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Author(s): Klimov, Victor Ivanovich

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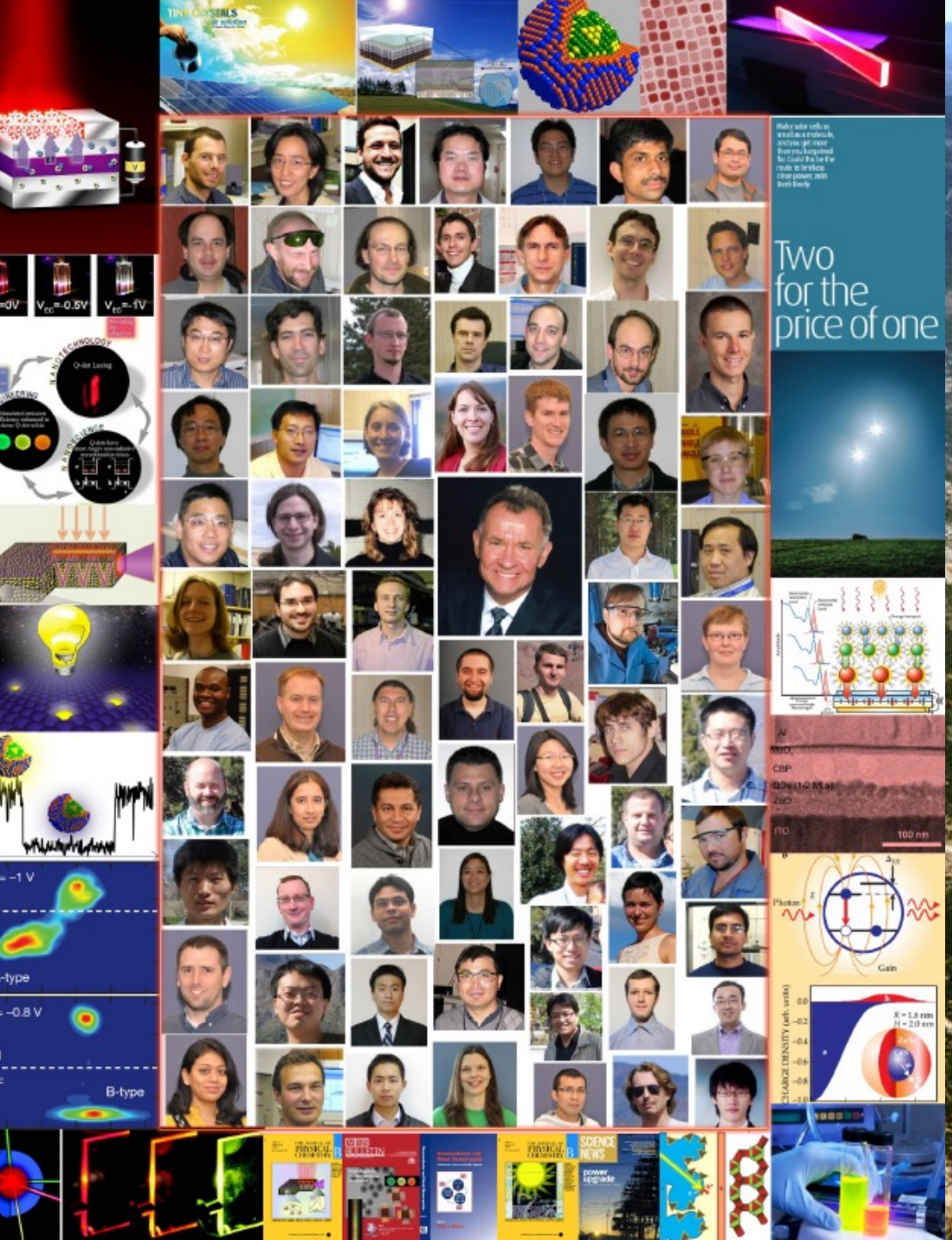
Los Alamos Quantum Dots



Prospects & Challenges of Colloidal Quantum Dot Laser Diodes

Victor I. Klimov

Nanotechnology and Advanced Spectroscopy Team

&

Center for Advanced Solar Photophysics

Los Alamos National Laboratory

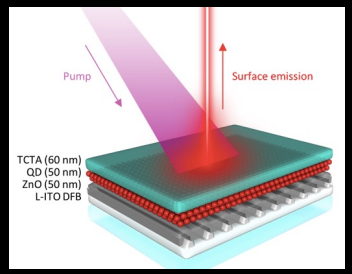
Los Alamos, NM

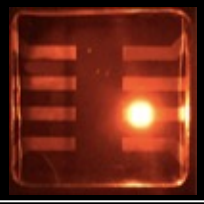
klimov@lanl.gov

http://casp.lanl.gov

http://quantumdot.lanl.gov

2020

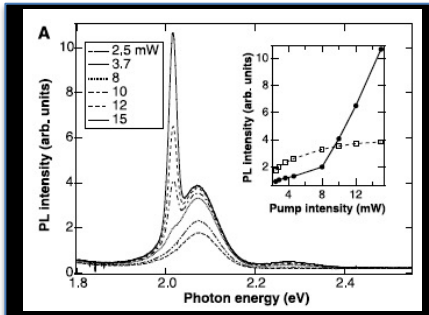


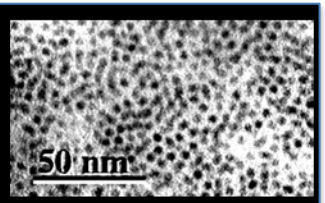


Nature Comm. **11,** 271 (2020)

Dual function laser/LED devices

2000

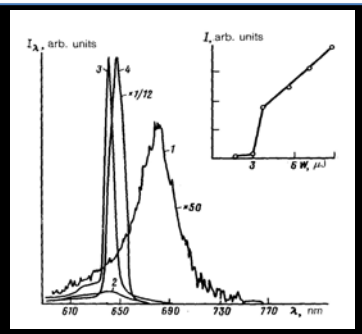




Science. **290**, 314 (2000)

ASE/lasing with colloidal QDs

1991



LETP Lett. **54,** 442 (1991)

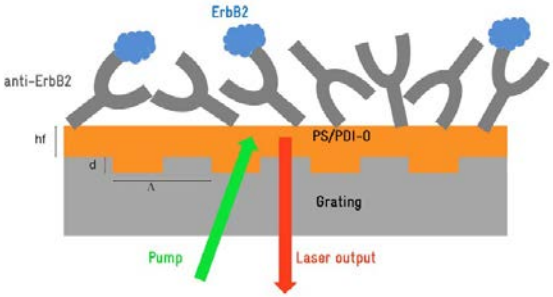
Lasing with glass-embedded NCs

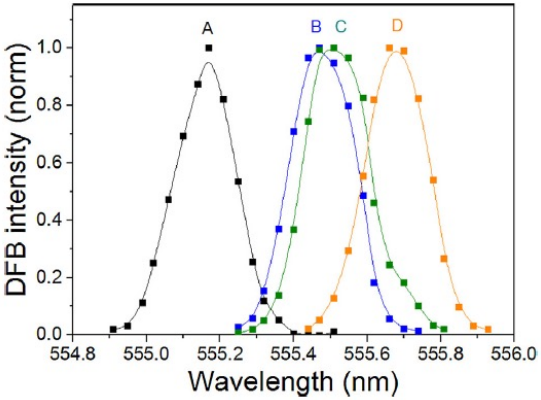
Ultra-Low-Threshold, Highly-Flexible, Solution-Processible Lasers: *Do We Need Them*?

NanoTechnology & Advanced Spectroscopy Team

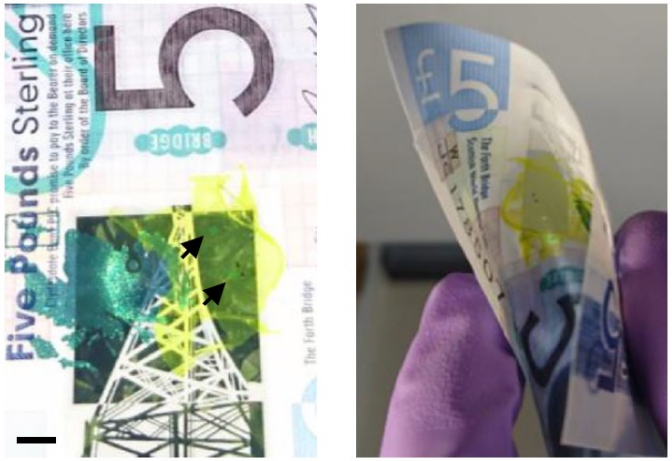
Optical communications & interconnects

Ultrahigh-gain chem/bio sensing



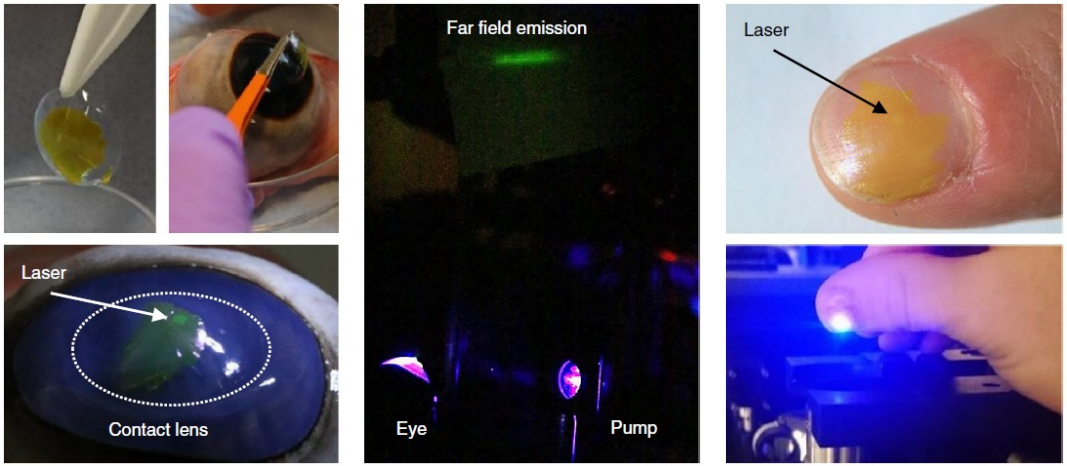


"Ultimate" Security



Banknotes

Wearable devices



Eye diagnostics

Lasing nail polish?

Polymer Lasers…still Not with Electrical Pumping

NanoTechnology & Advanced Spectroscopy Team

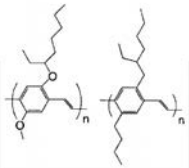
Solution-based polymer laser: Moses et al., APL 60, 3215 (1992);
Solid-state polymer laser, Tessler et al., Nature 382, 695 (1996)

ADVANCED MATERIALS

Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers**

By *Michael D. McGehee* and *Alan J. Heeger**

Light-emissive polymers are outstanding laser materials because they are intrinsically "4-level" systems, they have luminescence efficiencies higher than 60% even in undiluted films, they emit at colors that span the visible spectrum, and they can be processed into optical quality films by spin casting. The important materials issues are reviewed and the prospects for making polymer diode lasers are discussed.



Organic Semiconductor Lasers

I. D. W. Samuel* and G. A. Turnbull

Organic Semiconductor Centre and Ultrafast Photonics Collaboration, SUPA, School of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, U.K.

ACCOUNTS of chemical research

Article

pubs.acs.org/accounts

Organic Micro/Nanoscale Lasers

Wei Zhang,[†,‡] Jiannian Yao,[†,‡] and Yong Sheng Zhao*[,†,‡]

[†]Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
[‡]School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Polymer lasers: recent advances

Materials Today 7 (9), 28 (2004).

Ifor D. W. Samuel[†] and Graham A. Turnbull*

Review

SCI

Received: 18 April 2011 Revised: 13 July 2011 Accepted: 20 July 2011 Published online in Wiley Online Library: 12 October 2011

(wileyonlinelibrary.com) DOI 10.1002/pi.3173

Recent advances in solid-state organic lasers

Sébastien Chénais* and Sébastien Forget*

Polym. Int. 61 (3), 390 (2011).

CHEMICAL REVIEWS

Review

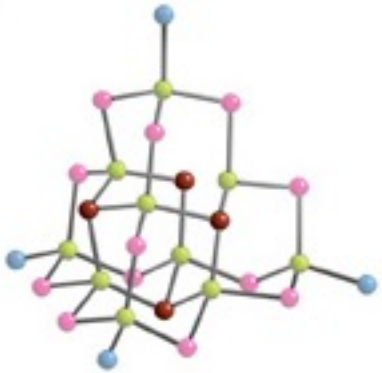
pubs.acs.org/CR

Organic Lasers: Recent Developments on Materials, Device Geometries, and Fabrication Techniques

Alexander J. C. Kuehne*[,†] and Malte C. Gather*[,‡]

[†]DWI–Leibniz Institute for Interactive Materials, RWTH Aachen University, Forckenbeckstr. 50, 52056 Aachen, Germany
[‡]Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom

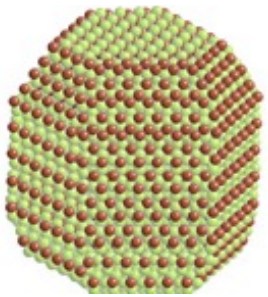
Semiconductor Nanocrystals: *Quantum Dots Made in a Chemical Beaker*



$Cd_{10}Se_4(SePh)_{12}(PPr_3)_4$

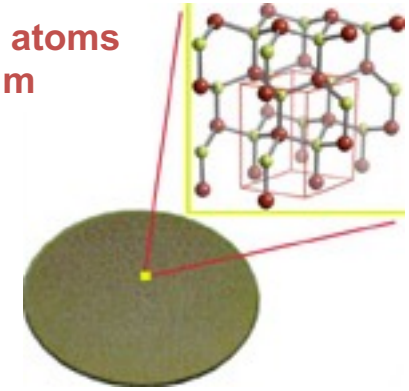
Cluster Molecule

100 atoms
2 nm



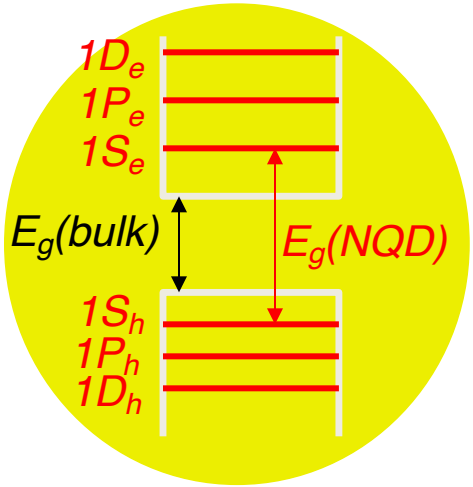
Quantum Dot Regime

100,000 atoms
20 nm



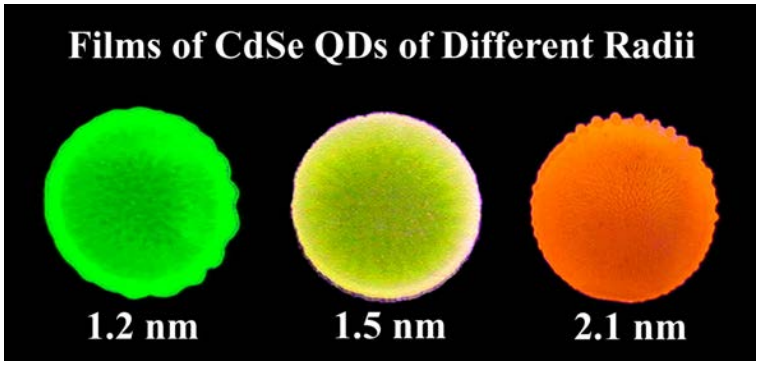
Bulk CdSe

- **Extreme quantum confinement**

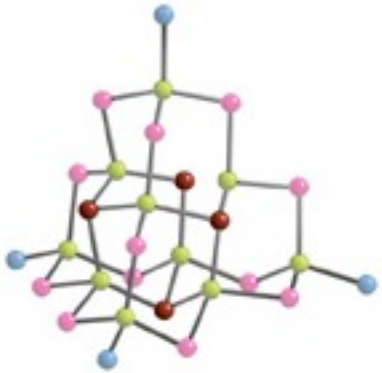


$$E_g(NQD) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2 m_{eh} R^2}$$

quantum confinement term (> 200 meV)



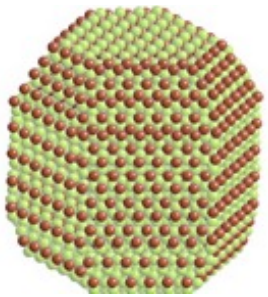
Semiconductor Nanocrystals: *Quantum Dots Made in a Chemical Beaker*



$Cd_{10}Se_4(SePh)_{12}(PPr_3)_4$

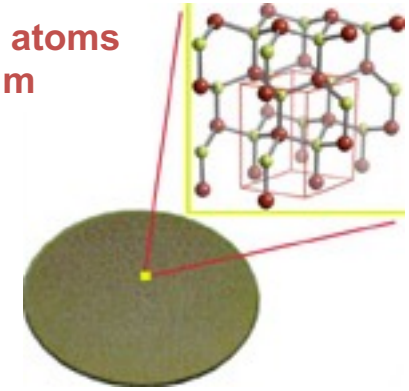
Cluster Molecule

100 atoms
2 nm



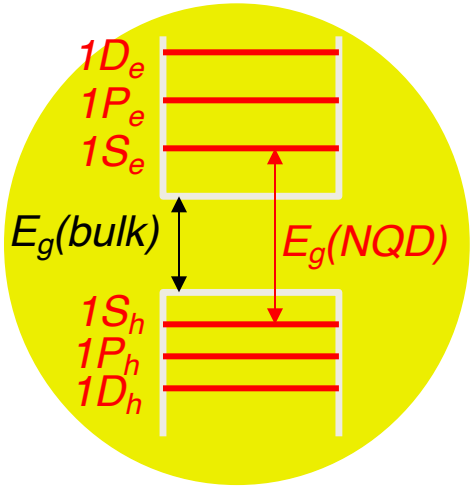
Quantum Dot Regime

100,000 atoms
20 nm



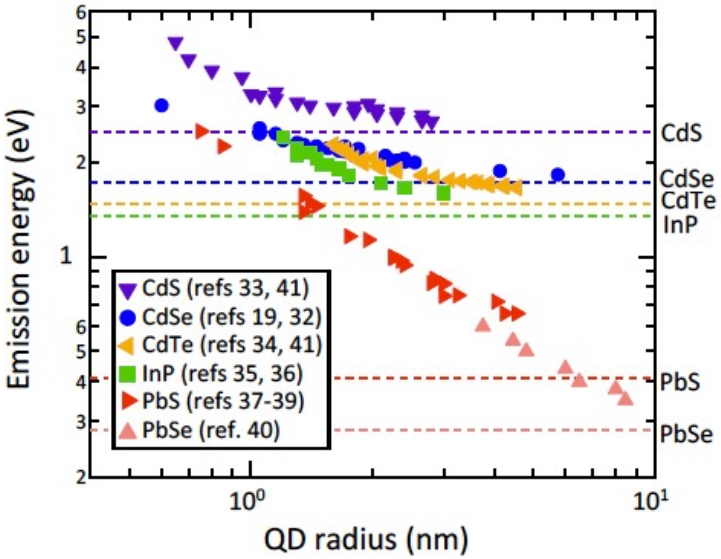
Bulk CdSe

- **Extreme quantum confinement**



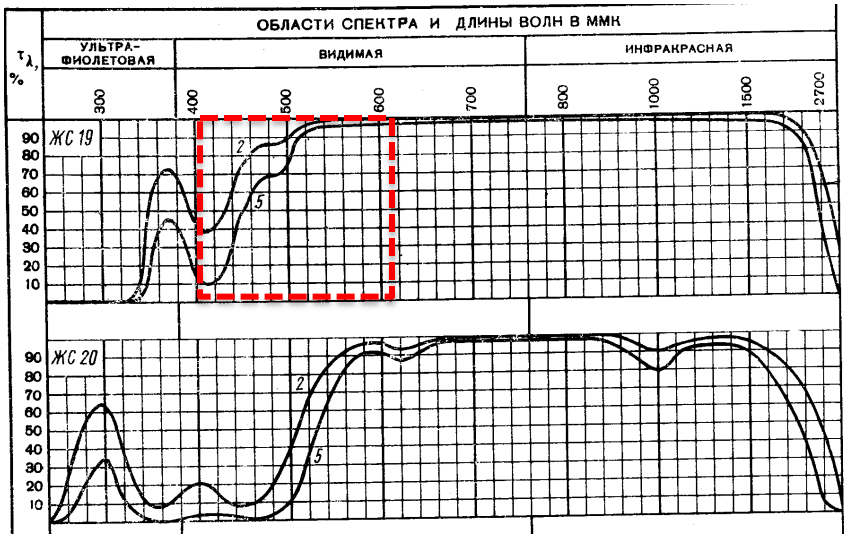
$$E_g(NQD) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2 m_{eh} R^2}$$

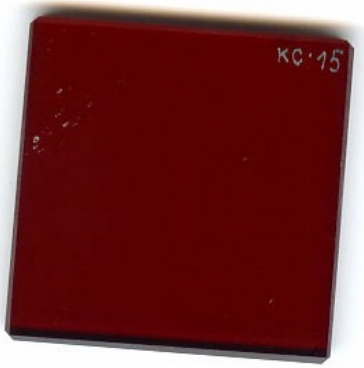
quantum confinement term (> 200 meV)

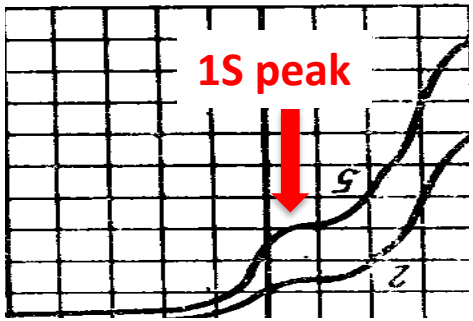


Commercial Samples of Quantum Dot Samples…
…back in the 1970s (…probably much earlier)

- **Low-pass Cut-off filters ($CdSe_xS_{1-x}$ -doped glass)**







RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 50, NUMBER 11 15 SEPTEMBER 1994-I

Biexciton effects in femtosecond nonlinear transmission of semiconductor quantum dots

V. Klimov,* S. Hunsche, and H. Kurz
Institut für Halbleitertechnik II, Rheinisch Westfälische Technische Hochschule Aachen, Sommerfeldstrasse 24, D-52074 Aachen, Germany

(Received 21 March 1994; revised manuscript received 5 July 1994)

The dynamics of carrier-induced absorption changes in CdSe quantum dots are investigated with femtosecond spectroscopy. After excitation with 4-eV photons a redshift of the lowest optical transition is observed in the initial phase of carrier relaxation. This shift is attributed to a biexciton effect where two electron-hole pairs interact via the Coulomb potential.

The samples under investigation are thin plates (thickness $d = 280\ \mu m$) prepared from commercially available CdS_xSe_{1-x} doped glass KC-19. Raman spectra of the samples exhibit only the CdSe-related LO-phonon peak. Therefore, the samples are considered as doped with pure CdSe. Transmission electron microscopy (TEM) examination ut 5.7 nm

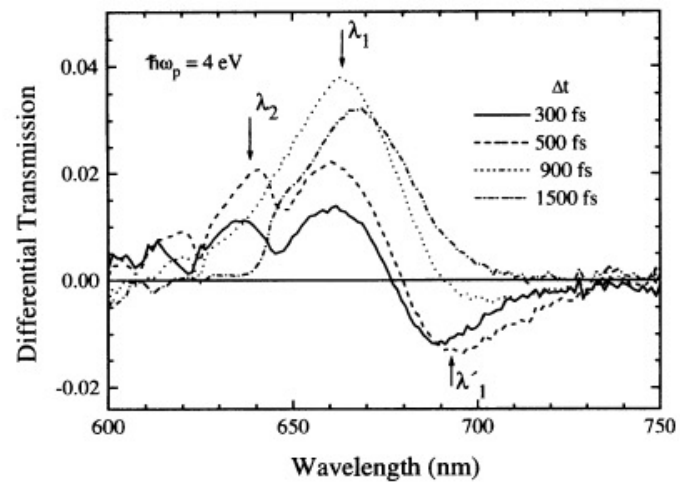
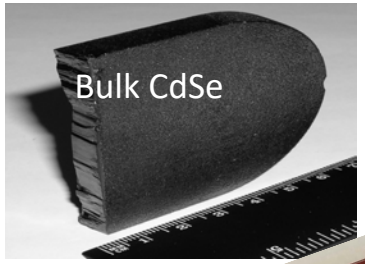


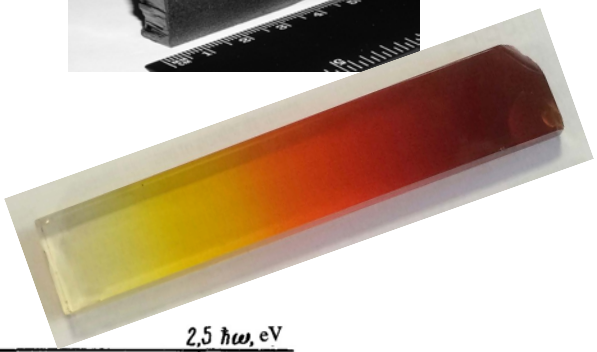
FIG. 1. DTS of the CdSe NC's ($T = 300$ K) at different delay between pump and probe pulses.

First Quantum Dot Samples: *Effects of Size Quantization in Semiconductor Doped Glasses*

- **Quantum dots in glass matrices (late 1970s - early 1980s)**

Alexey Ekimov





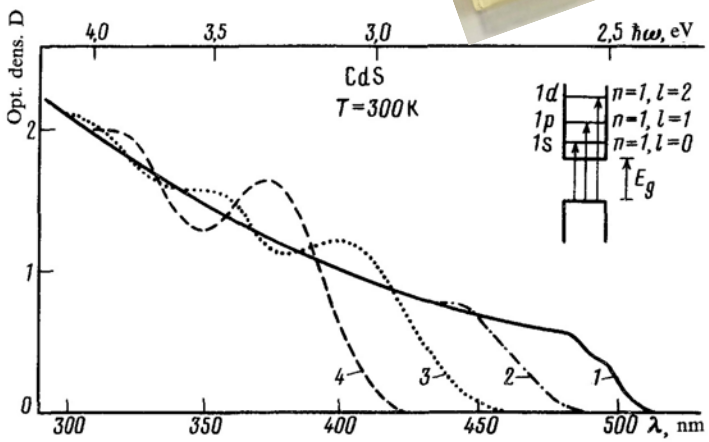


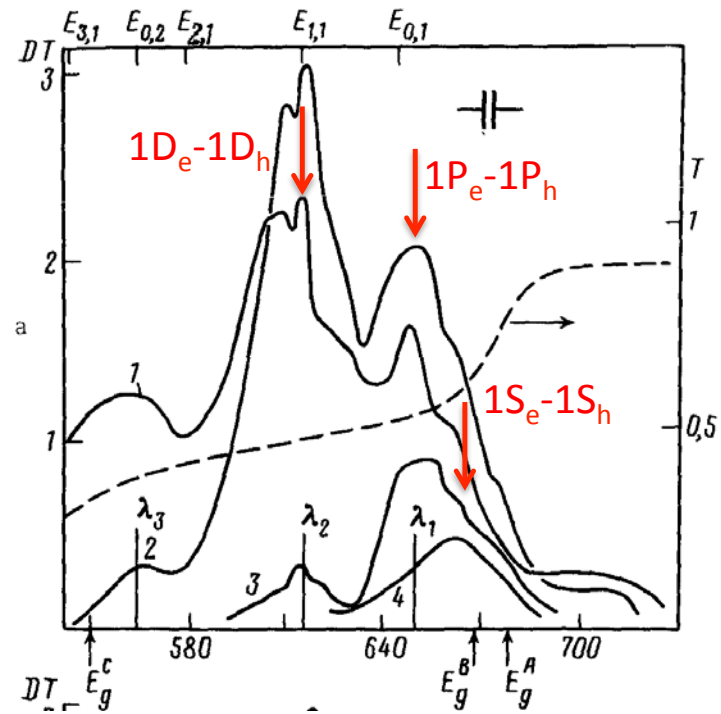
FIG. 1. Absorption spectra of samples containing microscopic CdS crystals of various radii. 1—$\bar{a}$ = 380 Å; 2—$\bar{a}$ = 32 Å; 3—$\bar{a}$ = 19 Å; 4—14 Å.

Manifestation of dimensional quantization levels in the nonlinear transmission spectra of semiconductor microcrystals

Yu. V. Vandyshev, V. S. Dneprovskiĭ, and V. I. Klimov
M. V. Lomonosov Moscow State University

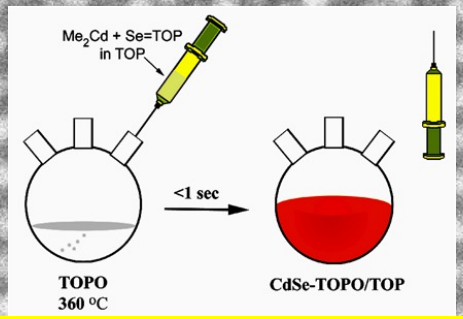
(Submitted 19 February 1991)
Pis'ma Zh. Eksp. Teor. Fiz. **53**, No. 6, 301–306 (25 March 1991)

Brightening peaks attributable to transitions between dimensional quantization levels are recorded in the transmission spectra of CdSe microcrystals (80 and 300 K) excited by picosecond light pulses. The dynamics of transmission restoration, which is explained on the basis of a model of discrete level filling in the conduction and valence bands, is investigated.



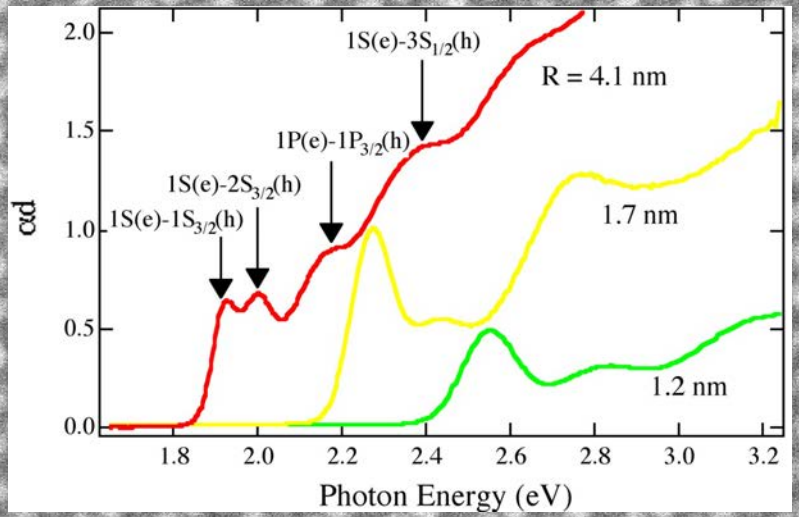
Problem: *Colloidal Quantum Dots Highly Efficient Emitters… but Difficult Lasing Material*

- **Colloidal quantum dots**



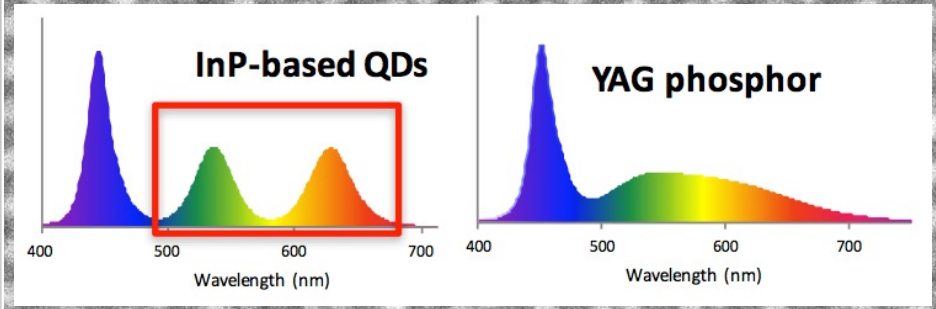
R = 10—50 Å, ΔR/R = 4—7%

C. Murray, D. Norris, and M. Bawendi, *J. Am. Chem.* Soc. **115**, 8706 (1993).



- **Quantum dot TVs**

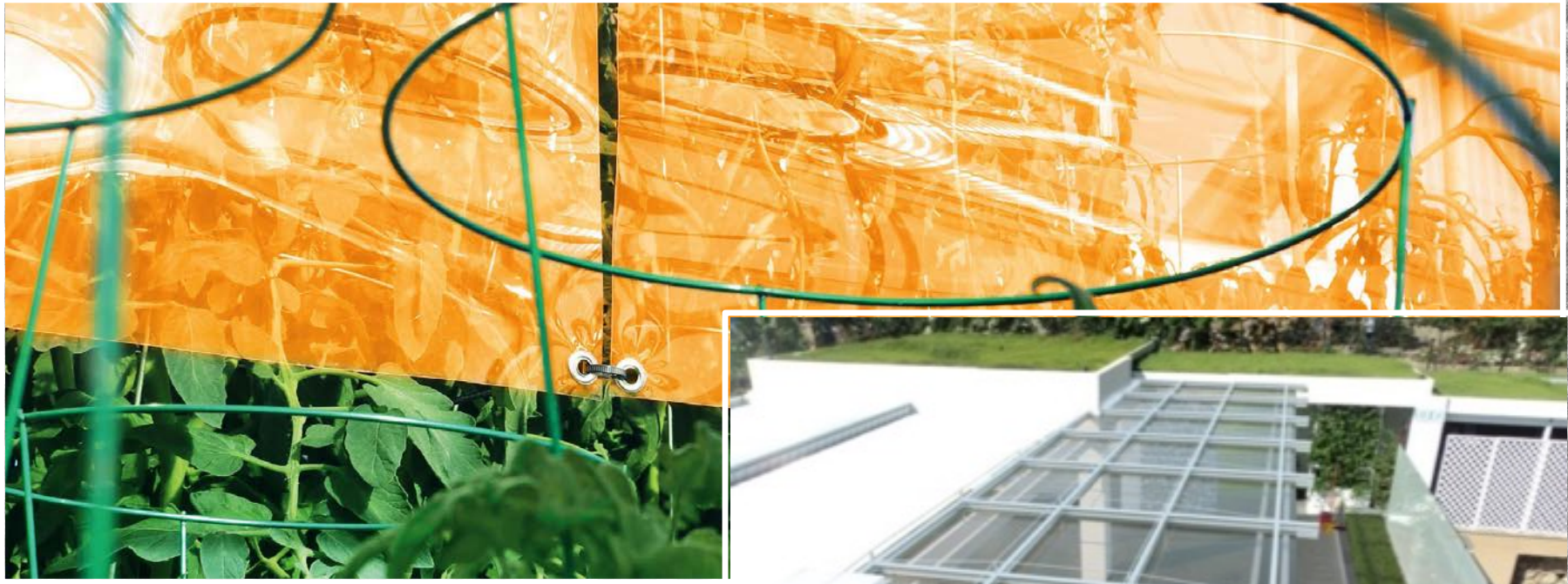
Samsung TV – JS9500



9

Luminescent Solar Concentrators and Color-Converting Films

- Quantum dot greenhouse film (UbiQD, Los Alamos, NM, USA)

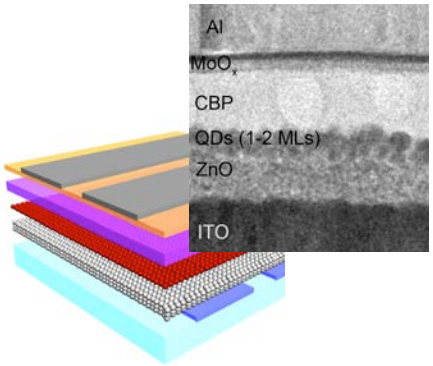


- Quantum dot "solar windows" ('Glass to Power', Milan, Italy)

Towards Colloidal Quantum Dot Laser Diodes

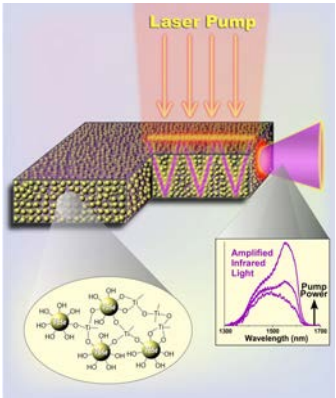
QD-LEDs

M. Achermann, V. I. Klimov, *et al., Nature* **429**, 642 (2004)
W.-K. Bae, *et al., MRS Bulletin* **38**, 721 (2013)
W.-K. Bae, et al. *Nature Comm.* **4**, 2661 (2013)



QD-lasers

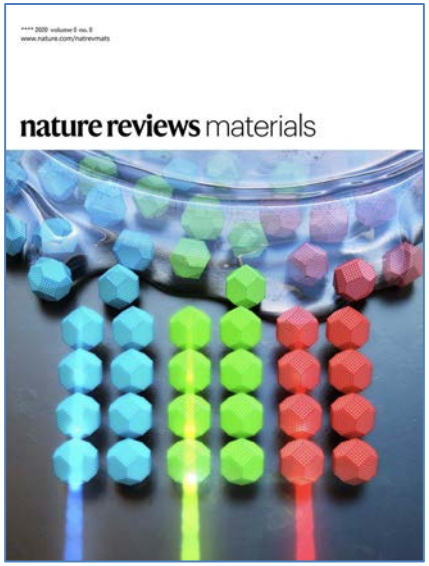
V. Klimov *et al.*, *Science* **287**, 1011 (2000)
V. Klimov, et al. *Nature* **447**, 441 (2007)
Y.-S. Park, V.I. Klimov et al. *Nano Lett.* **15**, 7319 (2015)



QD-laser diodes

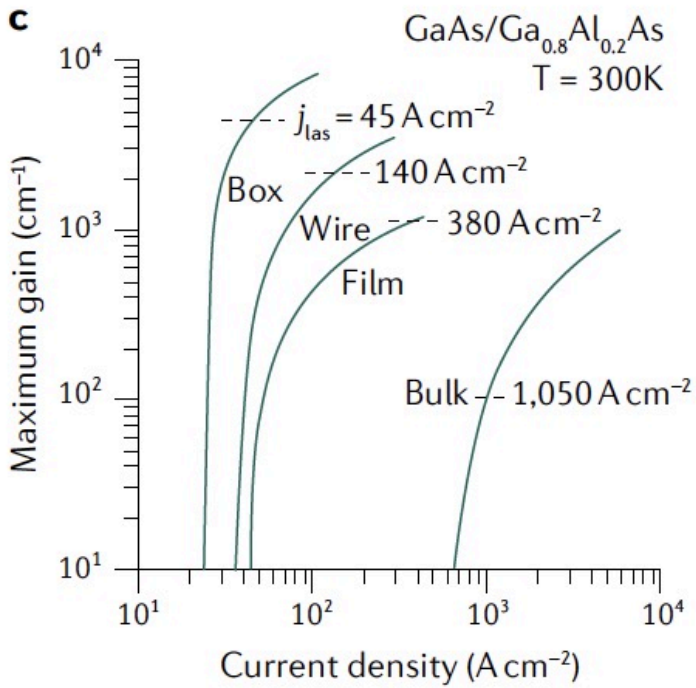
J. Lim, Y.S. Park, V.I. Klimov, *Nature Mater.* (2018)

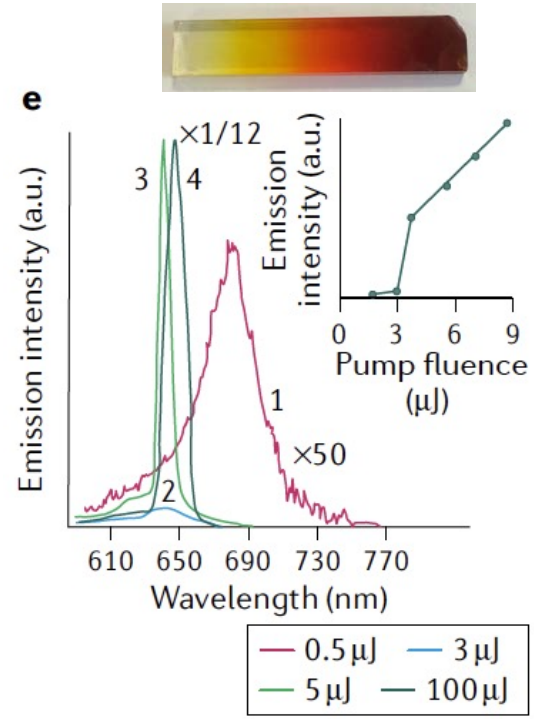
Quantum Dot Lasing… a Bit of History



Y.-S. Park, …V.I. Klimov *et al.*, **Colloidal quantum dot lasers**, *Nat. Rev. Mat.* Feb. 15, 2021

Fig. 1 | **Quantum dot lasing: from the theoretical concept to the practical demonstration**





<u>Theoretical concept</u>: Arakawa & Sakaki, *Multidimensional quantum well laser and temperature dependence of its threshold current*. APL **40** (1982).
Asada, Miyamoto & Suematsu, *Gain and the threshold of three-dimensional quantum-box lasers*. IEEE J. Qu. El. **22** (1986)

<u>First demonstration</u> (glass-embedded CdSe nanocrystals in a FP cavity, *T* = 80 K):
Vandyshev, … Klimov, *Lasing on a transition between quantum-well levels in a quantum dot*. JETP Lett. 54, 442 (1991)

Nanocrystal Lasing & Auger Recombination:
Significance of X-X interactions in Nanocrystals

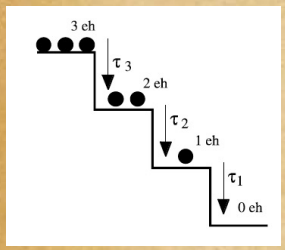
NanoTechnology & Advanced Spectroscopy Team

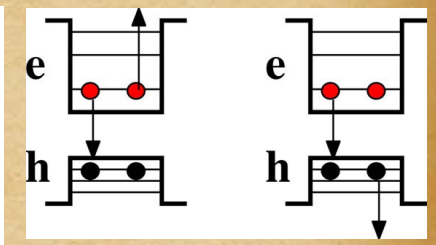
SCIENCE VOL 287 11 FEBRUARY 2000

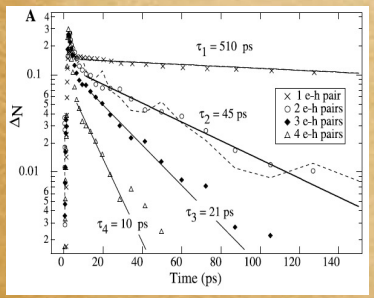
REPORTS

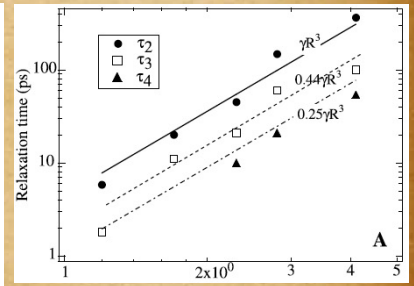
Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots

V. I. Klimov,[1*] A. A. Mikhailovsky,[1] D. W. McBranch,[1]
C. A. Leatherdale,[2] M. G. Bawendi[2]









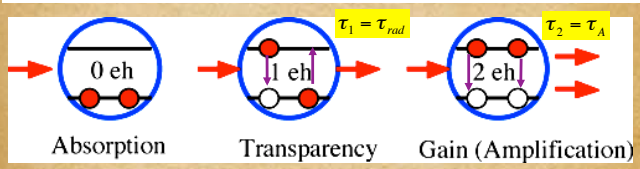
NC radius (nm)

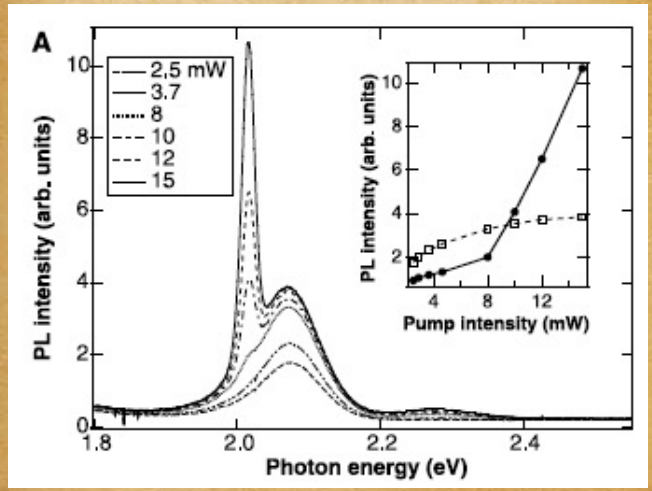
13 OCTOBER 2000 VOL 290 SCIENCE

REPORTS

Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots

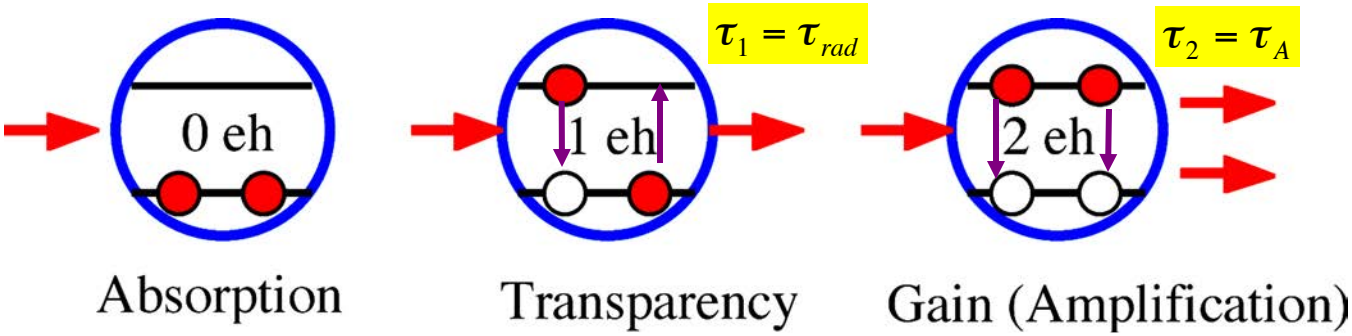
V. I. Klimov,[1*] A. A. Mikhailovsky,[1] Su Xu,[1] A. Malko,[1]
J. A. Hollingsworth,[1] C. A. Leatherdale,[2] H.-J. Eisler,[2]
M. G. Bawendi[2*]





Ultrasmall Q-dot Paradox: *Optical Gain due to Nominally Nonemissive Species*

- **Optical amplification (and lasing) threshold in NQDs: N > 1 e-h pairs per dot -> Gain is dominated by biexcitons!**



- **Nonradiative Auger recombination threshold: N > 1 e-h pairs per dot**

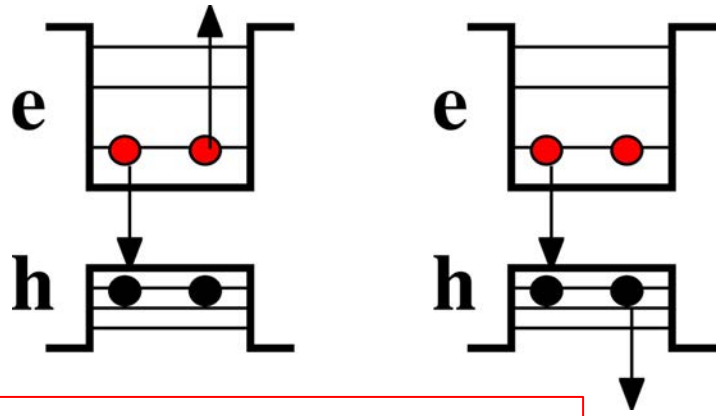
Auger decay:

$\tau_{XX,A} \approx 6 - 360\ ps\ (\tau_A \propto R^3)$

Radiative decay:

$\tau_{X,rad} \approx 20$ ns

$\tau_{XX,rad} \approx 5$ ns



CdSe Q-dots:
V. Klimov *et al.*, *Science* **287**, 1011 (2000)
CdSe Q-rods:
H. Htoon, et al., *Phys. Rev. Lett.* **91**, 227401 (2003)

Biexciton PL quantum yield: ~50 ps/5000 ps = ~1%

Two Tricks: *Close-Packed Nanocrystal Solids & Short-Pulse Optical Excitation*

NanoTechnology & Advanced Spectroscopy Team

- **Possible Solution:** ***Increased rates of stimulated emission (SE) in dense QD assemblies***

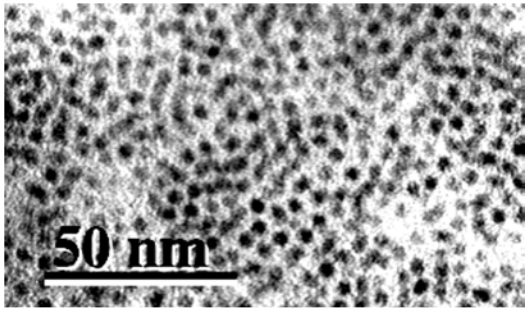
SE rate scales linearly with QD concentration

$$\tau_{st} \propto \frac{1}{Gain} \propto \frac{1}{\phi\sigma_g}$$

σ_g – *gain cross section (gain per dot)*

ϕ – *volume fraction of semiconductor*

For $\tau_{st} < \tau_{2.A}$, ϕ must be > 0.5%

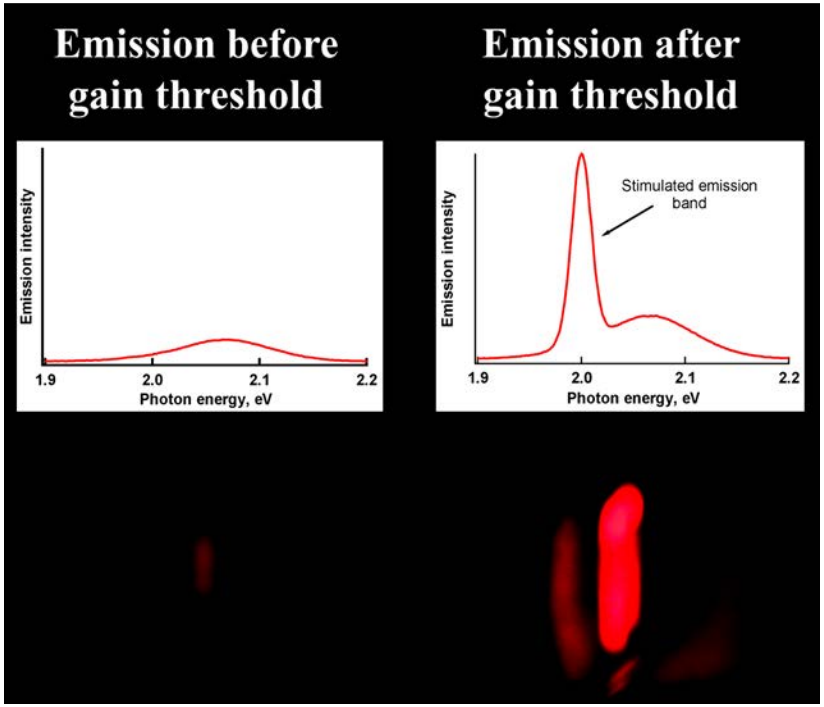


ϕ is *ca*. 15 - 20% in QD solids

13 OCTOBER 2000 VOL 290 SCIENCE

Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots

V. I. Klimov,[1*] A. A. Mikhailovsky,[1] Su Xu,[1] A. Malko,[1] J. A. Hollingsworth,[1] C. A. Leatherdale,[2] H.-J. Eisler,[2] M. G. Bawendi[2*]



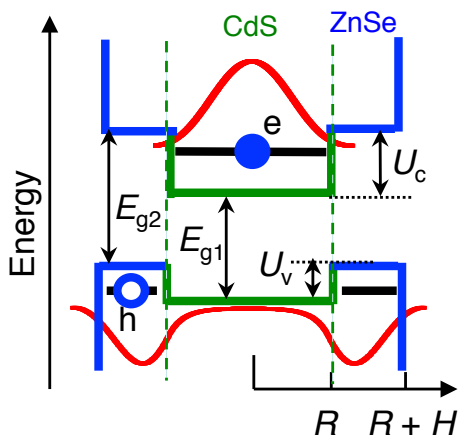
Single-Exciton Optical Gain *via* Strong Exciton-Exciton Repulsion in Type-II QDs

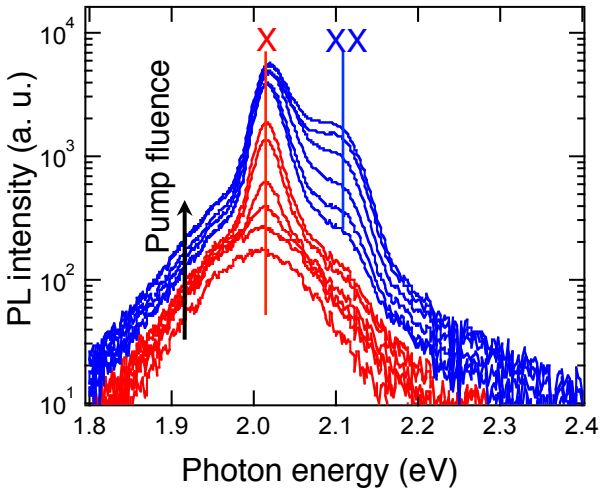
Vol 447|24 May 2007|doi:10.1038/nature05839 nature

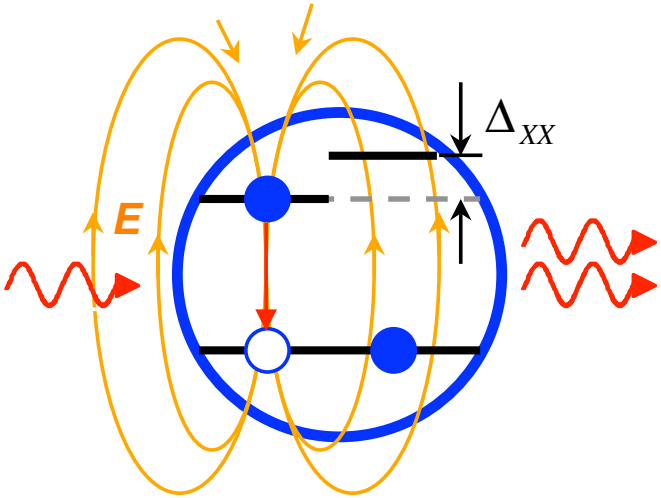
Single-exciton optical gain in semiconductor nanocrystals

Victor I. Klimov[1], Sergei A. Ivanov[1], Jagjit Nanda[1], Marc Achermann[1], Ilya Bezel[1], John A. McGuire[1] & Andrei Piryatinski[1]

Nanocrystal quantum dots have favourable light-emitting properties. They show photoluminescence with high quantum yields, and their emission colours depend on the nanocrystal size—owing to the quantum-confinement effect—and are therefore tunable. However, nanocrystals are difficult to use in optical amplification and lasing. Because of an almost exact balance between absorption and stimulated emission in nanoparticles excited with single electron–hole pairs (excitons), optical gain can only occur in nanocrystals that contain at least two excitons. A complication associated with this multiexcitonic nature of light amplification is fast optical-gain decay induced by non-radiative Auger recombination, a process in which one exciton recombines by transferring its energy to another. Here we demonstrate a practical approach for obtaining optical gain in the single-exciton regime that eliminates the problem of Auger decay. Specifically, we develop core/shell hetero-nanocrystals engineered in such a way as to spatially separate electrons and holes between the core and the shell (type-II heterostructures). The resulting imbalance between negative and positive charges produces a strong local electric field, which induces a giant (~100 meV or greater) transient Stark shift of the absorption spectrum with respect to the luminescence line of singly excited nanocrystals. This effect breaks the exact balance between absorption and stimulated emission, and allows us to demonstrate optical amplification due to single excitons.

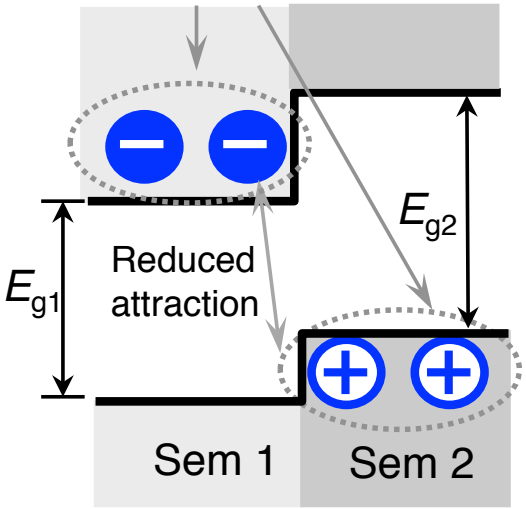






Optical gain

Enhanced repulsion



Lasing Threshold: *CW Excitation*

Continuous wave (cw) excitation

cw photon flux

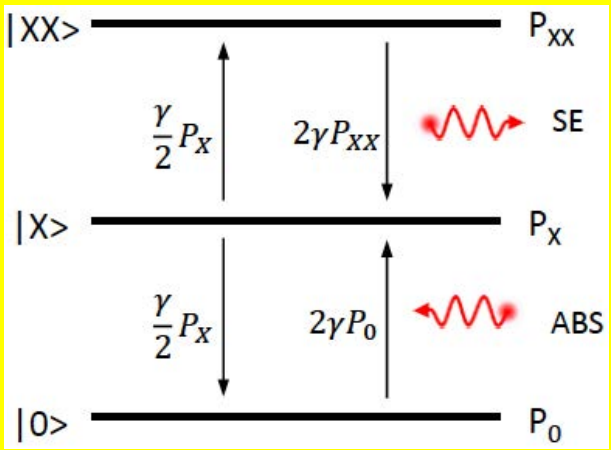
Critical per-dot population inversion
$\Delta_{las} \sim (\tau_{XX})^{-1/2}$

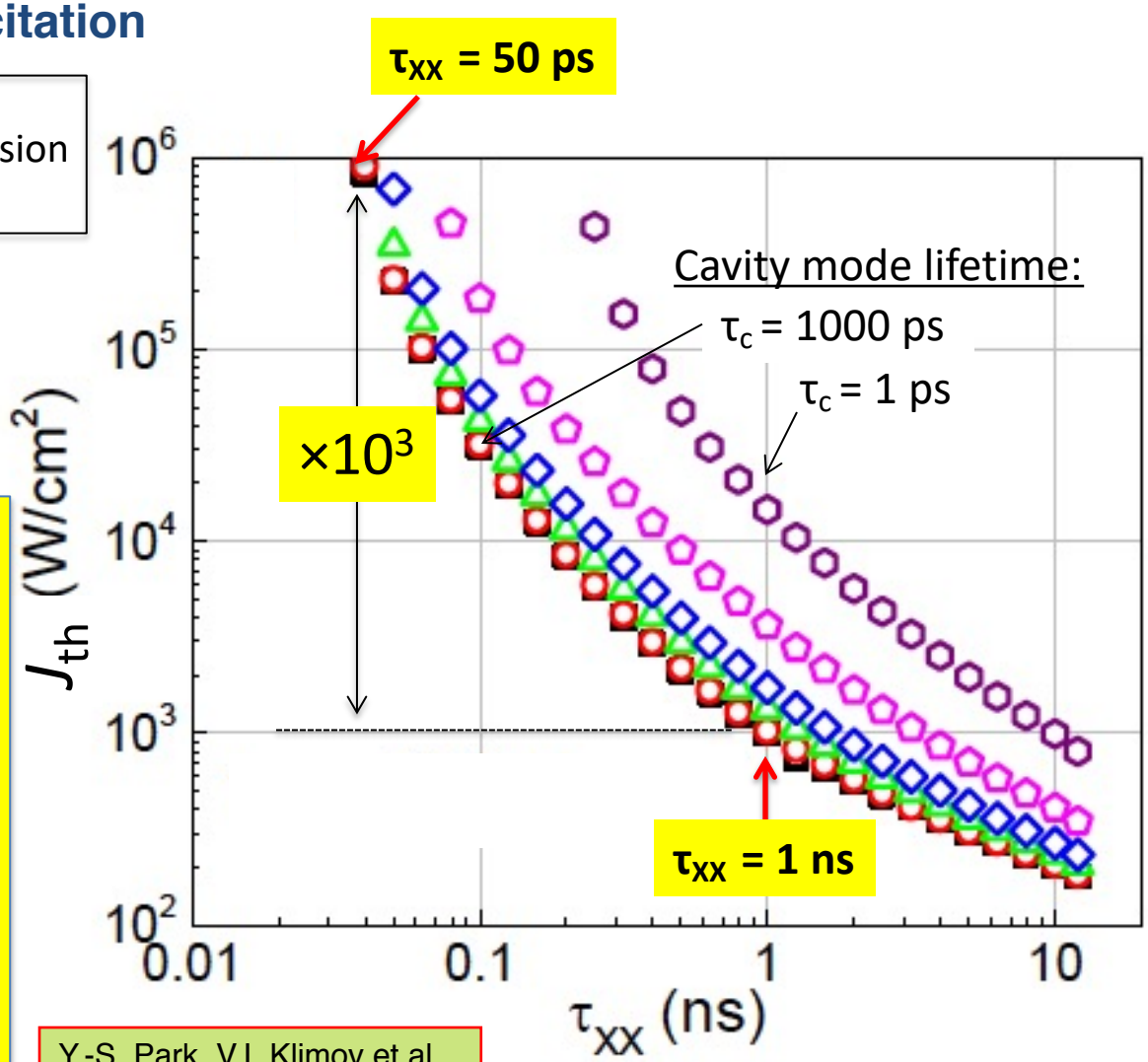
$$\sigma_{abs} J_{th} = \Delta_{las}/\tau_{gain} = \Delta_{las}/\tau_{XX}$$

$$J_{th} \sim 1/(\tau_{XX})^{3/2}$$

Per-dot population inversion

$$\Delta = \left(P_{XX} - P_0\right)$$





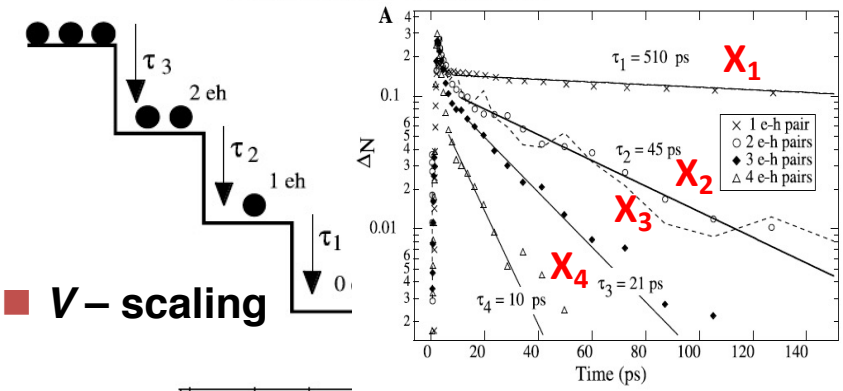
Y.-S. Park, V.I. Klimov et al.
Nano Lett. **15**, 7319 (2015)

Auger Recombination: *Universal Size-Dependent Trend ("V-scaling")*

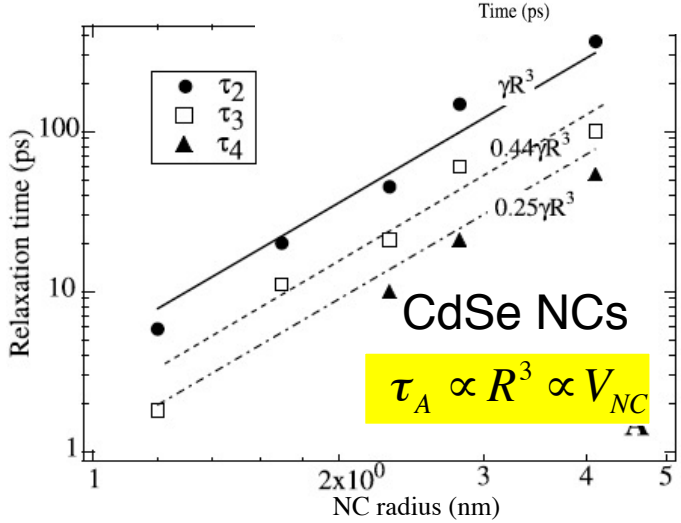
SCIENCE VOL 287 11 FEBRUARY 2000

Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots

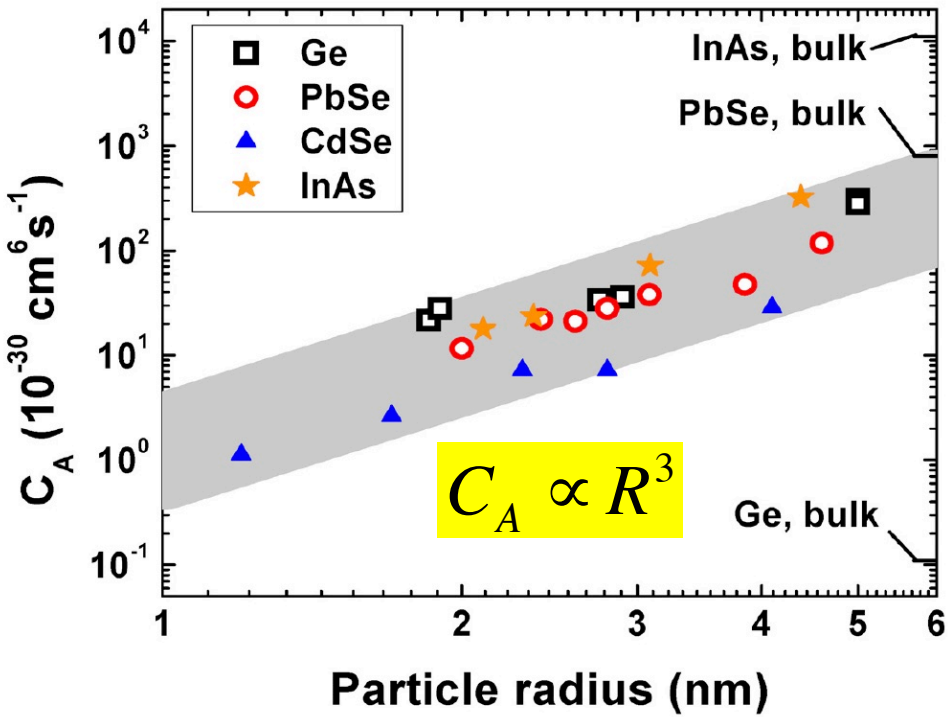
V. I. Klimov,[1*] A. A. Mikhailovsky,[1] D. W. McBranch,[1]
C. A. Leatherdale,[2] M. G. Bawendi[2]



- ***V* – scaling**



- **Generality of *V* – scaling:**



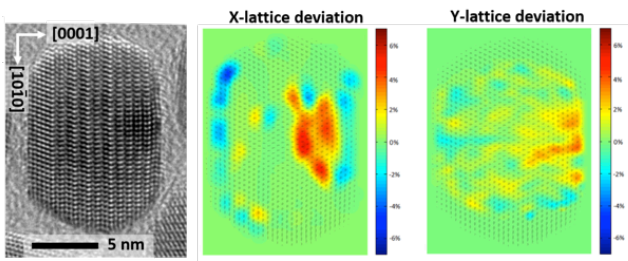
$$\tau_{2A} \propto 1/\left(C_A n^2\right) \propto \left(R^6 / C_A\right) \propto R^3$$

I. Robel et al. *Phys. Rev. Lett.* **102** 177404 (2009)
V-scaling for QDs of direct and indirect gap semiconductors

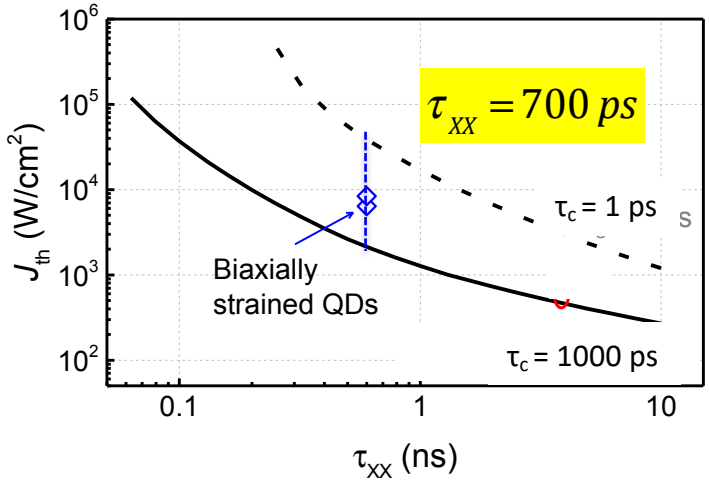
Cw Lasing with Bi-axially Strained "Giant" CdSe/CdS Quantum Dots

NanoTechnology & Advanced Spectroscopy Team

Thick-shell CdSe/CdS QDs: Extended XX Auger lifetime (τ_{XX} = 650 ps)



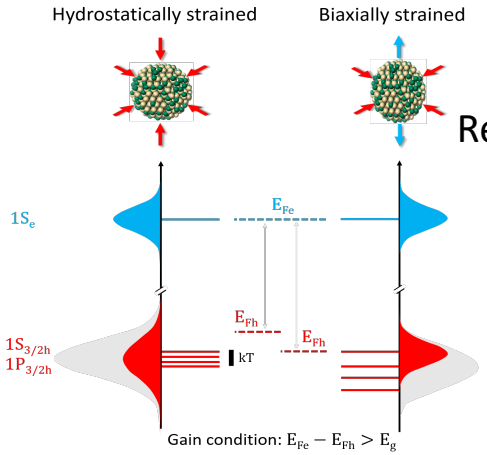
Sargent, Klimov, Rosenthal, et al. *Nature* **544** (2017)



Y.-S. Park, et al. *Nano Lett.* **15**, 7319 (2015)

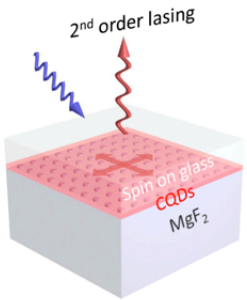
Expected cw lasing threshold: 2.5 – 30 kW/cm^2

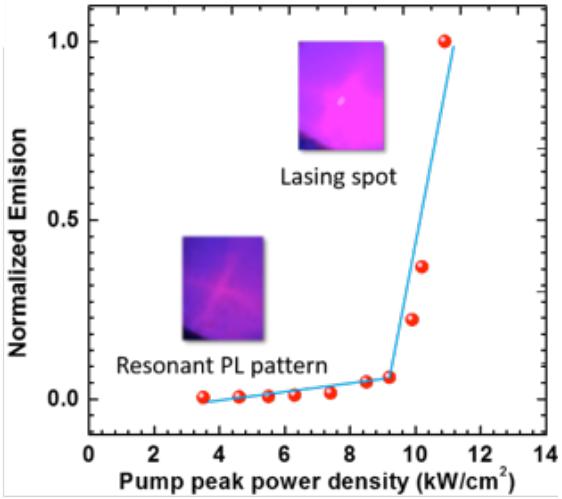
Bi-axial strain increases light-heavy hole splitting



Reduced effective VB-edge degeneracy & reduced gain thresholds

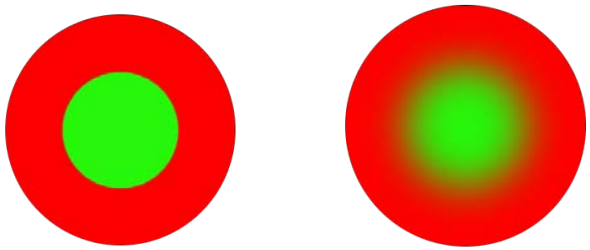
Demonstrated cw lasing threshold: ~10 kW/cm^2



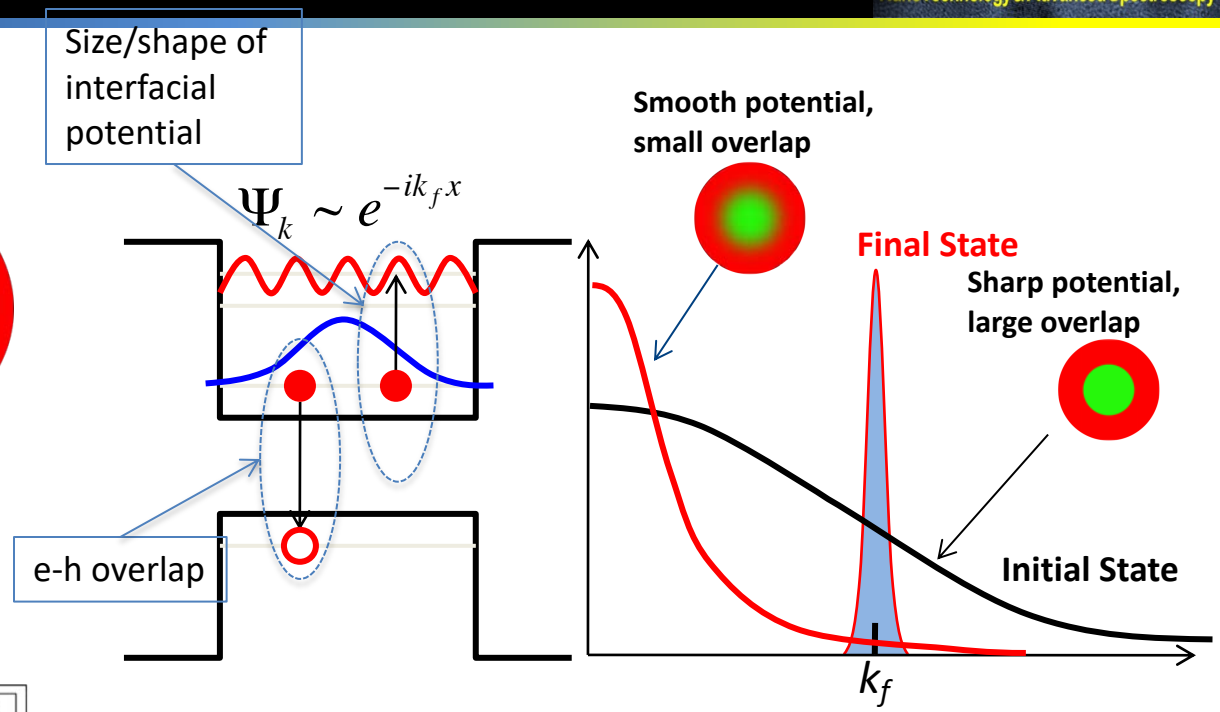


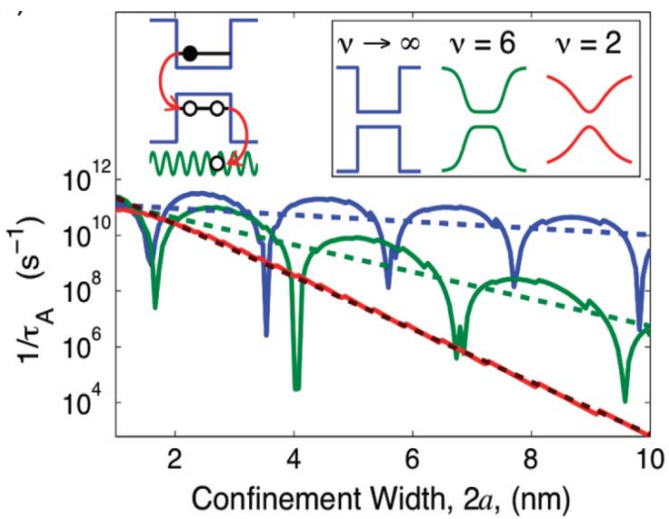
Suppression of Auger Recombination *via* Wavefunction Engineering in Fourie Space

Effect of interfacial potential on Auger decay



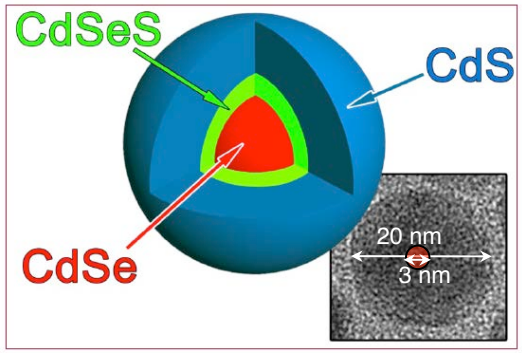
G. Cragg & Al. L. Efros, *Nano Lett.* (2010)





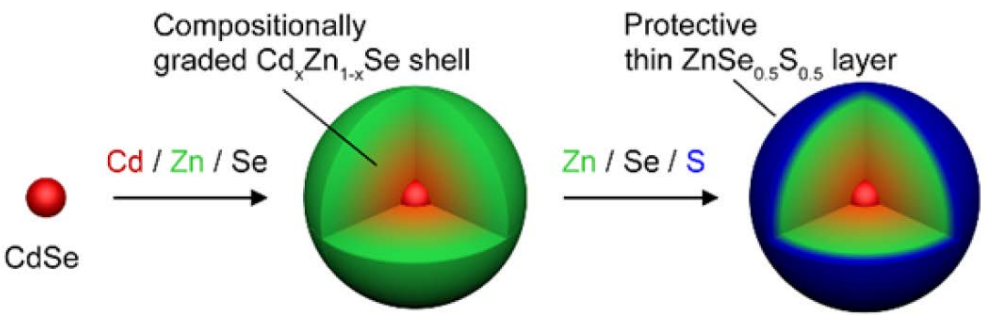
Uncontrolled interfacial alloying and Auger decay

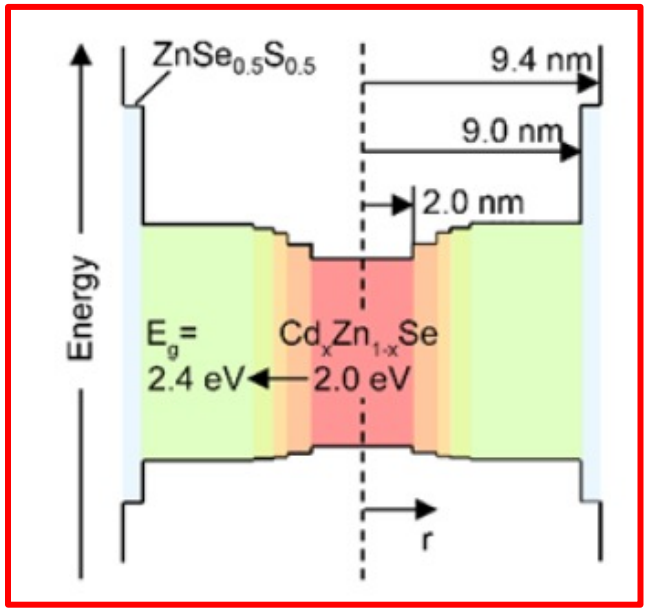
F. Garcia-Santamaria, et al. Nano Lett. (2011)



Novel Type-I "Giant" Quantum Dots with a Continuously Graded Shell

- **Type-I "giant" QDs with a continuously grade shell**



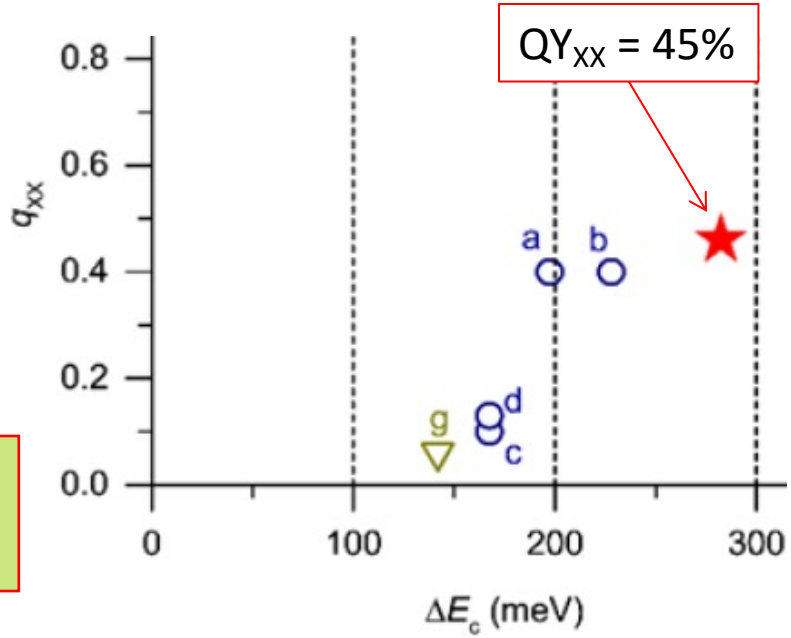


J. Lim, Y-H. Park, V.I. Klimov, *Nat. Mater.* 2018

- **Record high XX PL QYs**

$$\tau_{XX,Auger} = 2.4\,ns$$

$$QY_{XX} = \frac{\tau_{XX}}{\tau_{XX,rad}} = \frac{\tau_{XX,A}}{\left(\tau_{XX,rad} + \tau_{XX,A}\right)}$$



nature nanotechnology

ARTICLES

PUBLISHED ONLINE: 16 OCTOBER 2017 | DOI: 10.1038/NNANO.2017.189

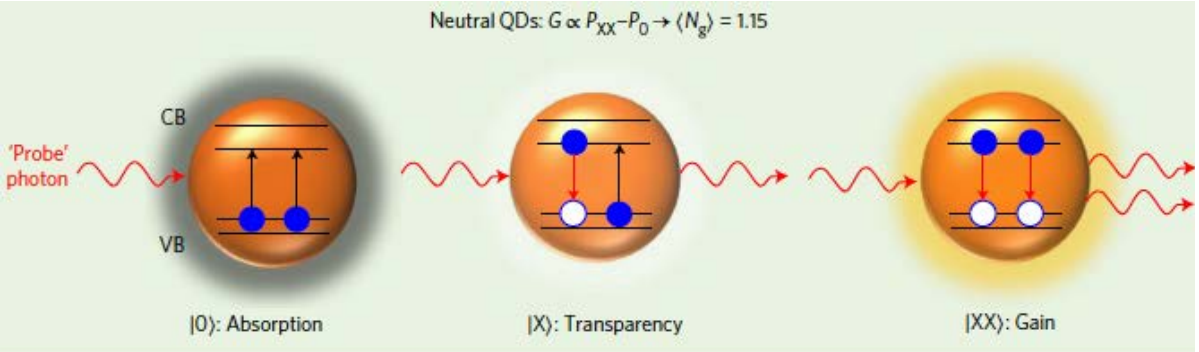
NanoTechnology & Advanced Spectroscopy Team

Towards zero-threshold optical gain using charged semiconductor quantum dots

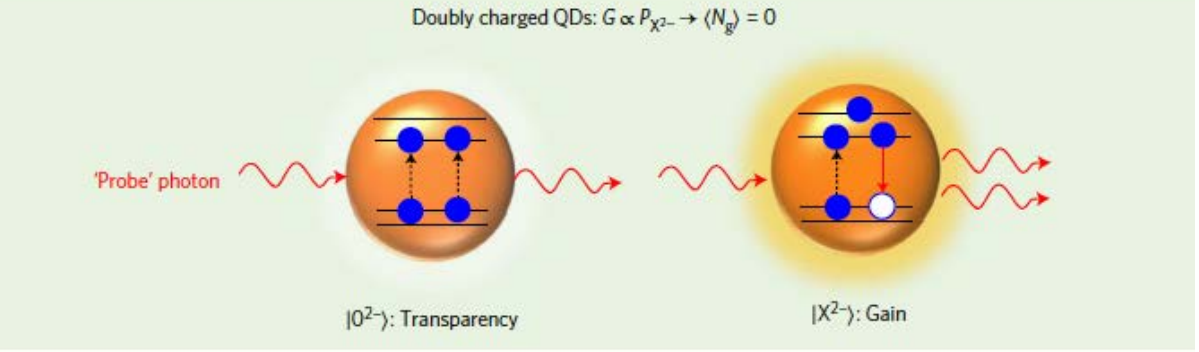
Kaifeng Wu[1†], Young-Shin Park[1,2], Jaehoon Lim[1] and Victor I. Klimov[1*]

Colloidal semiconductor quantum dots are attractive materials for the realization of solution-processable lasers. However, their applications as optical-gain media are complicated by a non-unity degeneracy of band-edge states, because of which multiexcitons are required to achieve the lasing regime. This increases the lasing thresholds and leads to very short optical gain lifetimes limited by nonradiative Auger recombination. Here, we show that these problems can be at least

- **"Standard" biexciton gain**



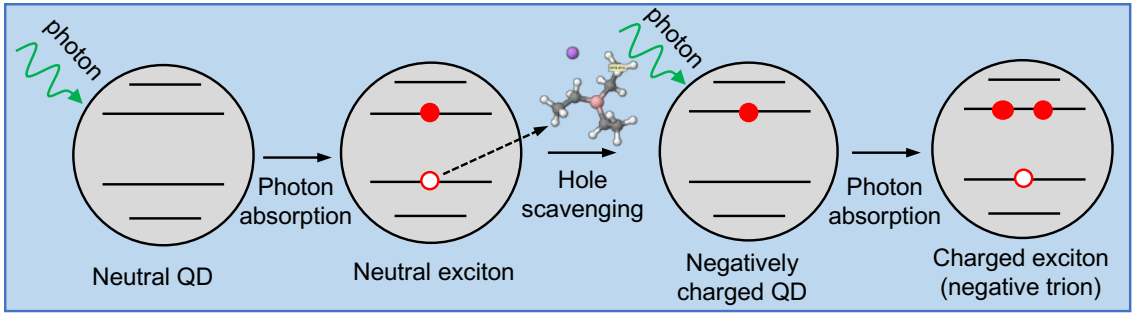
- **Doubly-charged-exciton gain (zero-threshold!)**



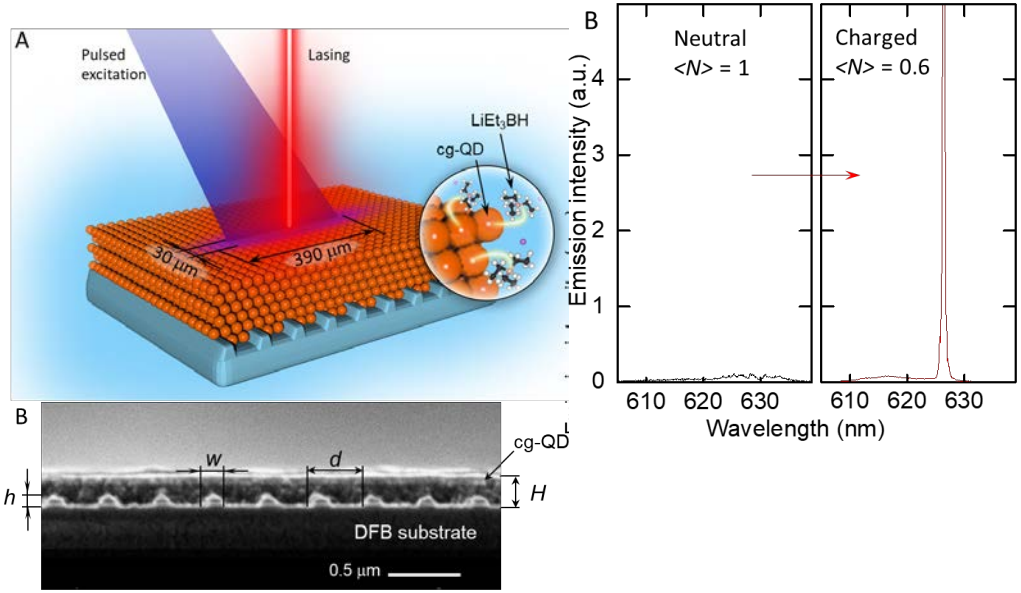
Sub-Single Exciton Lasing with Charged Quantum Dots: *Exploiting "Zero-Threshold" Gain Concept*

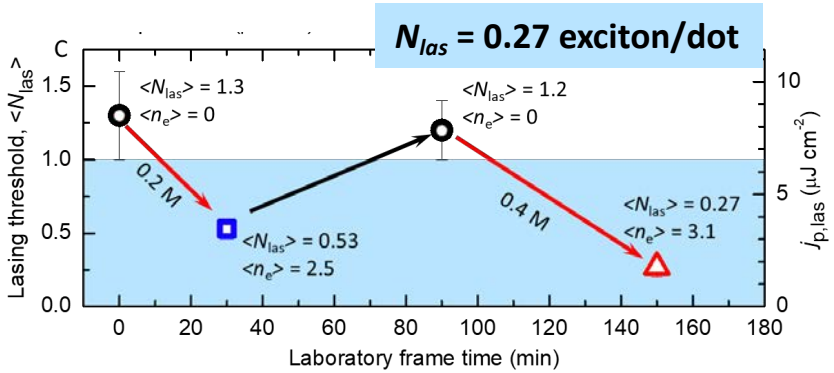
NanoTechnology & Advanced Spectroscopy Team

Photochemical reduction for controlled charging of QDs



Sub-single-exciton lasing using charged QDs

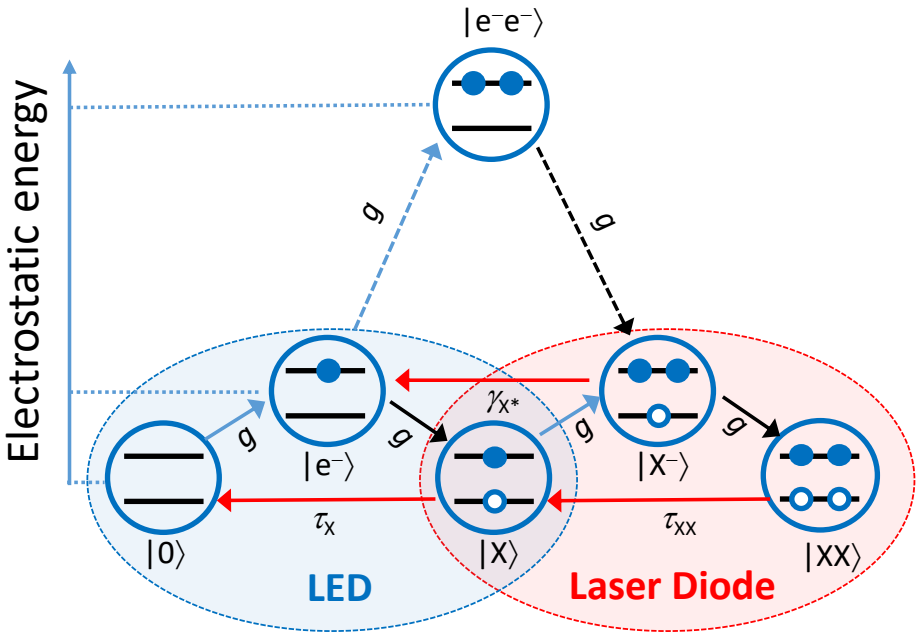




O. Kozlov, V.I. Klimov, *et al.*, *Science* **365**, 672 (2019)

Challenges of Colloidal QD Laser Diodes (QLDs)

Operational cycle: LED vs. QLD



P_0	> 0.9
P_X	< 0.1
P_{XX}	0

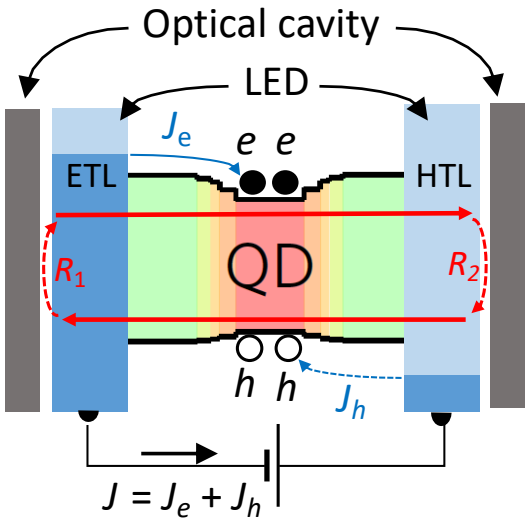
Sufficient for $L \approx 10^6$ cd m^{-2}

P_0	0
P_X	~0.5
P_{XX}	~0.5

Half saturated gain: $G_{½} = 0.5G_0$

H. Jung, N. Ahn, V.I. Klimov, *Nat. Phot., in press* (2021)

Integration of optical cavity & realization of lasing with an ultrathin EL-active QD layer

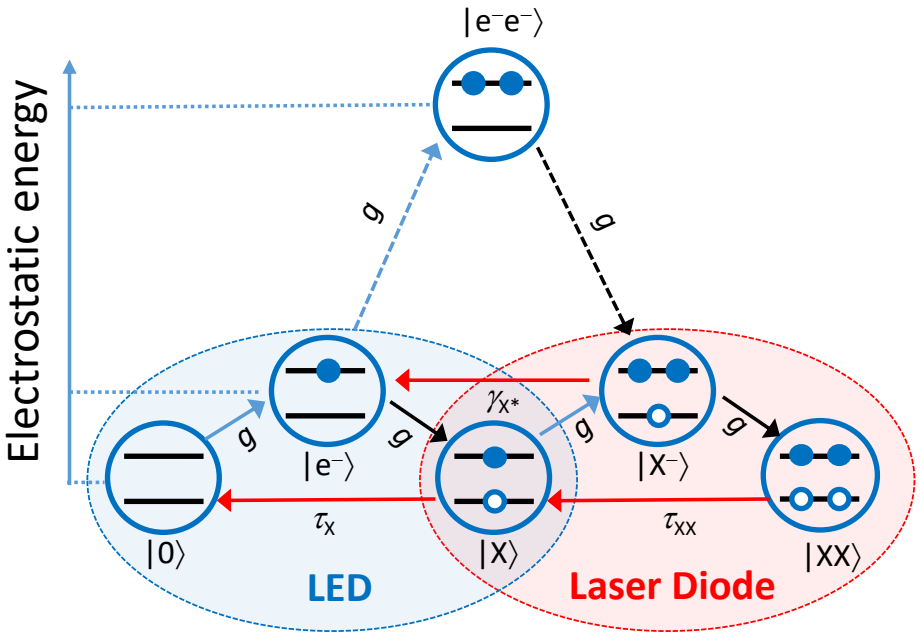


Related sub-challenges:

- *Avoid disruption of charge injection pathways*
- *Avoid quenching of lasing modes by charge-conducting layers*
- *Realization of lasing with ultrathin optical gain medium (< 5 QD monolayers) that can be excited electrically*

Challenges of Colloidal QD Laser Diodes (QLDs)

Operational cycle: LED vs. QLD



P_0	> 0.9
P_X	< 0.1
P_{XX}	0

Sufficient for $L \approx 10^6$ cd m^{-2}

P_0	0
P_X	~0.5
P_{XX}	~0.5

Half saturated gain: $G_{½} = 0.5G_0$

H. Jung, N. Ahn, V.I. Klimov, *Nat. Phot., in press* (2021)

Excitation rate for $G_{½} = 0.5G_0$

$$g_{½} = (2\tau_{XX})^{-1}[1 + (1 + 12\tau_{XX}/\tau_X)^{1/2}]$$

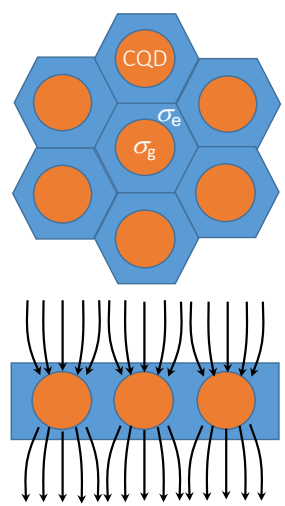
or

$$g_{½} \approx 1/\tau_{XX} \quad \text{if } \tau_{XX} \ll \tau_X$$

Conversion to current density (j)

Electrical cross-section: $\sigma_e \approx (1/f)\sigma_{geom}$

Areal filling factor: $f < 1$



$$j = efg/\sigma_{geom}$$

$$j_{½} \approx ef/(\tau_{XX}\sigma_{geom})$$

Estimations of $j_{½}$

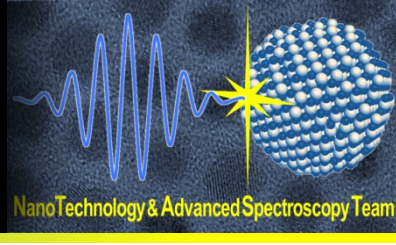
R = 3 nm, f = 0.5

$\tau_{XX} \approx$ 110 ps

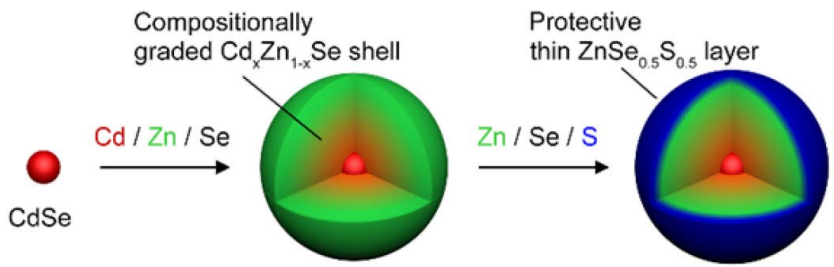
$j_{½}$ = 2.5 kA cm^{-2}

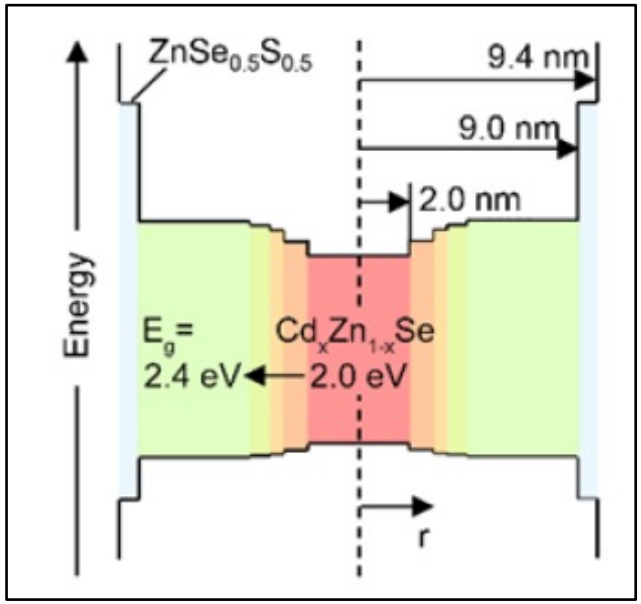
Standard colloidal QD LED: j < 1 A cm^{-2}

Type-I "Giant" Quantum Dots with a Continuously Graded Ultra-Thick Shell



Type-I "giant" QDs with a continuously grade shell





J. Lim, Y-H. Park, V.I. Klimov, *Nature Mater.* **17**, 42 (2018)

Y-H. Park, J. Lim, V.I. Klimov, *Nature Mater.* **18**, 249 (2019)

Long biexciton lifetimes & large electrical cross-sections

$\tau_{XX} \approx 1.3$ ns

$R \approx 9$ nm, $\sigma_{geom} \approx 3\times10^{-12}$ cm^2

$$j_{1/2} \approx ef/(\sigma_{geom}\tau_{XX})$$

Estimation of *j* for half-saturated gain: $j_{1/2}$

$j_{1/2} \approx 22$ A cm^{-2}

Estimation of *j* at the gain threshold ($G = 0$): j_0

$j_0 \approx 7$ A cm^{-2}

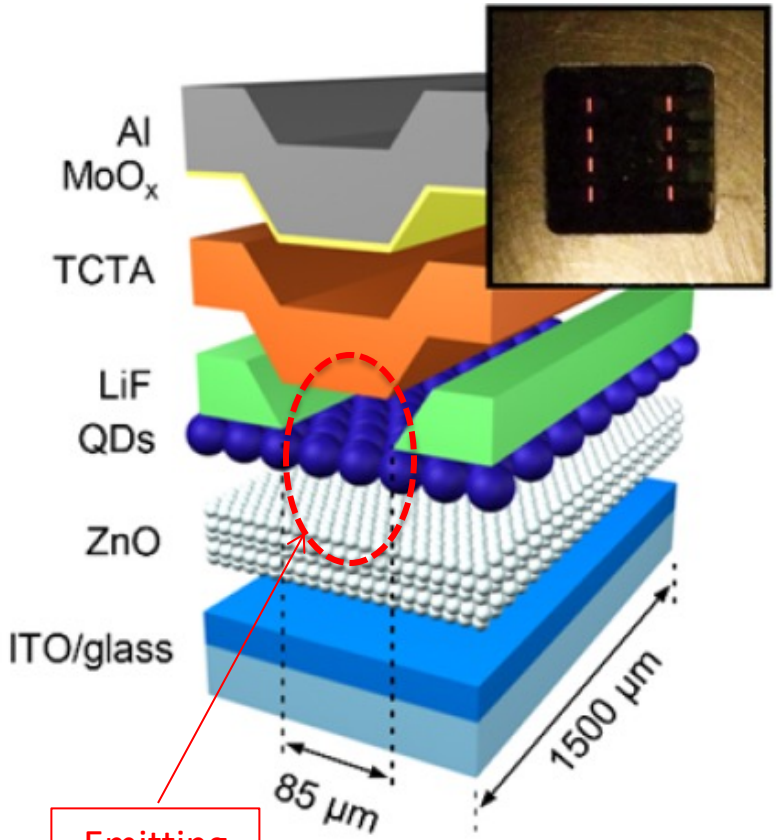
Standard colloidal QD LED:
$j < 1$ A cm^{-2}

nature materials
ARTICLES
PUBLISHED ONLINE: 20 NOVEMBER 2017 | DOI: 10.1038/NMAT5011

Optical gain in colloidal quantum dots achieved with direct-current electrical pumping

Jaehoon Lim[1,2†], Young-Shin Park[1,2†] and Victor I. Klimov[1*]

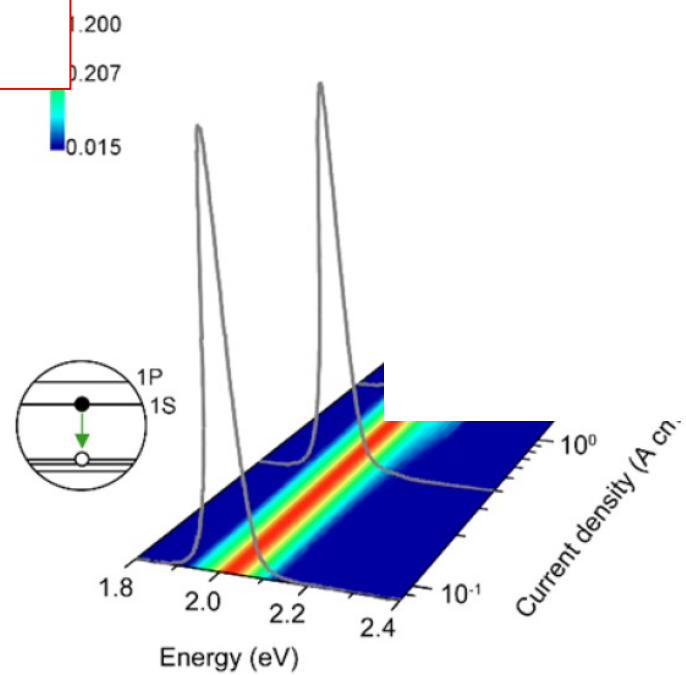
NanoTechnology & Advanced Spectroscopy Team



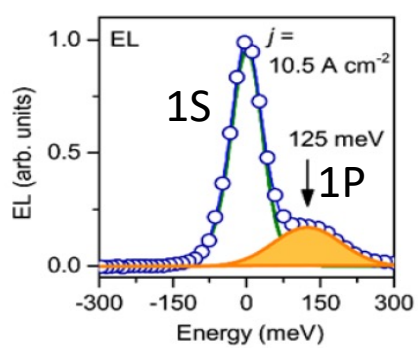
Emitting region

J. Lim, Y.S. Park, V.I. Klimov, *Nature Mater.* **17** (2018)

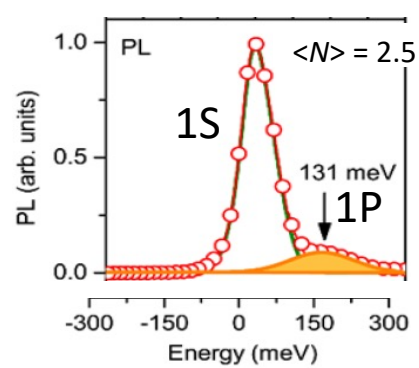
1P emission in EL



Electroluminescence

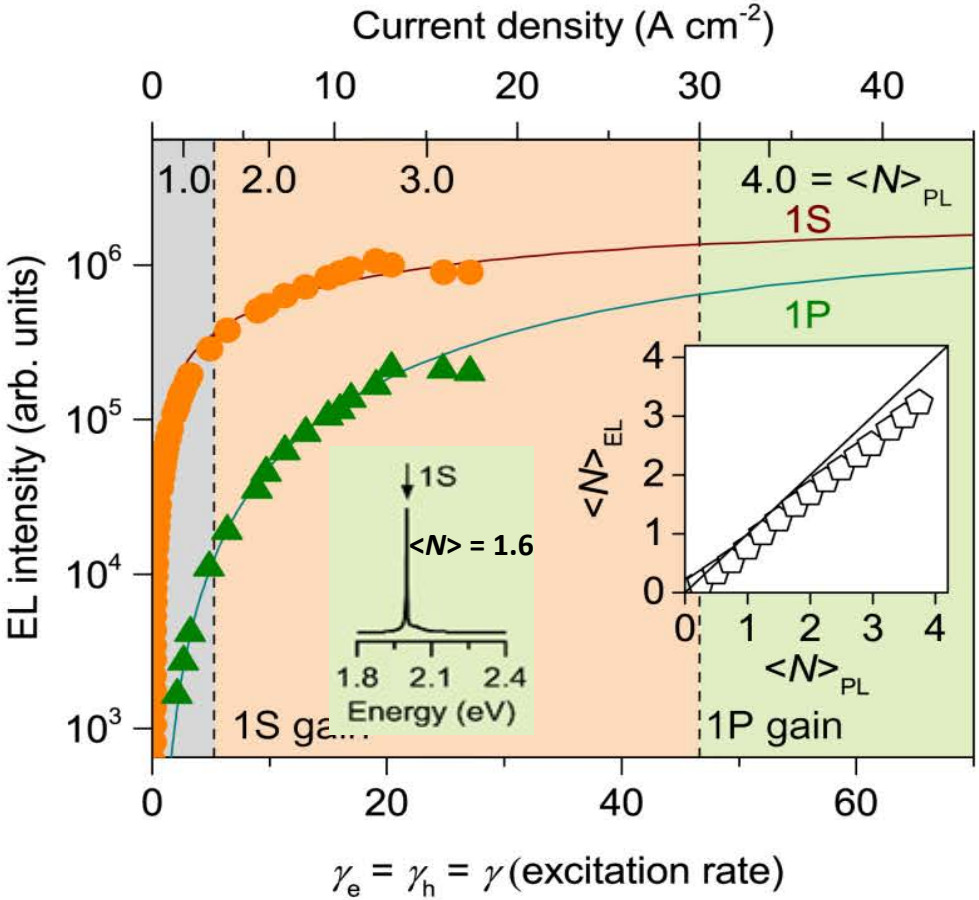


Photoluminescence



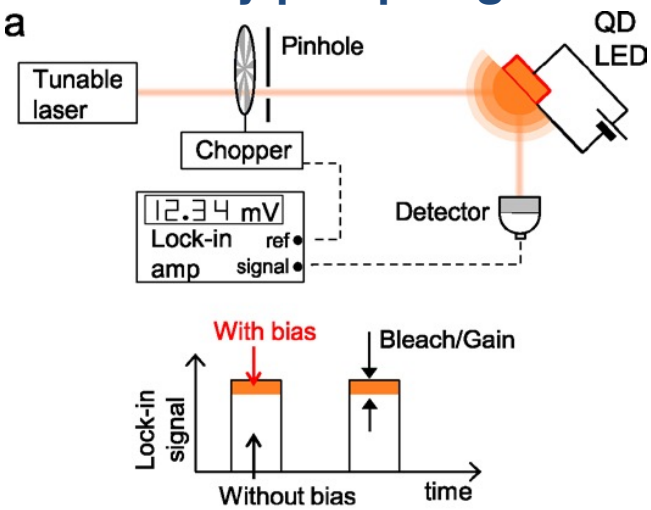
Population Inversion and Light Amplification Achieved Using Direct-Current Electrical Pumping

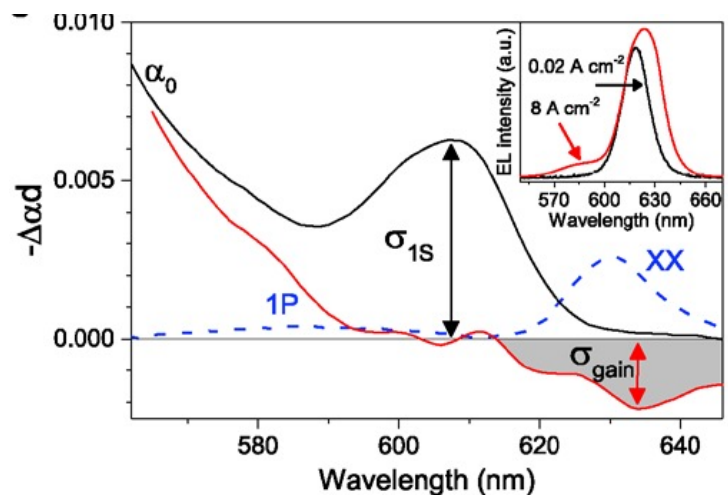
1P emission with electrical pumping



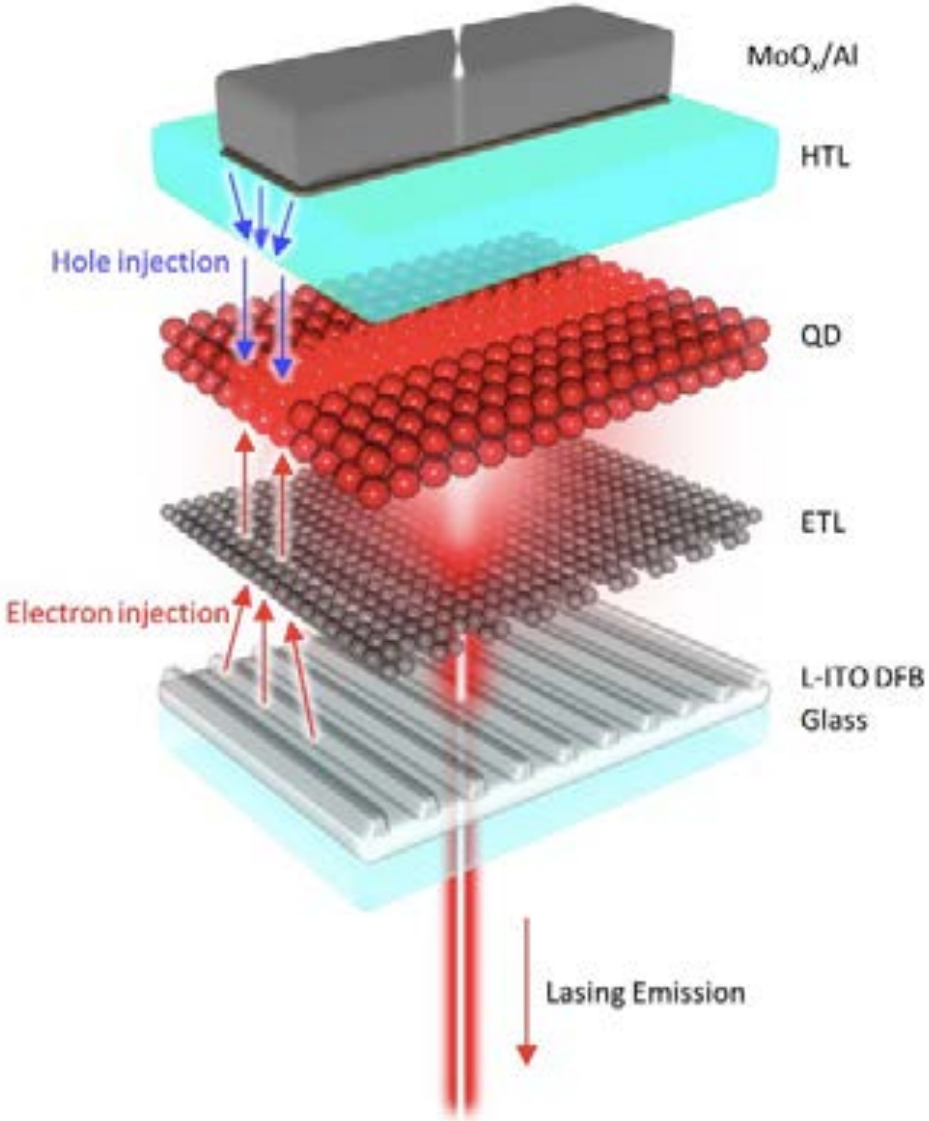
J. Lim, Y.S. Park, V.I. Klimov, *Nature Mater.* **17** (2018)

Electrically pumped gain

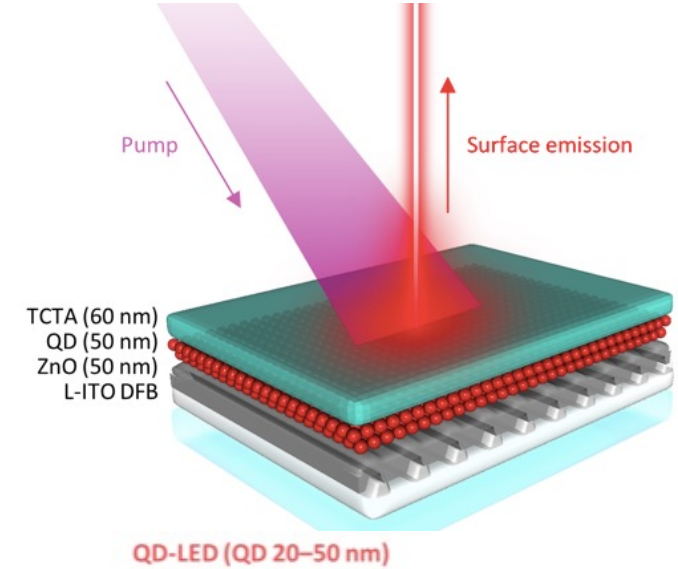


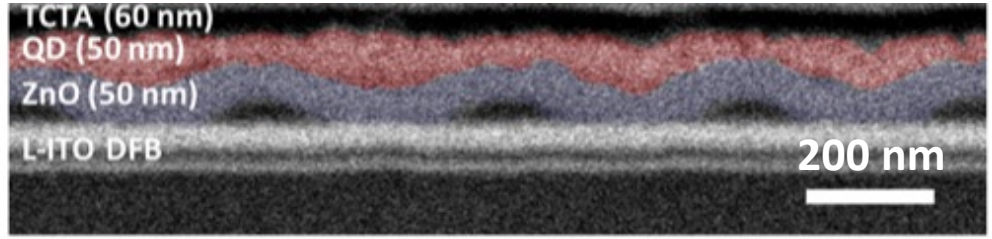


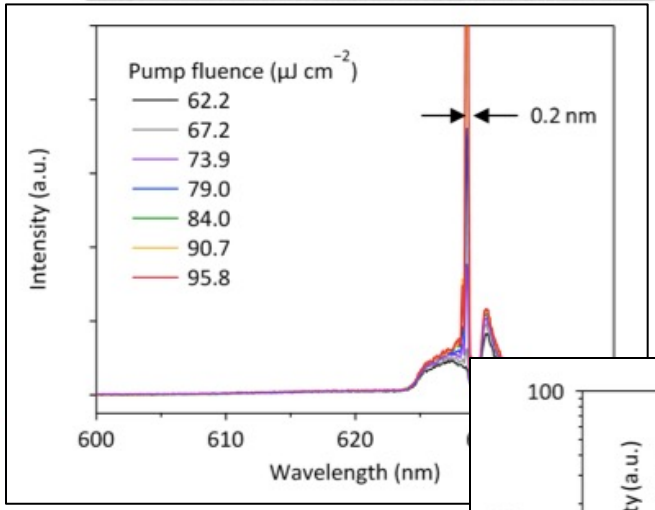
Colloidal QD Laser Diode (QLD)

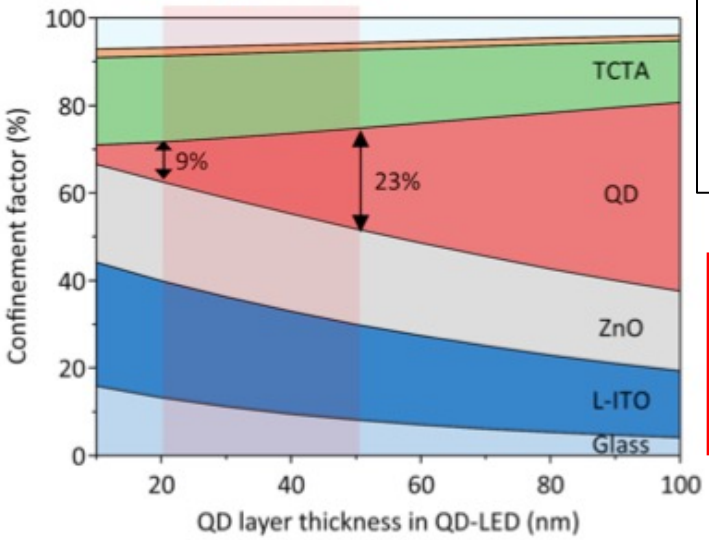


Lasing with Ultrathin QD layers (3 ML or less)

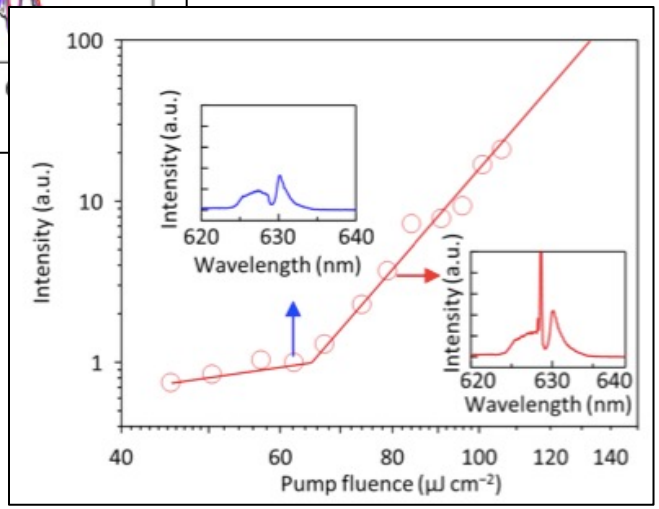




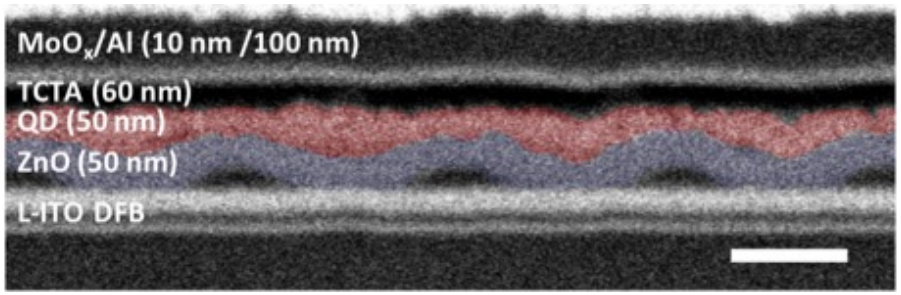


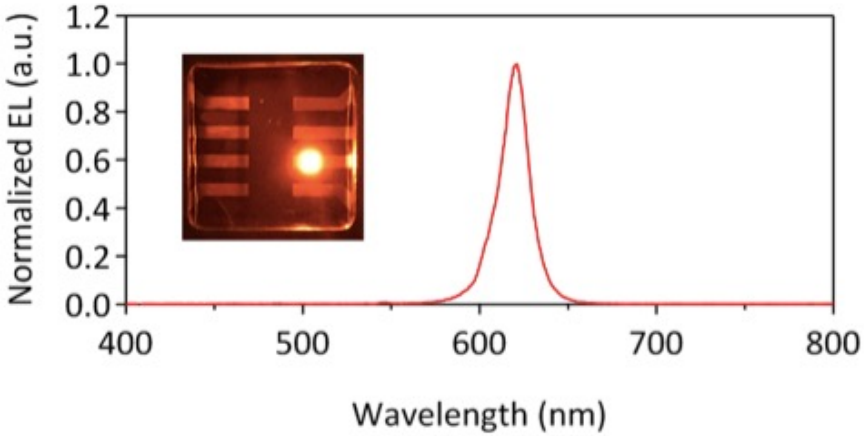


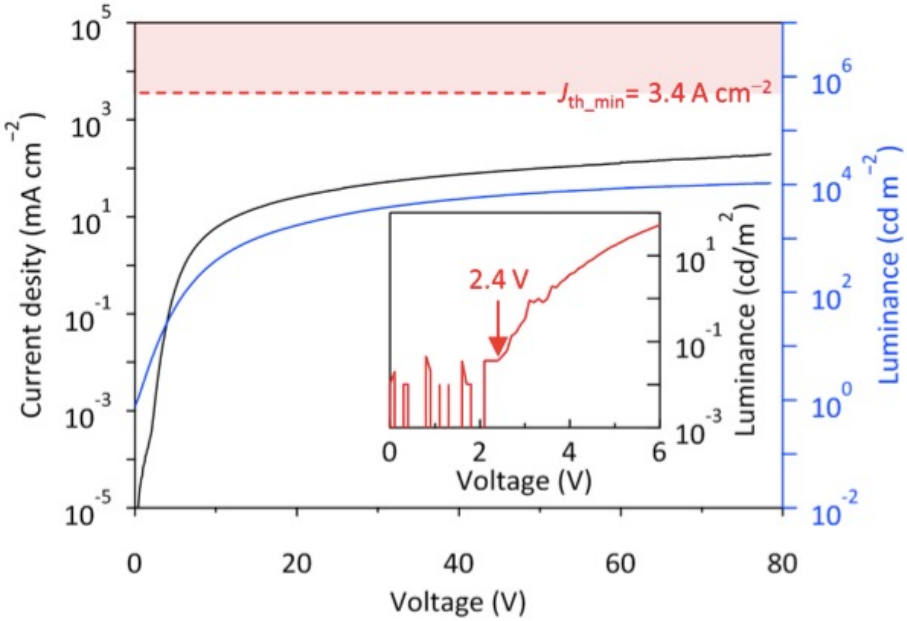
J. Roh, Y.S. Park, I. Fedin, V.I. Klimov, *Nature Comm. in press* (2019)

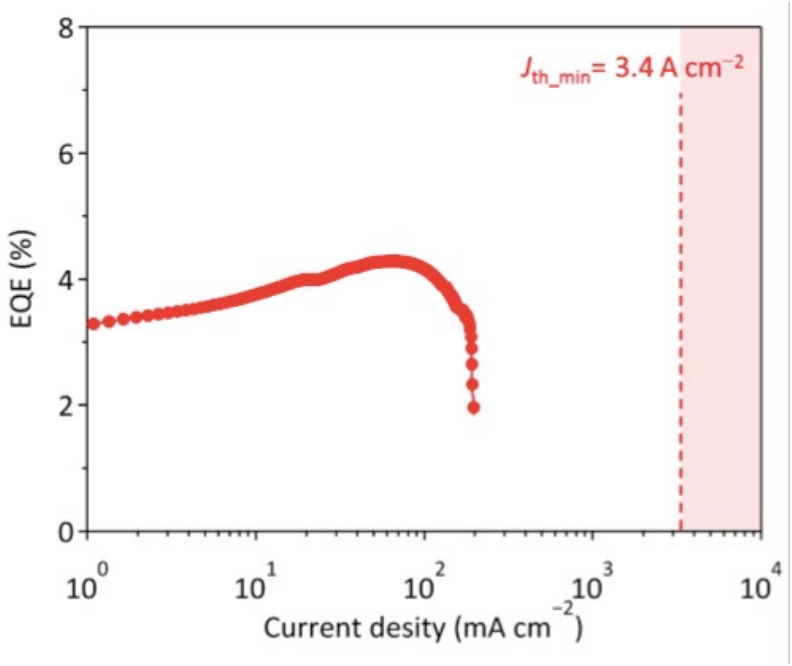


Electroluminescence from Lasing Device (3 QD MLs)



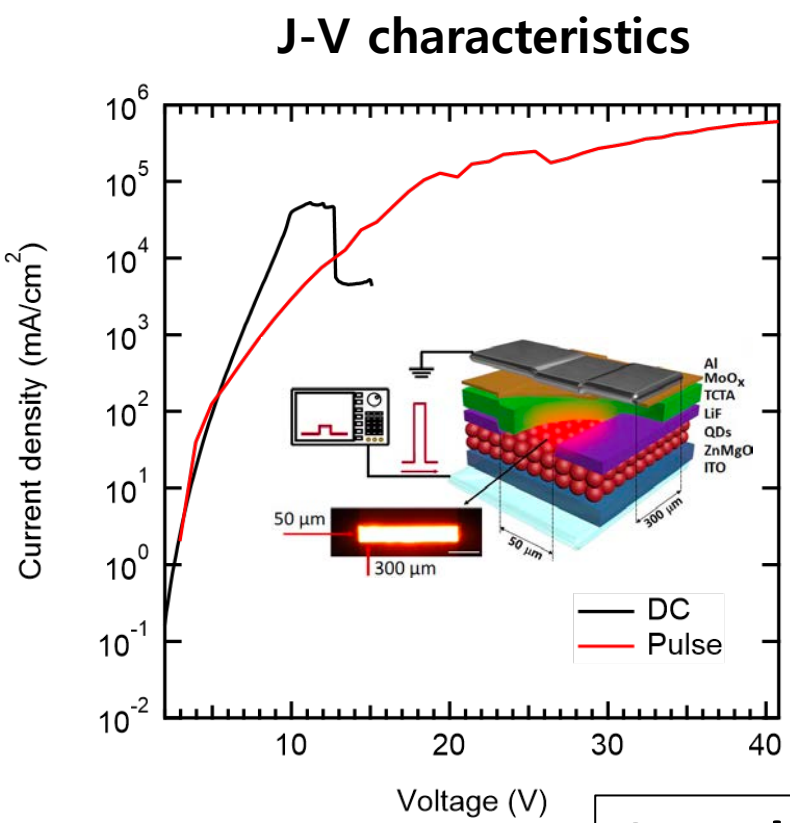


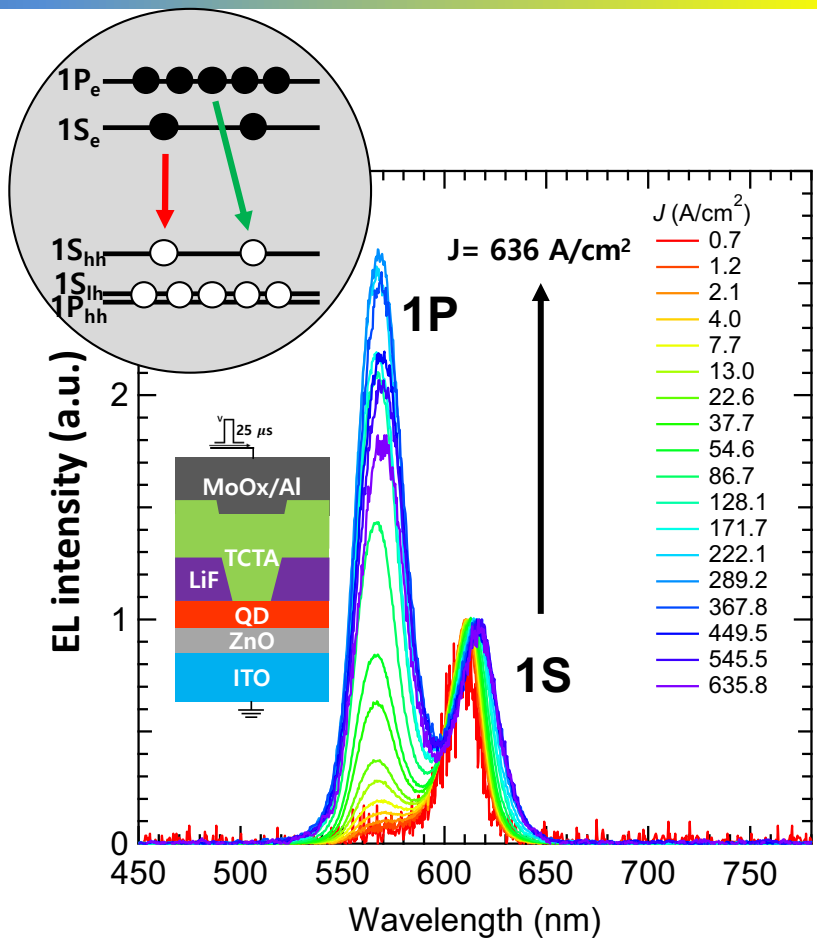




Colloidal QD-LED with Ultrahigh Current Densities up to 1000 A cm^{-2}

- **Pulsed QD-LED with current focusing**



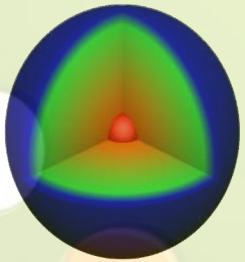


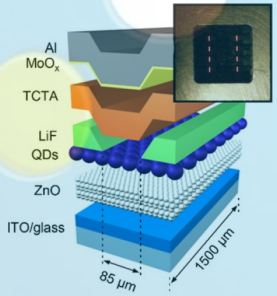
H. Jung, N. Ahn, V.I. Klimov, *et al.*, *Nat. Phot., under review* (2021)

Complete population inversion of 1S & 1P transitions using quasi-d.c. electrical pumping!

We are Ready to Put Together the Colloidal QD Laser Diode Puzzle

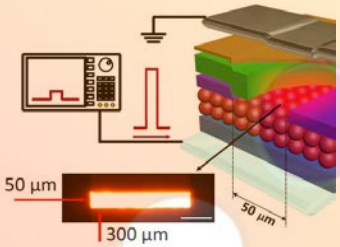
✓ cg-QDs with suppressed Auger decay

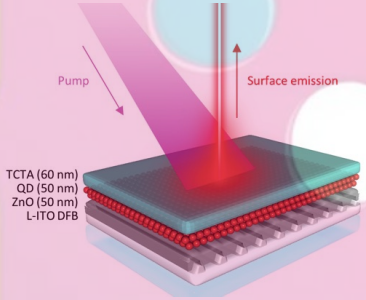




✓ Highly effective current focusing

✓ j ~ 1000 A cm^{-2} with pulsed excitation

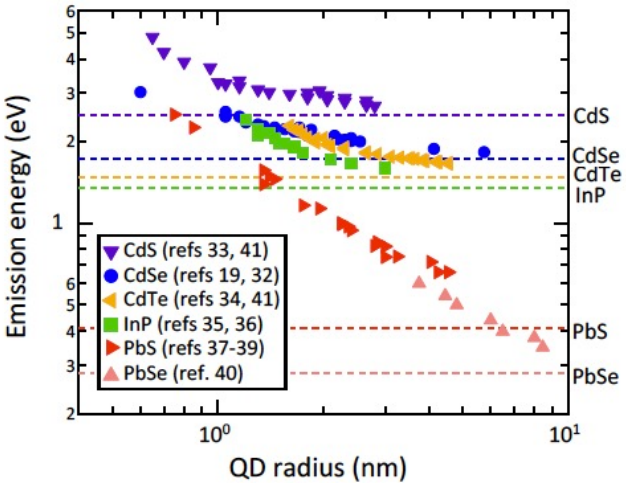




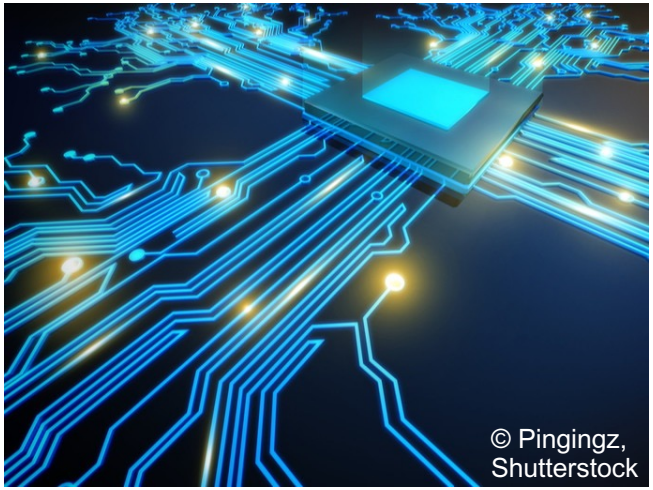
✓ Integrated cavity

End Result

- **Highly versatile, color selectable, inexpensive solution-processable gain media for on-chip optical amplifiers and lasers**

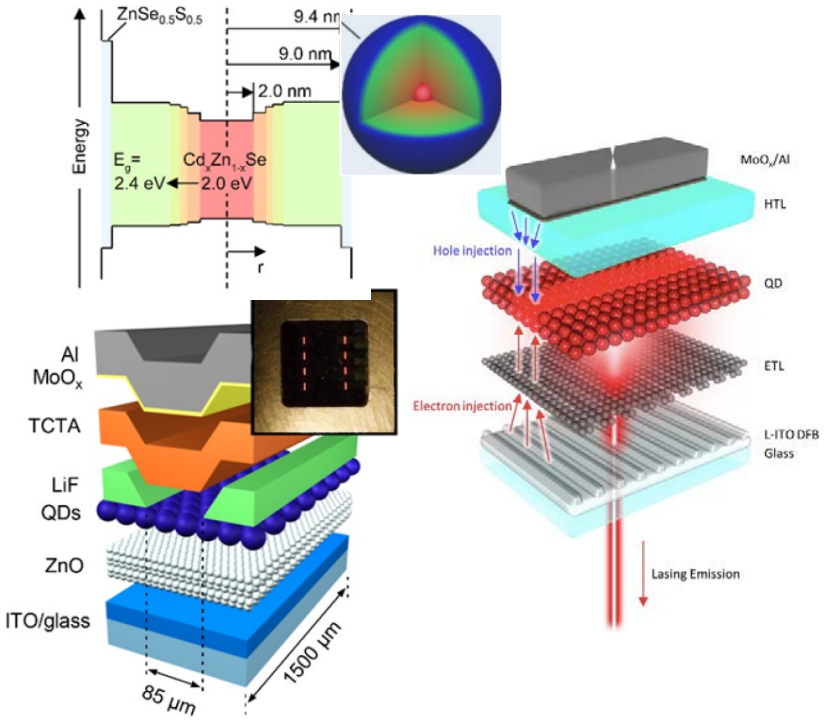


- **New materials platform for implementing highly integrated active photonic circuits (classical and quantum)**



Summary & Acknowledgements

- Suppression of Auger decay via continuous shell grading in type-I "giant" QDs (~50% bi-X PL QYs)
- Population inversion with dc electrical pumping (current focusing)
- Dual-function lasing/EL device
- LEDs with J of 1000 A/cm^2 (1P PL > 1S PL)



Jaehoon Lim

Jeongkyun Roh

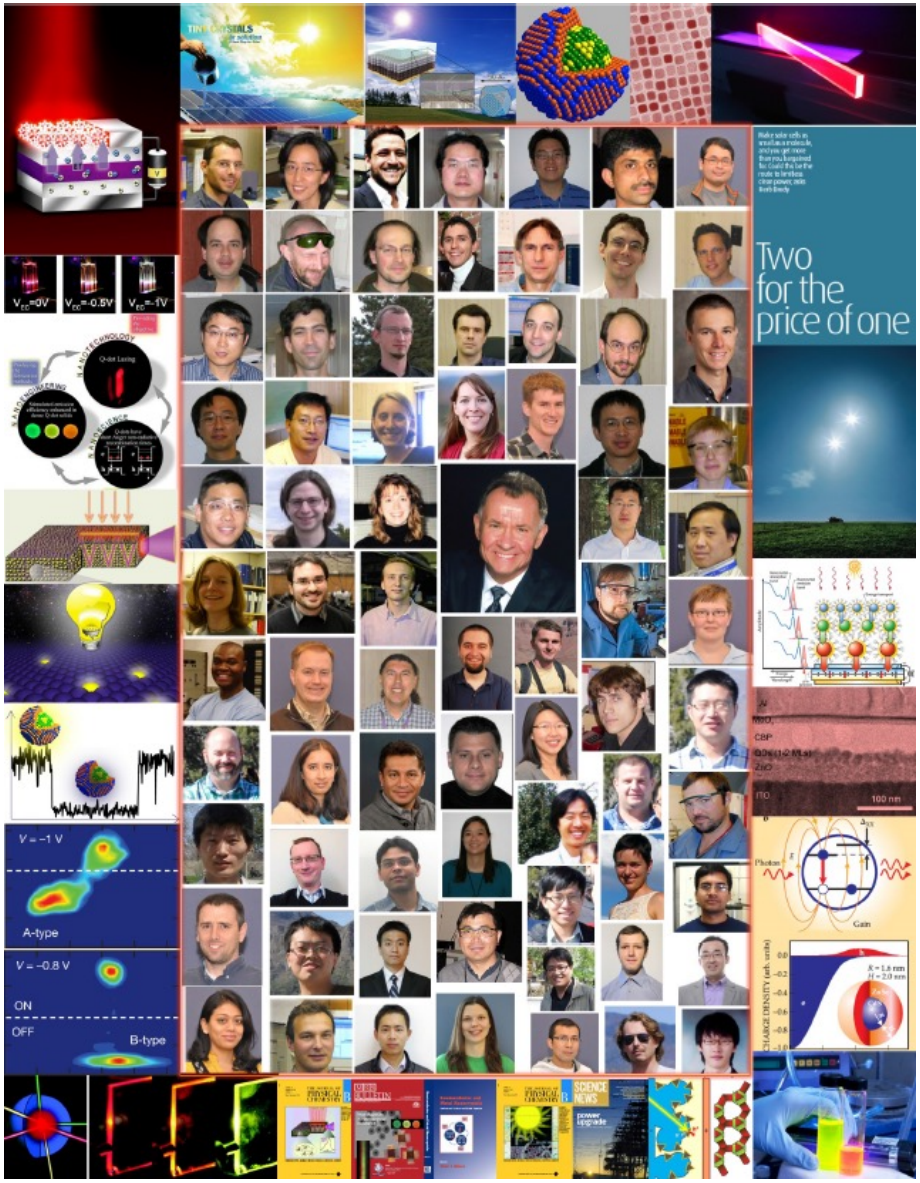
Heeyoung Jung

Young-Shin Park

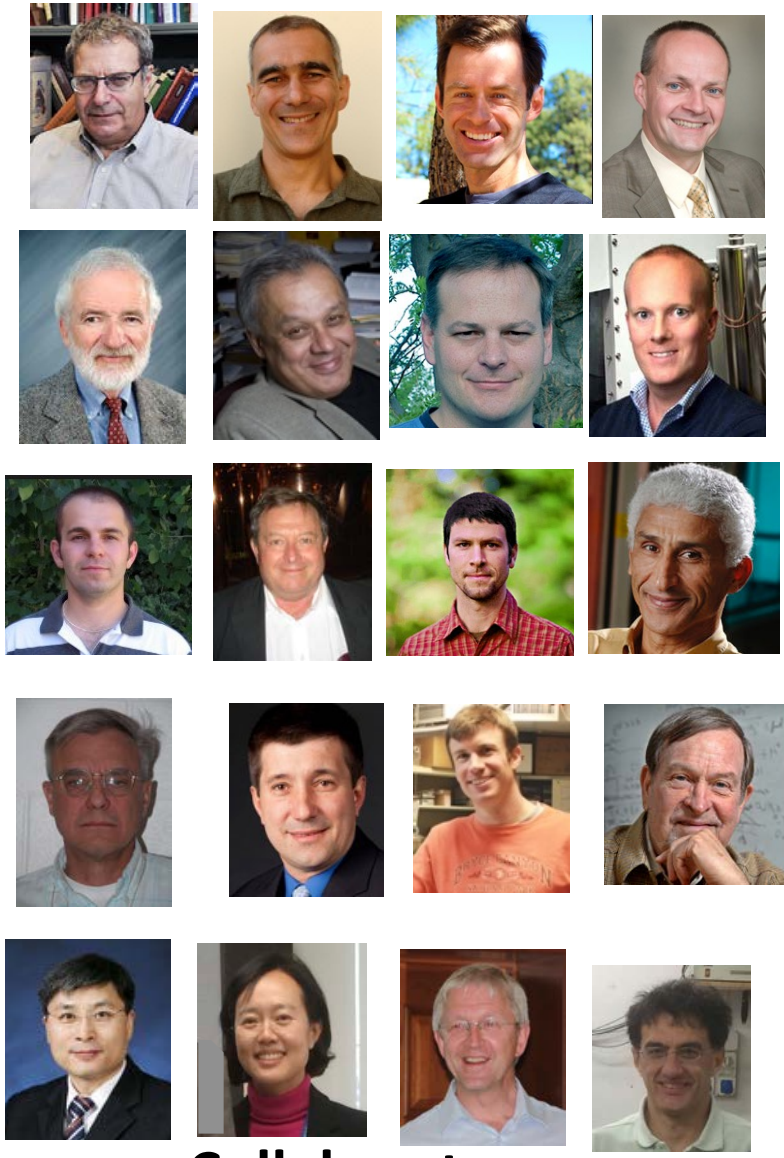
Namyoung Ahn

Nanotechnology & Advanced Spectroscopy Team

Los Alamos Quantum Dots



Members: ***Past & Present (>80)***



Collaborators

Job Openings at Los Alamos: *Postdoctoral & Student Positions*

NanoTechnology & Advanced Spectroscopy Team

Nanotechnology and Advanced Spectroscopy Team

- **Ultrafast Spectroscopy**
- **Single-Dot Spectroscopy**
- **Synthetic Inorganic/Organic Chemistry with Nanoscience emphasis**
- **Solution Processible Devices (PVs, LEDs, Lasers)**

Contact: Victor Klimov, klimov@lanl.gov
Phone: (505) 665-8284, Fax: (505) 667-0440
http://quantumdot.lanl.gov
http://casp.lanl.gov

Job Openings at Los Alamos: *Postdoctoral & Student Positions*