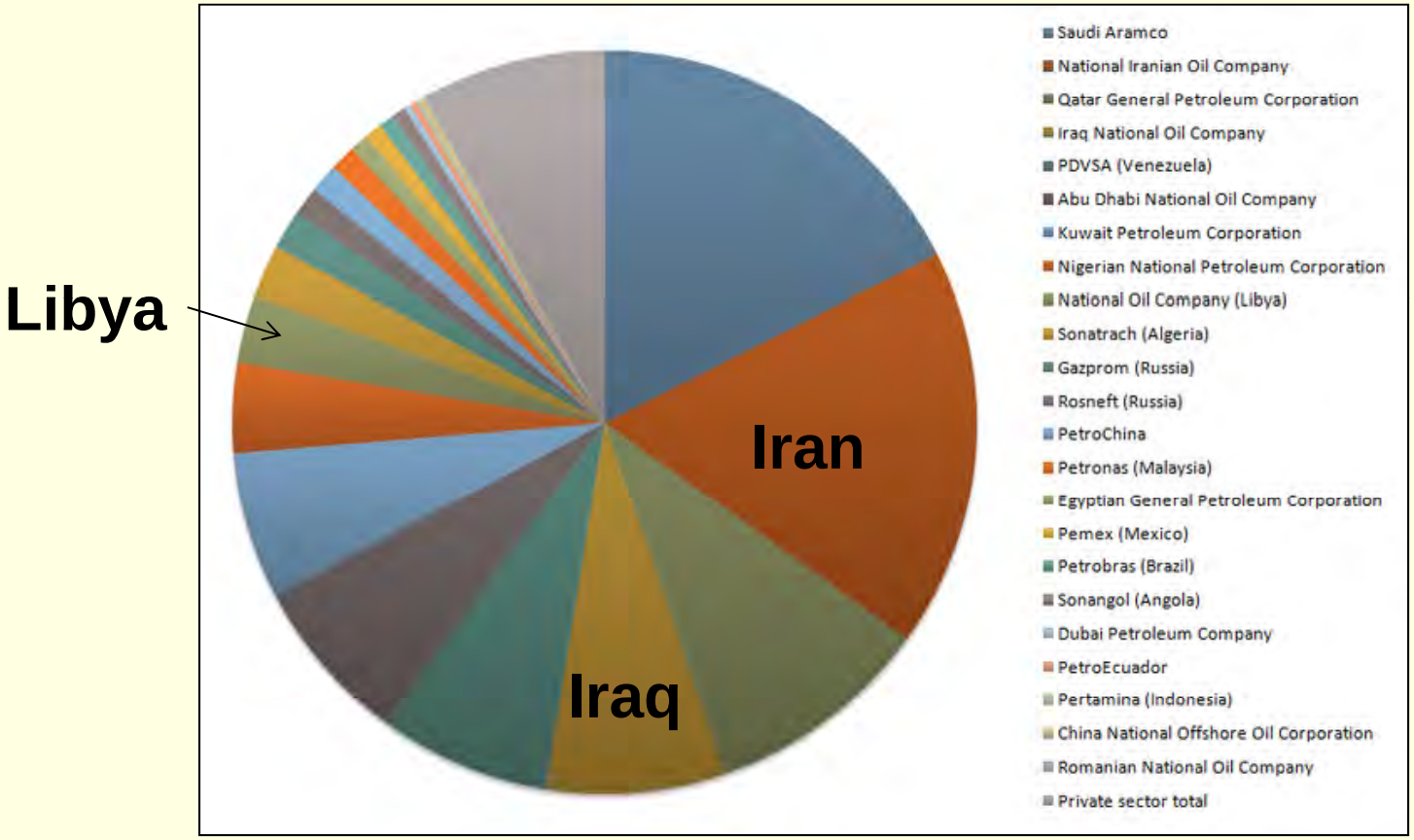
**Run out in few hundreds of years**

**Limited**

**Unlimited**

# Total World Reserves Today

***The 50 Largest Oil Companies = 1.73 Trillion Barrels***




**The U.S. is <u>not</u> on this list**

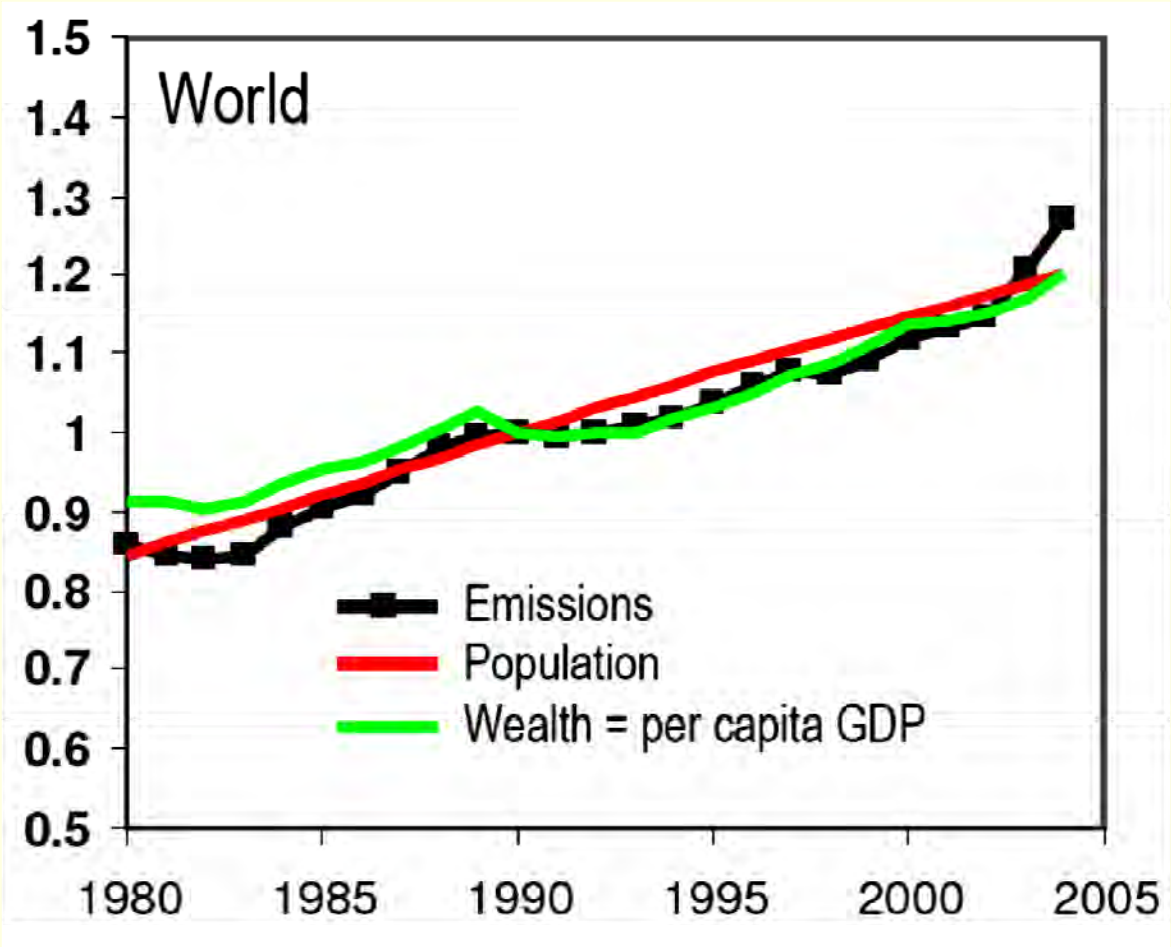
# Regional Instability and Threats to National Security

Libya: March 2011

**Oil Price "Roller Coaster": $100+ per Barrel and Rising**

# $CO_2$ Emissions, Population and Wealth

***Fossil Fuel Consumption Dominates Emissions***




IPCC report

# Energy Demands:

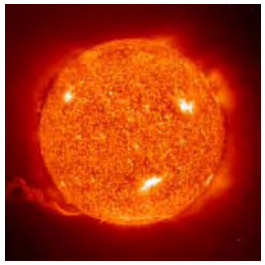
Energy consumed on Earth:

$4.1 \times 10^{20}$ J/yr

13 TW

Expected to double by: 2050

Expected to triple by: 2100

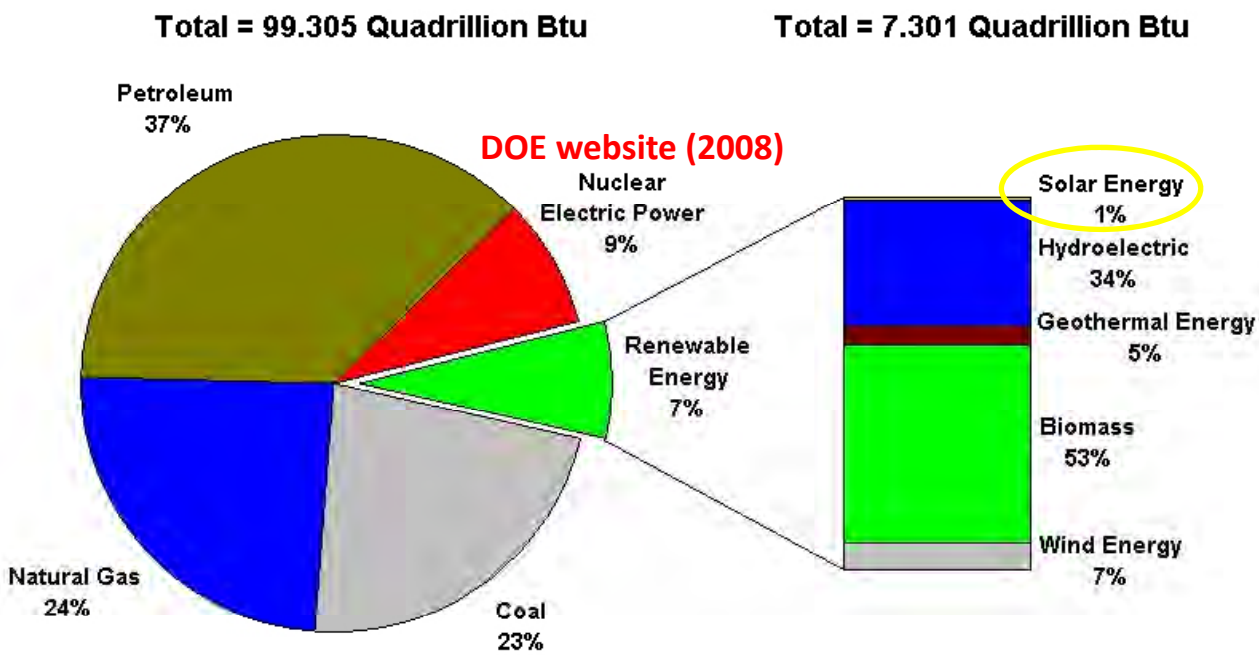


Energy from Sun striking Earth:

$4.3 \times 10^{20}$ J/hr

Mechanisms powered by Sun:

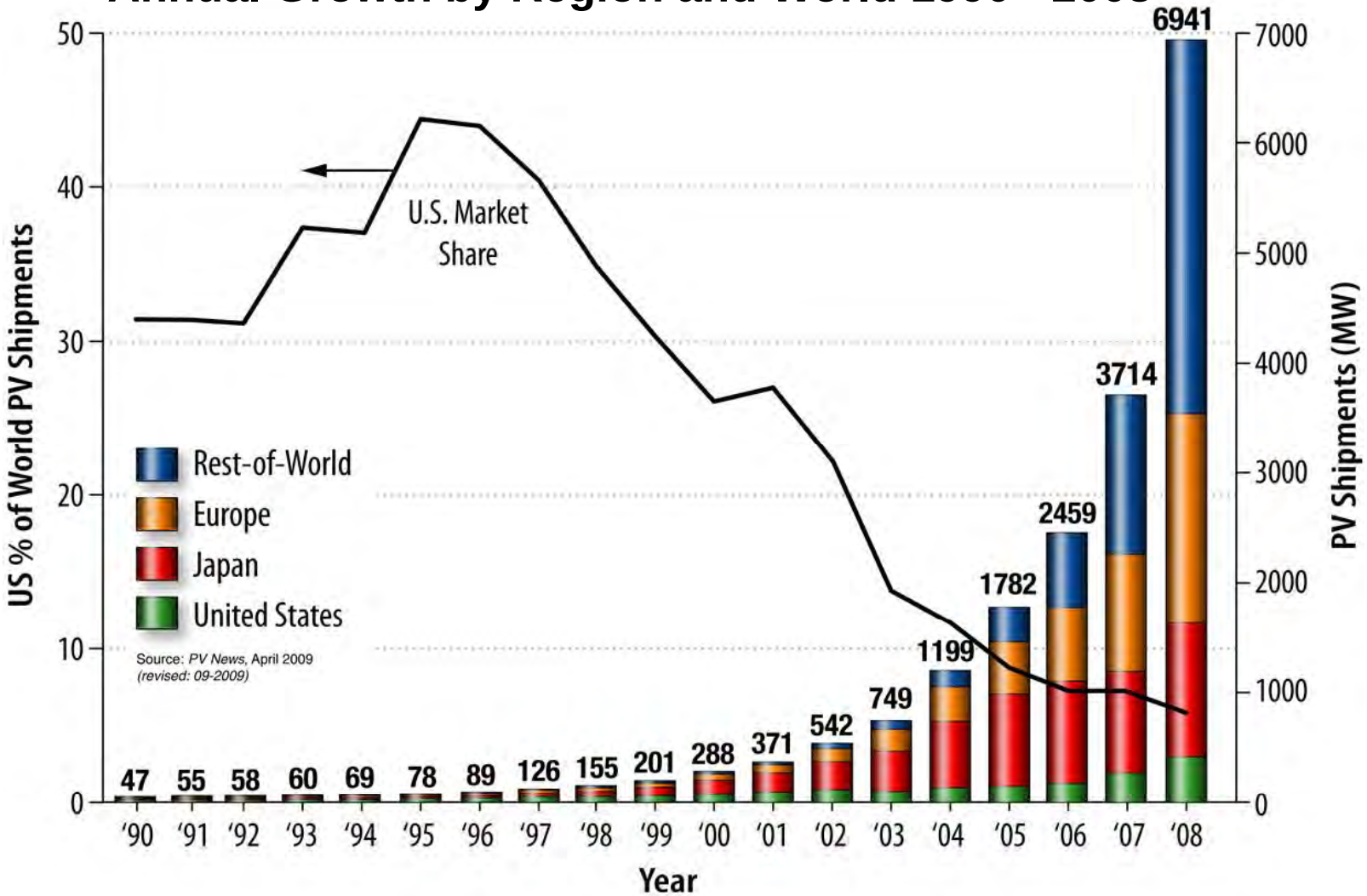
- Global wind/ocean currents
- Photosynthesis
- Evaporation/condensation




N.S. Lewis and G. Crabtree, "Basic Research Needs for Solar Energy Utilization: report of the Basic Energy Sciences Workshop on Solar Energy Utilization, April 18-21, 2005"

# Photovoltaic: A Thriving Global Industry & Markets

## Regional PV Shipment Growth in MWp
## Annual Growth by Region and World 1990 - 2008



# Nanotechnology for Renewable Energy (NRE)

www.solarenergy.ku.edu

- Judy Wu, Kansas University (PI)
- Jun Li, K-State University (co-PI)
- Francis D'Souza, Wichita-State U(Co-PI)

29 research groups from three Kansas research universities
in biology, chemistry, engineering and physics
Plus a broad collaboration nationally (NREL, ORNL, ANL, SNL, LANL, Ames, NASA),
internationally (Finland, Japan, China, Canada) and with industry network

# KANSAS EPSCoR

Partners in Science & Technology

PI: Kristin Bowmen-James

Three research subprojects:

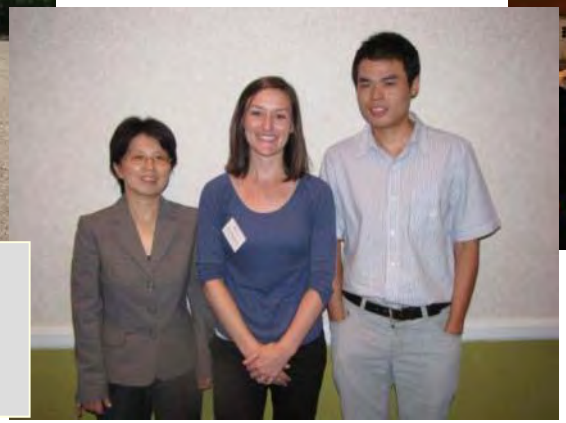
1. *Biofuels and Climate Change* (***BCC***)
2. *Climate Change and Mitigation* (***CCM***)
3. *Nanotechnology for Renewable Energy* (***NRE***)

These three research initiatives are linked with a diversity/workforce development project:

4. *Climate Change in Indigenous Communities* (***Pathways***)

A unique platform for research interaction and collaboration in energy, environment, economy, and interdisciplinary education

## REU Field trip to wind farm



**Poster award winners: Lina Zhao, Caitlin Rochford and Guowei Xu**

**Dr. Harrington (CCM):**

## Consilience and Collaboration:

**The Changing Nature of Scholarship**

**In collaboration with the Pathways, recruited Haskell student Michael Dunaway to NRE REU 2010-2011 NSF Graduate Research Fellowship**

**Dr. Abruna (Cornell): emc$^2$**

**High school students Terry Han, Richard Lu and Jonathan Gregory spent summer 2010 on solar Robot**

# NSF STEM renewable energy Scholarships program

**Judy Wu (PI), Cindy Berrie, Lucas Miller (Haskell), Val Smith, Barbara Twarog, Susan Williams**

**A renewable energy/nanotechnology course, seminars, field trips and outreach activities and renewable energy focused research with one of more than three dozen KU faculty mentors.**

**Oct. 1 2011 Kickoff picnic-KU football game (51 applications received and 14 funded, 3-year project 07/15/2011-07/14/2014)**

# Strong <u>Interdisciplinary</u> Team

***Broad Background***

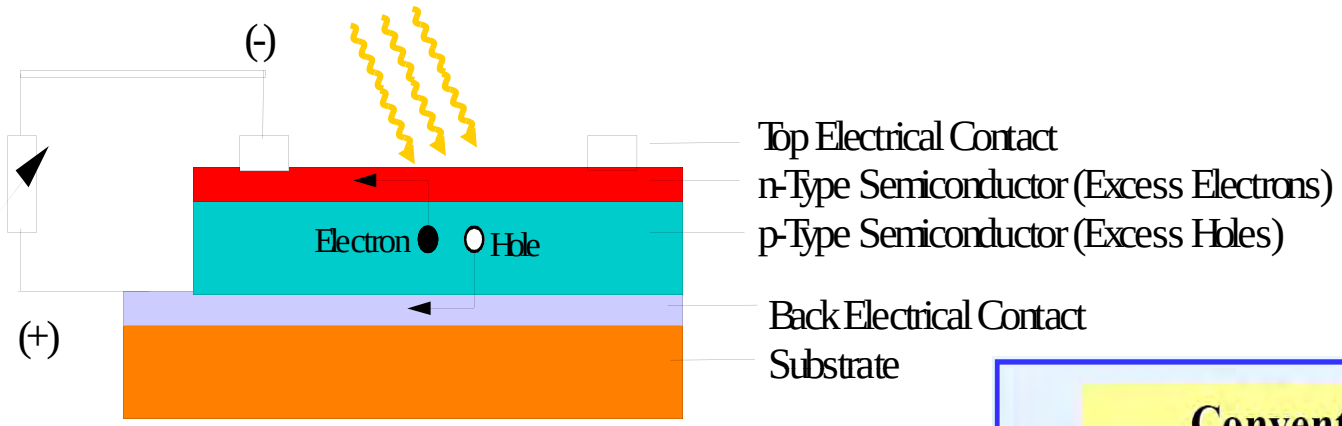
- **Nano-Structured Materials** (biological and synthetic)
- **Devices** (nanoscale to microscale)
- **Systems** (biofuels, integrated circuits)
- **Multi-Scale Characterization** (nanoscale,environmental)

***Unique Approaches***

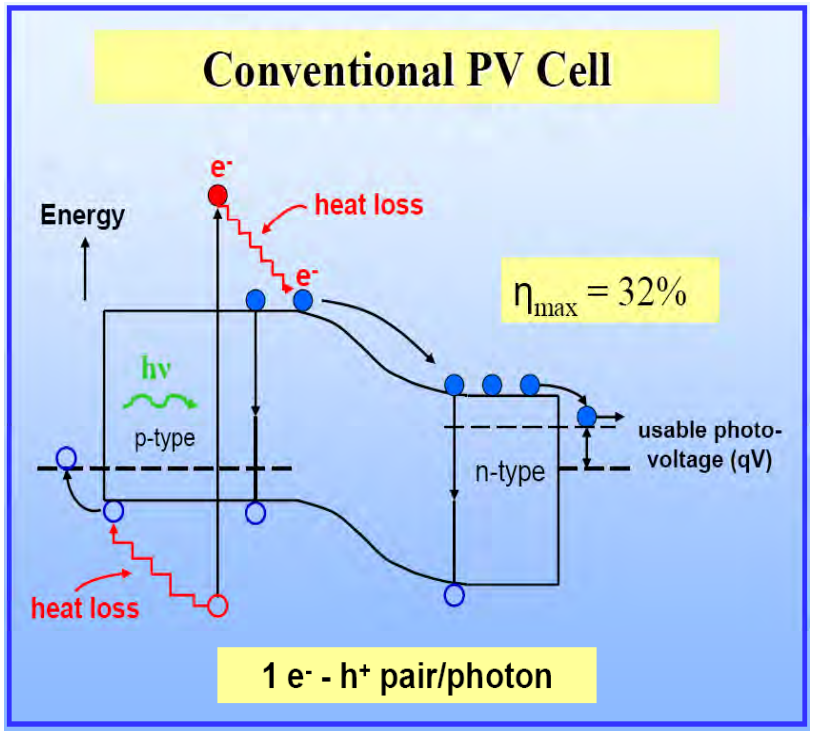
- **Solar energy capture, conversion occur at nanoscale**
- **Consists of multiple steps at multiple scales**
- **Involves biology, chemistry, physics, engineering, etc.**
- **Many "nano" tools were not available until recently**

# Principle of Semiconductor Solar Cells

## Devices That Convert Sunlight Directly Into DC Electricity



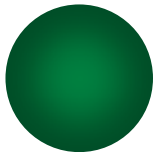

**Manipulation of photon absorption and electron transport at nanoscale is the key to high efficiency and low cost solar cells.**



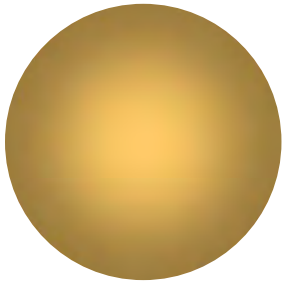
# The Relative Size of Things

Hydrogen

Carbon

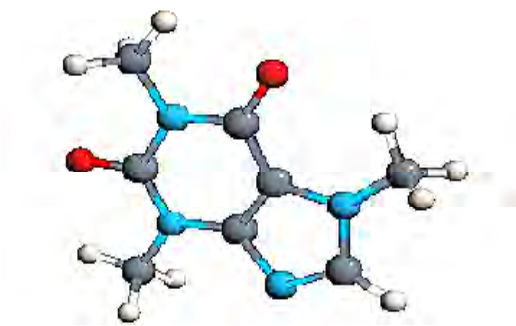


Gold



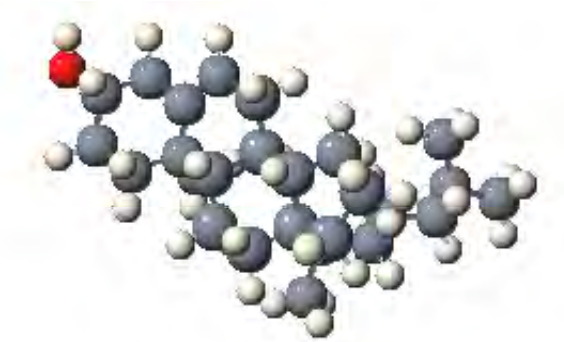
Diameter: ~0.1 nm

Caffeine



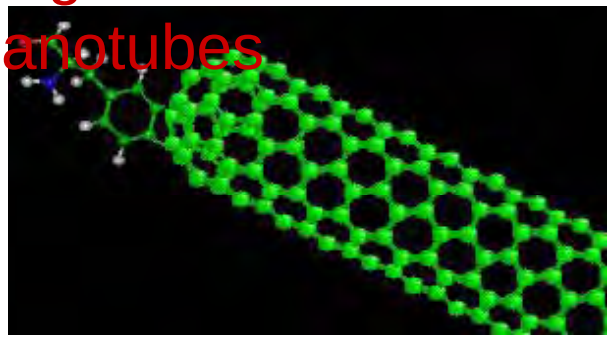
~0.8 nm

Cholesterol



~1.5 nm

Single-Wall Carbon Nanotubes



Diameter: 1-2 nm

Length: up to millimete

**The ability to tweak things at nanoscales allows us to design materials and devices with desired properties**

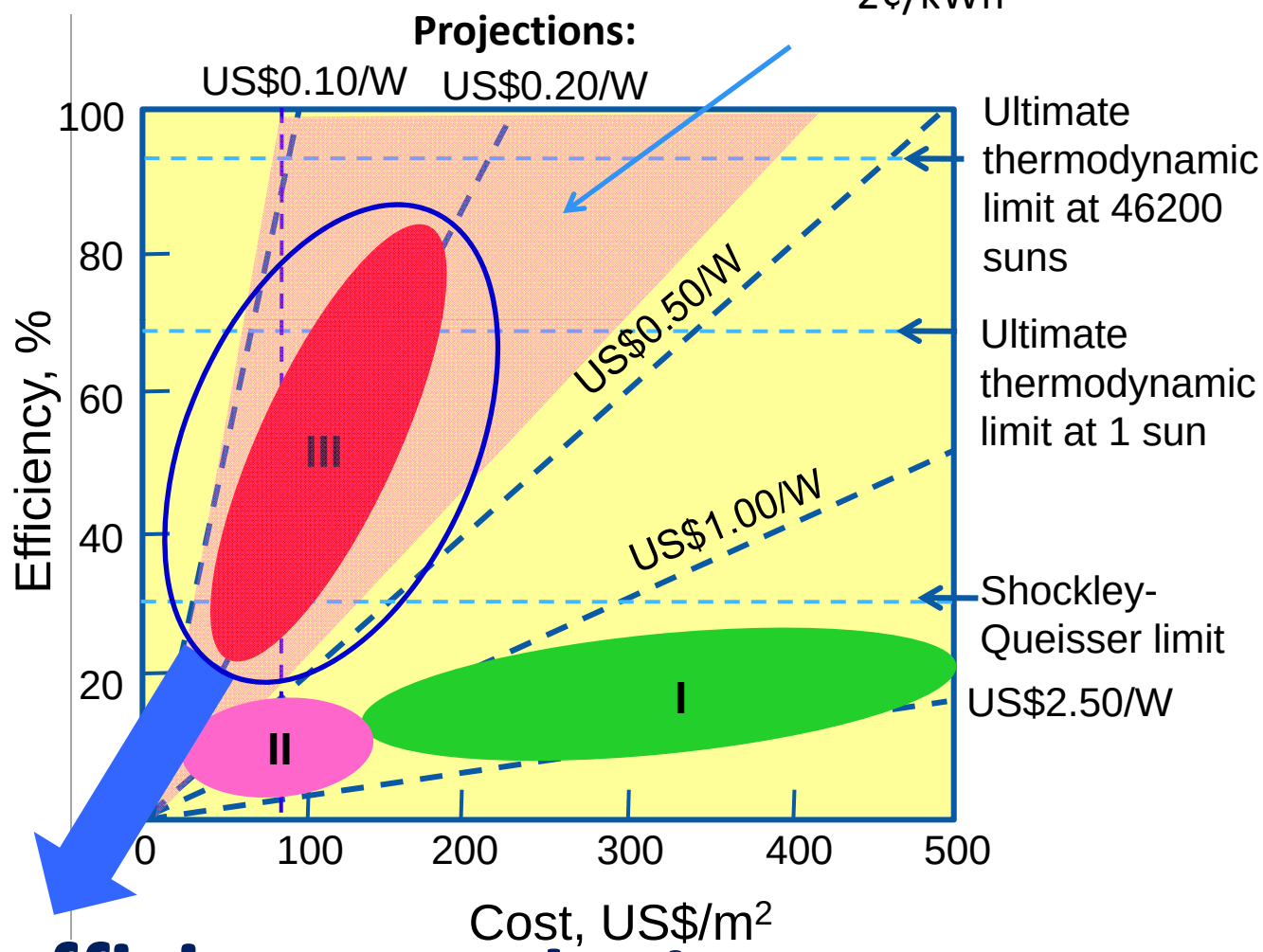
# Three Generations of Solar Cells

I) <u>Wafer based</u>
Silicon
Lab record: 25%
Module record: 23%

II) <u>Thin-film</u>
Different semiconductor(s)
Reduced material cost
Lab record: 26% (GaAs)
17% (CdTe)
10% (a-Si)
Module record: 20% (pc-Si)

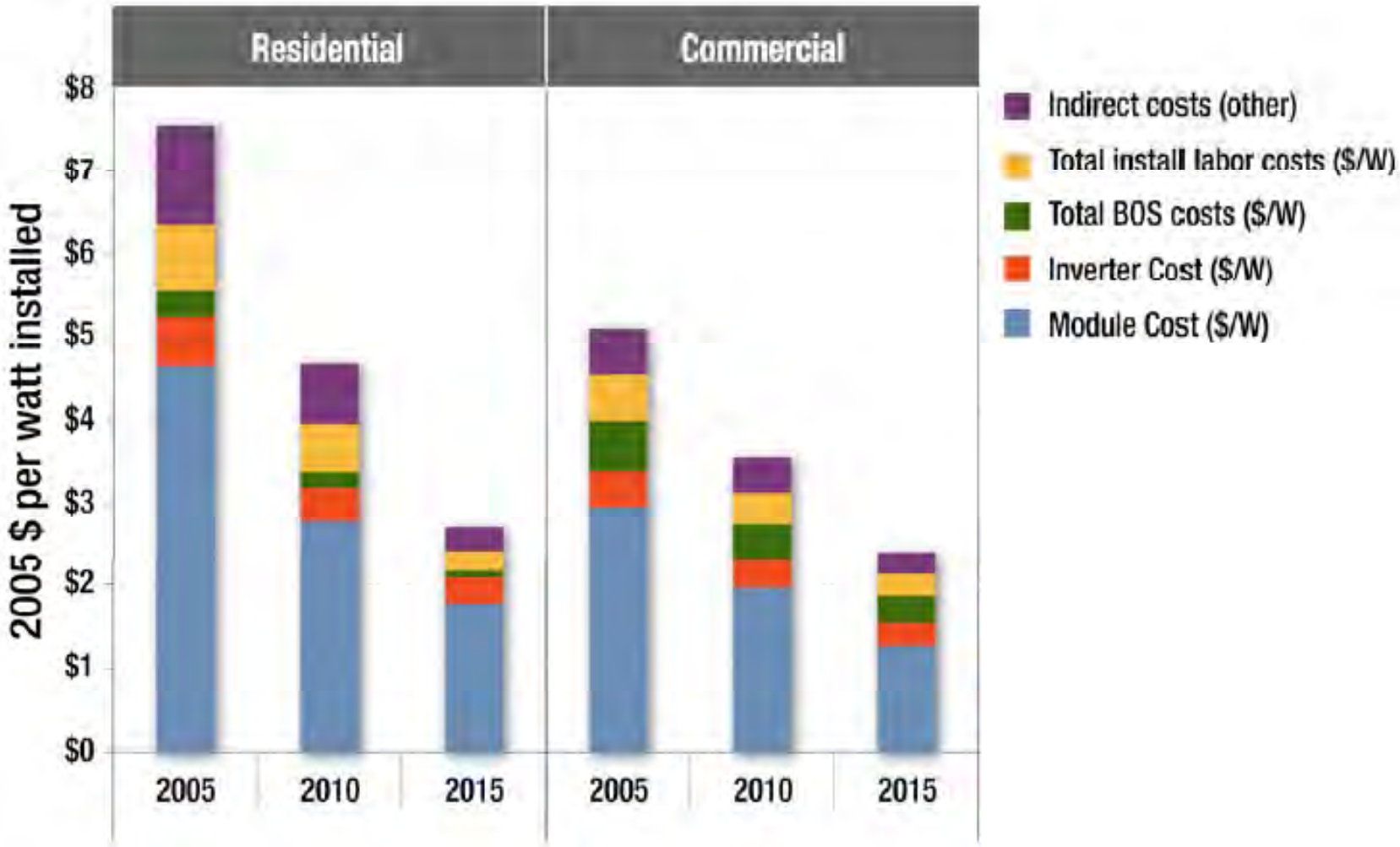
III) <u>Advanced thin-film</u>
Circumvent 1st gen. theoretical limit
Maintain low cost
Lab record: 34% (tandem)
Module record: ---

**Goals:** ~ 30¢/$W_P$
~ 2¢/kWh




**Enhancing efficiency, reducing cost**

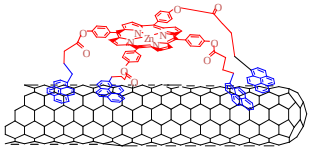
# Reducing PV system costs to grid parity will require significant reduction in the cost of all components



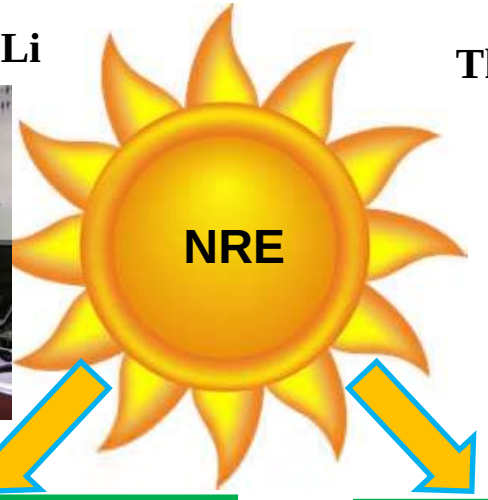

**Much of the cost reduction will have to be on the module level**

**Theme 1 leader: Jun Li**

Broad-band photosensitizer

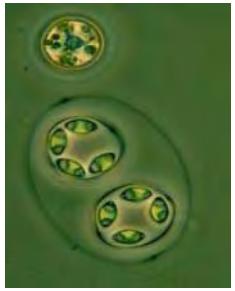


(D'Souza, Rillema-WSU)




**Theme 2 leader: Keith Hohn**

Algae



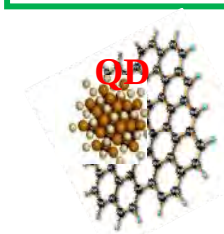
(Smith-KU)

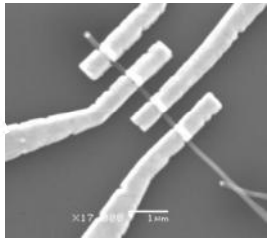
## Advanced solar cells--electricity:

- Cost-performance balanced solar cells
- Energy storage and distribution

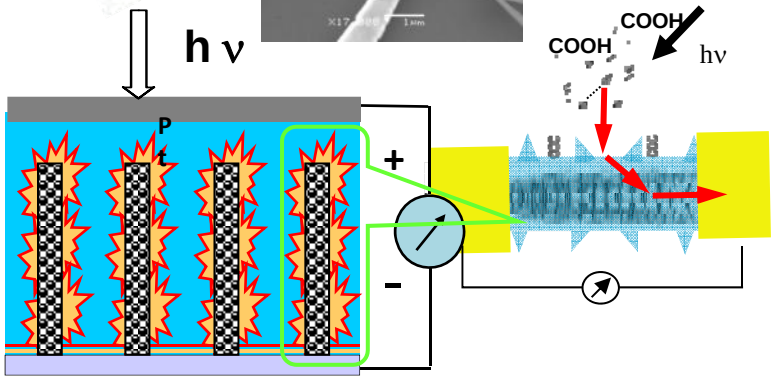
## Biomass to biofuel

- To improve environment
- To reduce reliance on fossil fuels
- To produce 36 Billions gal by 2022



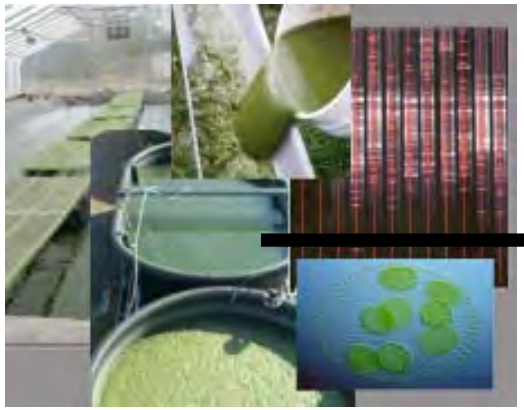



(Wu-KU)



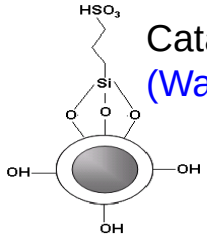

(Jun Li-KSU)

Nanostructured dye-sensitized solar cells



Algae production

(Schneegurt-WSU, Smith, Sturm-KU)



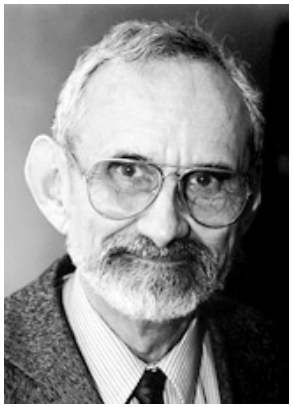
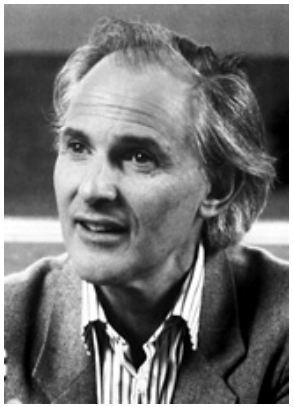
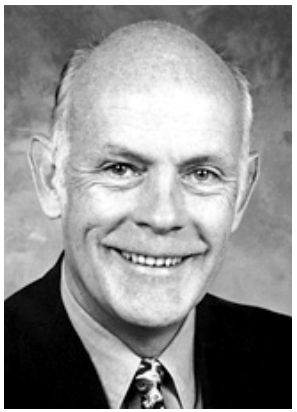

Catalysts for hydrolysis

(Wang & Hohn-KSU)

Biodiesel

(Williams-KU)

# Fascinating Carbon Nanostructures

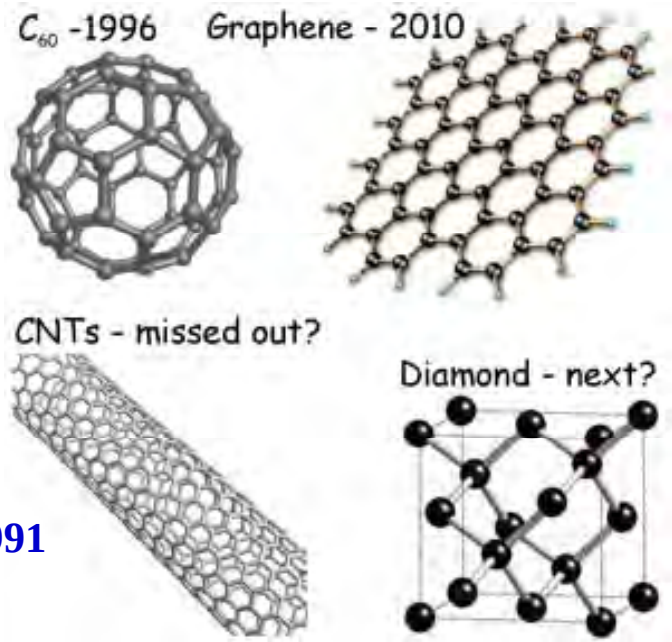




**Robert F. Curl Jr. Sir Harold W. Kroto Richard E. Smalley**

**Andre Geim** **Konstantin Novoselov**

**1996 Nobel Prize in chemistry for discovery of fullerenes**

**S. Ijima, 1991**




**2010 Nobel Prize in physics for the pioneer work on graphene**

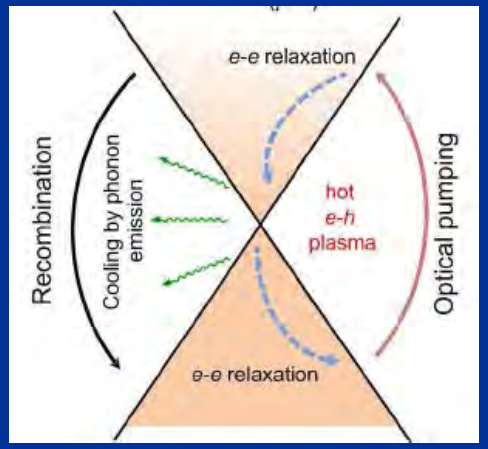
# Electronic Properties of Carbon Nanotubes

- **CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.**
- **Strength to weight ratio 500 time > for Al, steel, titanium; one order of magnitude improvement over graphite/epoxy**
- **Thermal conductivity ~ 3000 W/mK in axial direction with considerably smaller values in radial direction**
- **Ballistic electron transport and high current carrying capability in axial direction of single CNTs~ $10^7$-$10^9$ A/cm$^2$, better than any metal**
- **Band gap~0.4-1.2 eV**

Carbon Nanotubes:
Science and Applications,
M. Meyyappan, CRC Press, 2004.

# Electronic Properties of Graphene

- **Massless Dirac fermions with high Fermi speed $V_f$~$10^6$ m/s**
- **high mobility $\mu$ ~$10^6$ $cm^2/Vs$**
- **Electric conductivity $\sigma = en\mu$**—high conductivity $\sigma$ at low carrier density n due to high $\mu$; $\sigma_{min}$ **~$4e^2/h$ even at low carrier density**
- **Optical transmittance: T ~97.9%**




- Transparent conductors
- IR detectors
- Bio-/chemical-sensors

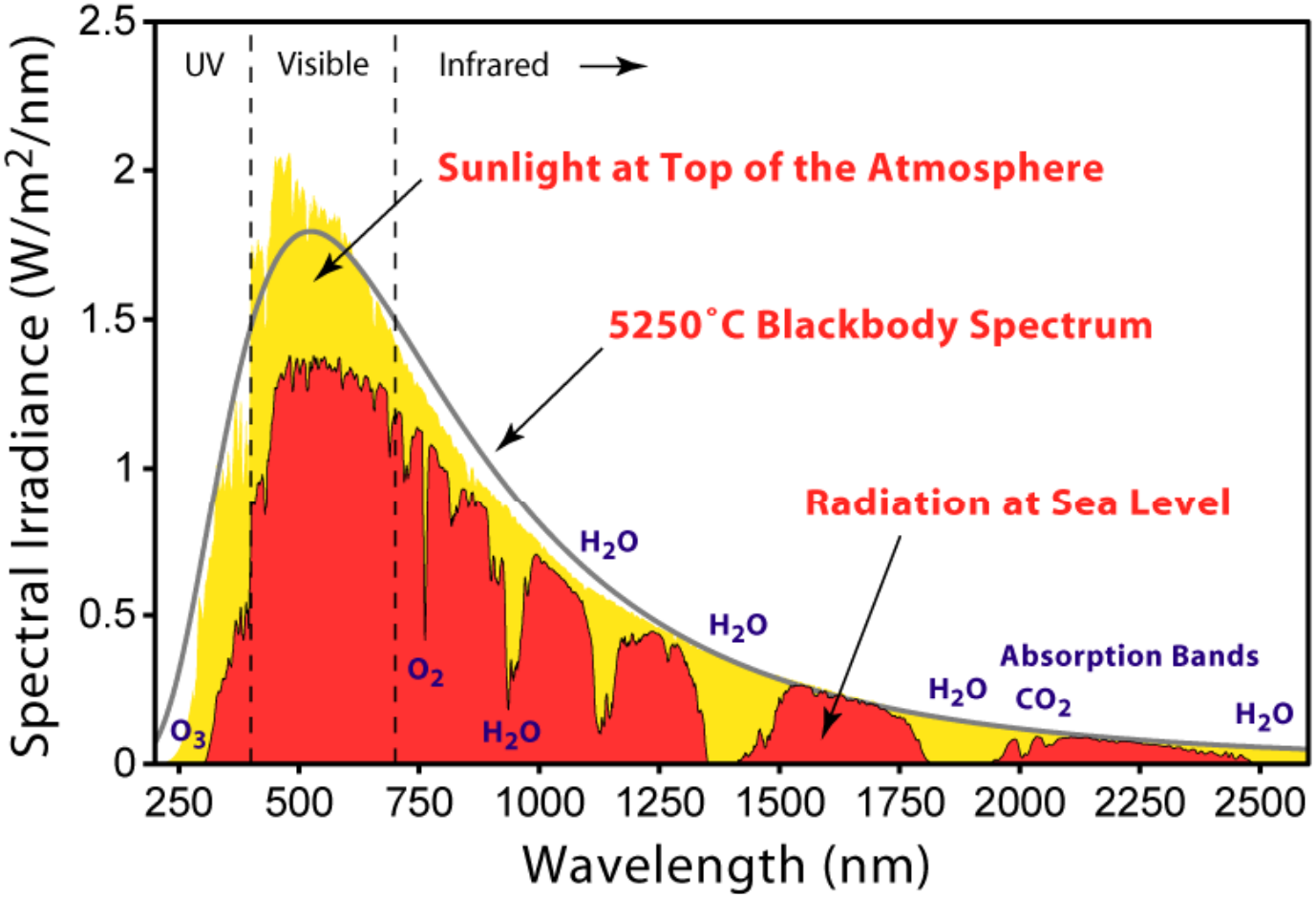
**P. Avouris, Nano Letters 10, 4285(2010)**

# Fascinating Carbon Nanostructures

- **Unique electronic and mechanical properties**
- **Light weight**
- **Low cost**
- **Non-toxic and no environmental impact**

**Could we use carbon nanostructures for solar cells?**
**Could we use more carbon nanostructures for solar cells?**
**Could we make all carbon nanostructures solar cells?**

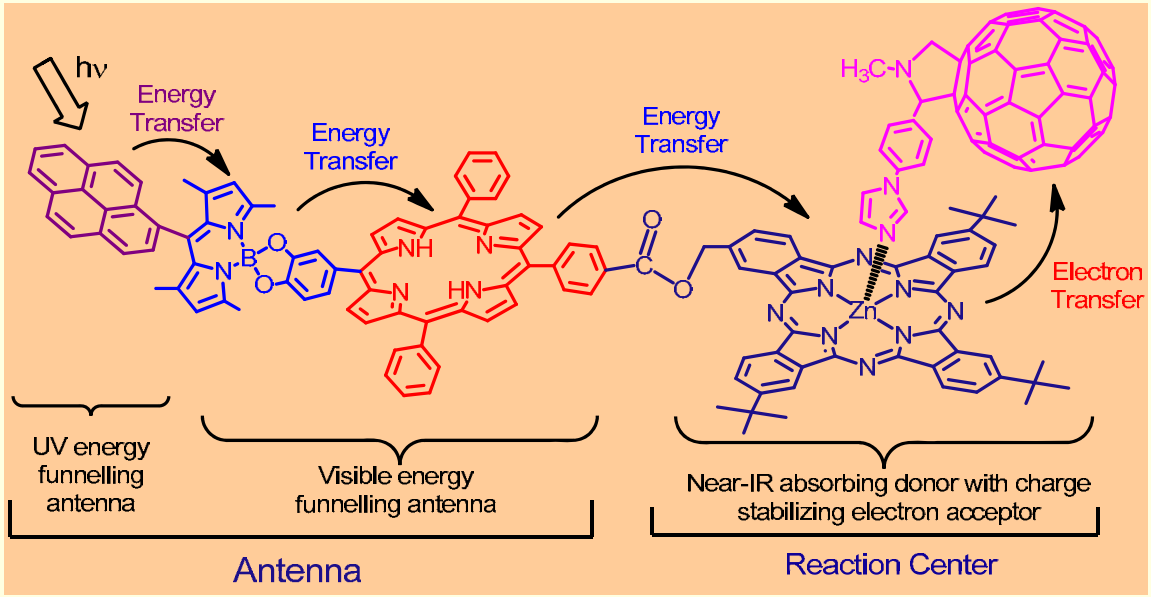
# Solar Radiation Spectrum

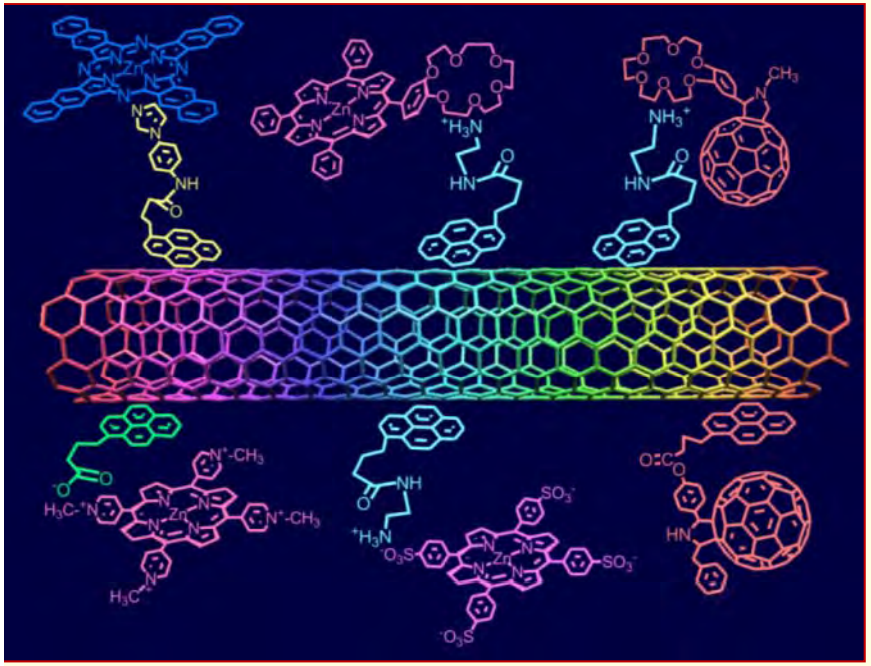


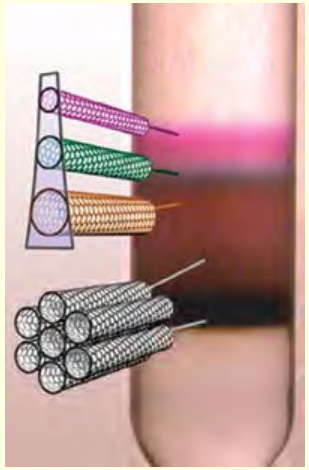

**Broad band-- Catch more photons in solar spectrum**

**Francis D'Souza and Paul Rillema-WSU**

## Broad Band Capturing Antenna-Reaction Mimics for Efficient Solar Energy Harvesting Devices



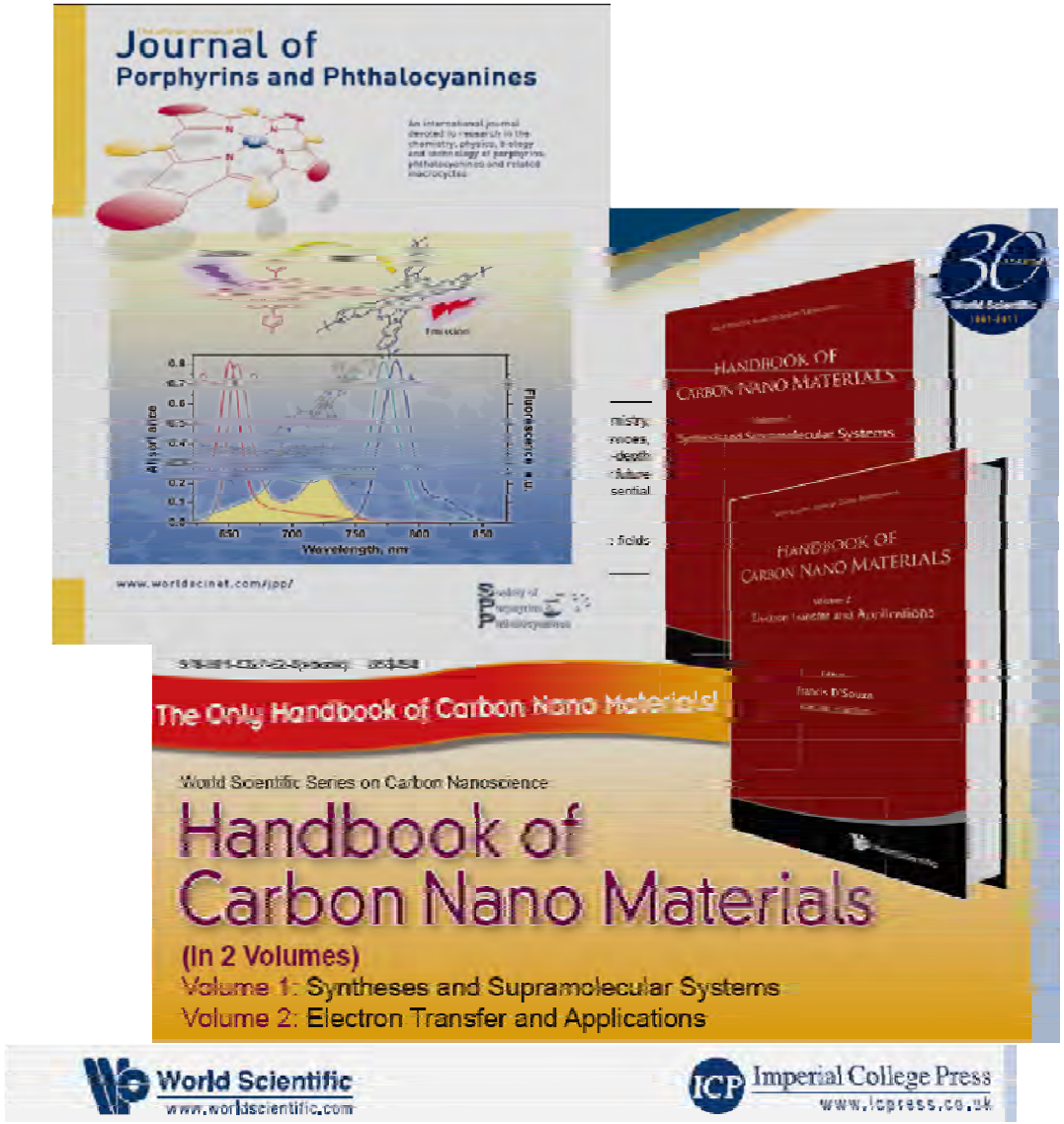





## Size Sorted Carbon Nanotube Based Donor-Acceptor Architectures for Energy Harvesting Applications

# Nature Inspired Carbon Nanomaterials for Broad-band Light Energy Harvesting—

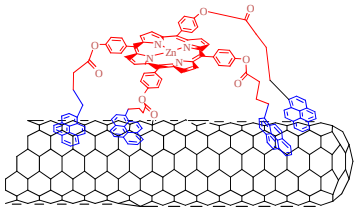
*D'Souza, Rillema (WSU)*

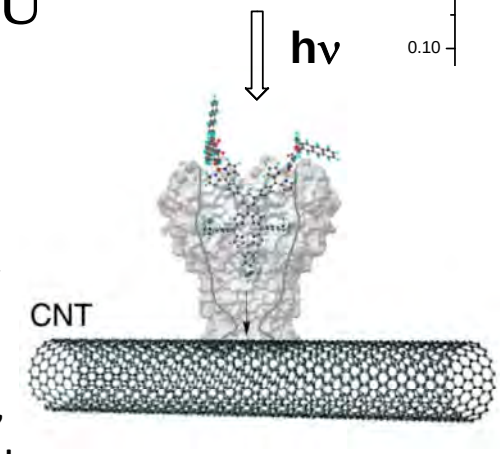



Accomplishment:

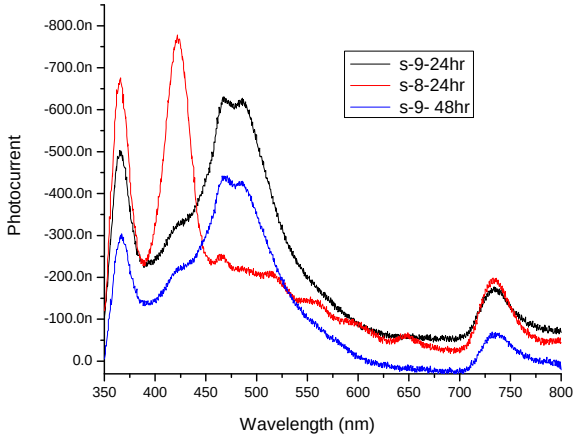
Design and synthesis of low cost materials for broad-band absorption of solar lights

# **Protein and Quantum Dots-Based Solar Cells—** Bossmann, D'Souza-WSU, Chikan-KSU & Wu-KU

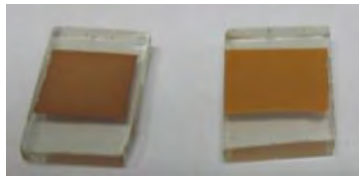





Experimental conditions: acetonitrile, /$I_3^-$ couple AM1.5 solar simulated light

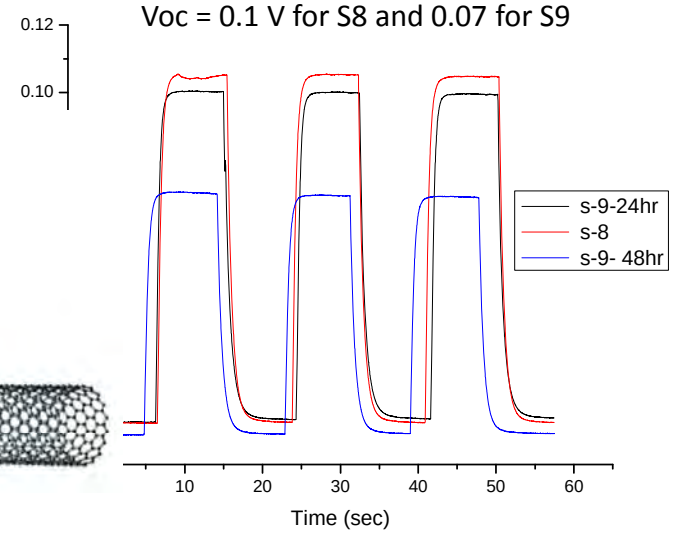



S8 S9

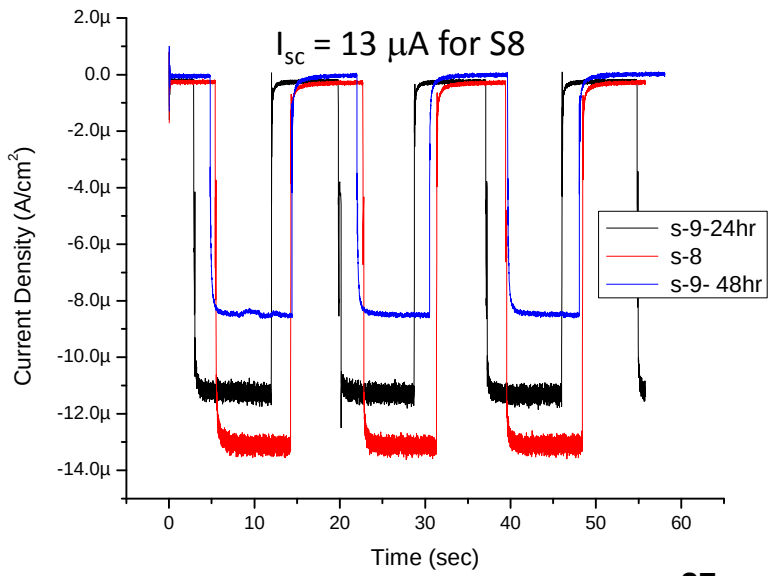


Potential Switching

Voc = 0.1 V for S8 and 0.07 for S9




Current Switching



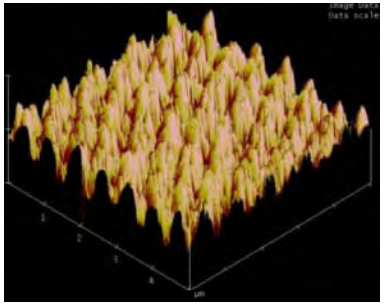

Accomplishment:

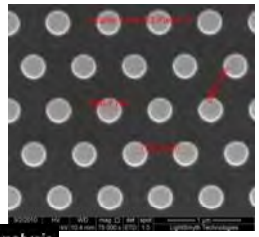
Low-cost self-assembly processes for advanced solar cells

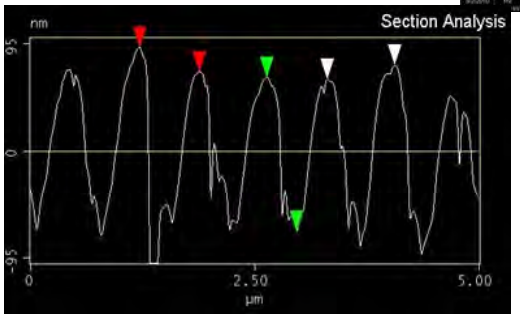
# Photonic dye-sensitized solar cells

## Hui, Wu (KU), D'Souza (WSU)

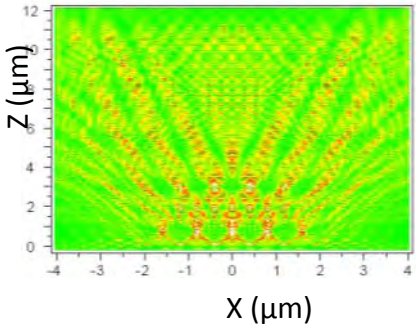
Photonic FTO



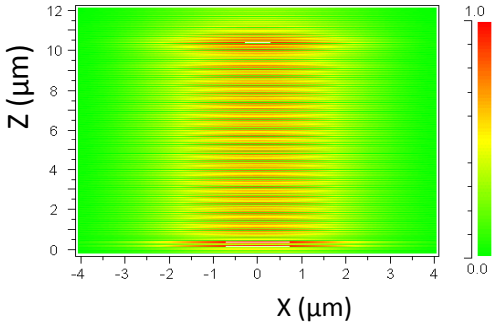


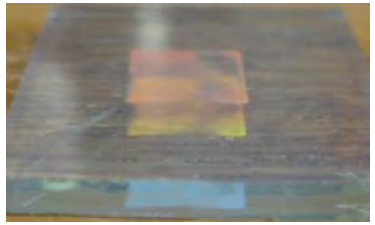


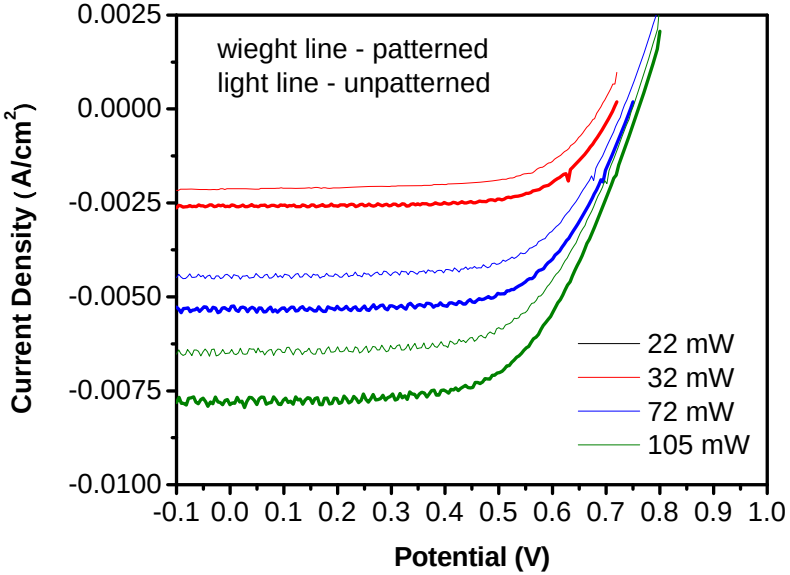

Power distribution




Power distribution,



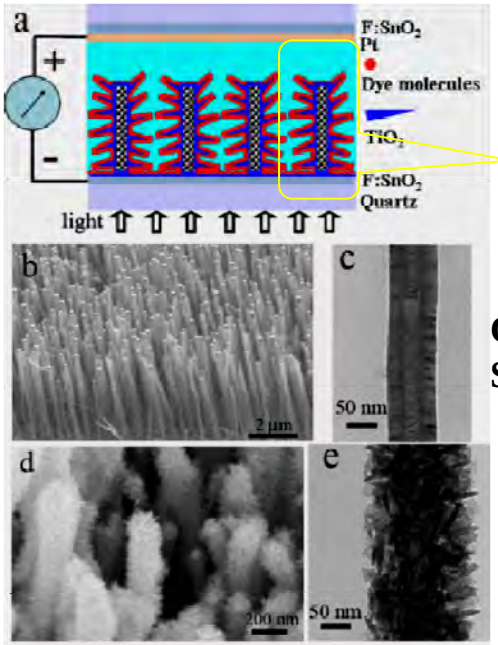



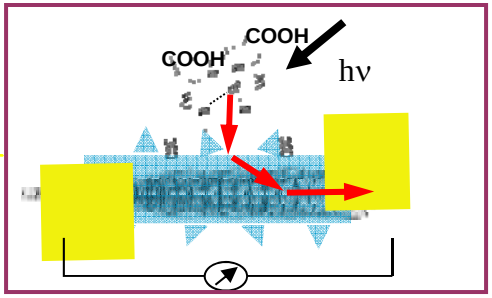


**Efficiency improved dramatically due to Enhanced light scattering through photonic FTO**

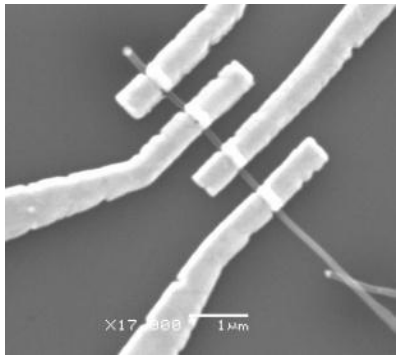
**F.L. Wang et al, submitted**

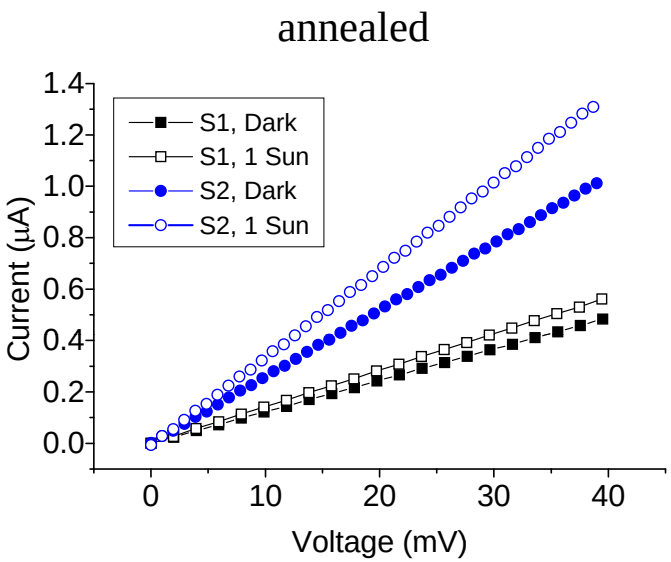
# 3D carbon-nanotube architectured solar cells— Li (KSU) and Wu (KU)




**CNF/TiO2 nanowire Dia: 90-140 nm**
**Spacing between probes: 1-1.5 µm**






Liu, J. et al. Novel Dye-Sensitized Solar Cell Architecture Using TiO2-Coated Vertically Aligned Carbon Nanofiber Arrays. *ACS Applied Materials & Interfaces* 2010.

Rochford, C.; et al,. *Applied Physics Letters* 2010, 97 (4), 043102.

Z.Z. Li et al, *Nanoscale Research Letters* 2010, 5, 1480.

Accomplishment:

- 3D architecture improves light absorption
- Regulated photoelectron pathway for high-efficiency charge transport

# Plasmonic photovoltaic

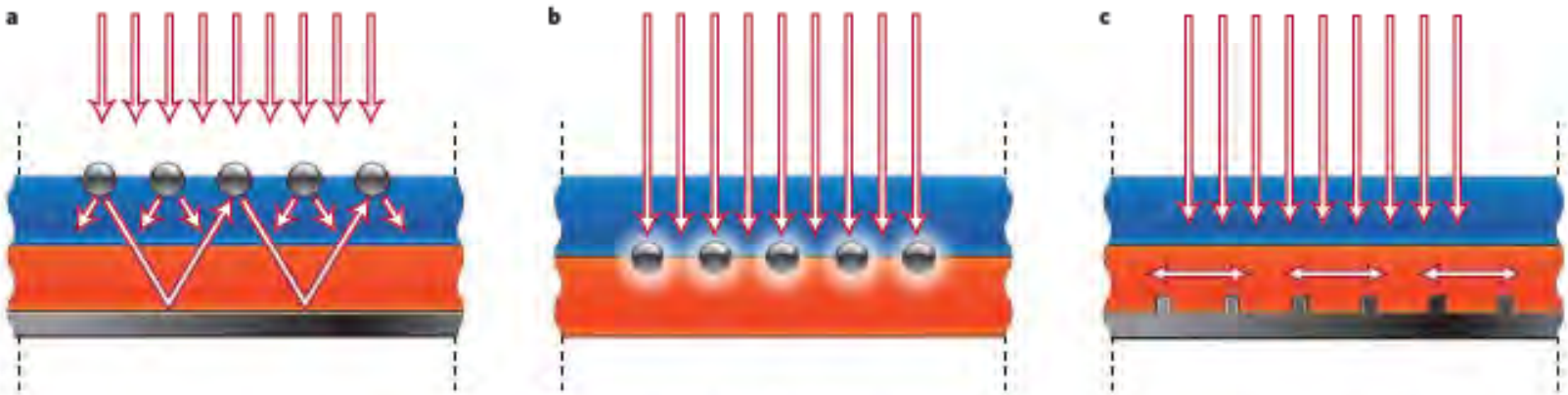
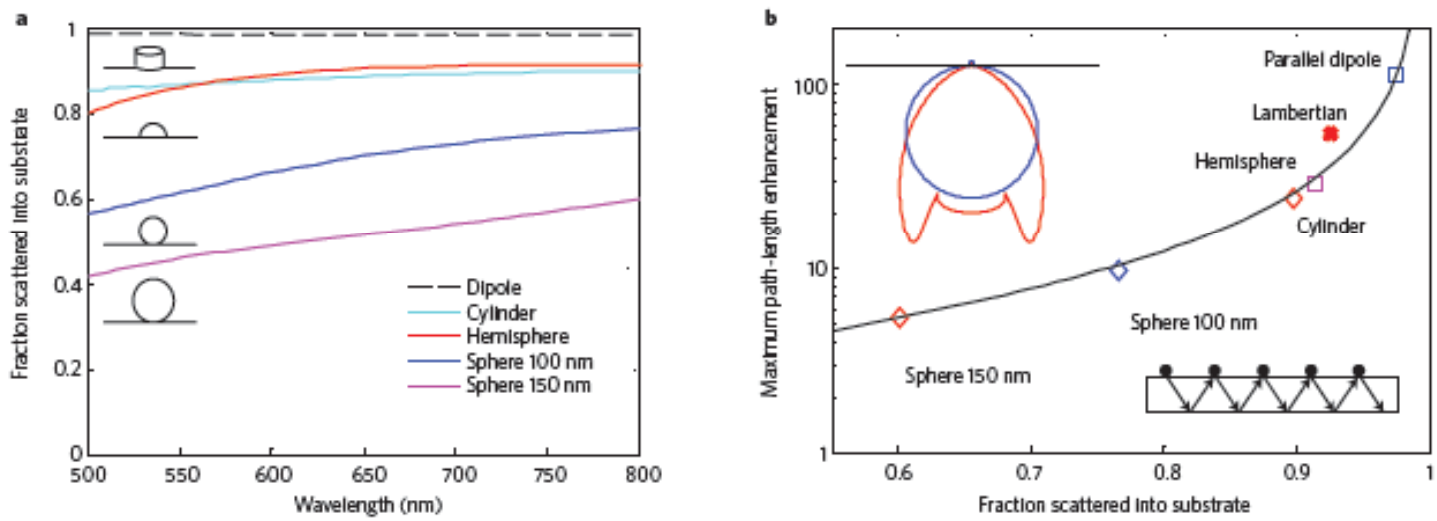


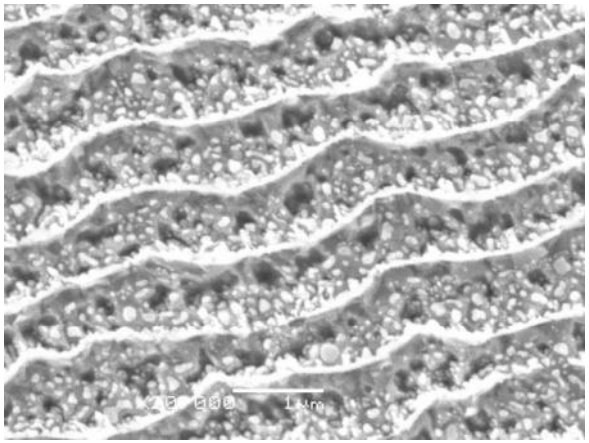

**Figure 2 | Plasmonic light-trapping geometries for thin-film solar cells. a**, Light trapping by scattering from metal nanoparticles at the surface of the solar cell. Light is preferentially scattered and trapped into the semiconductor thin film by multiple and high-angle scattering, causing an increase in the effective optical path length in the cell. **b**, Light trapping by the excitation of localized surface plasmons in metal nanoparticles embedded in the semiconductor. The excited particles' near-field causes the creation of electron–hole pairs in the semiconductor. **c**, Light trapping by the excitation of surface plasmon polaritons at the metal/semiconductor interface. A corrugated metal back surface couples light to surface plasmon polariton or photonic modes that propagate in the plane of the semiconductor layer.



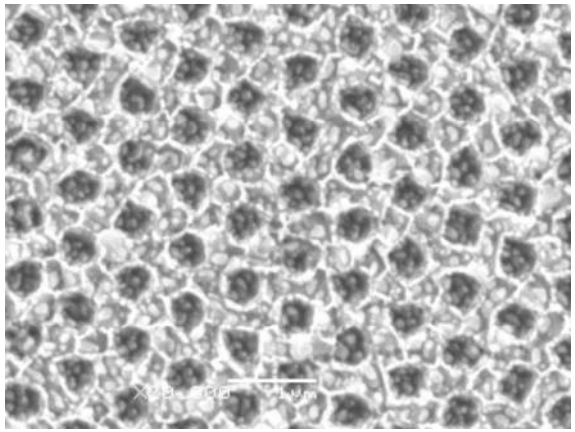

Atwater and Polman, Nat. Mat. Feb. 2010 | doi: 10.1038/nmat2629

# Plasmonic+Photonic FTO —Wu, Ren, and Hui (KU)

Au particles/nano line FTO

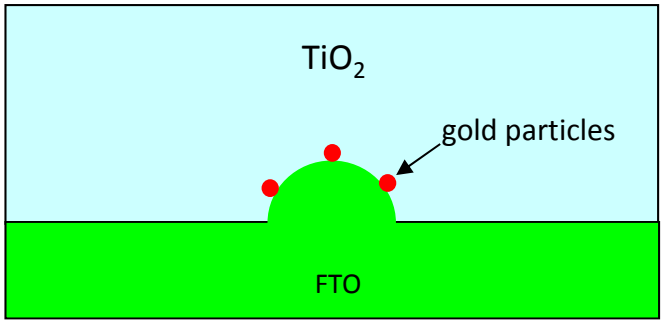


Au particles/nano pillar FTO

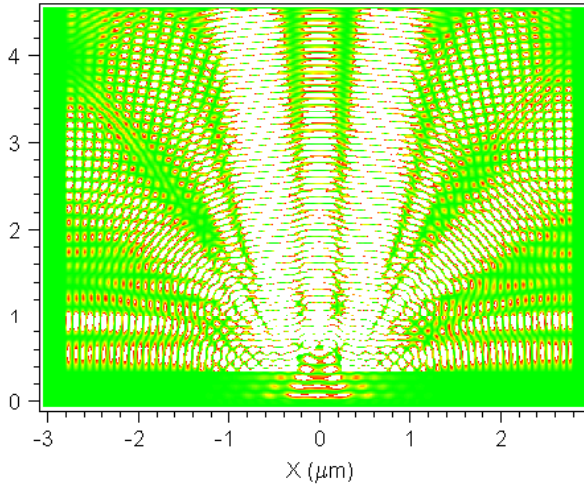


Significantly improved light absorption in thin film solar cells

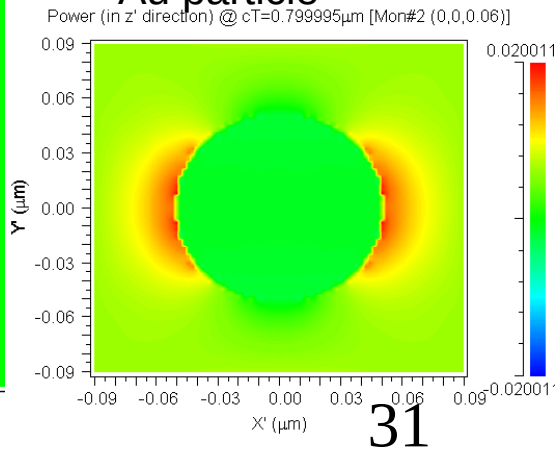
Ag nanoparticles on FTO photonic crystals



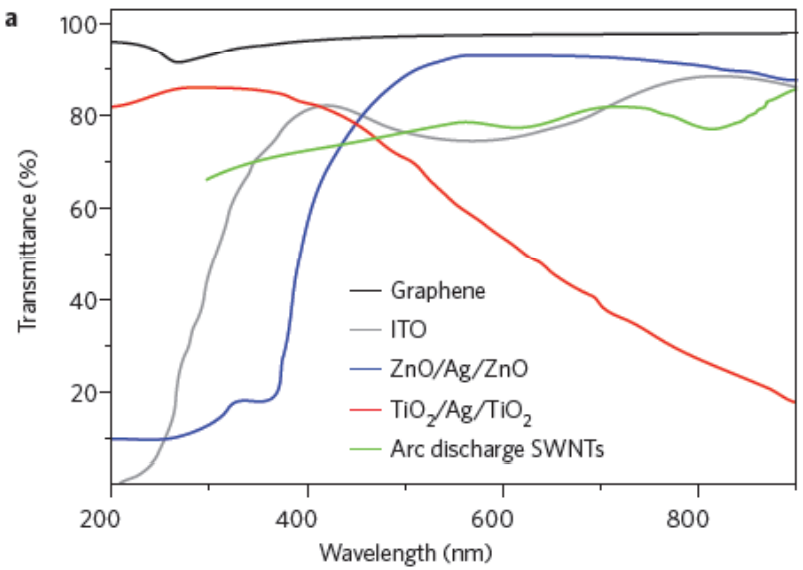

Power distribution

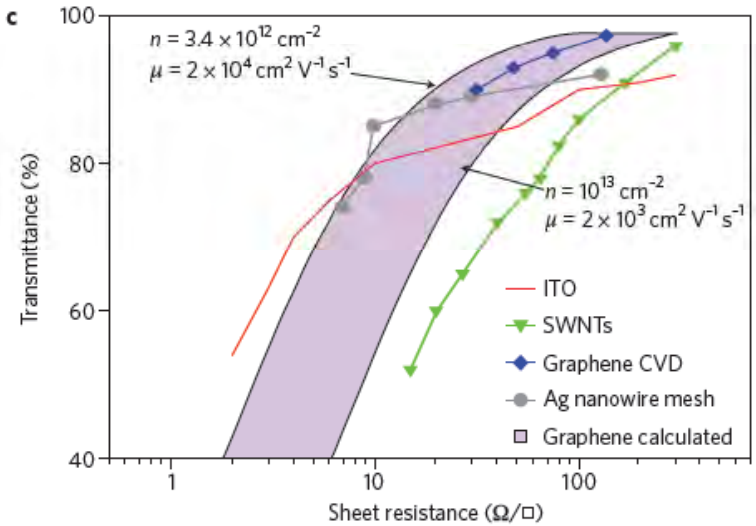



Localized Surface Plasmon of a spherical Au particle



# Graphene As Transparent Conductors




F. Bonaccorso et al., Nature Photinics 4, 611, 2010

**Pros**: Superior transparency

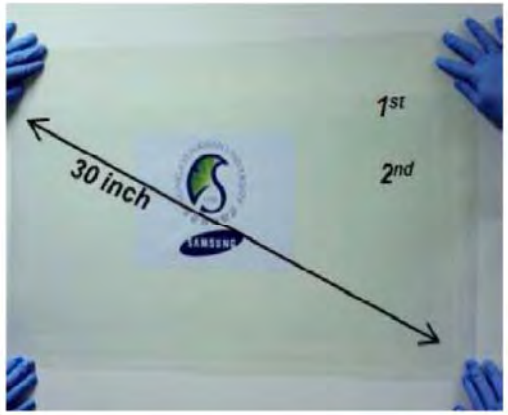
High mobility (~10,000 cm$^2$/Vs in small flakes)

Massive production, flexibility

Economically and environmentally friendly

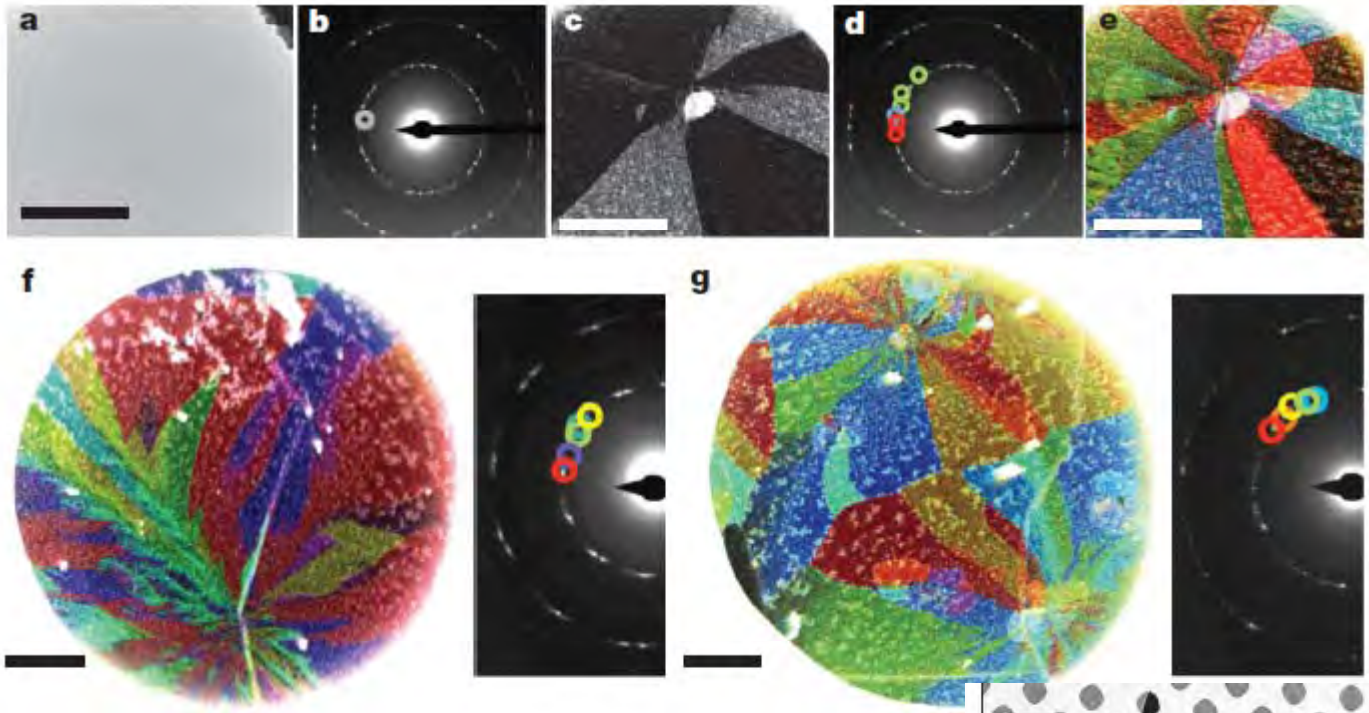
**Cons**: Relatively low sheet resistance in CVD graphene

**Needed:** advanced graphene nanostructures for solar cells and other opto-electronic applications



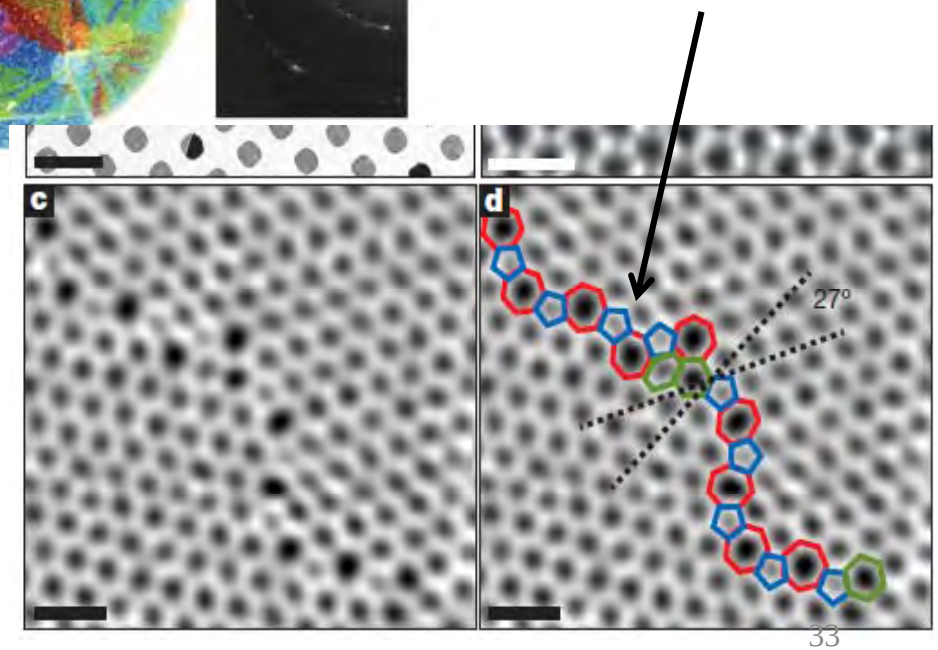

S. Bae et al, Nat. Nanotech. doi:10.1038/nnano.2010.132

# No epitaxy!-role of Cu substrate




S. Li, Sciece, 2009; S. Bae et al, Nat. Nanotech. doi:10.1038/nnano.2010.132

**Grain boundaries**

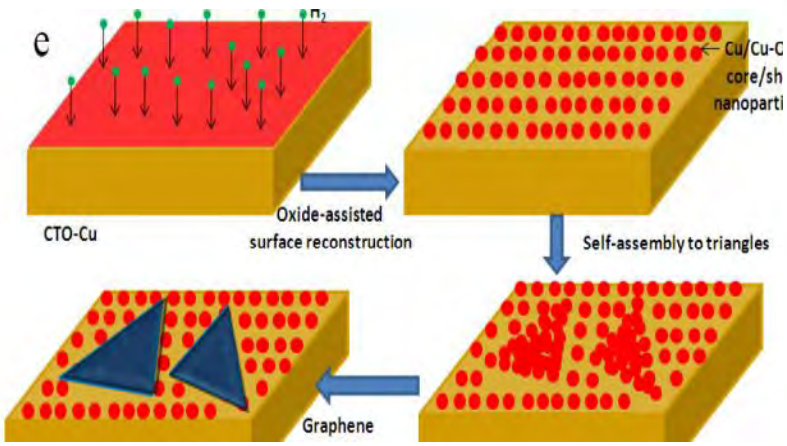



- On exfoliated graphene (single crystal) flakes: mobility up to 200,000 cm2/Vs
- On fabricated graphene (with GBs and defects)): mobility is in the range of 3,000-20,000 cm2/Vs

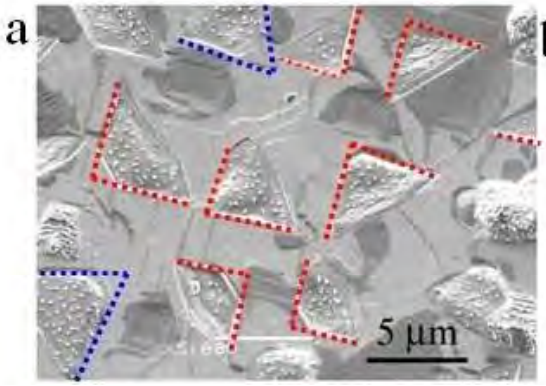
P. Huang et al, 2001, doi:10.1038/nature09718

# **Towards epitaxy of** graphene-NRE team, Ames, ANL, ORNL, NASA

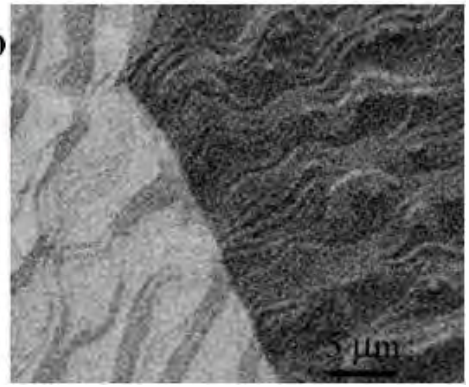
Oxide-assisted self-assembly



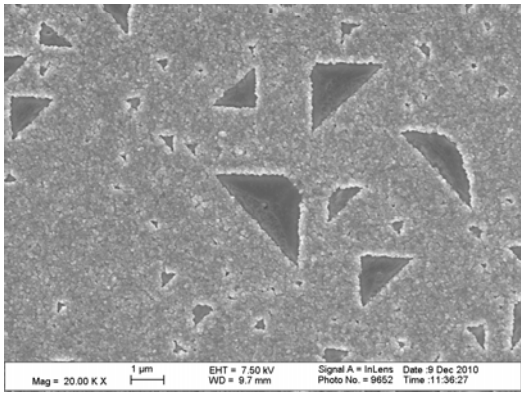

Cubic textured Cu

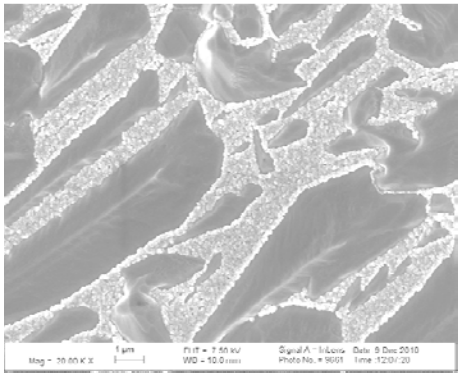



Polycrystalline Cu




Graphene nucleation at 5 min.



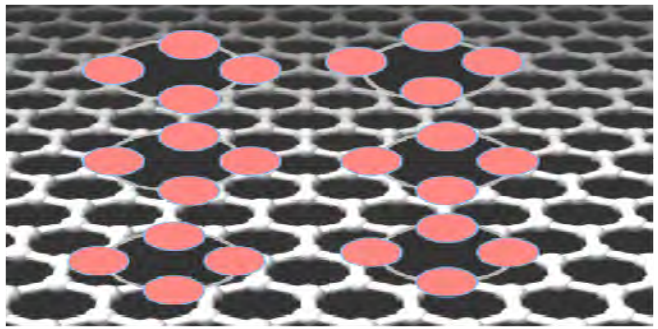


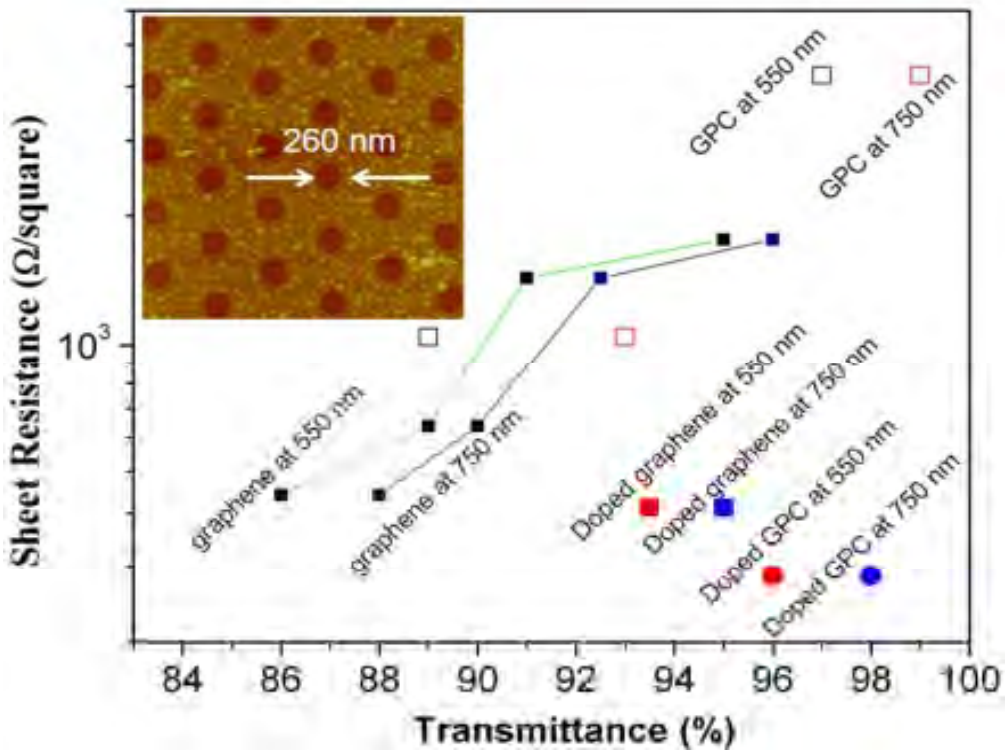
Aligning graphene grains to reduce effect of grain boundaries on electron mobility

Jianwei Liu, et al,, to appear in *Advanced Functional Materials.*

# Photonic Graphene- NRE, ANL

Graphene nanohole array
with chemical doping





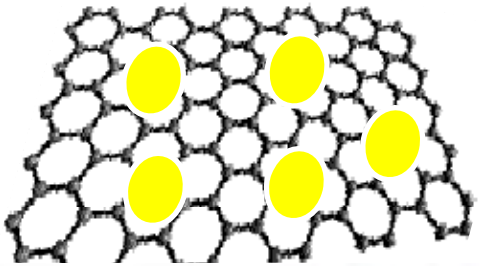

## Objectives:

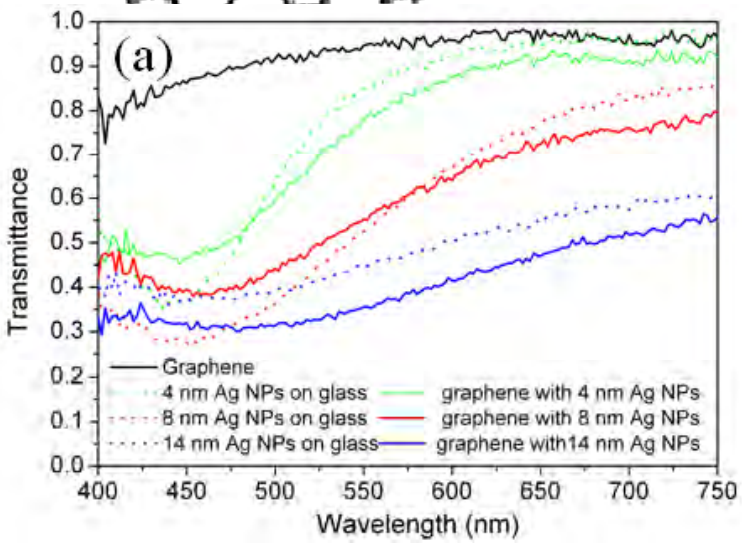
- High-performance, low cost, flexible transparent conductors for touch screens, solar cells, etc

Jianwei Liu, et al, "Graphene photonic crystal for broadband flexible transparent conductors", *Applied Physics Letters* **99**, 023111 (2011)

# Plasmonic Graphene-advanced transparent conductors (NRE, ANL, NREL, ISU, Arkansas)

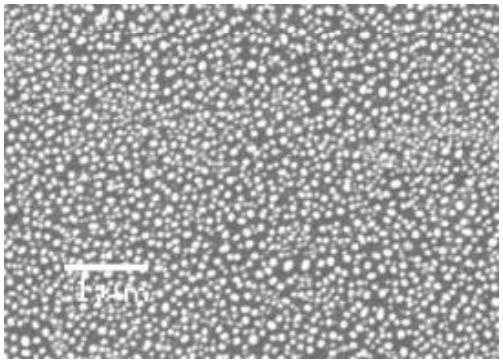
Graphene/metal nanopaticles —plasmonic graphene



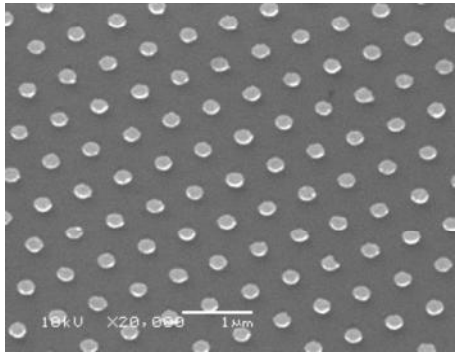


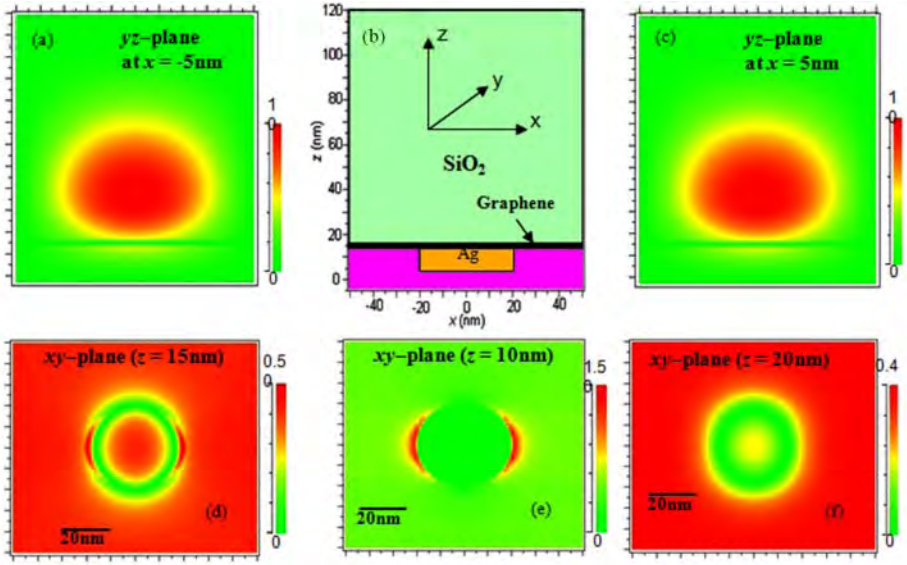

High-performance, low cost, flexible transparent conductors for touch screens, solar cells, etc

Self-assembled Ag nanoparticles on graphene
Diameter: 30-80nm



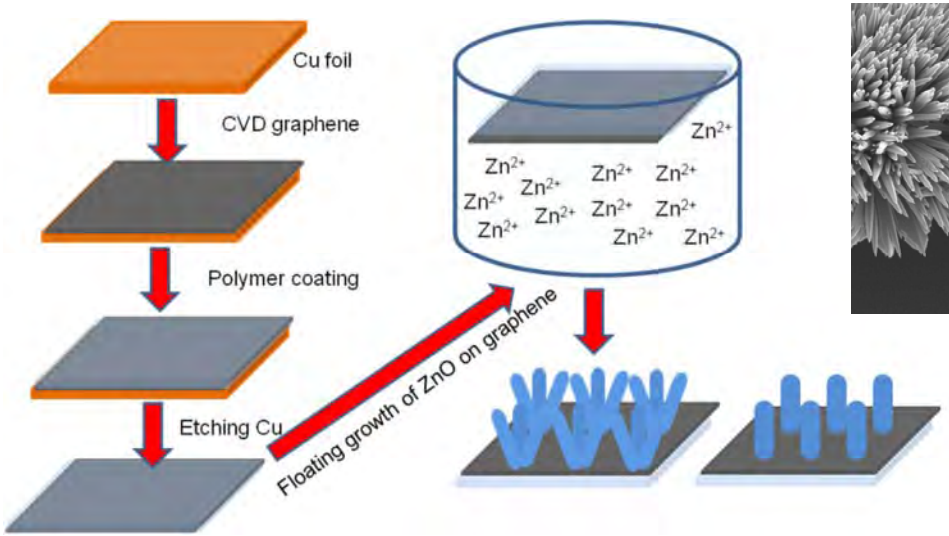
Ordered Ag nanoparticles on graphene
Diameter: 150-250nm

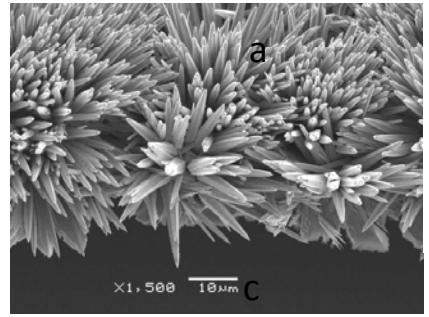


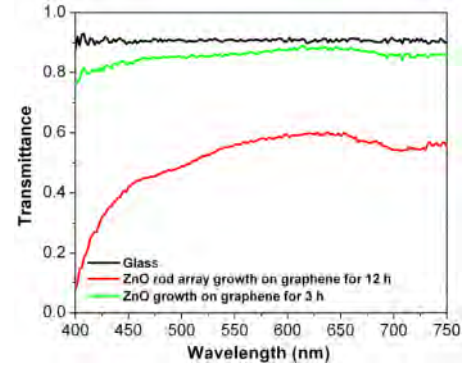


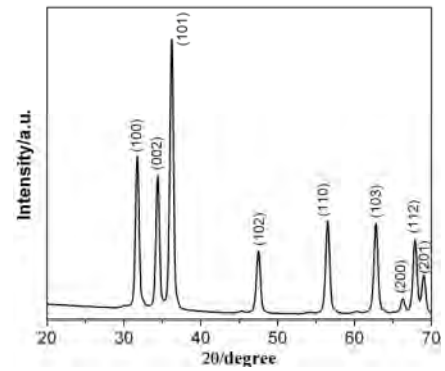

Guowei Xu et al, submitted.

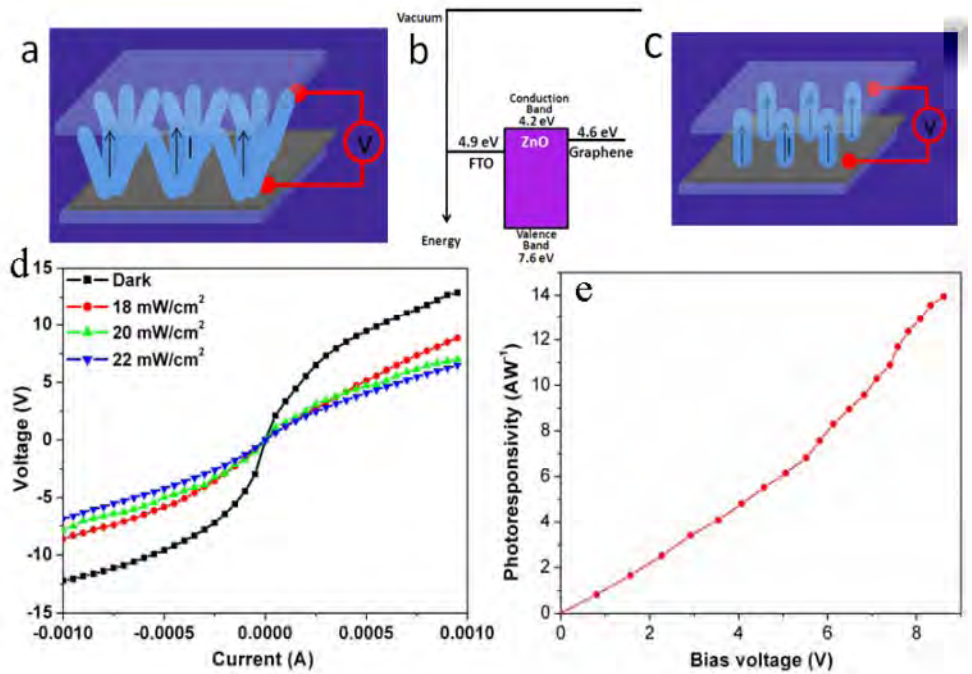
# ZnO nanorod/graphene hybrid nanostructures



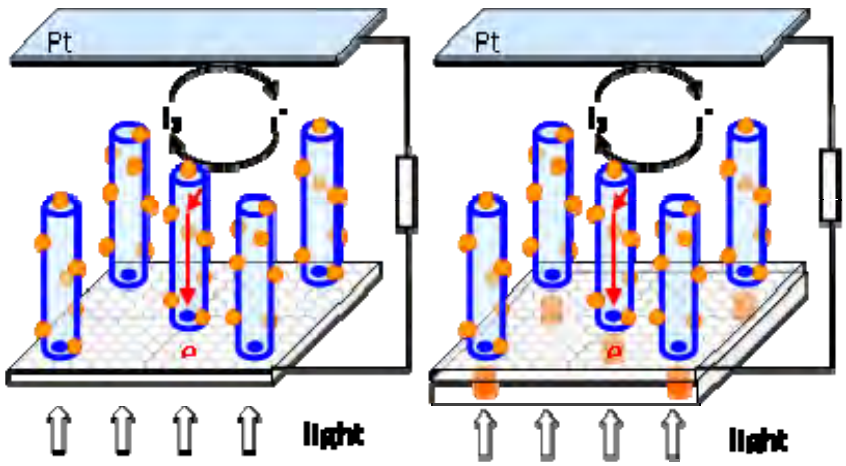




Semiconductor/graphene nanostructures with clean interface are promising for various opto-electronic device applications

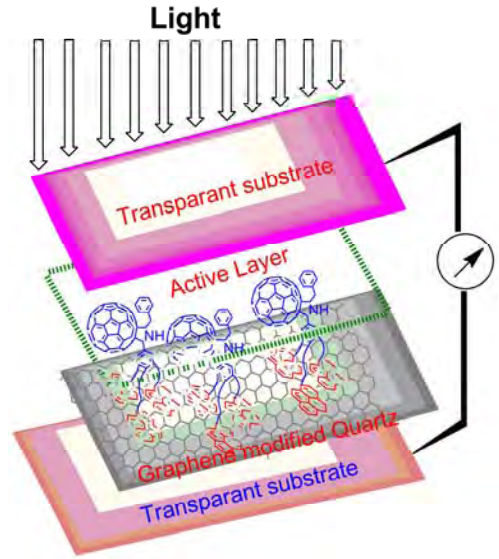
Jianwei Liu et al, submitted.

# Graphene-based plasmonic Photovoltaics --Ongoing with many collaborators

DSSC



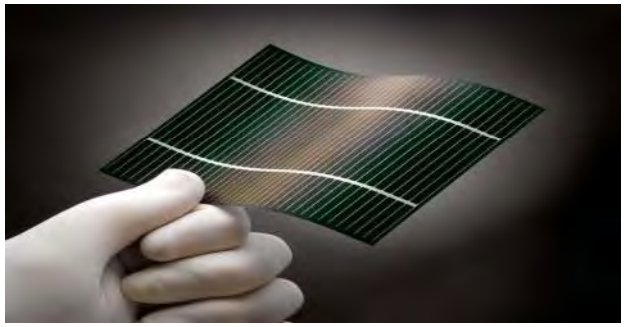

Si or OPV



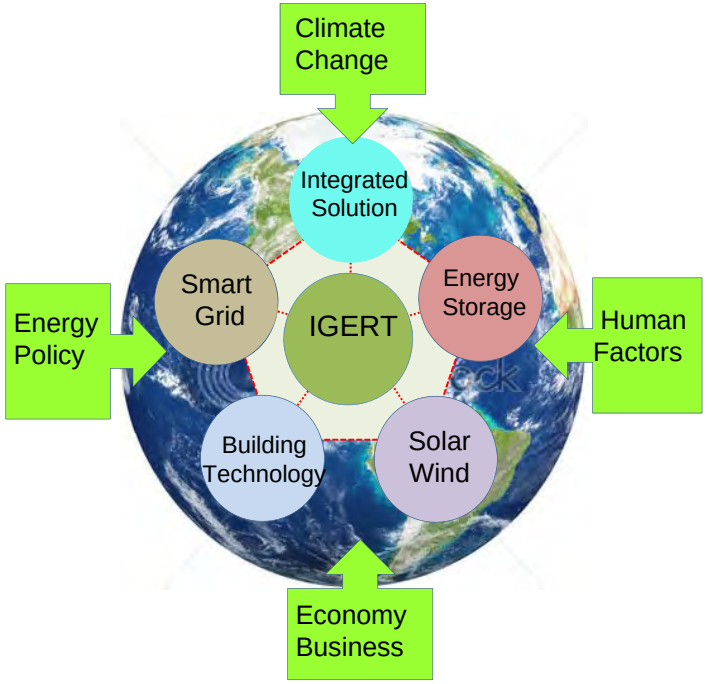

**We invite new collaborations!**

**(jwu@ku.edu)**

Flexible, cost-performance balanced, environmental friendly



## Developing Integrated Solutions for Sustainable Energy Generation, Distribution, Storage and Usage




**Built-environment:**

- 41% of national primary energy
- 73% in electricity
- A platform for energy research
- Tremendous business opportunity

(i.e. Black & Veatch, Burns & McDonnell, Westar, TradeWind, Schneider Electric, Treanor Architects ….)

Linkage also to: environmental/climate, economy, policy, social/human factors

# Summary

- **Carbon-based nanostructures provide a fascinating system for many optical and opto-electronic applications including solar cells, photodetectors, touch screens, etc.**
- **Design broad-band photosensitizers to catch more light in solar spectrum**
- **Develop photonic and plasmonic nanostructures to enhance light absorption in thin film solar cells**
- **Develop 3D architectures for high-efficient electron transfer and transport**

# Solar Future

iPhone (solar charged)

Solar farm

Solar power plane (NASA)

Solar powered house

Solar powered car

Review

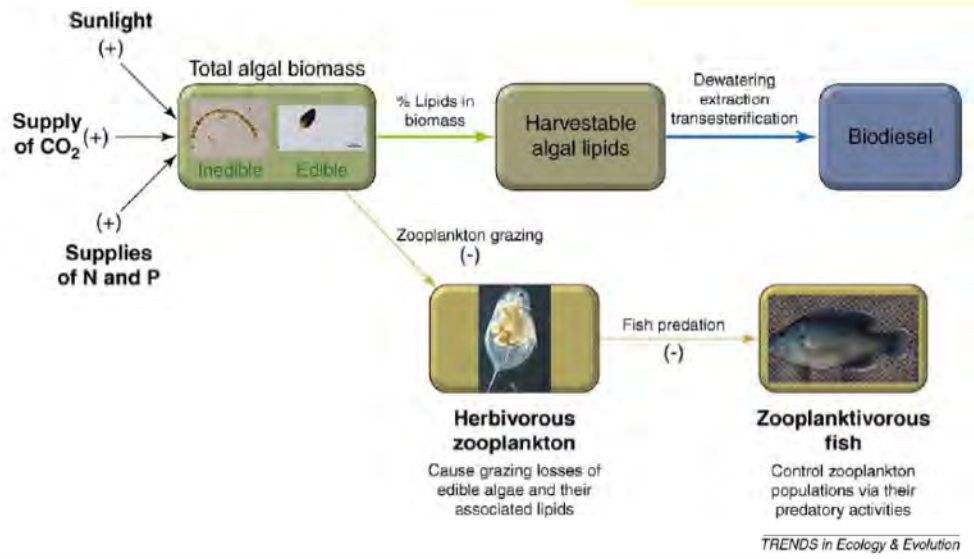
*Trends in Ecology and Evolution* Vol.25 No.5

# The ecology of algal biodiesel production

**Val H. Smith[1], Belinda S.M. Sturm[2], Frank J. deNoyelles[1,3] and Sharon A. Billings[1,3]**

[1] Department of Ecology and Evolutionary Biology, University of Kansas, Lawrence, KS 66045, USA
[2] Department of Civil, Environmental, and Architectural Engineering, University of Kansas, Lawrence, KS 66045, USA
[3] Kansas Biological Survey, University of Kansas, Lawrence, KS 66045, USA

**Sustainable energy production represents one of the most formidable problems of the 21st century, and plant-based biofuels offer significant promise. We summarize the potential advantages of using pond-grown microalgae as feedstocks relative to conventional terrestrial biofuel crop production. We show how pond-based algal biofuel production, which requires significantly less land area than agricultural crop-based biofuel systems, can offer additional ecological benefits by reducing anthropogenic pollutant releases to the environment and by requiring much lower water subsidies. We also demonstrate how key principles drawn from the science of ecology can be used to design efficient pond-based microalgal systems for the production of biodiesel fuels.**



# Using treated wastewater and top-down ecological control to grow high-yield algae

## Belinda Sturm, Val Smith-KU

Algae promise to be a major renewable energy problem-solver. They grow fast, trap carbon dioxide, and have the potential for high lipid contents which can result in high oil yields (see Table at bottom right). Algae also can be grown on land not suitable for agriculture, and don't displace food crops.

There are hurdles to mass production of algae that still must be addressed by scientists. It has been difficult to grow algae in outdoor settings and still get consistently high oil yields. Massive amounts of fresh water also are involved, so environmental costs could potentially outweigh the benefits.

University of Kansas researchers Belinda Sturm, assistant professor of environmental engineering, Val Smith and Jerry deNoyelles, professors of ecology and evolutionary biology, and Susan Williams, associate professor or chemical & petroleum engineering, are partnering with the Lawrence, KS wastewater treatment plant. This team is looking at ways to develop sustainable and consistently high oil yields from algae grown in outdoor bioreactors filled with treated wastewater (sewage).

An important component of the project is top-down ecological control, long used in lakes to limit algal blooms, and now used by the team in their bioreactors. They have introduced zooplankton predators (fish) to some of the tanks, to find out more about how to control algal losses to zooplankton grazing. The team believes that food webs in algal bioreactors can be manipulated to optimize nutrient recycling, maximize algal biomass yields, and create more stable and efficient systems for large-scale, algae-based biofuel production.

Initial results have been promising, and both scientists and wastewater plant professionals are pleased about yet another environmental benefit. Wastewater is filled with nitrogen and phosphorus. The wastewater-grown algae consume these pollutants, which are removed when the algae are harvested. This nutrient removal is a big plus, because the Midwest's wastewater treatment plants are under increasing pressure to send less nitrogen and phosphorus downstream to the Gulf of Mexico, which has a large area called the "dead zone" that is caused by excess nutrient inputs from the land.

*Val Smith, Jay Barnard, Belinda Sturm, and Jerry deNoyelles perform calculations at a bioreactor site.*

*Algal bioreactor tanks at KU's field station*

*Daniel Klapper, an undergraduate Chemical Engineering student, cleans an algal reactor.*

*Laboratory cultures of algae used to explore optimal conditions for lipid production*

### Oil Yield / Acre Per Year

**(gallons / acre)**

| Algae* | 4,000-38,000 |
|---|---|
| Oil Palm | 635 |
| Coconut | 287 |
| Jatropha | 207 |
| Rapeseed/Canola | 127 |
| Peanut | 113 |
| Sunflower | 102 |
| Safflower | 83 |
| Soybean | 48 |
| Hemp | 39 |
| Corn | 18 |

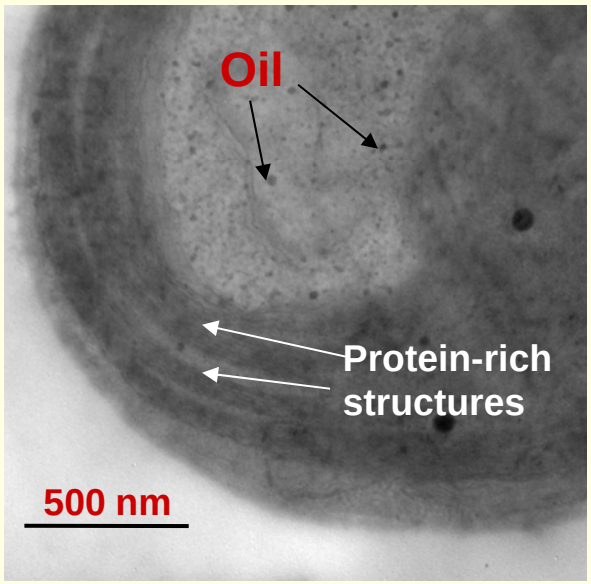
*** 4,000 is the range for the best cases; 38,000 is the theoretical maximum (Weyer et al., *Bioenerg. Res.* 2009).**

# Microscopic characterization of Biomass

## (Susan Sun-KSU, Wu and Sturm-KU)

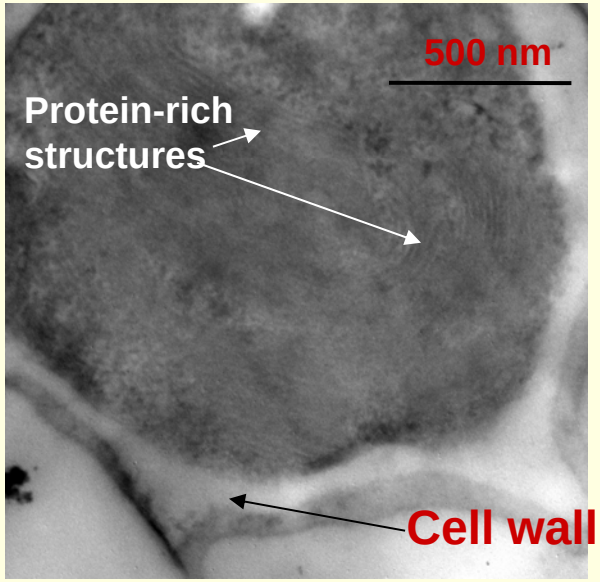
- Characterize algal cell morphology
- Identify algae cell ultrastructure among three species
  - Identify internal cell structures
  - Differentiate between oil and algae protein

***Scendesmus dimorphus***



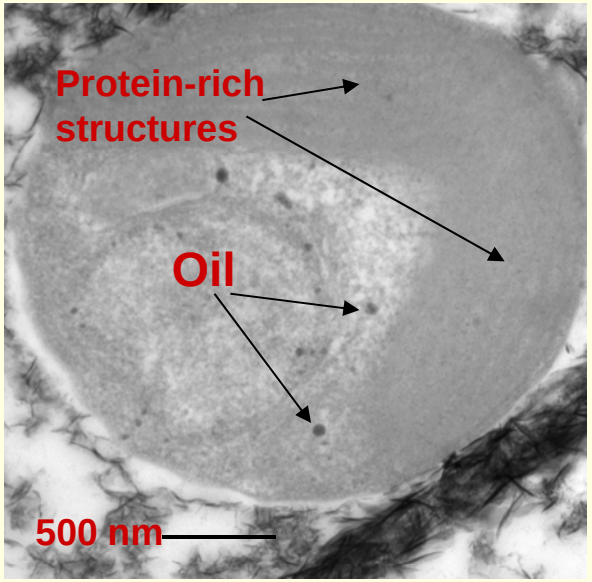

Transmission electron micrograph
34,000x magnification

***Chlorella protothecoides***




Transmission electron micrograph
34,000x magnification

***Nannochloropsis salina***

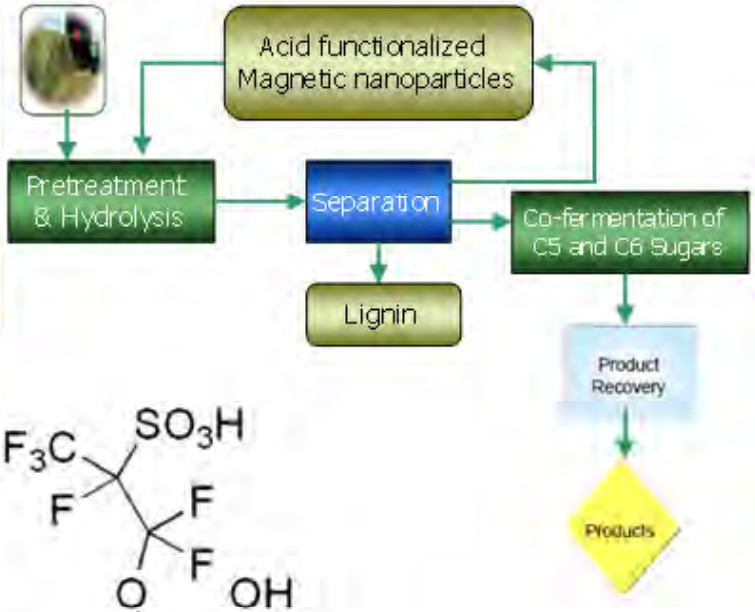


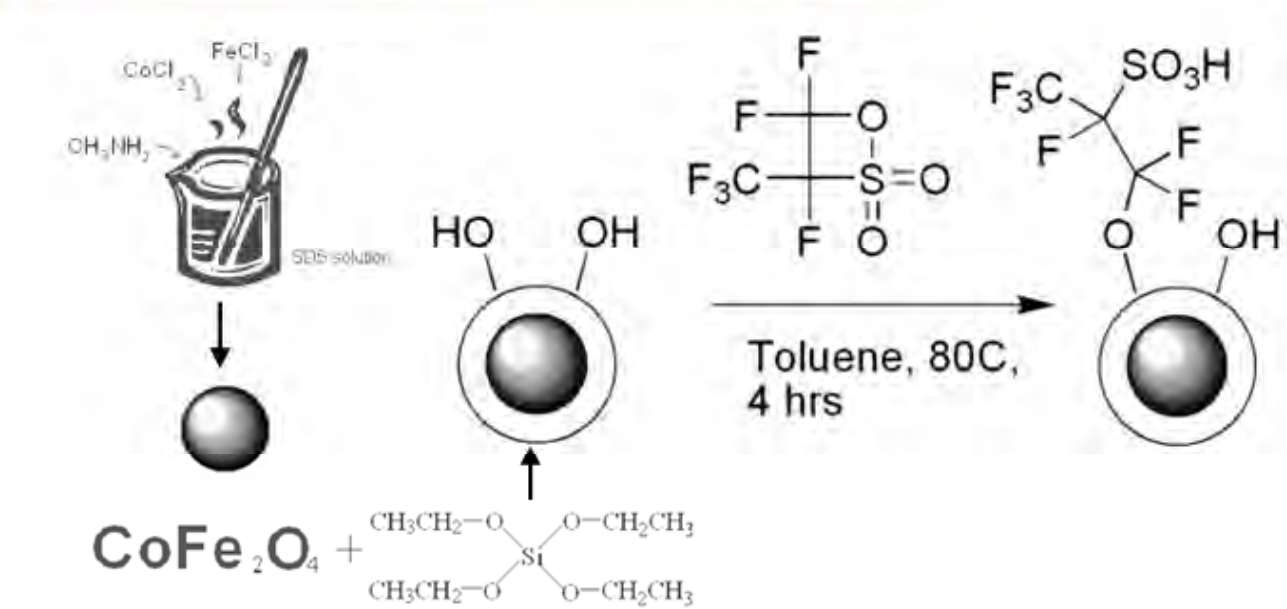

Transmission electron micrograph
25,000x magnification

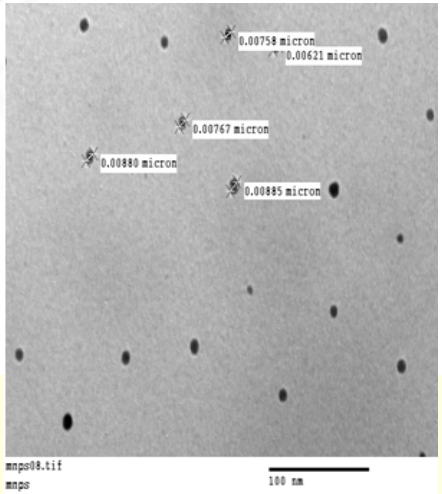
# Acid-functionalized nanoparticles for cellulose hydrolysis

## (Donghai Wang and Keith Hohn-KSU)

- Catalyst is easy to suspend in the biomass solution.
- Catalyst must have enough acidity to hydrolyze cellulose to glucose.
- Catalyst is easily separable and reusable.




**Three types of nanoparticles have been synthesized:**
**PFS = perfluoroalkyl-sulfonic acid nanoparticles,**
**AS = alkyl-sulfonic acid nanoparticles,**
**BCOOH = butylcarboxylic acid**