Outline of the course

1. Quantum Dot Solar Cells
2. Intro to Quantum dots
3. Schotty Devices
4. Depleted Heterojunction Devices
5. Doped PN devices
6. Increasing light absorption

How big is an exciton

Bohr Radius of an Exciton

$$r_B = \frac{\hbar^2 \varepsilon}{e^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right)$$

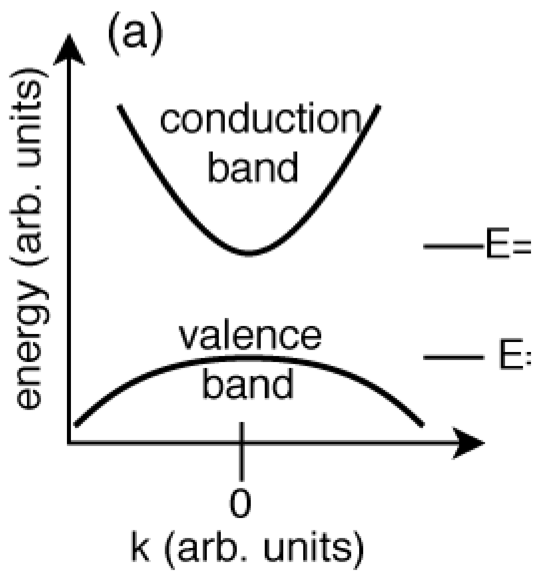
What is an effective mass?

$E = p^2 / 2m$

$dE/dp = p / m$

$d^2E/dp^2 = 1 / m$

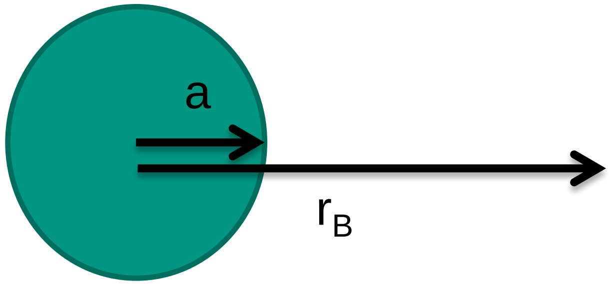
Effective mass proportional to the inverse of the curvature of the energy vs. momentum band diagram



Are holes or electrons heavier?

Quantum Size effect, what if the material is smaller than the size of the exciton?

1. Energy levels become discrete
2. These discrete levels are size dependent

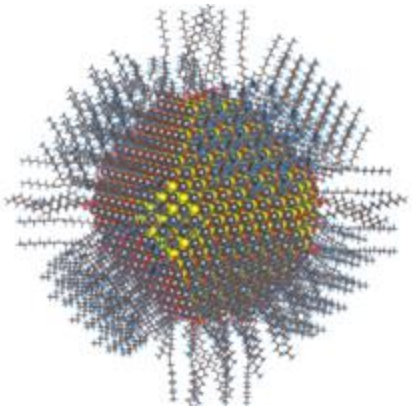


$$E_{\text{confinement}} = \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \frac{\hbar^2\pi^2}{2\mu a^2}$$

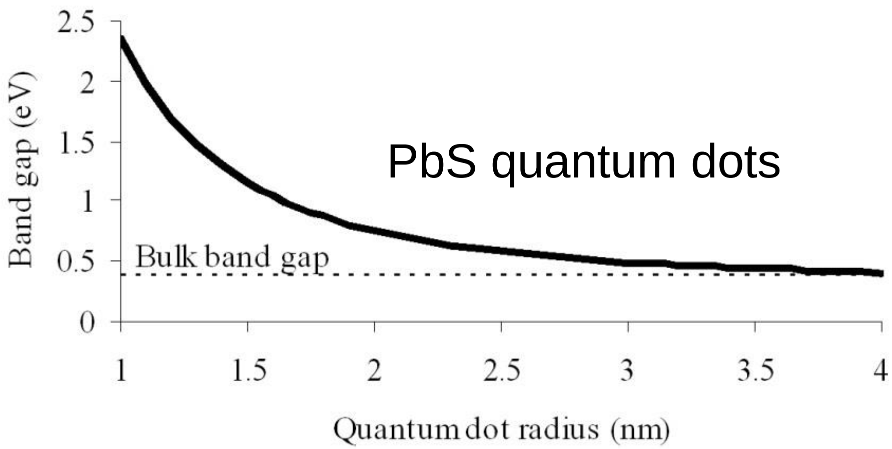
$$E_{\text{exciton}} = -\frac{1}{\epsilon_r^2}\frac{\mu}{m_e}R_y = -R_y^*$$

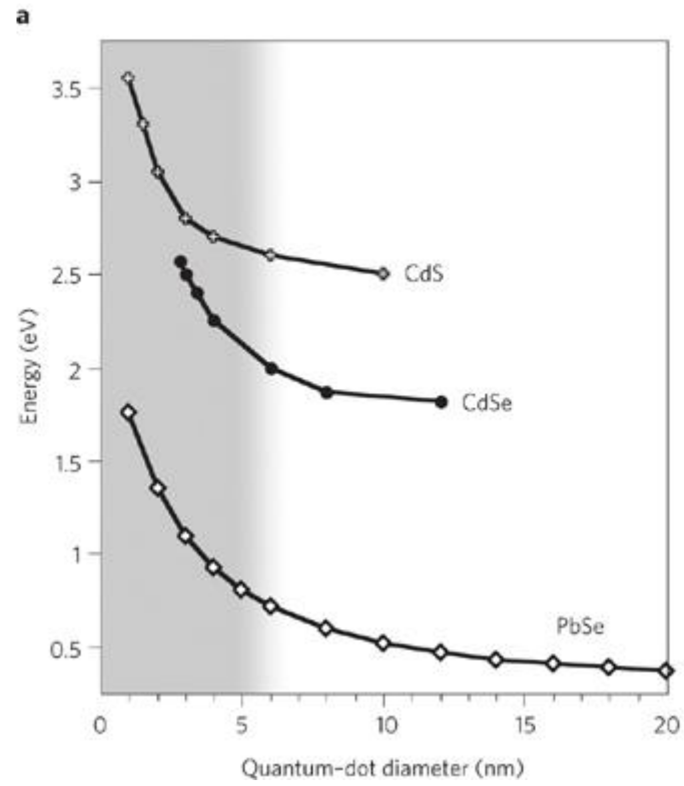
$$E = E_{\text{bandgap}} + E_{\text{confinement}} + E_{\text{exciton}}$$

$$= E_{\text{bandgap}} + \frac{\hbar^2\pi^2}{2\mu a^2} - R_y^*$$



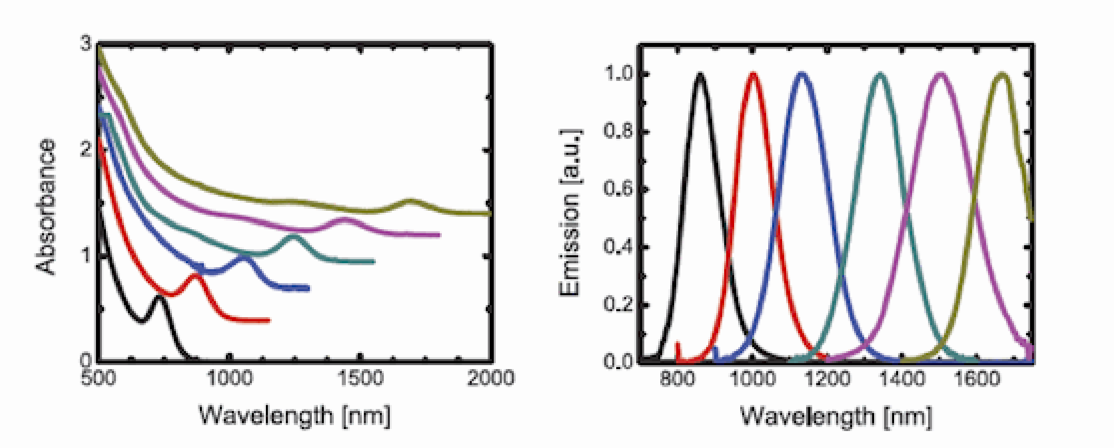
How does this look? Part 1





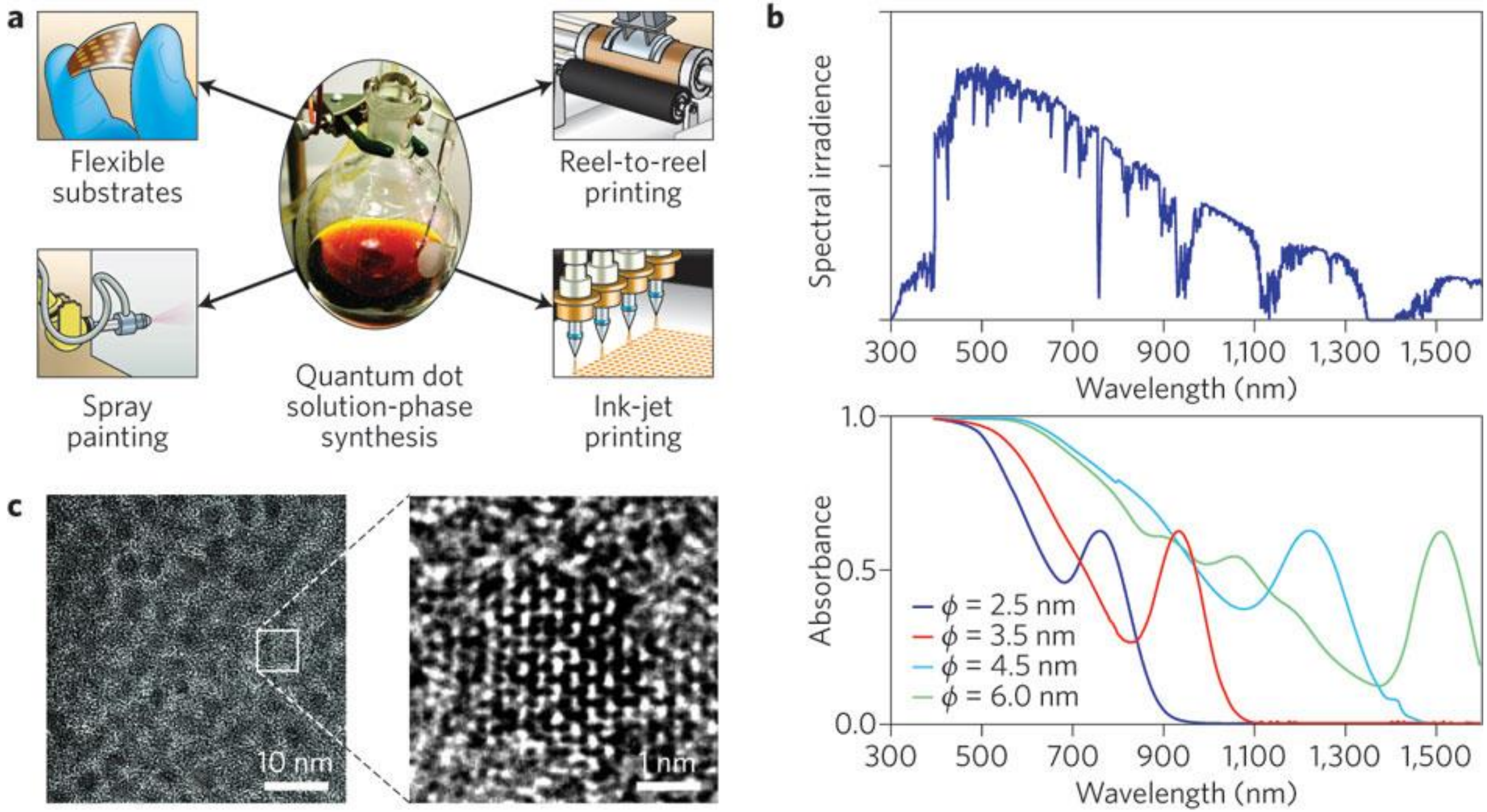
How does this look? Part 2

CdSe



PbS

PbS is at the moment quite promising



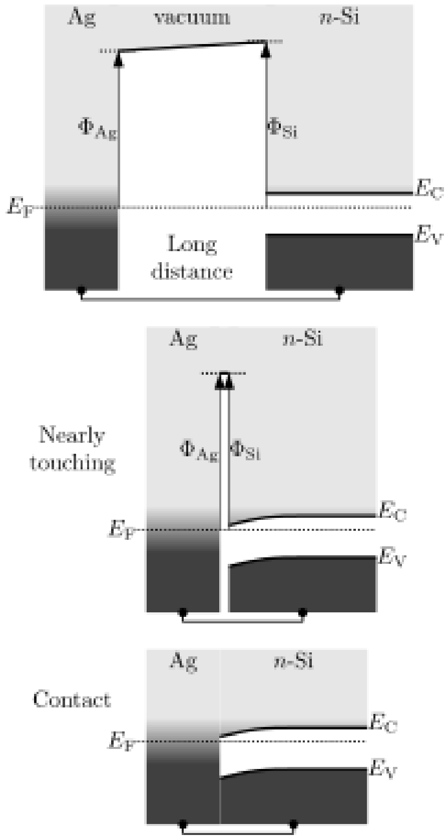
Nature Photonics 6, 133–135 (2012)
doi:10.1038/nphoton.2012.33

Useful for solar cells?

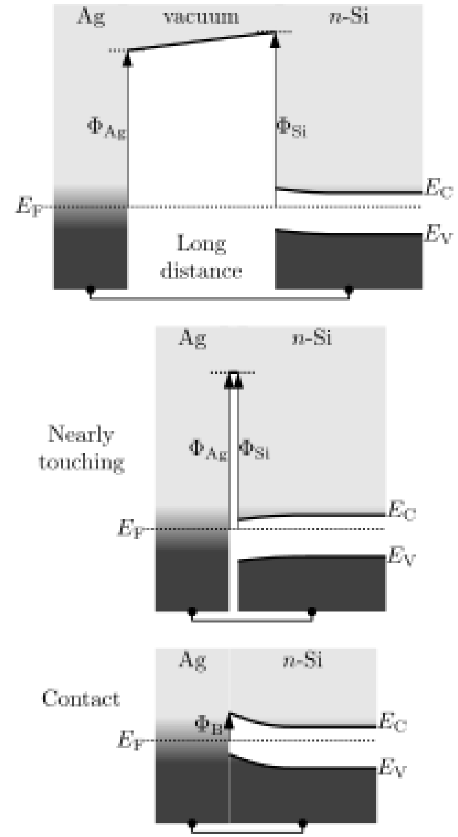
- Perhaps.
- What is the optimum bandgap for a single junction solar cell?
- Are there any quantum dots in this energy range

- What types of device can we make from them?
- Schottky structure
- Depleted heterojunction
- Bulk heterojuction

Metal Semiconductor Junctions

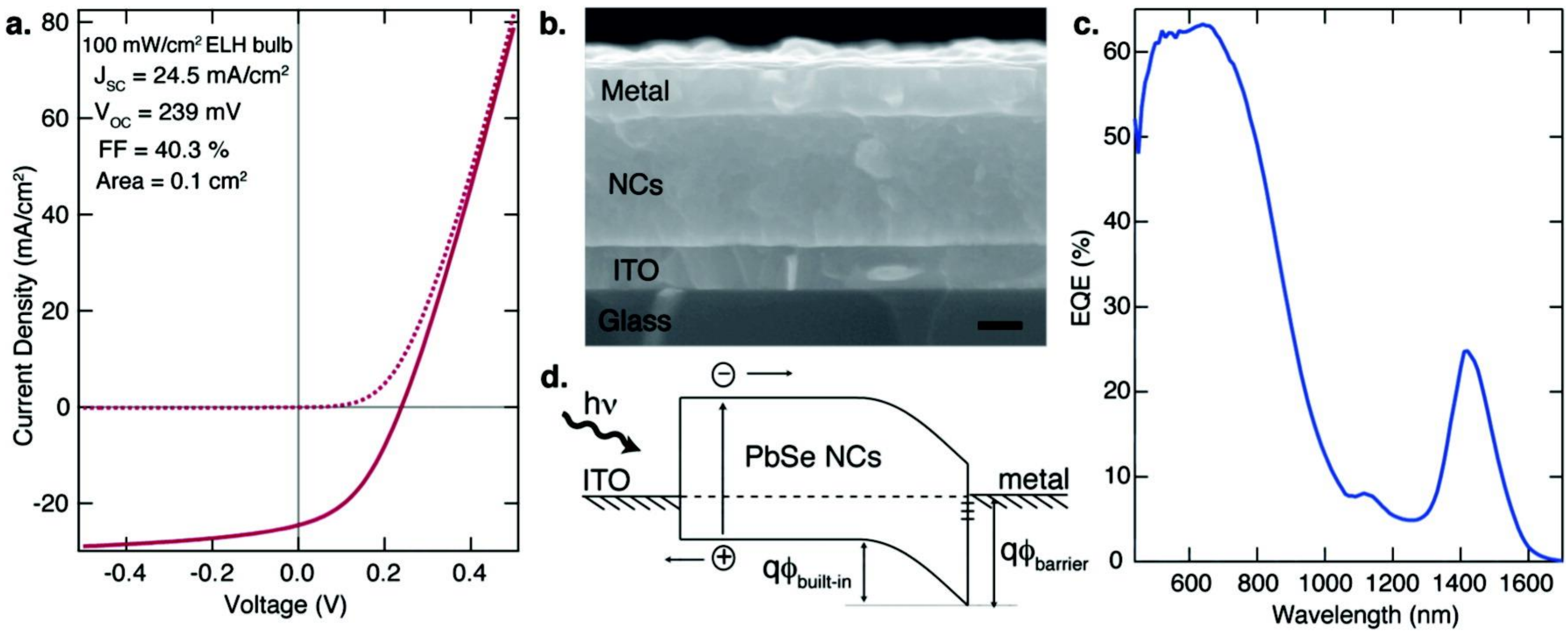


Without Fermi level pinning



With Fermi level pinning

Schottky Junction Solar Cells: What are the problems?

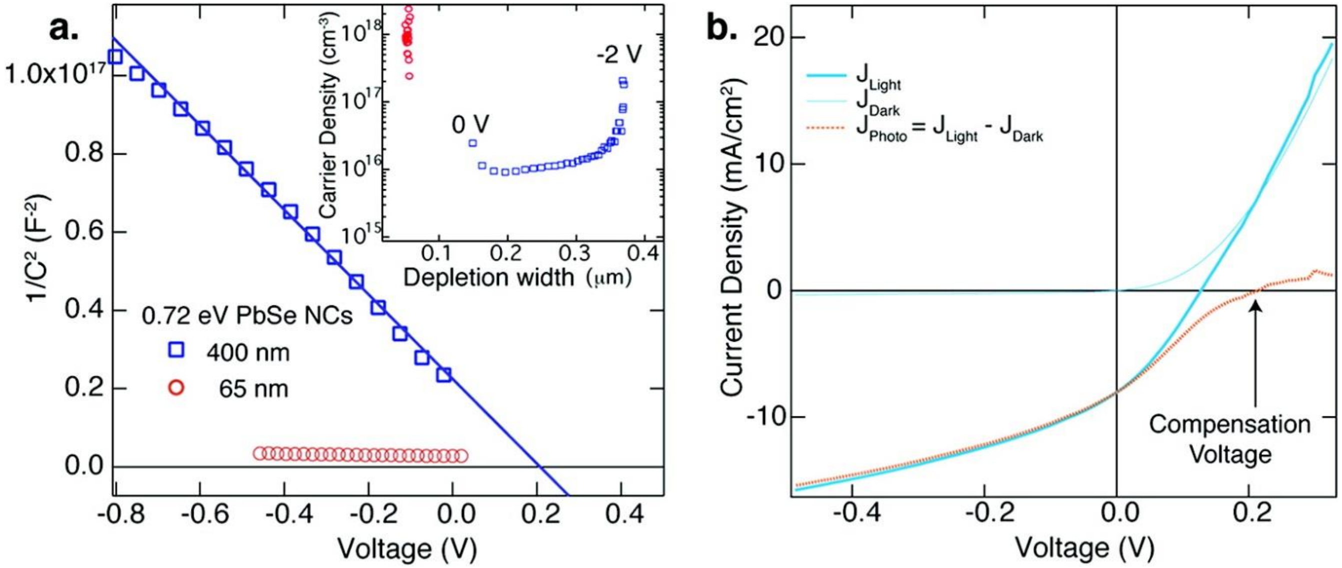


http://pubs.acs.org/doi/full/10.1021/nl802476m

$$W = \sqrt{\frac{2\varepsilon\varepsilon_0(\phi_{bi} - V)}{qN}} \qquad (1)$$

$$N = \frac{1}{A^2}\frac{2}{q\varepsilon_0\frac{d}{dV}\left(\frac{1}{C^2}\right)} \qquad (2)$$

N is the free carrier density at the edge of the depletion layer



Analysis of the Schottky barrier. (a) Mott−Schottky plots at 1 kHz for devices with a thin (65 nm, red) and thick (400 nm, blue) NC layer. The capacitance of the thin device is larger and changes little with reverse bias. A linear fit shows that the built-in potential of the thick device is 0.2 V. Note that smaller NCs yield larger built-in potentials (not shown), as expected from Figure 2a. The inset shows the carrier concentration at the edge of the depletion layer for both devices. The thick device has an equilibrium depletion width of ~150 nm, while the thin device is fully depleted. (b) *J*−*V* characteristics of the thick device. The photocurrent (*J*Light − *J*Dark) equals zero at a compensation voltage of 0.2 V.

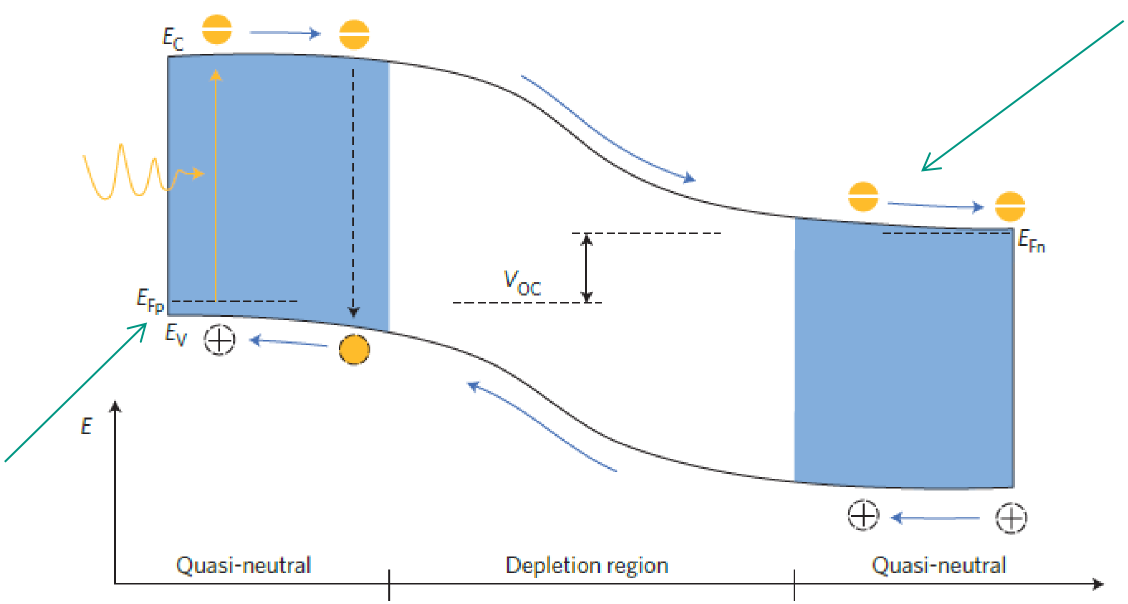
Published in: Joseph M. Luther; Matt Law; Matthew C. Beard; Qing Song; Matthew O. Reese; Randy J. Ellingson; Arthur J. Nozik; *Nano Lett.* **2008,** 8, 3488-3492.
DOI: 10.1021/nl802476m

Schottky Structures

- Fermi-level pinning at the quantum dot metal interface
  - Limits Voc
- Easy hole injection at the electron injecting contact, high backward current limits FF and Voc
- Light comes through the ITO contact, so light absorption is strongest far away from the region in where photocurrent generation is best. Limits Jsc

Depleted Heterojunction

- Junction between n-type wide-bandgap semiconductor and p-type quantum dot solid
  - N-type semiconductors → TiO_2, ZnO, CdS
  - P-type quantum dot solids CdSe, PbS, PbSe
- What limits the device thickness?

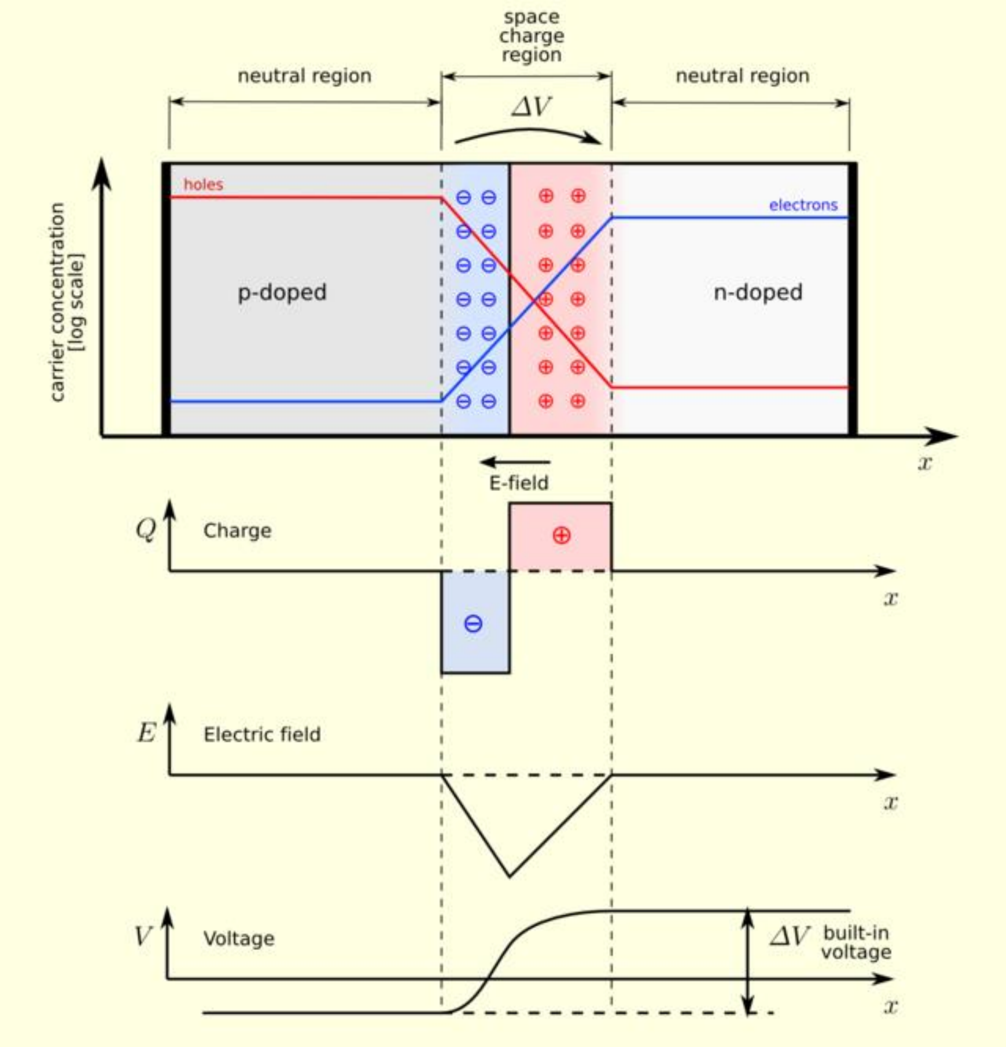


Hint:
How are charges transported here?

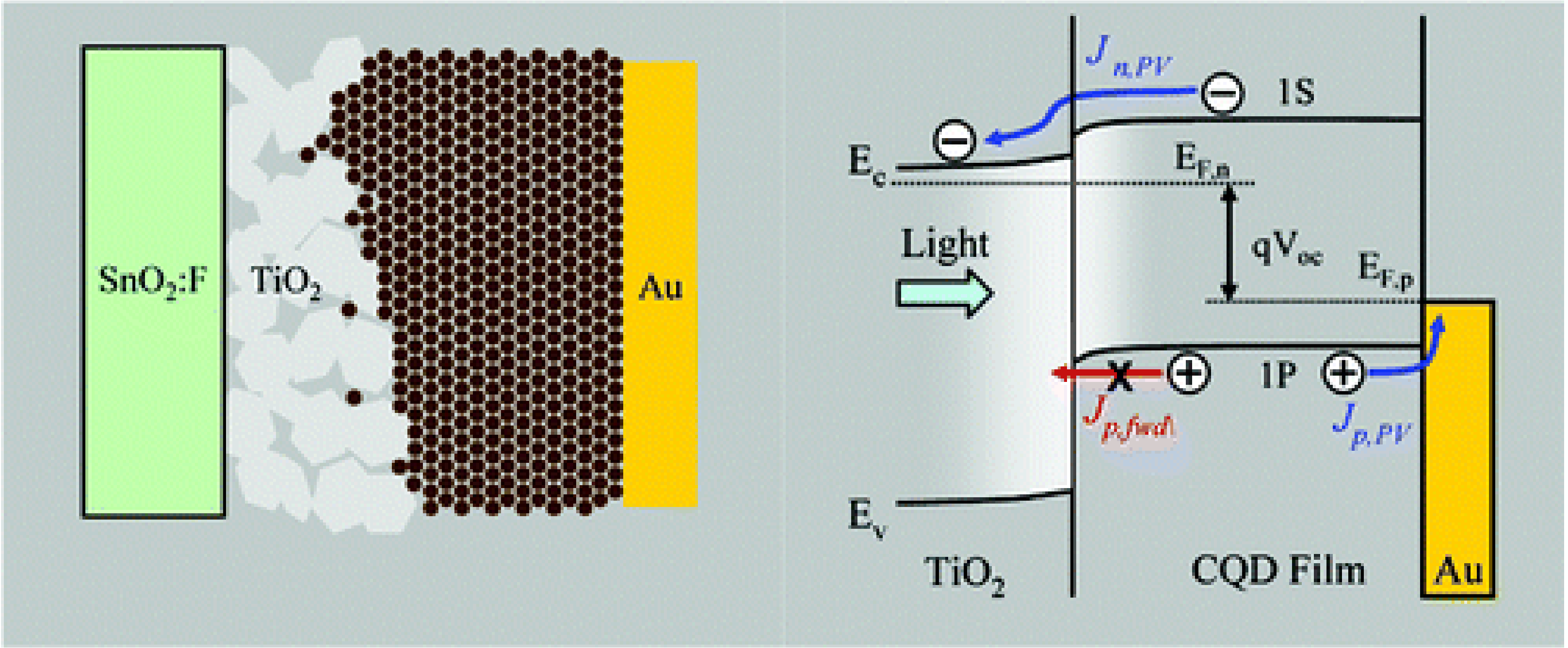
Hint:
And here?

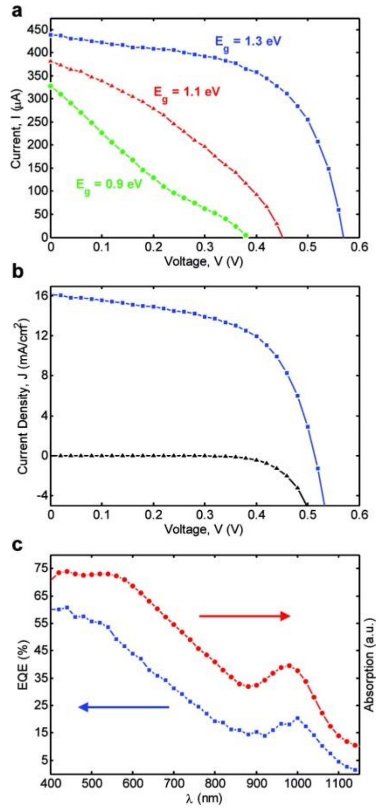
Depletion Region

- Electrons diffuse from the n material into the p
- Holes diffuse from the p material into the n
- After diffusion, these carriers can recombine.
- This leaves the dopants in the n and p regions uncompensated in a region with no free carriers
- A field is created in this depletion region.



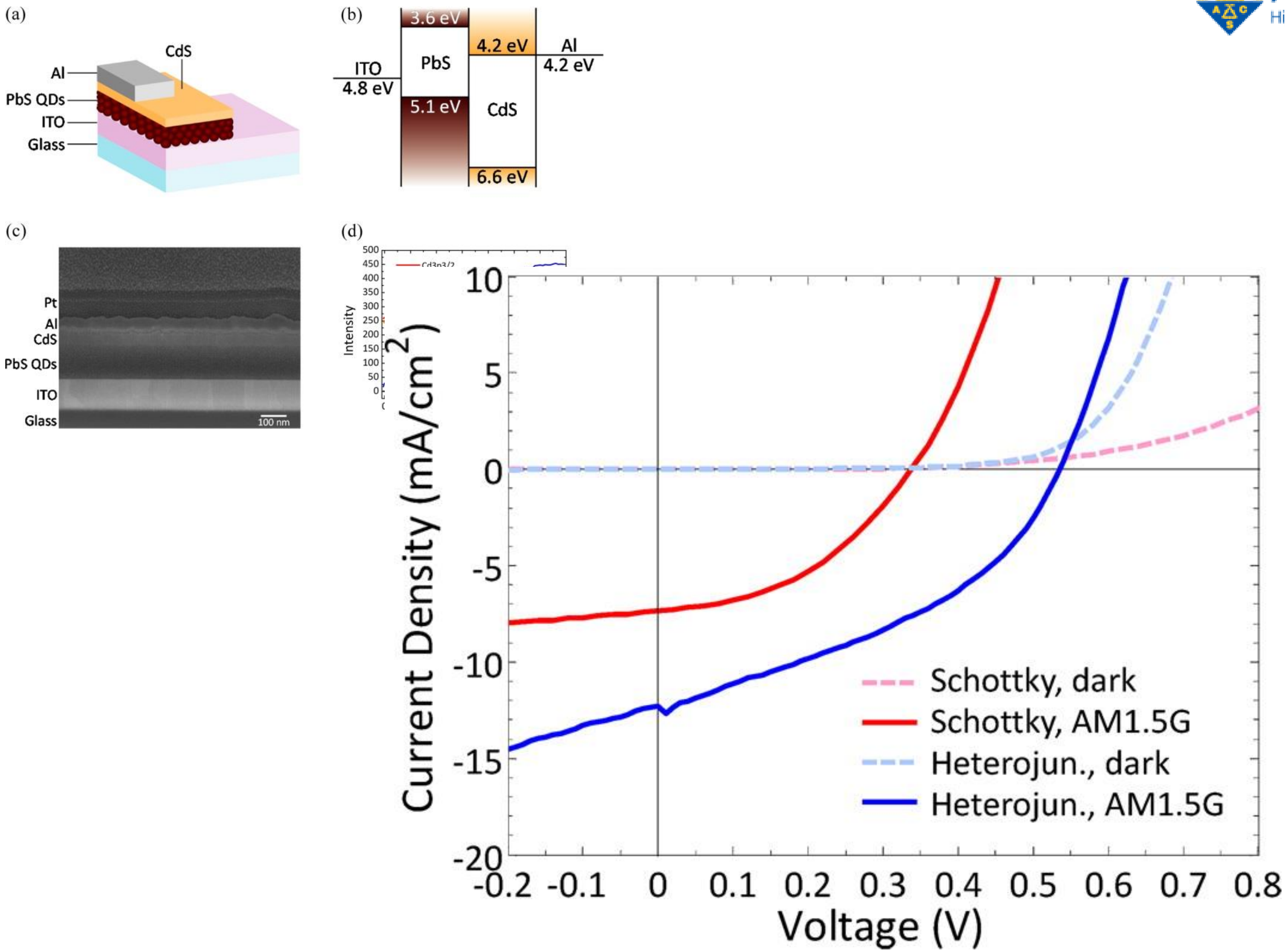
Depleted Heterojunction





(a) Unapertured I−V response of FTO/porous TiO2/PbS QD/Au photovoltaic devices from three different CQD sizes (device area 0.03 cm2). (b) Apertured dark and illuminated J-V curves for the champion device yielding short-circuit current of 16.2 mA/cm2, open-circuit voltage of 0.51 V, fill factor of 58% and PCE of 5.1% under 94% of one sun illumination. Here the device had a 0.06 cm2 contact area that was apertured down to a 0.05 cm2 device area to eliminate any lateral collection of photogenerated carriers. (c) Apertured external quantum efficiency and absorption spectra for a champion device based on PbS CQDs having a bandgap of 1.3 eV (~960 nm first excitonic peak).

Published in: Andras G. Pattantyus-Abraham; Illan J. Kramer; Aaron R. Barkhouse; Xihua Wang; Gerasimos Konstantatos; Ratan Debnath; Larissa Levina; Ines Raabe; Mohammad K. Nazeeruddin; Michael Grätzel; Edward H. Sargent; *ACS Nano* **2010,** 4, 3374-3380.
DOI: 10.1021/nn100335g



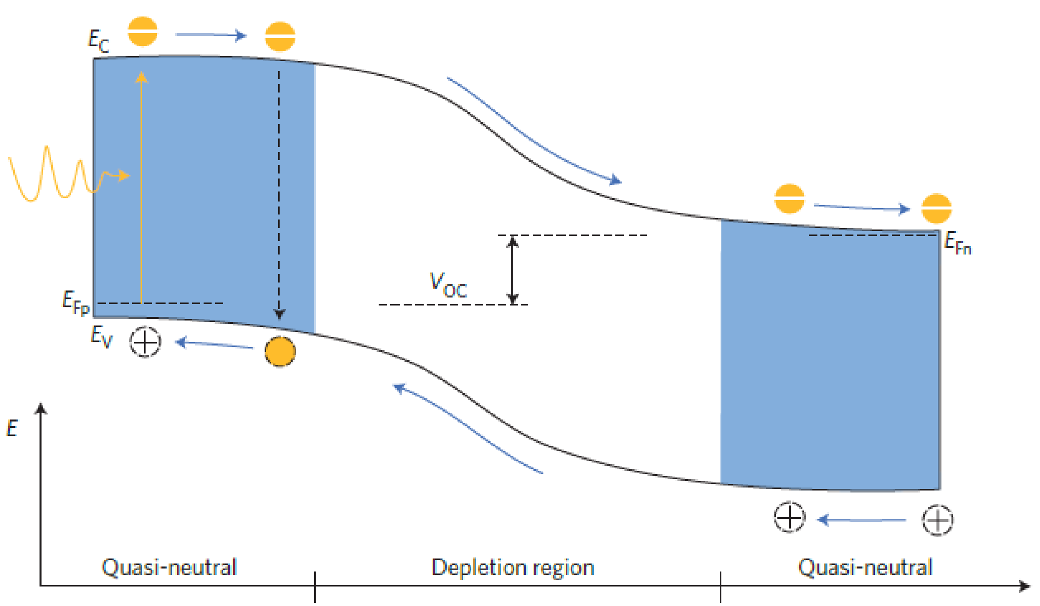
J–V characteristics of typical PbS QD Schottky (red) and PbS QD/CdS heterojunction (blue) devices measured in the dark and under AM1.5G simulated solar illumination.

Published in: Liang-Yi Chang; Richard R. Lunt; Patrick R. Brown; Vladimir Bulović; Moungi G. Bawendi; *Nano Lett.* **2013,** 13, 994-999.
DOI: 10.1021/nl3041417

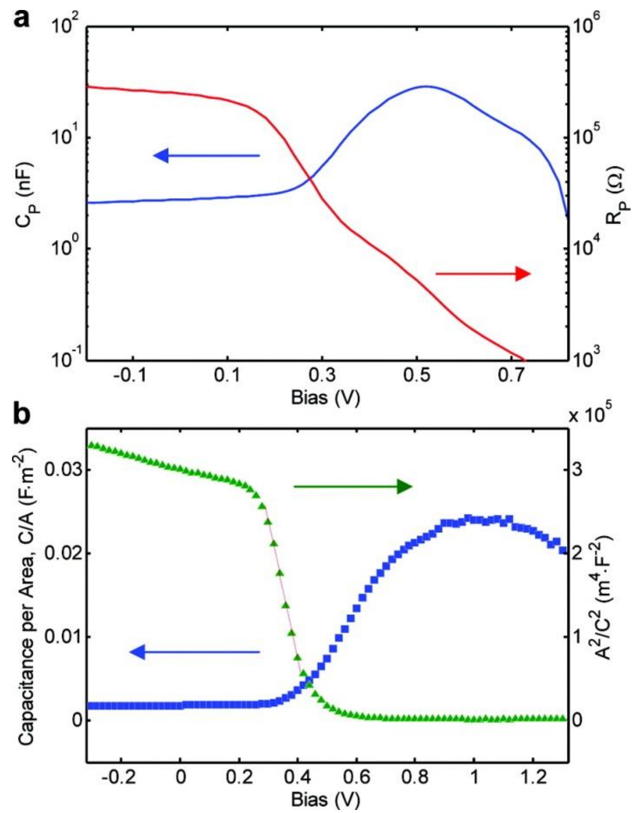
How wide is the depletion region

- Depends on the density of electrons and holes in the n and p type semiconductor.

$$W \approx \left[\frac{2\epsilon_r\epsilon_0}{q}\left(\frac{N_A + N_D}{N_A N_D}\right)(V_{bi} - V)\right]^{\frac{1}{2}}$$



$$N = \frac{1}{A^2} \frac{2}{q\varepsilon_0 \frac{d}{dV}\left(\frac{1}{C^2}\right)} \qquad (2)$$



Capacitance−voltage curves of (a) the champion TiO2/1.3 eV QD PV/Au device. The impedance was acquired at 1 kHz with a signal amplitude of 10 mV, and is represented here in terms of equivalent parallel resistance (Rp) and capacitance (Cp) for a device with contact area of 0.06 cm2. (b) a FTO/compact TiO2/1.3 eV PbS QD/Au structure. Mott−Schottky analysis was performed to arrive at approximate values for free carriers in 1.3 eV PbS QD films.

Published in: Andras G. Pattantyus-Abraham; Illan J. Kramer; Aaron R. Barkhouse; Xihua Wang; Gerasimos Konstantatos; Ratan Debnath; Larissa Levina; Ines Raabe; Mohammad K. Nazeeruddin; Michael Grätzel; Edward H. Sargent; *ACS Nano* **2010,** 4, 3374-3380.
DOI: 10.1021/nn100335g

Minority carrier diffusion length

$$L = \sqrt{D\tau}$$

$$D = \frac{\mu_q k_B T}{q}$$

How do we measure the mobility?

If mobility is known, then we can measure diffusion length in order to get lifetime
Or measure lifetime in order to get diffusion length.

Measurement of mobility. Time of Flight

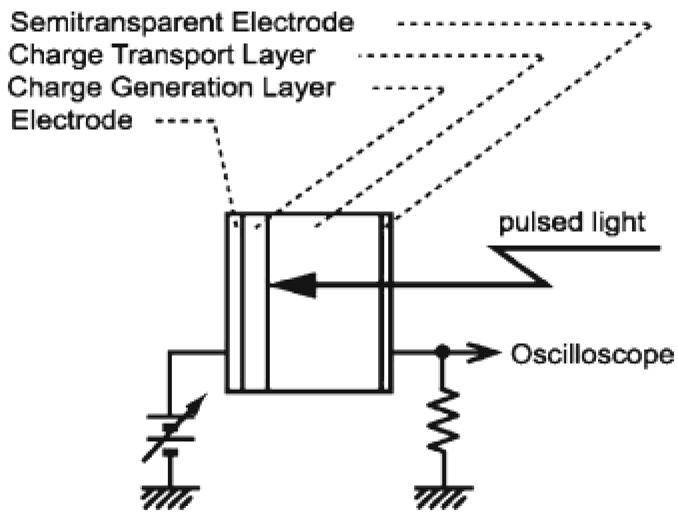


Fig. 3 Schematic diagram of apparatus for a time-of-fight method

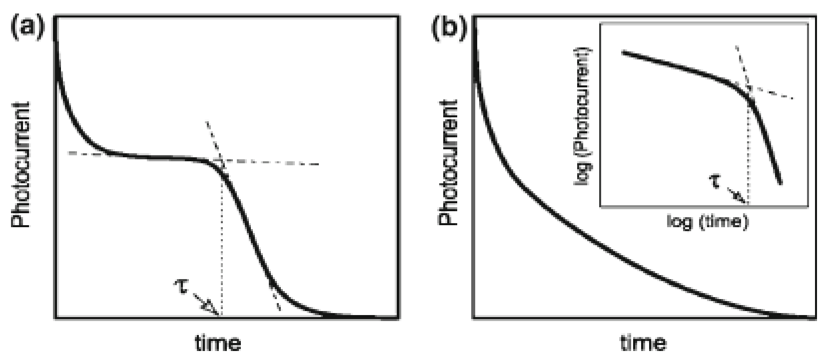


Fig. 4 Typical transient photocurrents: **a** non-dispersive; **b** dispersive. *Inset* double logarithmic plot

Opt Quant Electron (2009) 41:69–89
DOI 10.1007/s11082-009-9323-0

Charge mobility measurement techniques in organic semiconductors

Sanjay Tiwari · N. C. Greenham

$$\mu = \frac{d^2}{V\tau}$$

Measurement of mobility: CELIV

Karlsruhe Institute of Technology

Opt Quant Electron (2009) 41:69–89
DOI 10.1007/s11082-009-9323-0

Charge mobility measurement techniques in organic semiconductors

Sanjay Tiwari · N. C. Greenham

$$t_{\max} = d\sqrt{2/3\mu A}$$

Can measure thin sample without transparent electrodes.

Dispersive transport no problem.

If both hole and electrons present there are 2 peaks.

Further measurements are needed to determine which peak corresponds to which carrier

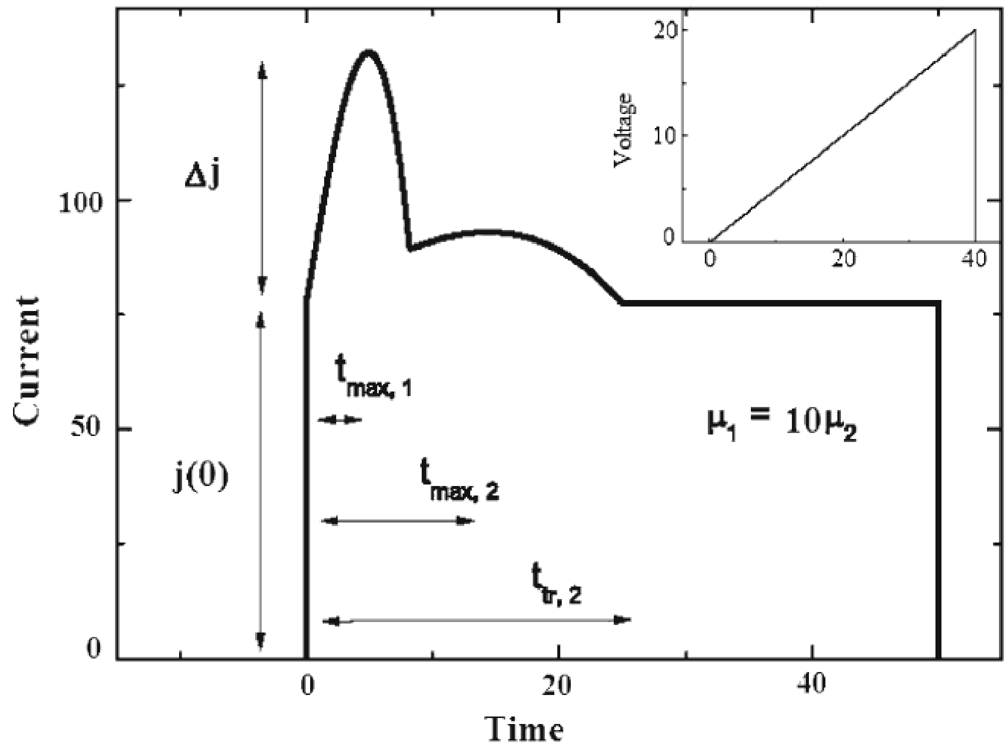
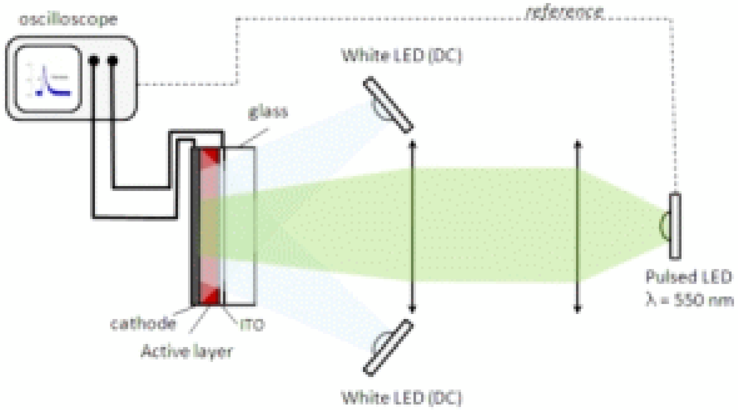
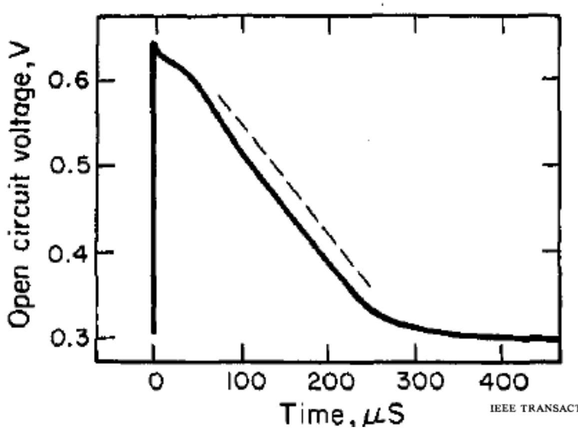


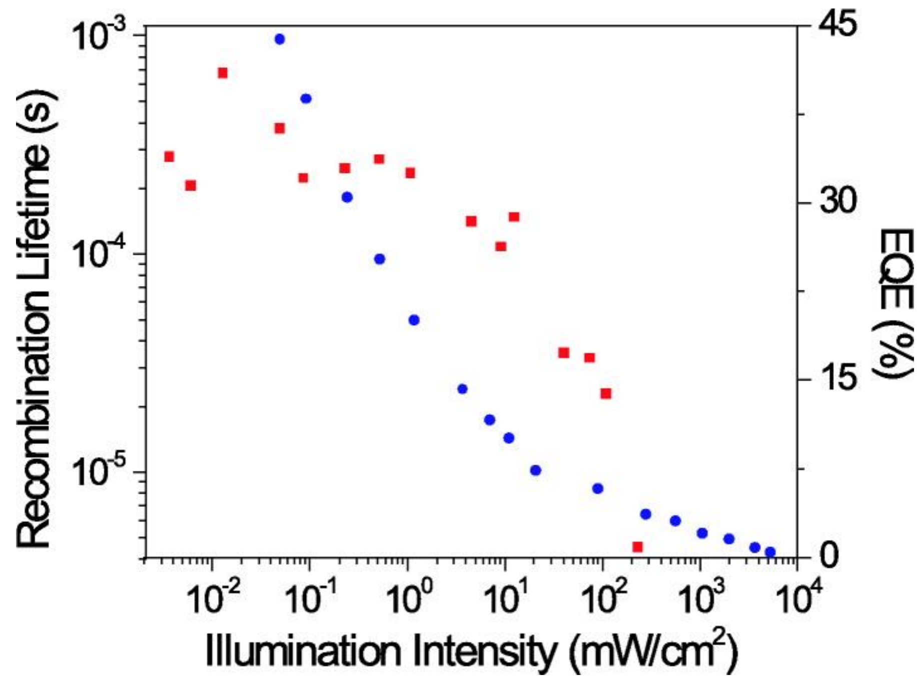
Fig. 8 Calculated CELIV transient

Carrier Lifetime: Transient Photovoltage



$$\tau = \frac{kT}{q}\left|\frac{1}{dV_{oc}/dt}\right|.$$





IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. ED-26, NO. 5, MAY 1979 733

Measurement of Minority Carrier Lifetime in Solar Cells from Photo-Induced Open-Circuit Voltage Decay

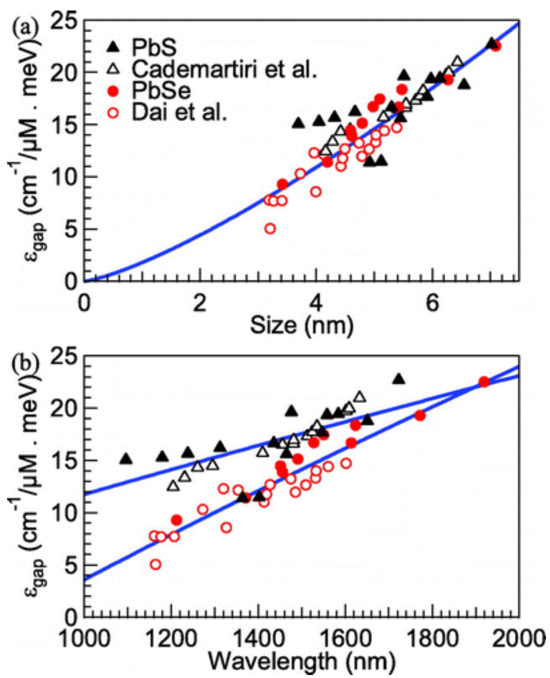
JOHN E. MAHAN, THOMAS W. EKSTEDT, ROBERT I. FRANK, MEMBER, IEEE, AND ROY KAPLOW

What fraction of light gets absorbed in the cell

- Depletion region + minority carrier diffusion length gives roughly 300 nm

$$I = I_0 e^{-\alpha(h\nu)l}$$

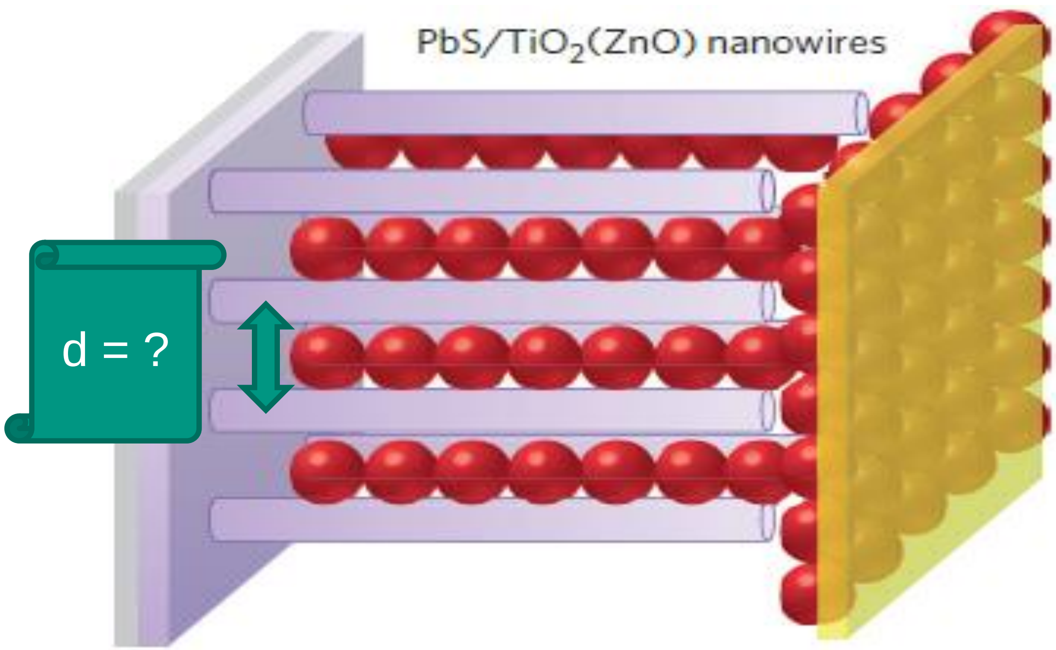
Beer- Lambert Law



Need roughly 1 µm film!

Bulk Heterojunction-type

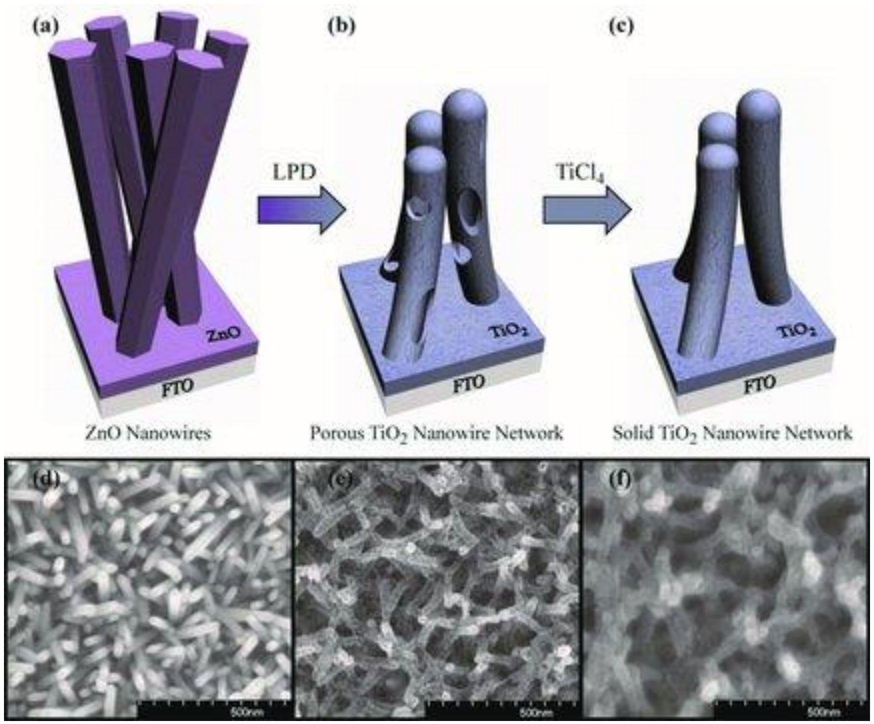
- What should the spacing between the TiO_2 pillars be?
  - Hint: remember the exciton diffusion length from organic semiconductors?
  - Hint 2: dots are not to scale, there could be many between the pillars.



Hint 1 was a Red Herring!

- Remember the exciton diffusion length was around 10 nm in the organic solar cells? Good.
- But that is irrelevant here.
- We just covered the relevant distance is the depletion region plus the minority carrier diffusion length.

- ZnO wires transformed into TiO_2, leads to efficiency of 7.2%



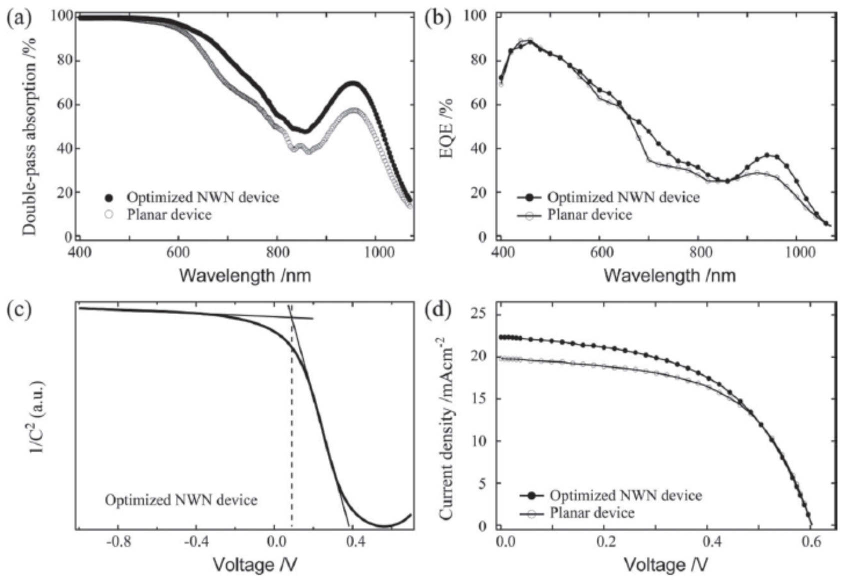
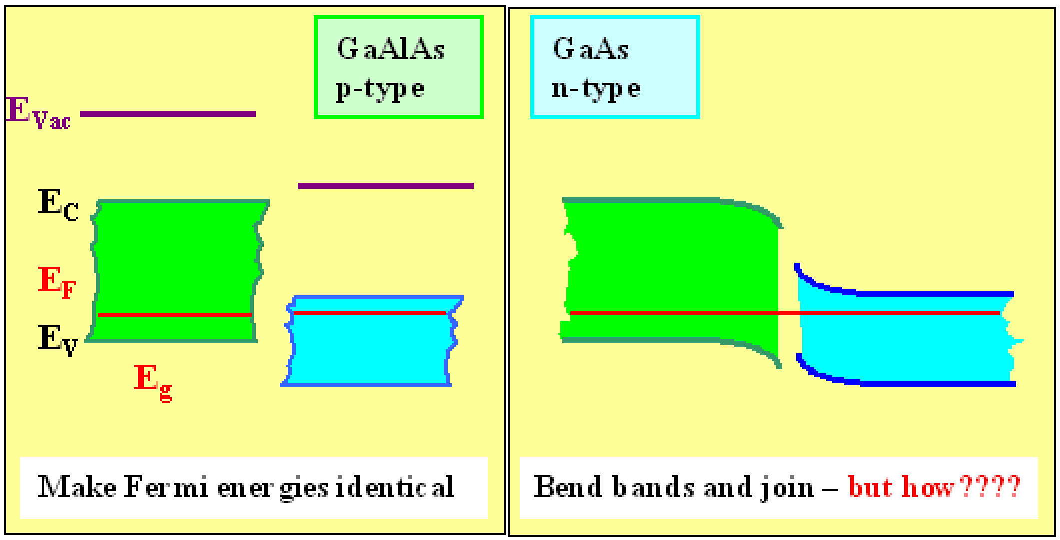


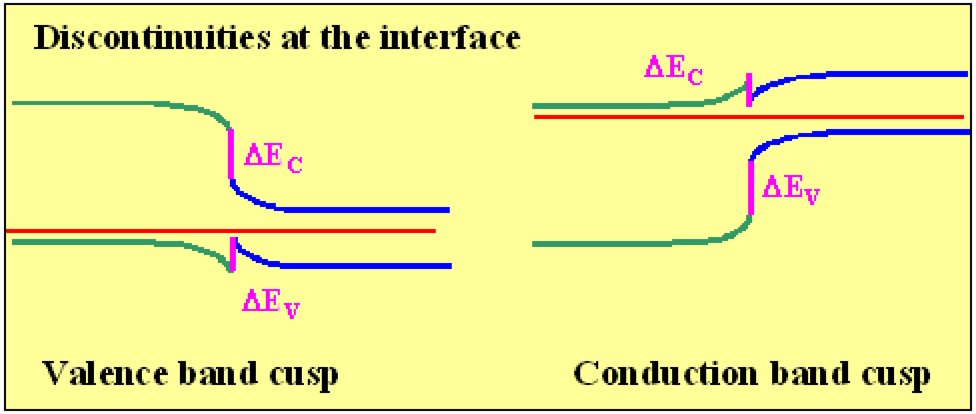
Figure 4. a) Double-pass optical absorption spectra of typical planar and NWN devices. b) External quantum efficiency spectra of the same devices. c) Capacitance^{-2} vs voltage curves for the NWN device showing that the device is substantially fully depleted even under slight forward bias. d) *J–V* curves under AM1.5 illumination of typical planar and NWN devices. The optimized NWN device shows the same open-circuit voltage as the planar counterpart, and a considerably increased photocurrent.

Band Bending

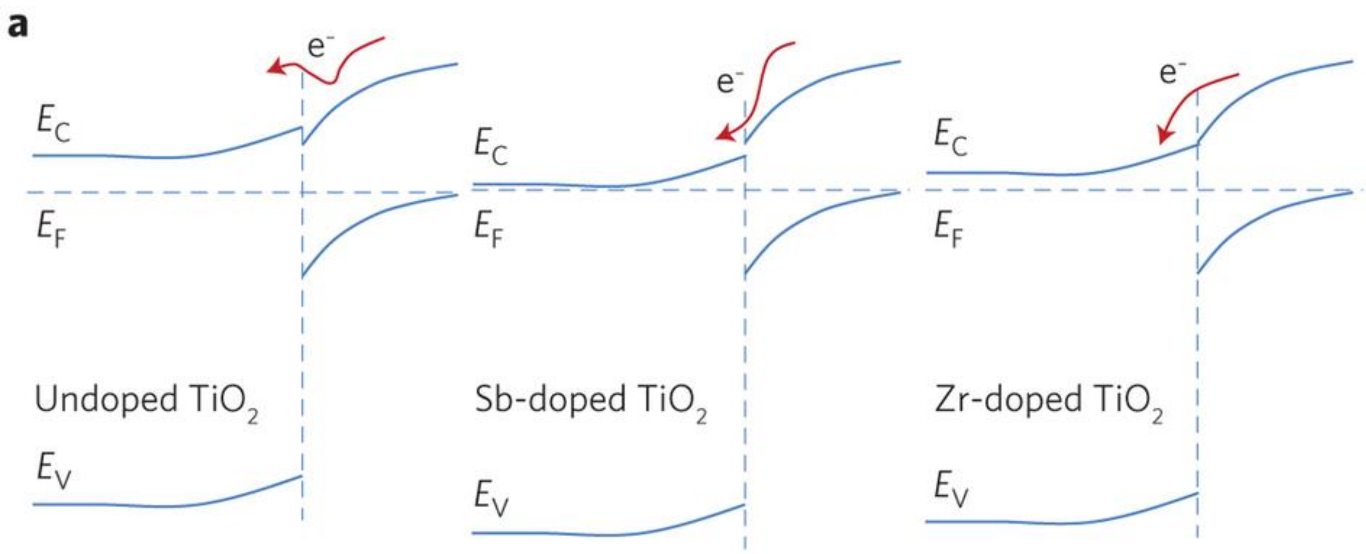
- **Band bending** refers to the local changes in the energy offset of a semiconductor's band structure near a junction, due to space charge effects. Because the common way to visualize the electron energy states and Fermi level in a material is to draw bands on an energy vs. distance plot (band diagram), band bending refers to bending observed in these diagrams and does not correspond to any physical (spatial) bending.
- The primary principle underlying band bending inside a semiconductor is space charge: a local imbalance in charge neutrality. Poisson's equation gives a curvature to the bands wherever there is an imbalance in charge neutrality. Why is there charge imbalance? Although one expects a homogeneous material to be charge neutral everywhere (since it must be charge neutral on average) there is no such requirement for interfaces. Practically all types of interface develop a charge imbalance, though for different reasons:
- At the junction of two different types of the same semiconductor (e.g., p-n junction) the bands vary continuously since the dopants are sparsely distributed and only perturb the system.
- At the junction of two different semiconductors there is a sharp shift in band energies from one material to the other; the band alignment at the junction (e.g., the difference in conduction band energies) is fixed.
- At the junction of a semiconductor and metal, the bands of the semiconductor are pinned to the metal's Fermi level.
- At the junction of a conductor and vacuum, the vacuum level (from vacuum electrostatic potential) is set by the material's work function and Fermi level. This also (usually) applies for the junction of a conductor to an insulator.

Junction between two semiconductors





This can be a problem at the PbS TiO_2 Interface



Where next?

- Discontinuities at the interface arise due to the different bandgaps of the semicondutors
- These discontinuities can cause trapping or decrease the open circuit voltage

- It would be nice to get rid of such discontinuities, and control the width of the depletion region.
- How could this be done?

Quantum Dot Doping

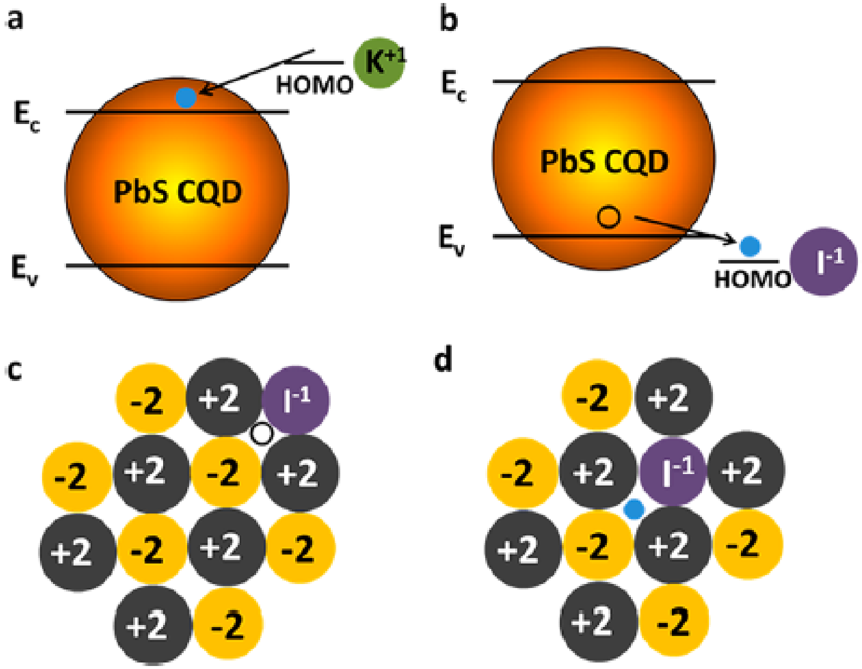
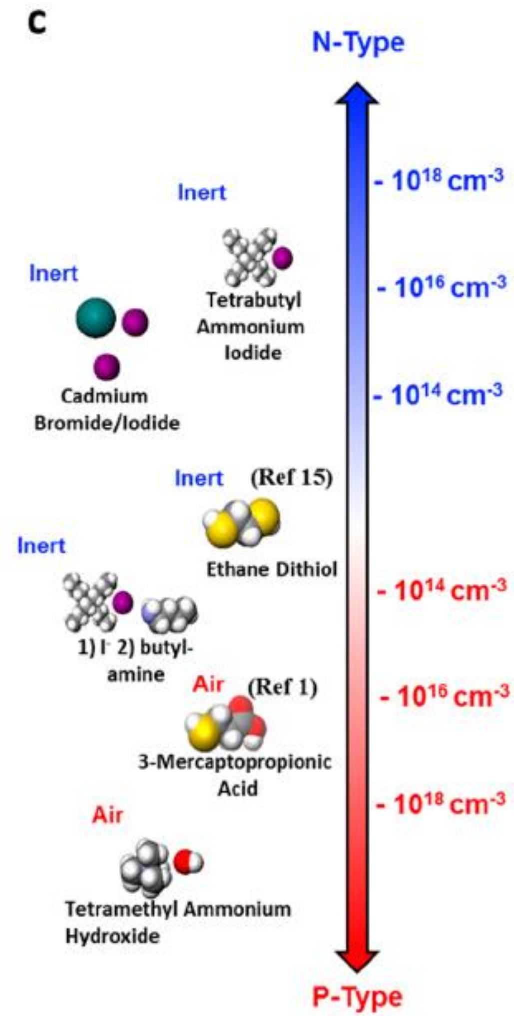
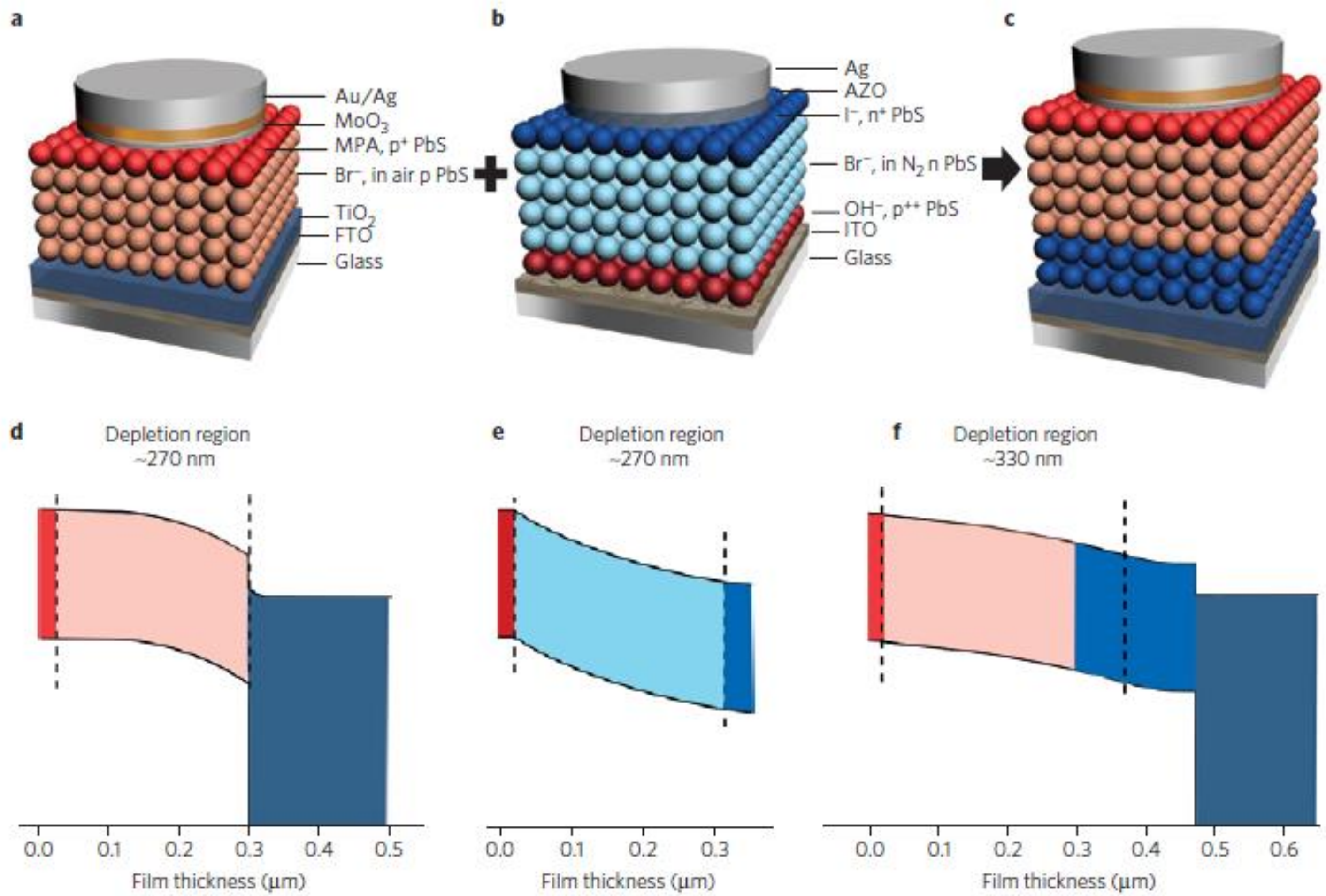


Figure 1. (a) Electron transfer from a remote cation (potassium) HOMO to a CQD conduction band, leading to n-type behavior; (b) transfer of electron from a CQD valence band to a remote anion (iodide) HOMO leading to p-type behavior; (c) atomic depiction of the scenario in part b; and (d) effect of iodine substitution for sulfur within the structure, leading to n-type character.



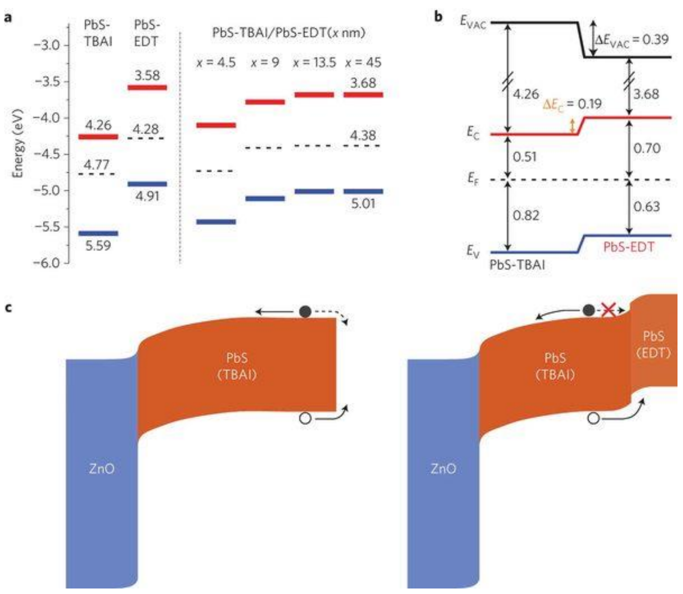
Graded PN junctions using QDs

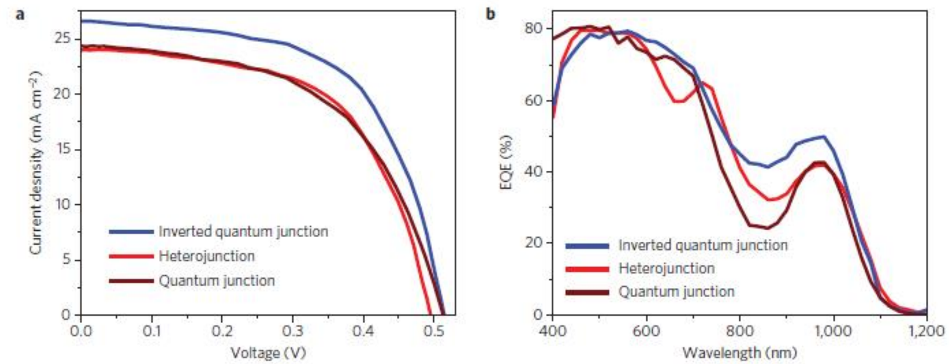


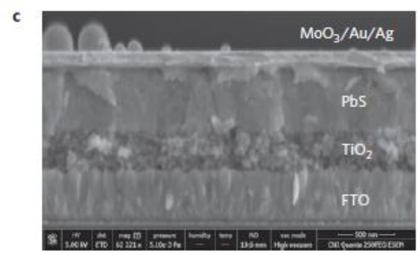
DOI: 10.1038/NMAT4007

Air-stable n-type colloidal quantum dot solids

Zhijun Ning[1], Oleksandr Voznyy[1], Jun Pan[2], Sjoerd Hoogland[1], Valerio Adinolfi[1], Jixian Xu[1], Min Li[3], Ahmad R. Kirmani[2], Jon-Paul Sun[4], James Minor[1], Kyle W. Kemp[1], Haopeng Dong[1], Lisa Rollny[1], André Labelle[1], Graham Carey[1], Brandon Sutherland[1], Ian Hill[4], Aram Amassian[2], Huan Liu[3], Jiang Tang[5], Osman M. Bakr[2] and Edward H. Sargent[1]*

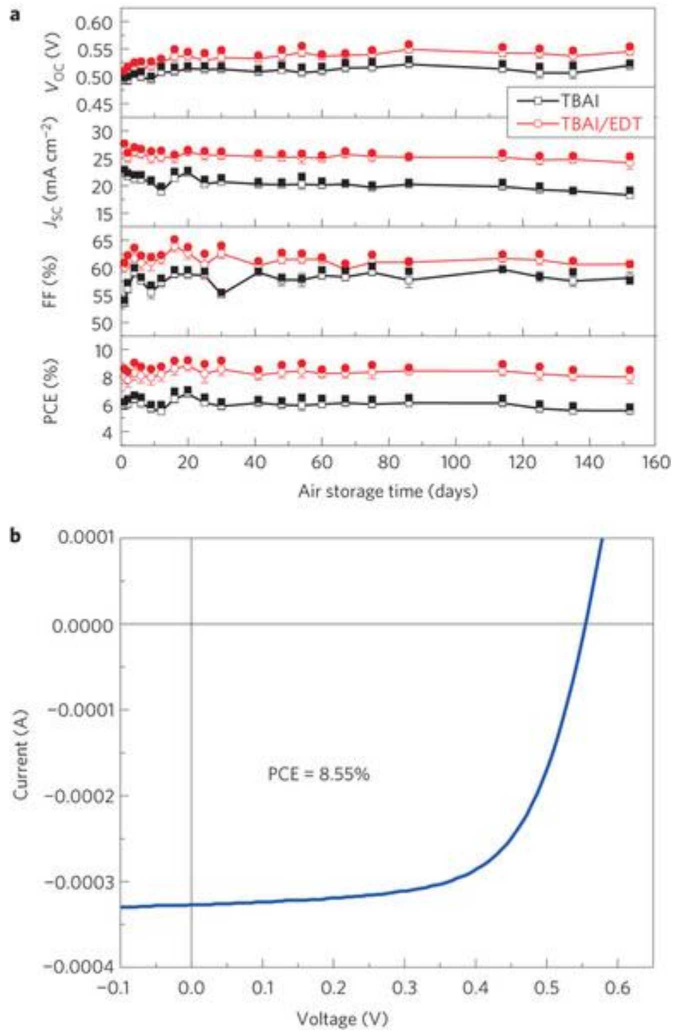






d

Type	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
Inverted quantum junction	0.51	26.6	0.59	8.0
Quantum junction	0.51	24.3	0.55	6.8
Heterojunction	0.49	24.0	0.59	6.9

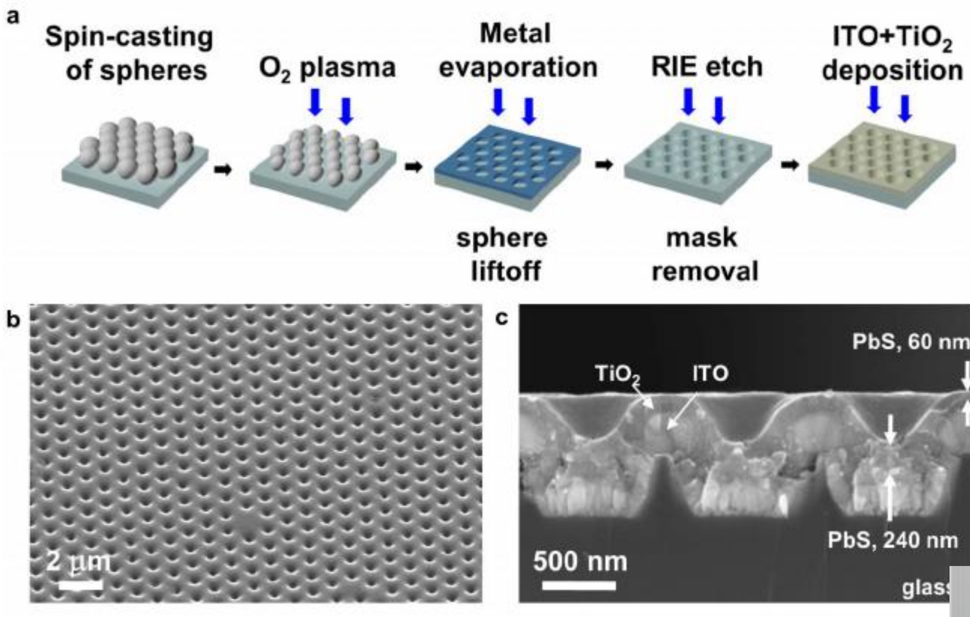


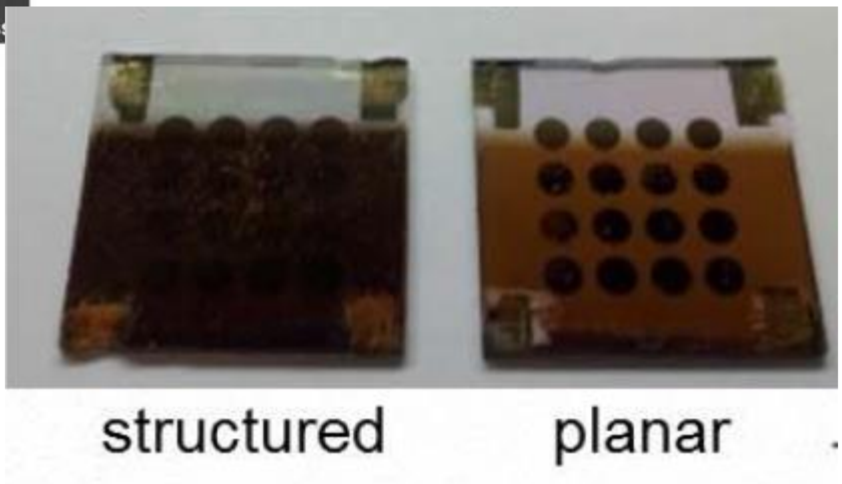
Nature Materials | Letter

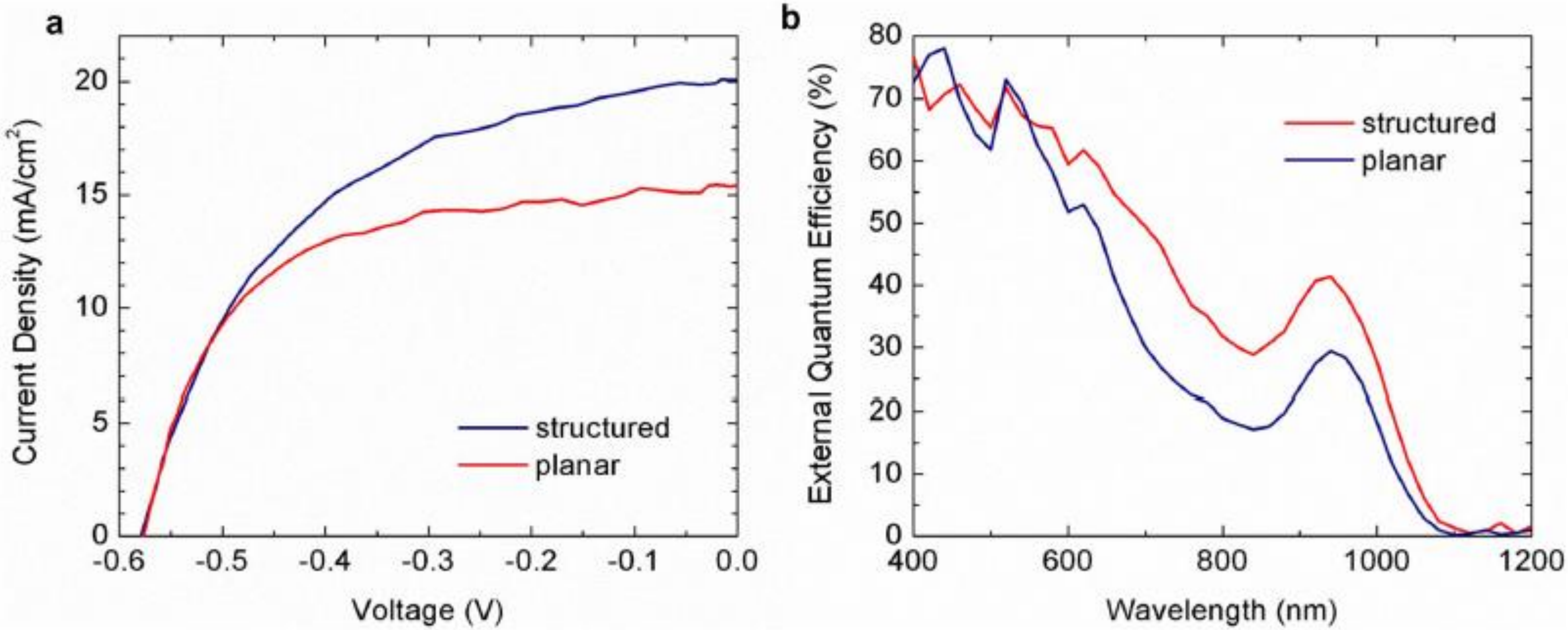
Improved performance and stability in quantum dot solar cells through band alignment engineering

Chia-Hao M. Chuang, Patrick R. Brown, Vladimir Bulović & Moungi G. Bawendi

Light scattering to increase absorption







Broadband solar absorption enhancement via periodic nanostructuring of electrodes

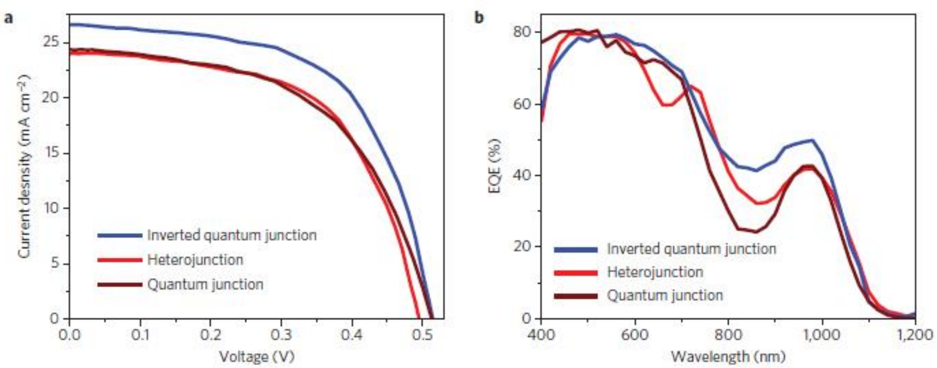
SCIENTIFIC REPORTS | 3 : 2928 | DOI: 10.1038/srep02928

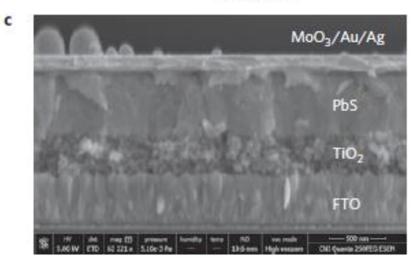
Michael M. Adachi[1], André J. Labelle[1], Susanna M. Thon[1]*, Xinzheng Lan[2], Sjoerd Hoogland[1] & Edward H. Sargent[1]

Lead Halide Perovskites

- Compared to quantum dot solar cells
- Absorption length and carrier diffusion length comparable
- Absorption length ~100 nm electron/hole diffusion lengths reported up to 1 μm

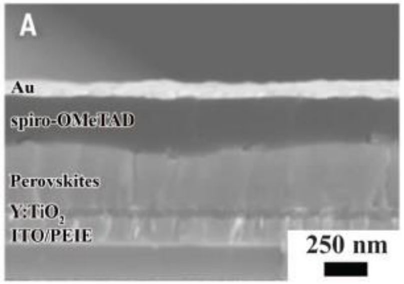
QD vs Perovskite

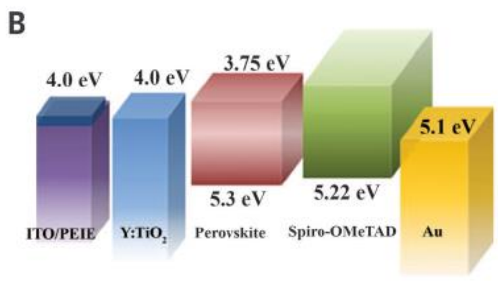


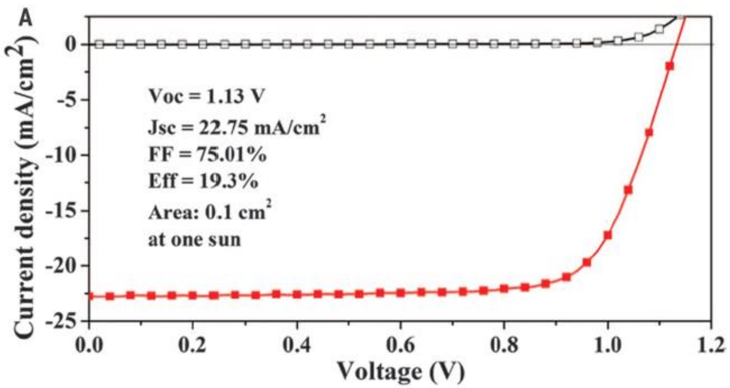


d

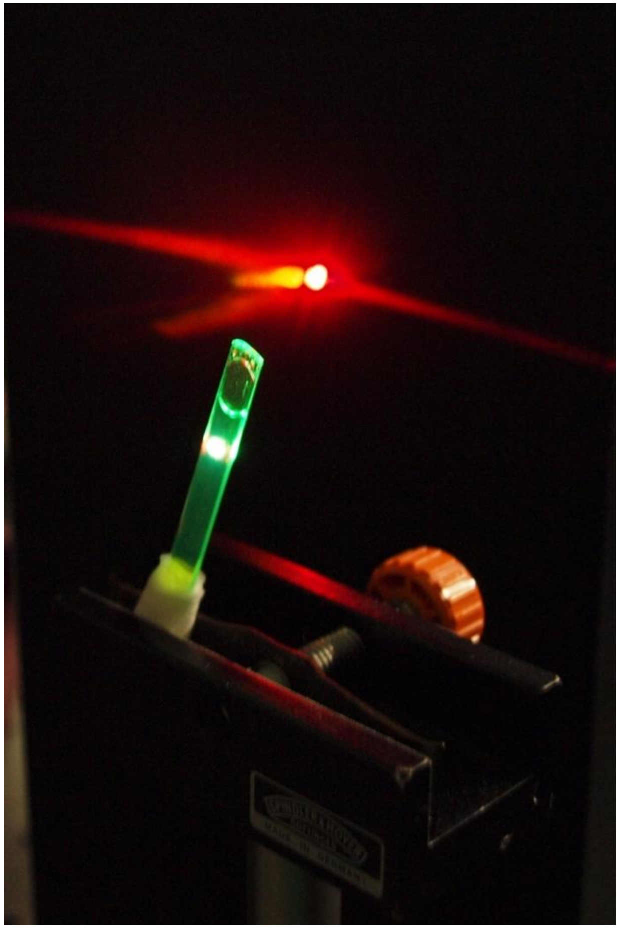
Type	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
Inverted quantum junction	0.51	26.6	0.59	8.0
Quantum junction	0.51	24.3	0.55	6.8
Heterojunction	0.49	24.0	0.59	6.9

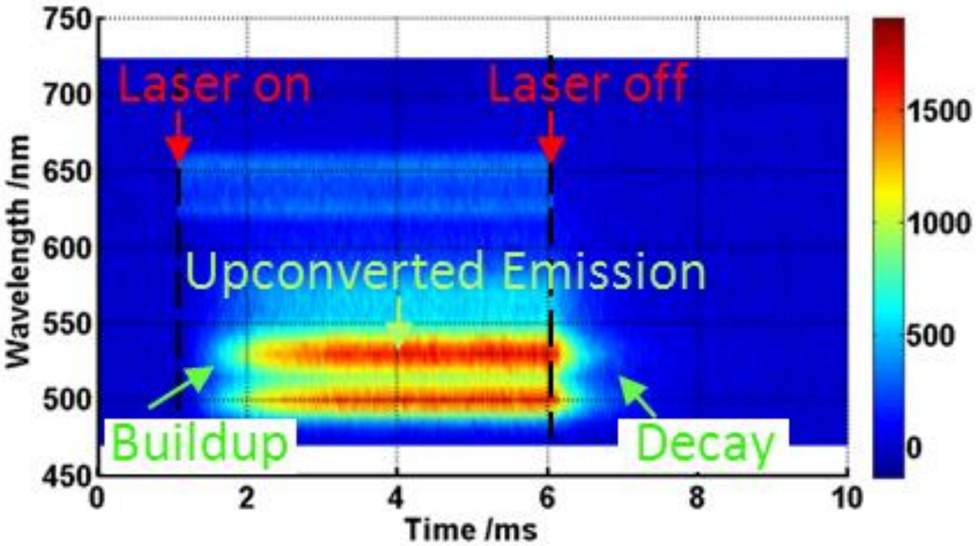


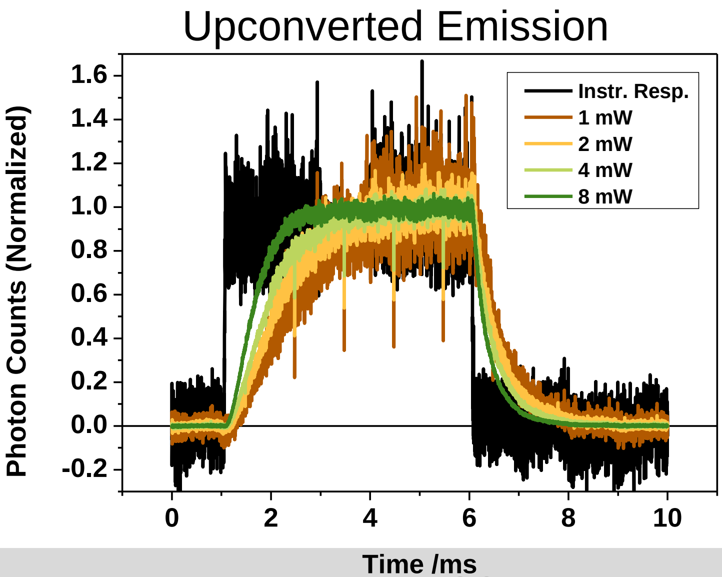




Photon Upconversion







Howard, I.A. et al. In preparation