Quantum dots: tiny materials whose properties are determined by their size

Lecture Series on Nobel Prizes 2023

January, 2024

Presented by

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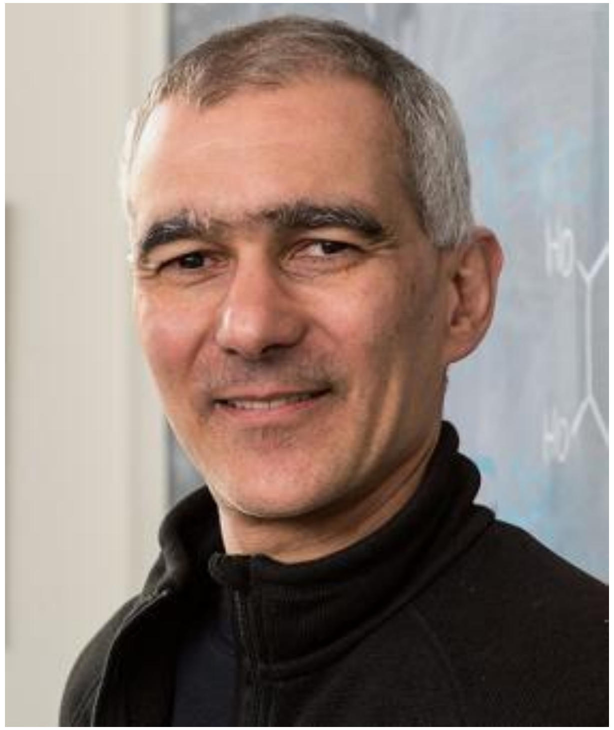
The Nobel Prize in Chemistry 2023

- The Nobel Prize in Chemistry 2023 was awarded to Moungi G. Bawendi, Louis E. Brus and Aleksey Yekimov "for the discovery and synthesis of quantum dots"



Prof. Moungi Bawendi
Massachusetts Institute of Technology

Prof. Louis E. Brus
Columbia University

Prof. Alexei Ekimov
Vavilov State Optical Institute

Presentation Outline

- Introduction to QDs
  - What are QDs and why are they so special
  - Basic theoretical background
- Discovery and synthesis of QDs
  - A chronological description of the challenges and milestones

1981
First observation of QDs
Prof. Alexei Ekimov

1983
First observation band gap as function of size
Prof. Louis Brus

1993
Development of a synthetic protocol to prepare high quality and consistent size
Prof. Moungi G. Bawendi

- Recent developments, challenges and future perspective
  - Applications in QLEDs and imaging
  - Single photon source and blinking

Introduction to QDs

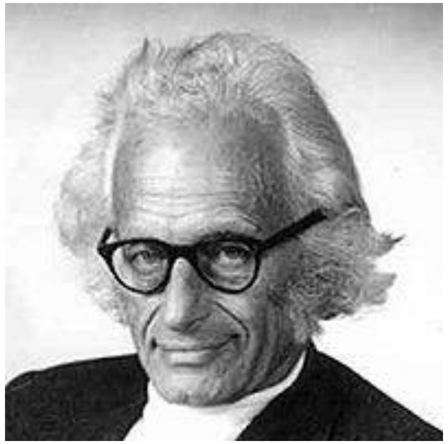
❖ Typically, properties of matter are defined by the atoms they are made of

Green dye

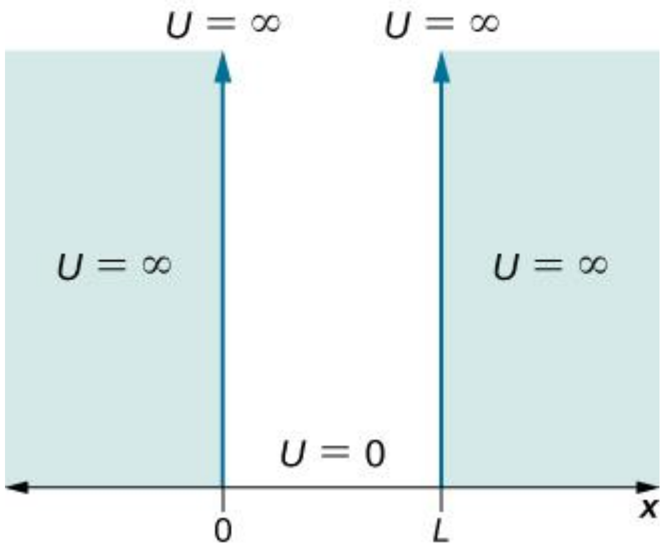
Red dye

Introduction to QDs

1937: Herbert Froehlich predicted that once particles were small enough—so-called nanoparticles—they would come under the strange spell of quantum mechanics



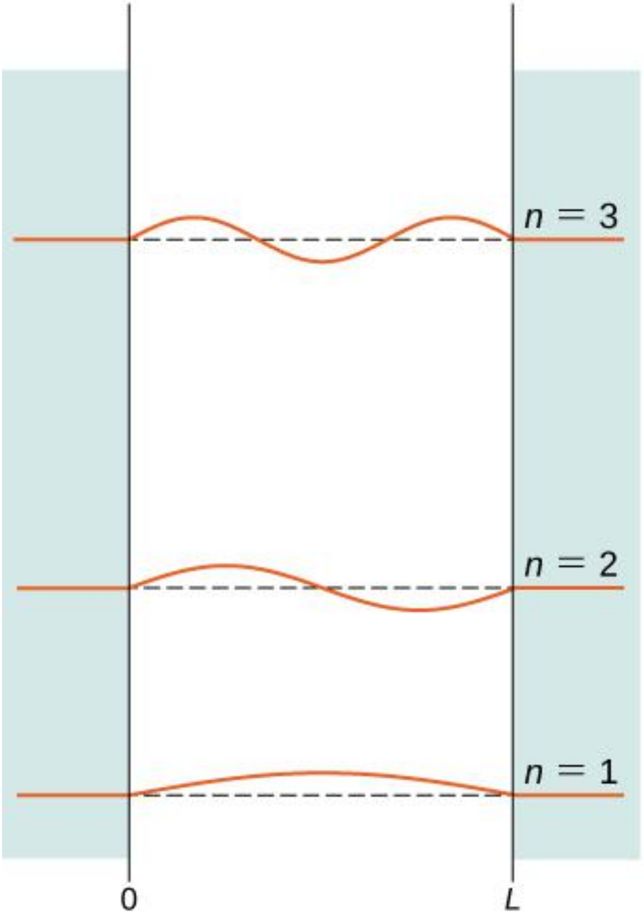
Herbert Fröhlich

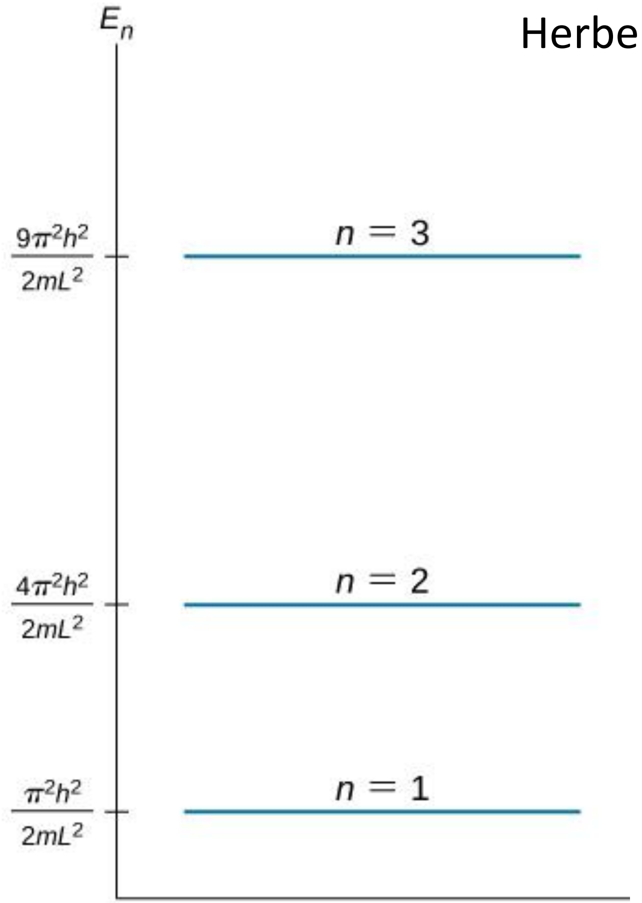


Particle-in-box problem

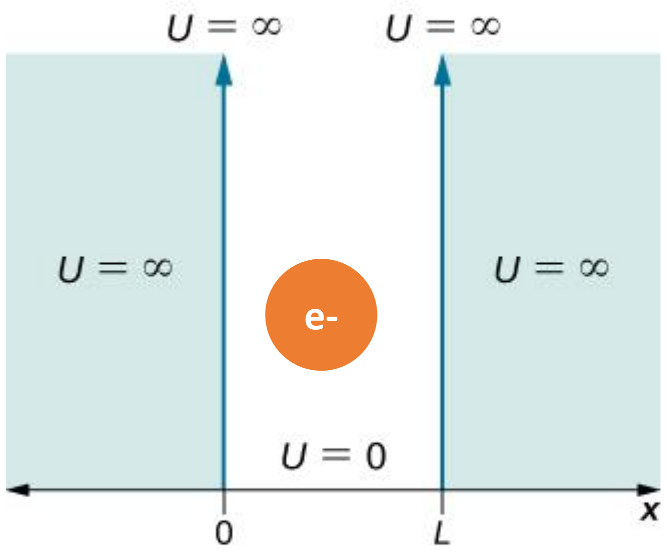
$$E_n = \frac{n^2 h^2}{8mL^2} \qquad \psi_n = ASin\frac{n\pi x}{L}$$

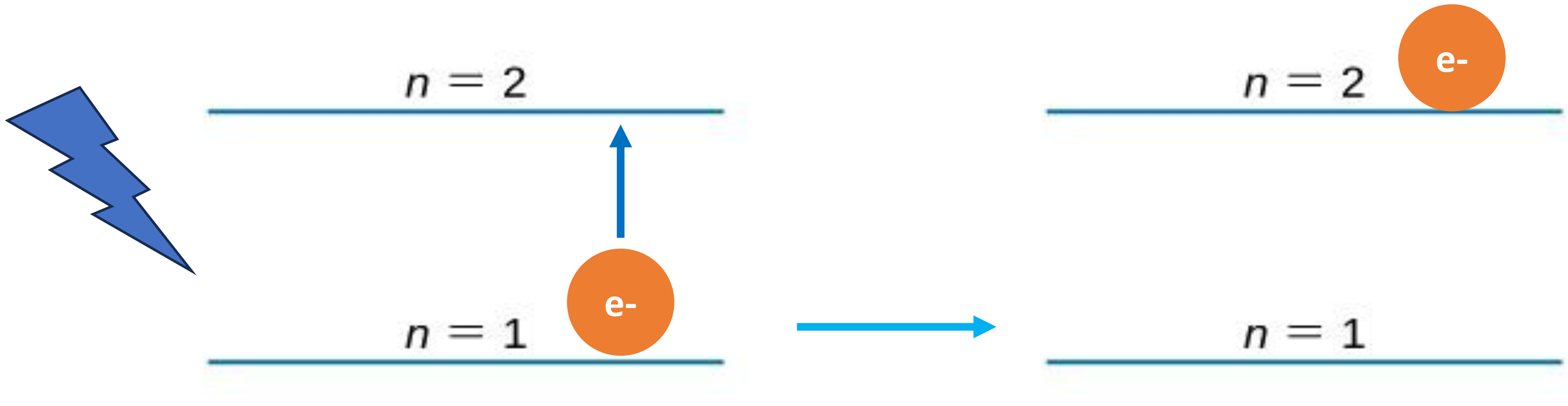
n=1,2,3……





Introduction to QDs





<u>Let's assume a scenario</u>

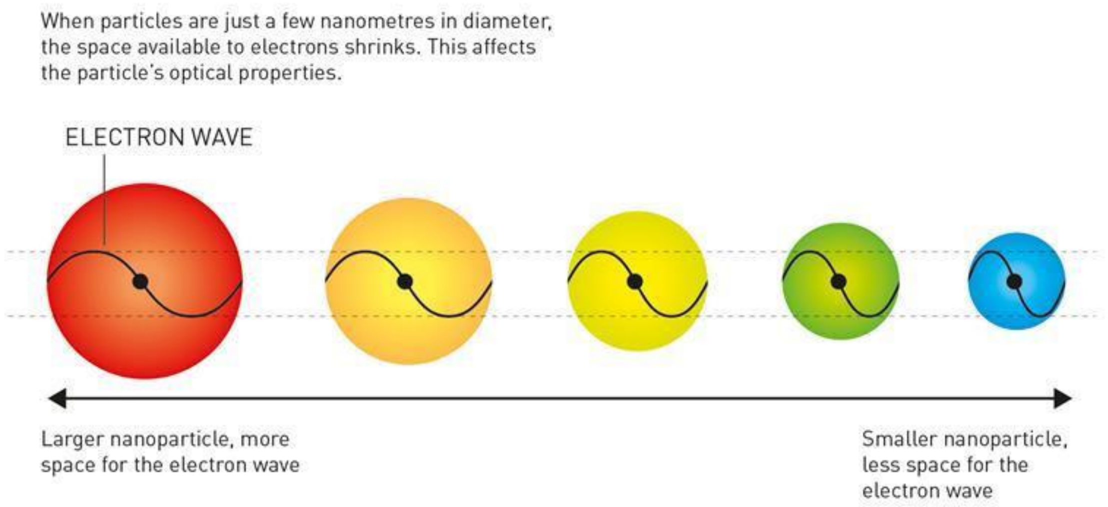
Particle= electron
L=0.6 nm

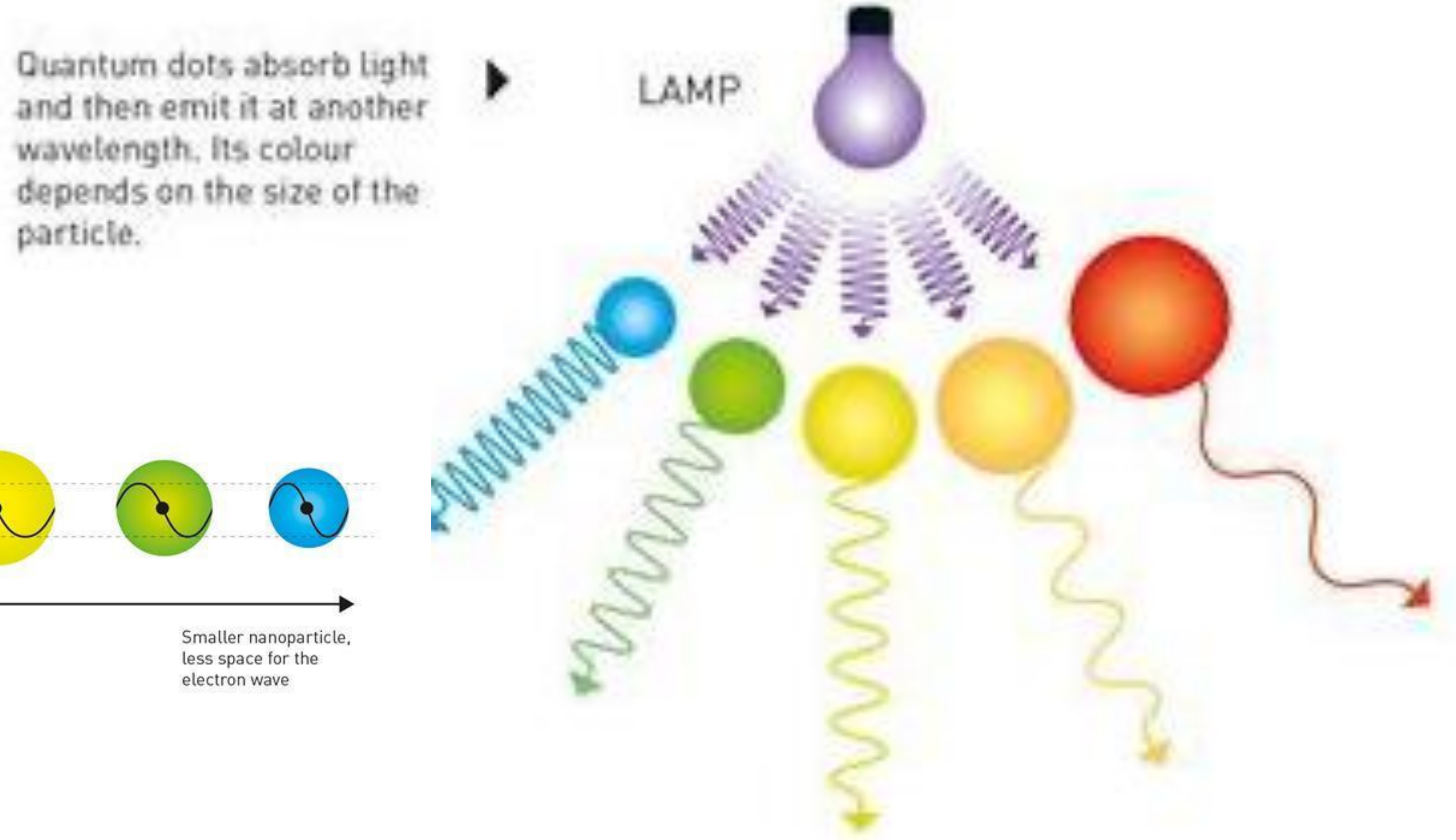
$$\Delta E_{1\rightarrow 2} = \frac{3h^2}{8mL^2} \sim 5\times 10^{-19}\, J$$

$$\lambda_{1\rightarrow 2} \sim 400\ nm$$

$$\boxed{\lambda_{n\rightarrow n+1} \propto L^2}$$

Introduction to QDs





https://www.chemistryworld.com/features/the-quantum-dot-story/4018219.article

The Journey to realize the size-dependent quantum effect

- Prof. Alexei Ekimov and Prof. Alexander Efros was studying origin of colors in Schott glasses

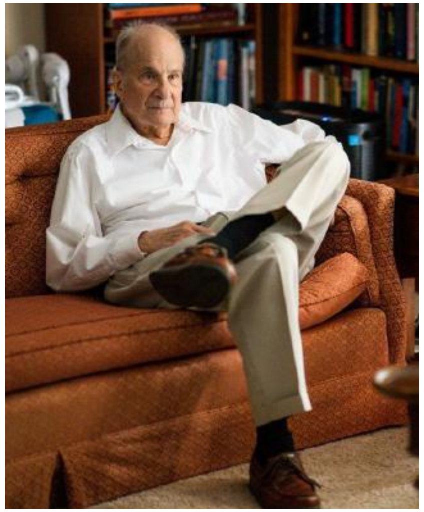
- They were heating glasses up to 700°C at varying rate and then studied the tiny semiconductor particles formed using X-rays.

- They found formation of tiny copper chloride crystals between 2 nm to 20 nm and they **attributed such size difference to the different color of glasses**.

Published in Russian language in Soviet Scientific Journal in 1981: Remained unnoticed..

The particles were frozen inside the glass so can't be used for any purpose.

m effect



- Prof. Lou
  Raman S

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RESEARCH ARTICLE | DECEMBER 01 1983

[No Title]

A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites

L. E. Brus

Check for updates

J. Chem. Phys. 79, 5566–5571 (1983)

https://doi.org/10.1063/1.445676 Article history

Share Tools

Large semiconductor crystals have intrinsic electronic properties dependent upon the bulk band structure. As the crystal becomes small, a new regime is entered in which the electronic properties (excited states, ionization potential, electron affinity) should be strongly dependent upon the electron and hole in a confined space. We address the possibility of a shift in the photochemical redox potential of one carrier, as a function of crystallite size. As a semiquantitative guide, one might expect a shift on the order of $h^2/8em^*R^2$ due to the kinetic energy of localization in the small crystallite. We model the elementary quantum mechanics of a charged crystallite using (a) the effective mass approximation, (b) an electrostatic potential for dielectric polarization, and (c) penetration of the carrier outside the crystallite in a cases of small effective mass. Shifts of several tenths of an eV appear possible in crystallites of diameter 50 Å. The carrier charge density reside near the crystallite surface if the effective mass is very small.

The journey to realize the size-dependent quantum effect

- Brus and Ekimov established the quantum size effects in colloidal nanocrystals but there was still a problem to be solved.

Their methods created quantum dots of unpredictable quality and size, often with defects; a reliable and consistent synthesis method was needed.

‘We struggled to get this colloidal synthesis under control because it was a kind of a black magic in the beginning; it was just a recipe’- Louis Brus

Paul Alivisatos

Michael L. Steigerwald

https://www.chemistryworld.com/features/the-quantum-dot-story/4018219.article

The journey to realize size-dependent quantum effect

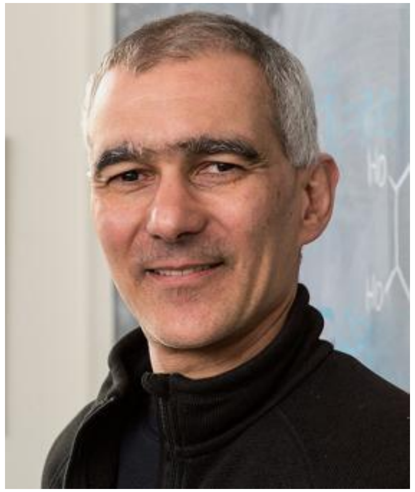
- A chronological description of the challenges and milestones

1981
First observation of QDs
Prof. Alexei Ekimov

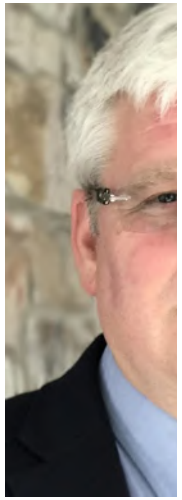
1983
First observation band gap as function of size
Prof. Louis Brus

1983----
optimization of synthesis process
Brus, Steigerwald, Alivasatos

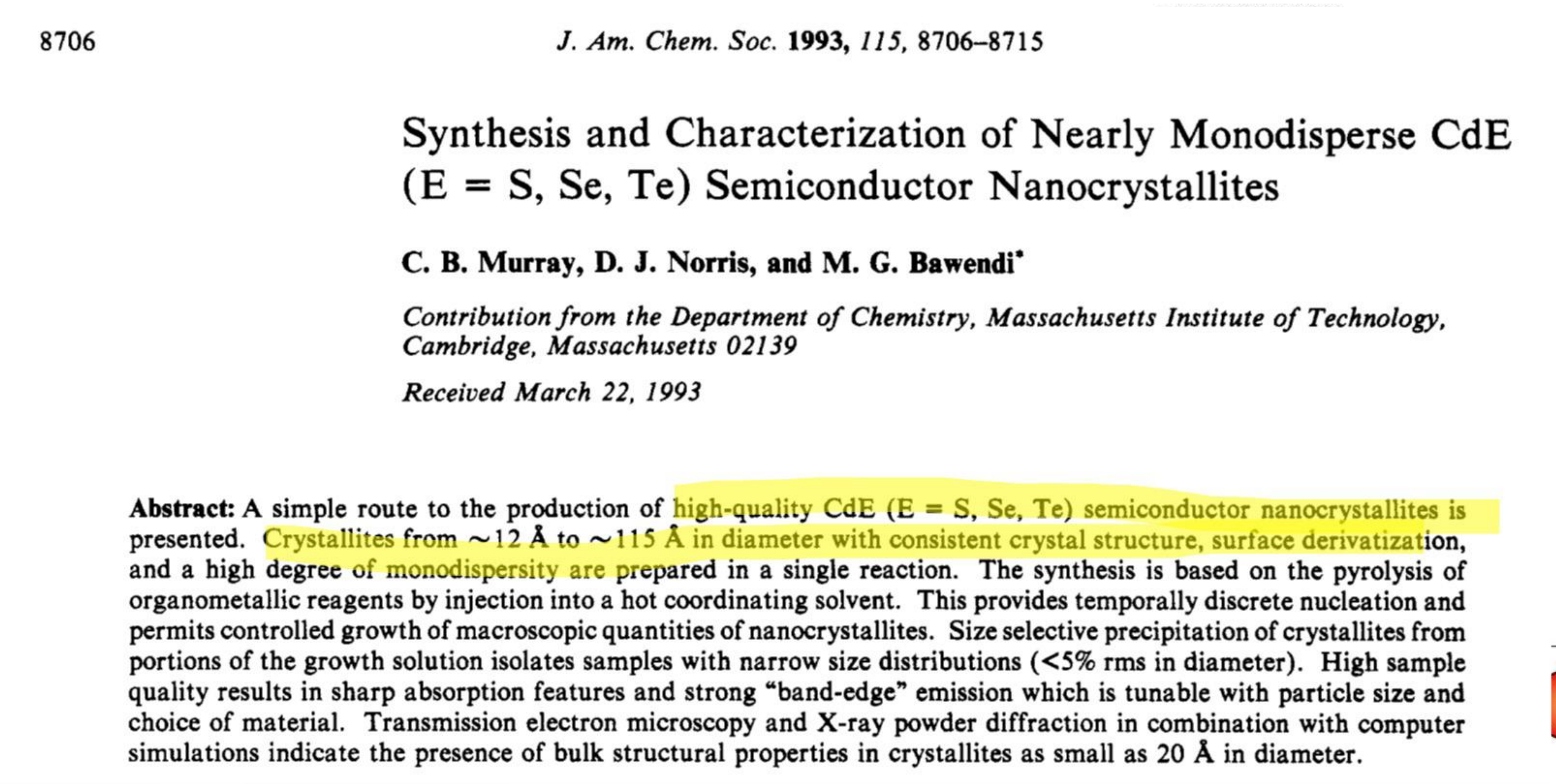
1987
Moungi Bawendi joined Brus's lab for short visit



The journey to realize size-dependent quantum effect: the synthesis of monodispersed QDs with tunable properties



Chris M



8706 *J. Am. Chem. Soc.* **1993,** *115,* 8706–8715

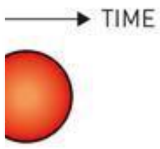
Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites

C. B. Murray, D. J. Norris, and M. G. Bawendi*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received March 22, 1993

Abstract: A simple route to the production of high-quality CdE (E = S, Se, Te) semiconductor nanocrystallites is presented. Crystallites from ~12 Å to ~115 Å in diameter with consistent crystal structure, surface derivatization, and a high degree of monodispersity are prepared in a single reaction. The synthesis is based on the pyrolysis of organometallic reagents by injection into a hot coordinating solvent. This provides temporally discrete nucleation and permits controlled growth of macroscopic quantities of nanocrystallites. Size selective precipitation of crystallites from portions of the growth solution isolates samples with narrow size distributions (<5% rms in diameter). High sample quality results in sharp absorption features and strong "band-edge" emission which is tunable with particle size and choice of material. Transmission electron microscopy and X-ray powder diffraction in combination with computer simulations indicate the presence of bulk structural properties in crystallites as small as 20 Å in diameter.

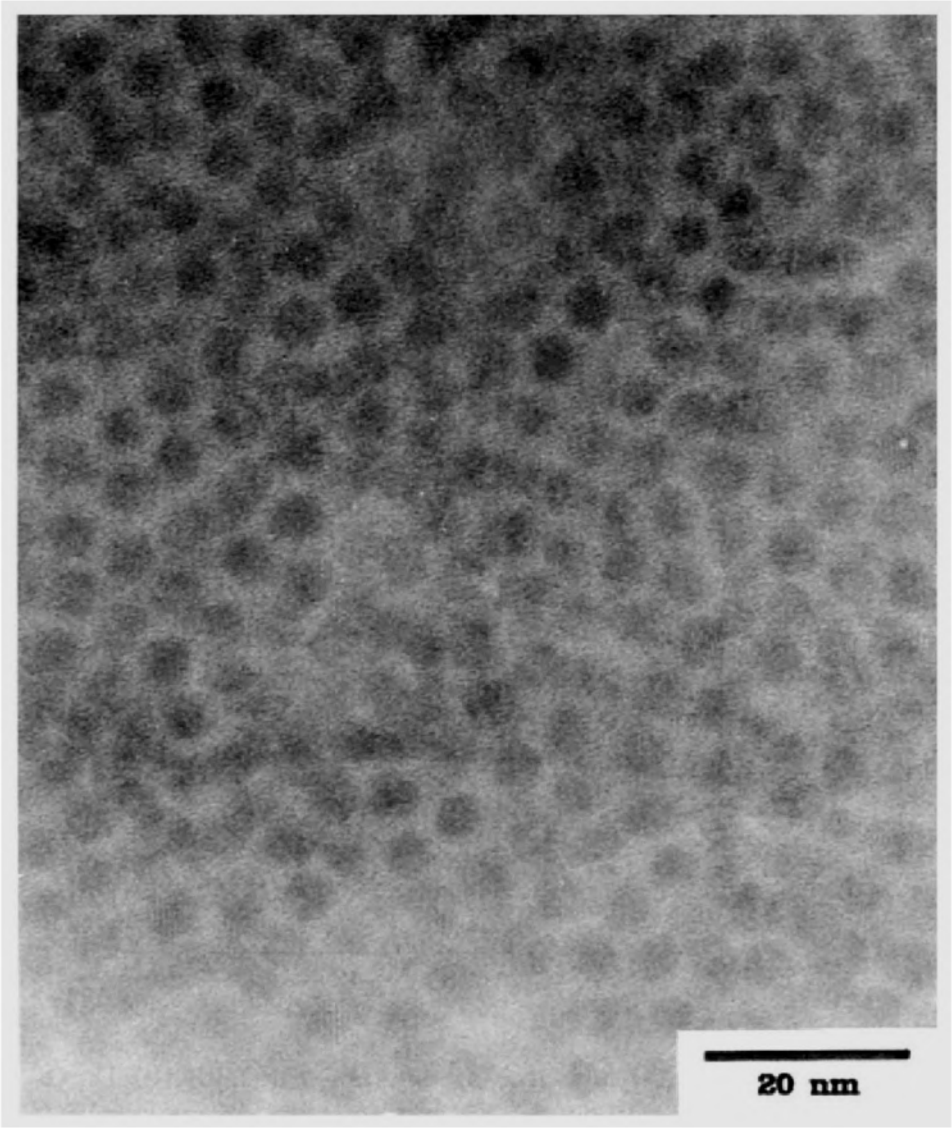


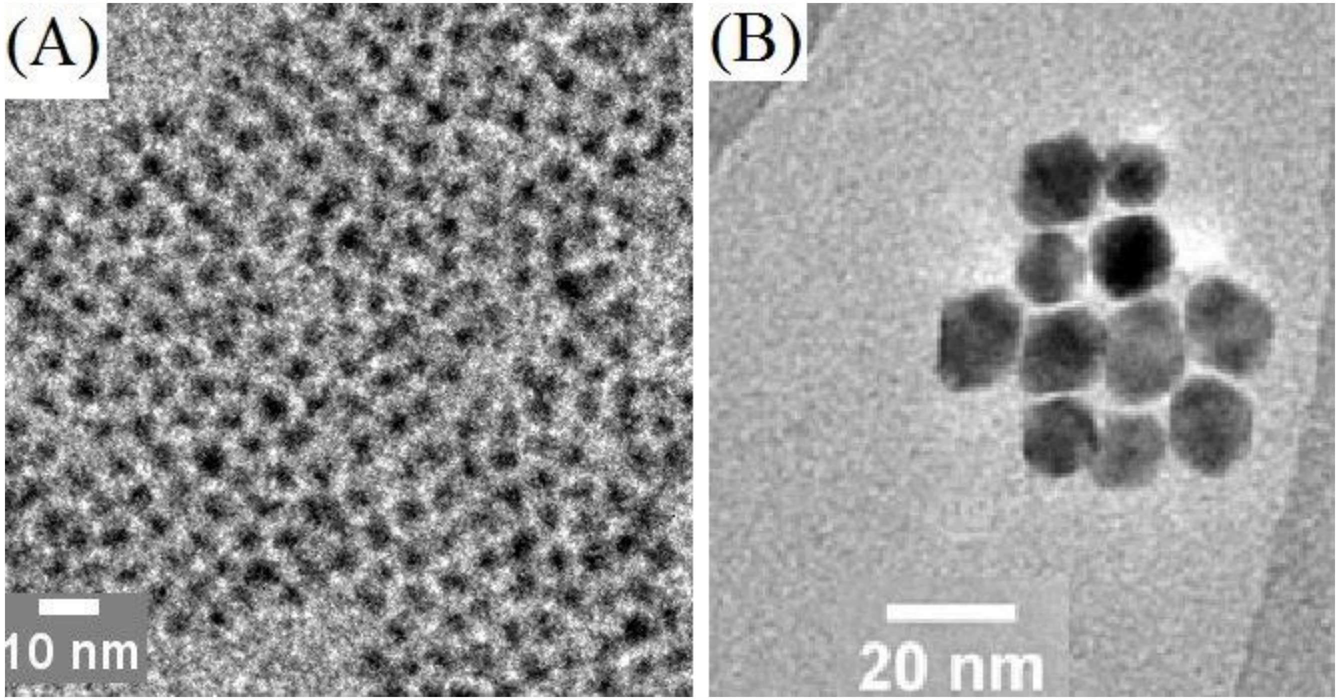
David Norris

Bawendi

https://www.chemistryworld.com/features/the-quantum-dot-story/4018219.article

Synthesis of Quantum Dots





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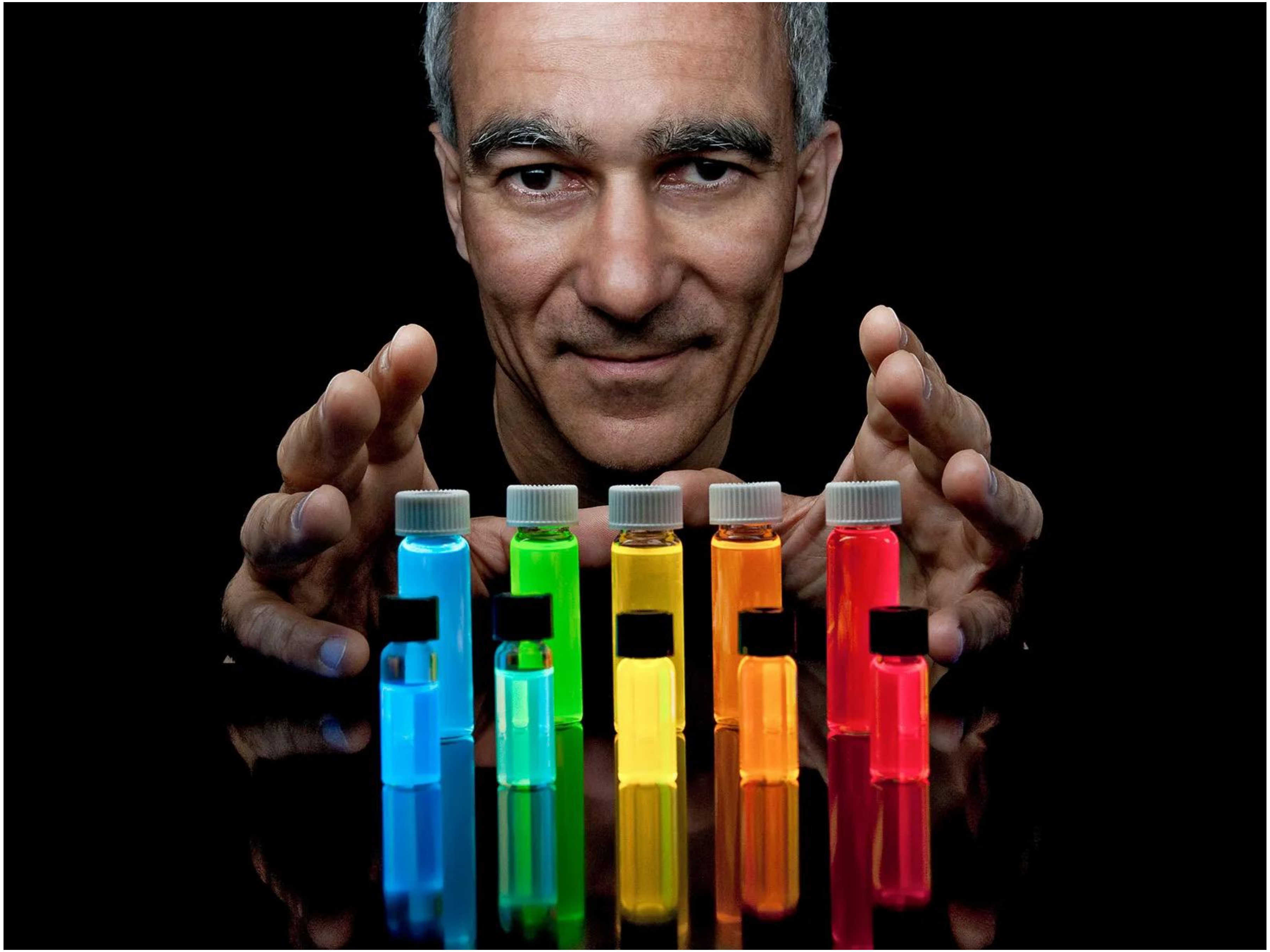
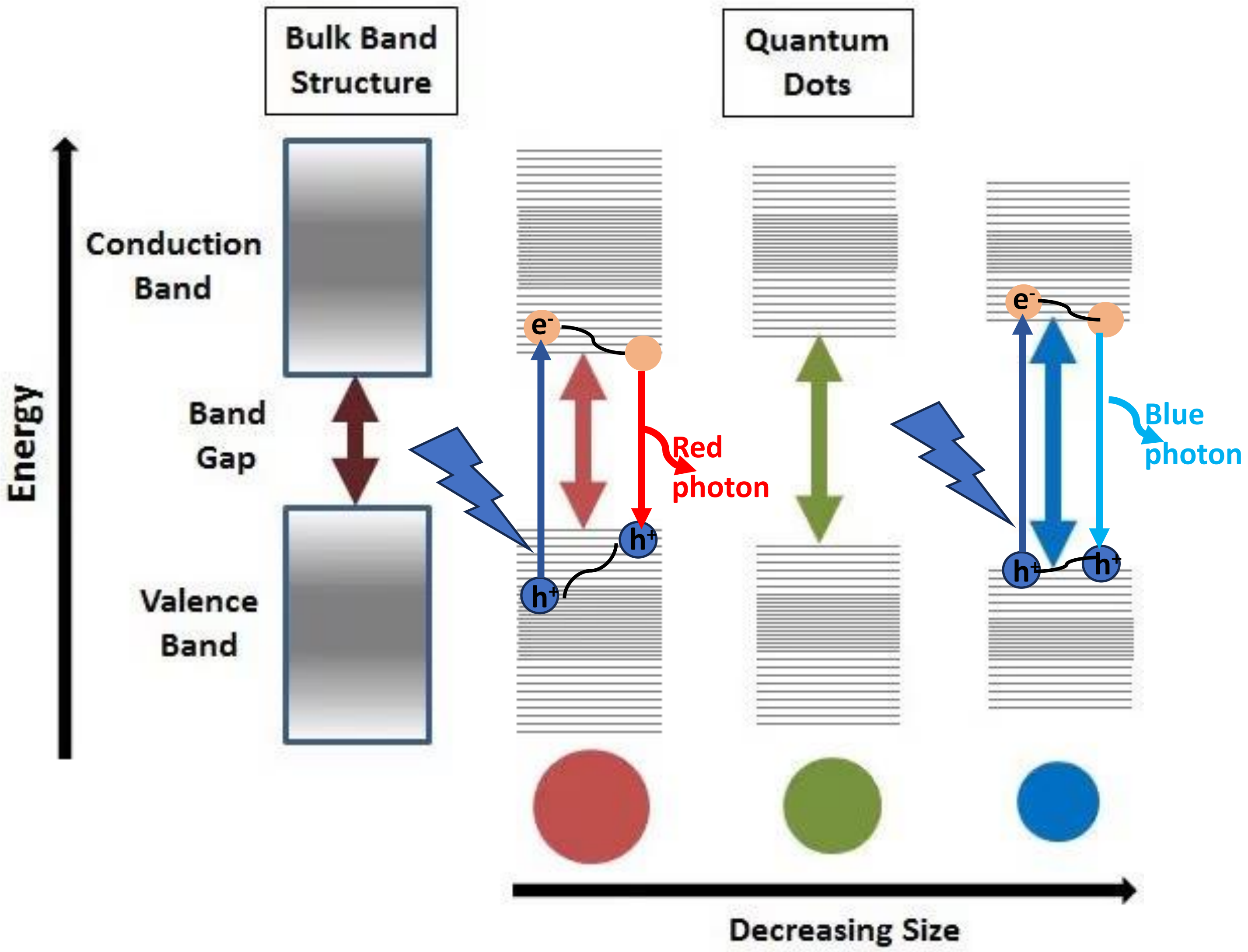


MIT; photograph, Len Rubenstein

The journey to realize size-dependent quantum effect

So, what are 'quantum dots'?

- ❑ Semiconductor nanocrystals with sizes between ~2-8 nm.
- ❑ Typically are chalcogenides (selenides, sulfides or tellurides) of metals like cadmium, lead or zinc



https://www.sigmaaldrich.com/IN/en/technical-documents/technical-article/materials-science-and-engineering/biosensors-and-imaging/quantum-dots

The journey to realize size-dependent quantum effect

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1993…..
Challenges and applications of QDs

Applications
Display application (Samsung)
Imaging applications
Single photon source

Better synthetic process
Removal of defects
core-shell QDs

New QD materials
Perovskite-based nanocrystals

Applications of QDs in QLED technology

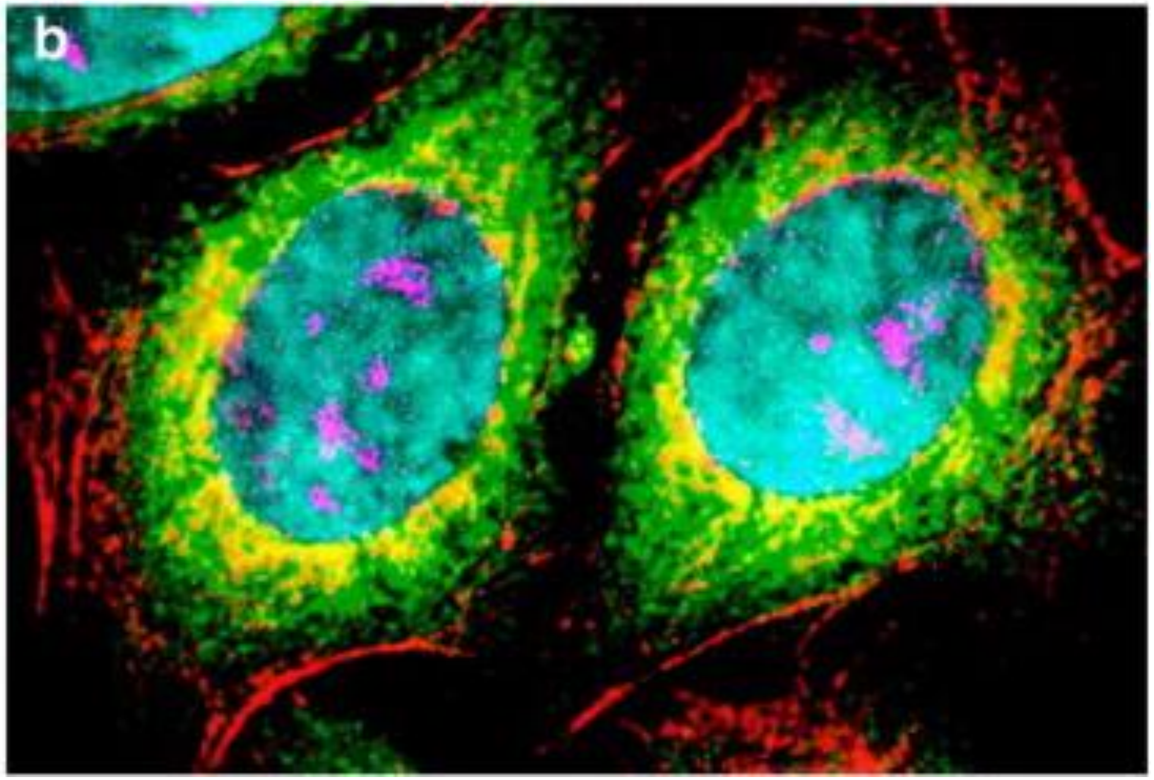
- ❖ Light-emission yield was low for typical QD materials
- ❖ Toxic materials could not be used from safety purpose
- ❖ Green and red colors are produced by QDs

‘Samsung deserves a lot of credit, they put a lot of money into the development of the technology so that they could use them in their own TVs,’ – Louis Brus.

‘Cadmium selenide is not consumer friendly, even if it’s completely protected, you don’t want to be using it,’ says Bawendi. ‘[Samsung] realised that and invested a lot of money in indium phosphide as a replacement to cadmium selenide, which is a harder material to make.’

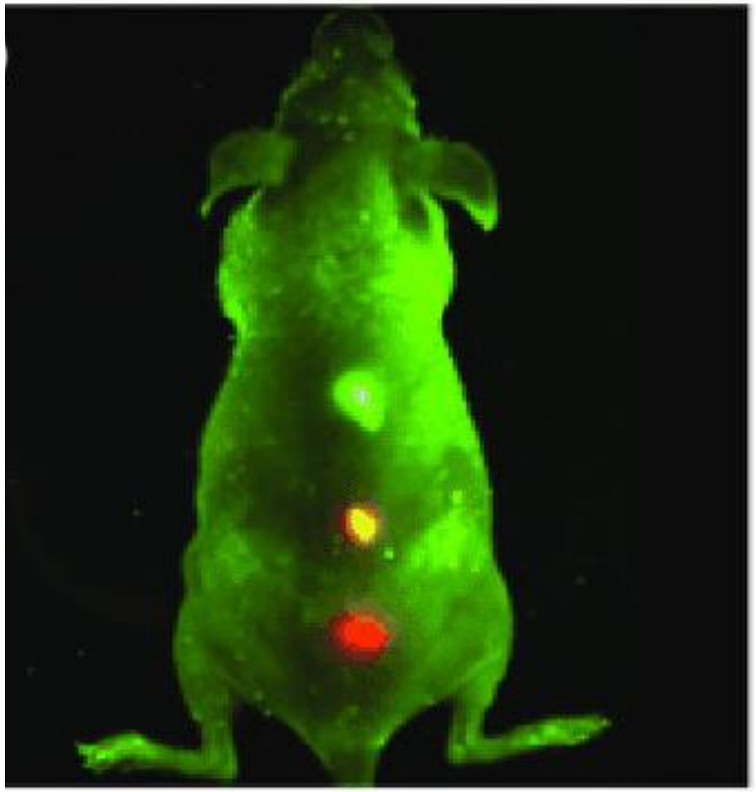
https://www.chemistryworld.com/features/the-quantum-dot-story/4018219.article

Applications of QDs in Imaging



Pseudo colored image of human epithelial cells by staining with five different sizes of QDs. Actin filaments — Red (705 nm), Nucleus — Cyan (655 nm), Ki67 protein — Magenta (605 nm), Microtubules — Green (565 nm), Mitochondria — Orange (525 nm).

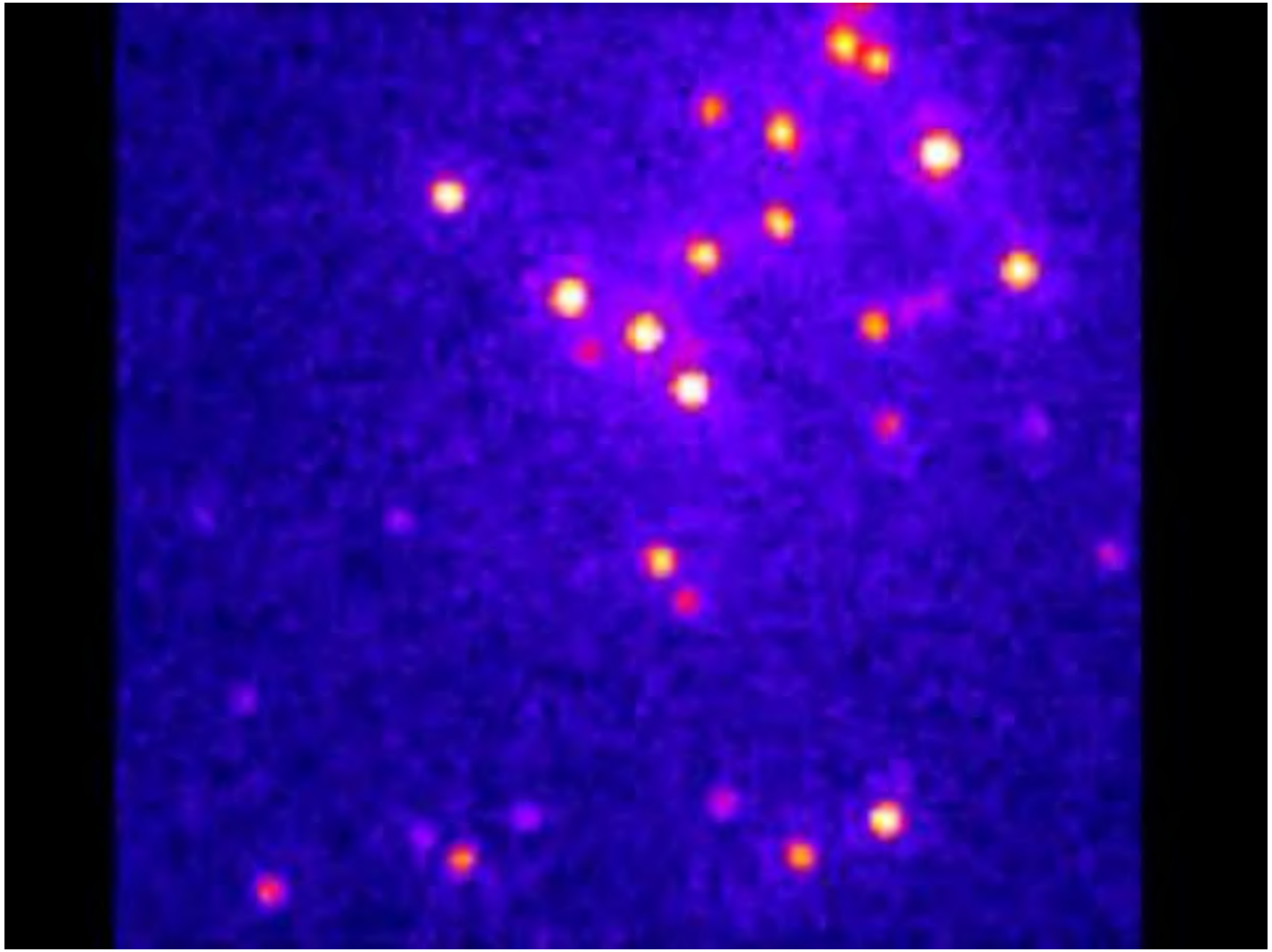
https://www.sciencedirect.com/science/article/pii/S0001868614002887

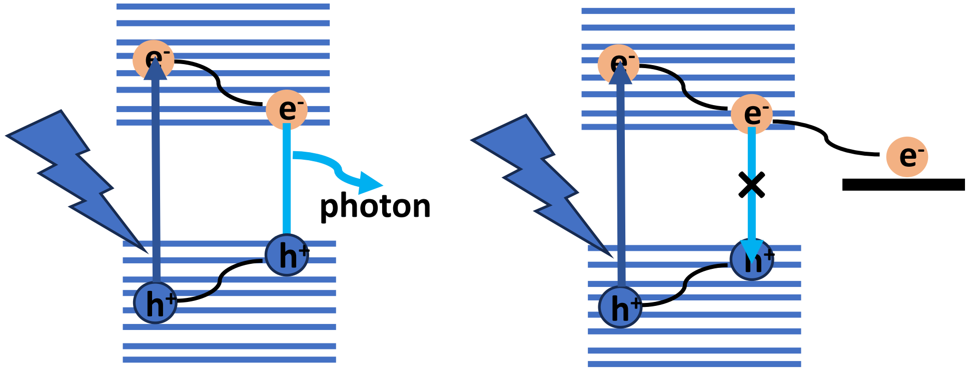


In vivo image of multicolor QDs injected into a live mouse

Nanomedicine (2006) 1(2)

Challenges: Defects and blinking





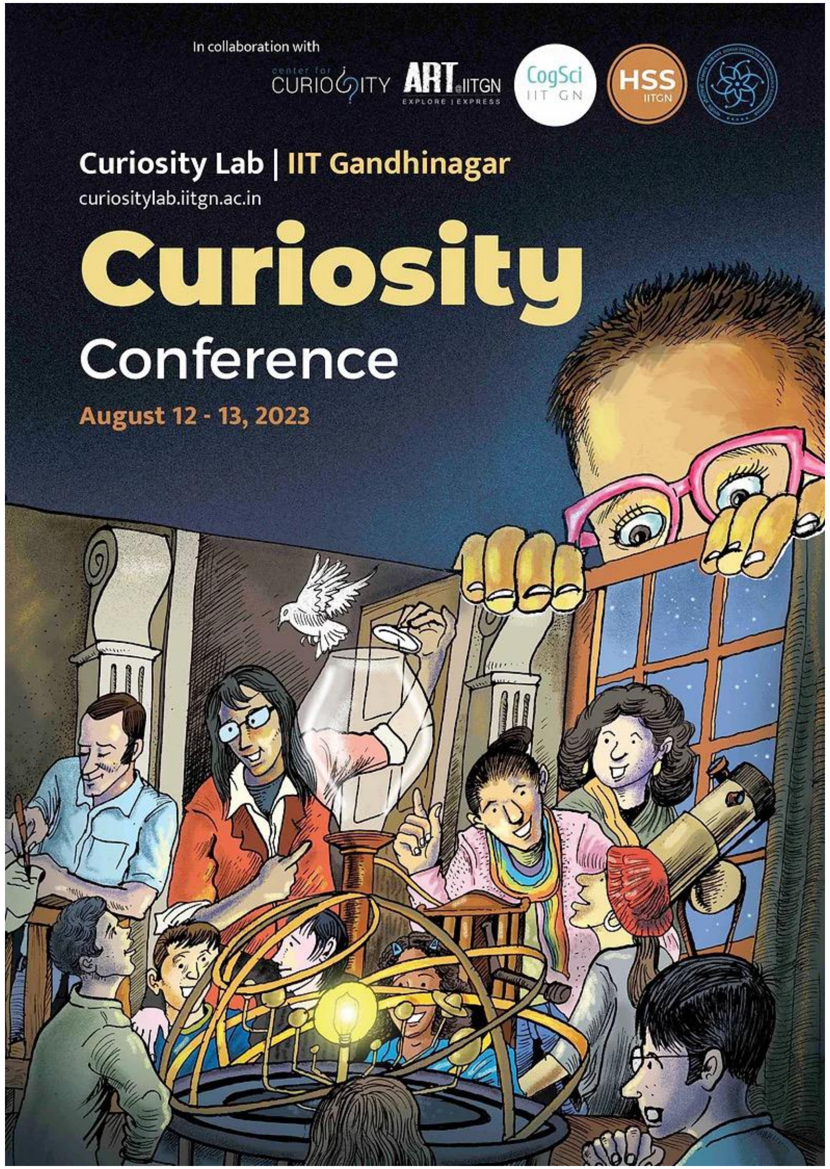
Ideal QD

Defect/trap on QD

- Impacts light emission efficiency
- Fluctuations affect the display and imaging applications

Source: youtube

Conclusions and take-home message



Follow your natural curiosity

Look carefully! Your **bad data (!)** could indicate something new

Source: wikipedia

Think outside the box