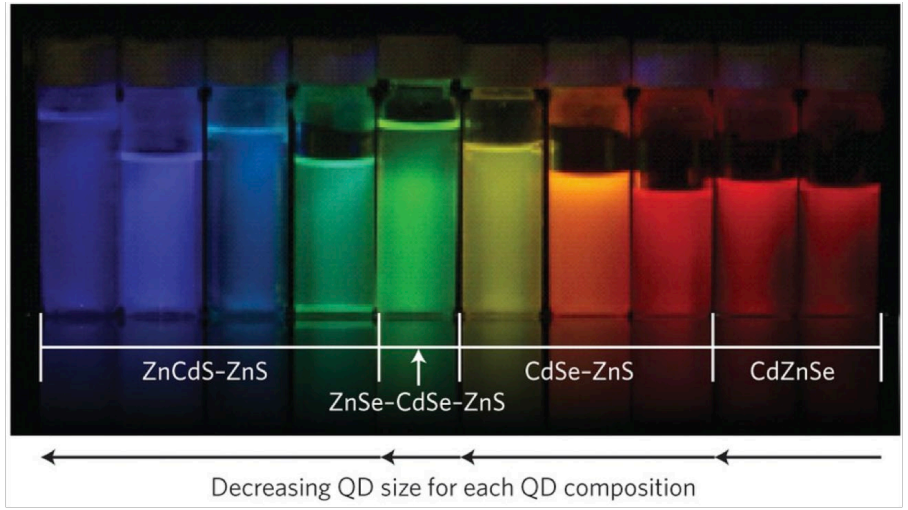
Colloidal Quantum Dot Technology in Industry

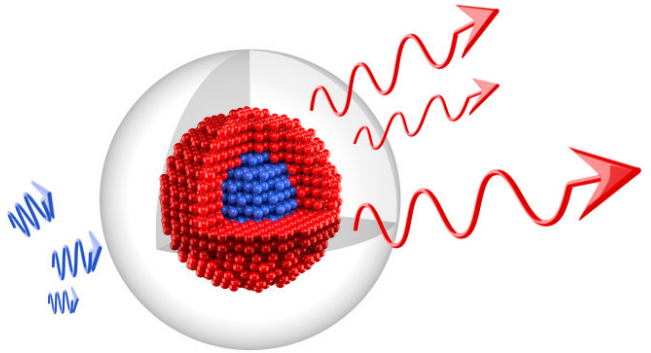
Dr. Jonathan Steckel, QD Industry Technology Leader and Entrepreneur

QD Technology and QD Product Development from QD Vision to Apple to STMicroelectronics

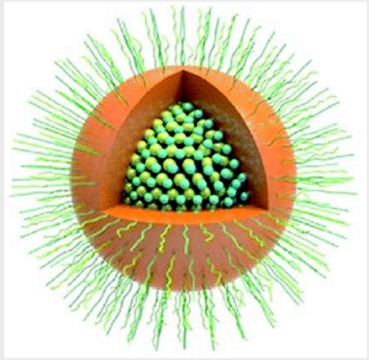
Class Outline

1. **Colloidal QD Material Technology**
2. **Colloidal QD Photoluminescence Technology**
3. **Colloidal QD Optoelectronic Device Technology**





https://www.osram.com/

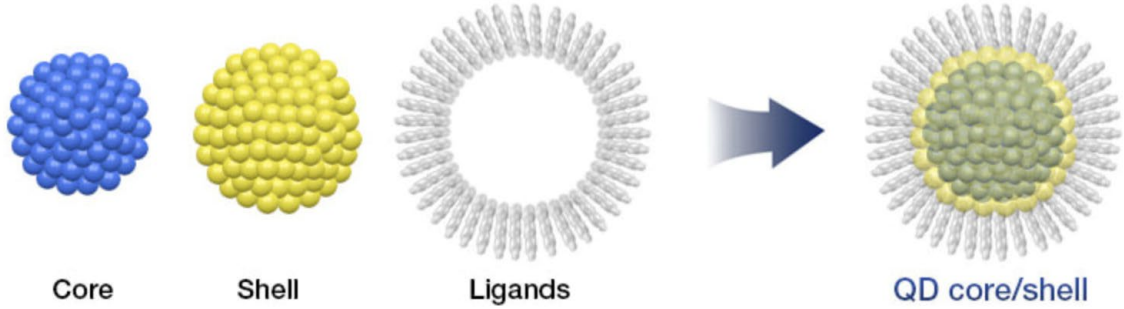


Colloidal QD Material Technology

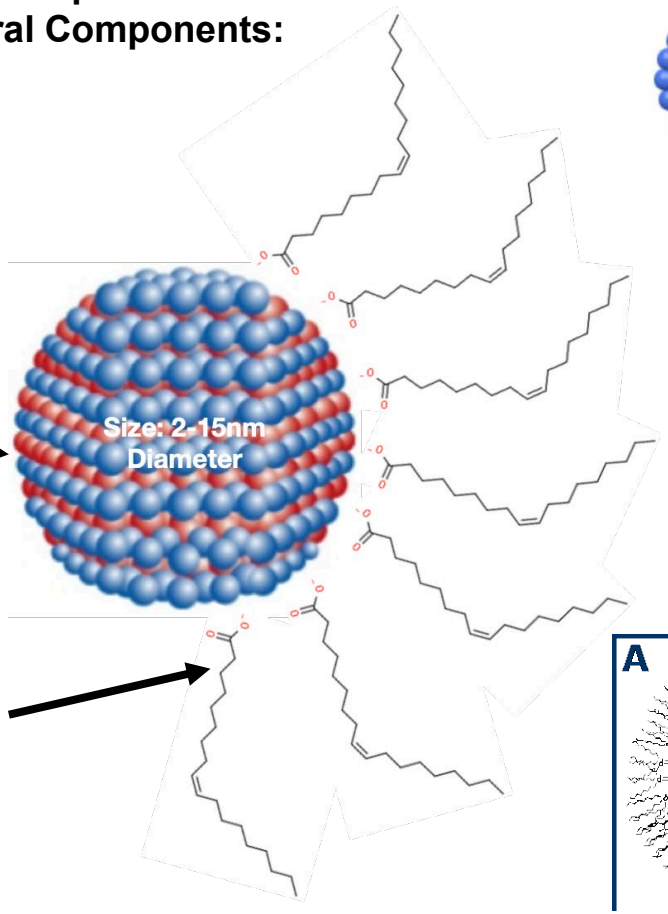
Colloidal Quantum Dot Technology

Quantum Dots (QDs) are Semiconductor Nanoparticles Comprised of Three Engineerable Structural Components:

1. Core (2-15nm diameter)
2. Shell (protect and passivate core)
3. Ligands (surface bound molecules)

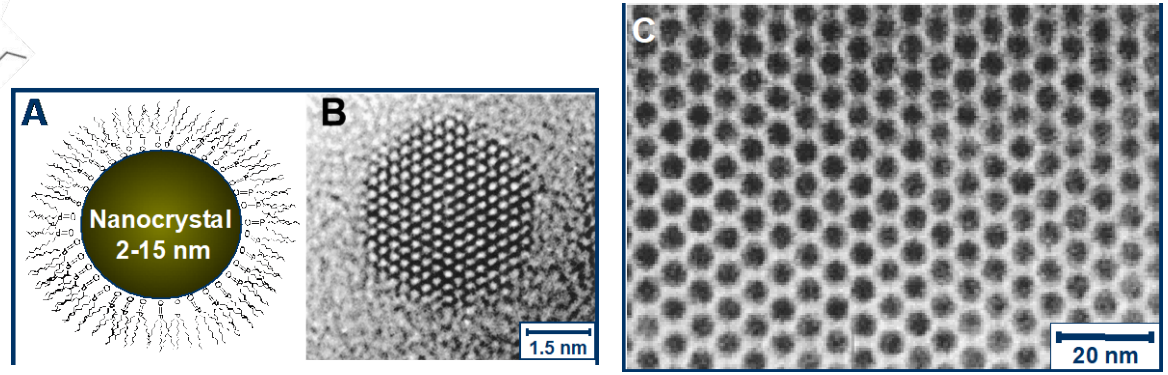


Semiconductor Core:
Size, shape and composition determine absorption & emission wavelength

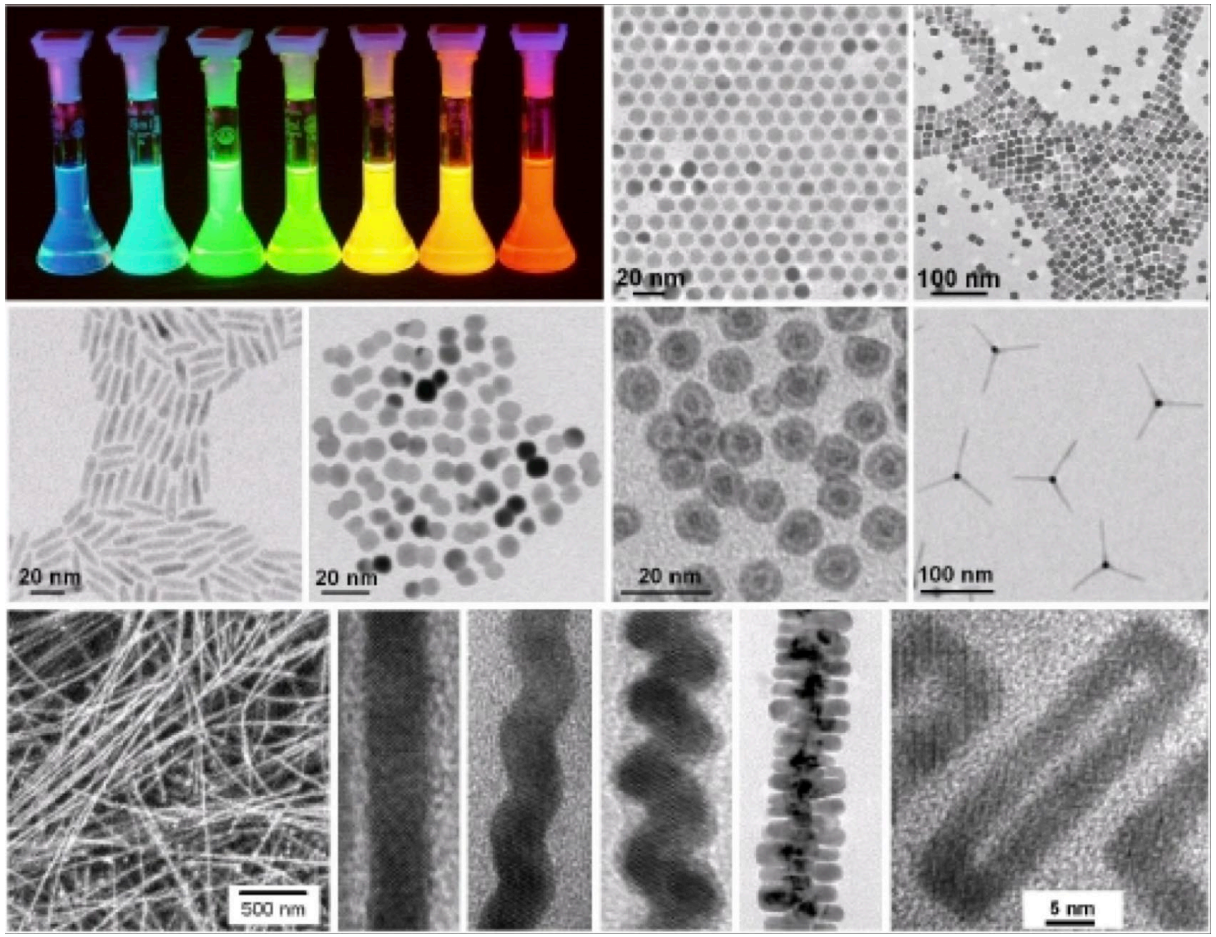


Semiconductor Shell:
Thickness and composition determine emission performance and wavelength

Ligands:
Organic aliphatic, organometallic, inorganic molecules that passivate, protect, and functionalise the semiconductor surface

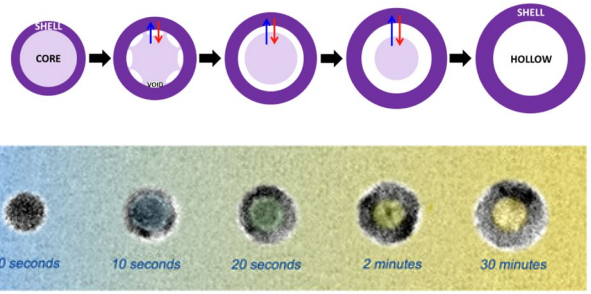


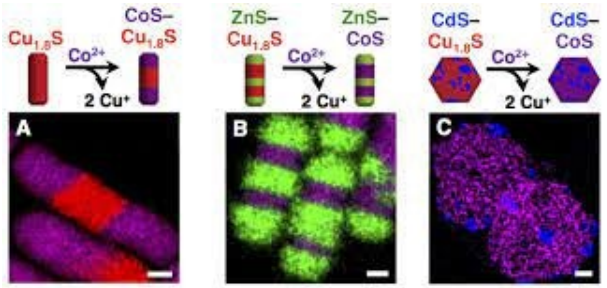
Colloidally Grown Semiconductor Nanoparticle Shape Control

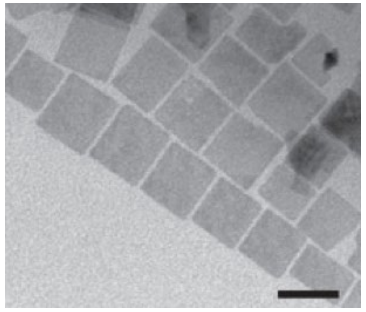


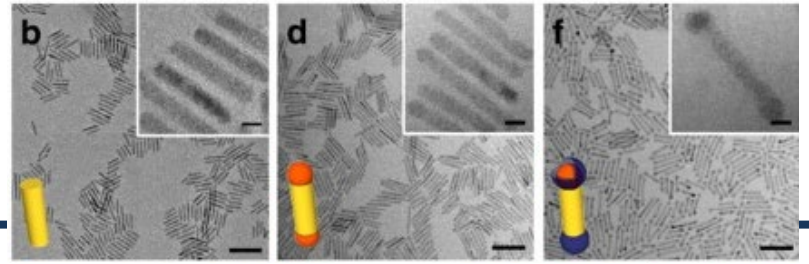
Colloidal synthesis enables unique nanoparticle shape control

- Rods
- Plates
- Branched
- Hollow
- Nested
- Striped
- Barbell

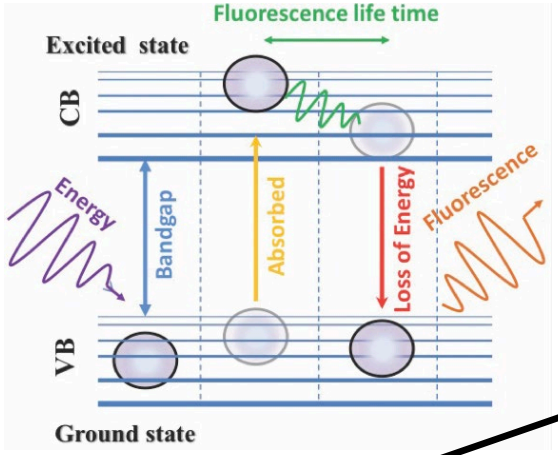


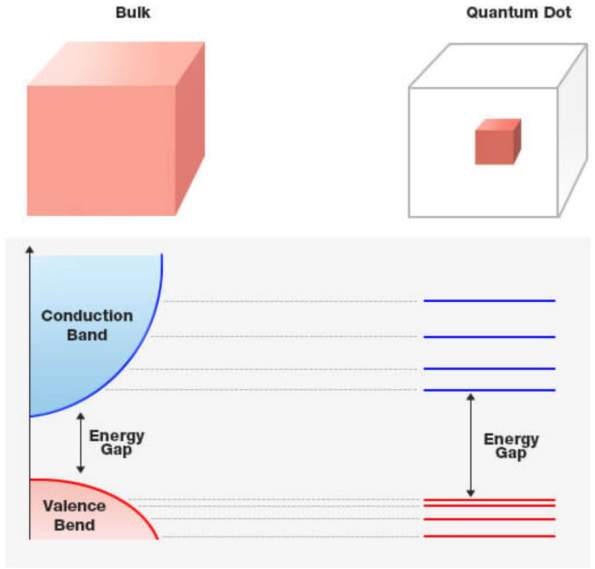




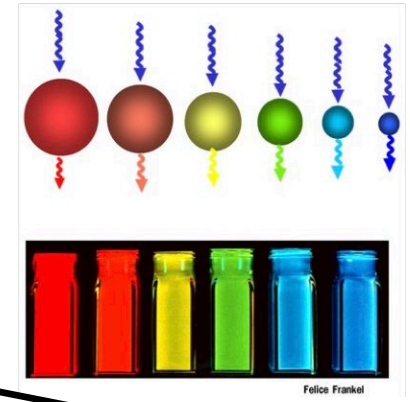


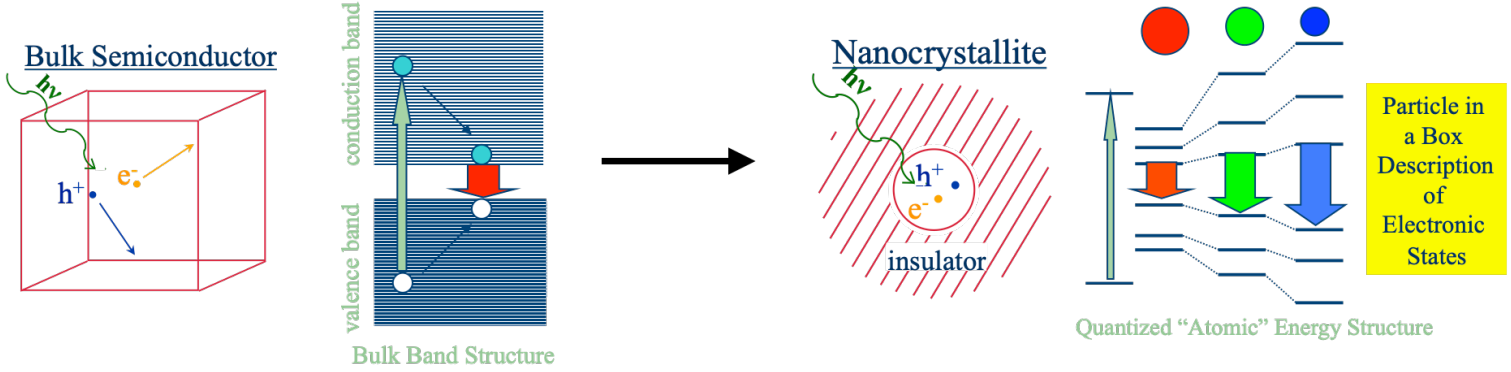
Particle in a Box Description of Electronic States



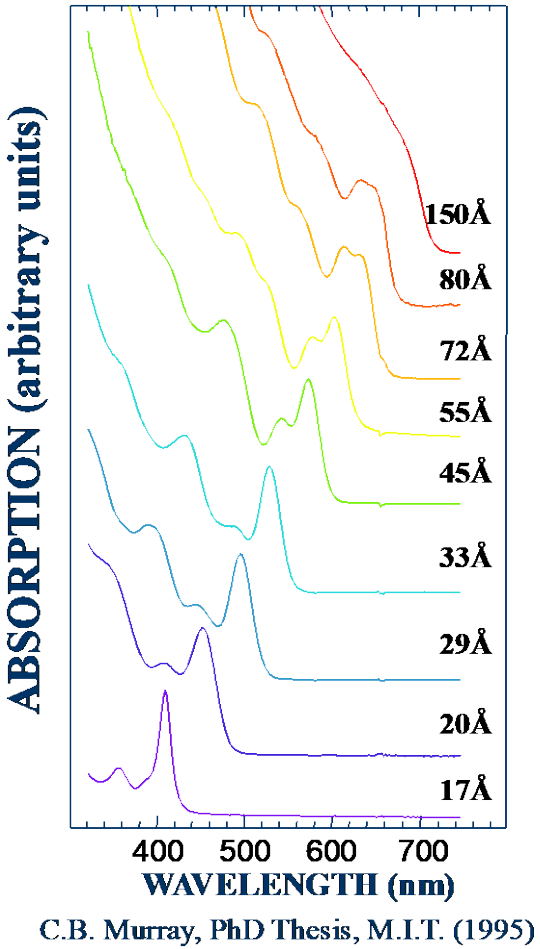


Size of QD provides lever for fine tuning color of emission



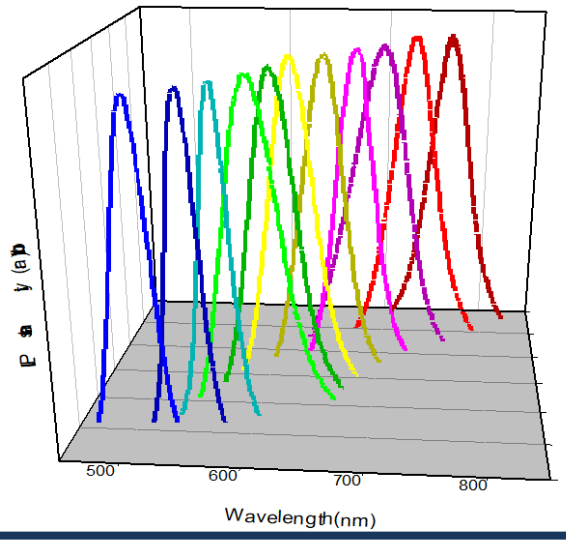


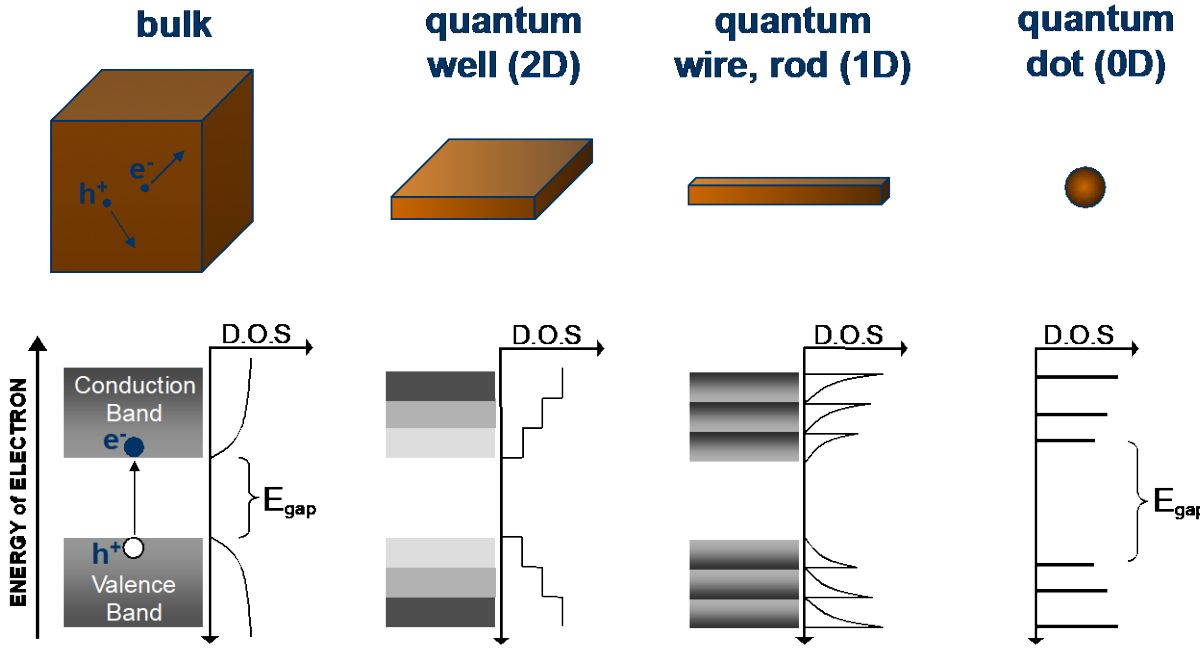
Quantum Confinement and "Seeing" Quantum Mechanics



C.B. Murray, PhD Thesis, M.I.T. (1995)

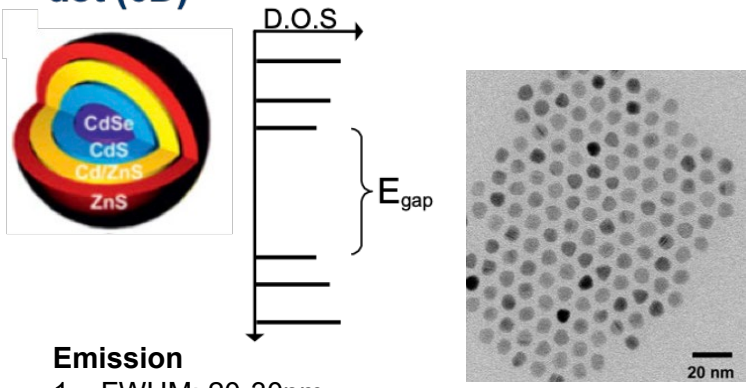
Photography by Felice Frankel





Functional Particle Shape and Physical Properties

quantum dot (0D)



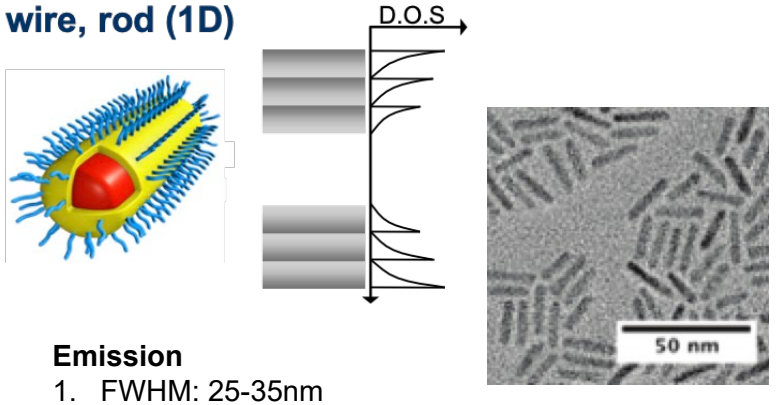
Emission
1. FWHM: 20-30nm
2. Degree of Linear Polarization: None
3. Profile: Non-directional

Excitation
1. Bi and tri-exciton efficiency dominate at high excitation
2. Ability to engineer Auger rate

Synthesis
1. Less strain tolerated
2. Core-shell lattice mismatch less tolerated
3. Fewer shell material choices available

Composition
1. Cd-free can be made (e.g. InP, ZnSe, CuInS)

quantum wire, rod (1D)



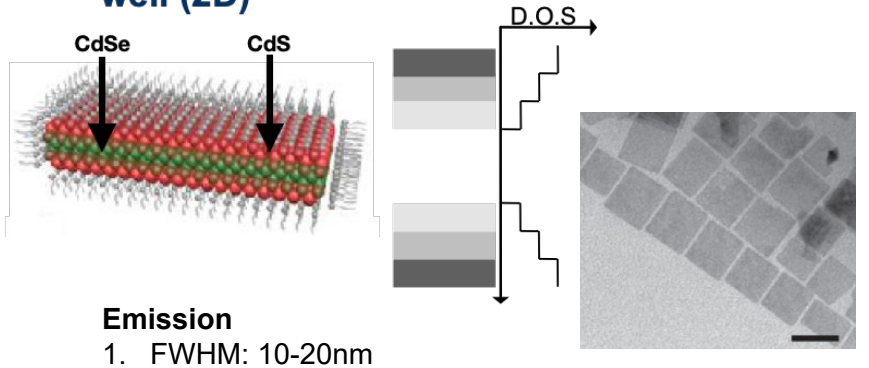
Emission
1. FWHM: 25-35nm
2. Degree of Linear Polarization: 0.6-0.8
3. Profile: Highly directional cone along a plane perpendicular and bisecting the long axis
4. Potential to double film light output

Excitation
1. Bi and tri-exciton efficiency dominate at high excitation
2. Ability to engineer Auger rate

Synthesis
1. Less strain tolerated
2. Core-shell lattice mismatch less tolerated
3. Fewer shell material choices available

Composition
1. Cd-free light emitters still very challenging

quantum well (2D)



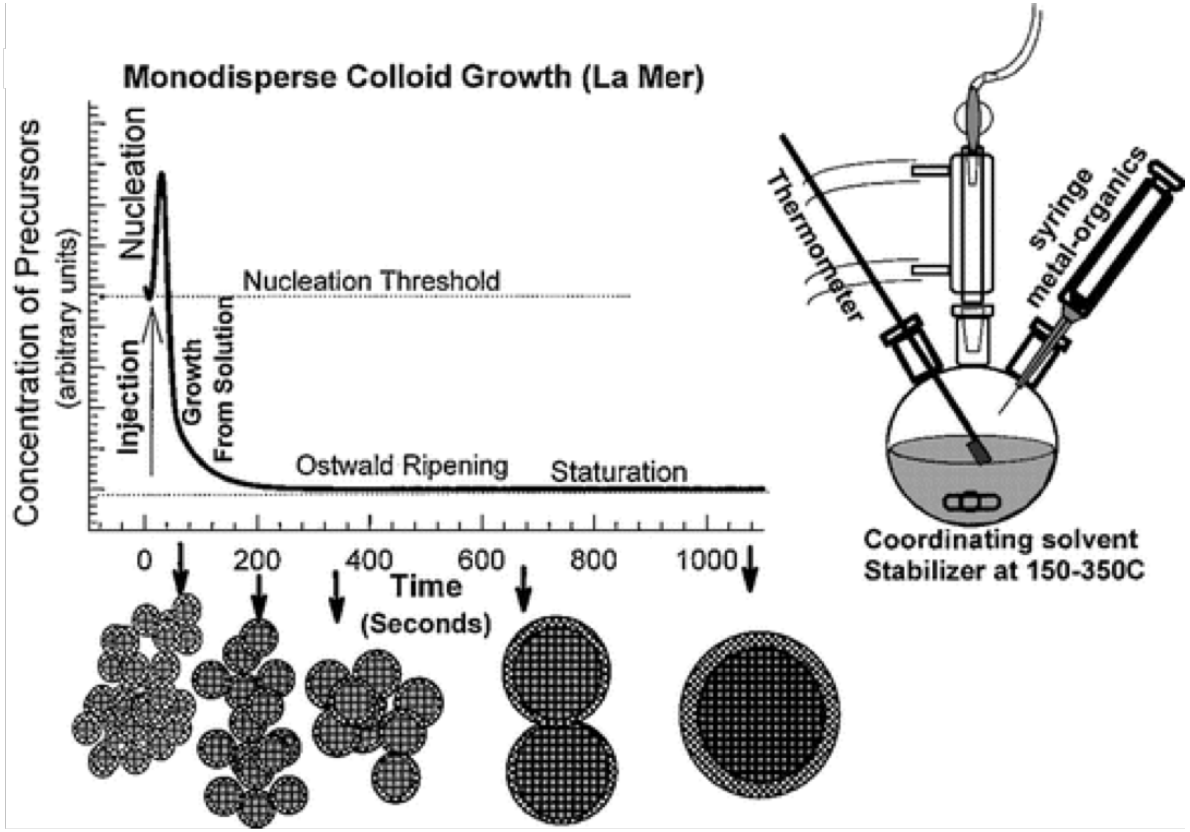
Emission
1. FWHM: 10-20nm
2. Degree of Linear Polarization: 0.9 from edge
3. Profile: Highly directional normal to the well plane
4. Potential to double film light output

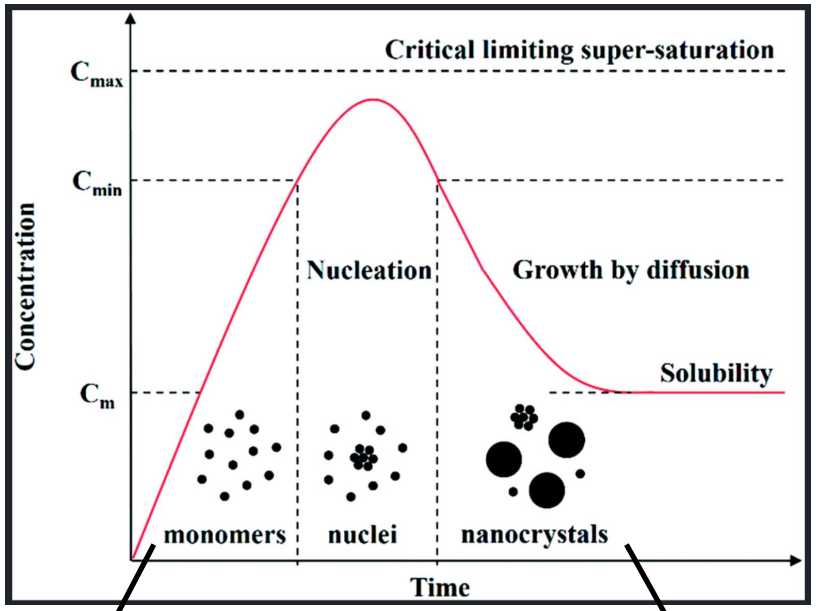
Excitation
1. Can excite much harder (DOS)
2. No Auger

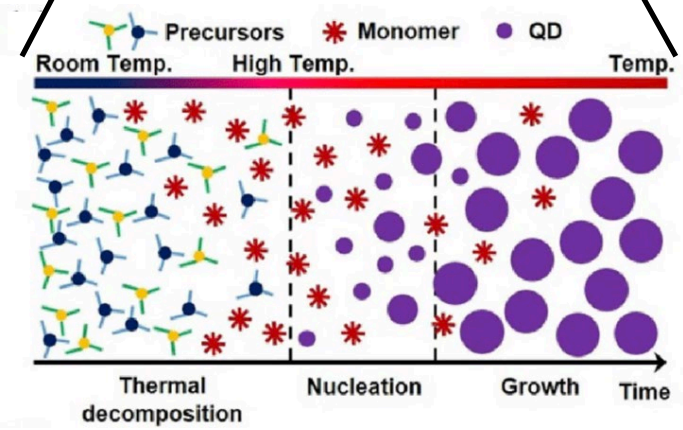
Synthesis
1. Up to 20% lattice strain tolerated by core
2. 10nm thick shells tolerated
3. Greater core-shell lattice mismatch tolerated
4. Greater shell material choices available for optimized charge injection and band alignment

Composition
1. Cd-free light emitters still very challenging

Colloidal Nanoparticle Nucleation and Growth



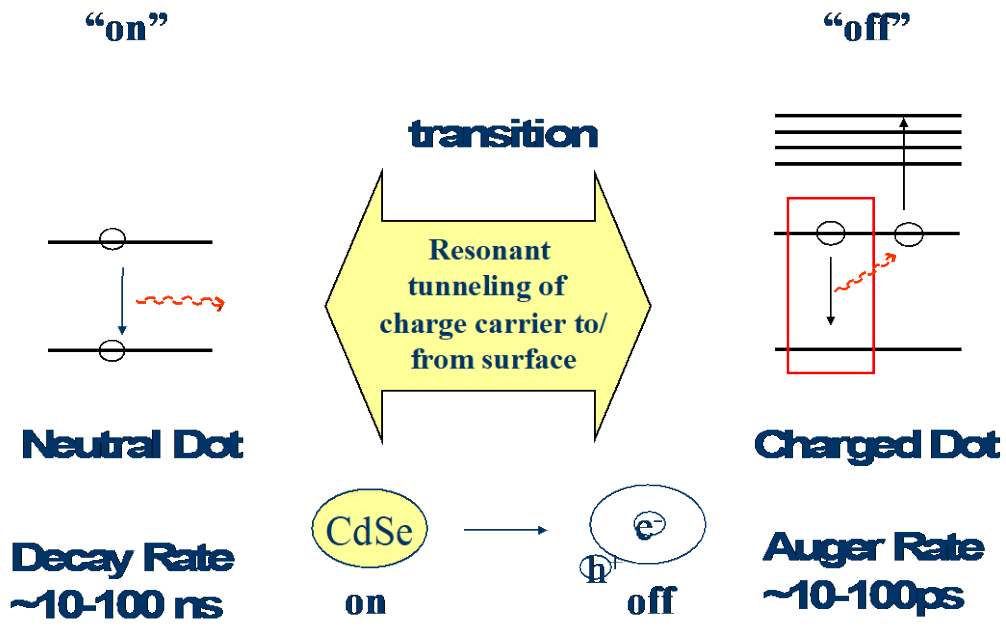


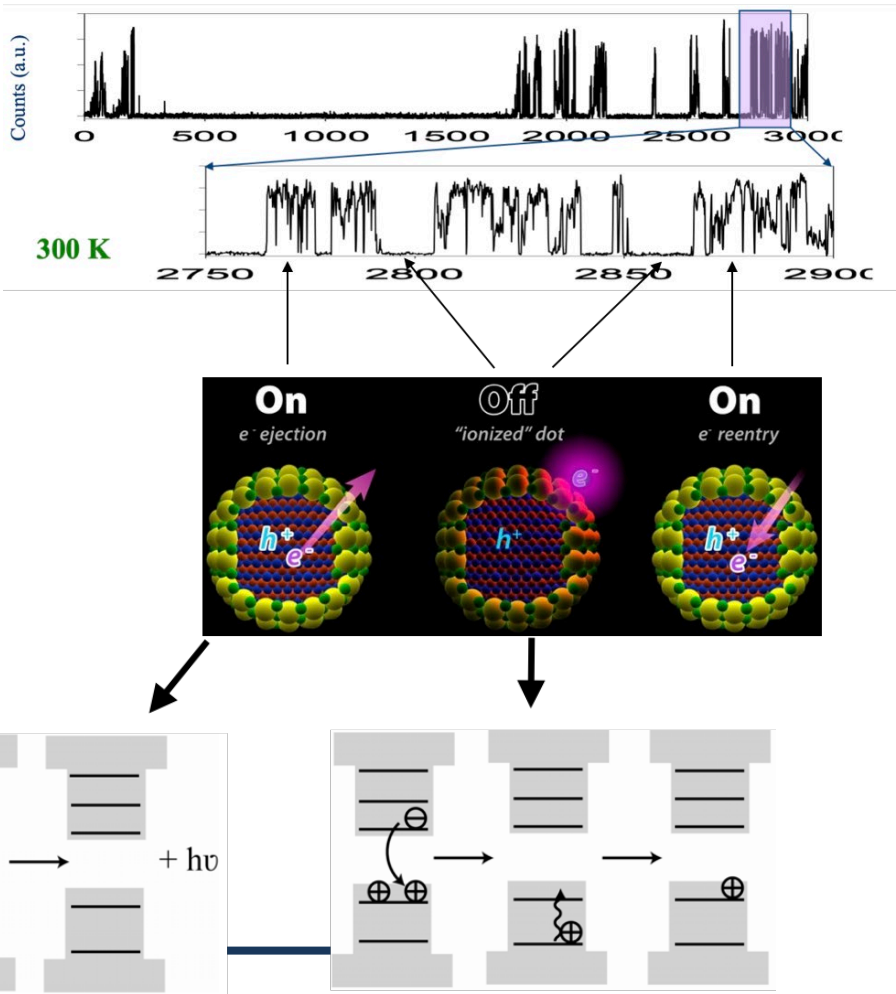


Shell Growth: QD Blinking and Auger Recombination

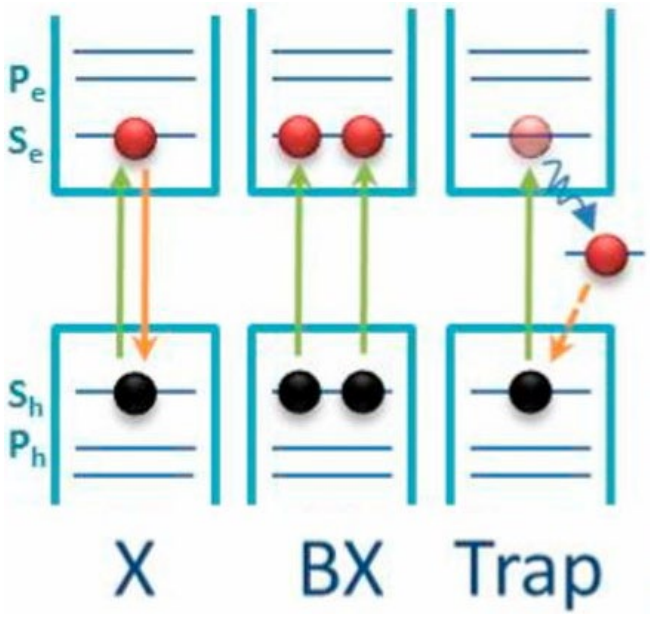
Heat, light, and chemically reactive species can cause surface changes

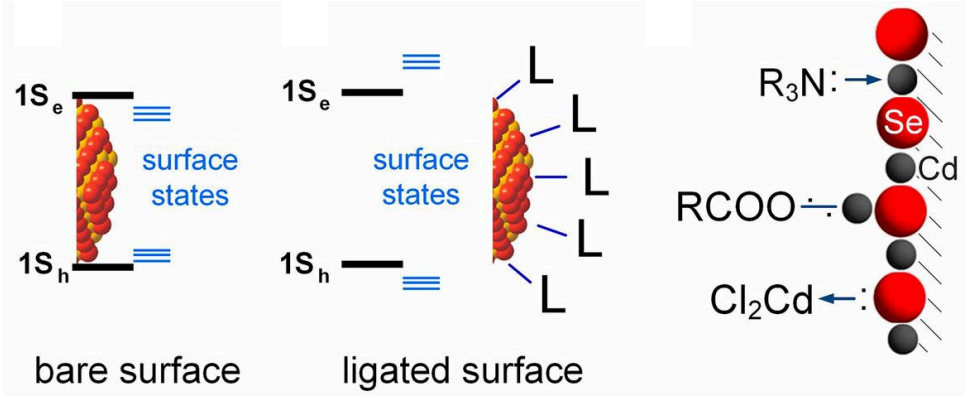
- Ligand loss/surface damage create surface states that trap electrons and holes
- Trapped surface charge lead to charged QDs which are “Off” QDs via Auger Recombination

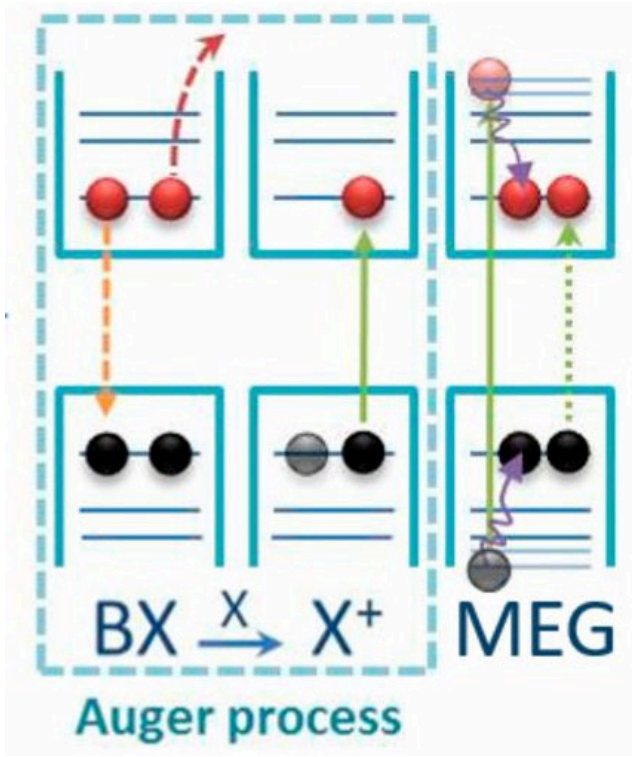




QD Carrier Dynamics Summary





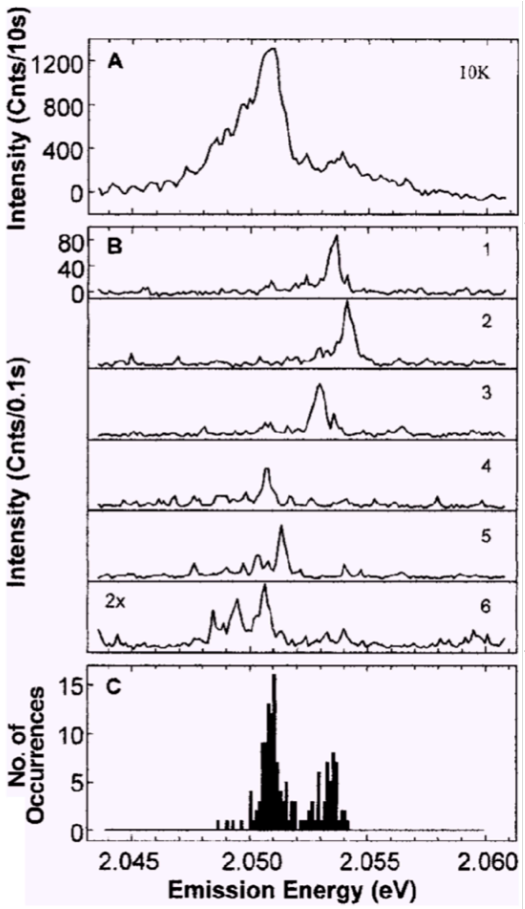


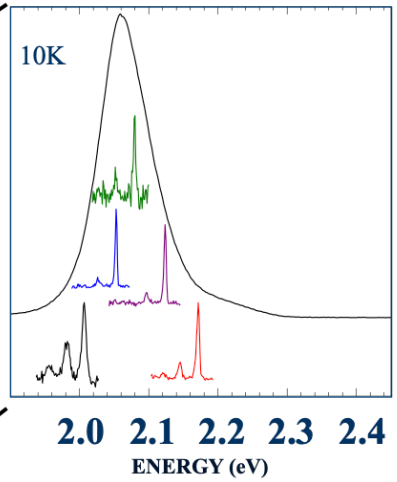
Absorption and Emission Processes in QDs

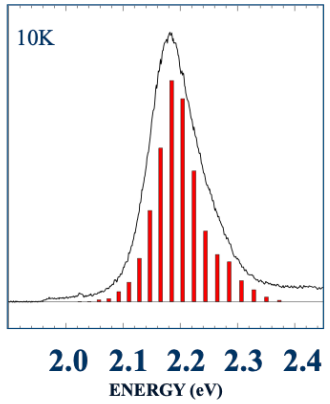
- (X): Single exciton → Band-edge absorption and emission
- (BX): Biexciton → Sequential absorption of two photons
- (Trap): Nonradiative decay → charge trapped into a mid-gap state followed by trap-to-band recombination
- (Auger Process): Nonradiative Auger process → Energy transfer from electron-hole recombination to a third carrier where it can become attached to a freshly formed exciton (X), creating a hole-hole-electron complex (trion, X+)
- (MEG): Multiple exciton generation → High energy electron-hole pair nonradiatively relaxes generating additional electron-hole pair (or pairs) across the band-gap from the cooling energy

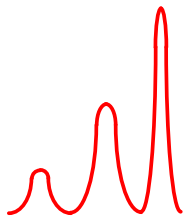
Building Devices from Colloidal Quantum Dots, Cherie R. Kagan, Efrat Lifshitz, Edward H. Sargent, Dmitri V. Talapin; *Science* 26 Aug 2016, Vol. 353, Issue 6302; DOI: 10.1126/science.aac5523

Origin of Linewidths: Rapid Spectral Fluctuations



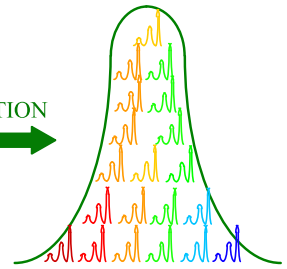




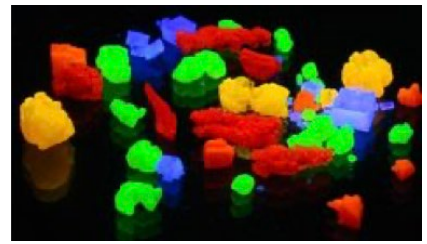


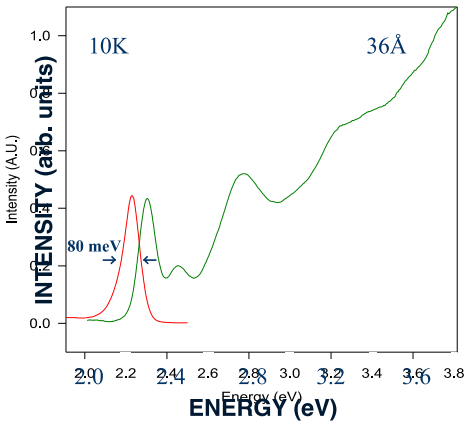
Single Nanocrystallite Emission Spectrum

SIZE DISTRIBUTION



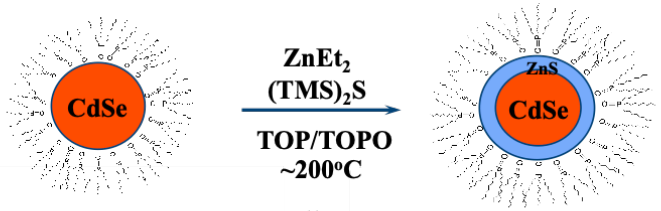
Inhomogeneous Emission Spectrum

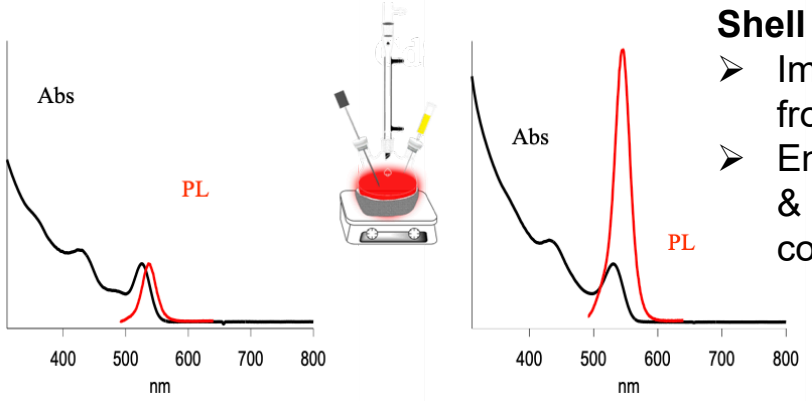




- Differences in QD size, shape and local environment produce inhomogeneous broadening
- Loss of spectral information
- Ensemble linewidths are significantly broader than predicted

Shell Growth: QD Design for Light-Emission



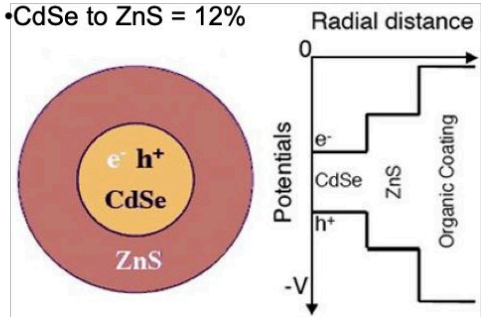


Shell Growth Provides:

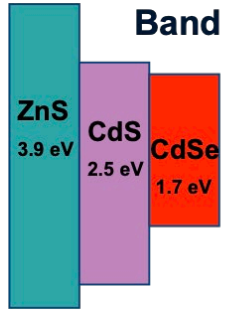
- Improved Stability (isolation of core from environment)
- Enhanced Efficiency (reduced Auger & blinking with maximized e^- and h^+ confinement in the core)

Critical Factors for Shell Growth

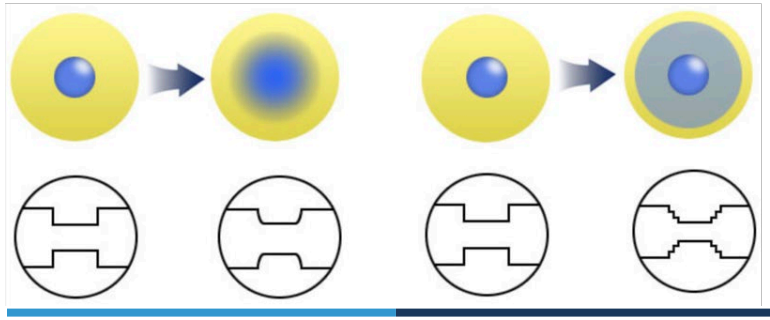
1. **Band Alignment**
2. **Lattice Mismatch**
   - CdSe to CdS = 3.8%
   - CdSe to ZnS = 12%



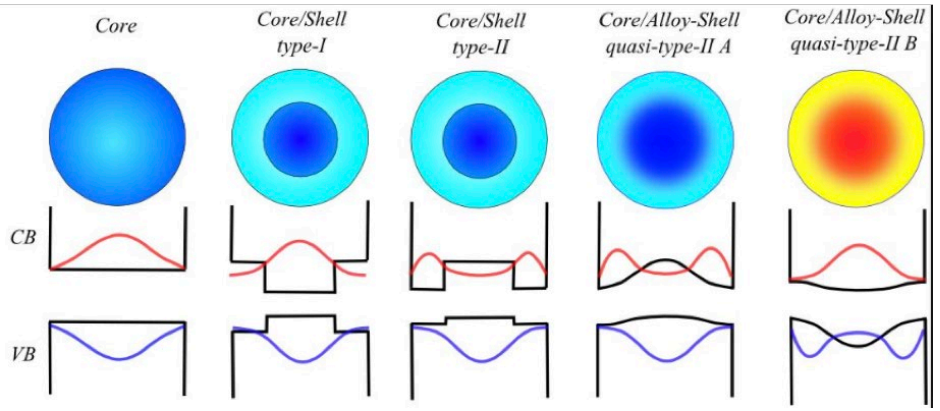
Band Alignment



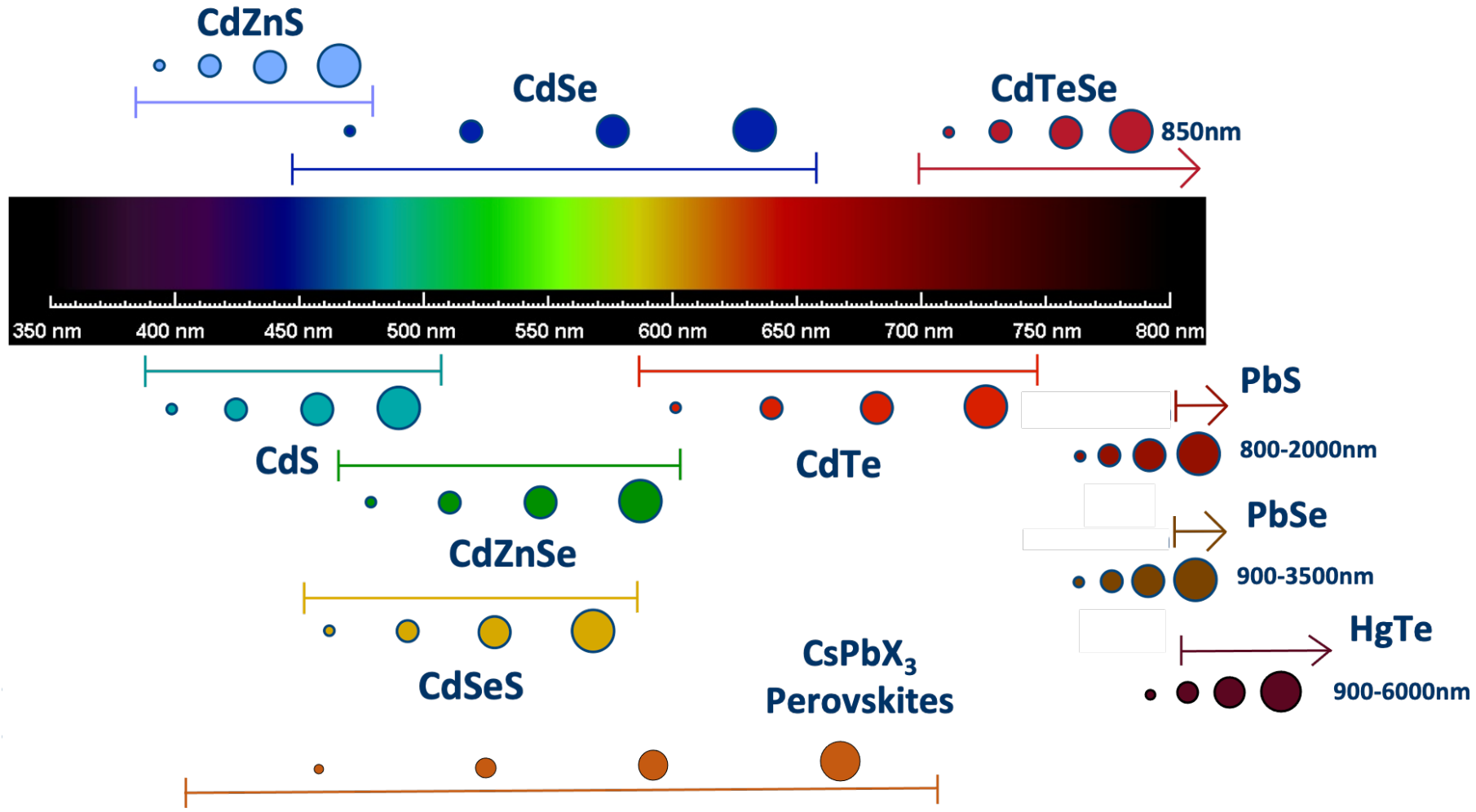
Highly Engineered Graded Shells with Interfacial Alloying



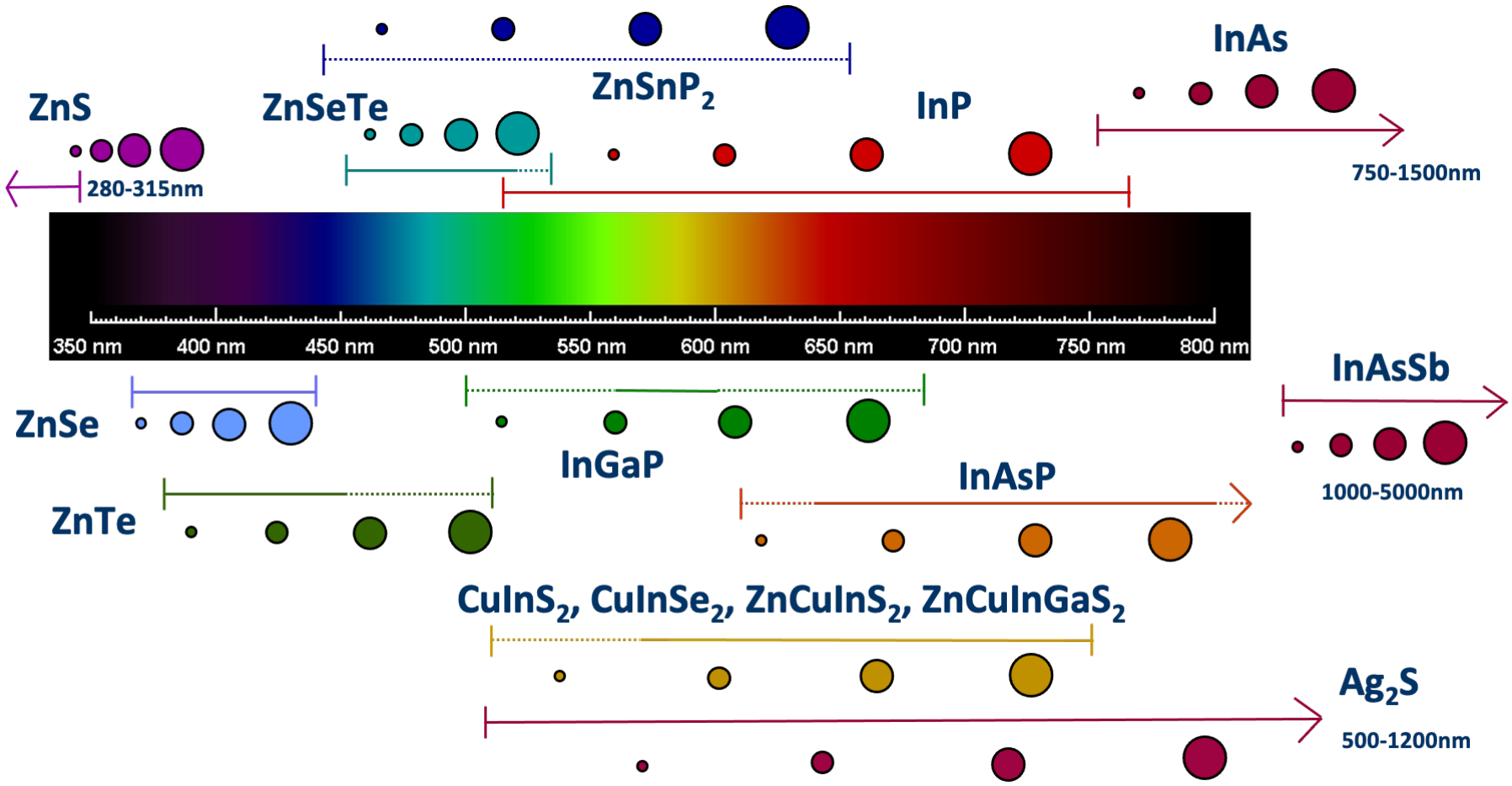
Core/Shell Types



Heavy Metal-Containing QD Spectral Tuning Ranges



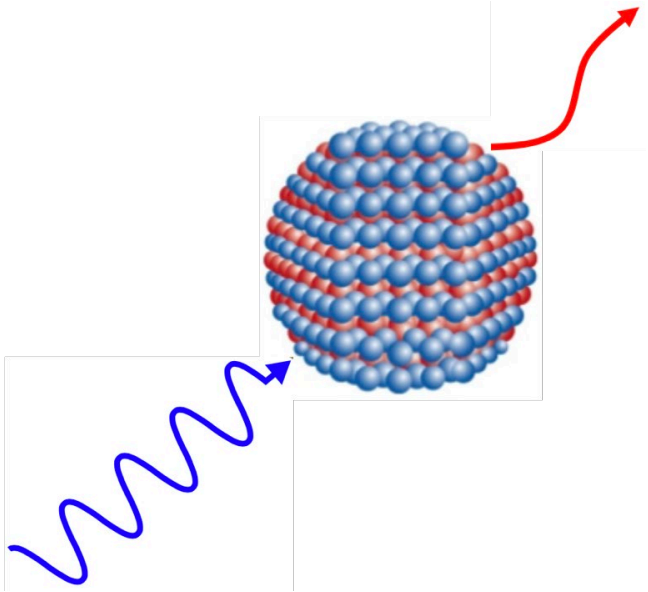
Heavy Metal-Free QD Spectral Tuning Ranges



QD Technology Modes of Operation

Photo-Active QD Technology

Photo-Luminescent



Optoelectronic QD Device Technology

Electro-Luminescent

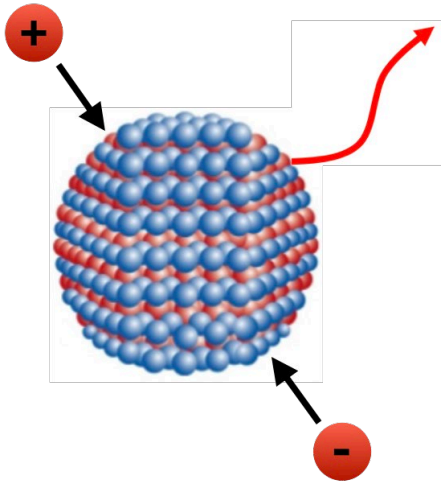
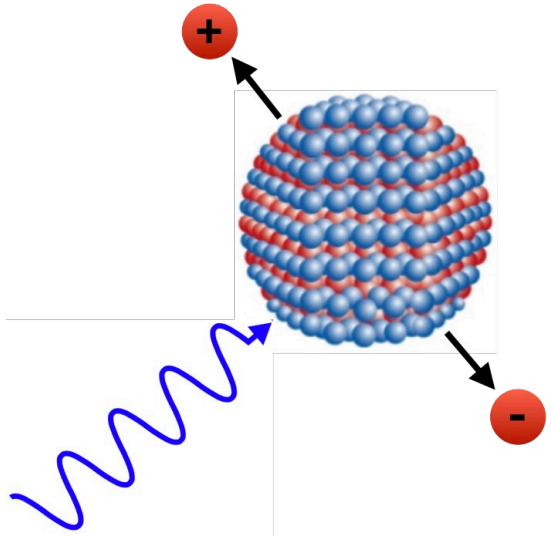
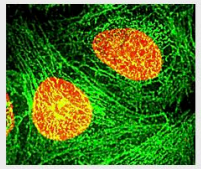
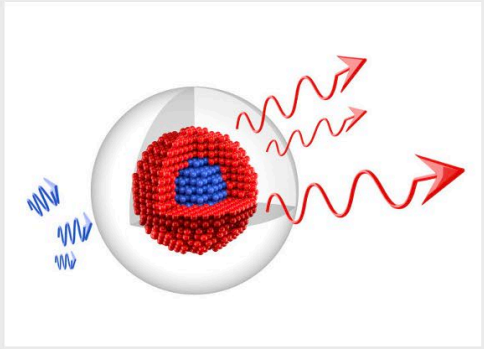


Photo-Electric



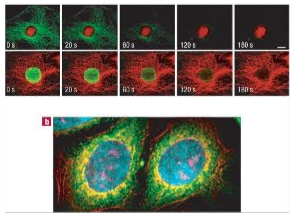




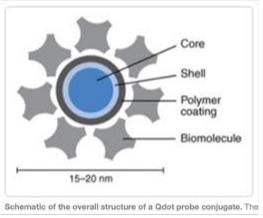
Colloidal QD Photoluminescence Technology

QD Photoluminescent Commercial Products Timeline

2002 →



Qdot Probes



Schematic of the overall structure of a Qdot probe conjugate. The

QD Corp.

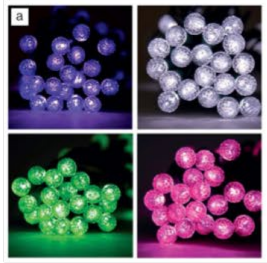
↓

Invitrogen

↓

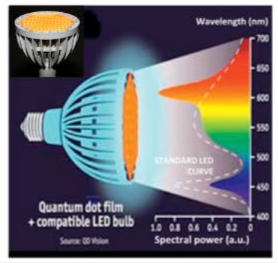
ThermoFisher SCIENTIFIC

2008-2010

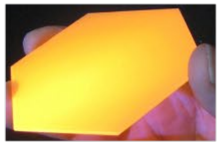


Evident Technologies
Christmas Tree Lights

2009-2010



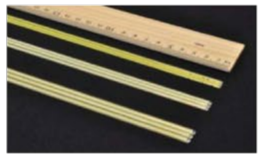
Nexxus Lighting/QD Vision
QD/LED Lamp

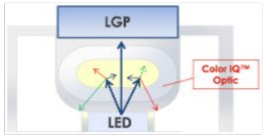


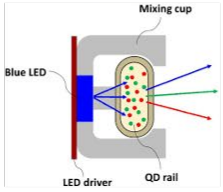
Quantum Light™ Optic

2013-2016

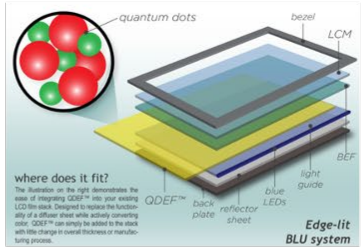
QD Vision
Color IQ™ Optic



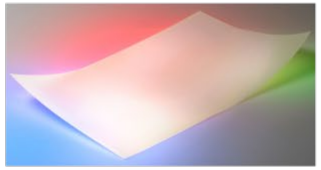


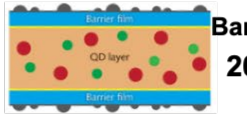


2013 →



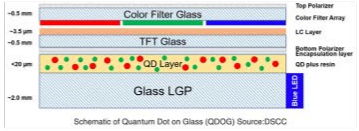
Nanosys/3M
QDEF™ Film





Barrier Film 2013

↓ **QDs on Glass 2019**



Schematic of Quantum Dot on Glass (QDOG) Source:DSCC

2018 →

UbiQD
Luminescent Greenhouse Films

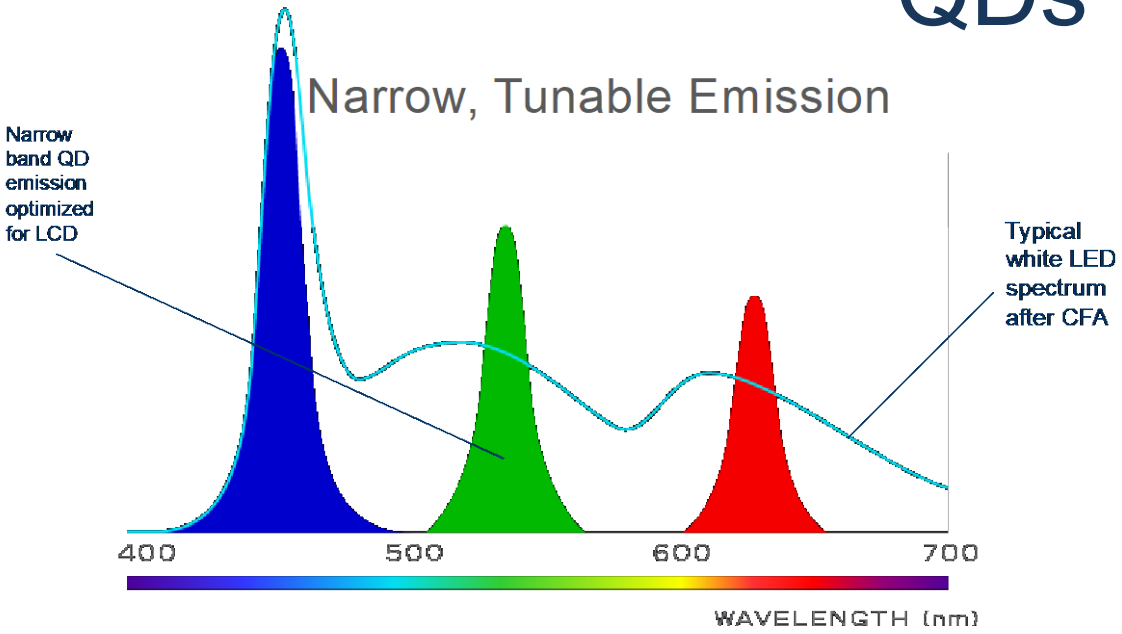
CIS (Copper, Indium, Sulphide) QDs

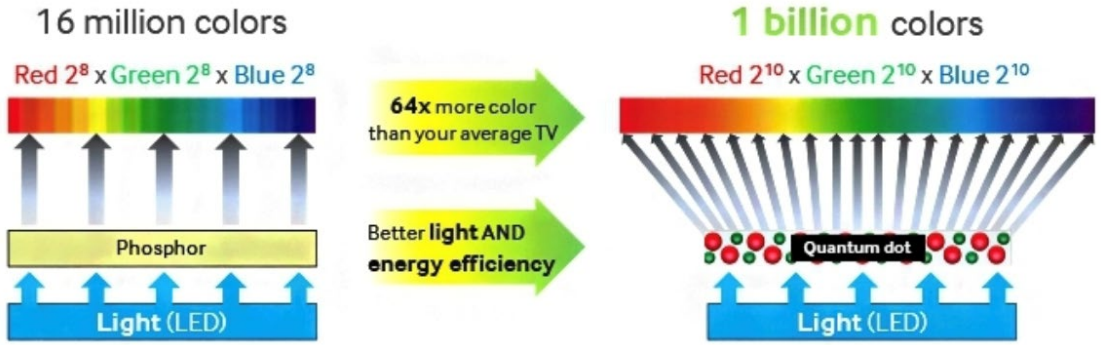
2019 →

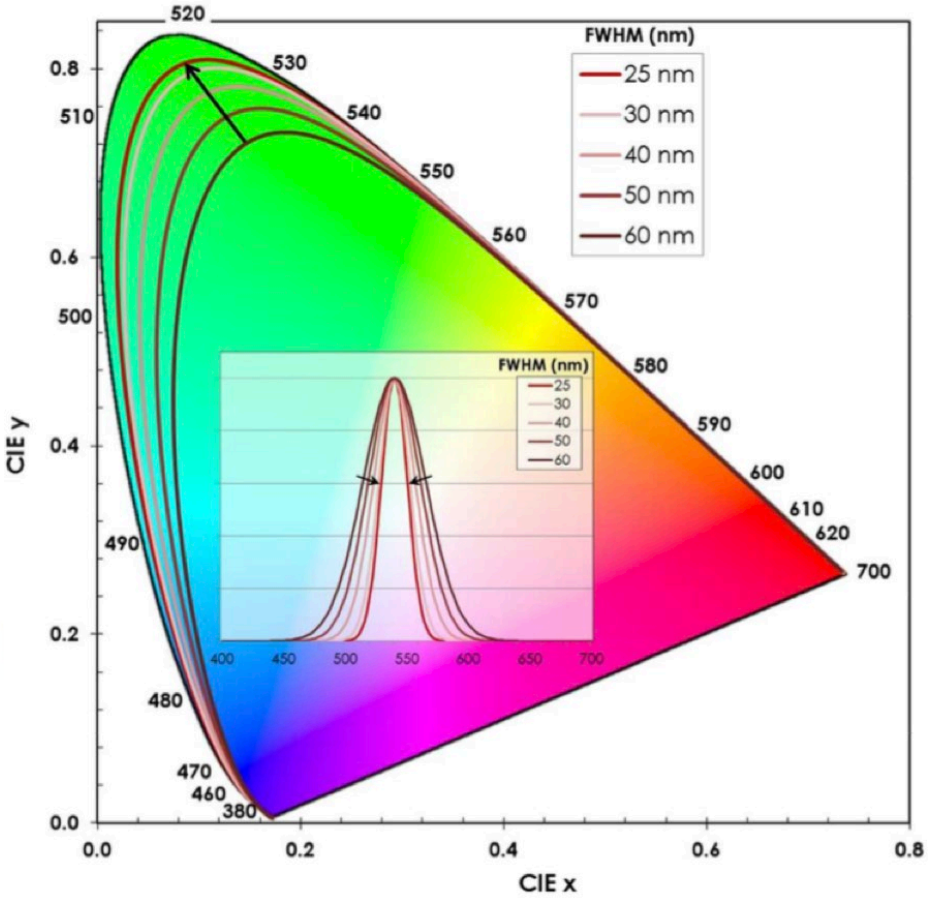
OSRAM/PLT
LED Osconiq S & E (QD)

Developed for Area Lighting & Downlight Applications

QDs for Displays



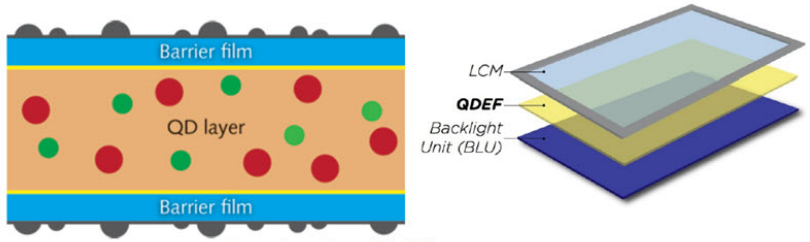




Colloidal Quantum Dot Technology

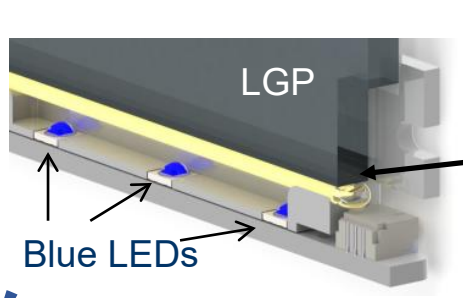
2013

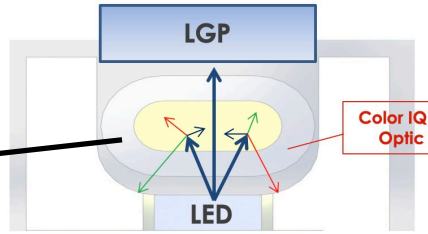
Nanosys/3M QDEF™ QD Film



Source: Laser Focus World, Nanosys

QD Vision Color IQ™ Optic

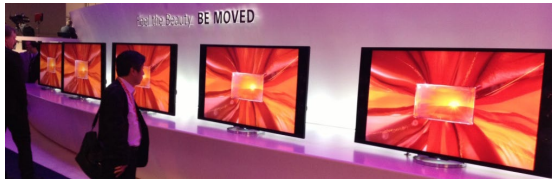




2021

2021 QLED TVs and Monitors: Samsung, LG, HP, Vizio, TCL, Hisense

2013 Amazon's Kindle Fire HDX 7″



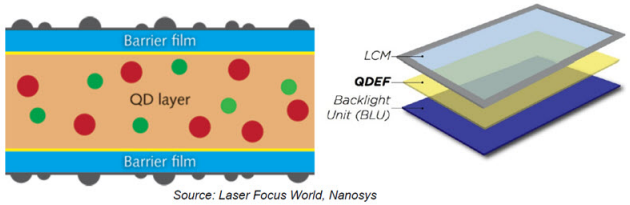
2013 Sony BRAVIA™ TVs:
X9200A, X9000A/X900A, W950A, W900A, W850A

LCD Display Innovation

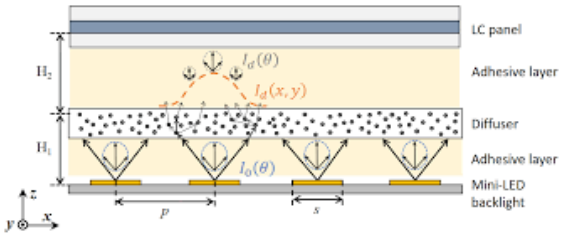
What Has Allowed LCD Displays to Continue to Compete with OLED

- QD Technology = Improved color and light/energy efficiency
- 2D Local Dimming = Improved contrast and HDR
- Cost = LCD display panel manufacturing is very mature

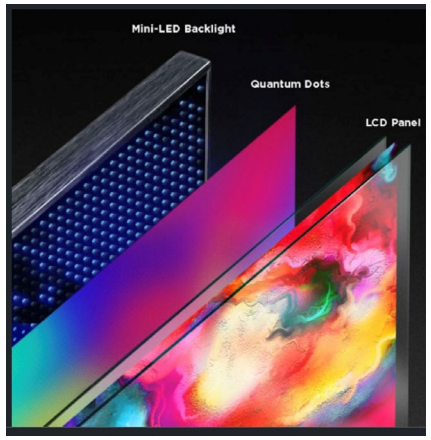
QD Film Technology

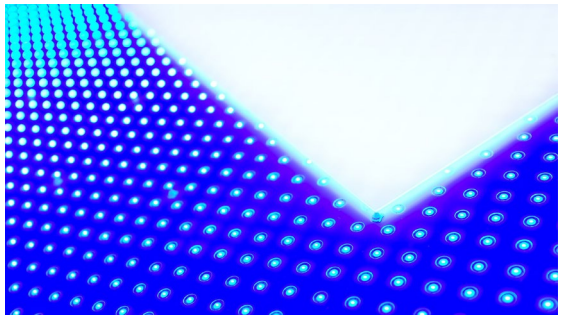


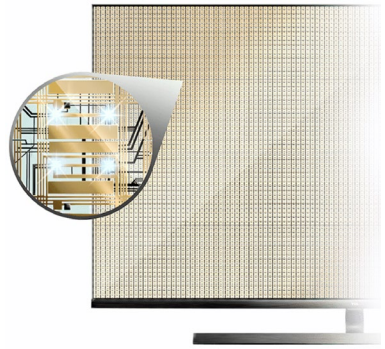
Source: Laser Focus World, Nanosys



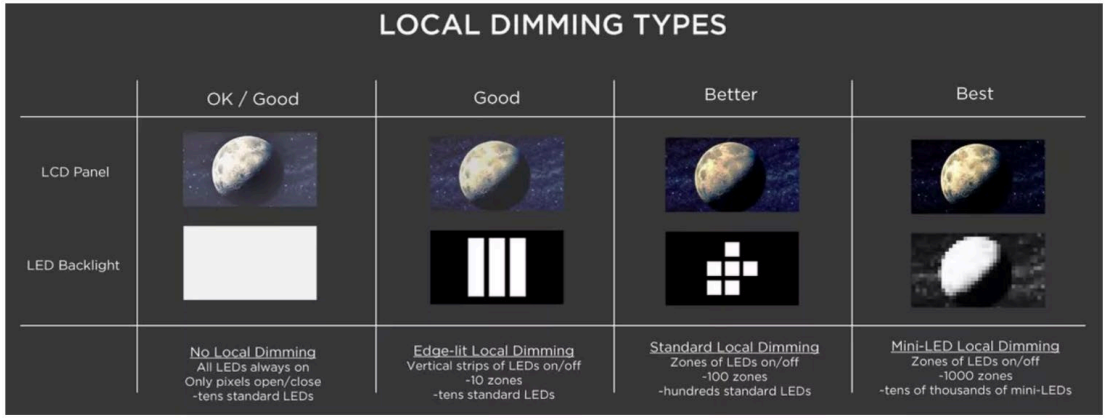
https://www.cnet.com/







Local Dimming Technology



TCL's comparison of LED backlight types using the 8-Series with mini-LED as the "Best" example.

LIGHT-EMITTING DIODE TV TECHNOLOGIES COMPARED

	Standard LED	QLED	OLED	Mini-LED	MicroLED
Size range	15-inch and up	32-inch and up	42-inch and up	55-inch and up	88-inch and up
Typical 65-inch price	$800	$900	$2,000	$1,000	N/A
US TV brands	All	Samsung, TCL	LG, Sony	LG, Samsung, TCL	Samsung
Based on LCD tech	Yes	Yes	No	Yes	No

QD-LCD TVs Projected to Continue to Out-Sell WOLED TVs

Samsung Q900 8K QLED TV
Samsung 49" CRG90 QLED Gaming Monitor

Vizio P-Series Quantum X
Vizio P-Series Quantum
Vizio M-Series Quantum

HP Pavilion 27

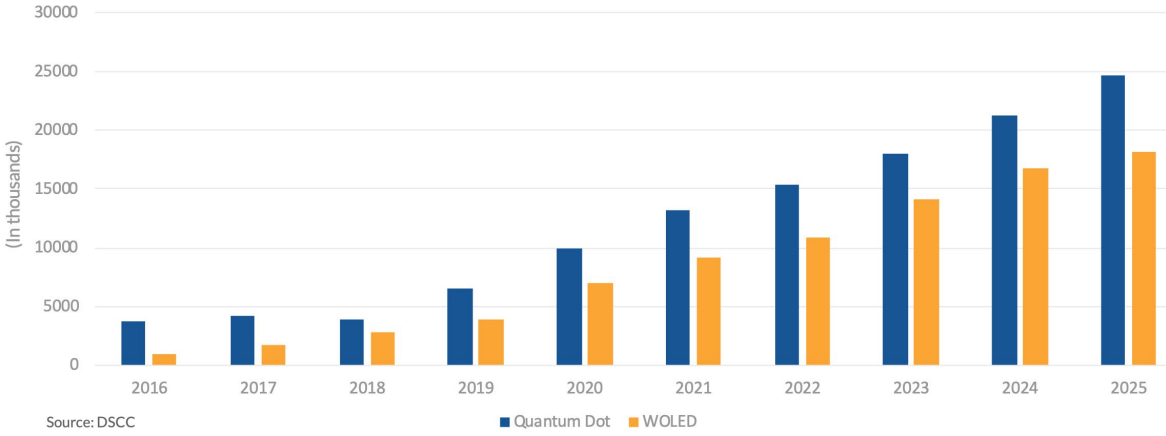
LG QNED MiniLED 99 & 90 Series 75" & 86" 8K TVs

HP Omen X Emperium

Hisense H9F

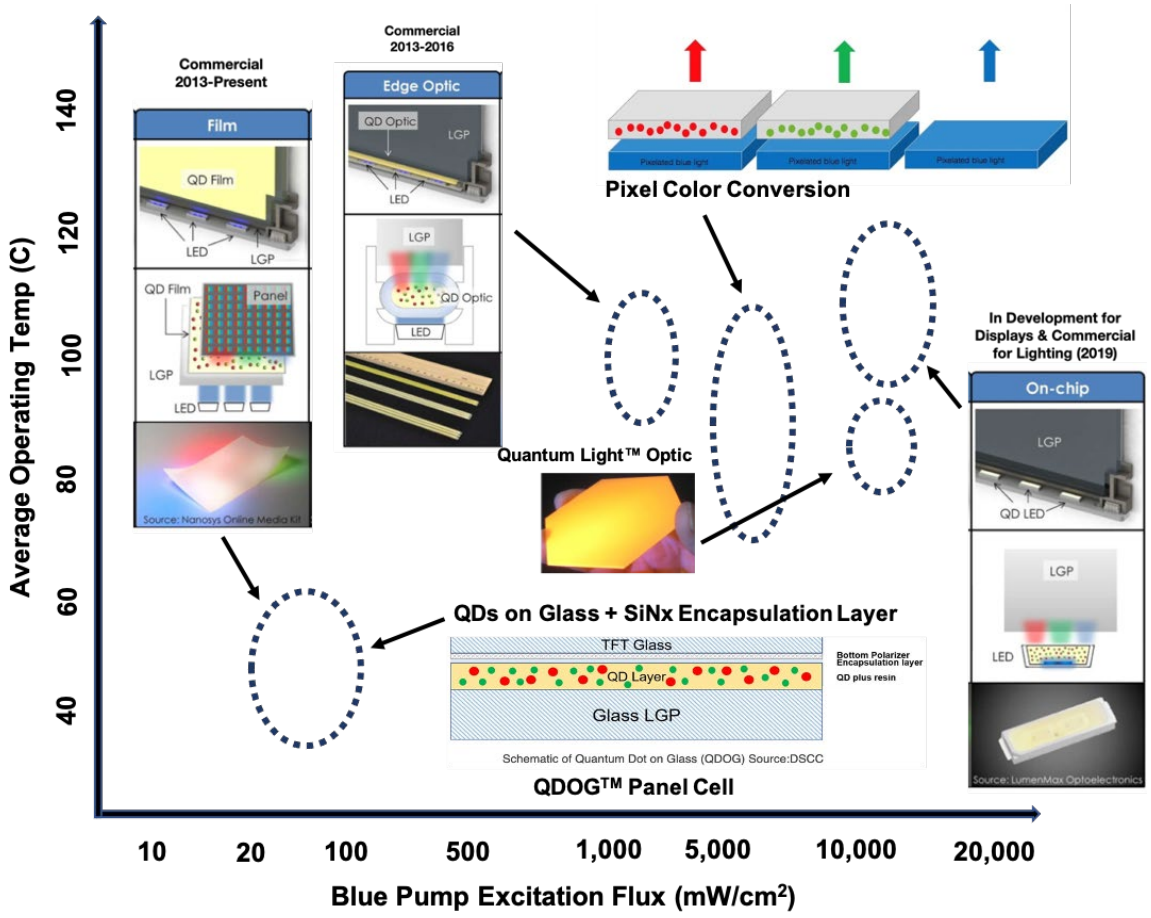
Hisense U9F

TCL X10 8K QLED TV



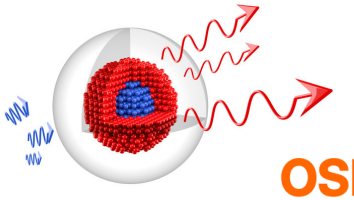
Source: DSCC

QD Integration into Displays and Lighting: Macro-to Nano-Encapsulation



Macro- to Nano-Encapsulation

Nexxus R30 LED Array



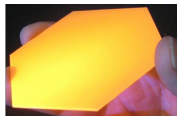
OSRAM
Opto Semiconductors
https://www.osram.com/

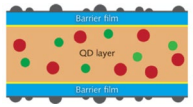
QD Vision's Quantum Light™ Optic
- Macro-encapsulation
- QDs sandwiched between two glass plates

Osram's Osconiq S 3030 QD & Osconiq E 2835
- Special encapsulation technology to protect QDs from moisture and other external influences

2009 → **2021**

Macro-Encapsulated QDs
- Glass & barrier film to protect QDs from oxygen & water





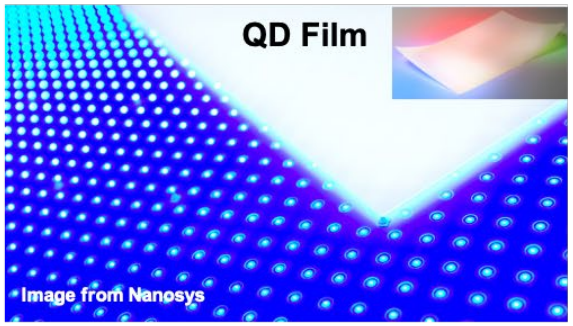
Nano-Encapsulated QDs
- QDs with a protective shell to improve stability towards chemical species, oxygen & water

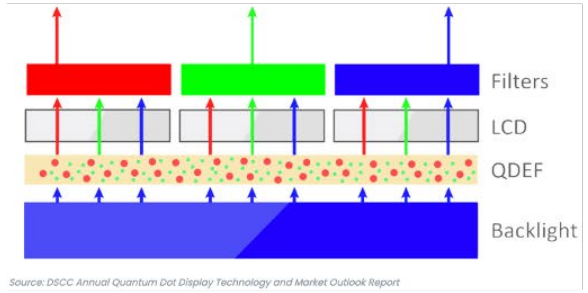
QD Photoluminescent Technology in Displays

Non-Emissive Displays | **Emissive Displays**

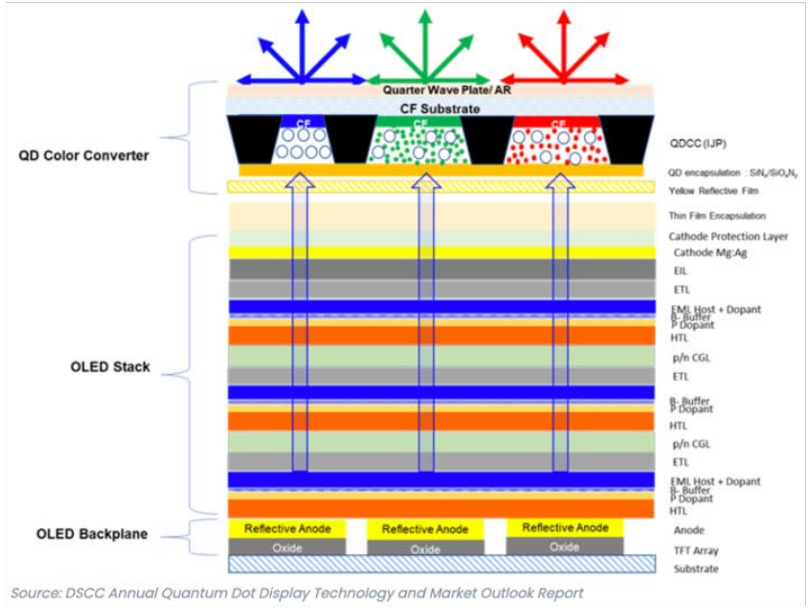
Commercial (2021) → **Very Soon (2022/2023)** → **Near Future (2023+)**

QD Film: LCD BLU's

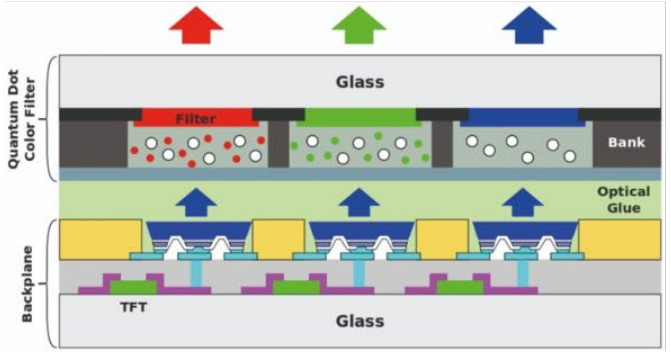




QD Pixel Color Conversion: OLED



QD Pixel Color Conversion: Micro-LED



https://compoundsemiconductor.net/article/111556/Making_MicroLED_Displays_With_A_Fluidic_Assembly_Process/feature

Samsung's QD OLED Structure

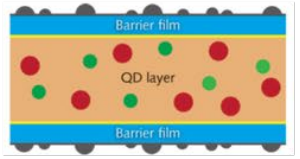
https://www.displaysupplychain.com/blog/dscc-releases-new-annual-quantum-dot-display-technology-and-market-outlook-report

The Evolution of QDs in Displays

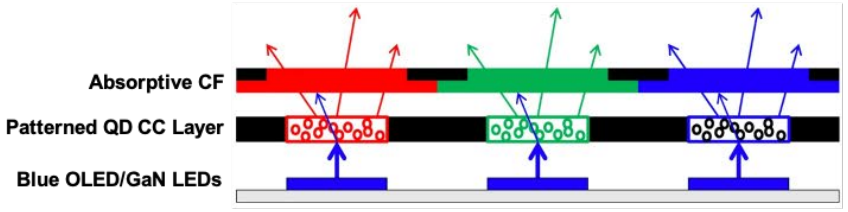
Non-Emissive Displays | **Emissive Displays**

2021 → **Photoluminescence** 2023 → 2025 → **Electroluminescence** 2030 →

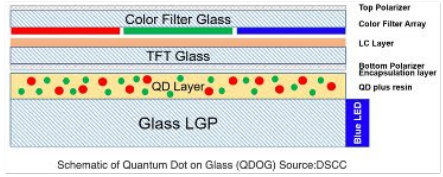
QD Film



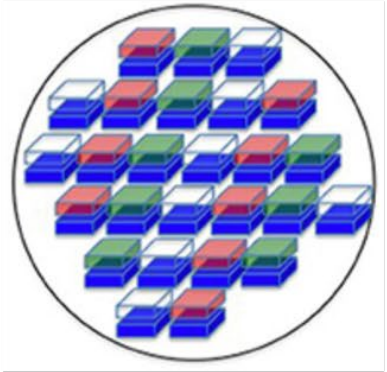
QD Pixel Color Conversion



QDs on Glass

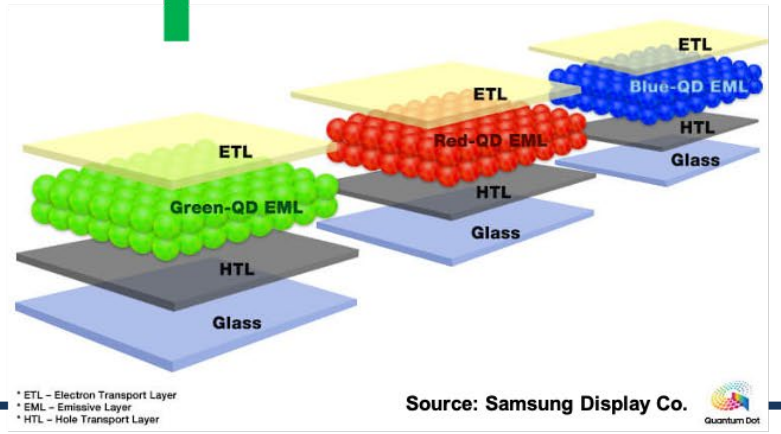


Schematic of Quantum Dot on Glass (QDOG) Source:DSCC



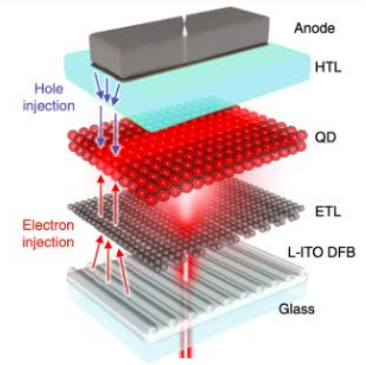
Source: Samsung Newsroom

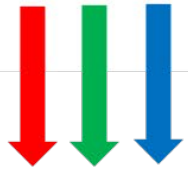
QD-LEDs



Source: Samsung Display Co.

QD-Lasers

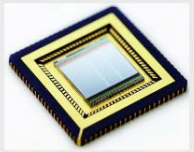


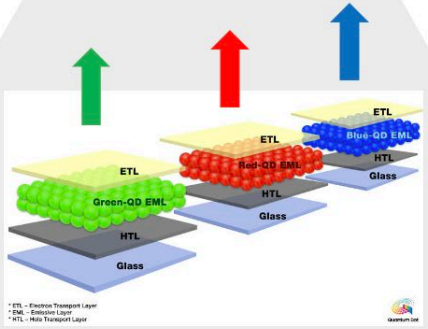


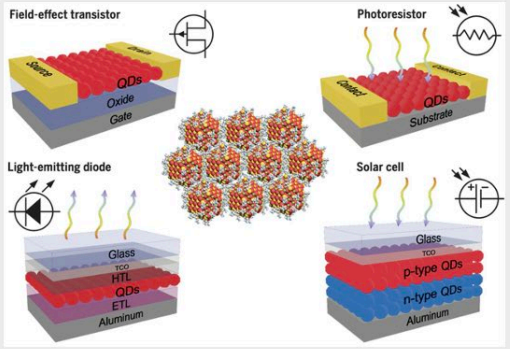
Lasing Emission

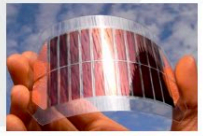
https://www.frontiersin.org/articles/10.3389/fchem.2019.00252/full

Huang, Y., Hsiang, EL., Deng, MY. et al. Mini-LED, Micro-LED and OLED displays: present status and future perspectives. Light Sci Appl 9, 105 (2020) (2020)11:271 | https://doi.org/10.1038/s41467-019-14014-3





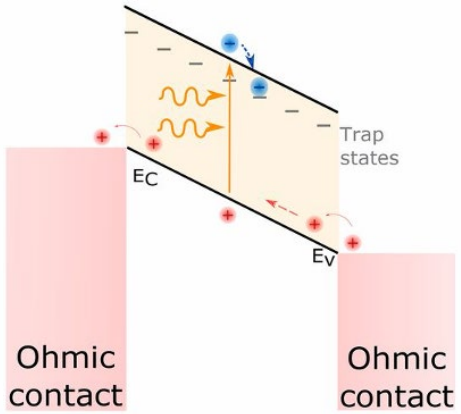




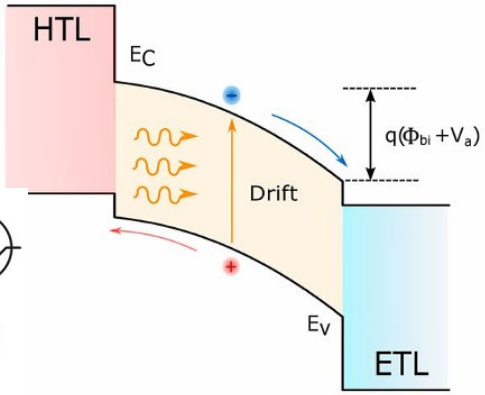
Colloidal QD Optoelectronic Device Technology

QD Optoelectronic Devices Overview

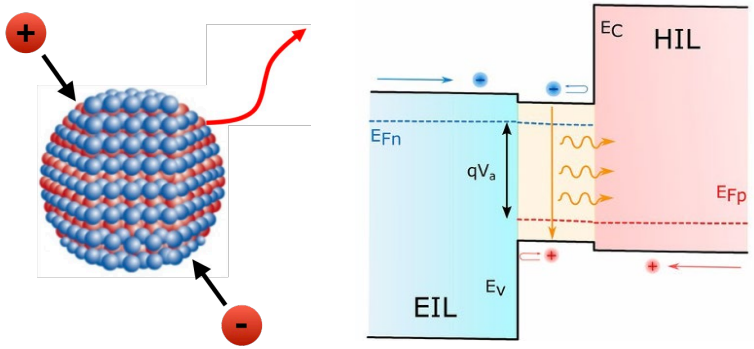
Photoconductors

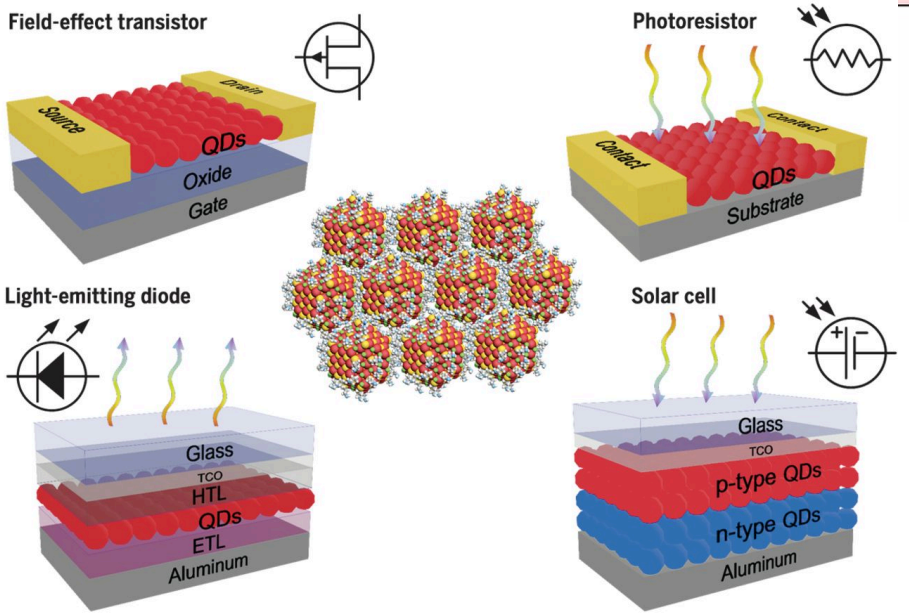


Photodiodes

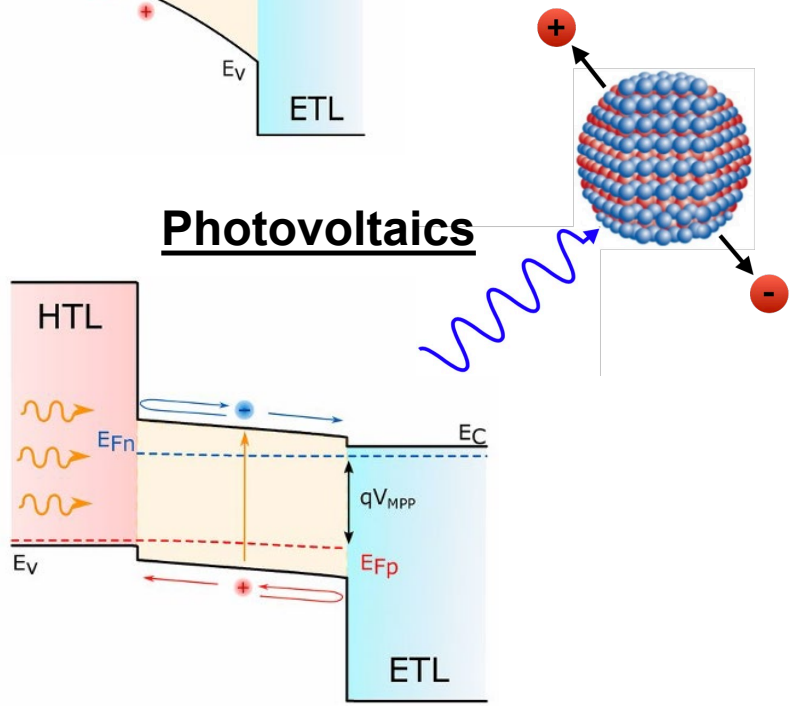


Light-Emitting Devices





Photovoltaics



Building Devices from Colloidal Quantum Dots, Cherie R. Kagan, Efrat Lifshitz, Edward H. Sargent, Dmitri V. Talapin; *Science* 26 Aug 2016, Vol. 353, Issue 6302; DOI: 10.1126/science.aac5523

The Commercialization of QD Optoelectronic Devices

2018-2021 → 2023 → 2025 → 2027 → 2030

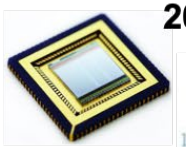
QD Image Sensors

2018

SWIR VISION SYSTEMS

2021

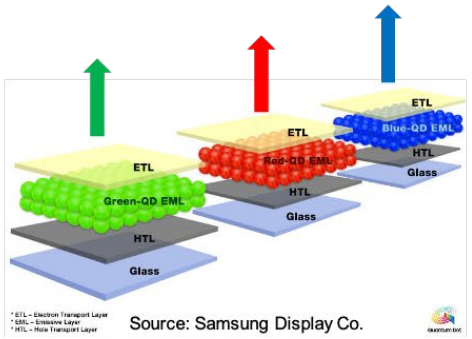
EMBERION



2021

life.augmented

QD-LEDs for Displays

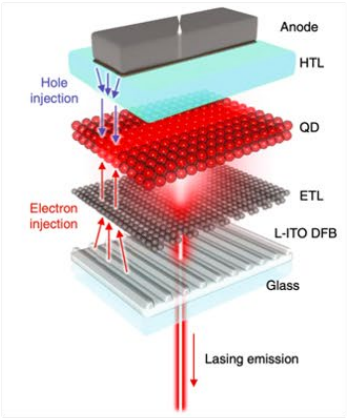


Source: Samsung Display Co.

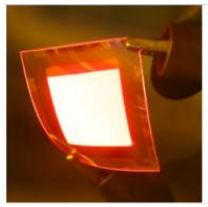
QD-LEDs for Lighting

H. Chen, et al. SID Symp. Dig. Tech. Pap. 47, 50-52 (2016)

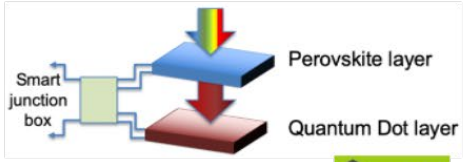
Electrically Pumped QD Lasing



QD-LEDs for Photomedicine

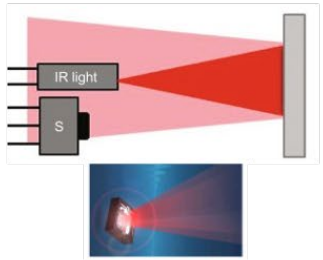


QD Solar Cells



QD Solar
Harvesting the Sun

QD-LEDs for Active Sensing

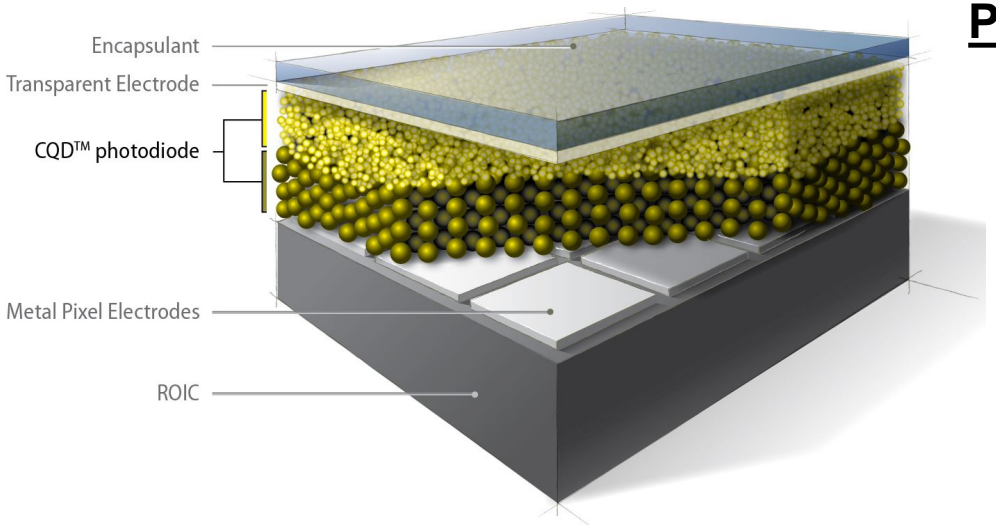


https://doi.org/10.1038/s41467-019-14014-3

Chen, H. et al. “Quantum dot light emitting devices for photomedical applications” Journal of the Society for Information Display 25 3 (2017): 177-184

The Two Types of QD Image Sensors

QD Vertical Stack Image Sensor Technology



Photodiode

Leveraging this Approach:

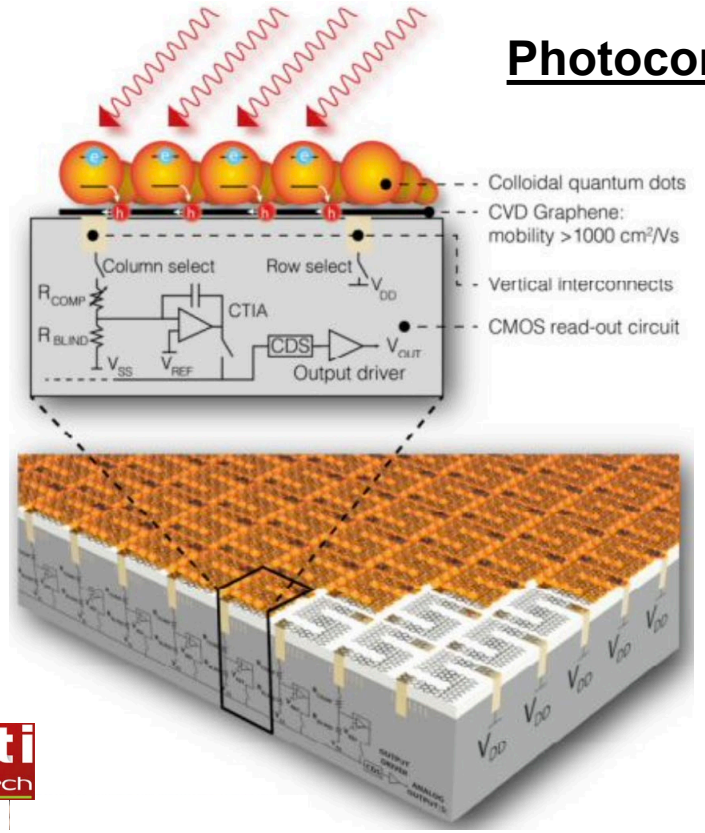
SWIR VISION SYSTEMS

life.augmented

imec

QD-Graphene Image Sensor Technology

Photoconductor



Leveraging this Approach:

EMBERION

qurv

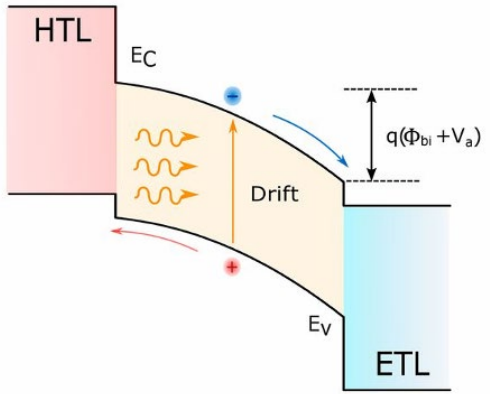
leti ceatech

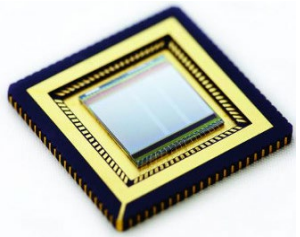
http://image-sensors-world.blogspot.com/2018/11/quantum-dot-swir-cameras.html

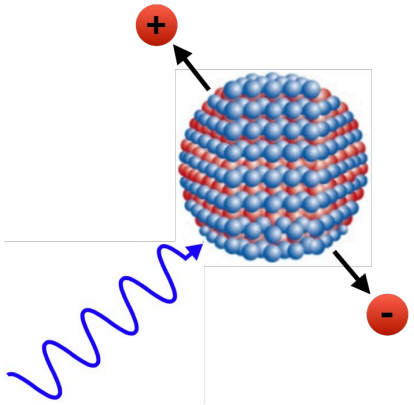
https://image-sensors-world.blogspot.com/2017/01/worlds-first-graphene-integration-onto.html

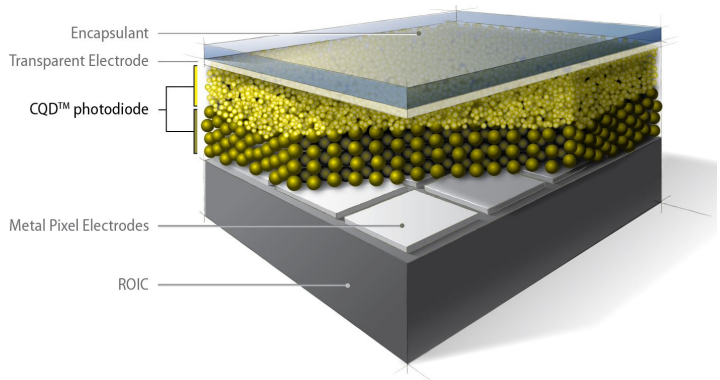
Strong Synergy Between QD Sensors & QD Photovoltaics

QD Photodiodes



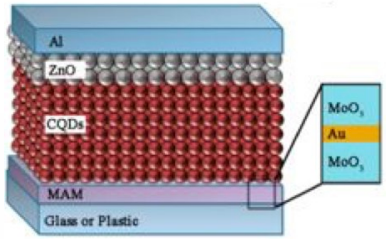


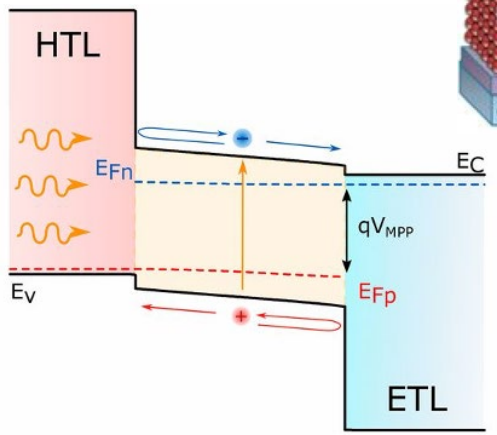


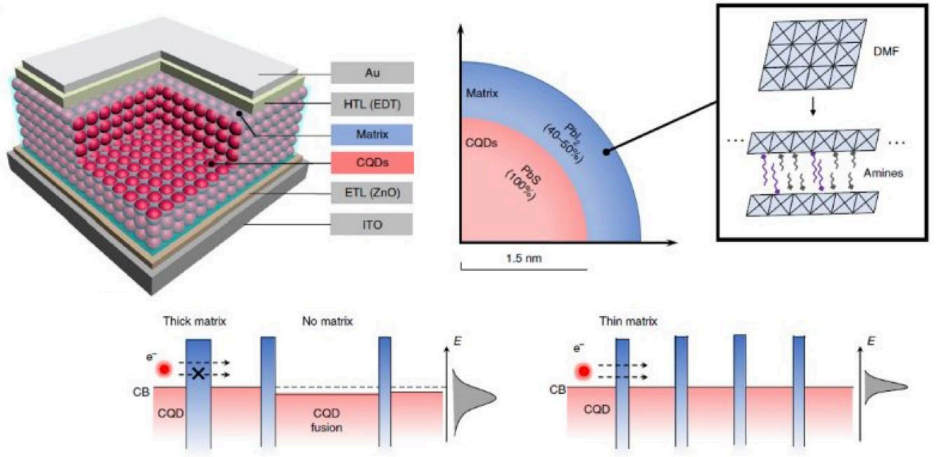


QD Vertical Stack Image Sensor Technology

QD Photovoltaics



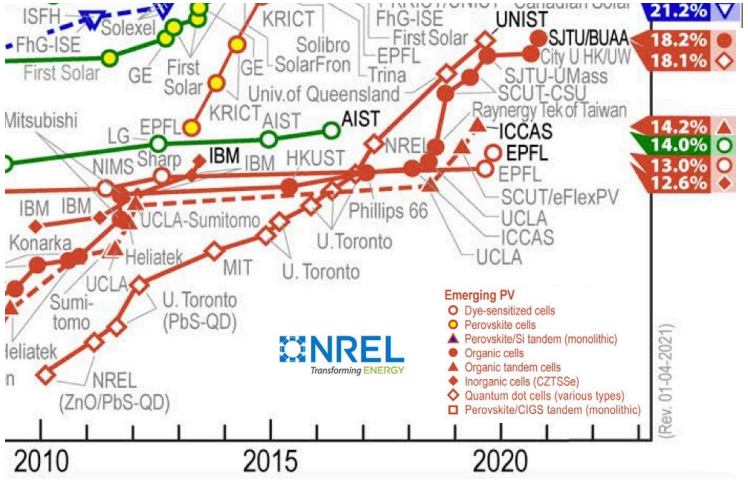




http://image-sensors-world.blogspot.com/2018/11/quantum-dot-swir-cameras.html

Nat Energy 5, 79–88 (2020). https://doi.org/10.1038/s41560-019-0535-7

State-of-the-Art QD Photovoltaic Devices



Best NREL Certified QD Research Cell Efficiencies

Materials		PCE
Pb based QD	PbS CQD	12.1%
	$CSPbI_3$	14.1%
Non-toxic QD	InZnP	1.2%
	$AgBiS_2$	6.3%
	$CuInS_2$	1.2%

→ 13.8%

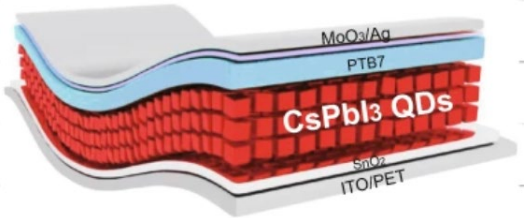
→ 18.1%

Energy Environ. Sci., 2020,13, 404-431

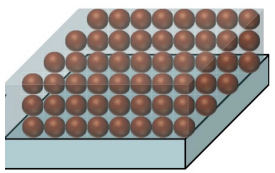
Published Year	PCE (%)	Reference (Type of Active Layer)
2008	2.1	PbSe [19]
2009	3.4	PbSe [20]
2010	2.9~5.1	PbS [21-23]
2011	5.1~5.7	PbS [24-27]
2012	5.4~7.4	PbS [28-31]
2013	7.3~8.4	PbS [32-34]
2014	6.1~8.6	PbS [35-38]
2015	7.3~9.0	PbS [39-41]
2016	9.0~10.6	PbS [12, 42-46], $CsPbI_3$ [47]
2017	10.4~11.6	PbS [48-53], $CsPbI_3$ [54]
2018	10.6~12.5	PbS [2, 55-62], $CsPbI_3$ [63, 64]
2019	10.4~16.6	PbS [65], $CsPbI_3$ [66, 67], Etc.[18]

Energy Environ. Sci., 2020,13, 404-431

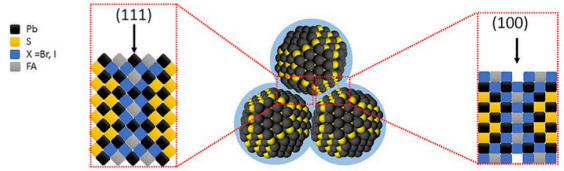
$CsPbI_3$ QD Solar Cells



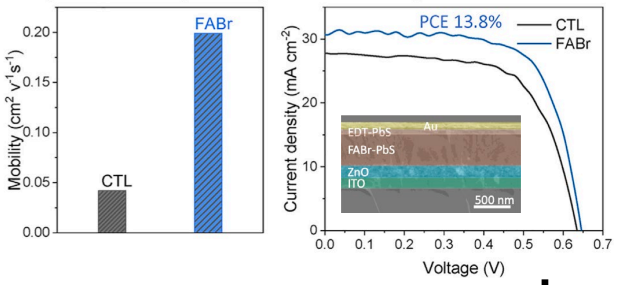
https://doi.org/10.1038/s41467-020-20749-1



Perovskite monolayer bridged quantum dots



Improved mobility and improved solar cell performance



https://doi.org/10.1016/j.joule.2020.05.011

PbS QDs NREL 3-4% — 2010

PbS QDs U. Toronto 4-6% — 2011

PbS QDs MIT 8% — 2012

PbS QDs U. Toronto 10-12% — 2013

$CsPbI_3$ QDs NREL 13.4% — 2014

$CsPbI_3$ QDs U. Queensland 16.6% — 2015

$CsPbI_3$ QDs UNIST 18.1% — 2016

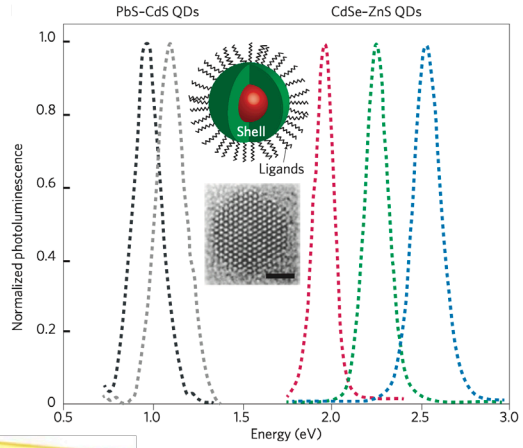
PbS QDs U. Toronto 13.8% — 2017

2018 2019 2020

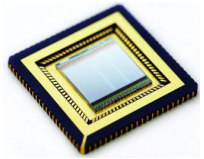
Nat Energy 5, 79–88 (2020). https://doi.org/10.1038/s41560-019-0535-7

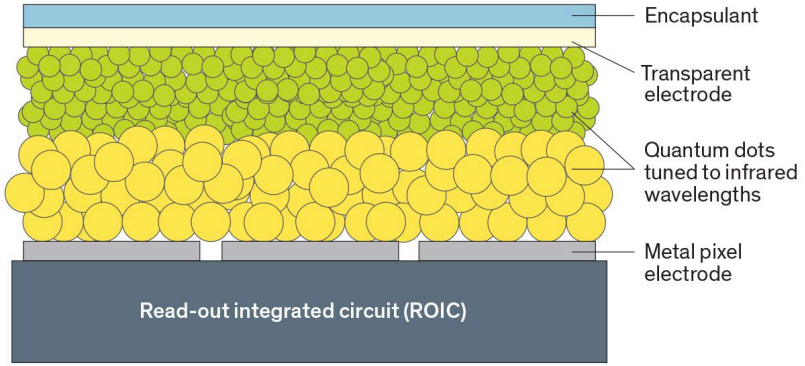
QD Sensors Will Help Drive The Commercialization of QD-LEDs

- **QD image sensors are the first commercial QD optoelectronic devices**
  - Solving new problems that do not exist in QD photoluminescence products
  - Uniting QD solution-based processing with traditional semiconductor wafer processing at scale
    1. Trace metal contamination in solutions
    2. Changing materials chemistry at QDs/semiconductor interfaces during device operation
    3. QD ligand, QD film, and QD device stack engineering



QD Image Sensors



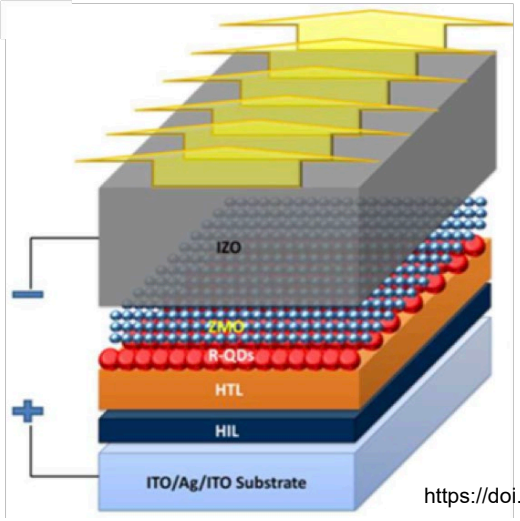


https://spectrum.ieee.org/consumer-electronics/audiovideo/move-over-cmos-here-come-snapshots-by-quantum-dots

QD Image Sensor Engineering Strategies and Know-How is Directly Applicable to QD-LEDs

2021 → **2025**

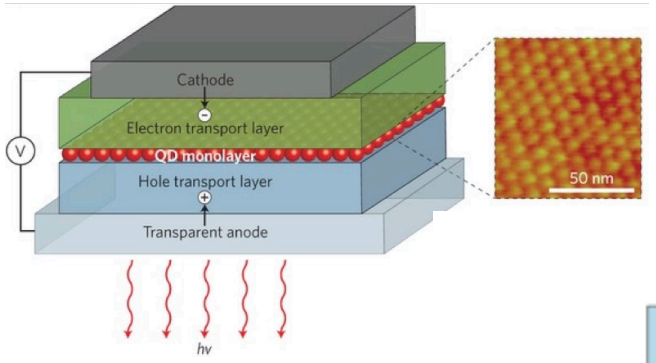
QD-LEDs

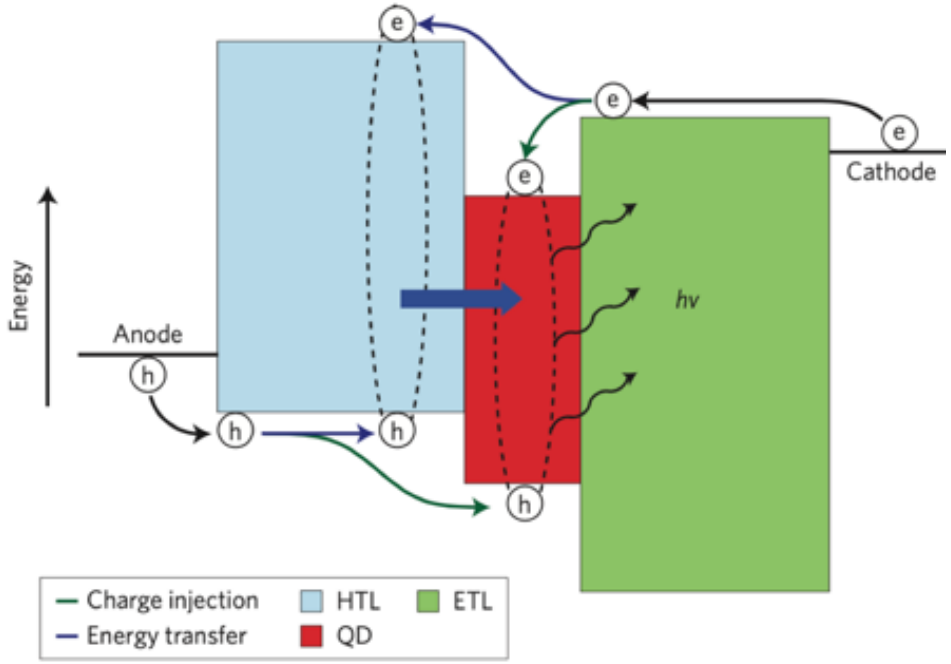


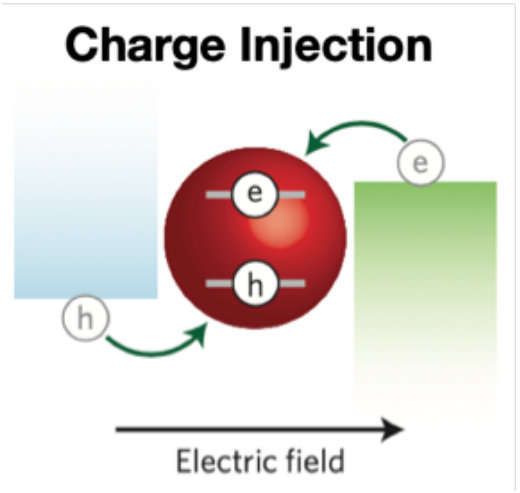
https://doi.org/10.3390/nano9111639

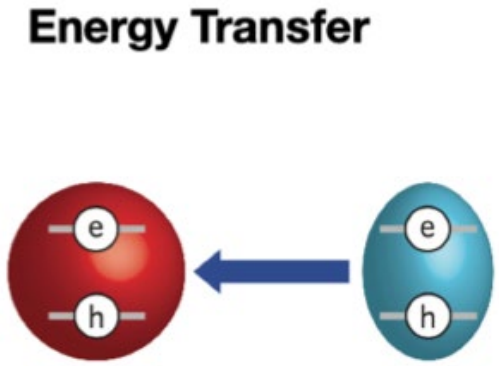
Shirasaki, Y., Supran, G., Bawendi, M. et al. Emergence of colloidal quantum-dot light-emitting technologies. Nature Photon 7, 13–23 (2013). https://doi.org/10.1038/nphoton.2012.328

QD-LEDs: QD Electroluminescence Excitation Mechanisms







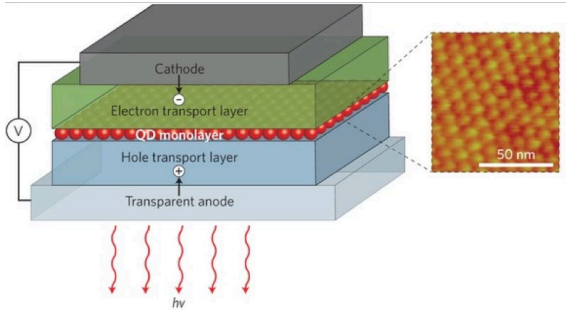


Shirasaki, Y., Supran, G., Bawendi, M. et al. Emergence of colloidal quantum-dot light-emitting technologies. Nature Photon 7, 13–23 (2013). https://doi.org/10.1038/nphoton.2012.328

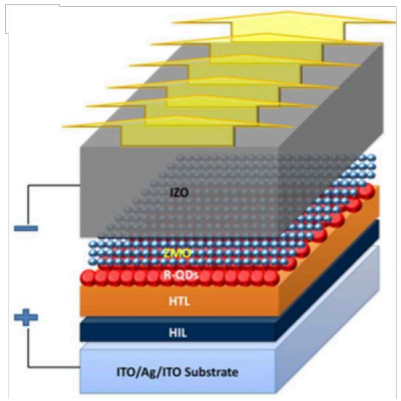
QD-LEDs: Device Stacks and Efficiency

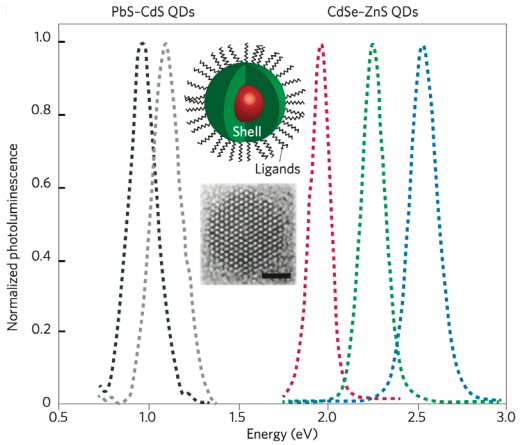
Device Structures

Bottom Emission (BE)



Top Emission (TE)



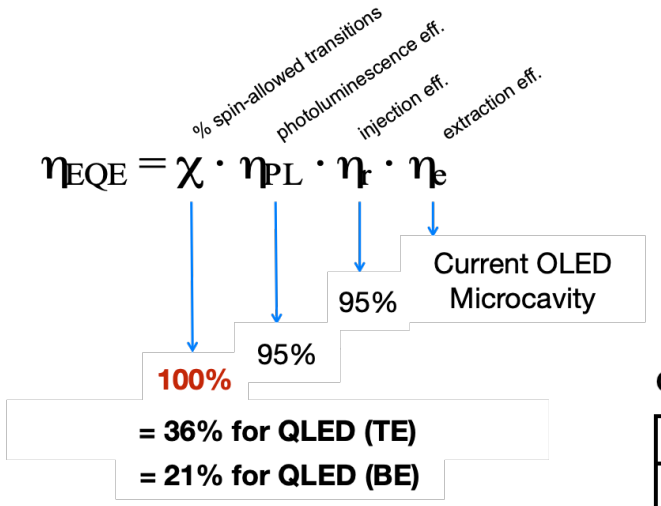


- **Visible: All the Pros of OLED with None of the Cons**
- **IR: Cheap, Tunable, Large Area**

Efficiency

100% Spin-Allowed Transitions for QDs

- **<25 meV energetic separation for the "bright" (spin-allowed) and "dark" (spin-forbidden) band-edge excitonic states**
- **Thermal mixing at RT = efficient crossing of excitons from dark states to higher energy bright states**



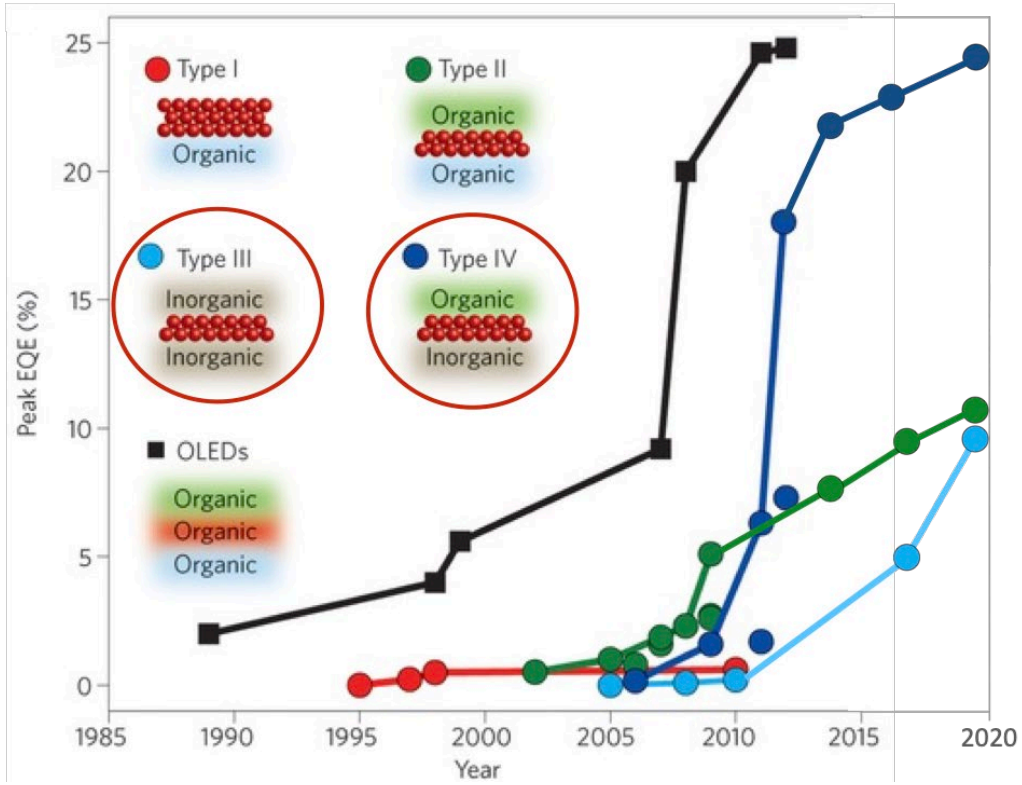
Current State-of-the-Art BE QD-LED Efficiency

QD Material	Bottom Emission
CdSe Red & Green	>20%
CdZnS Blue	**>20 %**
InP Red & Green	15-20%
ZnSe Blue	**15-20%**

https://doi.org/10.3390/nano9111639
https://doi.org/10.1038/s41566-020-00732-4

QD-LED Efficiency Progress Overtime

QD-LED Peak Efficiency Evolution

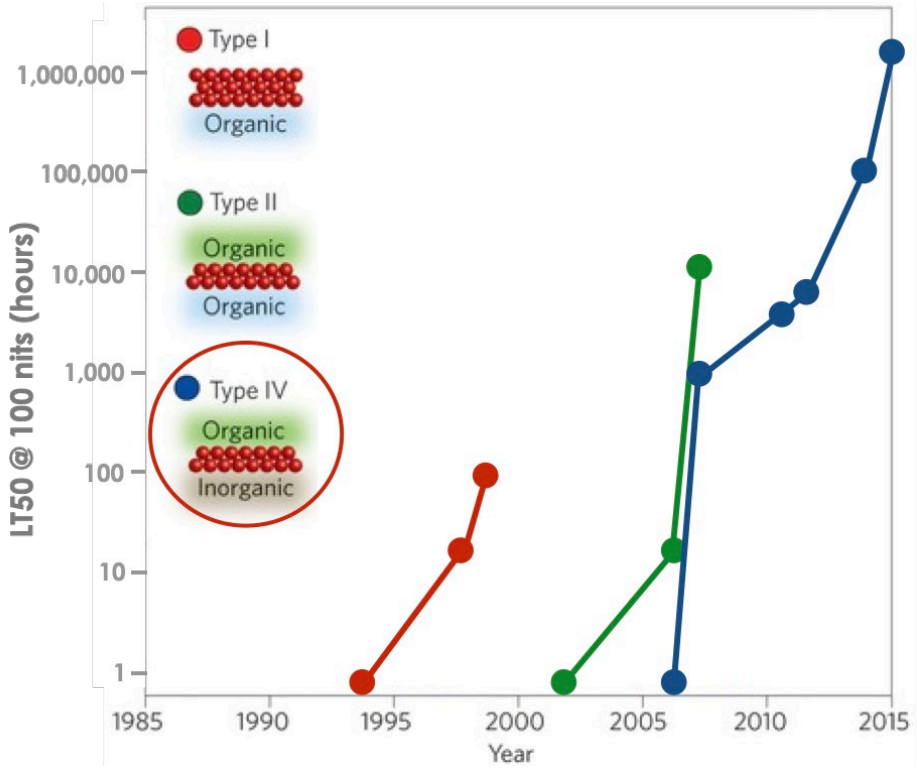


State-of-The-Art QD-LED Peak Efficiencies

Color	Cd-QD Peak EQE	Cd-Free QD Peak EQE
Red	>20%	>20%
Green	>20%	>15%
Blue	>20%	>15%

QD-LED Lifetime Progress Overtime

QD-LED Lifetime Evolution

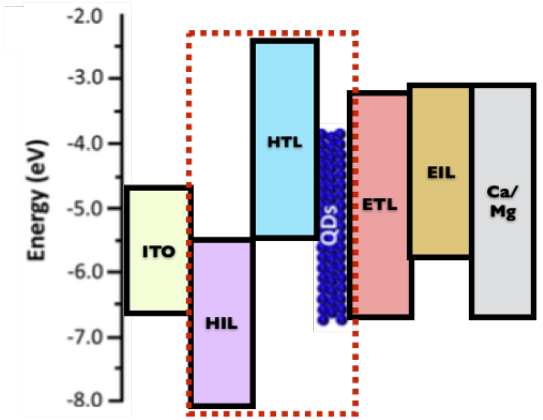


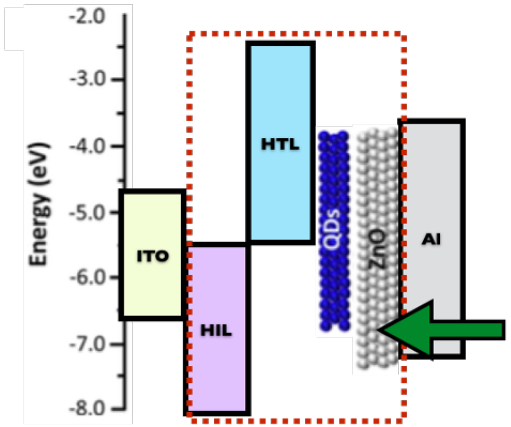
State-of-The-Art QD-LED Lifetimes

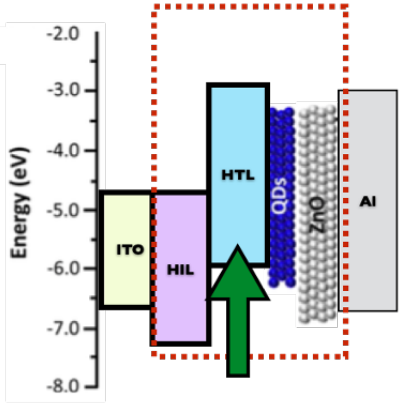
Color	Cd-QD Lifetime	Cd-Free QD Lifetime
Red	LT95 >10,000 hrs	LT95 >1,000 hrs
Green	LT95 >10,000 hrs	LT95 >500 hrs
Blue	LT95 >100 hrs	LT95 >10 hrs

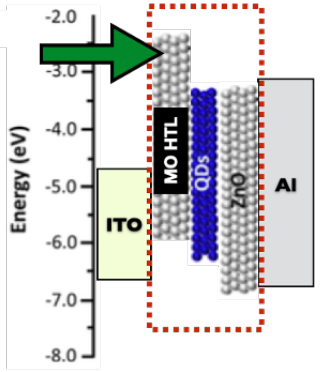
QD-LED Device Architecture Evolution

Early Architectures → **Most Mature Architecture** → **Advanced Architectures**









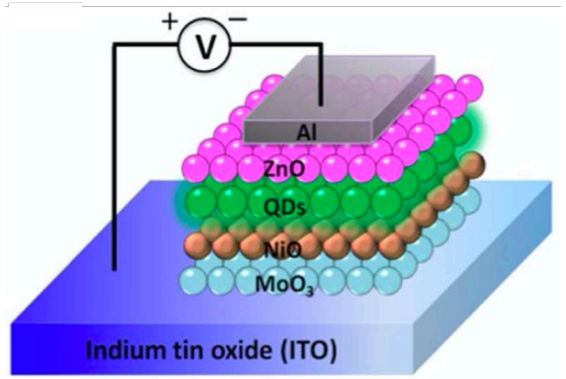
Early Architectures
- QDs surrounded by organics
- <10% EQE
- Very short lifetimes

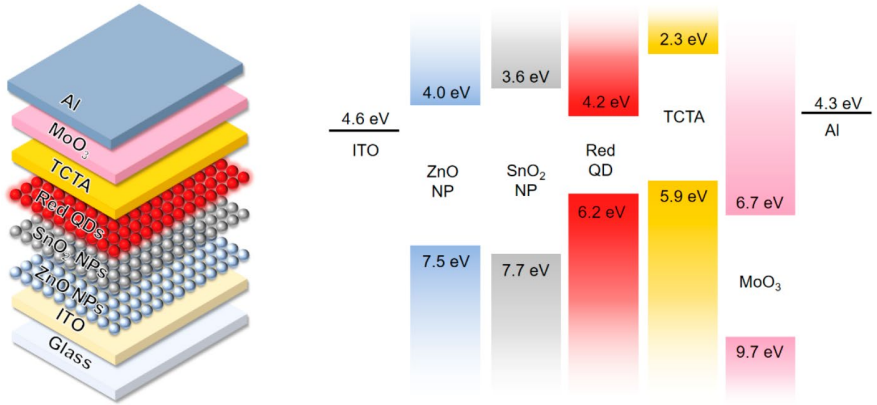
Current Architectures
- Introduction of ZnO NP ETL's
- >20% EQE
- >10x lifetime improvements

New Architectures
- Introduction of metal oxide NP HTL's and deeper HOMO organic HTL's
- Introduction of improved QD EML's
- Partial self encapsulation for enhanced resistivity toward oxygen and water

Solution Processed Layers

All-Inorganic QD-LED Device Stacks

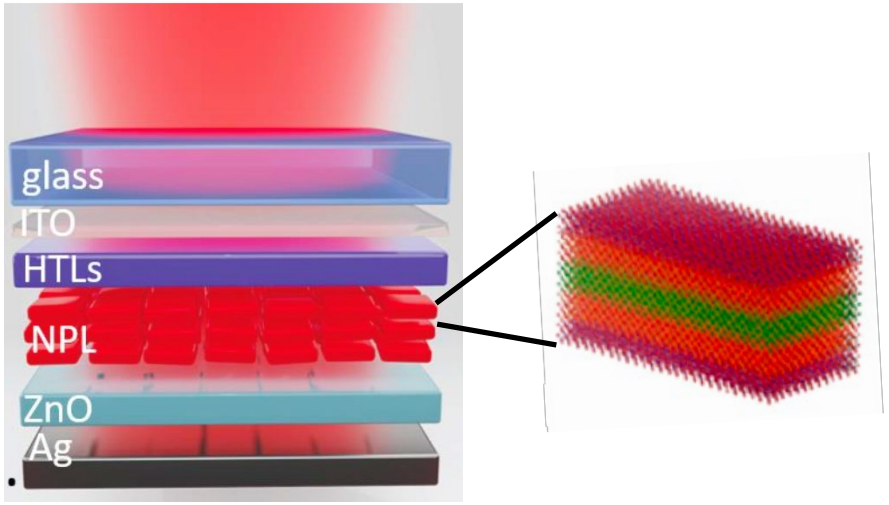


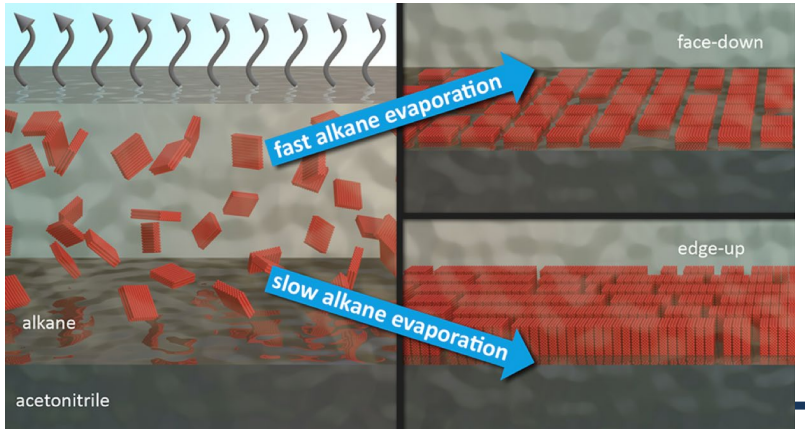


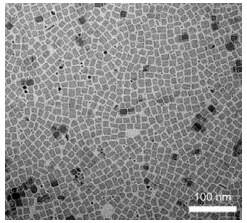
All-Inorganic QD-LED Architectures

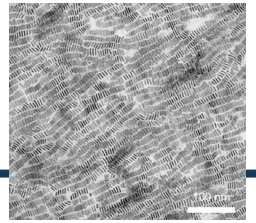
- High brightness (ability to support large current densities)
- Better lifetime
- Partial self-encapsulation for enhanced resistivity toward oxygen and water (reduced encapsulation requirements)
- More robust to solution processing and patterning in air
- More chemical and temperature resistant than organics

Colloidal Quantum Dot Technology





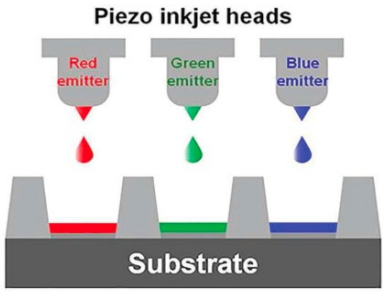




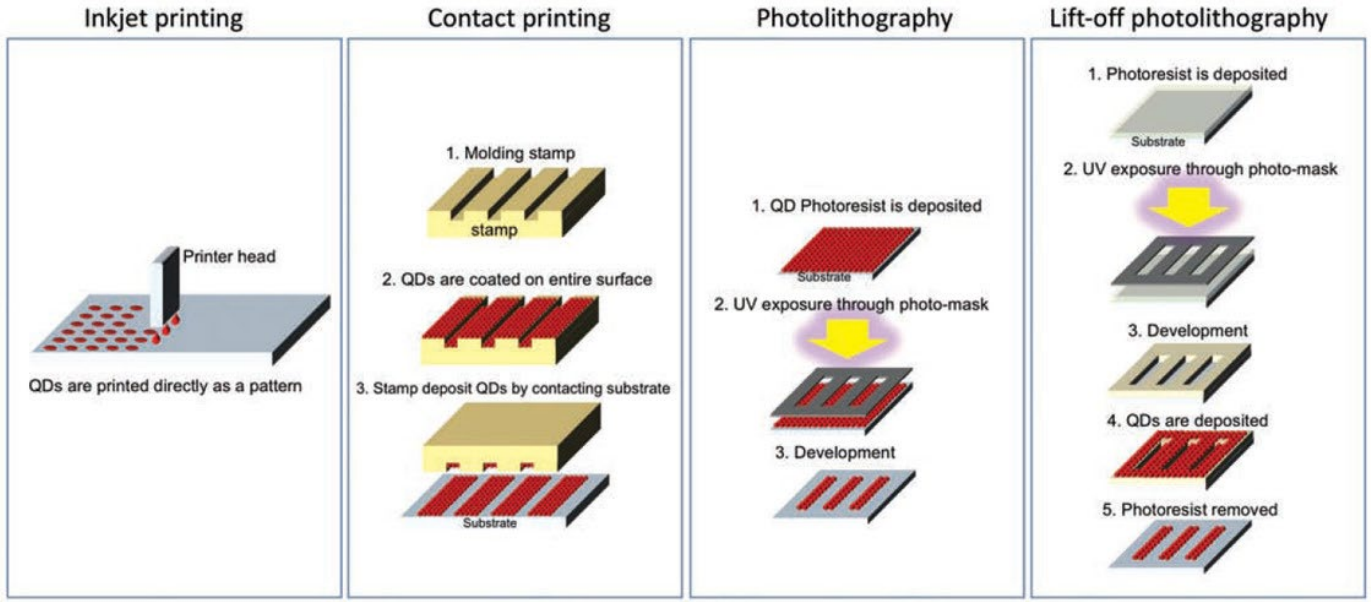
1. **Optical anisotropy improves light outcoupling**
   - Outcoupling of in-plane dipoles is 50% greater than isotropic dipoles
2. **Polarized light emission when aligned**
3. **No Auger recombination**
   - Excess injected charge will not quench emission
4. **No blinking**
   - “Always on” particles
5. **Ultra-narrow emission**
   - < 20nm FWHM
6. **Can “excite” much harder due to density of states**
   - Single-exciton and bi-excition emission is 100%
7. **Better suited to tune shell material to optimize charge injection and band alignment**
   - 20% core lattice expansion tolerated for shelling

https://dx.doi.org/10.1021/acs.nanolett.9b05270
ACS Appl. Mater. Interfaces 2020, 12, 19, 22058–22065

QD-LED Patterning Technology Overview



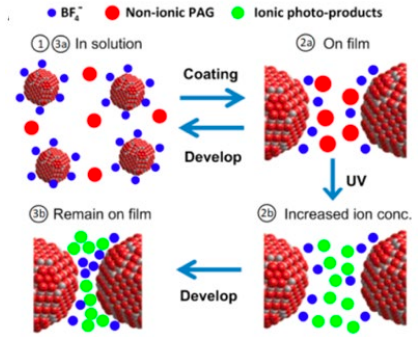
QD Solution Inkjet Printing



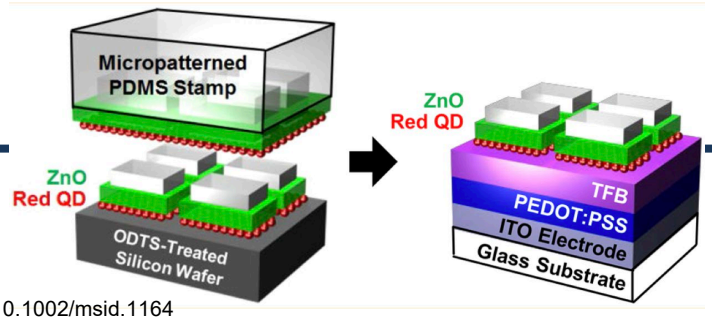
- **Most mature for RGB QD-LED displays**
- **Resolution limited**
- **Promising for large displays**

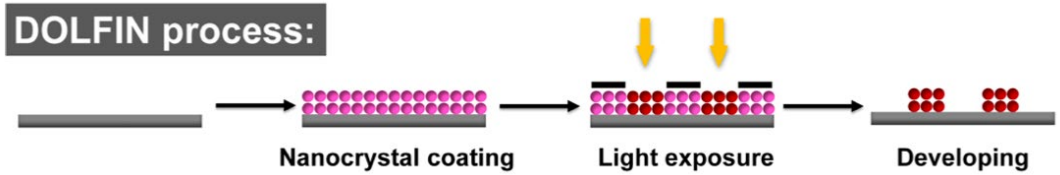
- **Very promising**
- **Early stage in maturity**

- **QD materials will likely prove to be more robust and compatible with these processes vs. OLED materials**



Multilayer Transfer Printing



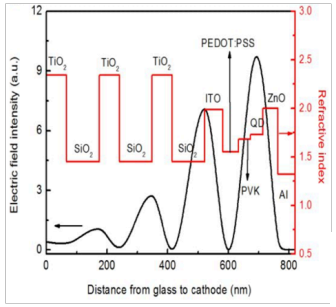


Direct Optical Lithography QD Patterning

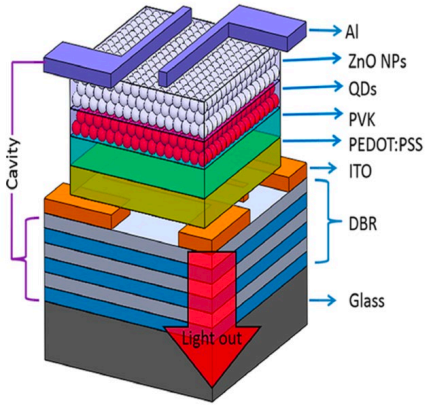
https://doi.org/10.1002/msid.1164
ACS Nano 2016, 10, 4920−4925
DOI: 10.1021/acsnano.5b06387
Adv. Mater. 2020, 2003805
DOI: 10.1002/adma.202003805

Electrically Pumped Colloidal QD Lasing

RI and standing wave electric field distribution in a conventional λ/2 red micro cavity QLED

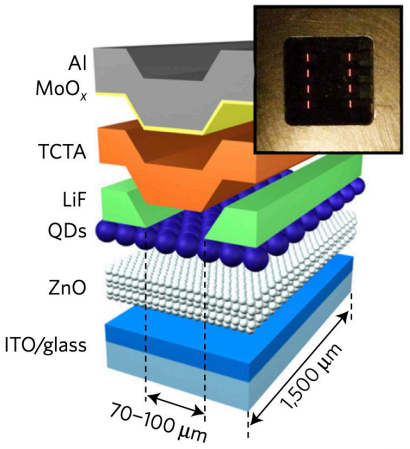


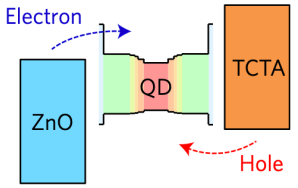
Strong Micro-Cavity QD-LEDs

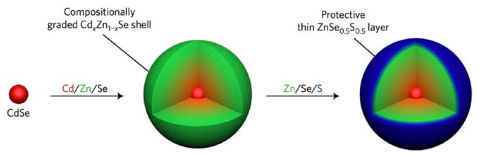


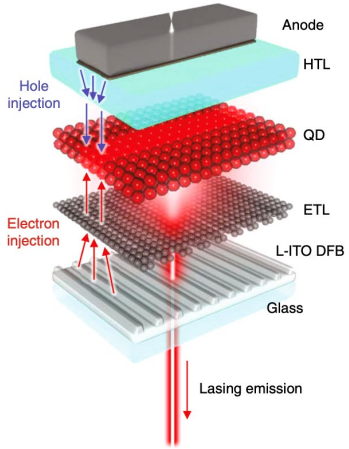
- **QD-Lasers will revolutionize the field of laser-based opto-electronics in the 2030's**

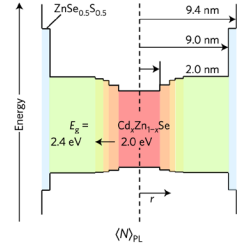
Electrically Pumped QD-Lasers



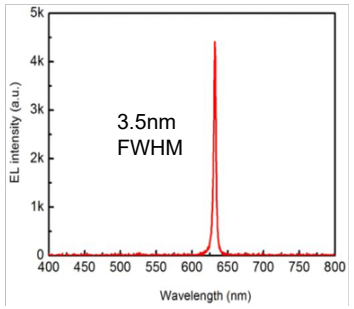






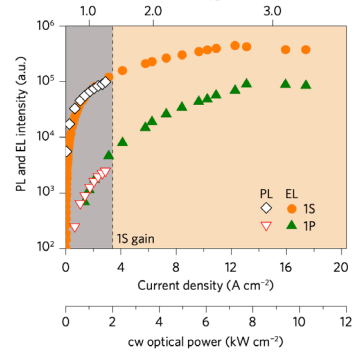


EL Spectrum with a Q Value of 180



- **QD laser fabrication has very challenging requirements that will be overcome in this decade**

1. The active light-amplifying medium
2. The pump mechanisms
3. The need for a high-quality feedback structure or optical cavity



ACS Appl. Nano Mater. 2020, 3, 5301−5310; https://dx.doi.org/10.1021/acsanm.0c00695
https://doi.org/10.1038/s41427-019-0141-y
https://doi.org/10.1038/s41467-019-14014-3
https://doi.org/ 10.1038/nmat5011

Thank You!