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

Think Ahead

Faculty of Engineering

School of Photovoltaic and Renewable Energy Engineering

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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….

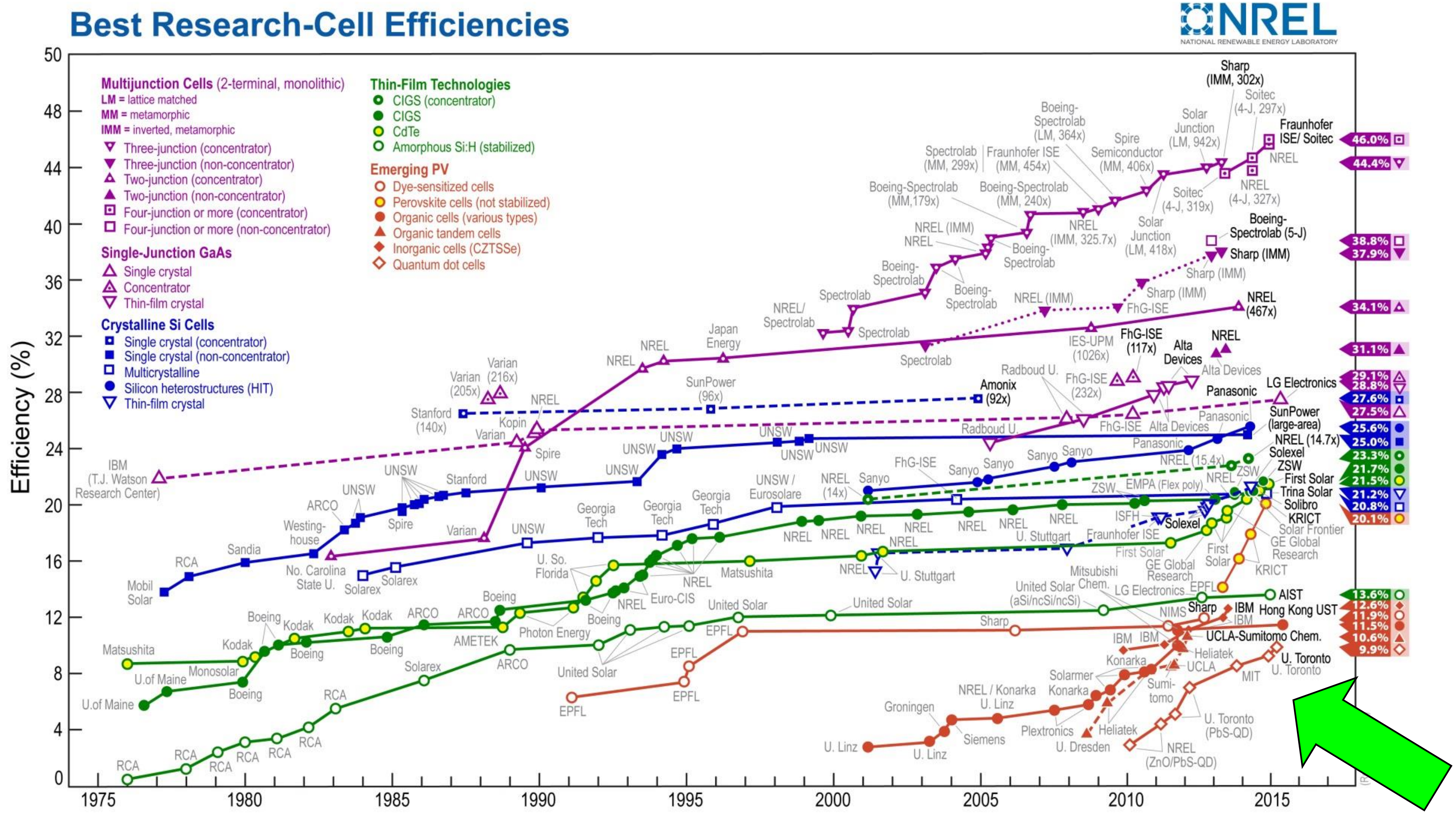
- Colloidal Quantum Dot Solar Cells (CQDSCs)
- Catechol surface modified TiO_2 nanoparticles (NPs)
- Net-negative carbon bioenergy systems
- Antimony sulfoiodide (SbSI) and related compounds as highly polarizable materials

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. Sargent 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”)
  - α-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

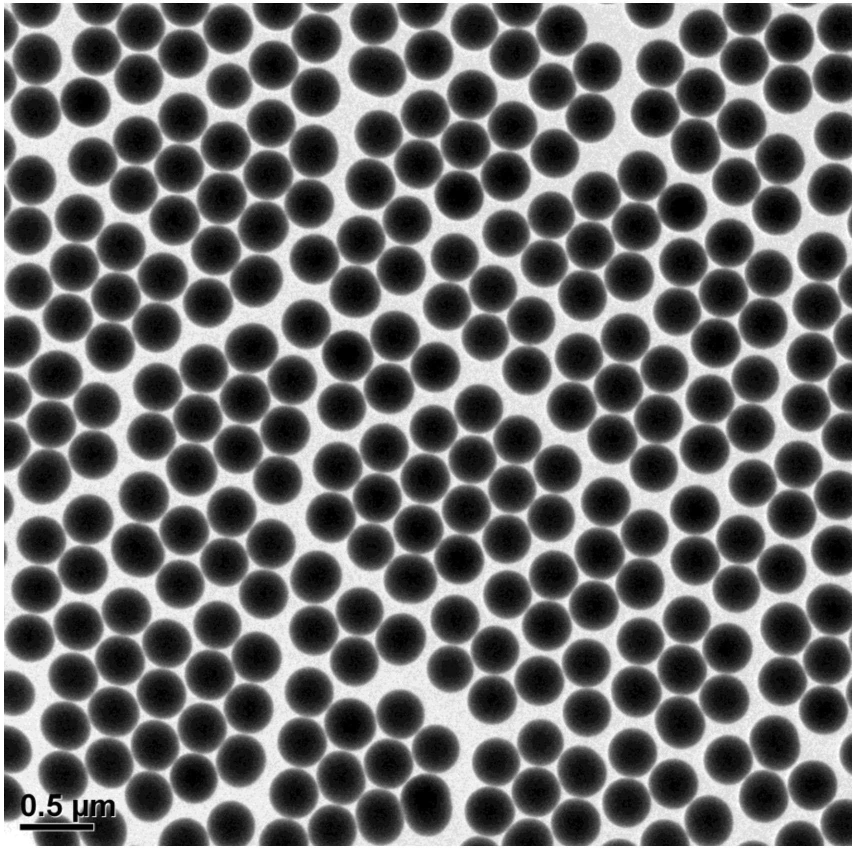


Figure. Silica nanoparticles ~300 nm diameter

CQDSCs – Shape and size monodispersity

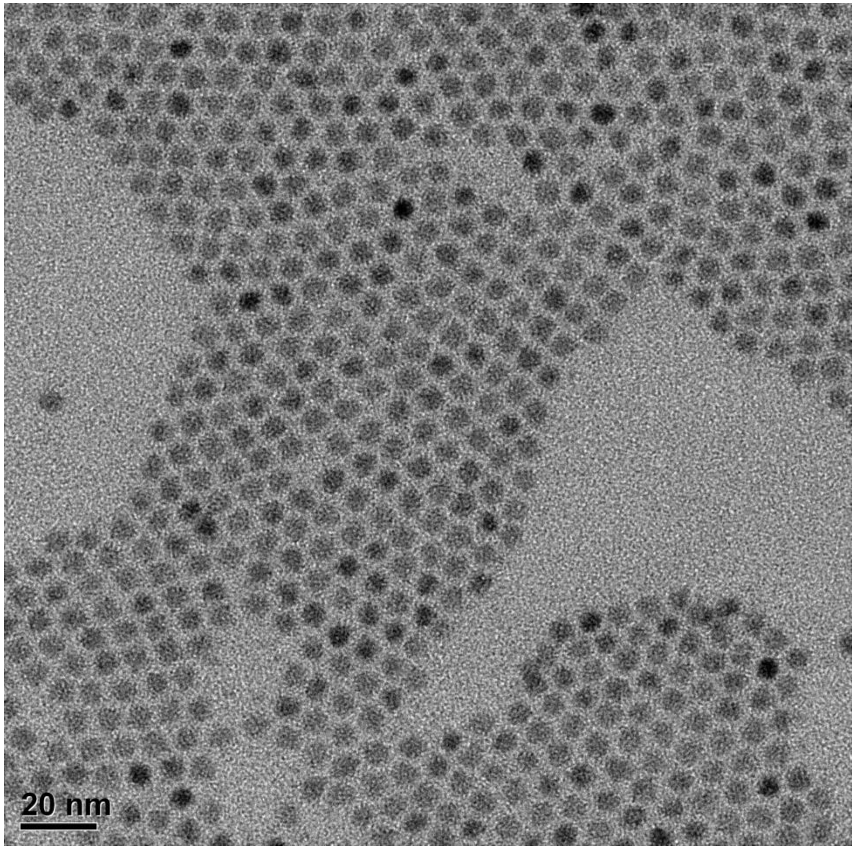
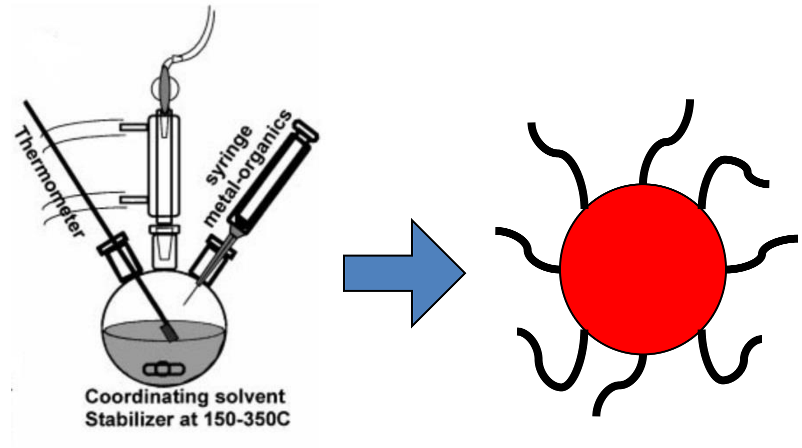
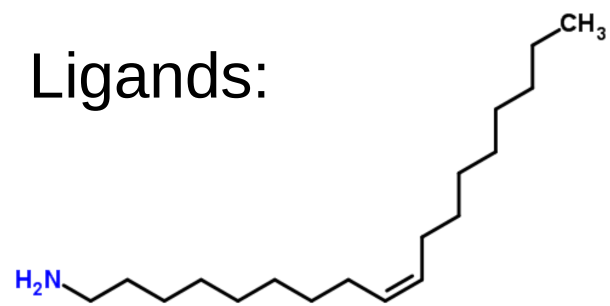


Figure. Bright field TEM of PbSe NPs



Ligands:



CQDSCs – Typical material parameters

- Mainly Pb-chalcogenides
- Bohr radii, a_B
  - PbS ~ 18 nm
- Sizes ~ 3-8 nm
- E_{gap} ~ 0.7 – 1.6 eV
- PbS $E_{g,bulk}$ ~ 0.4 eV

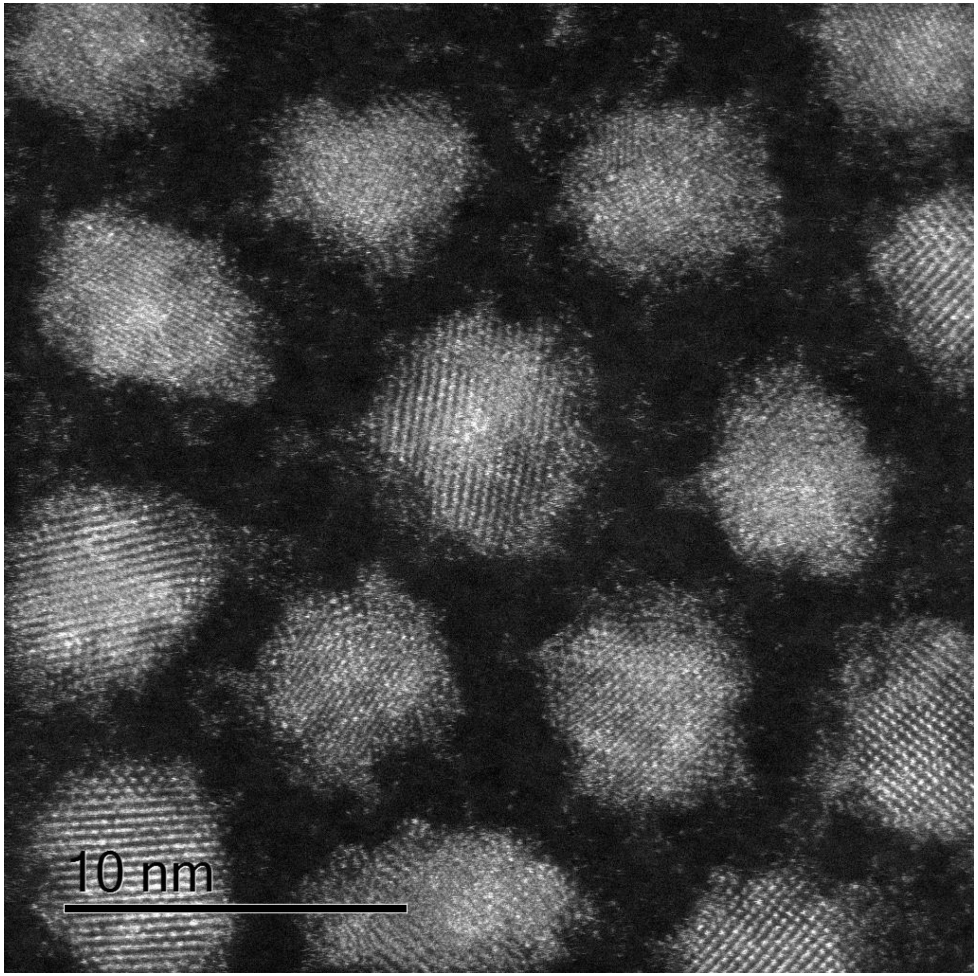
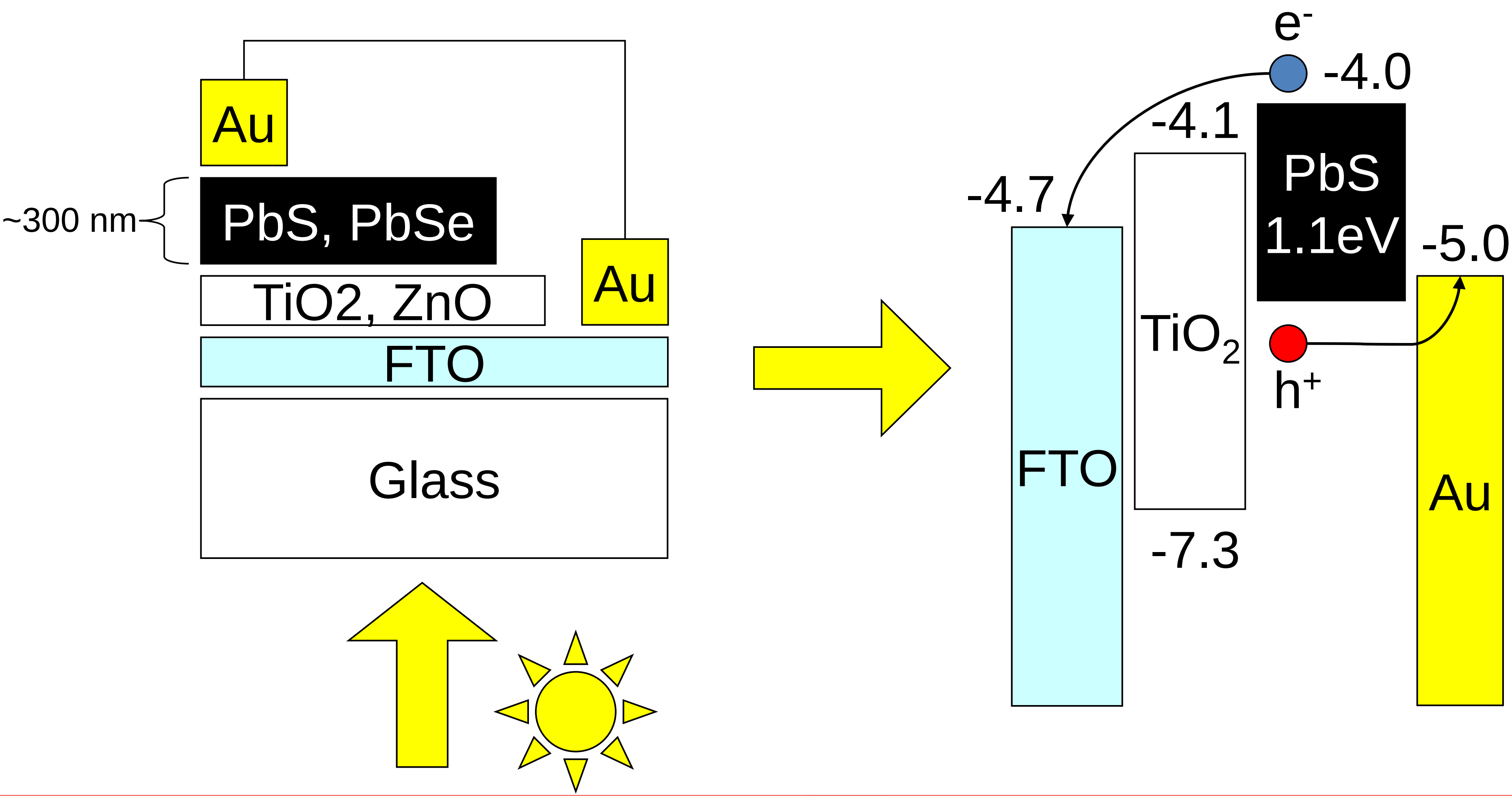
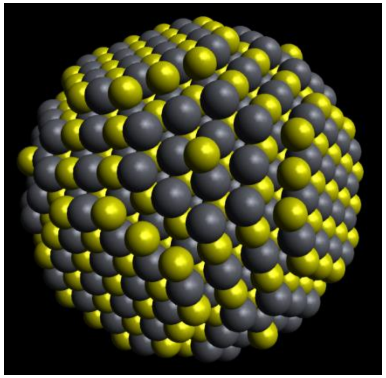


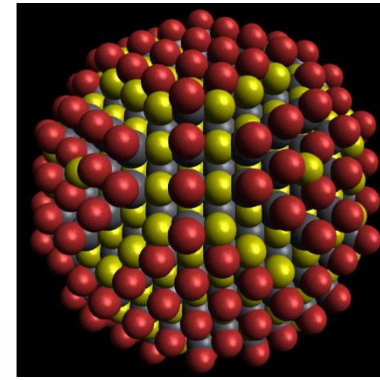
Figure. Atomic resolution dark field TEM image of Br-PbS QDs

CQDSCs – Cell structure



CQDSCs – Air stability





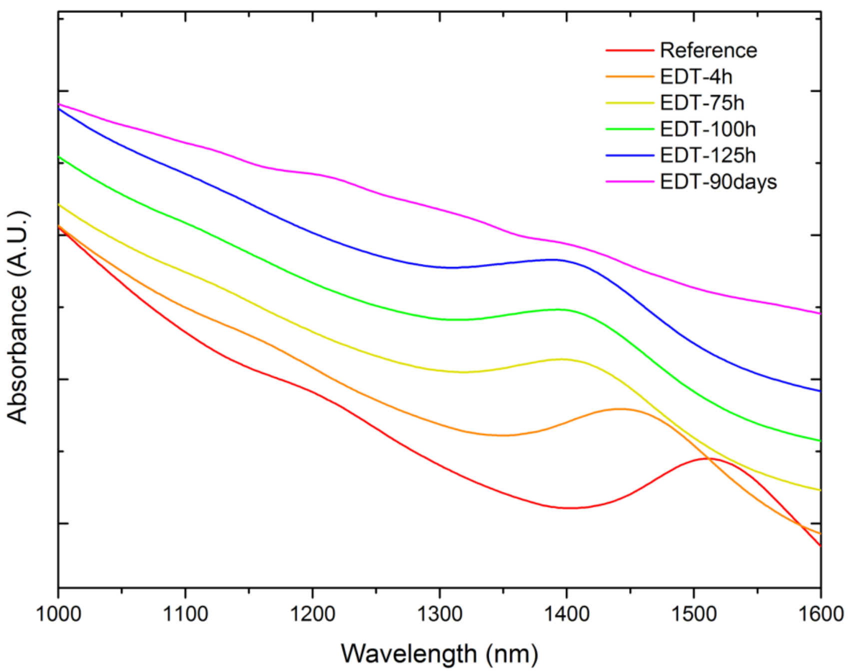


Figure. Unprotected PbSe UV-Vis showing a blue shift due to oxidation.

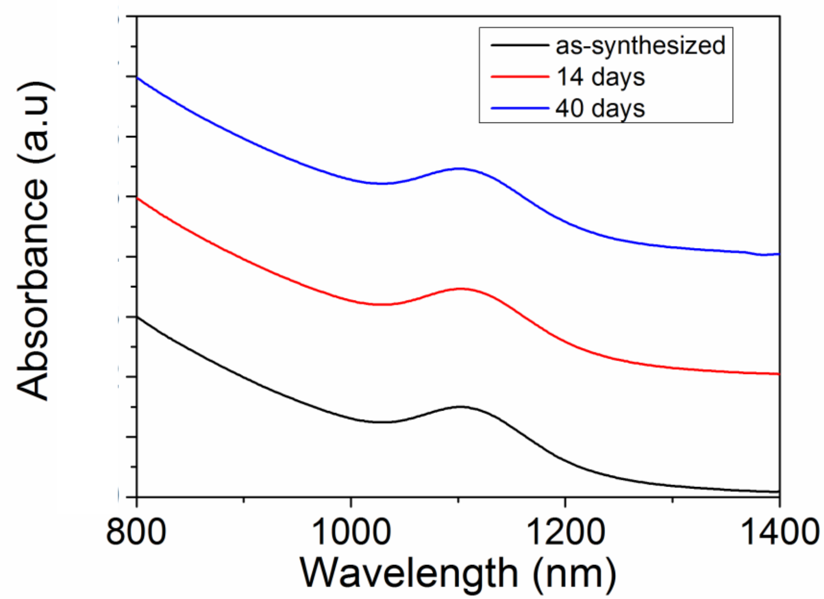


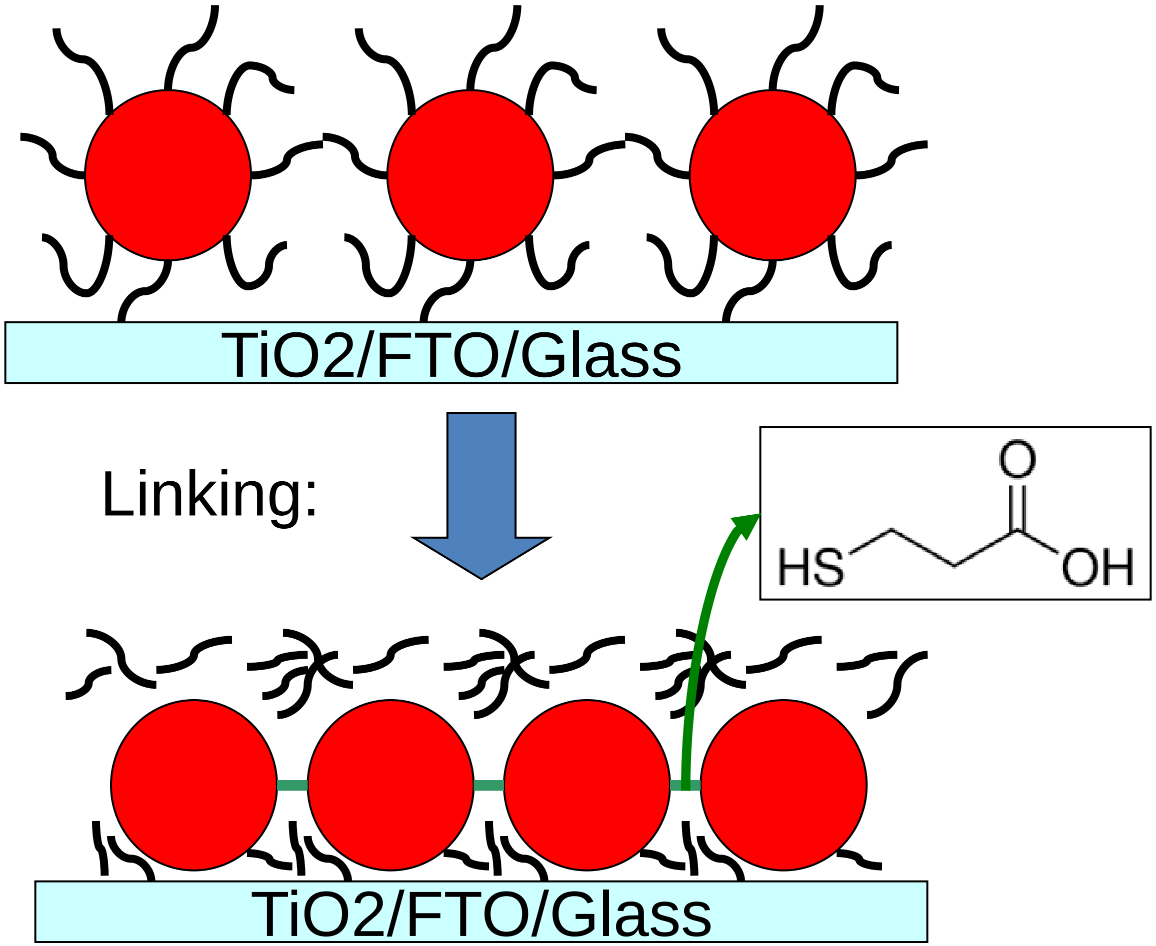
Figure. Bromine terminated PbS UV-Vis showing no blue shift after ~ 5 weeks.

Zhang et al, IEEE Conf, June 2015

Yuan, RSC Advances, in press, July 2015

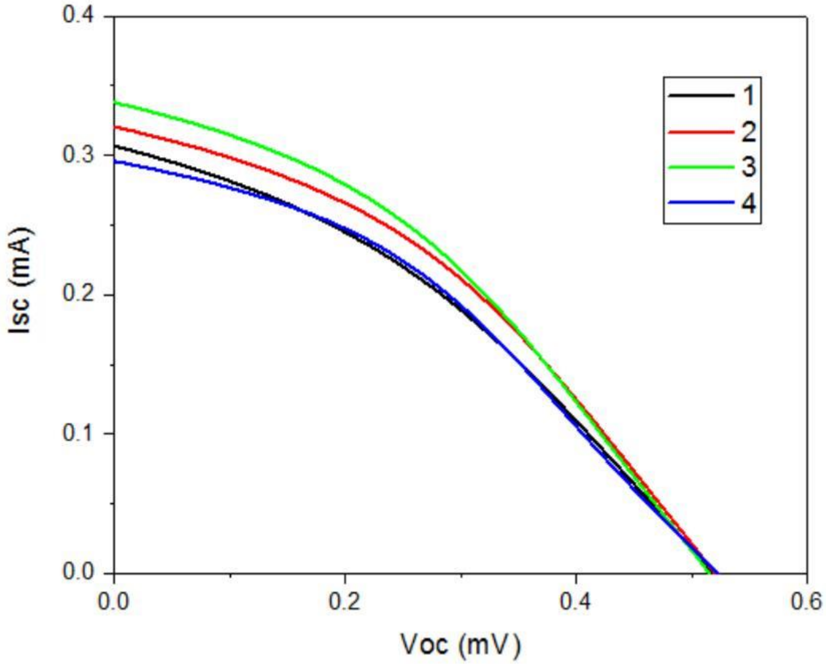
CQDSCs – Film fabrication & Linking

- "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

- Voc: 514.9 mV
- Jsc: 10.77 mA/cm2
- FF: 37.5%
- PCE: 2.08%
- Light soaking improved the curve
- World's best cells have more than double the current density and a better fill factor



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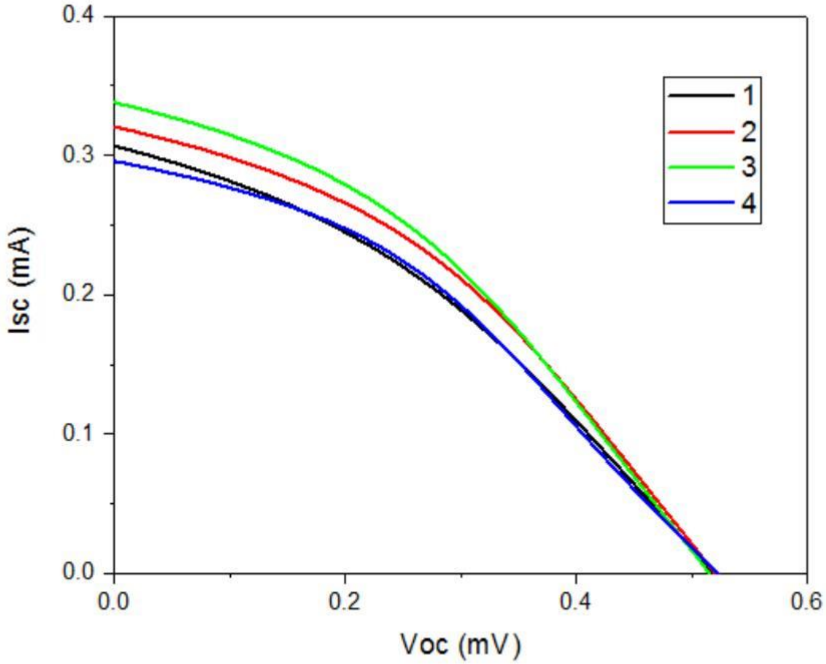
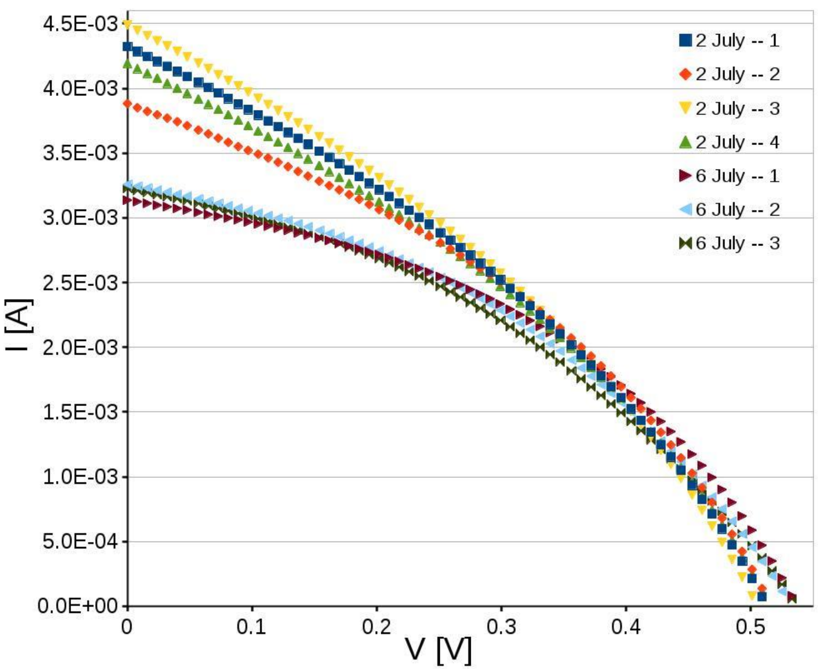
CQDSCs – Repeatability





2.1%, May 2015

2.47%, July 2015

CQDSCs – Further Work

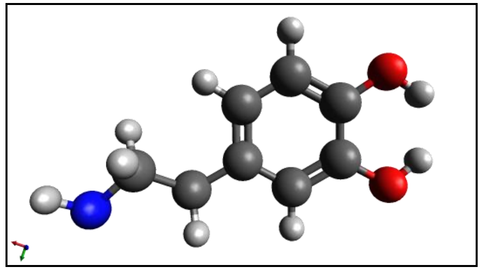
- Continue to improve efficiencies.
  - Film Continuity
  - Film Density
- Wide area devices
- Light trapping, plasmonics, hydrophillic QDs

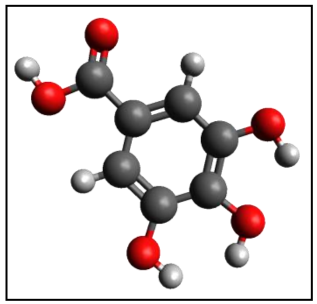
Catechol Surface Functionalized TiO_2 NPs

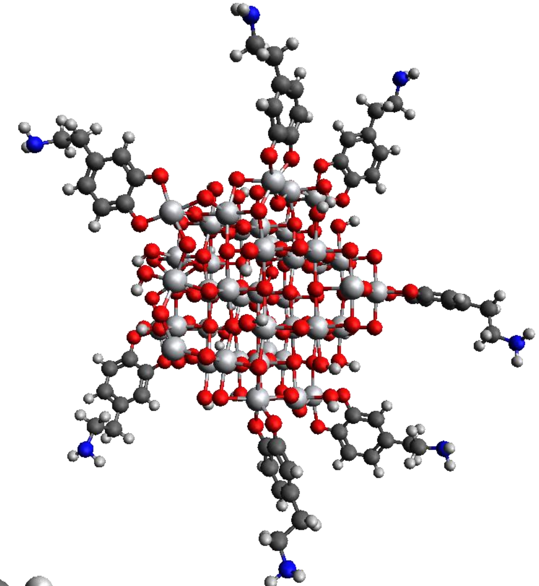
Shira Samocha, Vince Lorganzo,
Judy Hart

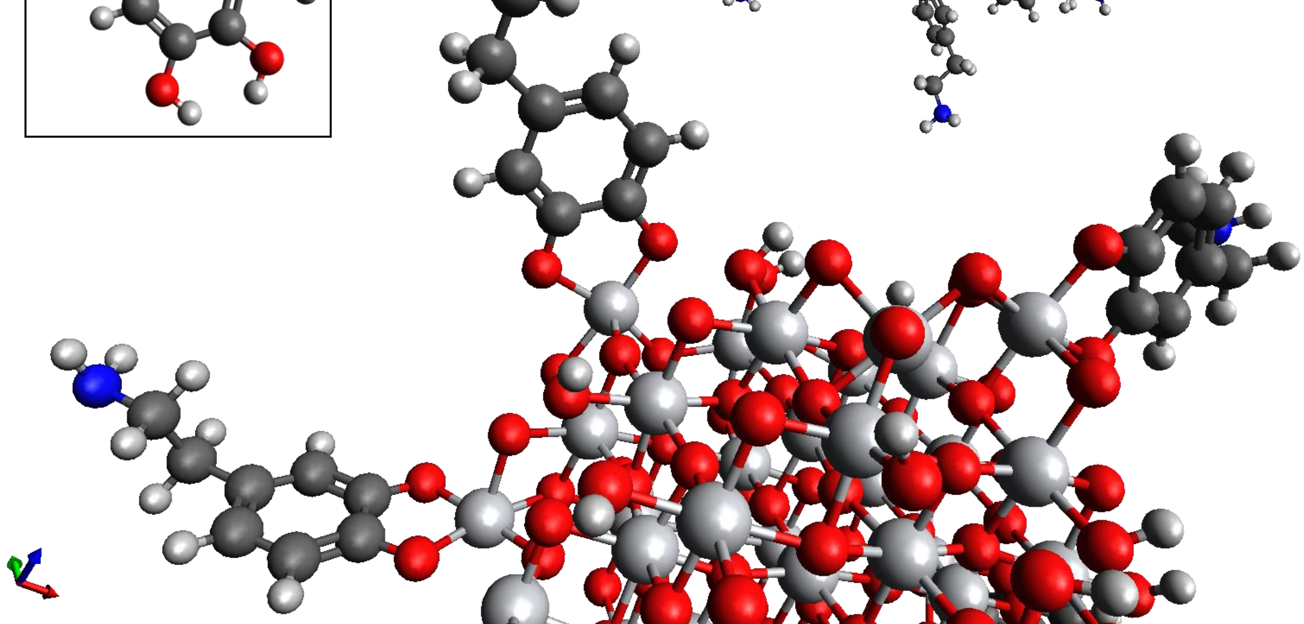
Catechol TiO_2 – NP Structure

- 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



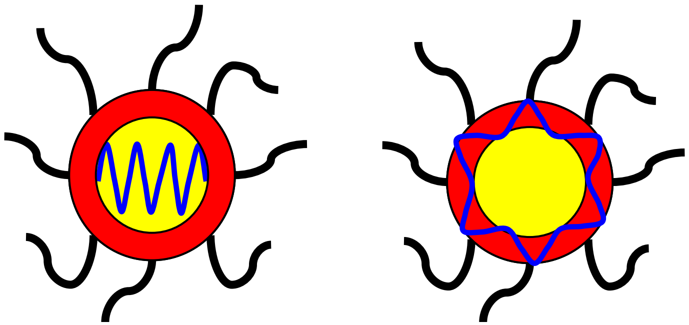






$C\text{-}TiO_2$ – Nanoparticle surface dipoles/ states

- With nanoparticles there is always a lot of surface
- Charge transfer across surface → strong surface dipole → 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



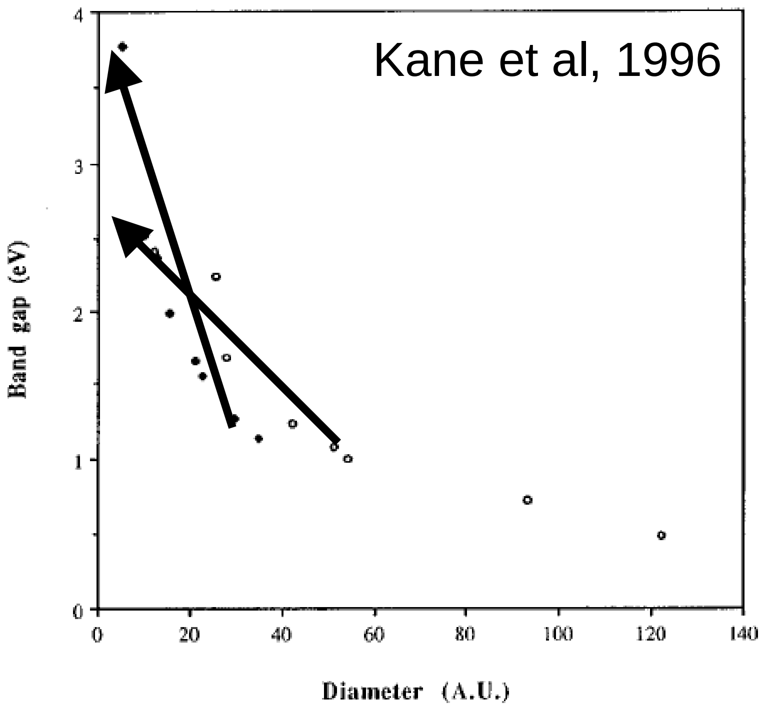
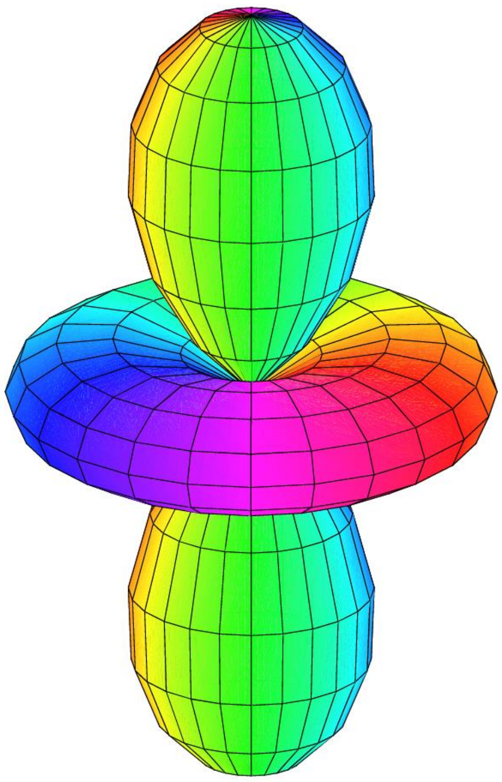


Figure 2. Band gap for PbS clusters. Black diamonds represent the temperature-adjusted calculations. Circles represent the experimental data of Wang et al.[9]

C-TiO_2 – LCAO/TB electronic bandstructure

Potential Energy + Kinetic Energy(**k**) = Total Energy(**k**)



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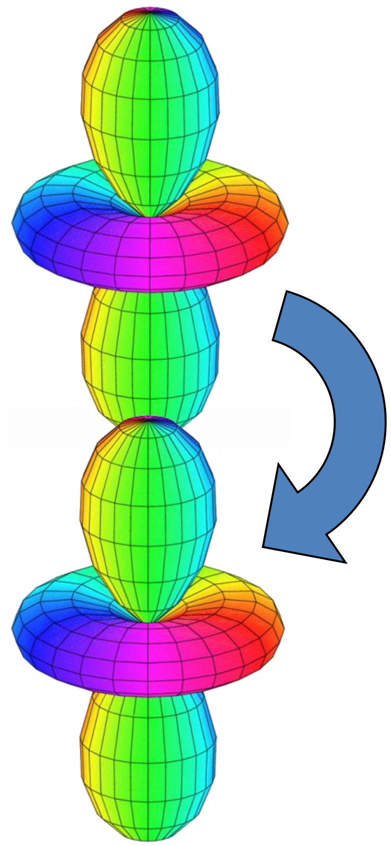

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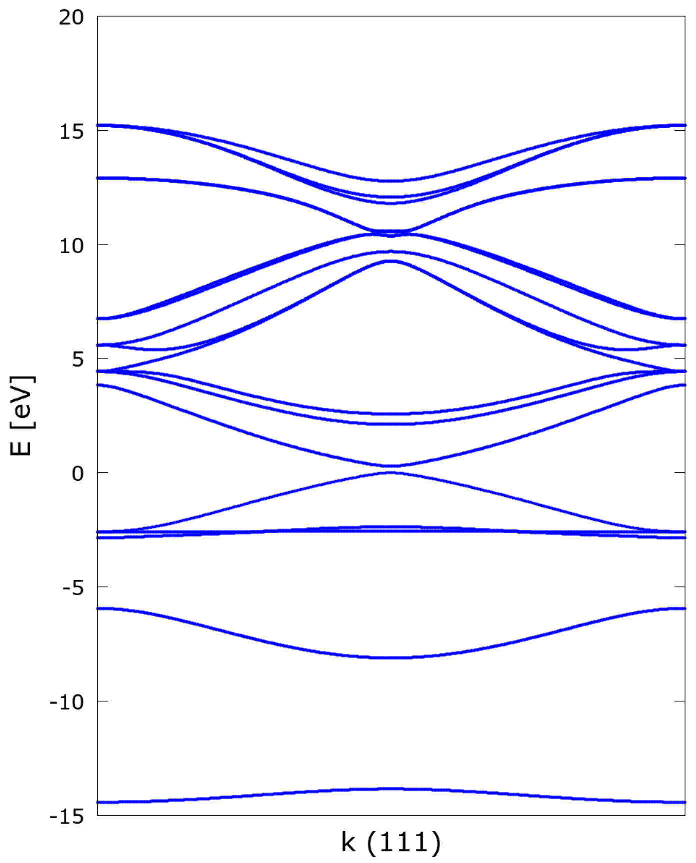
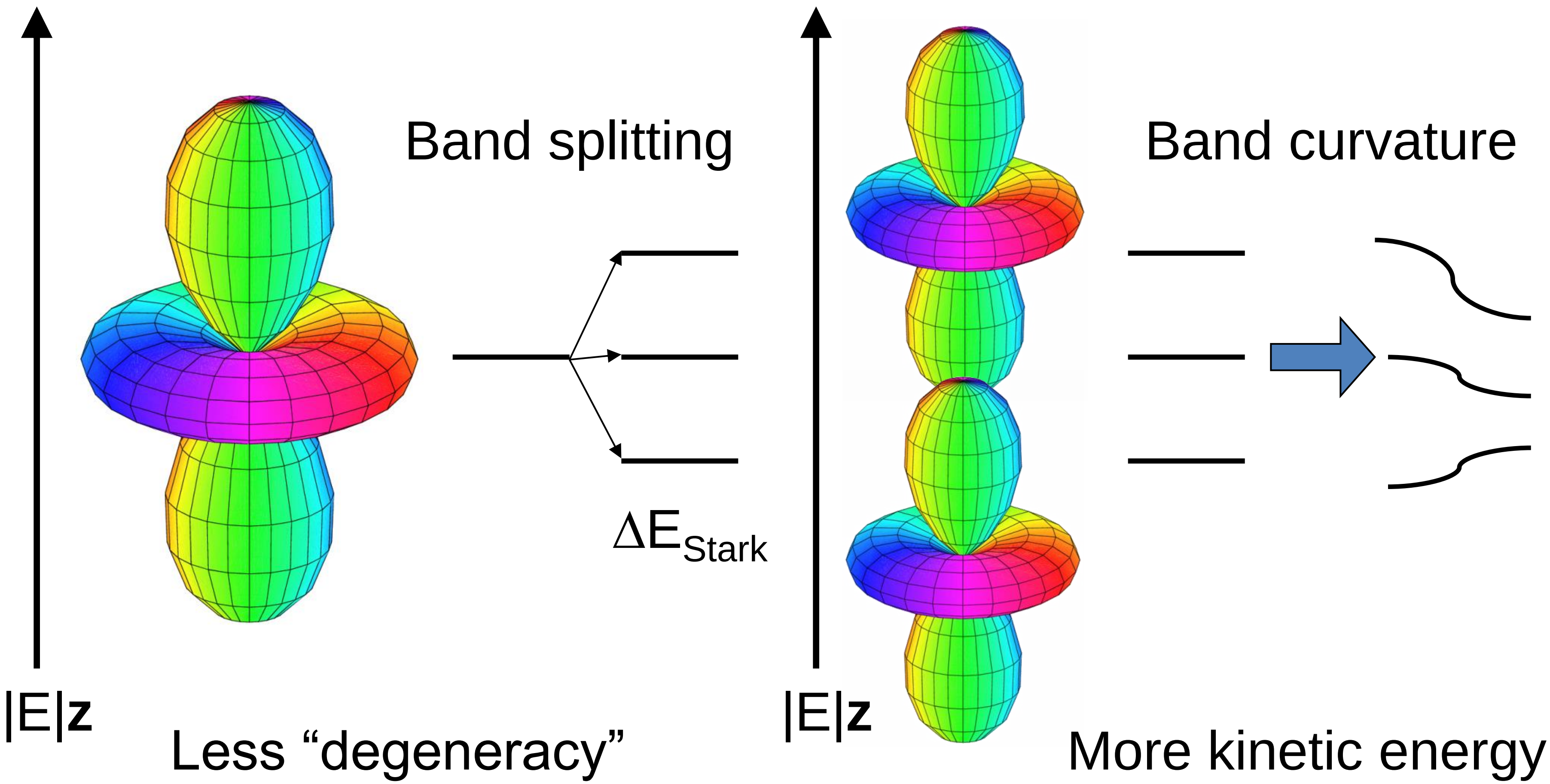
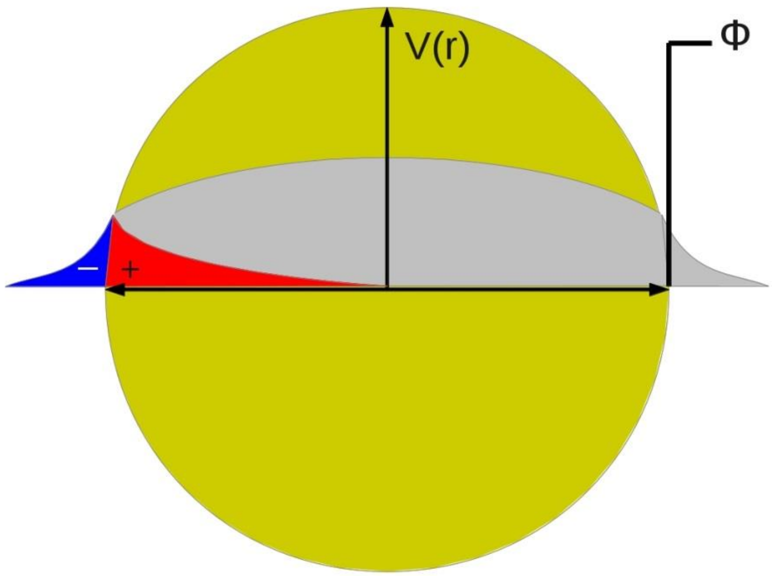
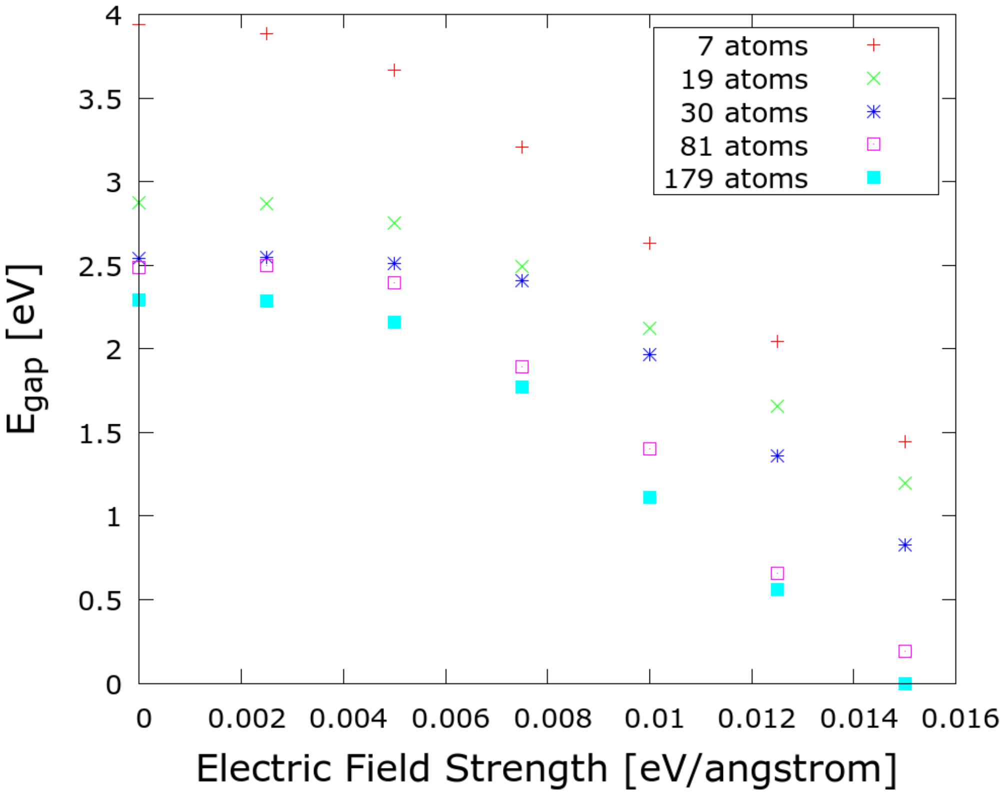


C-TiO_2 –Stark splittings due to surface dipoles



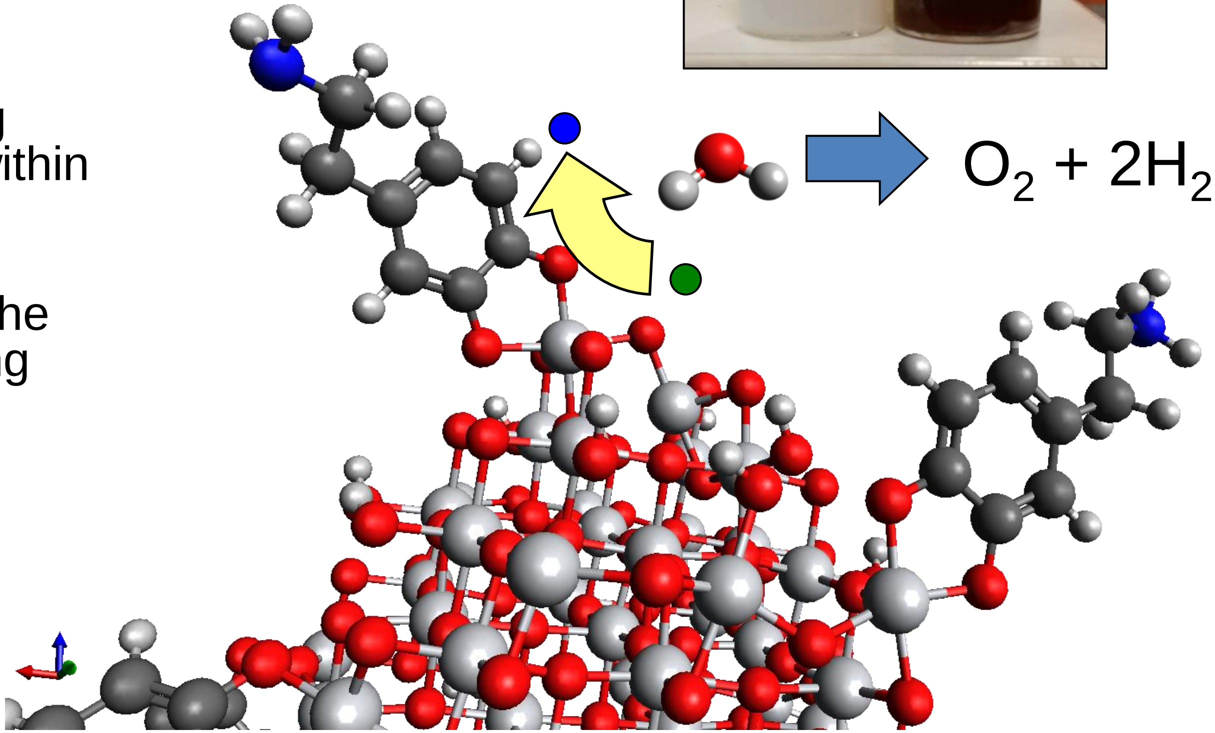
C-TiO_2 – Bandgap narrowing





C-TiO_2 -- Photocatalyst for solar hydrogen

- 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 ~2 eV – within reach using catechols
- Surface state created, catalysis happens at the surface, so worth trying

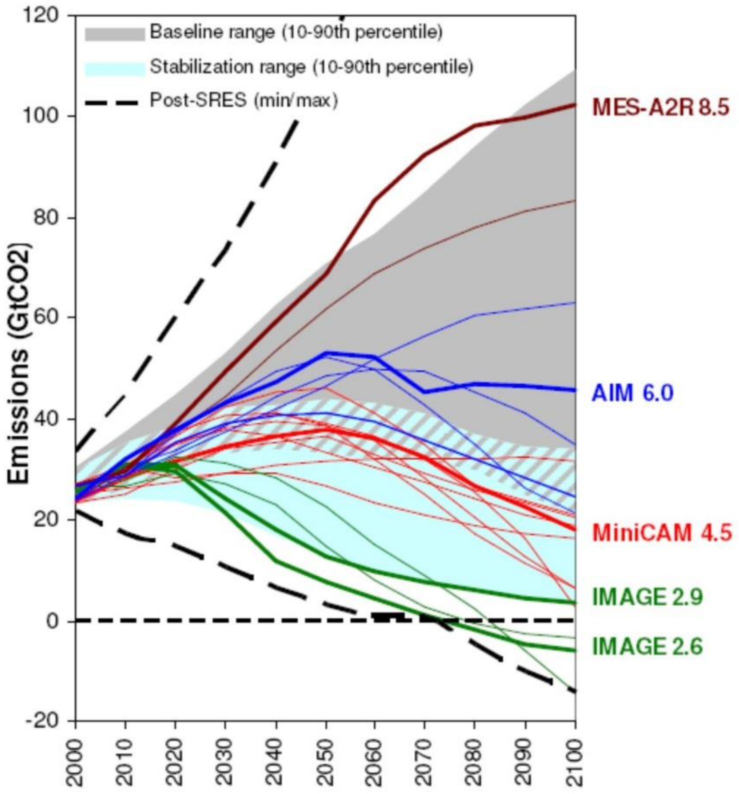


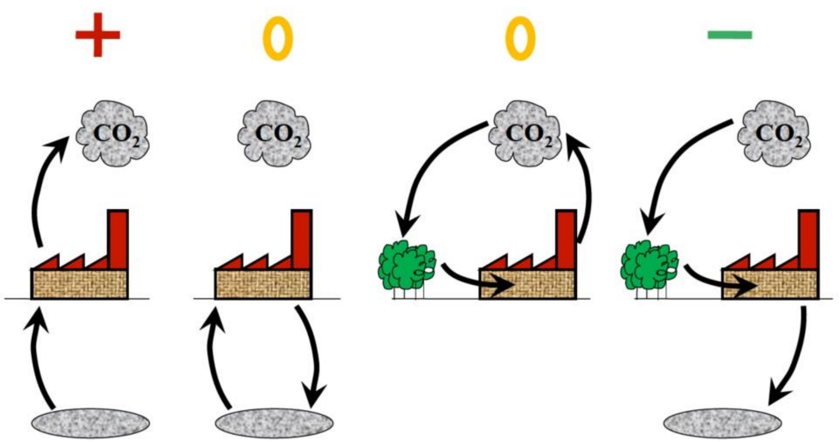
Bioenergy – Net-negative carbon bioenergy system

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.





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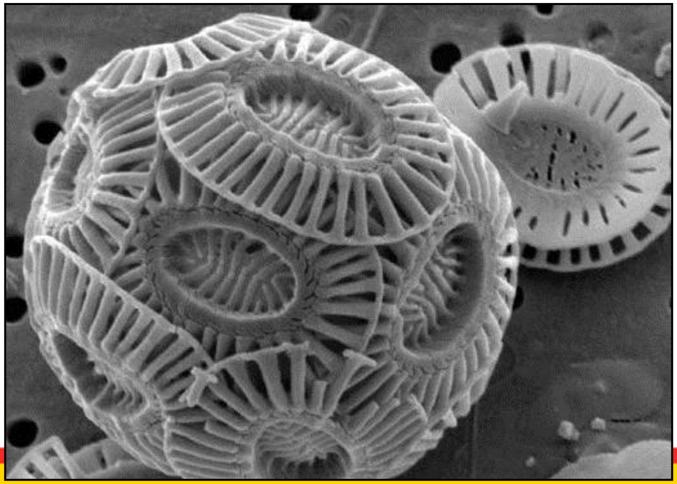
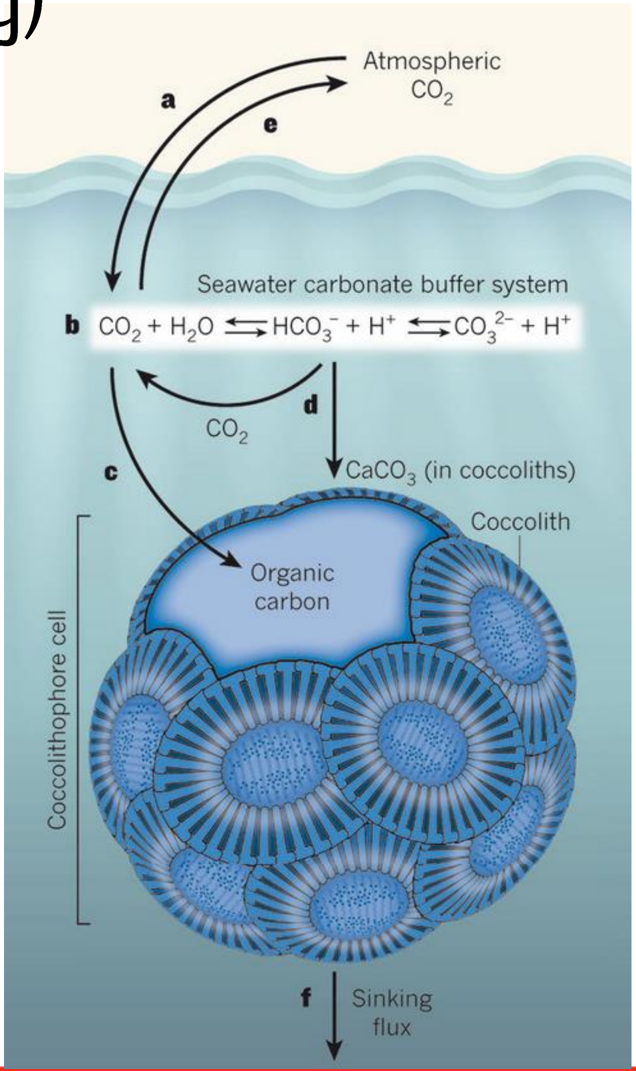
Bioenergy – Coccolithophorid algae (shell producing)

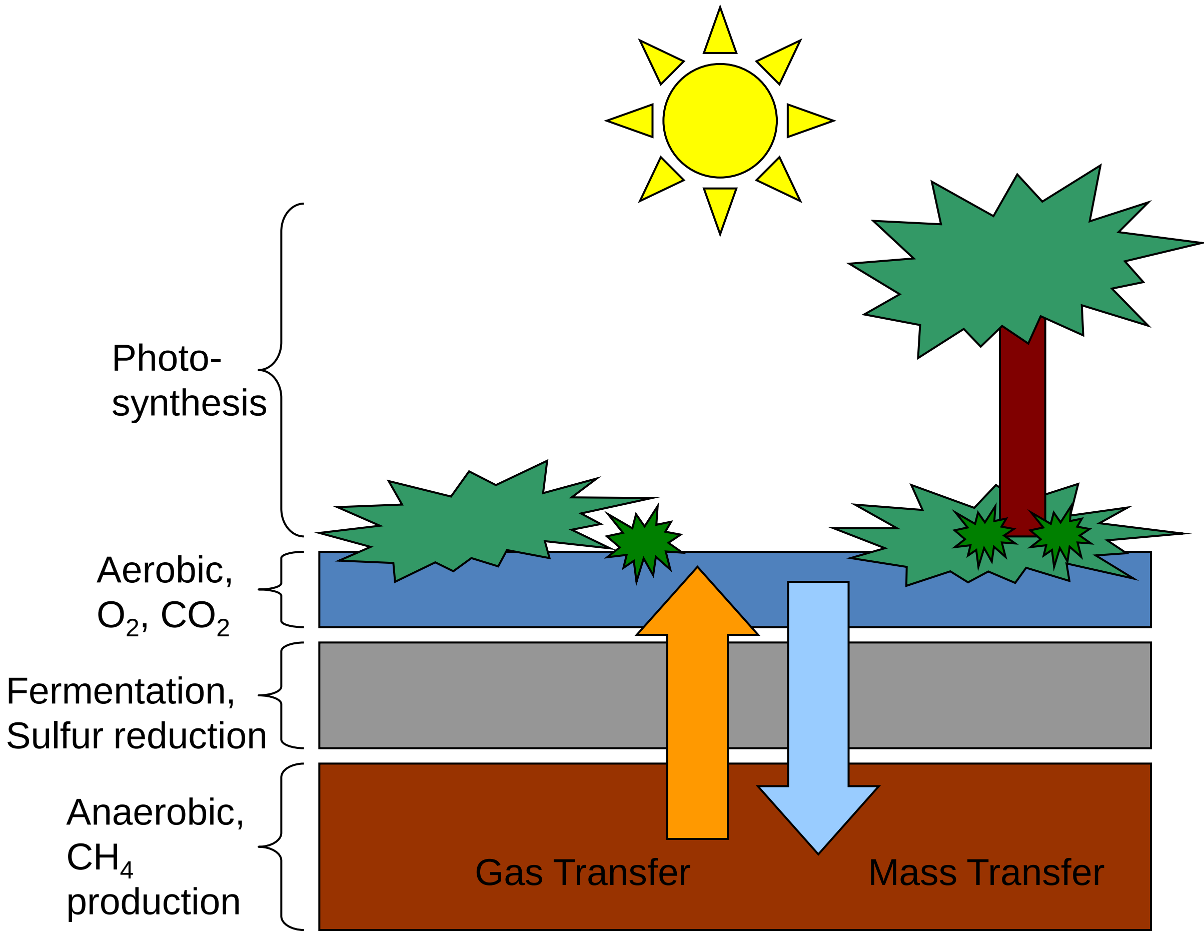
- Coccolithophorid algae
  - Carbohydrates, lipids, proteins → **biogas ($CH_4 + CO_2$)**
  - **Calcium carbonate ($CaCO_3$) → sequestration**
- "Shell producing" algae are abundant.
- Two common species:
  - Pleurochrysis Carterae
  - Emiliania Huxleyi





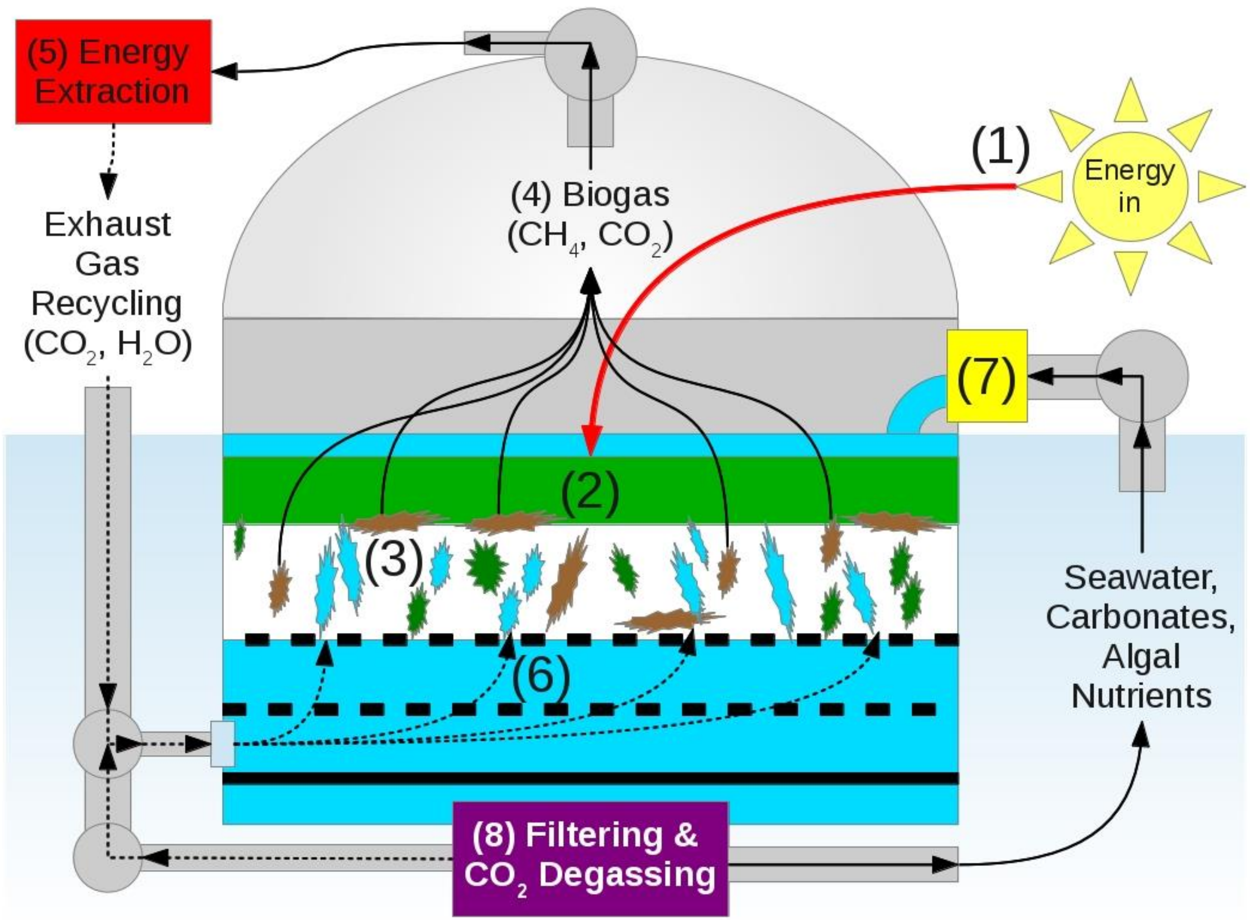
Bioenergy – Biomimetic concept

- 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?



Methanogens

Bioenergy – System structure



Bioenergy – System requirements

- Requirements
  - Oxygen/light tolerant methanogenic community
  - Photosynthesizing microbes with very high growth rates
  - high CO_2 tolerances (low O_2 environment)

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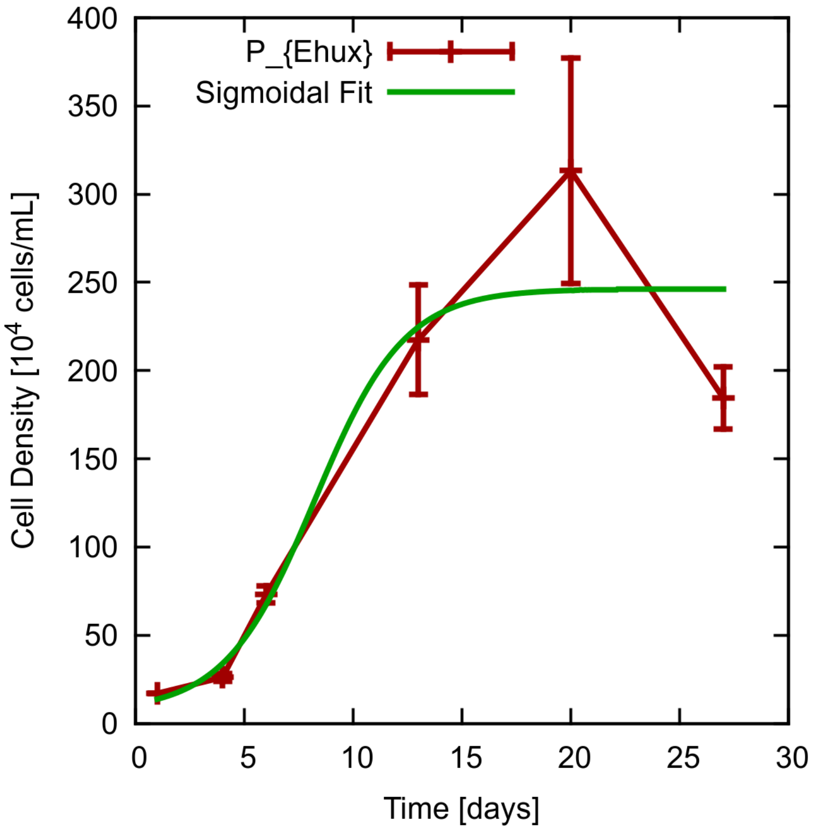
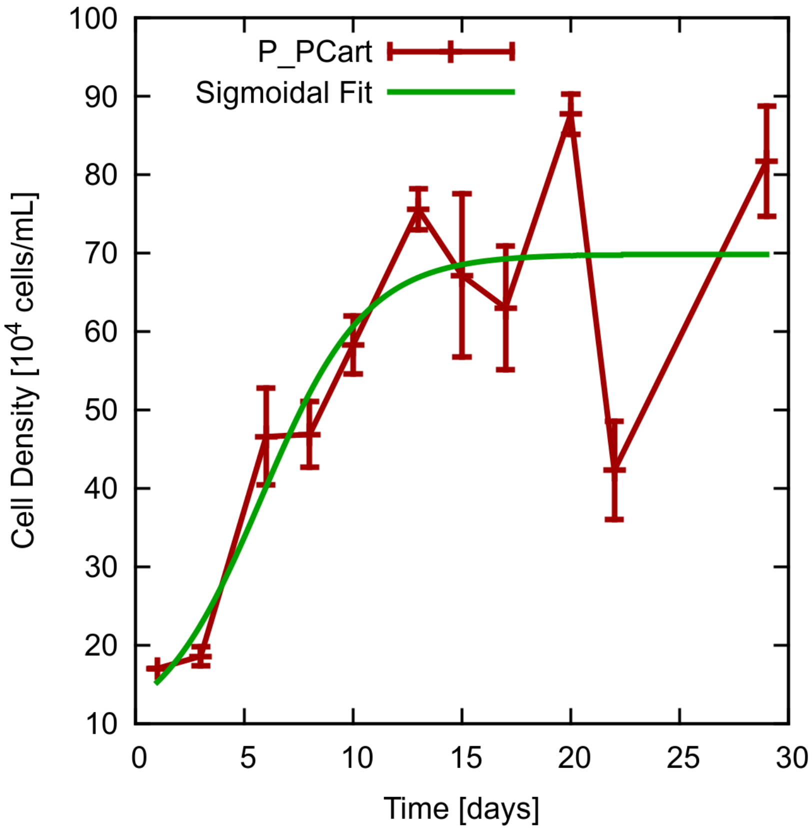
Bioenergy – Growth rates





Bioenergy – Oxygen and light dependence

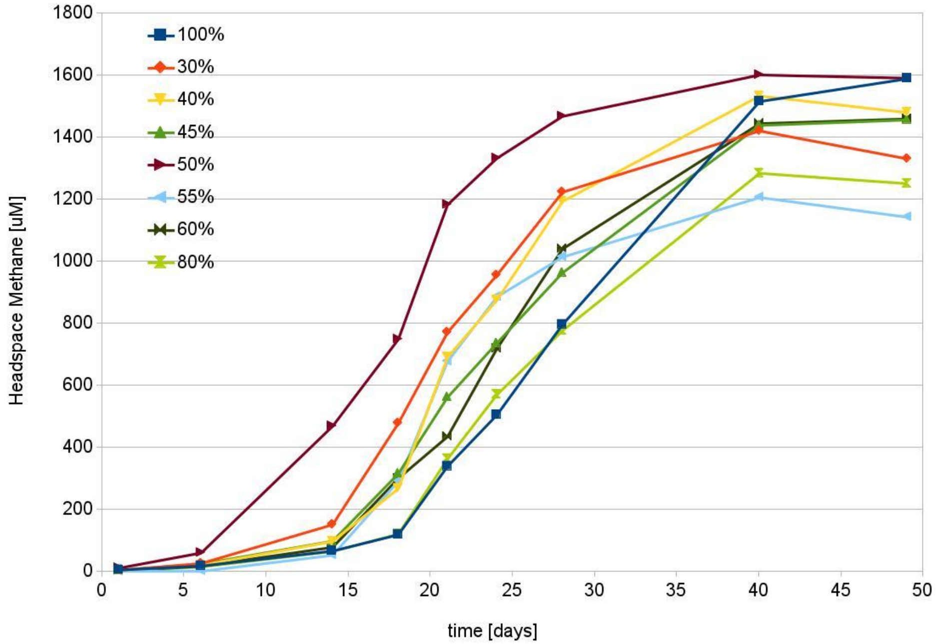


Figure. Varying initial headspace CO_2

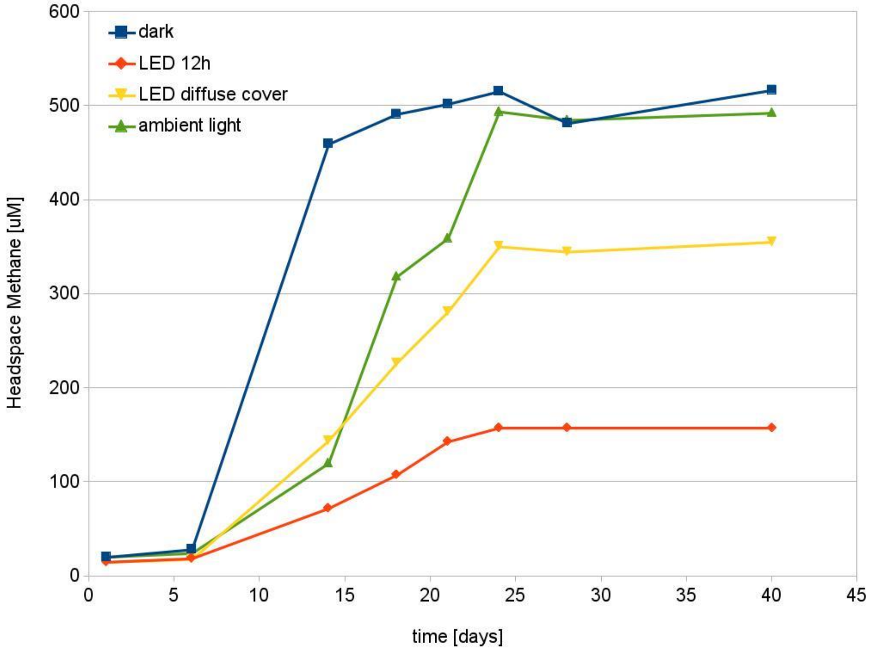
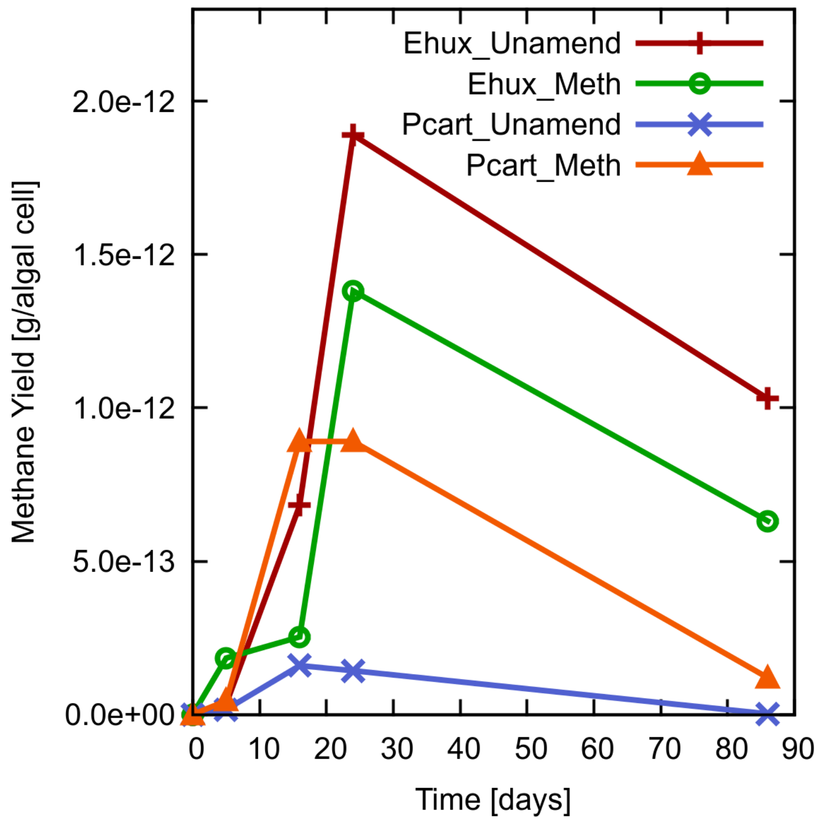


Figure. Light exposure

Bioenergy – Methane output

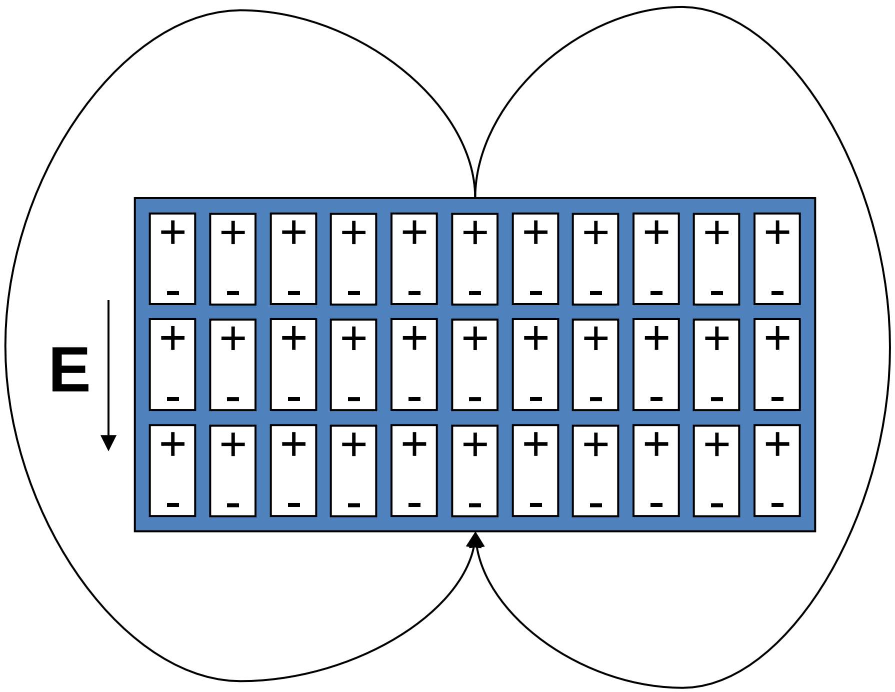
- Not in-situ yet… we're working on it.



Sulfohalide materials for solution processable solar cells

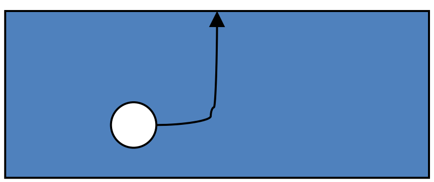
Sulfohalides – Motivation

- Ferroelectric – has high permittivity (ε_r), high polarizability and therefore possibly high screening
  - Si: ε_r ~ 11.7
  - Perovskite: ε_r ~ 60
  - Ferroelectric: ε_r ~ $1x10^4$
- Problems:
  - large bandgaps
  - Oxides
  - Unknown mobilities/ lifetimes

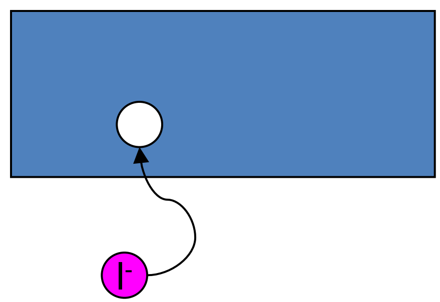


Sulfohalides – Defect removal, passivation, screening

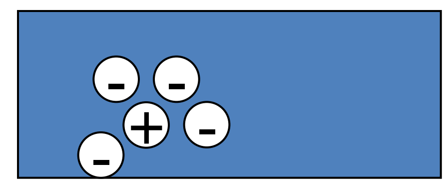
1. Remove defects
(fixing the problem)



2. Passivation
(masking the problem)

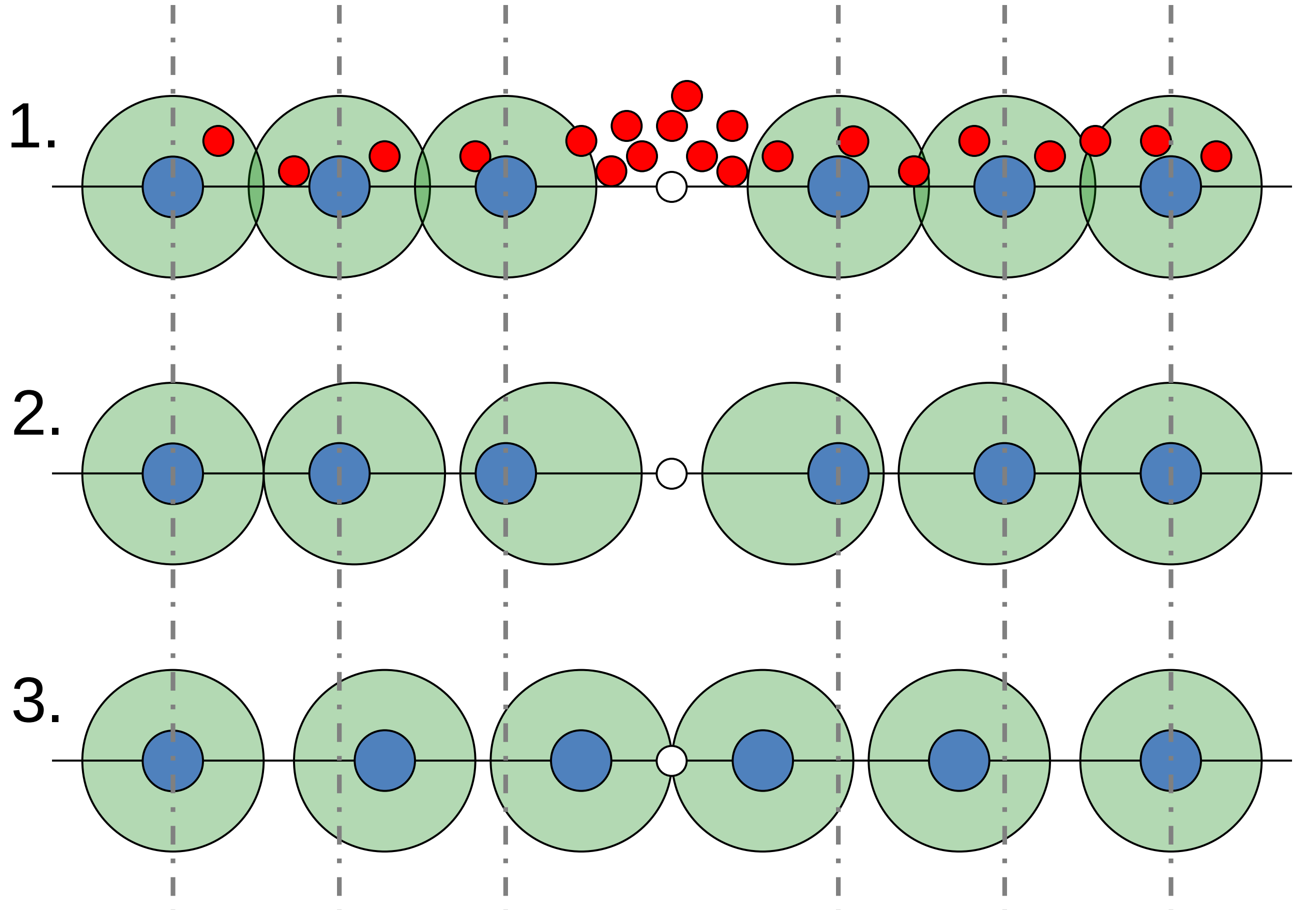


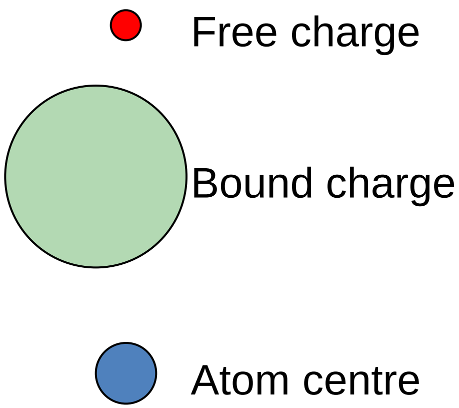
3. Screening
(disguising the problem)



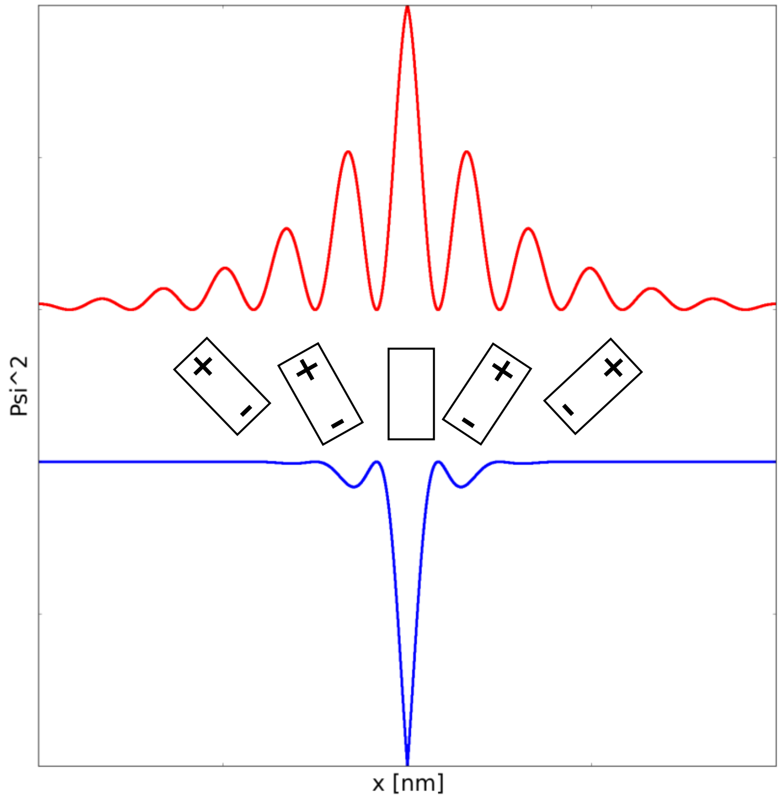
Sulfohalides – Connect er with distortions/vibrations and overall material polarizability

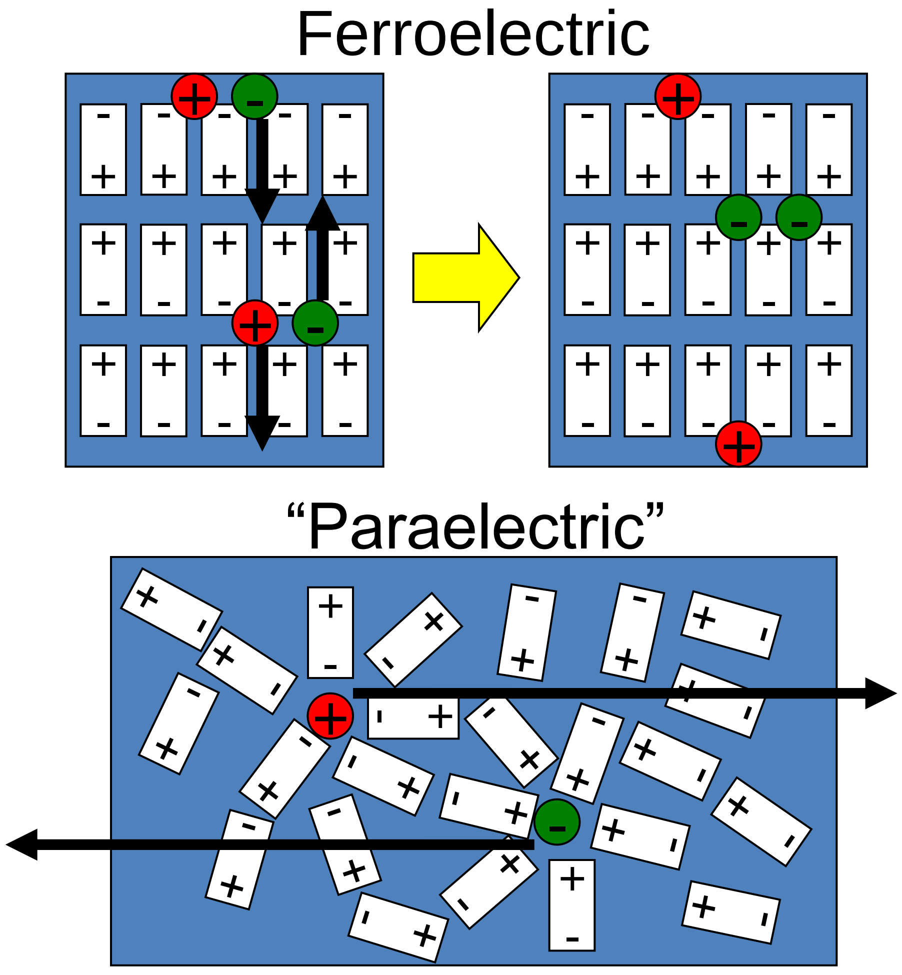
- $D = \varepsilon_0 {*} E + P$
  $\rightarrow \varepsilon_r = \varepsilon_0 + P/E$
- Dynamic process





Sulfohalides – Potential for charge segregation



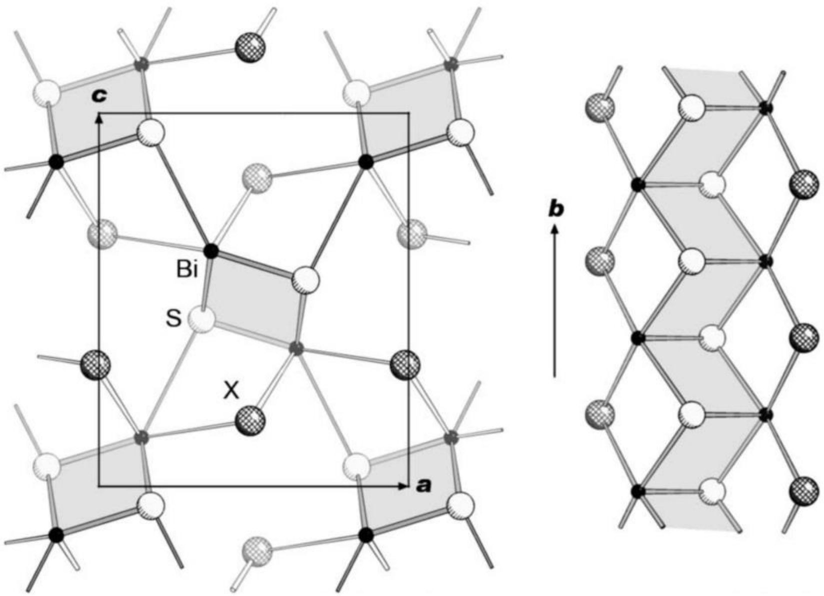


Electron contact

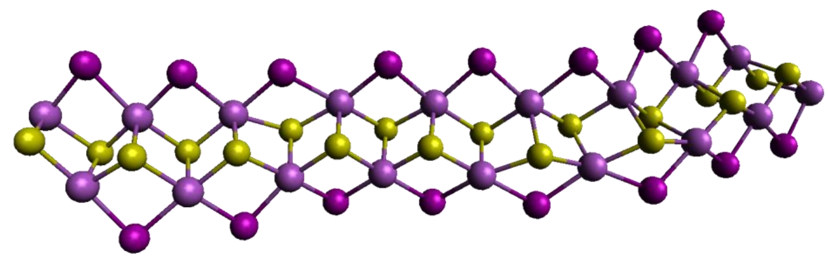
Potential difference between electrons and holes in the bulk of the material.

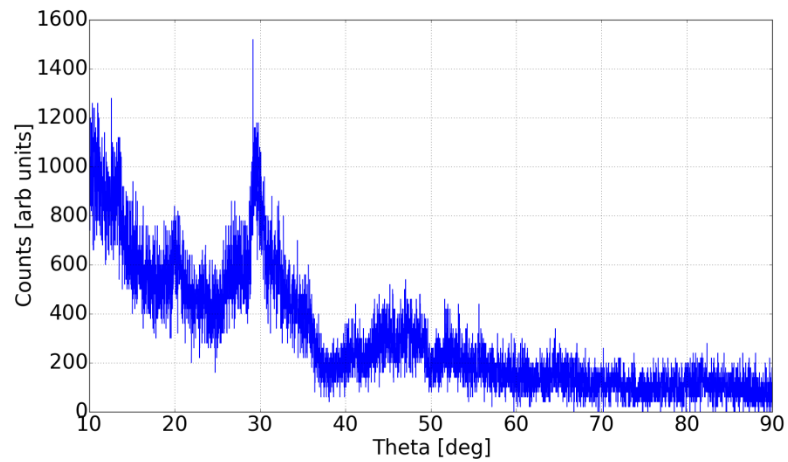
Hole contact

Sulfohalides -- Structure



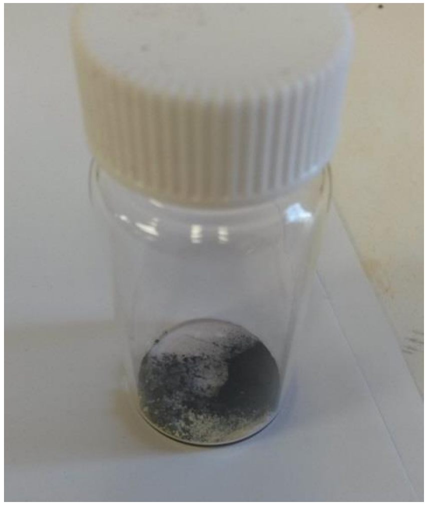
Keller, Act Cryst B, 2006



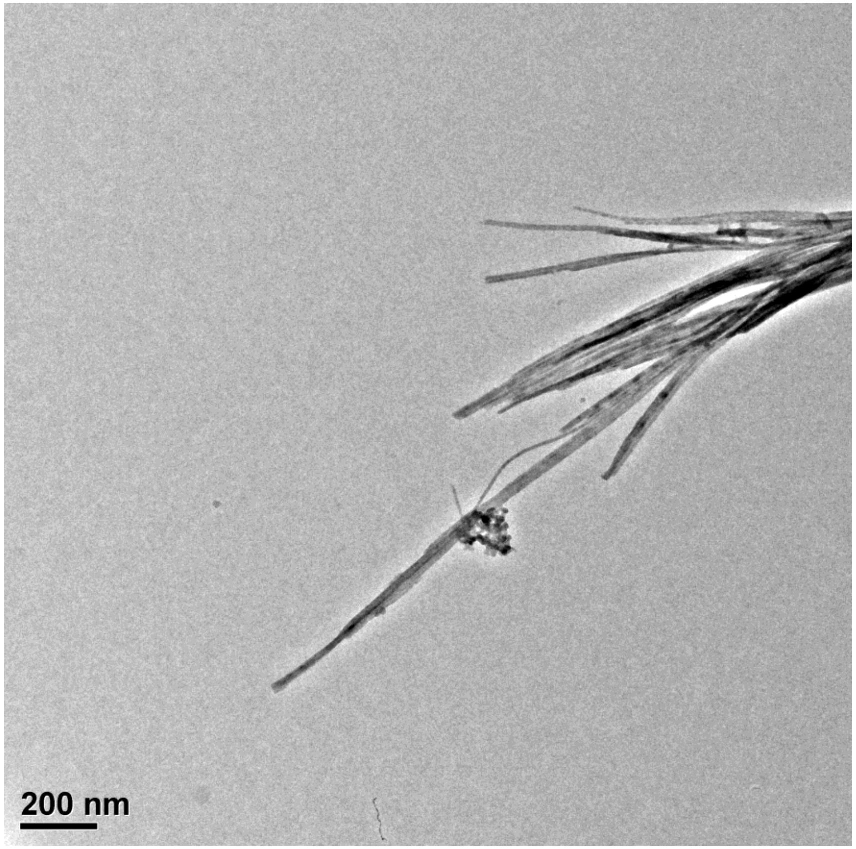


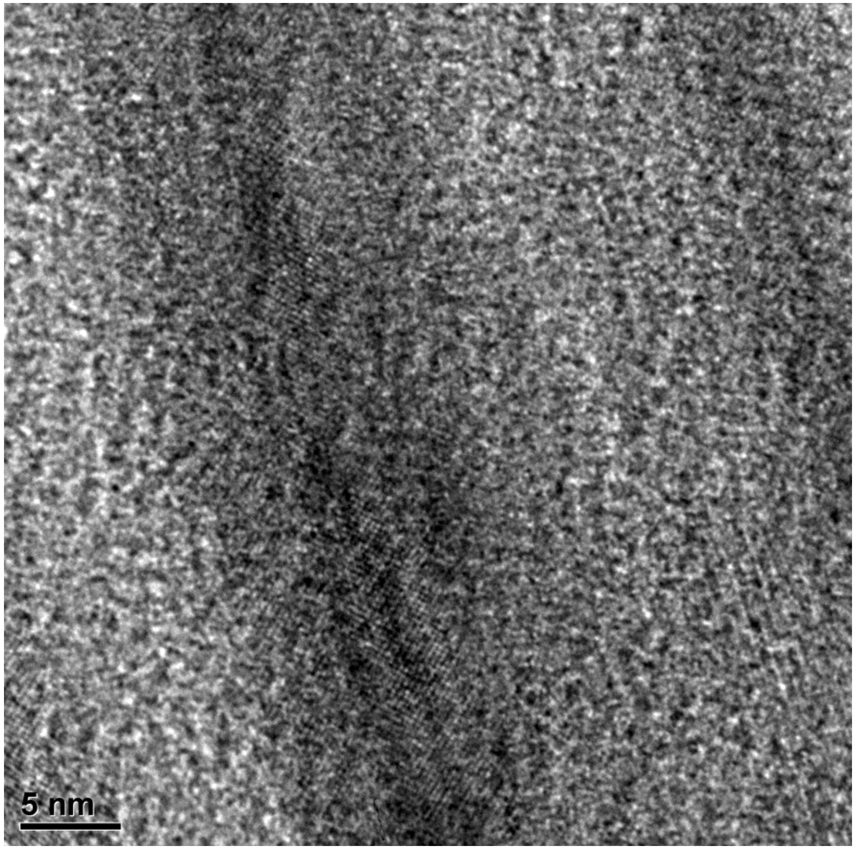
Sulfohalides – High permittivity semiconductor materials available from chemical synthesis

- SbSI, Eg ~ 1.8 eV
  - (top cell)
- SbSeI, Eg ~ 1.6 eV
  - (getting closer…)

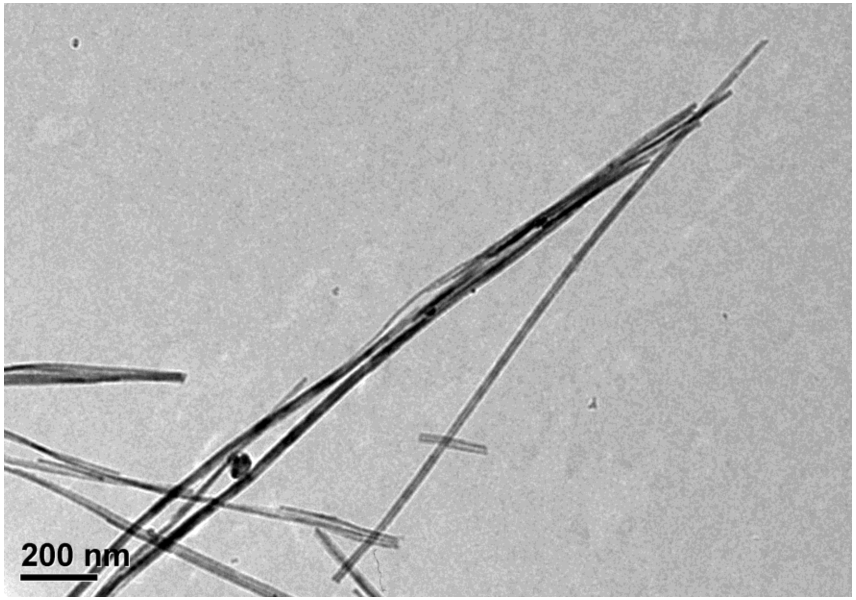


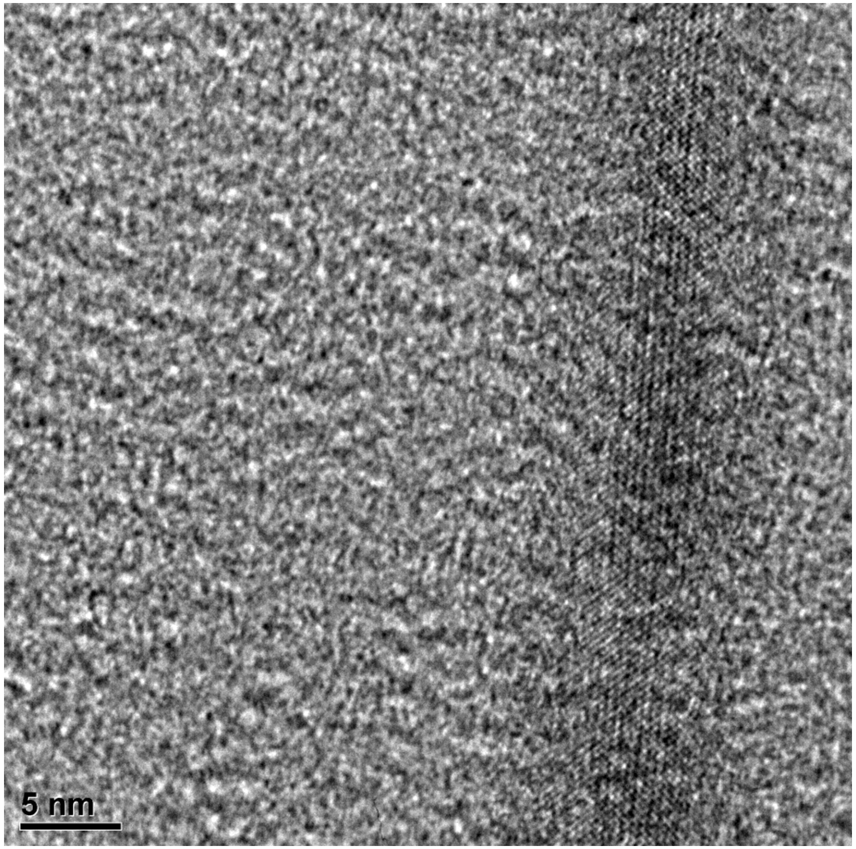
Sulfohalides – SbSeI TEM





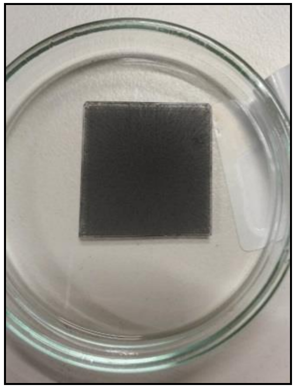
Sulfohalides – SbSeI TEM

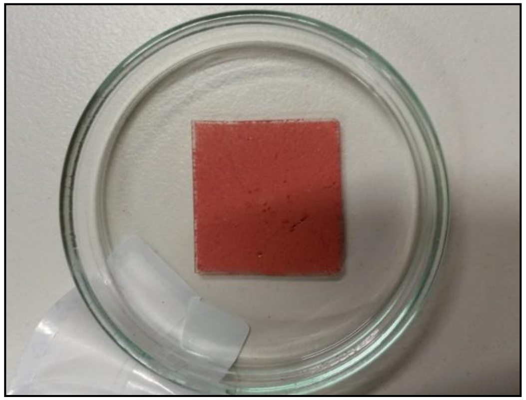


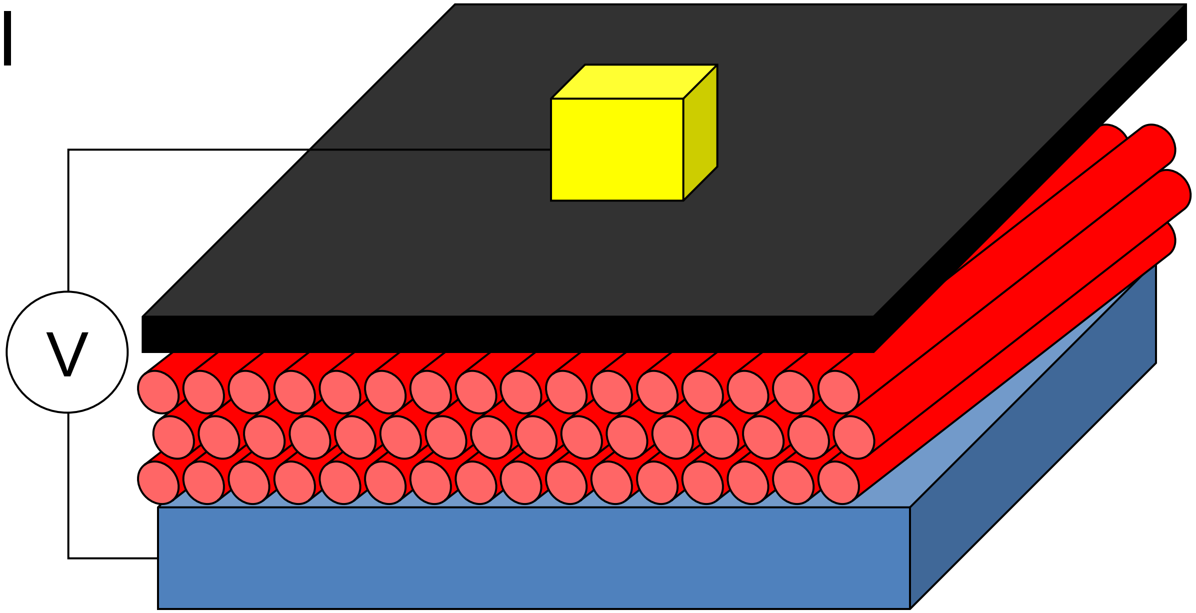


Sulfohalides – Thin film fabrication

- 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.

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