From solution processable solar cells to bioenergy: across the spectrum of renewable energy generation technologies

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SPREE Open Seminar
UNSW Sydney, Australia 2052
16 July 2015
Overview of Activities

- **Solution processable materials**
  - Colloidal Quantum Dot Solar Cells (CQDSCs)
  - Sulfohalides
  - Narrow bandgap oxides
- **Hot carrier dynamics modeling**
  - DFT/semiclassical electron-phonon bandstructures & transitions
- **Hot carrier dynamics experiment**
  - Inelastic X-ray Spectroscopy (IXS) @ Spring8 synchrotron, Japan
  - Ultra-fast PL/TA
- **All-optical hot carrier solar cells**
  - Plasmonics, nano-optics, photonic crystals, Purcell factor and hot luminescence
- **Photoelectrochemical cells**
  - ZnS
  - Catechols
- **Bioenergy**
  - Net-negative carbon energy systems
  - 2nd Generation Sugar Air Batteries/Fuel Cells
For today....

• Colloidal Quantum Dot Solar Cells (CQDSCs)

• Catechol surface modified TiO$_2$ nanoparticles (NPs)

• Net-negative carbon bioenergy systems

• Antimony sulfoiodide (SbSI) and related compounds as highly polarizable materials
Colloidal Quantum Dot Solar Cells

Lin Yuan, Zhilong Zhang, Naoya Kobamoto, Yicong Hu, Gavin Conibeer, Shujuan Huang

ARC DP 2014-2017
CQDSCs – Previous work

- E. Sargents et al, University of Toronto Canada / J. Tang et al, Wuhan, China
- NREL, M. Beard et al, Golden, Los Alamos USA/ LANL
- M. Bawendi et al, MIT USA
- Current record efficiency CQDSCs ~9.9%
CQDSCs – Motivation & Drawbacks

- Solution processable materials
  - Low processing temperatures
  - Low embodied energy
  - Inexpensive raw materials
- Novel quantum confinement effects/tunable bandgap
- Low material lifetime (surface area, passivation)
CQDSCs – Materials available

- Nanoparticles
  - PbS (QD)
  - PbSe (QD)
  - ZnO (“e-transport”)
  - $\alpha$-TiO$_2$ (“e-transport”)
  - SiO$_2$ (plasmonics)

- Solution processable materials (Sol-gel)
  - CaMnO$_3$, MnO$_x$
  - MoO$_{3-\delta}$
  - NiO$_x$
  - MoS$_2$
  - ZnS
  - CuS$_x$

Figure. Silica nanoparticles ~300 nm diameter
CQDSCs – Shape and size monodispersity

Figure. Bright field TEM of PbSe NPs

Ligands:
CQDSCs – Typical material parameters

- Mainly Pb-chalcogenides
- Bohr radii, \( a_B \)
  - \( \text{PbS} \sim 18 \text{ nm} \)
- Sizes \( \sim 3-8 \text{ nm} \)
- \( E_{\text{gap}} \sim 0.7 – 1.6 \text{ eV} \)
- \( \text{PbS } E_{g,\text{bulk}} \sim 0.4 \text{ eV} \)

Figure. Atomic resolution dark field TEM image of Br-PbS QDs
CQDSCs – Cell structure

- FTO
- PbS, PbSe
- TiO2, ZnO
- Glass

Solar cell diagram with energy levels and materials:

- FTO
- TiO2
- PbS
- PbSe
- Au

Energy levels and materials:

- FTO: -4.7
- TiO2: -4.1
- PbS: -4.0
- PbSe: -5.0
- Au: -7.3
- e\(^-\): -4.0
- h\(^+\): -5.0

Solar cell structure diagram with materials and layers:

- FTO
- PbS, PbSe
- TiO2, ZnO
- Glass
- Au

Energy band diagram:

- e\(^-\) at -4.0
- h\(^+\) at -5.0
- PbS at 1.1 eV

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CQDSCs – Air stability

Figure. Unprotected PbSe UV-Vis showing a blue shift due to oxidation.

Figure. Bromine terminated PbS UV-Vis showing no blue shift after ~ 5 weeks.

Zhang et al, IEEE Conf, June 2015
Yuan, RSC Advances, in press, July 2015
“Layer by layer” deposition procedure:
- Drop a few drops of colloidal solution on FTO (conductive) glass
- Spin coat
- Link
- Wash

Solid phase ligand exchange

Popular “linker” ligands: MPA and Iodine

QDs ideally spaced by a single molecule, or even one or two atoms
CQDSCs Results

- $\text{Voc}: 514.9 \text{ mV}$
- $\text{Jsc}: 10.77 \text{ mA/cm}^2$
- $\text{FF}: 37.5\%$
- $\text{PCE}: 2.08\%$
- Light soaking improved the curve
- World’s best cells have more than double the current density and a better fill factor
CQDSCs – Repeatability

2.1%, May 2015

2.47%, July 2015
CQDSCs – Further Work

• Continue to improve efficiencies.
  – Film Continuity
  – Film Density
• Wide area devices
• Light trapping, plasmonics, hydrophillic QDs
Catechol Surface Functionalized TiO$_2$ NPs

Shira Samocha, Vince Lorganzo, Judy Hart
Catechol TiO$_2$ – NP Structure

- Bandgap narrowing effect with specific molecule on the surface
- Gallic Acid, Ascorbic Acid, Dopamine, Tert-butyl catechol
- Anything with oxidation state greater than 4 and an ability to withstand strong chelation.
- Typically oxide materials
C-TiO$_2$ – Nanoparticle surface dipoles/ states

- With nanoparticles there is always a lot of surface
- Charge transfer across surface $\rightarrow$ strong surface dipole $\rightarrow$ bandgap reduction
- Can be explained with tight binding model for electronic bandstructure, perturbed at the surface.
- Surface Effects
  - Functionalization with ligands
  - Electric fields from depletion regions form interface dipoles

Figure 2. Band gap for PbS clusters. Black diamonds represent the temperature-adjusted calculations. Circles represent the experimental data of Wang et al.\textsuperscript{9}
Potential Energy + Kinetic Energy(\(k\)) = Total Energy(\(k\))
C-TiO$_2$ – Stark splittings due to surface dipoles

Band splitting

$\Delta E_{\text{Stark}}$

Less “degeneracy”

More kinetic energy

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C-TiO$_2$ – Bandgap narrowing
TiO$_2$ is known to be a good photocatalyst for water splitting (one of the first materials tried)

- Trouble is, it doesn’t absorb light very well
- Optimal water splitting bandgap of $\sim$2 eV – within reach using catechols
- Surface state created, catalysis happens at the surface, so worth trying

C-TiO$_2$ -- Photocatalyst for solar hydrogen

$O_2 + 2H_2 \rightarrow$
Bioenergy – Net-negative carbon bioenergy system

Melinda White, Campbell Griffin, Zhan Leo, Can Chu, Tracey Yeung, Louise Walsh, Peihang Zhang, Sheng Jiang, Sabrina Beckmann, Mike Manefield
Bioenergy – Motivation

• Answering the GCEP call for net-negative carbon energy systems.
Bioenergy – Coccolithophorid algae (shell producing)

- Coccolithophorid algae
  - Carbohydrates, lipids, proteins $\rightarrow$ biogas (CH4 + CO2)
  - Calcium carbonate (CaCO3) $\rightarrow$ sequestration
- “Shell producing” algae are abundant.
- Two common species:
  - Pleurochrysis Carterae
  - Emiliania Huxleyi
Bioenergy – Biomimetic concept

- Wetlands, marine canyons, mangroves are sources of biogenic methane
- Passive, self-contained
- Can this be mimicked in an industrial system with overall increased rates?
- Can that system be scalable?

Diagram:
- Photo-synthesis
- Anaerobic, \( \text{CH}_4 \) production
- Aerobic, \( \text{O}_2, \text{CO}_2 \)
- Fermentation, Sulfur reduction
- Gas Transfer
- Mass Transfer
- Methanogens

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Bioenergy – System requirements

• Requirements
  – Oxygen/light tolerant methanogenic community
  – Photosynthesizing microbes with very high growth rates
  – high CO$_2$ tolerances (low O$_2$ environment)
Bioenergy – Growth rates

![Graph showing cell density over time for two different species: P_{Ehux} and P_{PCart}. The graphs display sigmoidal fits to the data.](image_url)
Bioenergy – Oxygen and light dependence

Figure. Varying initial headspace CO$_2$

Figure. Light exposure
Bioenergy – Methane output

• Not in-situ yet… we’re working on it.
Sulfohalide materials for solution processable solar cells
Sulfohalides – Motivation

- Ferroelectric – has high permittivity ($\varepsilon_r$), high polarizability and therefore possibly high screening
  - Si: $\varepsilon_r \sim 11.7$
  - Perovskite: $\varepsilon_r \sim 60$
  - Ferroelectric: $\varepsilon_r \sim 1 \times 10^4$
- Problems:
  - large bandgaps
  - Oxides
  - Unknown mobilities/lifetimes
Sulfohalides – Defect removal, passivation, screening

1. Remove defects (fixing the problem)

2. Passivation (masking the problem)

3. Screening (disguising the problem)
Sulfohalides – Connect er with distortions/vibrations and overall material polarizability

- \( D = \varepsilon_0 \cdot E + P \)
- \( \varepsilon_r = \varepsilon_0 + \frac{P}{E} \)
- Dynamic process

1. Free charge
2. Bound charge
3. Atom centre
Sulfohalides – Potential for charge segregation

Potential difference between electrons and holes in the bulk of the material.

Electron contact

Hole contact

“Paraelectric”
Sulfohalides -- Structure

Keller, Act Cryst B, 2006
Sulfohalides – High permittivity semiconductor materials available from chemical synthesis

- SbSI, Eg ~ 1.8 eV  
  - (top cell)
- SbSeI, Eg ~ 1.6 eV  
  - (getting closer...)
Sulfohalides – SbSeI TEM
Sulfohalides – SbSeI TEM
Sulfohalides – Thin film fabrication

- Suspend the NWs
- Find appropriate p-type material
Summary

• CQDSCs at over 2% efficiency fabricated
• Catechol TiO$_2$ waiting for catalytic measurements
• Bioenergy has pieces assembled. System still required. Algal concentration and nutrient cycling ongoing
• High polarizability materials in-hand, detailed characterization required.
Thank you all for your support.

- Zhilong Zhang
- Lin Yuan
- Naoya Kobamoto
- Jeffrey Yang
- Hongze Xia
- Yu Feng
- ... and everyone else.

- Shujuan Huang
- Sabrina Beckmann
- Judy Hart
- Binesh Puthen Veettil
- Mike Manefield
- Ashraf Uddin
- Leigh Aldous
- John Stride
- Gavin Conibeer