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High-Performance Colloidal Quantum Dot Optoelectronic Devices

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Particles 2007
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Sargent Group at The University of Toronto

Current Research

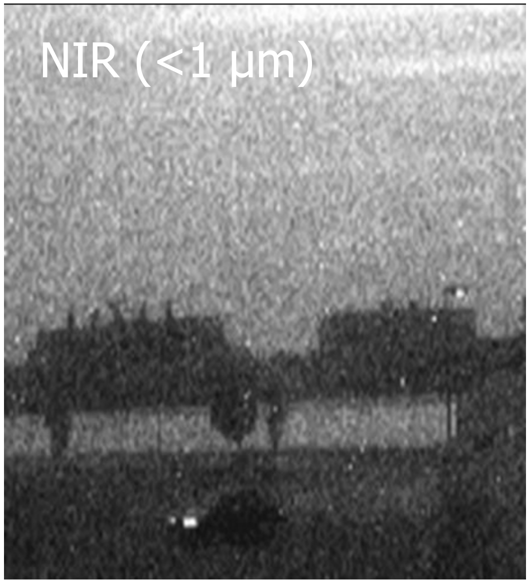
- Performance optimization of colloidal quantum-dot optoelectronic devices

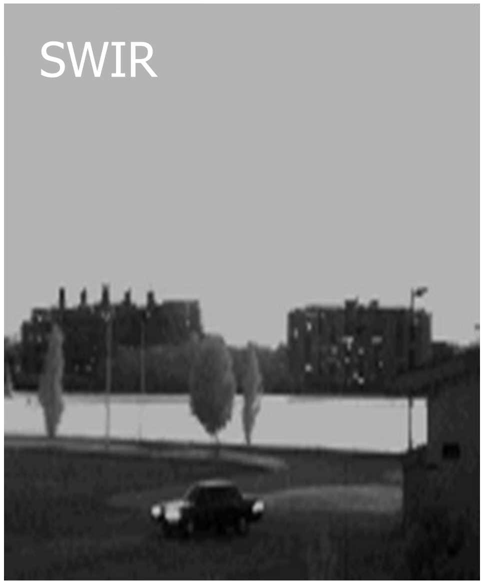
- PbS CQDs
  - short-wavelength infrared (SWIR) absorption and emission (1 um – 2 um)

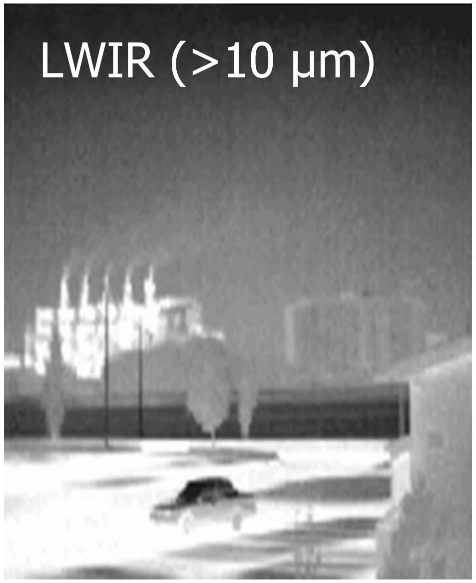
Photodetection	G. Konstantatos et al., Nature **442** 180 (2006)
Energy Conversion	E. Klem et al., Appl. Phys. Lett. **90**, 183113 (2007)
Photoemission and Lasing	S. Hoogland et al., Optics Express **42**, 3273 (2006)
Photomodulation	

Photodetection

Infrared (IR) Imaging





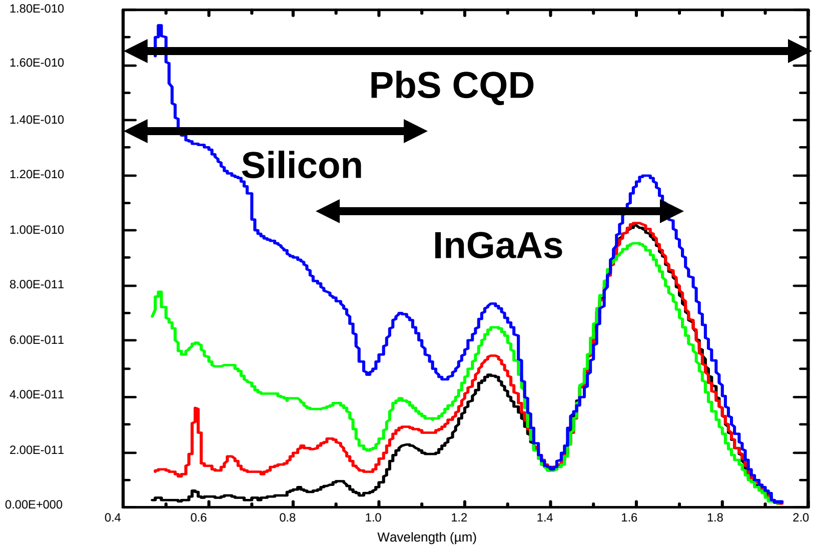


Naturally Occurring Illumination in SWIR

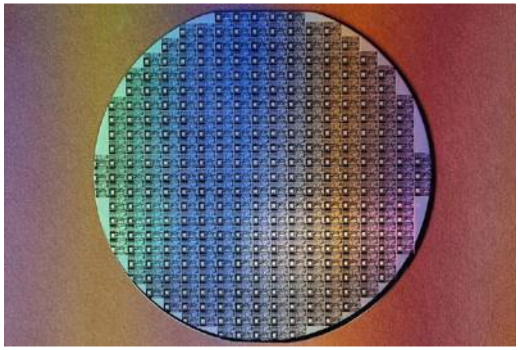
- 24 hour availability
- No dependence on artificial sources
- Emitted by hydroxyl (HO) radical reactions in upper atmosphere

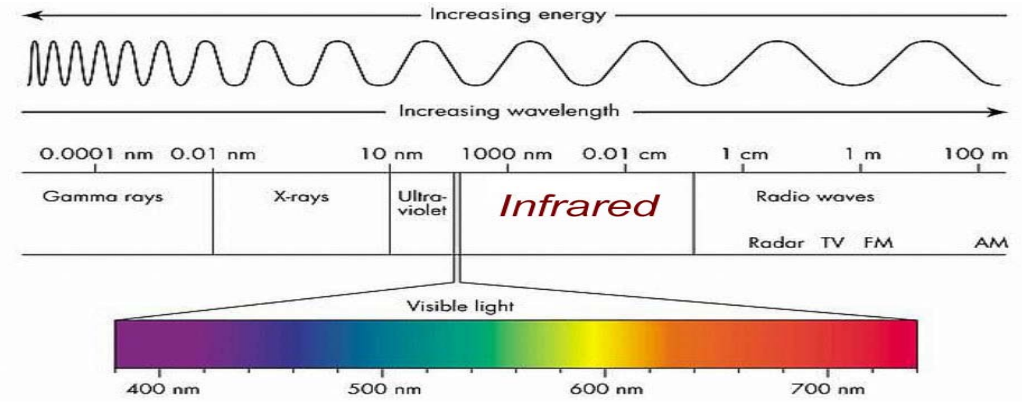
SWIR Imaging

- Reflected light – natural appearance
- Performance dependent on intensity



The Bandgap Problem





Silicon

- Ubiquitous, mature, platform for nearly all integrated circuits
- Bandgap at 1100nm prevents absorption or emission of light beyond 1100 nm

Infrared Optoelectronics

- Extensive applications in communication and imaging
    - night vision, thermal imaging, biomedical imaging, astronomy, etc.

- IR sensitive materials not structurally compatible with Si
    - high-cost, low yield mechanical hybridization of two semiconductor substrates

- Opportunity for development of IR materials suitable for direct Si integration

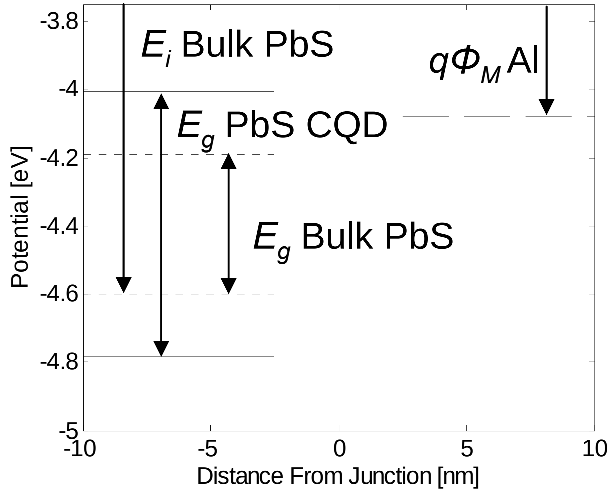
The Solution - Colloidal Quantum Dots

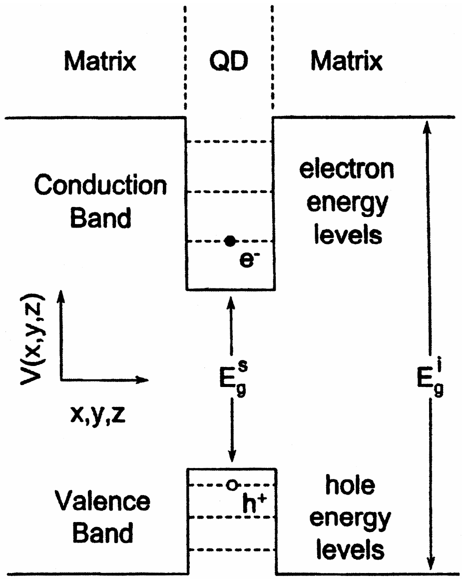
Lead Sulfide

- Group II-IV semiconductor
- 0.42 eV bulk bandgap

PbS Colloidal Quantum Dot (CQD)

- Crystalline semiconductor core
  - ~5 nm diameter
  - determines fundamental optoelectronic properties
- Oleate shell
  - Passivated surface bonds of core
  - Prevent NC aggregation
  - Provide solubility
- Quantum-Size-Effect
  - Controlled absorption and emission wavelengths





The Solution - Colloidal Quantum Dots

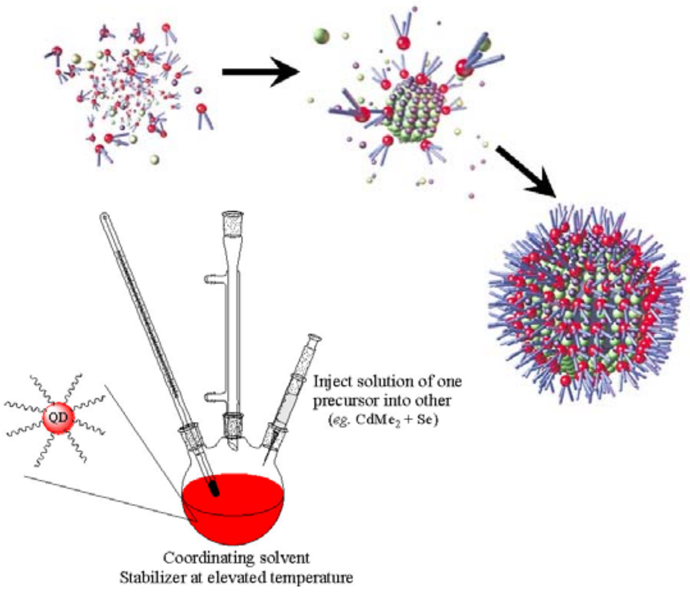
CQD Synthesis

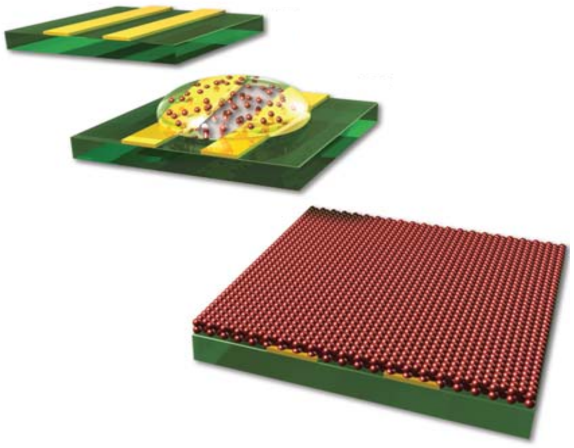
- Colloidal chemistry
    - Simple, cheap, fast

CQD Film Deposition

- Spin coating
    - CQDs suspended in organic solvents
    - Simple, cheap, fast

- Multiple advantages
    - No lattice matching of CQDs and substrate
    - No limitations on materials combinations
    - Near-ambient conditions
    - Large area deposition





Photodetector - Architecture and Operation

Structure

- CQD film between 2 ohmic contacts (Au)

Conductivity

- Transport of mobile holes injected from contacts
- Hopping or tunneling between proximal CQDs
- Ohmic I-V characteristics
    - for identical, efficiently injecting contacts

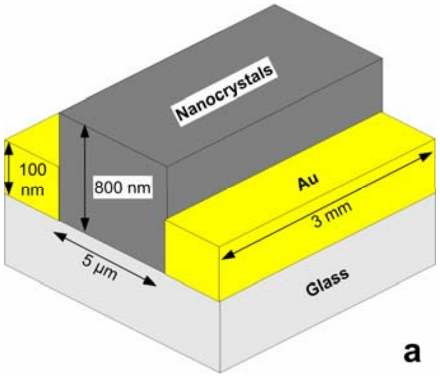
Photoconductivity

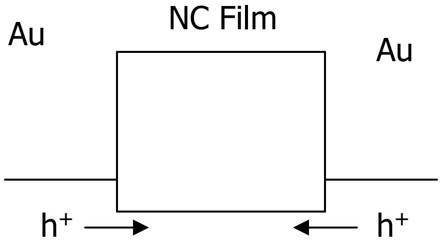
- Photogeneration of electron-hole pairs in CQDs
- In PbS, electrons captured in traps on surface of CQDs
- Holes are excess carriers and increase conductivity

High Detectivity (Sensitivity)

- High photoconductive gain
- Multiple carrier transit events for a single absorbed photon
- Gain = $T_{life} / T_{transit}$

- Tunable absorption spectrum
- Limited thermal noise – room temperature operation





G. Konstantatos et al., Nature **442** 180 (2006)

Photodetector - Optimization

Ligand Exchange

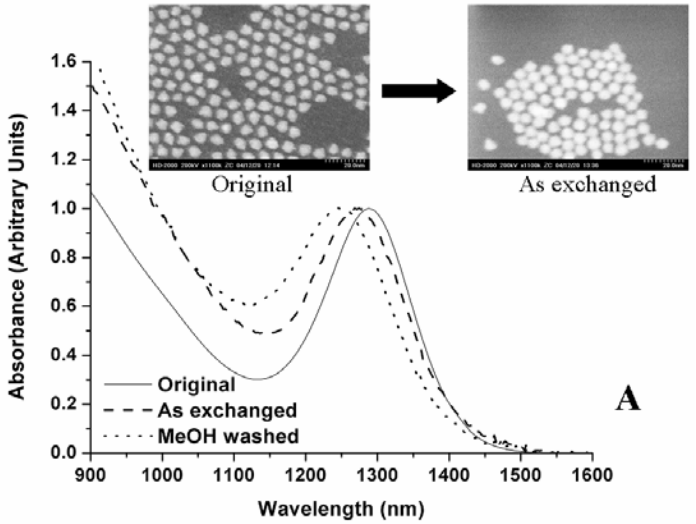
- As synthesized NCs – oleic acid (~2.5 nm)
- Solution phase exchange
- Primary butylamine ligand (~0.6 nm)
- Some oxidation
- Significant increase in conductivity
    - Increased mobility
    - Enables sensitization

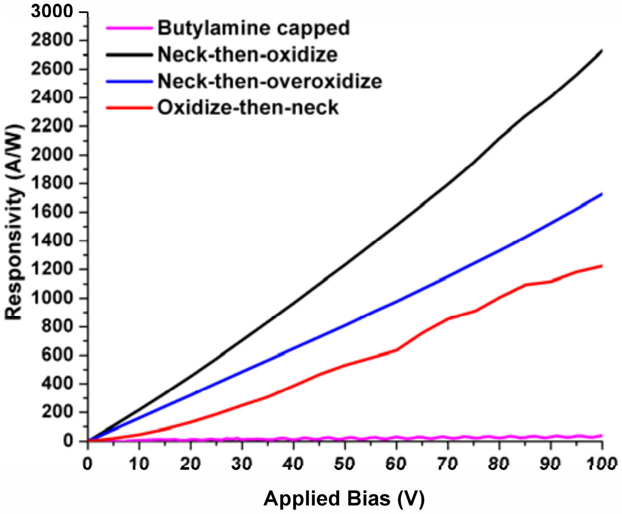
Sensitization

- Controlled oxidation of PbS
    - Oxides form electron traps
    - Increase hole lifetime
    - Maintain carrier pathways in film
- Observation of PbS0$_4$ – similar to bulk PbS

Independent Measurement of Gain

- Hole transit time ~0.5 µs
- Electron life time ~70 ms





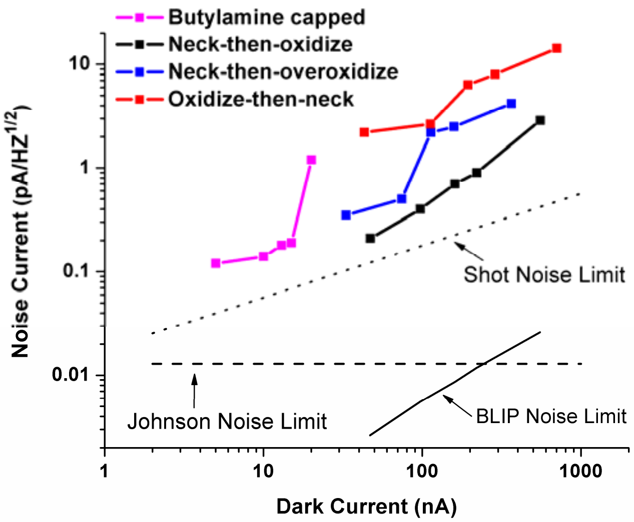
G. Konstantatos et al., Nature **442** 180 (2006)

Photodetector - Optimization

Sensitization and Noise

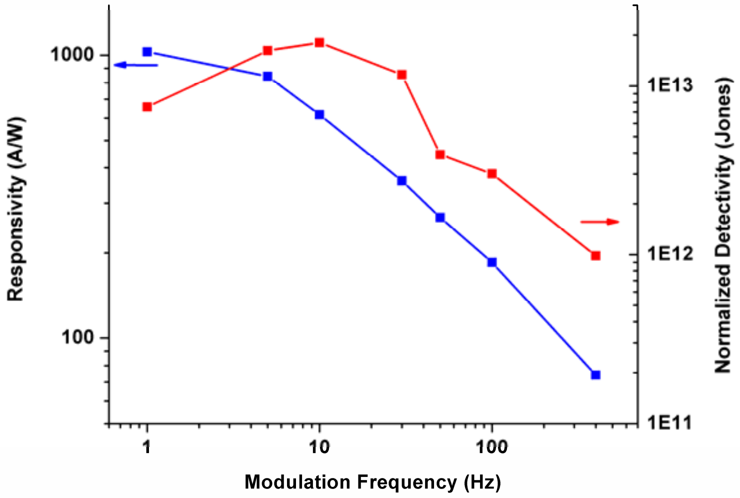
- Sensitization strategies
  - similar responsivities
  - dramatic differences in noise
- Minimal noise – neck-then-oxidize

- D* ~10^{13} Jones
  - FemtoWatts per cm^{-2}



Temporal Performance

- Speed limited by trap state lifetime
- 3-dB bandwidth 18 Hz
- D* > 10^{12} Jones up to 100 Hz
- Higher sensitivity than InGaAs at frequencies of interest for imaging applications



G. Konstantatos et al., Nature **442** 180 (2006)

Energy Conversion

Energy Conversion - Motivation

Solution Processed Solar Cells

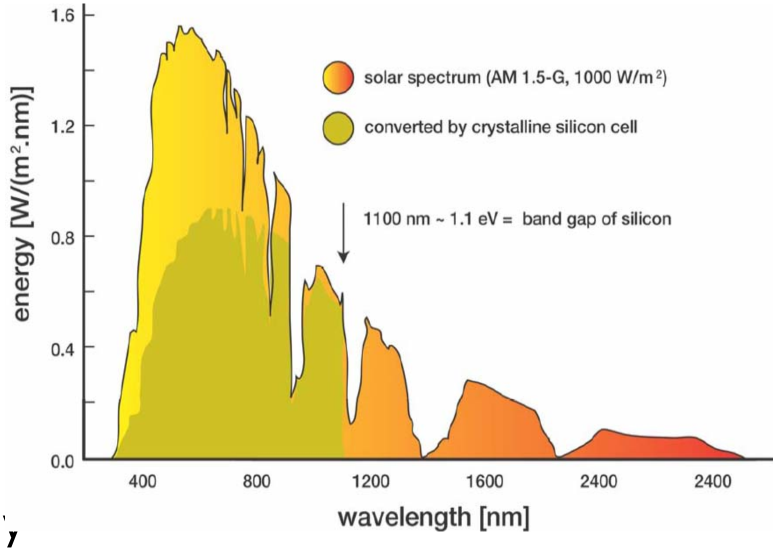
- low-cost
- large area
- substrate compatibility

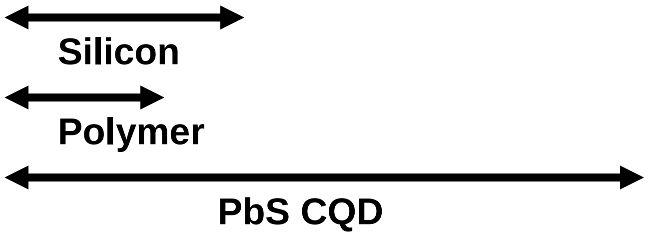
Current solution-processed devices

- Solar power conversion efficiency 3% - 5%
- Most limited to visible light absorption
- Sensitive to < 50% of available solar energ

PbS CQD photovoltaic devices

- Absorb light in visible and IR
- All cost and manufacturing benefits of organic photovoltaics





Silicon

Polymer

PbS CQD

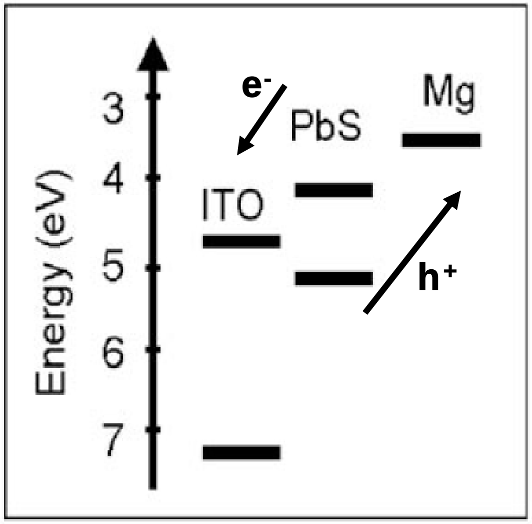
Energy Conversion – Device Architecture

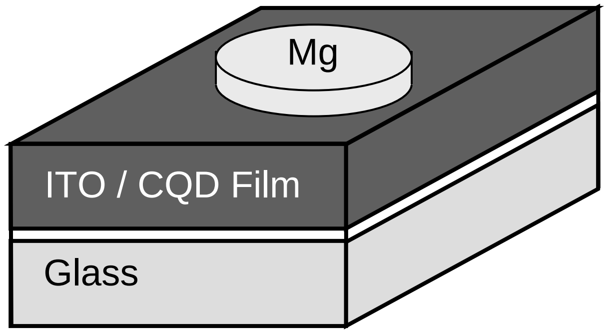
Architecture

- Type-II heterojunction
- Nanoporous metal oxide / infiltrated CQD film
- ITO – superior conductivity (~0.5 Ω.cm^{-1})
- Mg cathode – low work function

Operation

- Light absorption in PbS CQD film
- Charge separation at distributed ITO/CQD interface
- Hole transport in PbS CQD
- Electron transport in nanoporous ITO





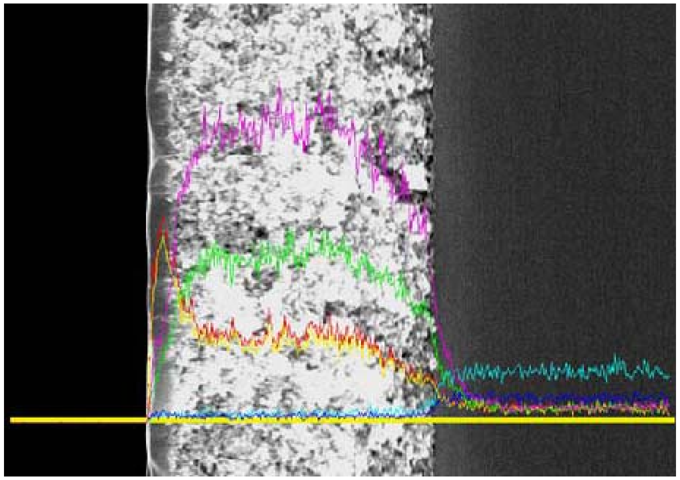
E. Klem et al., Appl. Phys. Lett. **90**, 183113 (2007)

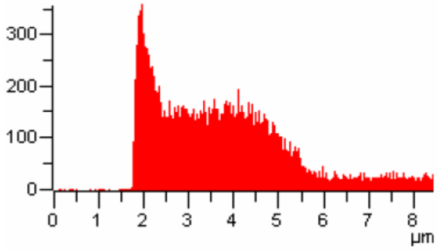
Energy Conversion – Device Architecture

Device efficiency limited by low mobility of CQD film

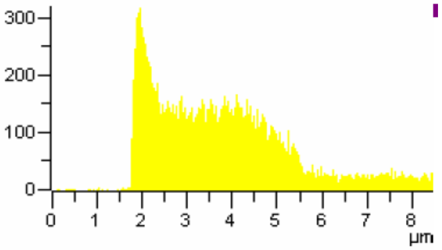
Bulk Heterojunction

- Reduce transport distance
  - before and after carrier separation
  - reduce recombination
- Increase scattering
  - increase absorption

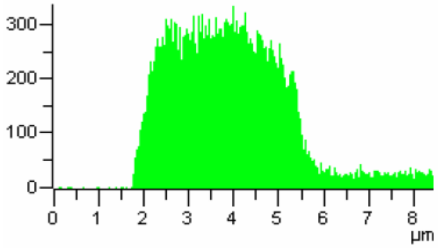




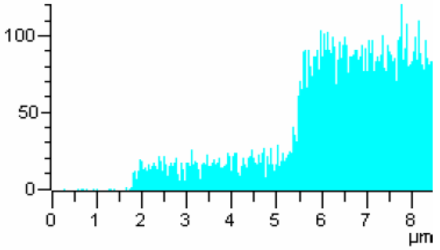
Lead Ma1



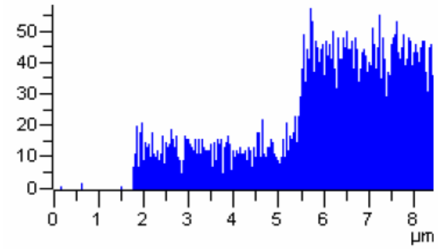
Sulfur Ka1



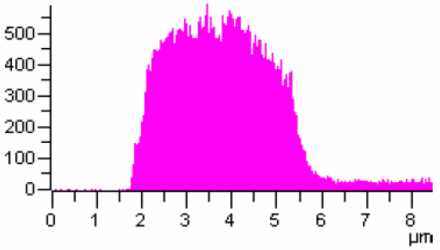
Tin La1



Gallium Ka1

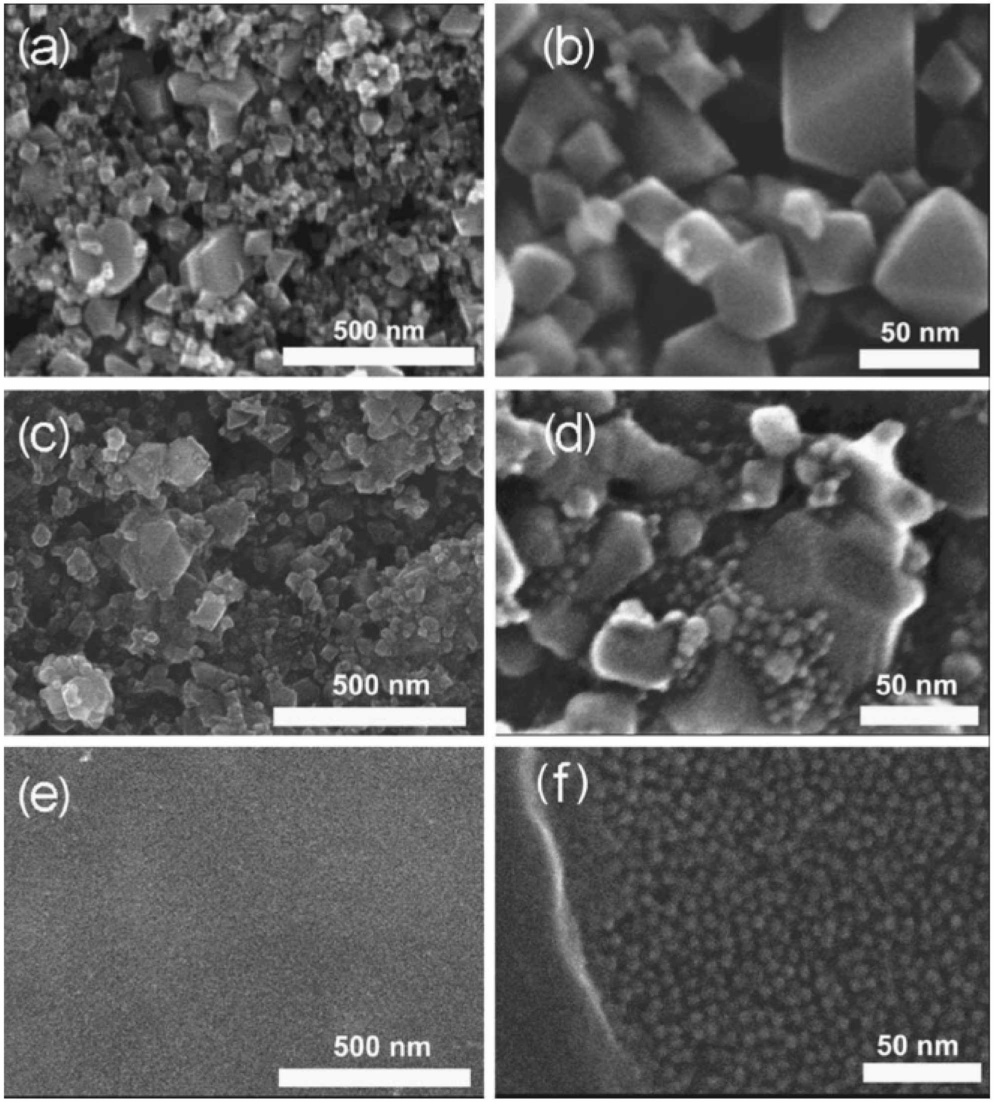


Arsenic Ka1



Indium La1

Energy Conversion - Optimization



Klem 2005

Nanoporous ITO

- High surface area – very rough

CQD Infiltration

- Soak substrate in PbS CQD soln.
- Exposed ITO – shorting

Linking CQDs

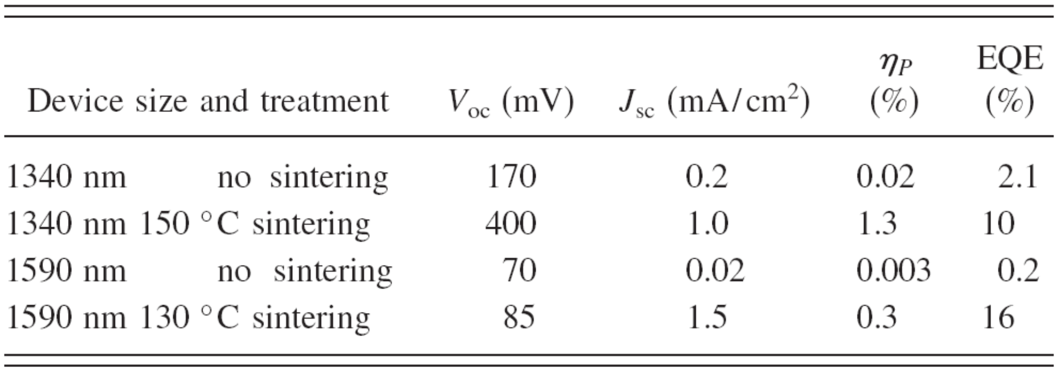
- Ethane dithiol (~0.7 nm long)
- Connects CQDs laterally & vertically
- Smooth continuous CQD films
- Coverage of ITO
- Eliminates shorting

Sintering

- Remove excess ligand
- Increase mobility
- Increase hole lifetime

E. Klem et al., Appl. Phys. Lett. **90**, 183113 (2007)

Energy Conversion - Optimization

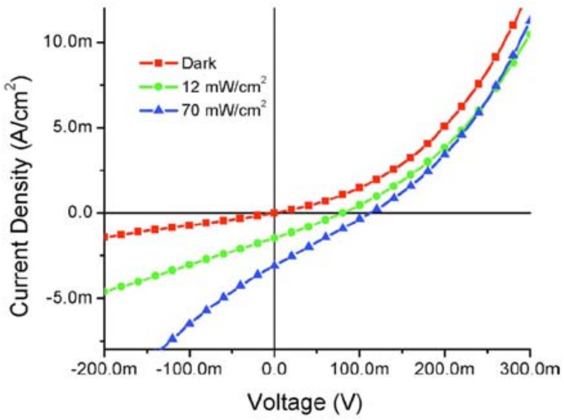


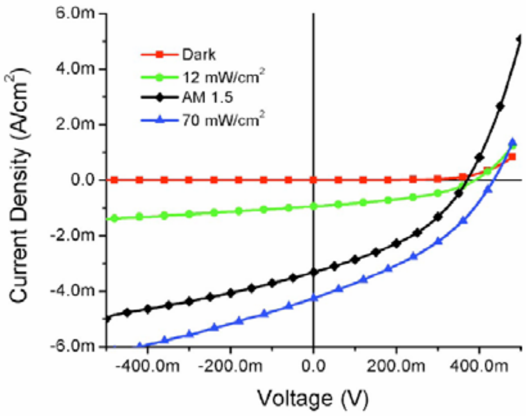
Device size and treatment	V_{oc} (mV)	J_{sc} (mA/cm^2)	η_P (%)	EQE (%)
1340 nm no sintering	170	0.2	0.02	2.1
1340 nm 150 °C sintering	400	1.0	1.3	10
1590 nm no sintering	70	0.02	0.003	0.2
1590 nm 130 °C sintering	85	1.5	0.3	16

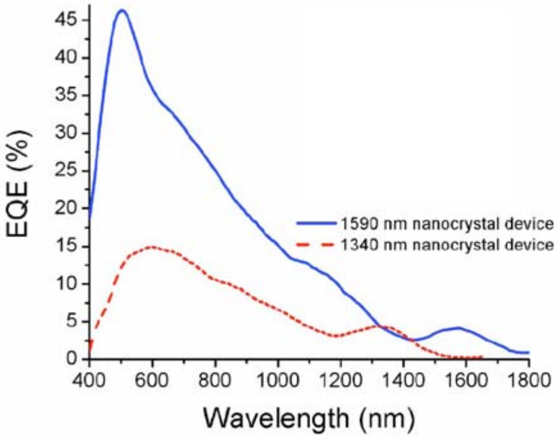
975 nm 12 mW.cm^{-2}

Performance

- 46% EQE at 500 nm
- > 5% at 1st excitonic feature
- Absorption beyond 1700 nm
- Suitable for integration in multi-junction solar cells







E. Klem et al., Appl. Phys. Lett. **90**, 183113 (2007)

Photoemission and Lasing

Lasing – Motivation

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Intel® Technology Journal

Optical Technologies and Applications

Integration of optoelectronic devices with Si

“Si compatible emitter is the missing link for integration as it would enable all optical components and drive electronics to be fabricated on a common substrate”

Mainstream semiconductor laser sources

Epitaxial lasers => strict lattice matching on single-crystal substrate
=> not monolithically integrable with Si

Silicon compatible sources

Silicon Raman laser => no electrical pumping possibilities
(Boyraz, *et al., Opt. Expr*. **12**, 5269 (2004)) => need seed laser at ~1.5 μm
(Rong, H.S., *et al., Nature*. **433**, 292 (2005))

Silicon laser => indirect bandgap – defects required for lasing
(Cloutier, *et al., Nat. Mat*. **4**, 887 (2005)) => unable to tune to 1.5 μm

Silicon quantum dot laser => low optical gain, no lasing
(Pavesi, *et al., Nature* **408**, 440 (2000)) => no evidence for 1.5μm operation

Lasing – Semiconductor Lasers

Quantum wells, wires, and dots

- Increase of confinement of carriers at energy band edge
- Tunable bandgap and emission

Emission wavelength

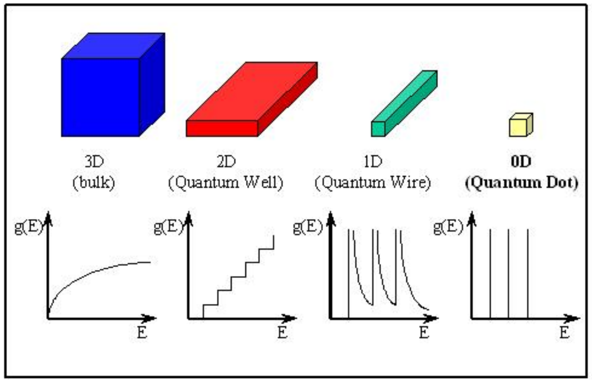
- Dependent on energy of carrier transition
- Carrier populations dependent on temperature
- Emission invariance for separation of states beyond kT

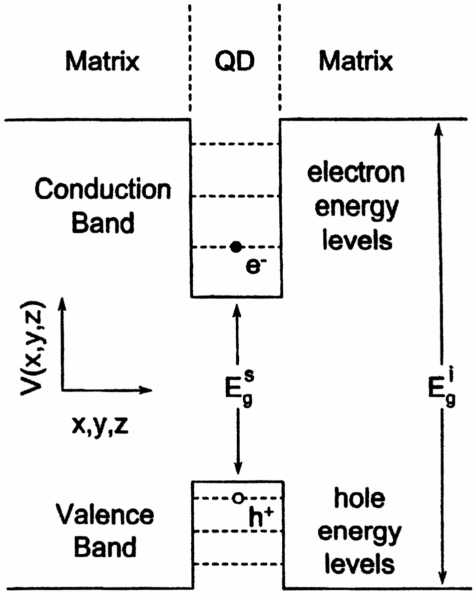
Epitaxial quantum dots

- Large compared to Bohr excition diameter
- Close spacing of confined states
- Require precise control of lattice mismatch

Colloidal quantum dots

- Much smaller diameter – very strong confinement
- Large state spacing's (100's meV)
- Excellent monodispersity (<5%)
- Compatible with wide range of substrates including Si





Lasing – Development of a CQD laser

For optically-pumped

- Material optical gain
- Resonator (with a large finesse)
- Lack of undue loss
- modal gain equal to resonator loss + excess loss

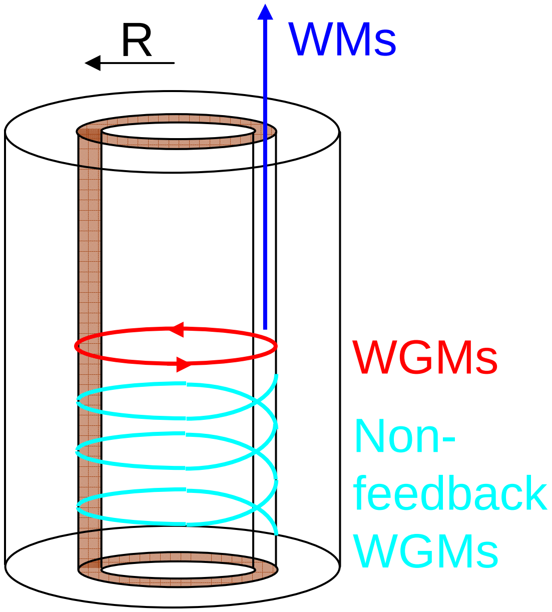
For electrically-pumped (additional to above)

- Injection of sufficient current density to feed gain required
- Confinement of carriers

CQD Laser Architecture

- Glass capillary substrate (R~50 um)
- Thin colloidal CQD film on inner-wall (<1 um)

- Whispering gallery mode resonator
  - Dependent on total internal reflection within film
  - Higher finesse than planar resonant structures



WM: Waveguide mode
WGM: Whispering gallery mode

S. Hoogland et al., Optics Express **42**, 3273 (2006)

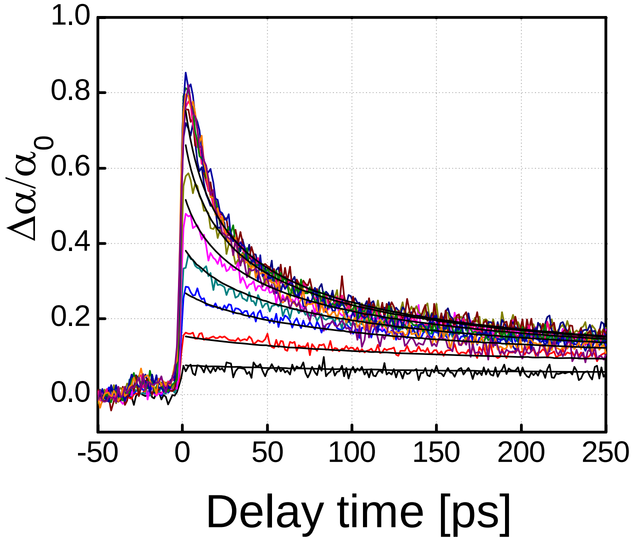
Lasing – Complications in PbS CQDs

Population Inversion

- Required for spontaneous emission

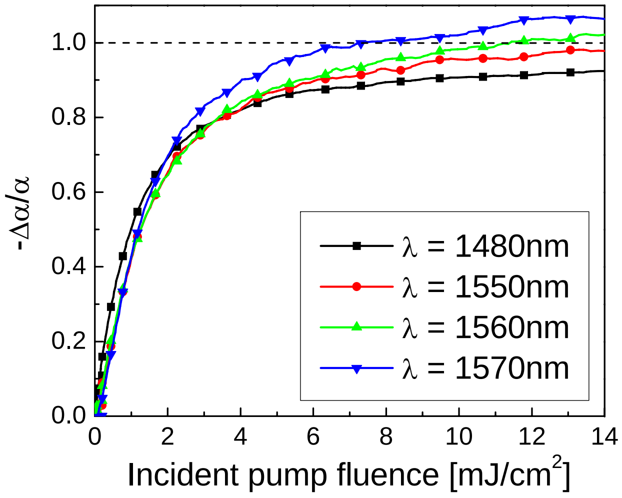
PbS CQDs

- 8-fold degeneracy of lowest energy states
- 4 excitons required to achieve transparency (inversion)
  - compared to 1 for Cd-based CQDs
- Increased Auger recombination of excited carriers
  - Fast (Tau~10 ns) recombination



Is it possible to ensure stimulated emission rate > Auger recombination rate?

- Transparency achieved when absorption change equals linear absorption
- Yes – at a pump power of 7.8 mJ.cm^{-2} at 1570 nm



Observed population inversion modest

- large packing fraction of CQD film required for gain
- Achieved though ligand exchange

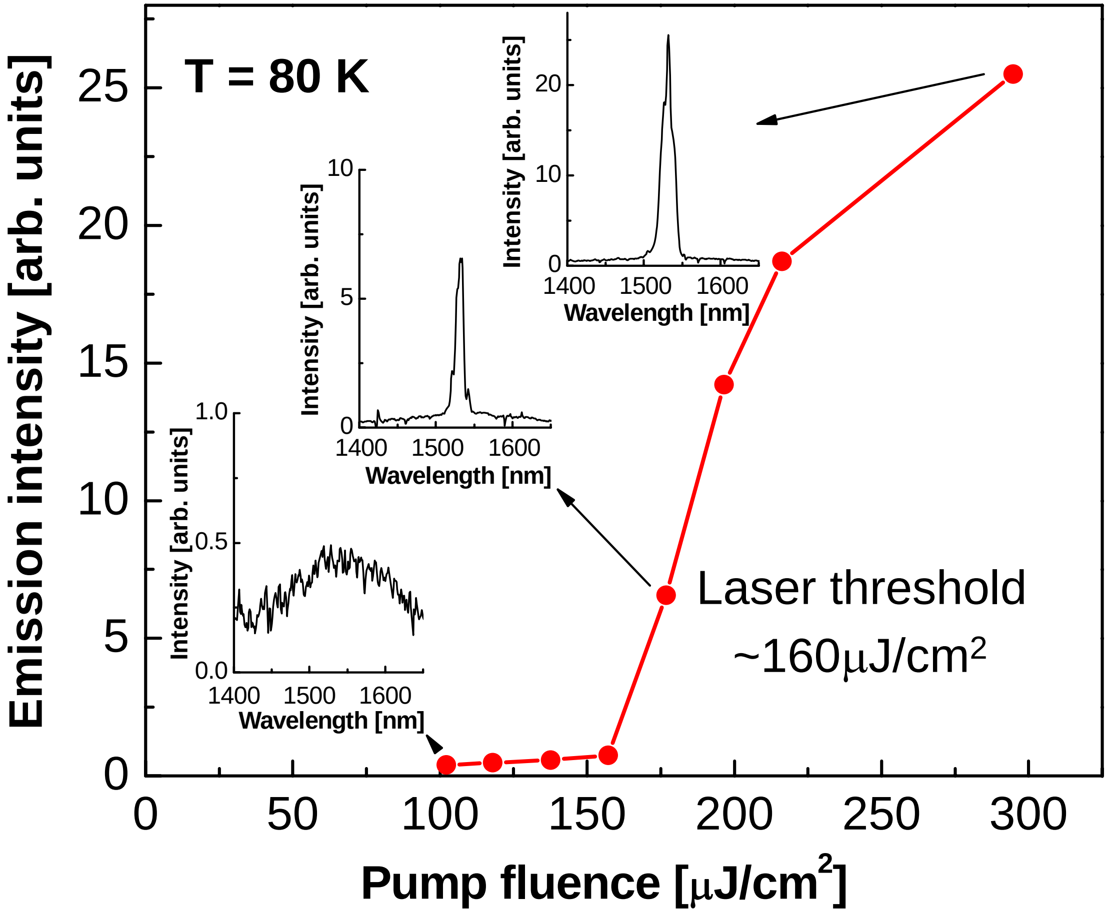
S. Hoogland et al., Optics Express **42**, 3273 (2006)

Lasing – Observation of Lasing in PbS CQD

Optically-pumped lasing

- Clear lasing threshold at ~169 uJ.cm^{-2}
- 1532 nm emission at 80K
  - Stable for several hours
- Temp sensitivity of emission
  - 0.03 nm/K
  - 10x smaller than current semiconductor QW lasers

First report of solution processed laser source!



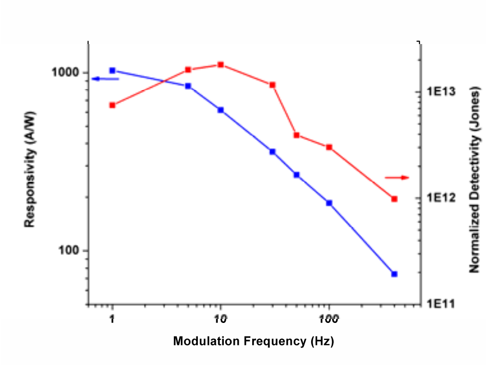
S. Hoogland et al., Optics Express **42**, 3273 (2006)

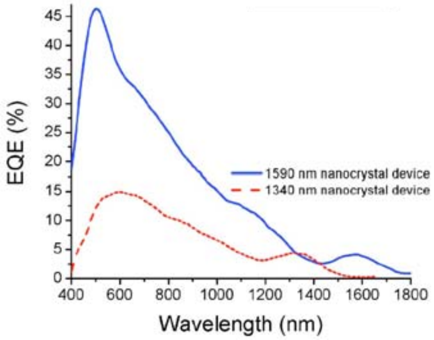
Conclusion

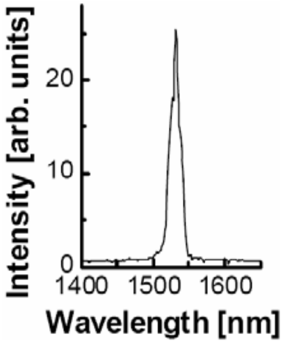
Conclusion

Demonstrated

- High sensitivity visible-IR photodetectors
- Photovoltaic energy conversion in visible-IR
- Lasing in IR







Colloidal quantum dot optoelectronic devices offer real advantages

- Useful-to-excellent performance
- Low-cost
- Potential for integration
- Access to IR wavelengths

Proven feasibility of high-performance CQD device applications !

Acknowledgements

Sargent Group

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