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Quantum Dot Solar Cells

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Case Western Reserve University



Our little dot



In 1990, Carl Sagan convinced NASA engineers to turn Voyager for one last, homeward look before leaving the solar system



"Look again at that dot. That's here. That's home. That's us. On it, everyone you love, everyone you know, everyone you ever heard of, every human being who ever was, lived out their lives Every hunter and forager, every hero and coward, every creator and destroyer of civilization, every king and peasant, every young couple in love, every mother and father, hopeful child, inventor and explorer, every teacher of morals, ... every saint and sinner in the history of our species lived there--on a mote of dust suspended in a sunbeam."

"....The Earth is the only world known so far to harbor life. There is nowhere else, at least in the near future, to which our species could migrate ... Like it or not, for the moment the Earth is where we make our stand."

-- Energy Secretary, Steve Chu

\$ per Watt Workshop held Aug. 11-12, 2010 [http://www1.eere.energy.gov/solar/dollar per watt.html].

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http://www1.eere.energy.gov/solar/pdfs/dpw_chu.pdf

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Global average temperatures from NASA's Goddard Institute for Space Studies (Columbia University). Data set follows methodology developed by J. Hansen.





Keeling curve, data from Mauna Loa, Hawaii.

Hansen, J., et al. (2006) "*Global temperature change*", PNAS 103: 14288-14293.





NATURE |VOL 395 | 29 OCTOBER 1998 Energy implications of future stabilization of Atmospheric CO_2 content M. Hoffert et al.

<u>Growth</u>

- Global energy consumption -- 1.6-1.7% per year.
- Includes for 1%/yr. efficiency improvement
- 28 TW global power consumption by 2050
- Population growth primarily in less-developed countries → increased C-intensity.
- ~15 TW of the ~30 TW should come from C-free sources in 2050.

<u>Health</u>

Coal-fired power plants:

- 59% of total U.S. sulfur dioxide pollution
- 18% of total nitrous oxides every year
- largest polluter of toxic mercury pollution

All U.S. power plants: release over 40% of U.S. CO₂

[Sources – U.S. DOE and U.S. EPA]

Acid rain, smog (ozone), soot → unhealthy ecosystems, respiratory problems, unhealthy lungs (incl. asthma)

A developmental toxin, affecting unborn children



Earth's key natural resources: water and air





Volume of Earth: $1.1 \times 10^{12} \text{ km}^3$ Volume of water: $1.4 \times 10^9 \text{ km}^3$ Volume of atmosphere: $4.2 \times 10^9 \text{ km}^3$

Photo & caption info: ADAM NIEMAN / SCIENCE PHOTO LIBRARY

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Happy Birthday (April 11) to Uncle Brooks!







Dirty energy, toxic food, air, and water



Burn a 100 W light bulb for a year:

 $\frac{876~\mathrm{kW}\cdot\mathrm{h}}{2.0~\mathrm{kW}\cdot\mathrm{h/kg}} = 438~\mathrm{kg}~\mathrm{of}~\mathrm{coal} = 966~\mathrm{pounds}~\mathrm{of}~\mathrm{coal}$

Ohio only ~85% coal, but also 5-10% transmission losses \rightarrow ~900 lbs. (~400 kg) coal to light that bulb (or four 25 W CFLs) in Ohio.

http://en.wikipedia.org/wiki/Coal



Coal energy density: ~24 MJ/kg



http://en.wikipedia.org/wiki/Mercury_in_fish



The upsides of carbon-free energy





The Sun (worth revering)

"Why Does the Sun Shine?" by They Might Be Giants

The sun is a mass of incandescent gas A gigantic nuclear furnace Where hydrogen is built into helium At a temperature of millions of degrees

Yo ho, it's hot, the sun is not A place where we could live But here on Earth there'd be no life Without the light it gives

We need its light We need its heat We need its energy Without the sun, without a doubt There'd be no you and me

- Theoretical: 1.2x10⁵ TW solar energy potential (1.76 x10⁵ TW striking Earth; 0.30 Global mean albedo)
- Energy in 1 hr of sunlight \leftrightarrow 14 TW for a year
- Practical: > On-shore electricity generation potential of ≈ 600 TW (10% conversion efficiency).
- *Photosynthesis*: 170 TW (90 TW land-based, and 80 TW aquatic)

Sunlight to electricity (photovoltaic conversion)

www.sciencegeek.net/tables/LosAlamosperiodictableColor.pdf

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Sunlight to electricity (photovoltaic conversion)

http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_2_4.html

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Top: space-charge density (ionized dopants) Middle: electric field Bottom: electrostatic potential

http://www.aerostudents.com/files/solarCells/CH4SolarCellOperationalPrinciples.pdf

Transport of free carriers occurs via drift (electric field) and diffusion (concentration gradient)

$$J_{n} = q\mu_{n}n(x)E + qD_{n}\frac{dn(x)}{dx}$$
$$J_{p} = q\mu_{p}p(x)E + qD_{p}\frac{dp(x)}{dx}$$

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Typical p-n (homo)junction crystalline silicon (c-Si) PV cell

http://en.wikipedia.org/wiki/File:Silicon_Solar_cell_structure_and_mechanism.svg

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Estimating depletion width for c-Si

$$W = \left[\frac{2K_{s}\varepsilon_{0}}{q}\left(\frac{N_{A}+N_{D}}{N_{A}N_{D}}\right)(V_{bi}-V)\right]^{1/2}$$

$$K_{s} \approx 11.9$$

$$\varepsilon_{0} = 8.85 x 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$$

$$\frac{10^{16} cm^{-3}+10^{19} cm^{-3}}{10^{35} cm^{-6}} \approx 10^{-16} cm^{3}$$

$$W \approx \left[1.3 x 10^{-13} V^{-1} m^{2} (V_{bi}-V)\right]^{1/2}$$

$$W \approx \left[3.3 x 10^{-13} V^{-1} m^{2} (V_{bi}-V)\right]^{1/2}$$

$$W \approx 330 \text{ nm}$$

$$V_{bi} \approx \frac{kT}{q} \ln\left(\frac{10^{16} cm^{-3} 10^{19} cm^{-3}}{2.2 x 10^{20} cm}\right) \approx 0.84 \text{ V}$$

http://ocw.tudelft.nl/fileadmin/ocw/courses/SolarCells/res00030/CH7_Thin_film_Si_solar_cells.pdf

Solar PV is a booming global industry 11000 10,660 10000 9000 But U.S. market share has 8000 fallen to about 5% of global PV Cell Production (MW) 7056 output - from more than 40% in 7000 the mid-1990s 6000 5000 Rest-of-World 4000 3746 China/Taiwan (Broken out from ROW since 2007) 3000 Europe 2450 Japan 2000 1782 United States Source: PV News, 1990-2010 1000 542 288 371 '08 '09 '90 '91 '97 '98 '99 '07 '03 '04 '05 '06 '07 '01

Worldwide production of solar photovoltaics – in Megawatts

Commercial Photovoltaics as of 2010

"2009 was historic in that for the first time ever, a thinfilm producer (CdTe-based First Solar) claimed the title of the largest cell/module manufacturer. In a year where most producers considered themselves fortunate to expand marginally, First Solar doubled its production, from 504 MW in 2008 to a staggering 1,011 MW: it alone made up 10% of global supply."

from May 2010 PV News: "26th Annual Data Collection Results: Another Bumper Year for Manufacturing Masks Turmoil" Standard Crystalline Si 8,020 75%

Attained vs. attainable efficiencies

Fig. 3. Performance gaps between best device efficiencies in the laboratory and attainable efficiencies for several solar cell technologies.

L.L. Kazmerski / Journal of Electron Spectroscopy and Related Phenomena 150 (2006) 105–135

Attained vs. attainable **open circuit photovoltage**

Cell Type	E _g at RT (eV)	V _{oc} ^{MAX} (V)	V _{oc} (V)	V _{oc} loss (V)	V _{OC} /V _{OC} ^{MAX} (%)
SC-Si	1.12	0.84	0.71	0.13	85
GaAs	1.42	1.14	1.02	0.12	90
InP	1.28	1.00	0.88	0.12	88
CdTe	1.45	1.17	0.84	0.33	72
CIGS	1.14	0.86	0.72	0.14	84
a-Si	1.7	1.42	0.86	0.56	61
DSS (black dye) (Red N719) (Red N3)	1.4 1.6 2.0	1.12 1.32 1.72	0.72 0.85 0.80	0.40 0.47 0.92	64 64 47
OPV	1.55	1.27	0.75	0.52	59

Attained vs. attainable short-circuit photocurrent

	Cell Type	E_{a} at RT	J _{SC} MAX	J _{sc}	J _{SC} /J _{SC} ^{MAX}
		ັ(eV)	(mA/cm ²)	(mA/cm ²)	(%)
	SC-Si	1.12	43.8	42.7	98
	GaAs	1.42	32.0	28.5	89
	InP	1.28	36.3	29.5	81
	CdTe	1.45	30.8	25.9	84
	CIGS	1.15	42	33.5	80
	a-Si	1.7	22.4	17.5	78
	DSS (black dye) (Red N719) (Red N3)	1.4 1.6 2.0	33.3 25.5 14.4	20.5 17.7 9.2	62 70 64
	OPV	1.55	26.9	14.7	55

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United States Photovoltaic Solar Resource : Flat Plate Tilted at Latitude kWh/m²/Day 2.34.2.48 6.³⁰ A.355 A.49 6.65° 6.78 6.60, 6.6A 6.22 6.35 A.221 - A.3A 4.06 4.20 4.60, 4.63 6.3° 6.1° 6.0° 5.9° 5.1° 5.6° 5.1° 5.3° 5.1° 5.0° 4.9° 4.1' 6.0° 5.3° 5.1° 5.5° 5.3° 5.3° 5.3° 5.0° 4.3° 4.1° 4.5° 2.2. 10° 3.9° 3.1° 3.2° 3.0° 2.9° 2.1° 2.0° 2.4° 2.5°

- High surface area devices \rightarrow
 - strong light absorption (dye-sensitized nanostructured TiO₂)
 - fast charge separation (proximity of photoexcited carriers to charge-separating interface)
- Customizable properties \rightarrow
 - Size-dependent optical properties
 - Controlled geometries e.g., efficient transport in oriented quantum rods, nanotubes
 - Controlled chemical functionalization for directed charge separation (surface chemistry)
- Novel effects? (multiple exciton generation, excitonic behavior)

Early history on Multiple Exciton Generation (MEG) in NCs

NCs of: IV-VI, II-VI, III-V, IV (e.g., PbSe, PbS, PbTe, CdSe, Si, InP), and SWNTs as well...

Spectroscopic Techniques: TA (interband, intraband), TRPL*, TRTS (THz), and quasi-cw PL*

(* shows red-shifted biexciton PL)

A. J. Nozik, *Physica E* **14**, 115 (2002).

R. Schaller and V. Klimov, *PRL* **92**, 186601 (2004). (PbSe QDs \rightarrow QY 2.2)

Ellingson, Beard, Efros, Nozik, et al., Nano Lett. **5**, 865 (2005). (PbSe, PbS QDs \rightarrow QY 3.0)

R. Schaller et al., App. Phys. Lett. 87, 253102 (2005). (CdSe \rightarrow QY 1.6 at 3.1E_g)

> J. Murphy et al., JACS **128**, 3241 (2006). (PbTe \rightarrow QY 3.0 at 4E_g)

R. Schaller *et al., Nano Lett.* **6,** 424-429 (2006). (PbSe \rightarrow QY of 7.0 at 8E_g) J. Pijpers *et al., J. Phys. Chem. C* **111**, 4146 (2007). (InAs/CdSe/ZnSe QDs \rightarrow QY 1.6 at 2.7E_g)

M. C. Beard *et al., Nano Lett.* **7**, 2506 (2007). (Si QDs \rightarrow QY 2.6 at 3.4E_g)

R. Schaller *et al.*, *Nano Lett.* **7**, 3469 (2007). (InAs/CdSe core/shell QDs \rightarrow QY of 1.95 at ~4.8E_{ρ})

J. Luther *et al., Nano Lett.* **7**, 1779 (2007). (Efficient MEG in PbSe QD films)

M. Tuan Trinh *et al., Nano Lett.* **8**, 1713 (2008). (PbSe QDs \rightarrow QY 1.7 at 4.8 8E_{σ})

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Annealed NC-based solar cell

Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution Ilan Gur, Neil A. Fromer, Michael L. Geier, A. Paul Alivisatos 21 OCTOBER 2005 VOL 310 SCIENCE

Figure 6 and 7: A laboratory sample of our nanoparticle ink. Nanoparticles shown to the right are an average of 20nm in diameter.

Good solar cells from nanoparticle inks (CIGS)

from NanoSolar white paper

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TEM of colloidal lead selenide QDs

PbSe exciton Bohr radius ~ 46 nm

Hines, M. A.; Scholes, G. D. Adv. Mater. 2003, 15, 1844

Sample synthesis recipe (Krauss et al., adapted from Hines and Scholes)

- heat together in a flask at 150 °C for 1 hr under N₂ flow (to make lead oleate):
 - 220 mg lead(II) oxide
 - 0.25 ml oleic acid (tech grade)
 - 9.75 ml 1-octadecene (ODE, tech grade)
- after cooling to 90-100 °C, quickly inject into the reaction flask 5 ml of 0.1 M hexamethyldisilathiane (0.5 mmol) dissolved in ODE
- immediately cool with an ice bath
- precipitate (methanol/butanol mixture), centrifuge and resuspend in nonpolar solvent (e.g., toluene, tetrachloroethylene, or hexanes).

PbO + 2
$$C_{18}H_{34}O_2 \xrightarrow{N_2, ODE}$$
 Pb(oleate)₂ + H₂O
< 122C

 $http://pubs.acs.org/doi/suppl/10.1021/nl0525756/suppl_file/nl0525756si20060213_112831.pdf$

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Colloidal PbSe QDs in tetrachloroethylene (TCE)

- Solution synthesis, typically at elevated temperature
- Inorganic crystalline core surrounded by organic capping molecules
- Most frequently suspended in organic solvents
- Can be stored stably either in powder or solution form

Colloidal semiconductor NCs have typical diameters of 1 nm to 10 nm

Colloidal quantum dot – scale

Coupling QDs within a film (or array)

Optical, Electronic, and Structural Properties of Uncoupled and Close-Packed Arrays of InP Quantum Dots Olga I. Mic´ic´ et al., 1998.

What could cause a decrease in QD-QD spacing to red-shift the exciton transition?

"This can cause (i) an increase in the average dielectric constant of the film, (ii) an increase in the inter-QD radiative coupling, and (iii) an increase in the inter-QD electronic coupling."

Strong Electronic Coupling in Two-Dimensional Assemblies of Colloidal PbSe Quantum Dots, Williams et al., ACS Nano (2009)

- i) Increased wavefunction extension
- ii) Increased FRET
- iii) Reduced barrier width for tunneling/hopping transport

$$a_B^* = \frac{4\pi\varepsilon\hbar^2}{m^*e^2}$$

Energy transfer (FRET):

 \Rightarrow R₀ \approx 8-9 nm for ~3 nm InP QDs

J. Phys. Chem. B 1998, 102, 9791-9796

Hopping/tunneling transport:

$$\Gamma_{ij} = \Gamma_0 \exp(-\beta d) \begin{cases} \exp\left[-\frac{E_j - E_i}{kT}\right] & E_j > E_i \\ 1 & E_i > E_j \end{cases}$$

Miller, Abrahams, Phys. Rev. 120, 745-755 (1960)

Liu, Hillhouse, Law, Nano Lett. (2010), 10, 1960.

Steady-state photoluminescence (1310 nm NCs)

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Time-resolved photoluminescence spectra

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Post-casting treatment of spin-cast films of PbSe NCs

"Microstructure of the spin-cast NC films before and after EDT treatment. (a) SAXS data, showing a ~16 Å decrease in the spacing between the NCs and a dramatic loss of superlattice order upon EDT treatment. Measurements were taken in air. (b, c) Planview SEM images of (b) an untreated film and (c) a treated film."

J. Luther, M. Law et al., ACS Nano 2, 271 (2008).

Layer by layer (LbL) fabrication of PbSe nanocrystal (NC) films. Nanocrystal films prepared by dip-coating, alternating between (1) PbSe NCs in hexane and (2) 0.1 M EDT in anhydrous acetonitrile, allowing the film to dry between each layer.

J. M. Luther, M. Law *et al.*, "Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol", *ACS Nano* **2**, 271 (2008).

Ligand exchange in PbX NC films

Schottky barrier nanocrystal-based solar cell

- Auger recombination typically occurs on ≤ 100 ps timescale (need fast exciton dissociation and/or diffusion to low density)
- High long-range mobility desired
- EQE > 100% would provide MEG process/concept confirmation

Plan view SEM image of PbSe NC films prepared by layer-by-layer dip coating onto ITO substrate. LbL film shown was produced using 10-20 dip coating cycles.

J. Luther, M. Law et al., ACS Nano 2, 271 (2008).

Grain boundary density considerations

e.g. CdTe

Rough estimates of grain boundary densities (boundary area / layer area)

<u>CdTe</u>: ~1 μ m grain size (assumed cubic grains, ~ 1 μ m thick layer):

$3 (\mu m^2 / \mu m^2)$

<u>**PbSe QD film</u></u>: ~5 nm "grain size" (assumed cubic grains 5 nm on a side, 1 \mum thick film):</u>**

600 (μm²/ μm²)

Nanocrystal-based solar cell

(a) J-V in dark and under 100 mW cm⁻² AM 1.5G ($E_g = 0.9 \text{ eV}$). (b) SEM cross-section of the stack (metal is 20 nm Ca / 100 nm Al). (c) EQE of a device with 140 nm-thick NC film and an efficiency of ~2.2% ($E_g = 0.95 \text{ eV}$). (d) Proposed equilibrium band diagram; band bending occurs at interface between the NCs and metal electrode. Schottky barrier height ($q\phi_{barrier}$) for p-type material is the difference between the valence band max. and the metal Fermi level.

J. M. Luther, M. Law, et al., Nano Lett. 8, 3488-3492 (2008).

(a) Dependence on NC size. Each point is the average of six devices from a single substrate. The line is a least-squares fit to the data. (b) Dependence on metal work function ($E_g = 0.82 \text{ eV}$). The best and average V_{oc} for each metal are shown, along with the standard deviation of six devices.

J. M. Luther, M. Law, et al., Nano Lett. 8, 3488-3492 (2008).

"Mott-Schottky plots at 1 kHz for devices with a thin (65 nm, red) and thick (400 nm, blue) NC layer. The thick device has an equilibrium depletion width of \sim 150 nm, while the thin device is fully depleted."

J. M. Luther, M. Law, et al., Nano Lett. 8, 3488-3492 (2008).

Relation between doping density and QD density? QD size ~ 6 nm dia., add 1 ligand ~0.5 nm, so V(QD) = $(4\pi/3)(3.2 \text{ nm})^3 = 1.3 \times 10^{-19} \text{ cm}^3$

Random packing of spheres \rightarrow ~ 0.64

- \rightarrow Vol. density of QDs ~ 5 x 10¹⁸ cm⁻³
- \rightarrow ~1 free carrier per 500 QDs

How/why?

T-dependent performance in PbS QD device

T. Ju et al., APL 97, 043106 2010

Luther et al., Adv. Mater. 2010, 22, 3704–3707

Layers of ZnO and PbS fabricated in air. Device shows good air stability over ~1,000 hrs.

Two-diode model for PbS/ZnO heterojunction device

Two-diode model equivalent circuit including a main diode between ZnO QD film with PbS QD film, and a Schottkydiode between PbS QD film with top contact Au or Ag.

"Quantum Dot Size Dependent J-V Characteristics in Heterojunction ZnO/PbS Quantum Dot Solar Cells", J. Gao et al, Nano Lett. 2011.

Figure 1. Typical characteristics of J-V in the dark and under 1 sun illumination, which shows the crossover and roll-over effects. The device structure is ITO/ZnO NC/PbS QD/Ag with PbS layer thickness of \sim 550 nm.

- 1. **Roll-over effect**, a fact of current limiting at positive voltage, is due to a hole transport barrier at Schottky-junction formed by PbS QD film with metal contact .
- 2. **Cross-over effect:** low forward current due to Schottky barrier at metal contact (hole transfer barrier).

Best Research-Cell Efficiencies

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- Energy intensity of materials and deposition
- Doping control within films
- Air/moisture tolerance (deposition and operation)

<u>Collaborators</u>: A. Nozik (NREL); M. Beard (NREL); J. Luther (NREL); M. Zamkov (BGSU)

<u>The University of Toledo, PVIC</u>: T. Bigioni (Chemistry); R. Collins and M. Heben (Physics); R. Jha (EE)

Ellingson Group Members: Tieneke Dykstra (UT-PVIC postdoc) Jianbo Gao (UT-PVIC postdoc @ NREL) Khagendra Bhandari, NC thin films Neale Haugen, laser spectroscopy Paul Roland, device characterization and spectroscopic ellipsometry Ryan Zeller, laser scribing Tyler Kinner (undergraduate), Earth-abundant NC synthesis

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- UT-PVIC startup funds
- National Renewable Energy Lab/DOE-EERE
- AFRL

Left to right: Julia Deitz, Ryan Zeller, Neale 'Ole' Haugen, Khagendra Bhandari, Paul Roland, Tieneke Dykstra, and Randy Ellingson