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DIPARTIMENTO DI FISICA

Nobel Preis inspired notes on

Chemistry 2023

Quantum dots

Bassano Vacchini @ FG3

Press release

PRESS RELEASE

4 October 2023

The Nobel Prize in Chemistry 2023

The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2023 to

Moungi G. Bawendi
Massachusetts Institute of Technology (MIT), Cambridge, MA, USA

Louis E. Brus
Columbia University, New York, NY, USA

Aleksey Yekimov
Nanocrystals Technology Inc., New York, NY, USA

“for the discovery and synthesis of quantum dots”

that is ...

PRESSMEDDELANDE

4 oktober 2023

Nobelpriset i kemi 2023

Kungl. Vetenskapsakademien har beslutat utdela Nobelpriset i kemi 2023 till

Moungi G. Bawendi
Massachusetts Institute of Technology (MIT), Cambridge, MA, USA

Louis E. Brus
Columbia University, New York, NY, USA

Aleksey Yekimov
Nanocrystals Technology Inc., New York, NY, USA

”för upptäckt och syntes av kvantprickar”

Awardees

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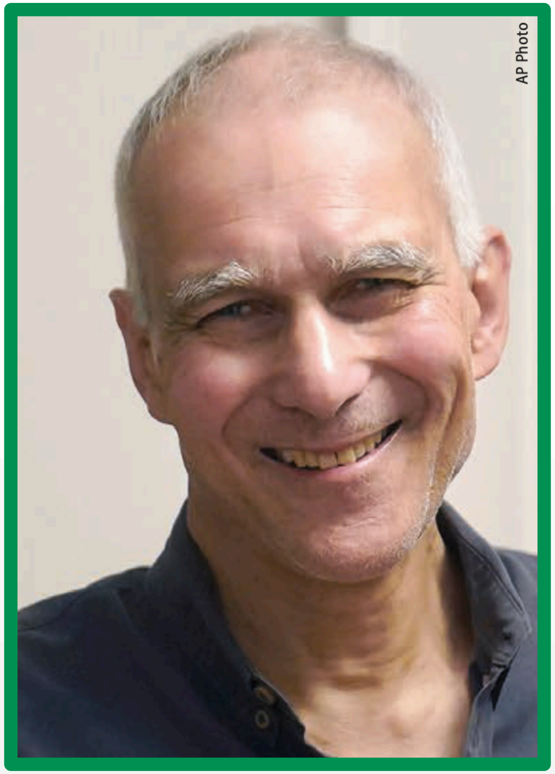
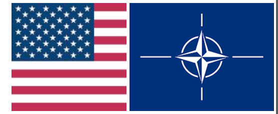
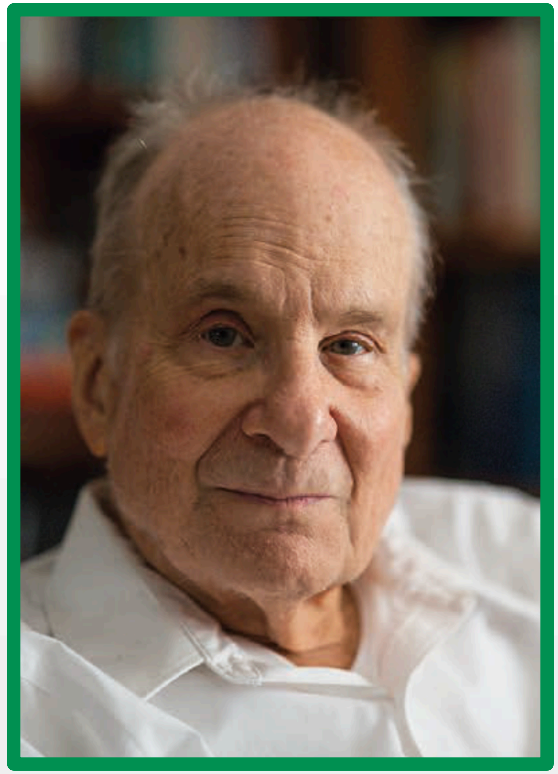


Moungi Gabriel Bawendi
born 1961 in Paris, France

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

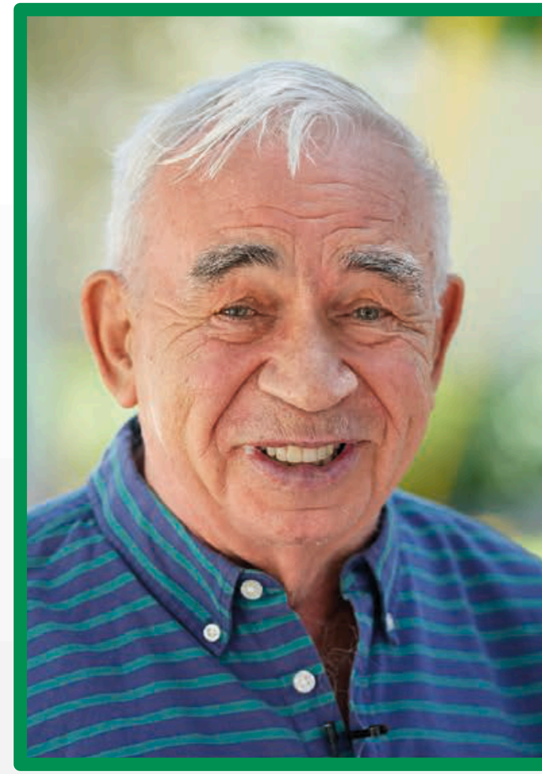




Louis Eugene Brus
born 1943 in Cleveland, OH, US

R. Rosetti und *L. Brus*, J. Phys. Chem. **86**, 4470 (1982)

eiserne vorhang



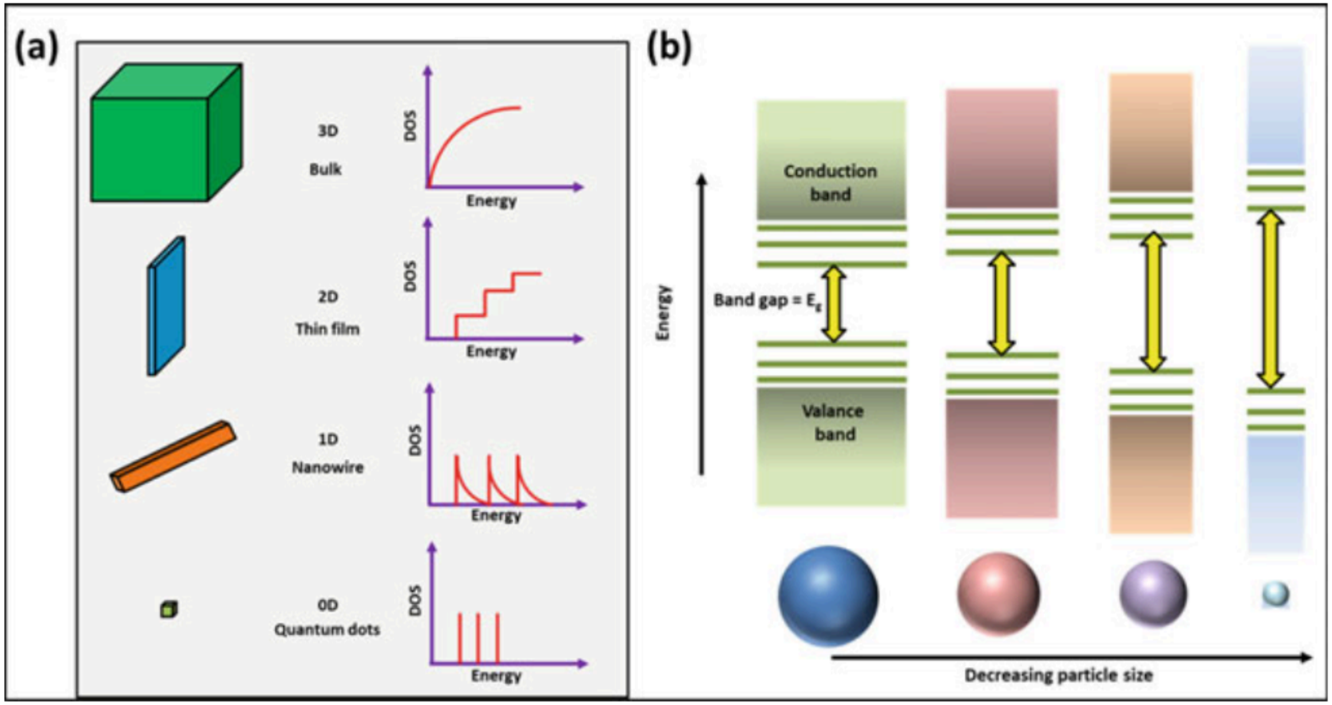
Aleksey Ivanovič Yekimov
born 1945 in the former USSR

A. I.Y. Ekimov und *A. A. Onushchenko*,
JETP Lett. **34**, 345 (1981)
translated from
A. I.Y. Ekimov und *A. A. Onushchenko*,
Pis'ma Zh. Eksp. Teor. Fiz. **34**, 363 (1981)

Scientific background

Density Of States in different samples

Bulk → quantum well → quantum wire → quantum dot
Dimensions 3 → 2 → 1 → 0



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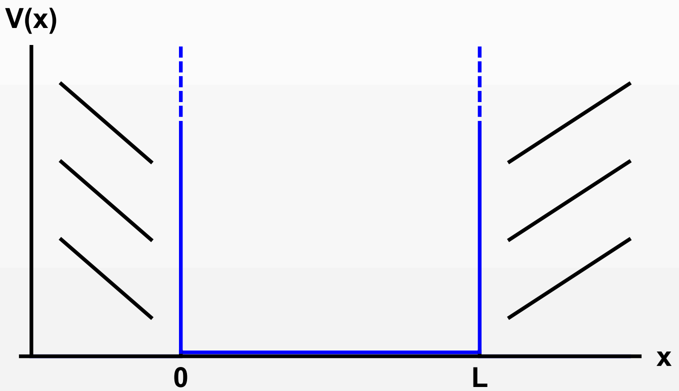
Scientific background

The basic theoretical concept underlying quantum dots is referred to as the 'particle-in-a-box' problem. When a quantum mechanical particle, such as an electron, is confined inside a 'box' with a size L comparable to the particle's de Broglie wavelength, the energies of the wave function's allowed eigenstates depend critically on L, and the energy spacing ΔE scales as $1/L^2$. This concept has been textbook material since the very early days of quantum mechanics.[6]



$$\Rightarrow \quad E_{n_x,n_y,n_z} = \frac{\pi^2\hbar^2}{2m_e}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

$$= \frac{\pi^2\hbar^2}{2m_e\bar{a}^2}\left(n_x^2+n_y^2+n_z^2\right)$$

$$E_n = \frac{\hbar^2\pi^2}{2mL^2}n^2$$

[6]In this respect the the Swedish Nobel Committee highly recommends the ***Dispense del corso di Fisica Generale 3*** used by students at the Math Department of UNIMI

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The heart of the matter

Size dependent quantum effects

Physica IV, no 5 Mei 1937

DIE SPEZIFISCHE WÄRME DER ELEKTRONEN KLEINER METALLTEILCHEN BEI TIEFEN TEMPERATUREN

von H. FRÖHLICH

Instituut voor Theoretische Natuurkunde der Rijks-Universiteit, Leiden

Zusammenfassung

Auf Grund des Sommerfeld-Bloch'schen Metallmodells ergeben sich bei tiefen Temperaturen grosse Unterschiede zwischen der spezifischen Wärme der Elektronen eines unendlich grossen Metalles und derjenigen kleiner Metallteilchen.

Nehmen wir z.B. an, dass das Teilchen die Form eines Würfels von der Seitenlänge L hat, so sind die Energieterme bekanntlich gegeben durch

$$E_n = \frac{\hbar^2\pi^2 n^2}{2m^* L^2},$$

wo

$$n^2 = n_x^2 + n_y^2 + n_z^2, \quad n_i = 1, 2, 3, \ldots .$$

ist. Da sich beinahe jede grosse ganze Zahl auf vielfache Weise als Summe dreier Quadrate darstellen lässt, folgt

$$\Delta E = \frac{\hbar^2\pi^2}{2m^* L^2}, \tag{2}$$

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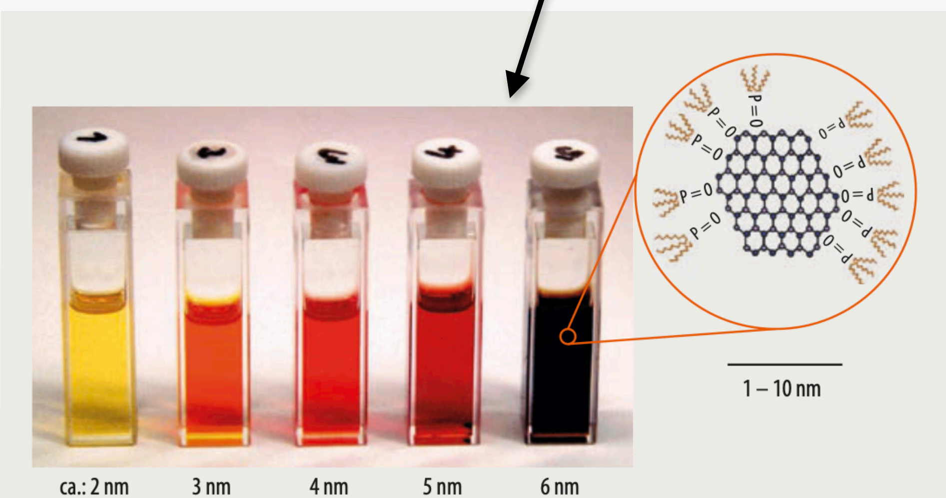
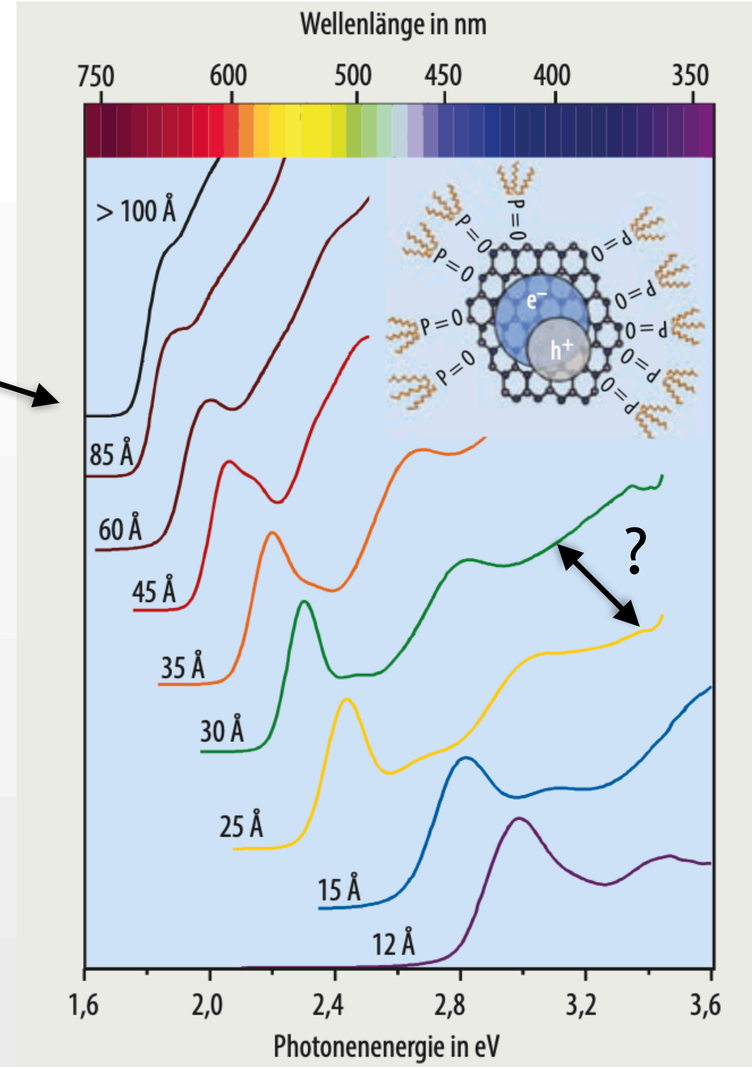
The heart of the matter

Size dependent quantum effects

size dependent emission and absorption in Cadmium selenide (CdSe) nanoparticles





Visible light relevant ranges

$$E \sim 2\text{-}3\,\text{eV}; \quad \lambda \sim 400\text{-}700\,\text{nm}; \quad \nu \sim 4\text{-}8 \times 10^{14}\,\text{Hz}$$

Original patterns and guiding formulae

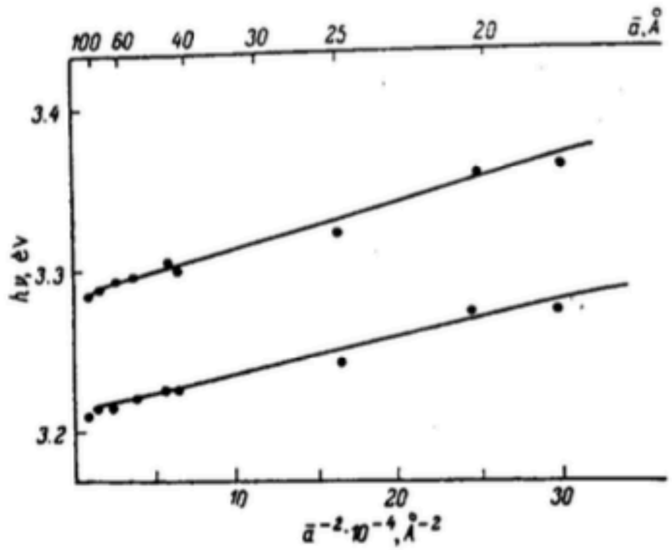


Fig. 2. Dependence of the spectral positions of exciton absorption lines at T = 4.2 K on the average radius a^{-} of CuCl nanocrystals in glass. The energy of the absorption line increases proportional to $^{-2}$. Reproduced from A.I. Yekimov and A.A. Onushchenko, *JETP Lett* 1981, *34*, 345–349.

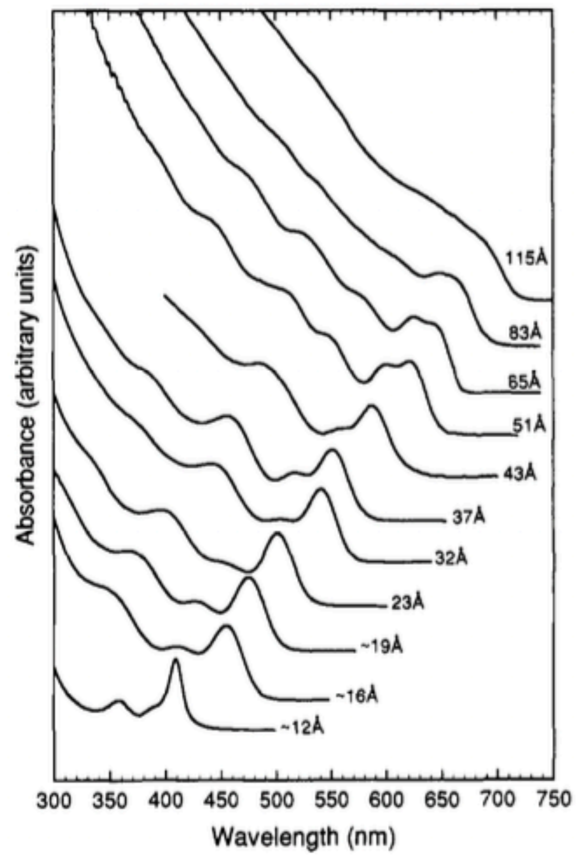


Fig. 4. Room-temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from ~12 to 115 Å. Reproduced from C.B. Murray, D.J. Norris, and M.G. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).

from *Scientific Background to the Nobel Prize in Chemistry 2023*

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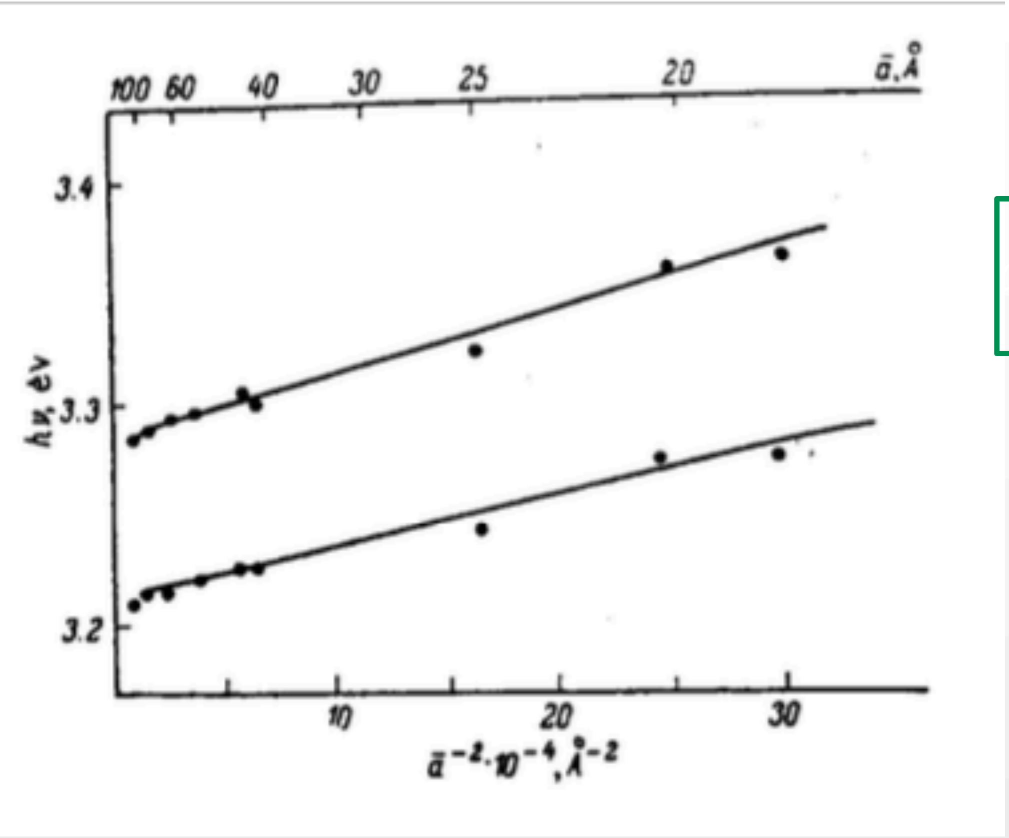
Original patterns and guiding formulae

Absorption frequency $(\bar{a})$



$$\nu_{\mathrm{Bohr}}(\bar{a}) = \frac{\delta E_n}{h} = \delta n \, \frac{\hbar \pi}{4 m_{\mathrm{e}}} \frac{1}{\bar{a}^2}$$

$$\frac{\hbar \pi}{4 m_{\mathrm{e}}} \sim 10^{-3} \, \mathrm{m}^2/\mathrm{s}$$

$$\delta n \sim 3$$

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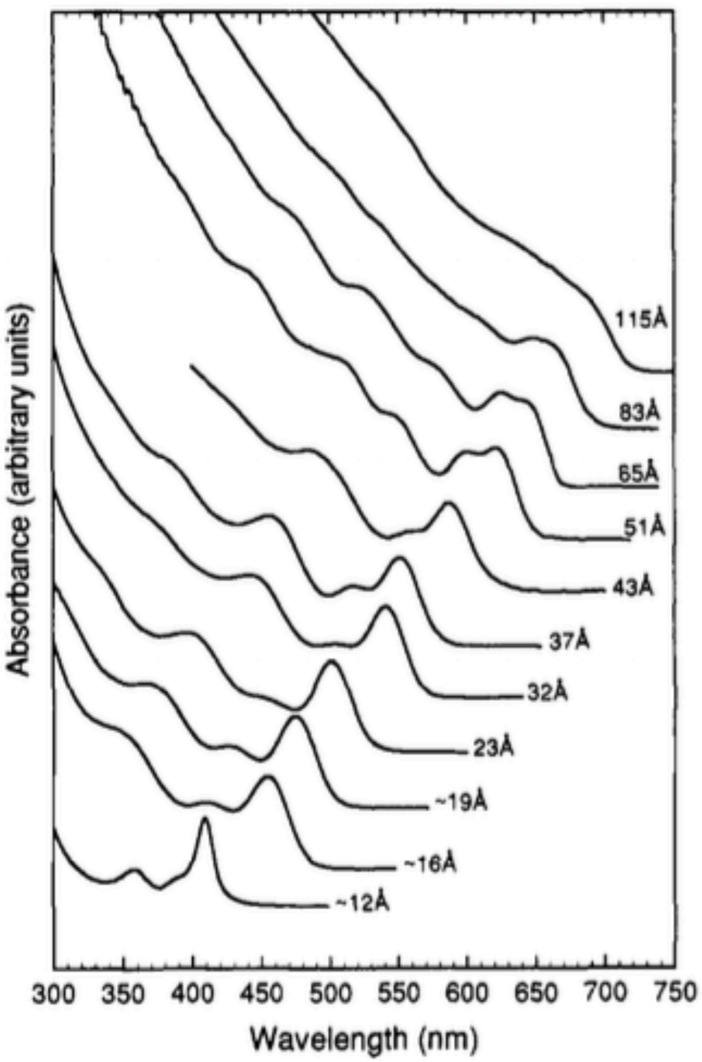
Original patterns and guiding formulae

Absorption intensity $(\lambda; \bar{a})$



$$\nu_{\mathrm{Bohr}} = \nu_{\mathrm{light}} \iff \bar{a}^2 = \delta n \frac{\pi}{4} \frac{\hbar}{m_{\mathrm{e}} c} \lambda$$

$$\nu_{\mathrm{Bohr}} = \delta n \frac{\hbar \pi}{4 m_{\mathrm{e}}} \frac{1}{\bar{a}^2}$$

$$\nu_{\mathrm{light}} = \frac{c}{\lambda}$$

$$\frac{\hbar}{m_{\mathrm{e}} c} \sim 10^{-12}\mathrm{m}$$

$$\bar{a}(\text{Å}) \sim \sqrt{\lambda(\mathrm{nm})}$$

$$\frac{\hbar}{m_{\mathrm{e}} c} = \alpha a_o \quad \begin{cases} a_o = \dfrac{\hbar^2}{me^2} = \text{Bohr radius} \\ \alpha = \dfrac{e^2}{\hbar c} = \text{fine structure constant} \end{cases}$$

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Detailed achievements

In the early 1980s, **Aleksey Yekimov** succeeded in creating size-dependent quantum effects in coloured glass. The colour came from nanoparticles of copper chloride and Yekimov demonstrated that the particle size affected the colour of the glass via quantum effects.

Quantum size effect in three-dimensional microscopic semiconductor crystals

A. I. Ekimov and A. A. Onushchenko
S. I. Vavilov State Optics Institute

(Submitted 29 July 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 6, 363–366 (20 September 1981)

The exciton absorption spectrum of microscopic CuCl crystals grown in a transparent dielectric matrix has been studied. The size of the microscopic crystals was varied in a controlled manner from several tens of angstroms to hundreds of angstroms. There is a short-wave shift (of up to 0.1 eV) of the exciton absorption lines, caused by a quantum size effect.

PACS numbers: 61.60. + m, 71.35. + z

Detailed achievements

A few years later, **Louis Brus** was the first scientist in the world to prove size-dependent quantum effects in particles floating freely in a fluid.

4470 *J. Phys. Chem.* **1982**, *86*, 4470–4472

Electron–Hole Recombination Emission as a Probe of Surface Chemistry in Aqueous CdS Colloids

R. Rossetti and L. Brus*

Bell Laboratories, Murray Hill, New Jersey 07974 *(Received: July 8, 1982; In Final Form: September 14, 1982)*

Luminescence has been observed from dilute aqueous CdS colloidal solutions following irradiation above the semiconductor band gap. The emission is attributed to radiative recombination of short-lived ($\tau < 5$ ns) h^+ with e^- in small particles of hydrodynamic radius $\simeq$200 Å. The luminescence quantum yield is sensitive to surface-adsorbed species that are able to undergo reduction. PbS and *p*-benzoquinone cause 50% luminescence quenching at $\simeq 10^{-5}$ M concentration, corresponding to far less than a monolayer surface coverage. These results demonstrate that recombination emission in small CdS particles can be used as a probe of the h^+ and e^- surface chemistry and physics.

Detailed achievements

In 1993, **Moungi Bawendi** revolutionised the chemical production of quantum dots, resulting in almost perfect particles. This high quality was necessary for them to be utilised in applications.

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

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

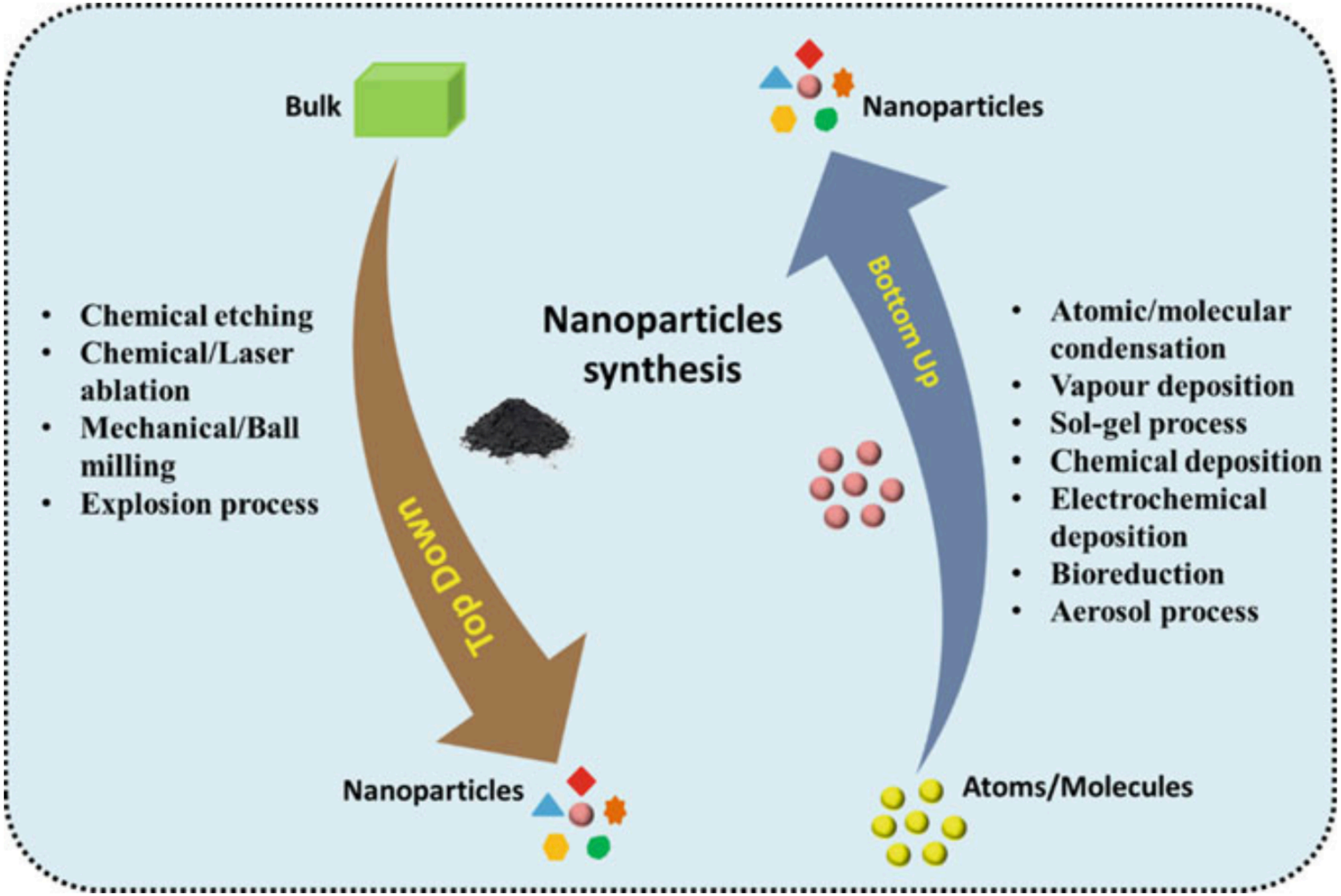
C. B. Murray, D. J. Norris, and M. G. Bawendi*

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.

Production strategies



Top down: bulk → nano   Bottom up: nano → atom

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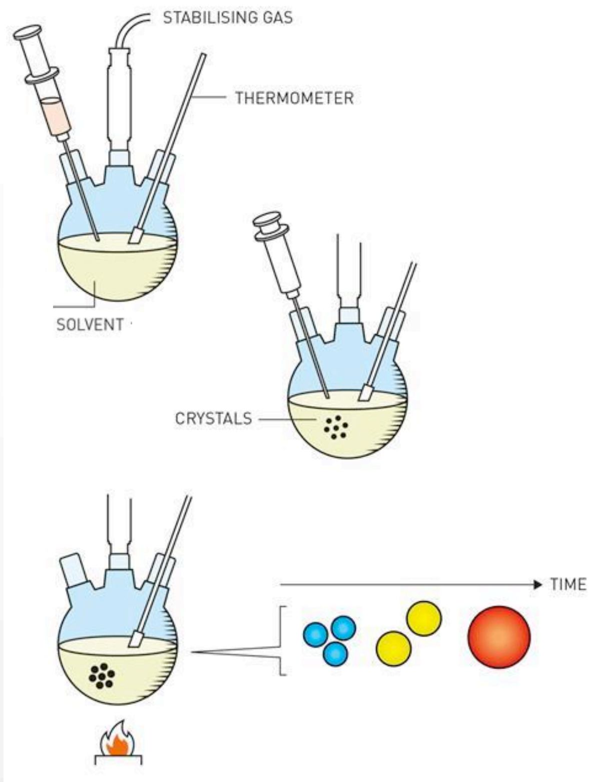
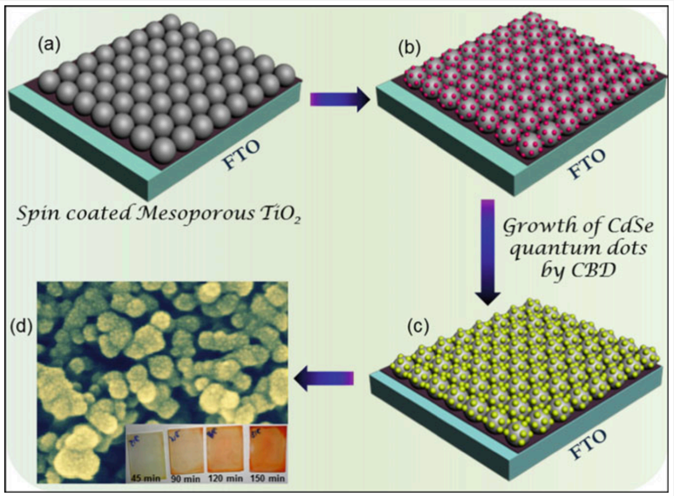
Production strategies

- hot injection of organometallic reagents into a hot solvent leading to nucleation taking place at well-defined times





- lattice structures slightly different in size from those of the material upon which the films are grown

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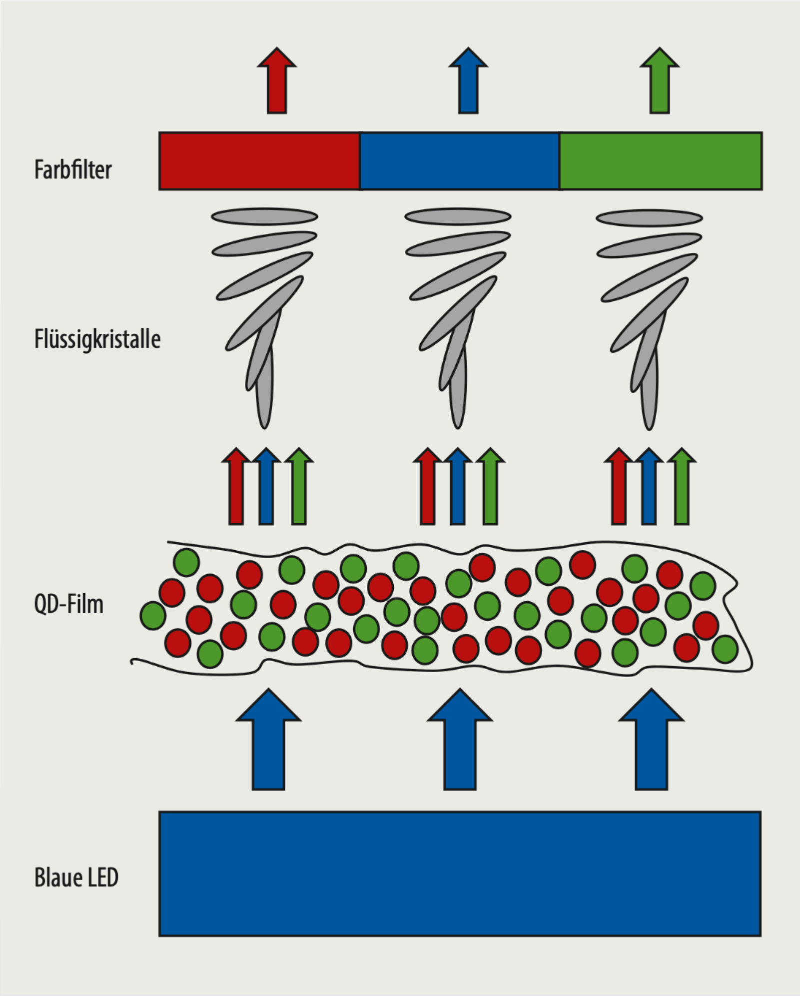
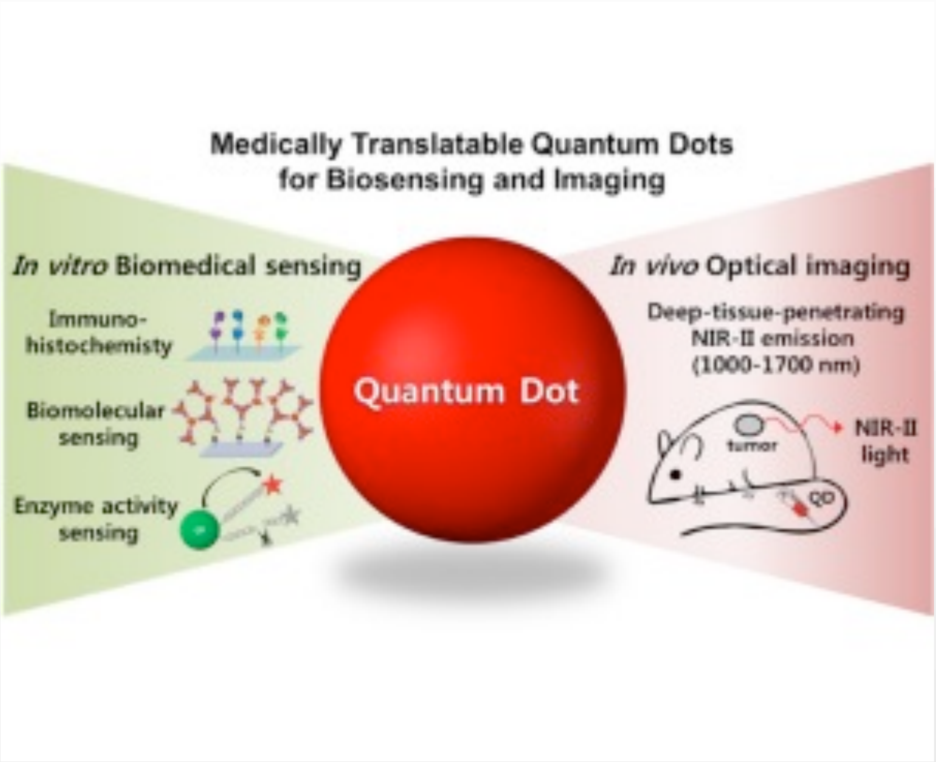
Applications

QLED displays



Q Dots-based biosensors



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Group picture

Finally, a picture!

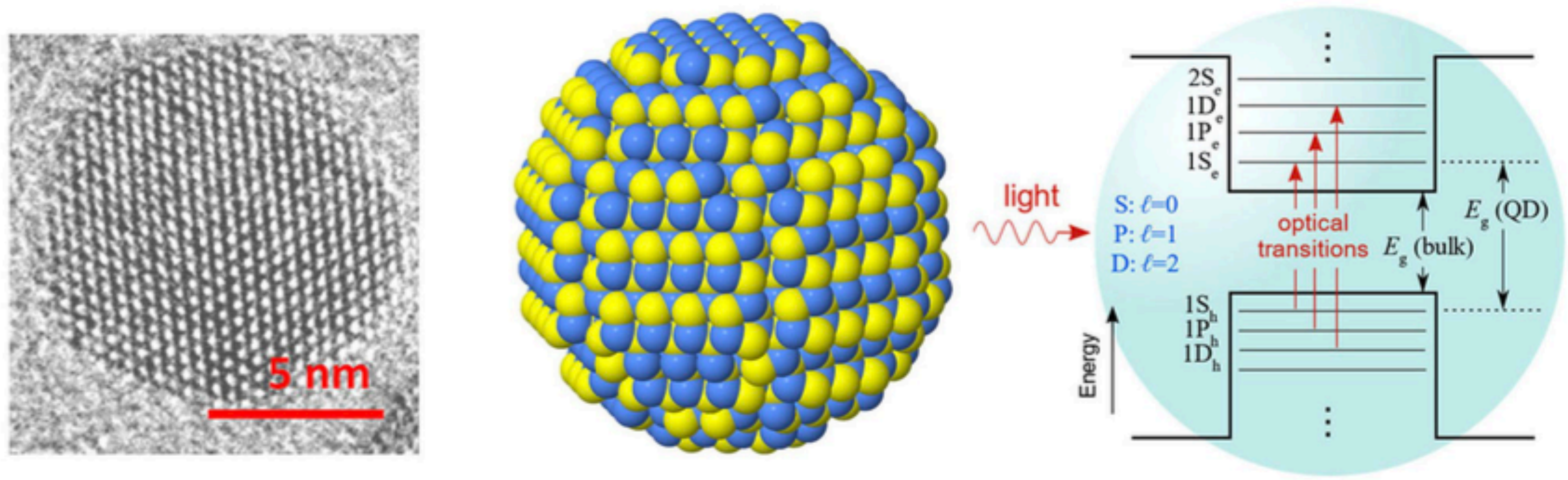

Fig. 3. Illustration of quantum dots. Left: transmission electron microscope image of a CdSe nanocrystal. Centre: Atomic structure of a nanocrystal. Right: Electronic states in a core-shell quantum dot, with the dot itself in the centre bracketed by a wide-bandgap shell. Reproduced from A. L. Efros and L.E. Brus, *ACS Nano* **15**, 6192 (2021).

Sources

The Nobel Prize in Chemistry 2023

Press release

Scientific motivation

DPG announcement

Physik Journal article

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