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

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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

Fossil challenges
- Finite supply
- Secure access
- Environmental pollution
- Greenhouse gases

EIA-Energy Information Administration
Fossil Energy Resources are **Limited**

<table>
<thead>
<tr>
<th>Resource</th>
<th>Energy Potential (TWy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil and gas (conventional)</td>
<td>1,000</td>
</tr>
<tr>
<td>Oil and gas (unconventional)</td>
<td>2,000</td>
</tr>
<tr>
<td>Coal</td>
<td>5,000</td>
</tr>
<tr>
<td>Methane clathrates</td>
<td>20,000</td>
</tr>
<tr>
<td>Oil shale</td>
<td>30,000</td>
</tr>
<tr>
<td>Uranium (conventional)</td>
<td>370</td>
</tr>
<tr>
<td>Uranium (breeder)</td>
<td>7,400</td>
</tr>
<tr>
<td>Sunlight on land</td>
<td>30,000 per year</td>
</tr>
<tr>
<td>Wind</td>
<td>2,000 per year</td>
</tr>
<tr>
<td>Fusion (if successful)</td>
<td>250,000,000,000</td>
</tr>
</tbody>
</table>

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 not on this list
Regional Instability and Threats to National Security

Oil Price “Roller Coaster”: $100+ per Barrel and Rising

Libya: March 2011
CO$_2$ Emissions, Population and Wealth

*Fossil Fuel Consumption Dominates Emissions*

IPCC report
Energy Demands:

Energy consumed on Earth:

- 4.1x10^20 J/yr
- 13 TW

Expected to double by: 2050

Expected to triple by: 2100

Energy from Sun striking Earth:

- 4.3x10^20 J/hr

Mechanisms powered by Sun:
- Global wind/ocean currents
- Photosynthesis
- Evaporation/condensation

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

Source: PV News, April 2009
(revised: 09-2009)
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
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

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

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): emc²
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 Interdisciplinary 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

Gold
Diameter: ~0.1 nm

Hydrogen

Carbon

Diameter: ~0.8 nm

Caffeine

Cholesterol

Diameter: ~1.5 nm

Single-Wall Carbon Nanotubes
Diameter: 1-2 nm
Length: up to millimeters

The ability to tweak things at nanoscales allows us to design materials and devices with desired properties
Three Generations of Solar Cells

I) Wafer based
   Silicon
   Lab record: 25%
   Module record: 23%

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

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

Goals:
~ 30¢/W
~ 2¢/kWh

Projections:
US$0.10/W US$0.20/W

Enhancing efficiency, reducing cost
Reducing PV system costs to grid parity will require significant reduction in the cost of all components.

<table>
<thead>
<tr>
<th></th>
<th>Residential</th>
<th>Commercial</th>
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<tbody>
<tr>
<td>2005</td>
<td>$8</td>
<td>$8</td>
</tr>
<tr>
<td>2010</td>
<td>$6</td>
<td>$5</td>
</tr>
<tr>
<td>2015</td>
<td>$4</td>
<td>$3</td>
</tr>
</tbody>
</table>

2005 $ per watt installed

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

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

1991 S. Ijima

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 $\sim$ 200 GPa.
- **Strength to weight ratio 500 time** $>$ for Al, steel, titanium; one order of magnitude improvement over graphite/epoxy
- Thermal conductivity $\sim$ 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 $\sim$ $10^7$-$10^9$ A/cm$^2$, better than any metal
- Band gap $\sim$ 0.4-1.2 eV

Electronic Properties of Graphene

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

- 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

Potential Switching
\( \text{Voc} = 0.1 \text{ V for S8 and 0.07 for S9} \)

Current Switching
\( I_{sc} = 13 \mu\text{A for S8} \)

Accomplishment:
Low-cost self-assembly processes for advanced solar cells
Photonic dye-sensitized solar cells
Hui, Wu (KU), D’Souza (WSU)

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)


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 Photonics 4, 611, 2010

**Pros:** Superior transparency

High mobility (~10,000 cm²/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

- 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

S. Li, Science, 2009; S. Bae et al, Nat. Nanotech. doi:10.1038/nnano.2010.132
P. Huang et al, 2001, doi:10.1038/nature09718
Towards epitaxy of graphene-NRE team, Ames, ANL, ORNL, NASA

Oxide-assisted self-assembly

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

Photonic Graphene- NRE, ANL

Graphene nanohole array with chemical doping

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

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

Graphene/metal nanoparticles — plasmonic graphene

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

- Ordered Ag nanoparticles on graphene
  Diameter: 150-250nm

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

Guowei Xu et al, submitted.
ZnO nanorod/graphene hybrid nanostructures

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

Graphene-based plasmonic Photovoltaics -- Ongoing with many collaborators

DSSC

Si or OPV

Flexible, cost-performance balanced, environmental friendly

We invite new collaborations!
(jwu@ku.edu)
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
The ecology of algal biodiesel production

Val H. Smith¹, Belinda S.M. Sturm², Frank J. deNoyelles¹,³ and Sharon A. Billings¹,³

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

Oil Yield / Acre Per Year (gallons/acre)

<table>
<thead>
<tr>
<th>Algae*</th>
<th>4,000-38,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Palm</td>
<td>635</td>
</tr>
<tr>
<td>Coconut</td>
<td>287</td>
</tr>
<tr>
<td>Jatropha</td>
<td>207</td>
</tr>
<tr>
<td>Rapeseed/Canola</td>
<td>127</td>
</tr>
<tr>
<td>Peanut</td>
<td>113</td>
</tr>
<tr>
<td>Sunflower</td>
<td>102</td>
</tr>
<tr>
<td>Safflower</td>
<td>83</td>
</tr>
<tr>
<td>Soybean</td>
<td>48</td>
</tr>
<tr>
<td>Hemp</td>
<td>39</td>
</tr>
<tr>
<td>Corn</td>
<td>18</td>
</tr>
</tbody>
</table>

* 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

*Scenedesmus dimorphus*  *Chlorella protothecoides*  *Nannochloropsis salina*

- Oil
- Protein-rich structures
- Cell wall

Transmission electron micrograph
34,000x magnification

Transmission electron micrograph
34,000x magnification

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