# Quantum Dots – Seeds of Nanoscience

KUNGL.
VETENSKAPS-
AKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

## THE NOBEL PRIZE IN CHEMISTRY 2023

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


©Johan Jarnestad/The Royal Swedish Academy of Sciences

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

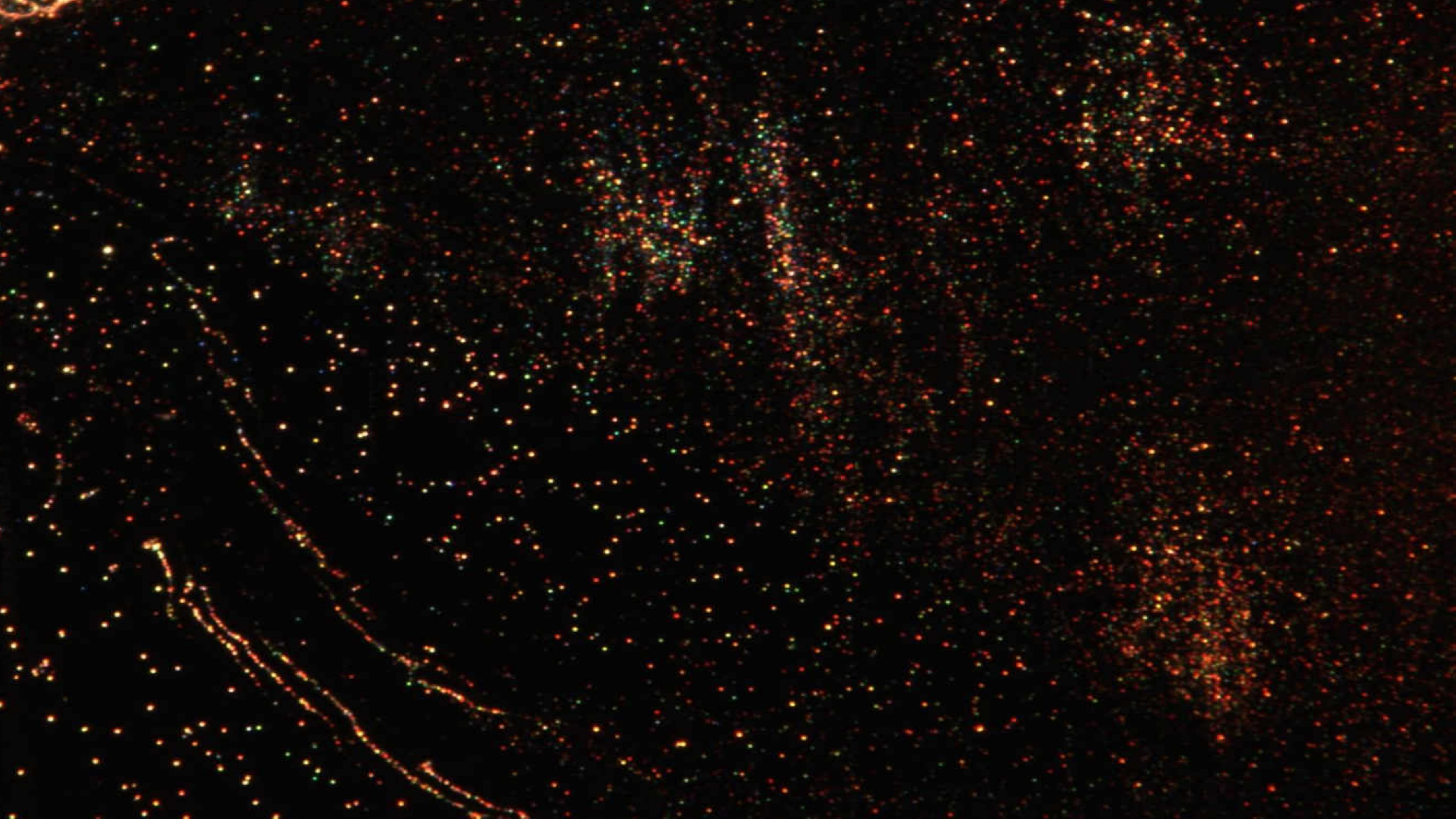
**Louis E. Brus**
Columbia University, New York, NY, USA

**Alexei I. Ekimov**
Nanocrystals Technology Inc., New York, NY, USA

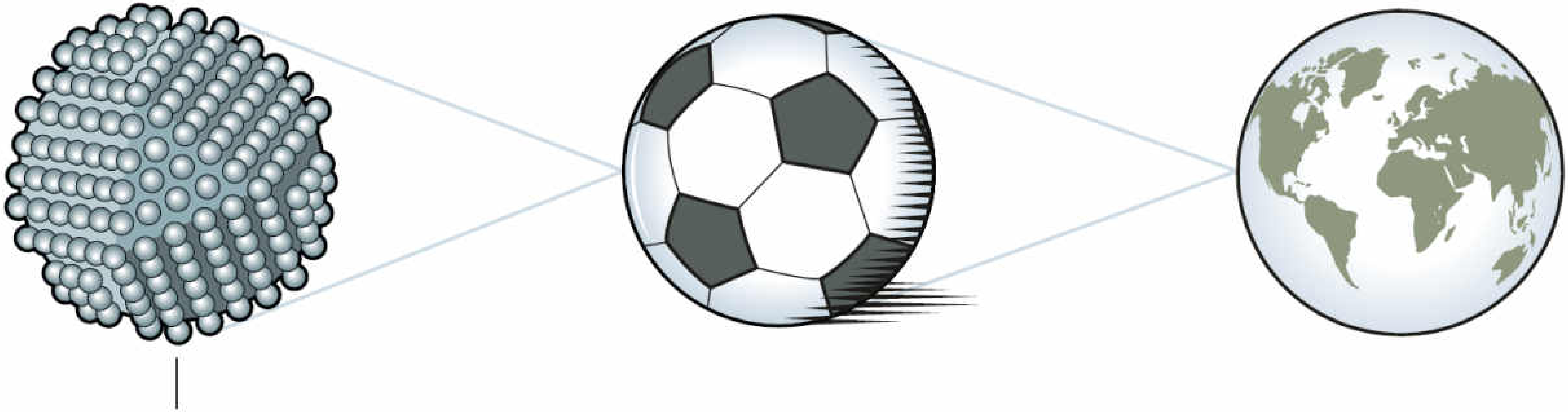
*‘for the discovery and synthesis of quantum dots’*

Faraday, 1857

Faraday’s gold preserved in Royal Institution. From the site, http://www.rigb.org/rimain/heritage/faradaypage.jsp



# How small are these ‘Quantum Dots’?



A quantum dot is a crystal that often consists of just a few thousand atoms. In terms of size, it has the same relationship to a football as a football has to the size of the Earth.

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# Remembering pioneers

**Michael Faraday** – Divided metals

**Lord Kelvin** – Melting depends on size?

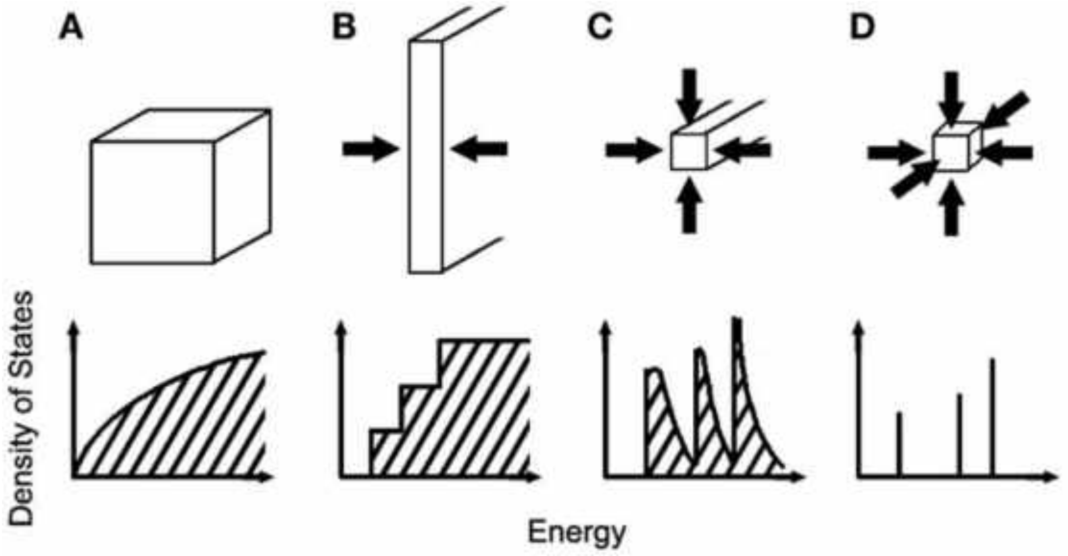
**Richard Feynman**, Nobel Prize 1965 – Plenty of room at the bottom

**Robert F. Curl, Harold W. Kroto and Richard E. Smalley** Nobel Prize 1996

**Andre Geim and Konstantin Novoselov**, Graphene, Nobel Prize 2010

**Jean Pierre Sauvage, J. Fraser Stoddart, and Bernard Lucas Feringa**, Molecular machines Nobel Prize 2016

# Quantum effects arise when particles shrink in size



Energy levels of semiconductor crystallites with different dimensionalities.

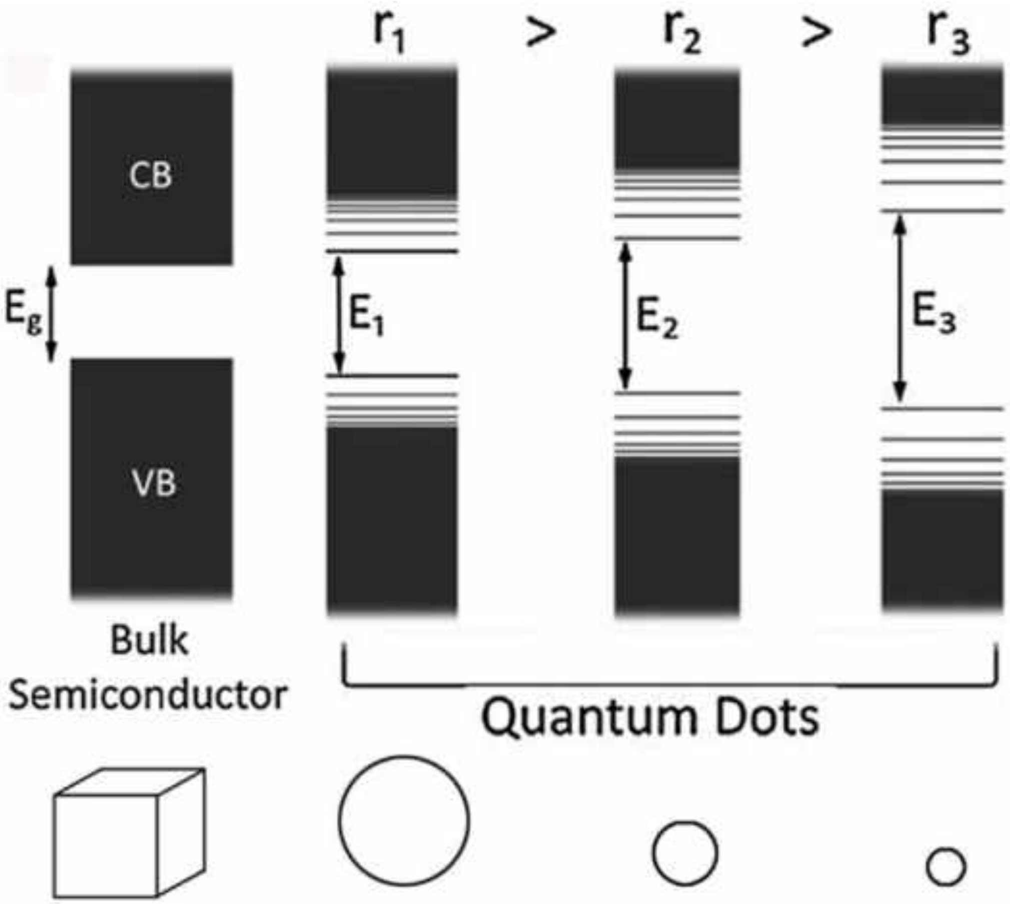
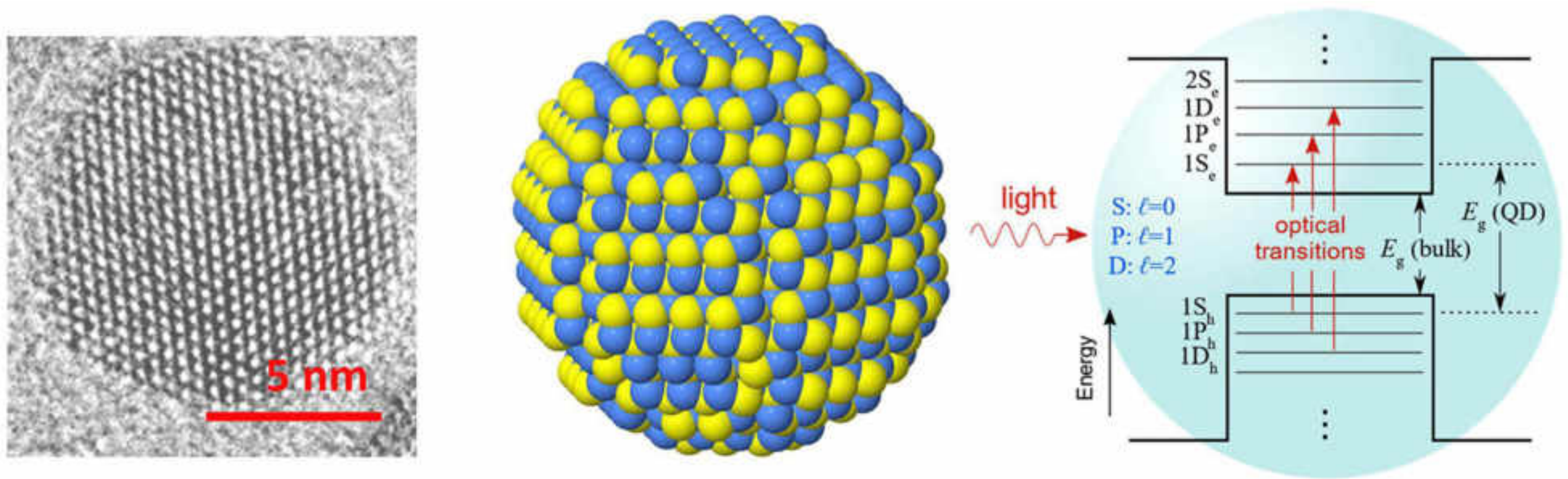


Illustration of size-dependent bandgap.

G. Dong, H. Wang, G. Chen, Q. Pan, J. Qiu, Frontiers in Materials 2015, 2.

# Illustration of quantum dots



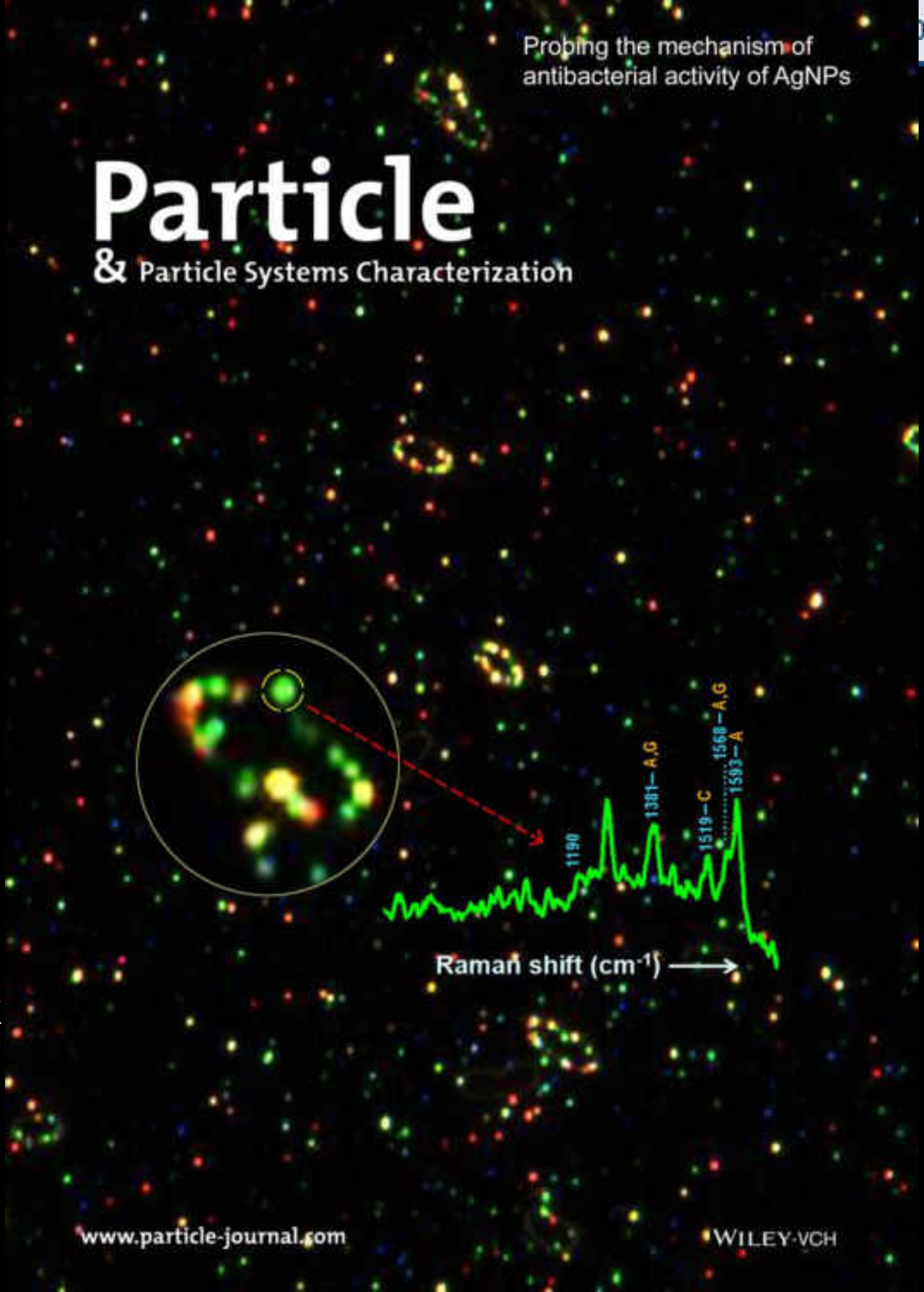
Left: transmission electron microscope image of a CdSe nanocrystal. Centre: Atomic structure of a nanocrystal. Right: Electronic states in a core-shell quantum dot, with the dot itself in the centre bracketed by a wide-bandgap shell.

A. L. Efros and L.E. Brus, ACS Nano 15, 6192 (2021).

**Today, 'quantum dot' refers to a nanostructure in which quantum mechanical effects manifest themselves in the electronic structure.**

- Either through quantum size effects, many-body interactions (excitonic states) or high surface-to-volume ratio such that surface states dominate the electronic structure.
- In addition to a small size comparable to the carriers' de Broglie wavelength, it is now recognized that the quantum phase coherence length (typically limited by inelastic scattering) needs to exceed the system size.

Lycurgus cup; in transmitting light (left) and the site, http://www.thebritishmuseum.ac.uk



Probing the mechanism of antibacterial activity of AgNPs

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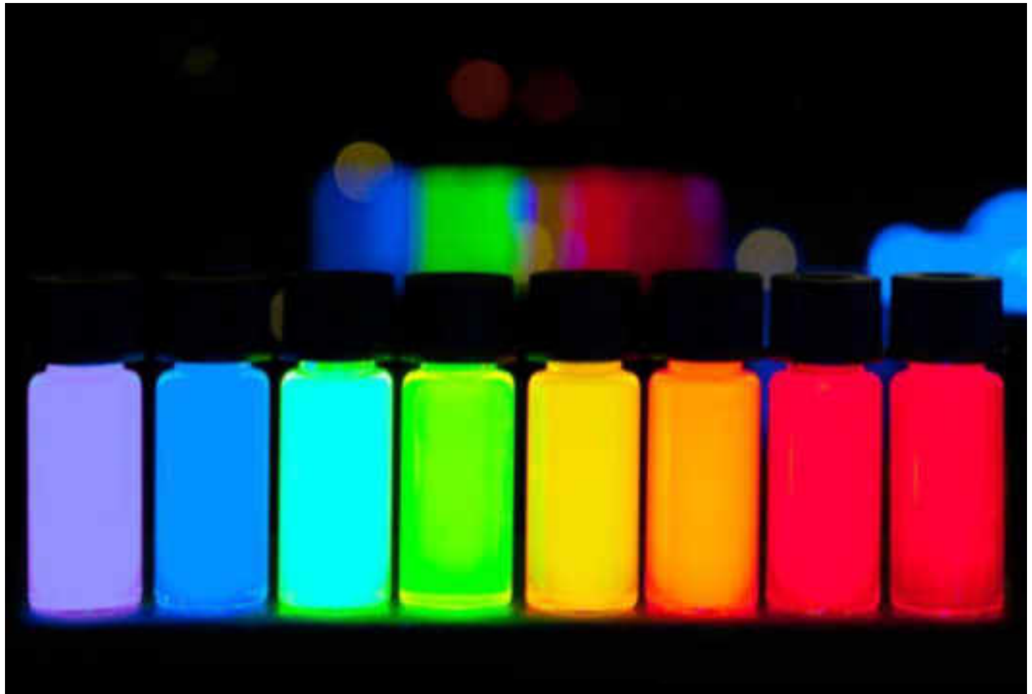
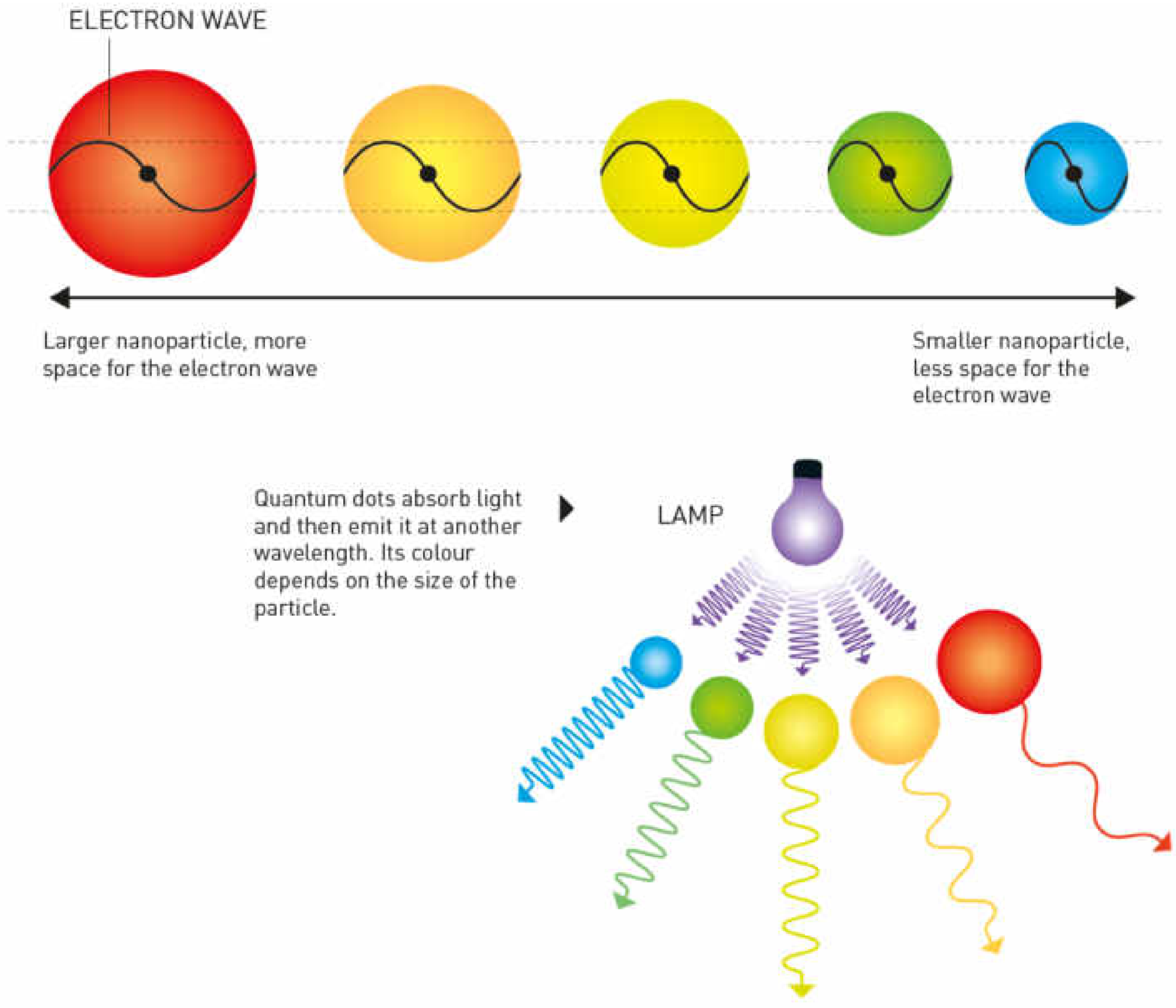
# ‘They added colour to nanotechnology’



Vials of quantum dots with gradually stepping emission from violet to deep red.



Larger nanoparticle, more space for the electron wave

Smaller nanoparticle, less space for the electron wave

Quantum dots absorb light and then emit it at another wavelength. Its colour depends on the size of the particle.

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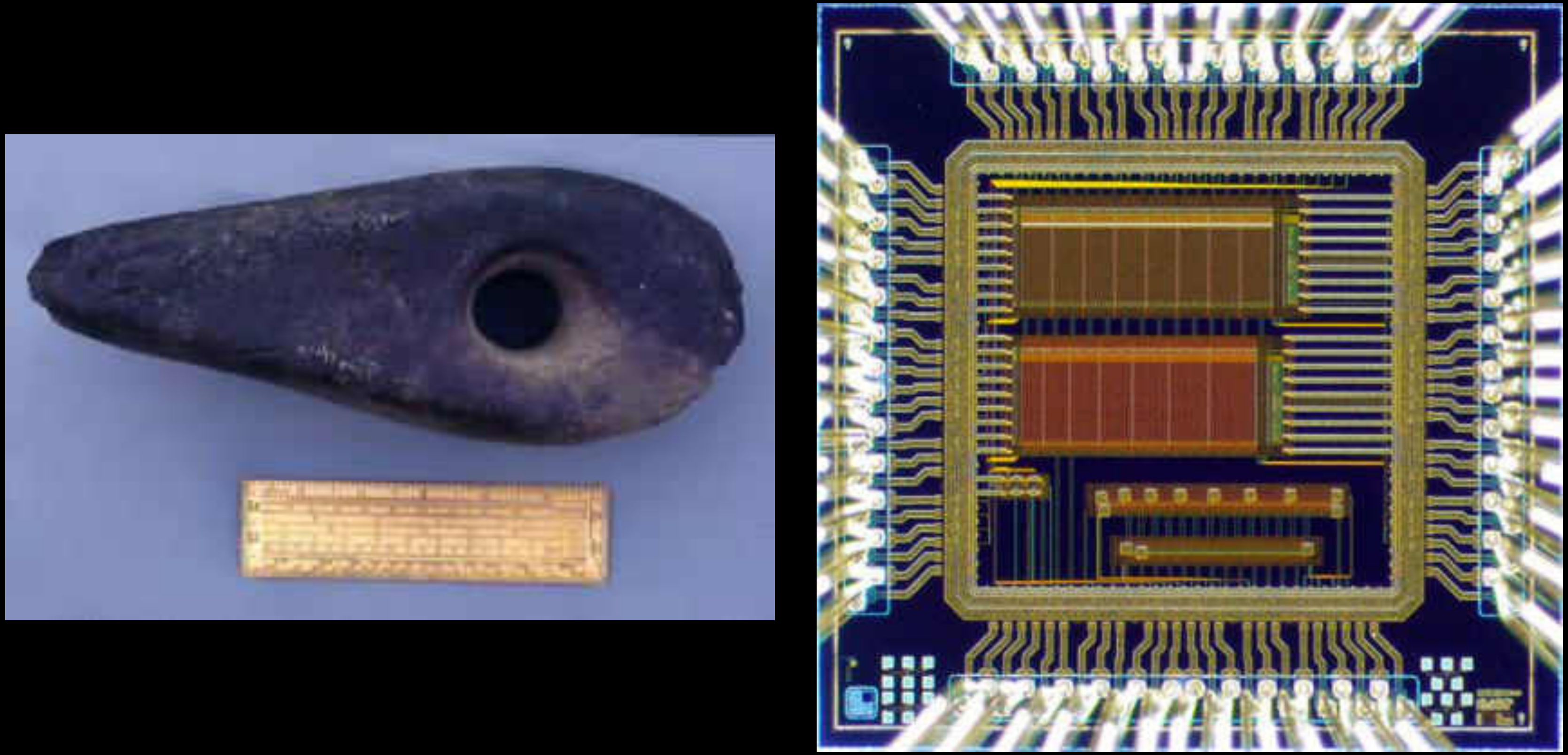
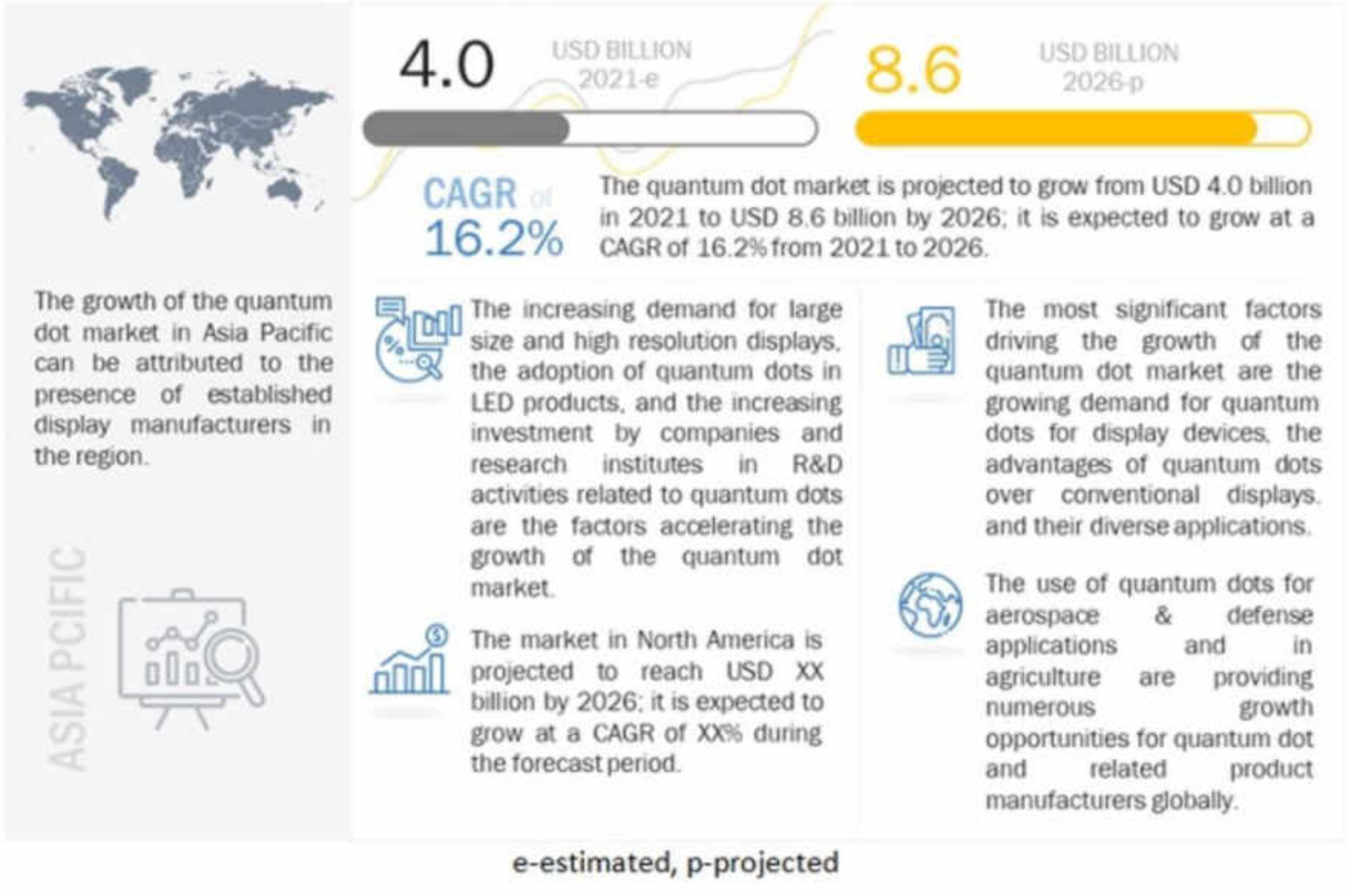
# Technology is about manipulating objects



Growth of civilization reduced the size of objects manipulated

# Quantum dot market



4.0 USD BILLION 2021-e

8.6 USD BILLION 2026-p

CAGR of 16.2%

The quantum dot market is projected to grow from USD 4.0 billion in 2021 to USD 8.6 billion by 2026; it is expected to grow at a CAGR of 16.2% from 2021 to 2026.

The growth of the quantum dot market in Asia Pacific can be attributed to the presence of established display manufacturers in the region.

ASIA PCIFIC

The increasing demand for large size and high resolution displays, the adoption of quantum dots in LED products, and the increasing investment by companies and research institutes in R&D activities related to quantum dots are the factors accelerating the growth of the quantum dot market.

The market in North America is projected to reach USD XX billion by 2026; it is expected to grow at a CAGR of XX% during the forecast period.

The most significant factors driving the growth of the quantum dot market are the growing demand for quantum dots for display devices, the advantages of quantum dots over conventional displays, and their diverse applications.

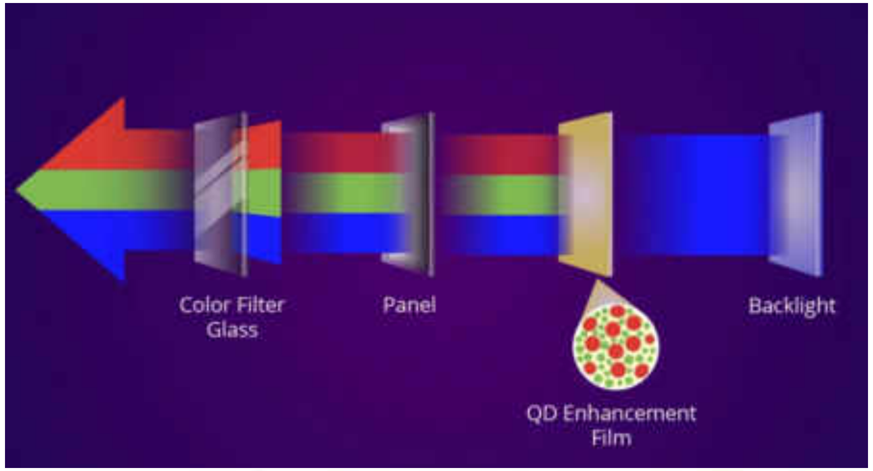
The use of quantum dots for aerospace & defense applications and in agriculture are providing numerous growth opportunities for quantum dot and related product manufacturers globally.

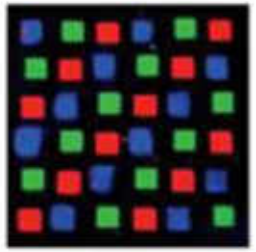
e-estimated, p-projected

https://www.marketsandmarkets.com/Market-Reports/quantum-dots-qd-market-694.html

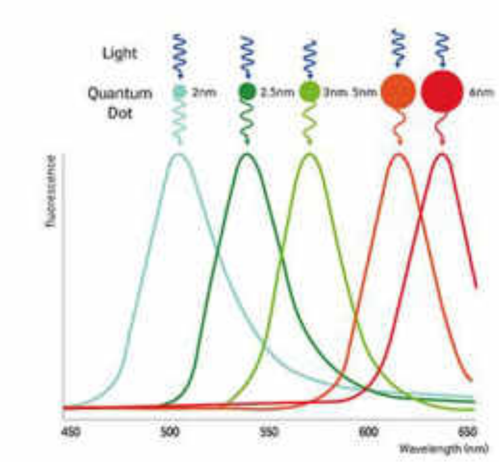
# Quantum dot (QLED) displays

## QLED Panel Layers

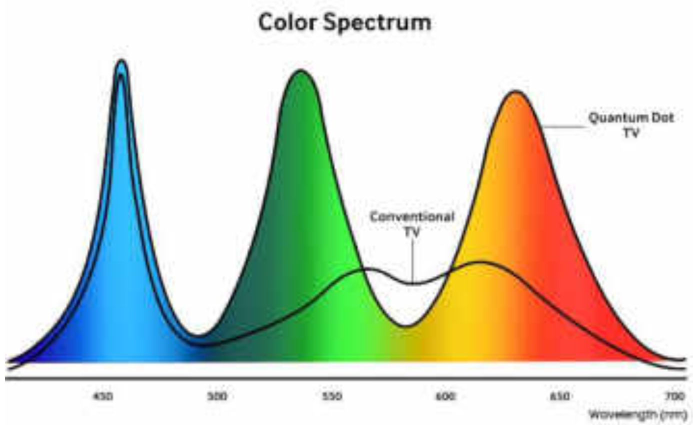


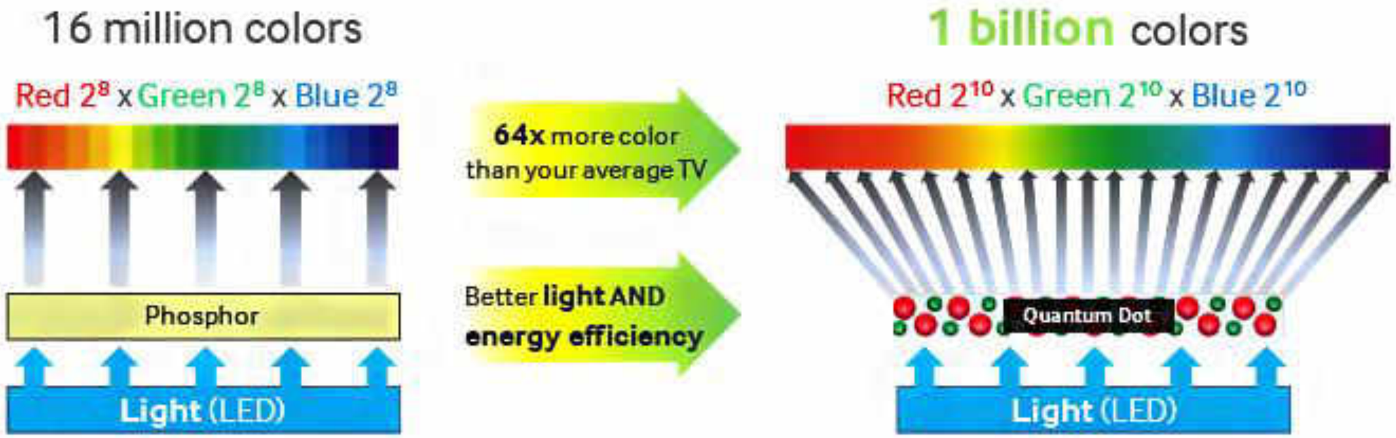


## Color depends on the size of the QDs



## Energy efficient





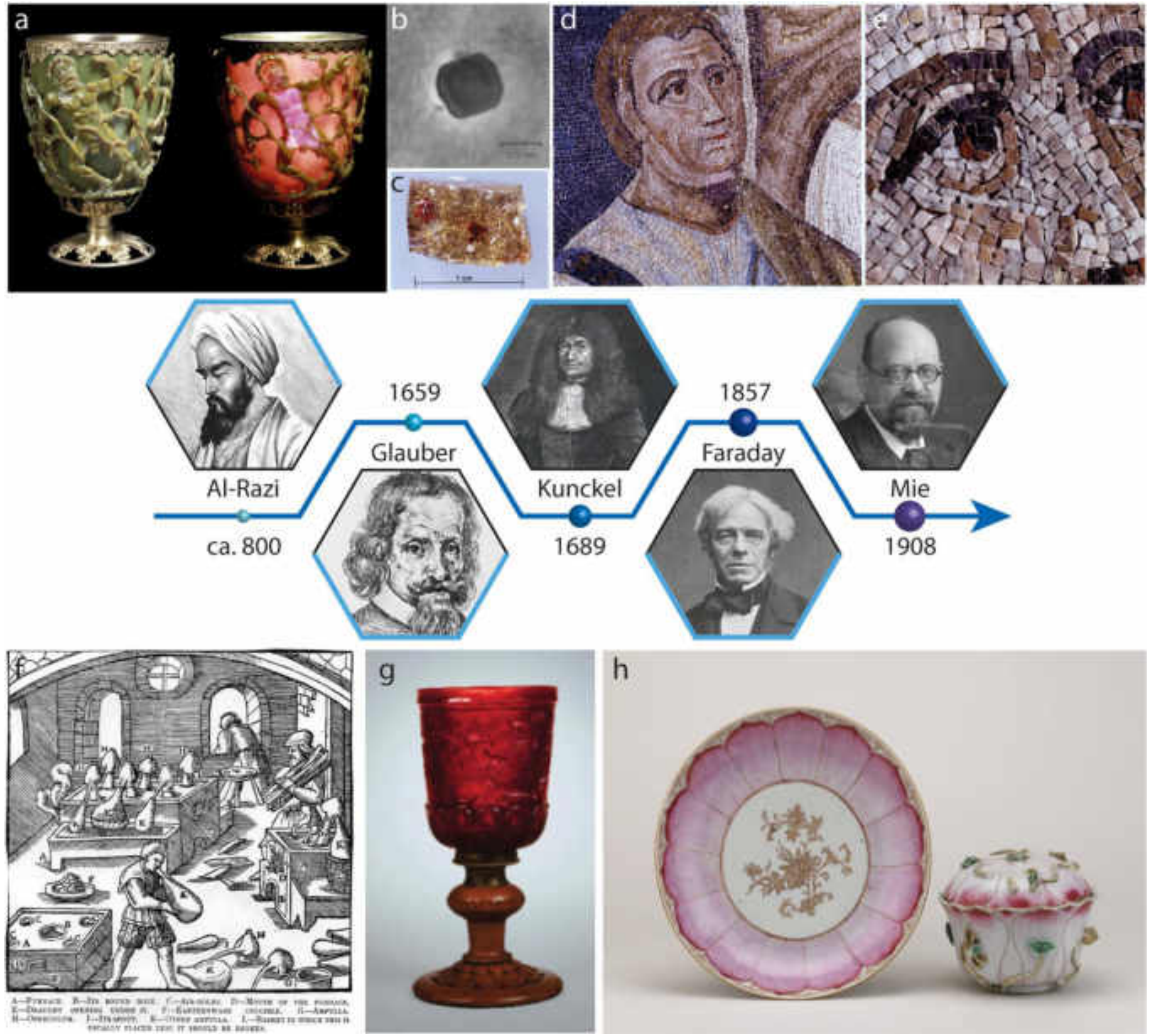
## Capable of displaying wide color gamut

# Discovery of quantum size effects

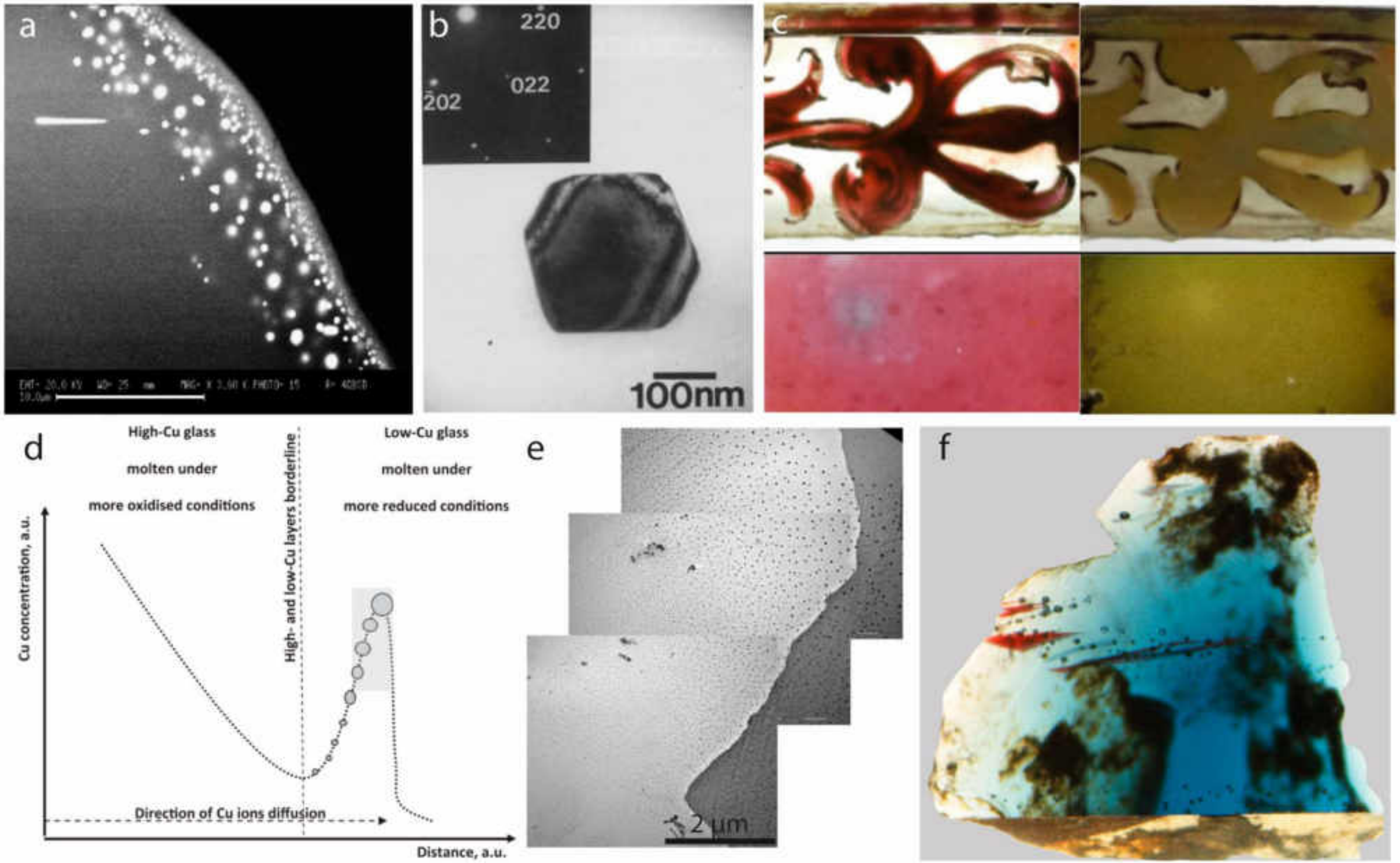
## Part I : Quantum dots in glass matrix

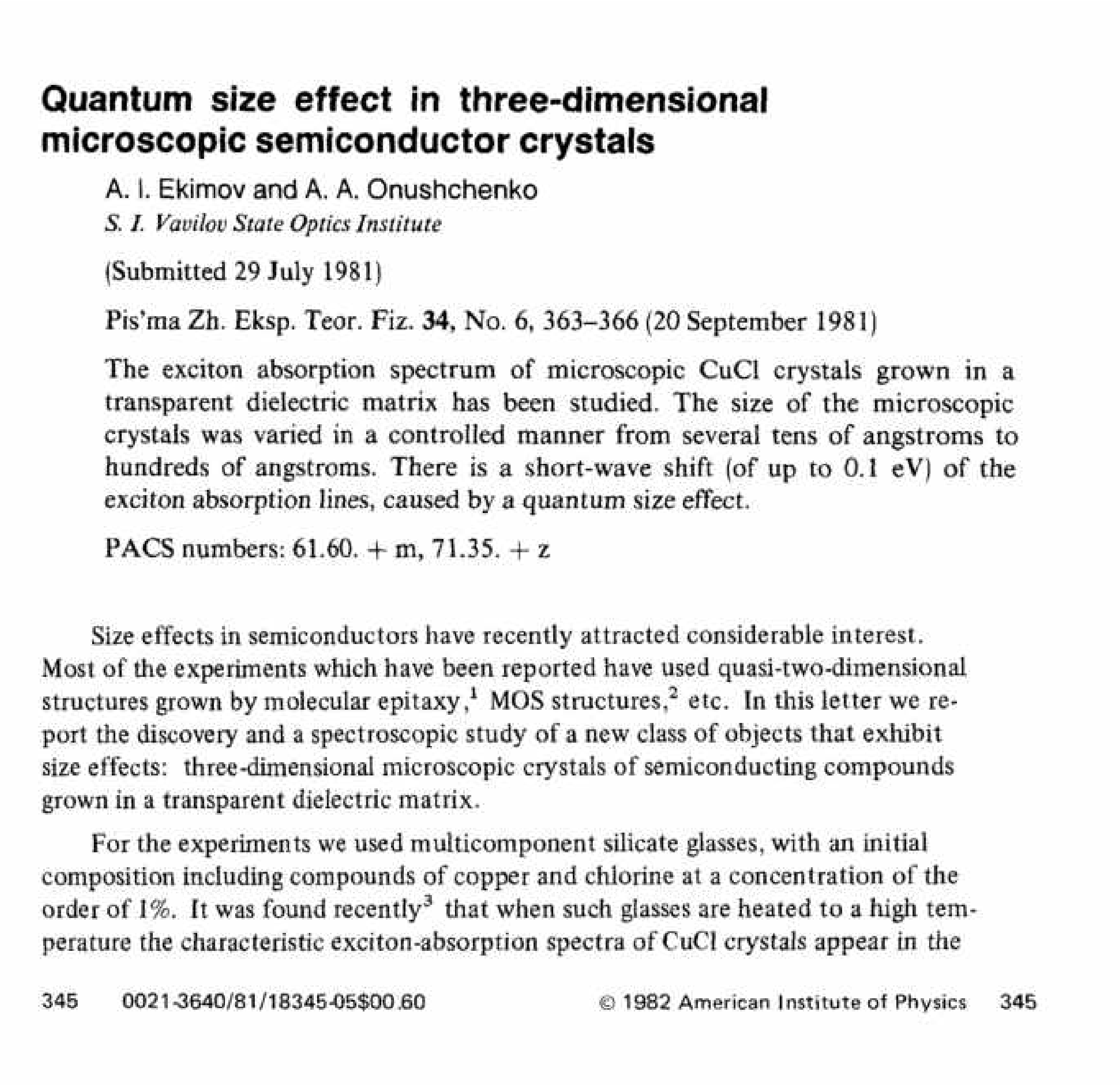
**Alexey I. Ekimov**

# Use of gold nanocrystals throughout the centuries



# Nanocrystals in glass throughout history





# 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)

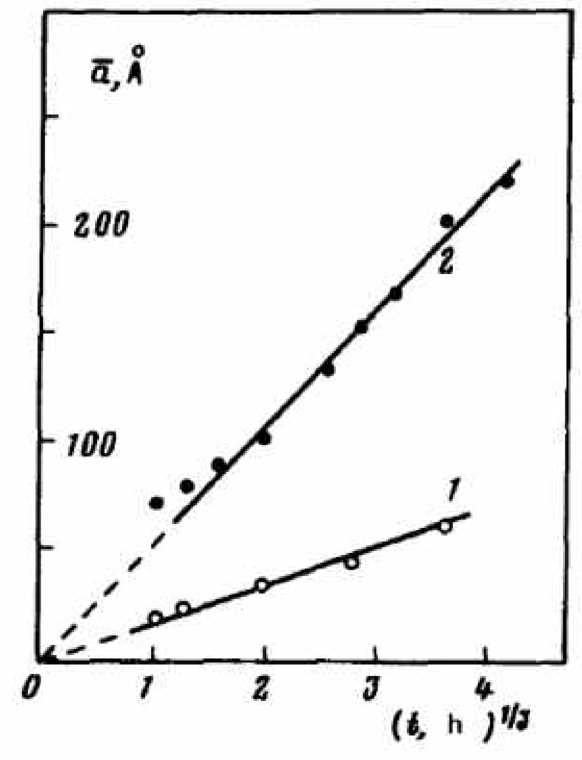
The exciton absorption spectrum of microscopic CuCl crystals grown in a transparent dielectric matrix has been studied. The size of the microscopic crystals was varied in a controlled manner from several tens of angstroms to hundreds of angstroms. There is a short-wave shift (of up to 0.1 eV) of the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

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

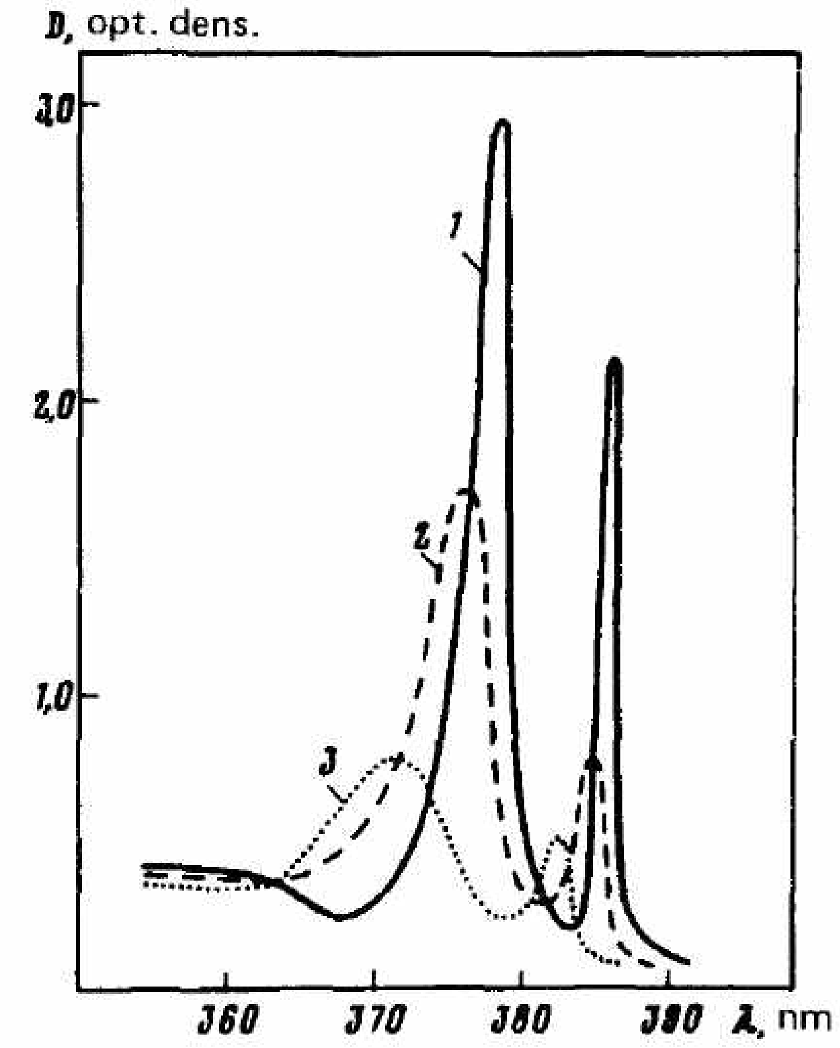
Size effects in semiconductors have recently attracted considerable interest. Most of the experiments which have been reported have used quasi-two-dimensional structures grown by molecular epitaxy,[1] MOS structures,[2] etc. In this letter we report the discovery and a spectroscopic study of a new class of objects that exhibit size effects: three-dimensional microscopic crystals of semiconducting compounds grown in a transparent dielectric matrix.

For the experiments we used multicomponent silicate glasses, with an initial composition including compounds of copper and chlorine at a concentration of the order of 1%. It was found recently[3] that when such glasses are heated to a high temperature the characteristic exciton-absorption spectra of CuCl crystals appear in the

# Observation of quantum size effects in microscopic CuCl crystals in Schott glasses

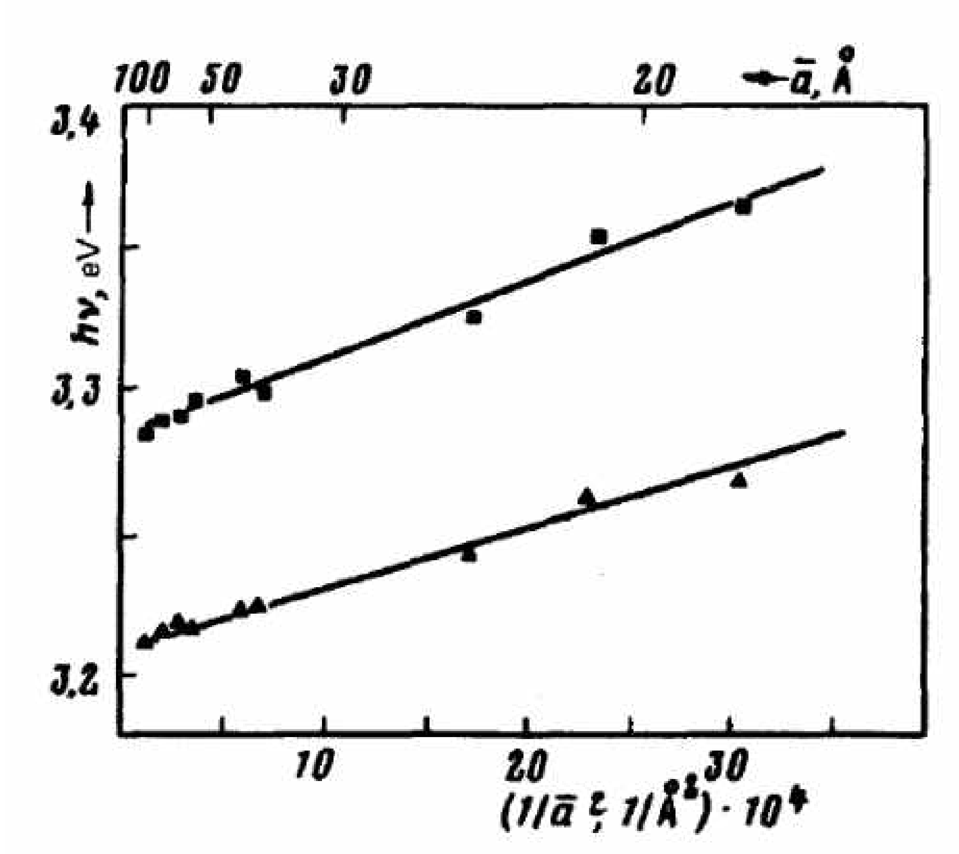


Dependence of the average radius of the CuCl crystals on the duration of heat treatment: 1 - 550°C; 2 - 625°C.



Absorption spectra of microscopic CuCl crystals at T=4.2 K with different average radii: 1 - 310 Å, 2 - 100 Å, c - 25 Å.

A.I. Ekimov and A.A. Onushchenko, JETP Lett 1981, 34, 345–349.



Dependence of the spectral positions of exciton absorption lines at T = 4.2 K on the average radius ā of CuCl nanocrystals in glass. The energy of the absorption line increases proportional to $\bar{a}^{-2}$.

Photon energy $\hbar\omega$ of the exciton absorption line:

$$\hbar\omega = E_g - E_{ex} + \frac{\hbar^2\pi^2}{2M\bar{a}^2}$$

Here, $E_g$ is the bulk material's semiconductor bandgap, $E_{ex}$ is the exciton binding energy, and M is the charge carrier effective mass.

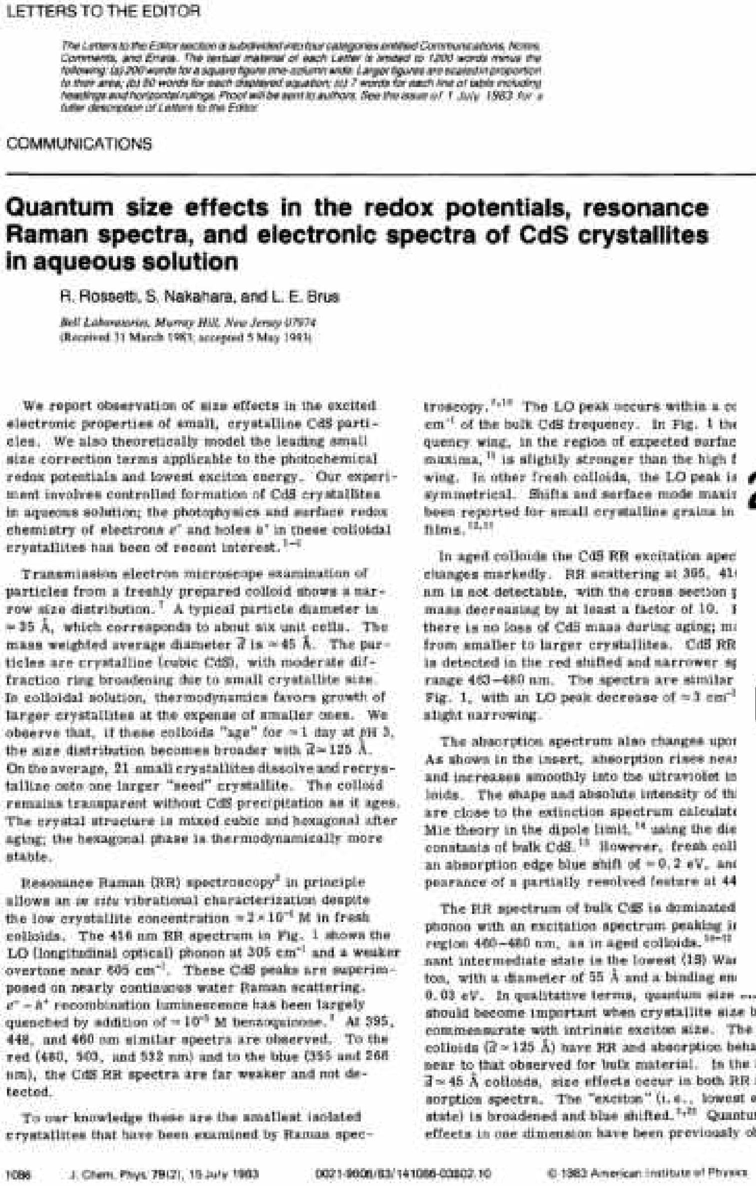
A.I. Ekimov and A.A. Onushchenko, JETP Lett 1981, 34, 345–349.
Ekimov, A.; Onushchenko, A. Sov Phys Semicond+ 1982, 16 (7), 775-778.

- Limitation of Ekimov's groundbreaking discovery was that his team's quantum dots were 'frozen' in glass and not suitable for further processing.

# Discovery of quantum size effects

## In colloidal quantum dots

**Louis E. Brus**



LETTERS TO THE EDITOR

*The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1983 for a fuller description of Letters to the Editor.*

COMMUNICATIONS

## Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution

R. Rossetti, S. Nakahara, and L. E. Brus

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 11 March 1983; accepted 5 May 1983)

We report observation of size effects in the excited electronic properties of small, crystalline CdS particles. We also theoretically model the leading small size correction terms applicable to the photochemical redox potentials and lowest exciton energy. Our experiment involves controlled formation of CdS crystallites in aqueous solution; the photophysics and surface redox chemistry of electrons $e^-$ and holes $h^+$ in these colloidal crystallites has been of recent interest.[1-4]

Transmission electron microscope examination of particles from a freshly prepared colloid shows a narrow size distribution.[7] A typical particle diameter is ≈35 Å, which corresponds to about six unit cells. The mass weighted average diameter $\bar{d}$ is ≈45 Å. The particles are crystalline (cubic CdS), with moderate diffraction ring broadening due to small crystallite size. In colloidal solution, thermodynamics favors growth of larger crystallites at the expense of smaller ones. We observe that, if these colloids "age" for ≈1 day at pH 3, the size distribution becomes broader with $\bar{d}$≈125 Å. On the average, 21 small crystallites dissolve and recrystallize onto one larger "seed" crystallite. The colloid remains transparent without CdS precipitation as it ages. The crystal structure is mixed cubic and hexagonal after aging; the hexagonal phase is thermodynamically more stable.

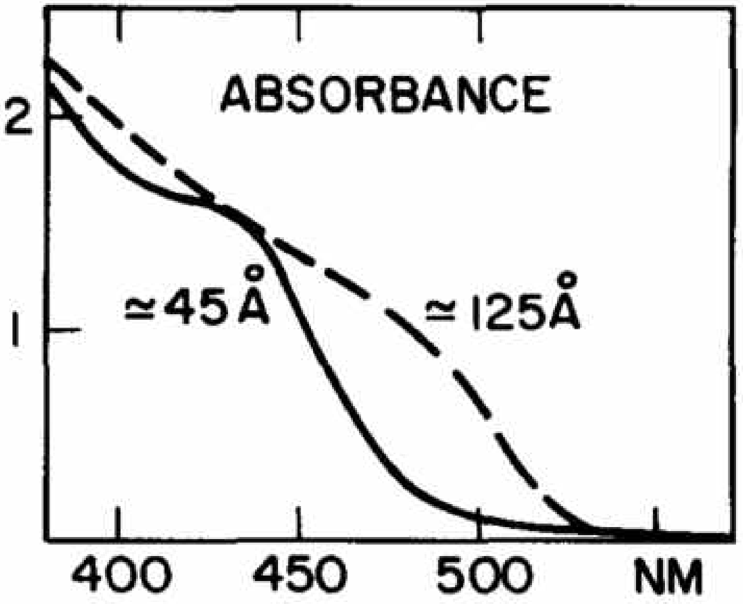
Resonance Raman (RR) spectroscopy[8] in principle allows an *in situ* vibrational characterization despite the low crystallite concentration ≈$2\times10^{-6}$ M in fresh colloids. The 416 nm RR spectrum in Fig. 1 shows the LO (longitudinal optical) phonon at 305 cm$^{-1}$ and a weaker overtone near 605 cm$^{-1}$. These CdS peaks are superimposed on nearly continuous water Raman scattering. $e^- - h^+$ recombination luminescence has been largely quenched by addition of ≈$10^{-3}$ M benzoquinone.[7] At 395, 448, and 460 nm similar spectra are observed. To the red (480, 503, and 532 nm) and to the blue (355 and 268 nm), the CdS RR spectra are far weaker and not detected.

To our knowledge these are the smallest isolated crystallites that have been examined by Raman spectroscopy.[9,10] The LO peak occurs within a c
cm$^{-1}$ of the bulk CdS frequency. In Fig. 1 th
quency wing, in the region of expected surfac
maxima,[11] is slightly stronger than the high f
wing. In other fresh colloids, the LO peak is
symmetrical. Shifts and surface mode maxi
been reported for small crystalline grains in
films.[12,13]

In aged colloids the CdS RR excitation spec
changes markedly. RR scattering at 395, 41
nm is not detectable, with the cross section p
mass decreasing by at least a factor of 10.
there is no loss of CdS mass during aging; m
from smaller to larger crystallites. CdS RR
is detected in the red shifted and narrower s
range 460–480 nm. The spectra are similar
Fig. 1, with an LO peak decrease of ≈3 cm$^{-1}$
slight narrowing.

The absorption spectrum also changes upo
As shown in the insert, absorption rises nea
and increases smoothly into the ultraviolet i
loids. The shape and absolute intensity of th
are close to the extinction spectrum calculat
Mie theory in the dipole limit,[14] using the di
constants of bulk CdS.[15] However, fresh col
an absorption edge blue shift of ≈0.2 eV, an
pearance of a partially resolved feature at 44

The RR spectrum of bulk CdS is dominated
phonon with an excitation spectrum peaking i
region 460–480 nm, as in aged colloids.[16-17]
nant intermediate state is the lowest (1S) Wa
ton, with a diameter of 55 Å and a binding en
0.03 eV. In qualitative terms, quantum size
should become important when crystallite size becomes commensurate with intrinsic exciton size. The aged colloids ($\bar{d}$≈125 Å) have RR and absorption behavior near to that observed for bulk material. In the fresh $\bar{d}$≈45 Å colloids, size effects occur in both RR and absorption spectra. The "exciton" (i.e., lowest excited state) is broadened and blue shifted.[1,20] Quantum size effects in one dimension have been previously observed



## Size effects in the excited electronic states of small colloidal CdS crystallites

R. Rossetti, J. L. Ellison,[a] J. M. Gibson, and L. E. Brus

*Bell Laboratories, Murray Hill, New Jersey 07974*

(Received 7 December 1983; accepted 25 January 1984)

This paper reports experimental studies of the development of bulk optical properties as a function of crystallite size for the inorganic direct gap semiconductor CdS. Small crystallites are synthesized via colloidal chemical techniques, and their optical properties are studied *in situ* at extreme dilution. The crystallites are characterized via high resolution transmission electron microscopy. Direct images show (111) lattice planes, and establish the crystallite structures as close to those of excised fragments of bulk CdS (zinc-blende cubic). Large crystallites (> 100 Å average diameter) show an optical absorption, in colloidal solution, close to that of bulk crystalline material. However, small crystallites of 30 Å average diameter show a large blue shift (~0.8 eV) in absorption edge (effective band gap), and an intensification of edge absorption relative to absorption at higher energy regions. These observations can be understood as quantum size effects resulting from confinement of an electron and hole in a small volume. 40 Å average size crystallites show a smaller shift (~0.25 eV), and corresponding changes in their fluorescence, and resonance Raman excitation, spectra.

### IOUCTION

s experiment explores the development of bulk spec-
: and electronic properties as a function of crystal-
n the semiconductor CdS. In general, semiconduc-
metals are materials in which the individual atomic
ular components undergo strong intercomponent
l bonding. The properties of the bulk material are
e in nature and entirely different than those of the
nt molecules. We attempt to understand how these
s develop as a function of size, and whether aggre-
ntermediate size have properties that are not char-
: of either the atomic or bulk limits.
: experimental approach to synthesis and character-
f small particles involves controlled reaction in a
elding extremely dilute colloidal crystallites, with
imension in the range 10–10$^3$ Å. Chemical interest
loped in the catalytic properties of such colloidal
nd semiconductors.[1-4] Colloidal semiconductors
tilized as photosensitizers, in that optical excitation
e band gap creates an electron and hole which may
ividually react with adsorbed molecular species.
tion naturally arises as to the correct physical de-
of the confined electron and hole, i.e., as to the
f the crystallite excited electronic states. This ques-
urn depends intimately upon the actual structure
of the aggregate. In this paper we characterize col-
dS crystallites with high-resolution transmission
microscopy (TEM), and correlate changes in dimen-
h changes in the electronic absorption, resonance
and fluorescence spectra.
: solubility product of CdS in water is so low
[illegible] ) that, if a dilute Cd$^{++}$ solution is mixed with S$^{-}$
solution at higher concentration, Cd$^{++}$ will exist almost entirely in the form of solid CdS when equilibrium is achieved. The size of the initial crystallites formed is controlled by kinetic considerations during mixing. Their stability, once formed, is influenced by the dynamic equilibrium

$$(\mathrm{CdS})_{\mathrm{crystal}} \rightleftharpoons (\mathrm{Cd}^{++})_{\mathrm{soln}} + (\mathrm{S}^{--})_{\mathrm{soln}}. \qquad (1)$$

This equilibrium is a function of both crystallite size and solvent dielectric constant. Small crystallites are less stable than large crystallites and tend to dissolve rapidly.[7] The dissolved ions can recrystallize on larger crystallites where thermodynamic stability is higher. The net effect is that mass transfers from smaller to larger crystallites as a function of time—an effect long known as "aging" or Ostwald ripening. In principle, such aging can be reduced, and thus the lifetime of small crystallites enhanced, in a solvent of low dielectric constant where dissolved ions are less stable than in water. The equilibrium is shifted to the left hand side in Eq. (1). We study an aqueous CdS colloid in both its initial and aged form. We also study a CdS colloid in acetonitrile, a solvent of lower dielectric constant (ε = 36), in which smaller crystallites are obtained.

In this manuscript we first establish experimentally that the colloidal particles are crystalline, and that the optical properties are a function of size. To our knowledge, this work (along with our earlier Communication[8]) is the first report of a correlation between semiconductor crystallite size and optical properties. We then compare these observations with the predictions of the elementary model of an electron and hole confined in a small crystallite.[9]

### II. EXPERIMENTAL

Both acetonitrile and aqueous colloids contain 0.1% by weight of styrene/maleic anhydride copolymer, a stabilizing agent used to prevent coagulation and flocculation. While the role of the copolymer is not fully understood, the dissolved copolymer has negative carboxylate groups which apparently complex with Cd$^{++}$ surface ions on the CdS crystallite.

The aqueous colloid was prepared by slowly injecting with a syringe 20 cc of $9.3\times10^{-3}$ M CdSO$_4$ solution into 100 cc of a stirring ≈$5\times10^{-3}$ M (NH$_4$)$_2$S solution (containing

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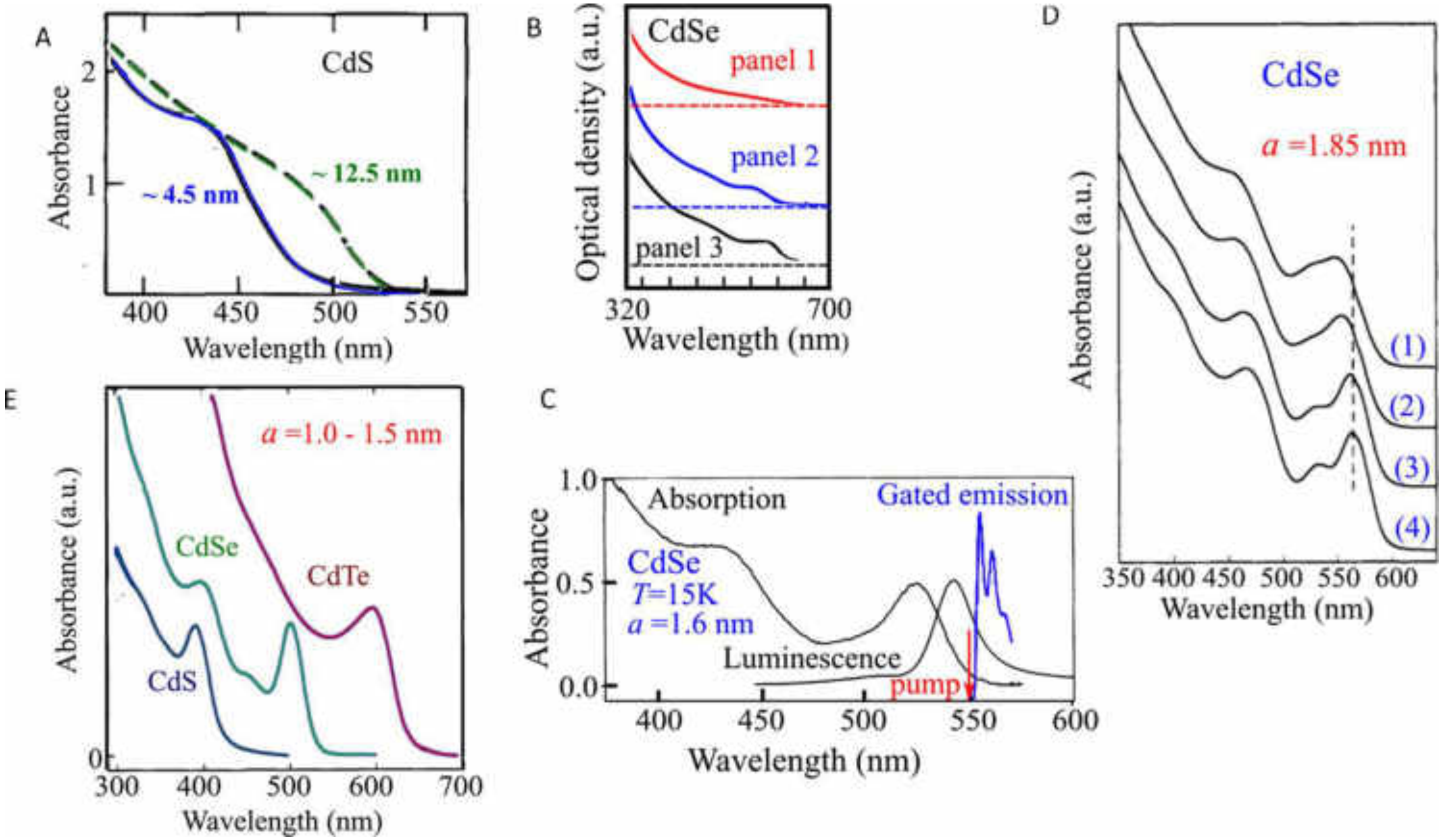
[a] Bell Laboratories undergraduate research student.

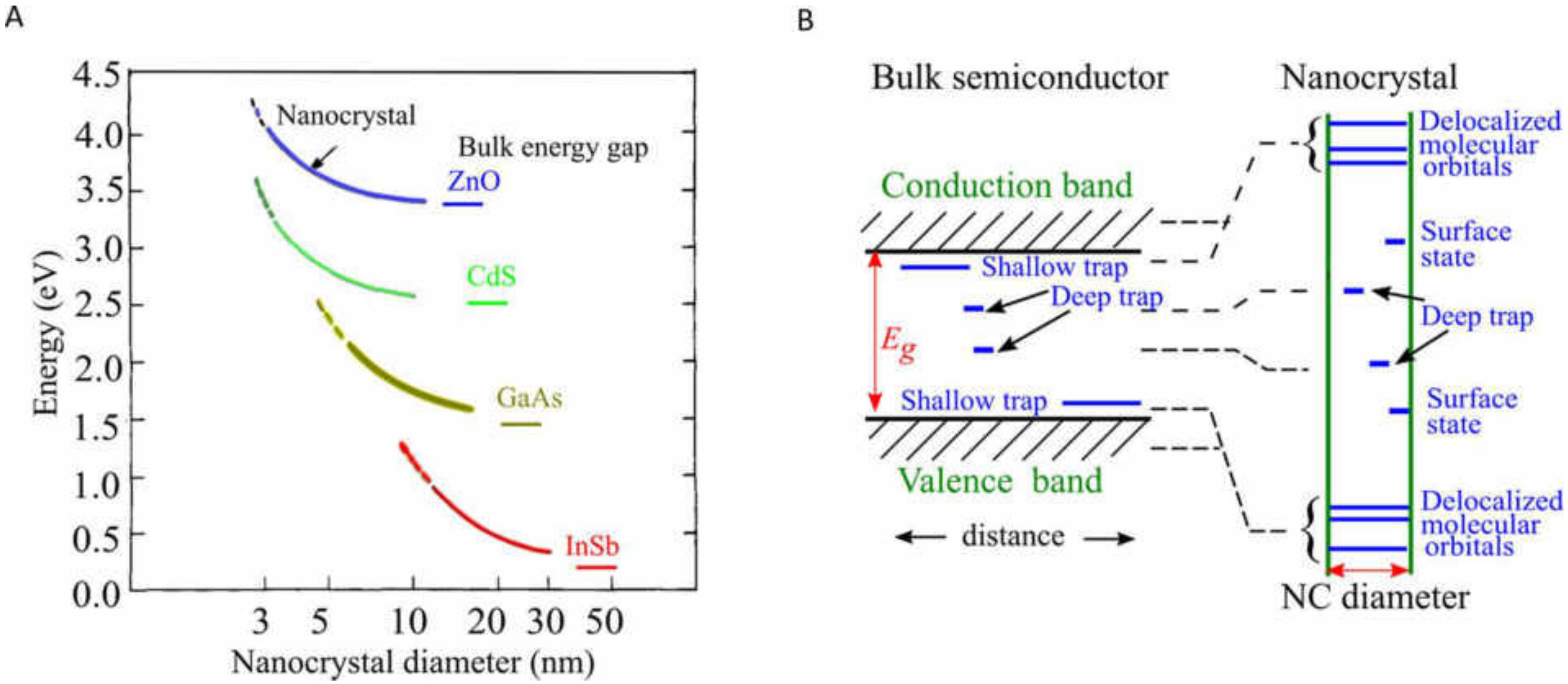
# Evidence of quantum size effects in colloidal nanoparticles



**Nucleation and growth of NCs in an aqueous solution.** (A) Room-temperature absorption spectra of “fresh” and aged for 1 day CdS NC in aqueous solution. (B) Room-temperature absorption spectra of CdSe NC grown by inverse micelle approach, before (panel 1) and after (panel 2) postreaction annealing as well as wurtzite CdSe NCs resulting from high-temperature refluxing (panel 3). (C) Photoluminescence from 1.6 nm radius CdSe NC and its resonance photoexcitation. (D) Sharpening of CdSe NC absorption spectra introduced by size-selective precipitation. (E) Absorption spectra of CdS, CdSe, and CdTe NCs.

Rossetti, R.; Nakahara, S.; Brus, L. E. J Chem Phys 1983, 79 (2), 1086-1088.
Rossetti, R.; Ellison, J. L.; Gibson, J. M.; Brus, L. E. Chem Phys 1984, 80 (9), 4464-4469.
Brus, L. E.  J Chem Phys 1983, 79 (11), 5566-5571.
Steigerwald, M. L.; Brus, L. E. Acc. Chem. Res. 1990, 23, 183−188.

# Theoretical ideas from 1980s



(A) Calculated size-dependent shift of the lowest exciton levels in strong confinement. (B) Spatial electronic state correlation diagram for bulk semiconductors and NCs.

Brus, L. E. J Chem Phys 1984, 80 (9), 4403-4409.
Brus, L. E. J Phys Chem 1986, 90 (12), 2555-2560.

- The discovery of quantum size effects in colloidal nanocrystals stimulated significant research efforts in understanding their optical and photochemical properties, in the hope of being able to use size to design desirable physical and chemical properties.
- Limited homogeneity and quality of the available nanocrystals, with variations in size, shape, crystallinity and surface electronic defects made it difficult to isolate inherently size-dependent behaviour. For example, luminescence from nanocrystals available in the late 1980s was typically limited by a quantum yield of only a few percent.

# Synthesis

## Improved universal synthetic methodology

**Moungi G. Bawendi**

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.

## I. Introduction

The study of nanometer sized crystallites provides an opportunity to observe the evolution of material properties with size. This intermediate size regime is where the collective behavior of bulk materials emerges from the discrete nature of molecular properties. The differing rates with which each of the bulk properties develops provides the possibility of observing and perhaps controlling novel behavior. Nonlinear optical effects from highly polarizable excited states and novel photochemical behavior are two such examples.[1]

The physical properties of semiconductor nanocrystallites are dominated by the spatial confinement of excitations (electronic and vibrational). Quantum confinement, the widening HOMO LUMO gap with decreasing crystallite size, and its implications for the electronic structure and photophysics of the crystallites have generated considerable interest.[1,2] A number of optical studies have begun probing the photoexcited states in such crystallites.[1,2]

Although considerable progress has been made in the controlled synthesis of II–VI semiconductor crystallites,[1,3] interpretation of sophisticated optical experiments often remains difficult due to polydispersities in size and shape, surface electronic defects due to uneven surface derivatization, and poor crystallinity. The study of an appropriate high quality model system is essential in distinguishing properties truly inherent to the nanometer size regime from those associated with variations in sample quality. Each sample must display a high degree of monodispersity (size, shape, etc.), regularity in crystallite core structure, and a consistent surface derivatization (cap).

This paper presents a relatively simple synthetic route to the production of high-quality nearly monodisperse (<5% rms in diameter) samples of CdE (E = S, Se, Te) nanometer size crystallites, with the emphasis on CdSe. The synthesis begins with the rapid injection of organometallic reagents into a hot coordinating solvent to produce a temporally discrete homogeneous nucleation. Slow growth and annealing in the coordinating solvent results in uniform surface derivatization and regularity in core structure. Size selective precipitation provides powders of nearly monodisperse nanocrystallites which can be dispersed in a variety of solvents. The crystallites are slightly prolate with an aspect ratio of 1.1 to 1.3. The average crystallite size, defined by its major axis, is tunable from ~12 to ~115 Å. Room temperature optical absorption and luminescence experiments show that the samples are of high optical quality. Transmission electron microscopy and X-ray powder diffraction are used in combination with computer simulations to characterize nanocrystallite structural features.

## II. Experimental Section

**General.** All manipulations involving alkylcadmium, silylchalconides, phosphines, and phosphine chalconides were carried out using standard airless procedures. Tri-*n*-octylphosphine [TOP] and bis(trimethylsilyl) sulfide [$(TMS)_2S$] were used as purchased from Fluka. Electronic grade (99.99+%) selenium and tellurium shot were purchased from Alfa. Anhydrous methanol, 1-butanol, pyridine, and hexane were purchased from a variety of sources. Tri-*n*-octylphosphine oxide [TOPO] was purchased from Alfa and purified by distillation, retaining the fraction transferred between 260 and 300 °C at ~1 Torr. Dimethylcadmium [$Me_2Cd$] was purchased from Organometallics Inc. and purified by filtration (0.250 μm) and vacuum transfer. Bis(trimethylsilyl)selenium [$(TMS)_2Se$] and Bis(*tert*-butyldimethylsilyl)tellurium [$(BDMS)_2Te$] were prepared via literature methods[3b,4] and stored at −35 °C in a drybox. Appropriate masses of selenium and tellurium shot were dissolved directly

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(1) Recent reviews include: (a) Brus, L. E. *Appl. Phys. A* **1991**, *53*, 465. (b) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113. (c) Wang, Y.; Herron, N. *J. Phys. Chem.* **1991**, *95*, 525. (d) Bawendi, M. G.; Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Phys. Chem.* **1990**, *41*, 477.

(2) Recent optical studies include the following: (a) Roussignol, P.; Ricard, D.; Flytzanis, C.; Neuroth, N. *Phys. Rev. Lett.* **1989**, *62*, 312. (b) Alivisatos, A. P.; Harris, A.; Levinos, N.; Steigerwald, M.; Brus, L. E. *J. Chem. Phys.* **1989**, *89*, 4001. (c) Peyghambarian, N.; Fluegel, B.; Hulin, D.; Migus, A.; Joffre, M.; Antonetti, A.; Koch, S. W.; Lindberg, M. *IEEE J. Quantum Electron.* **1989**, *25*, 2516. (d) Bawendi, M. G.; Wilson, W. L.; Rothberg, L.; Carroll, P. J.; Jedju, T. M.; Steigerwald, M. L.; Brus, L. E. *Phys. Rev. Lett.* **1990**, *65*, 1623. (e) Bawendi, M. G.; Carroll, P. J.; Wilson, W. L.; Brus, L. E. *J. Chem. Phys.* **1992**, *96*, 946. (f) Alivisatos, A. P.; Harris, T. D.; Carroll, P. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1989**, *90*, 3463. (g) O'Neil, M.; Marohn, J.; McLendon, G. *J. Phys. Chem.* **1990**, *94*, 4356. (h) Eychmuller, A.; Hasselbarth, A.; Katsikas, L.; Weller, H. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 79. (i) Wang, Y.; Suna, A.; McHugh, J.; Hilinski, E.; Lucas, P.; Johnson, R. D. *J. Chem. Phys.* **1990**, *92*, 6927. (j) Esch, V.; Fluegel, B.; Khitrova, G.; Gibbs, M.; Jiajin, X.; Chang, S. W.; Koch, S. W.; Liu, L. C.; Risbud, S. W.; Peyghambarian, N. *Phys. Rev. B* **1990**, *42*, 7450. (k) Ekimov, A. I.; Hache, F.; Schanne-Klein, M. C.; Ricard, D.; Flytzanis, C.; Kudryavtsev, I. A.; Yazeva, T. V.; Rodina, A. F.; Efros, Al. L. *J. Opt. Soc. Am. B* **1993**, *10*, 100.

(3) (a) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglas, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *110*, 3046. (b) Brennan, J. G.; Siegrist, T.; Carroll, P. J.; Stuczynski, S. M.; Brus, L. E.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 4141. (c) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649.

(4) Derry, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, *47*, 1354.

0002-7863/93/1515-8706$04.00/0

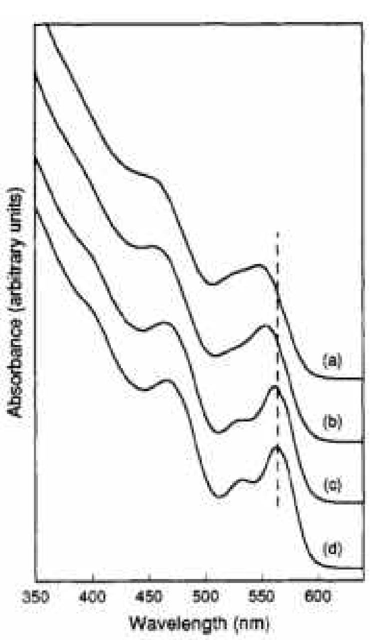


**Figure 1.** Example of the effect of size-selective precipitation on the absorption spectrum of ~37 Å diameter CdSe nanocrystallites. (a) Room temperature optical absorption spectrum of the nanocrystallites in the growth solution before size-selective precipitation. (b) Spectrum after one size-selective precipitation from the growth solution with methanol. (c) Spectrum after dispersion in 1-butanol and size-selective precipitation with methanol. (d) Spectrum after a final size-selective precipitation from 1-butanol/methanol.

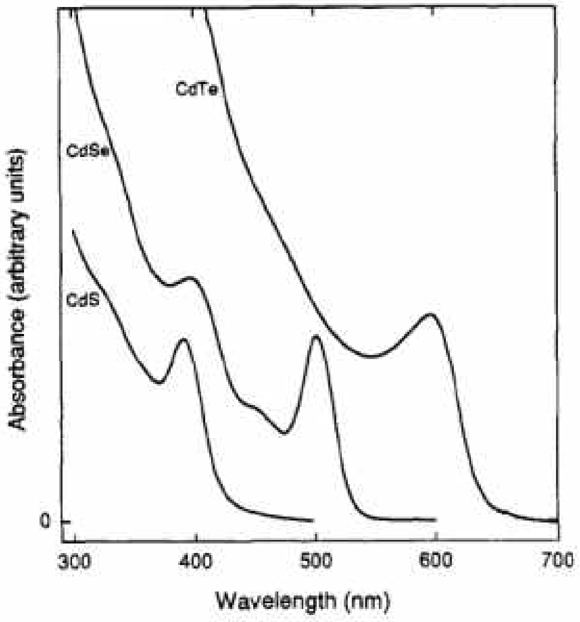
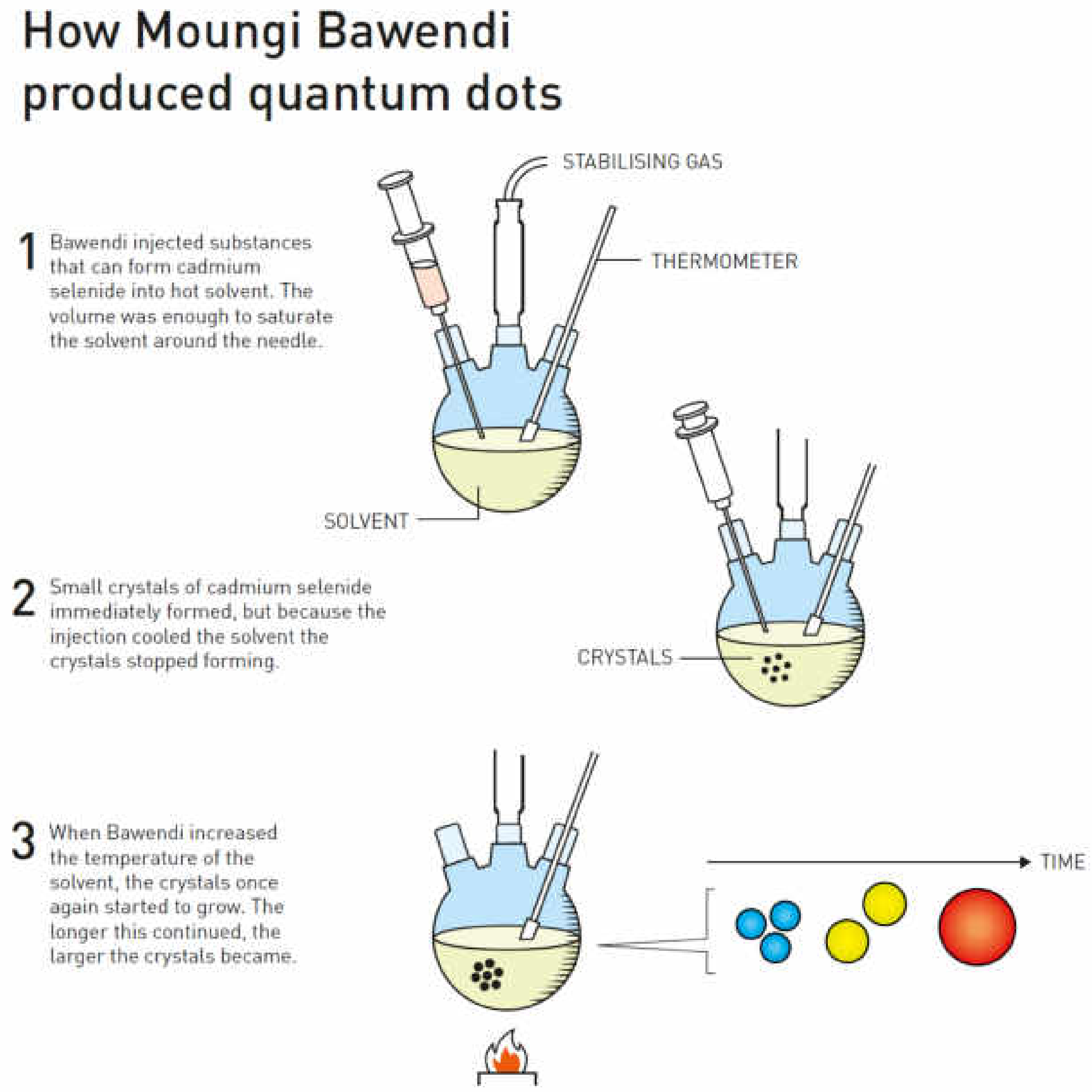


**Figure 2.** Room temperature optical absorption spectra of ~20–30 Å diameter CdS, CdSe, and CdTe crystallites.

# The hot-injection synthesis



How Moungi Bawendi produced quantum dots

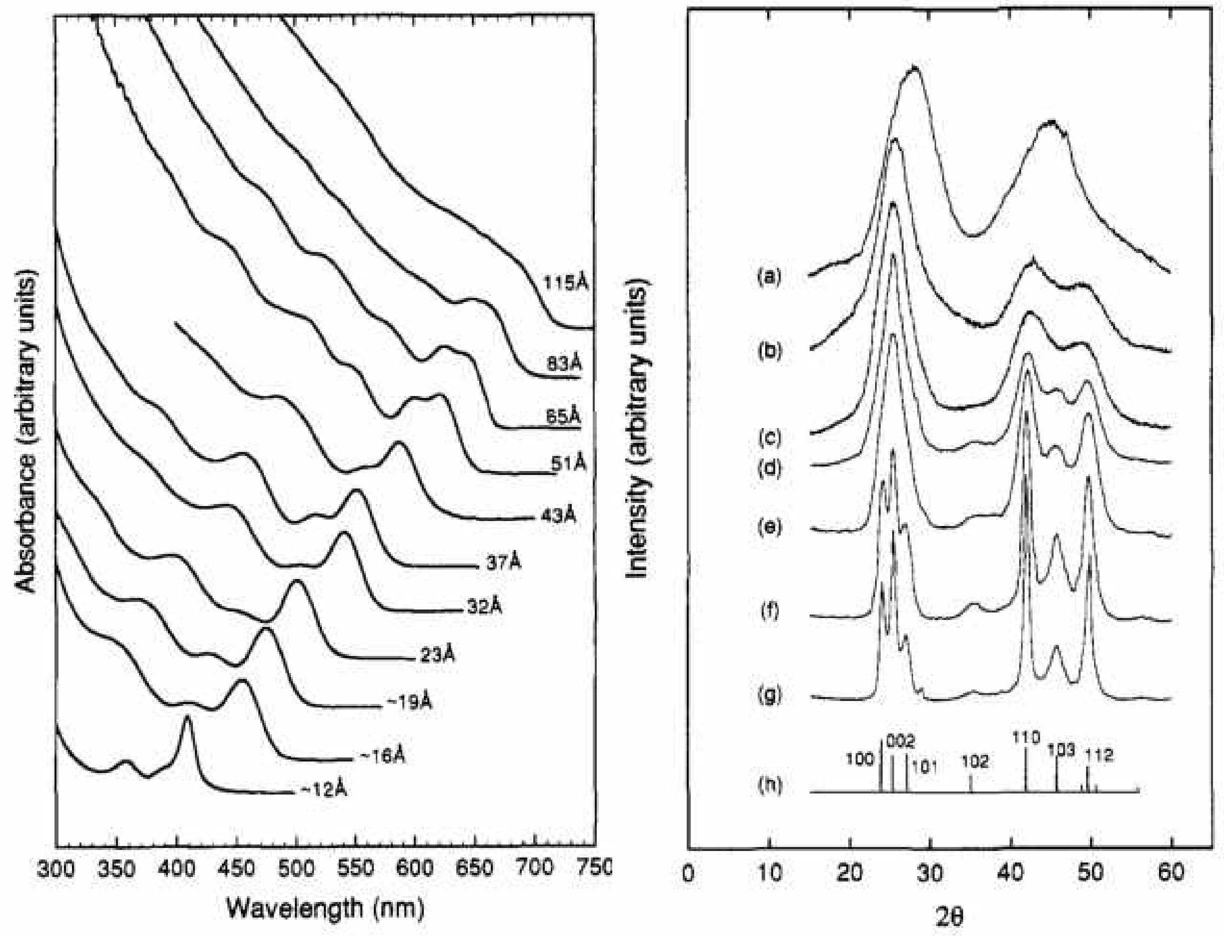
1 Bawendi injected substances that can form cadmium selenide into hot solvent. The volume was enough to saturate the solvent around the needle.

2 Small crystals of cadmium selenide immediately formed, but because the injection cooled the solvent the crystals stopped forming.

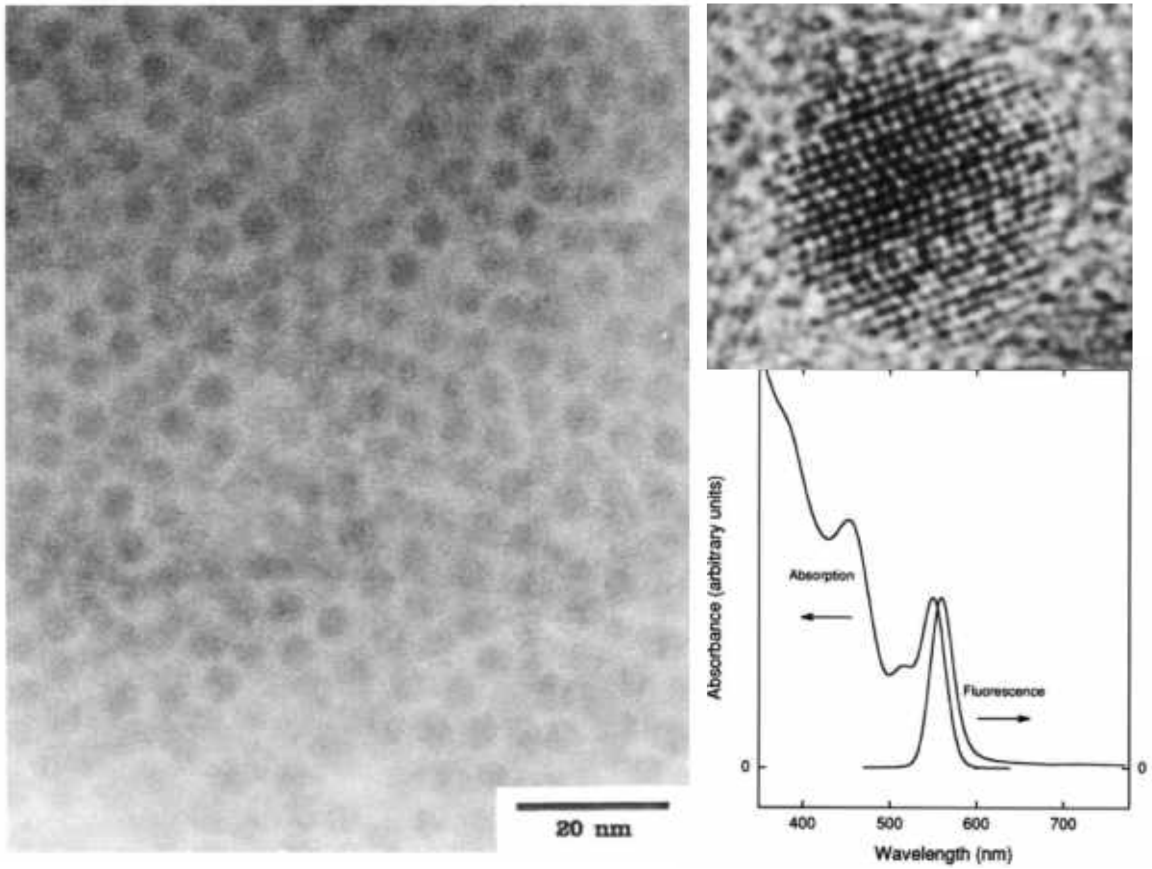
3 When Bawendi increased the temperature of the solvent, the crystals once again started to grow. The longer this continued, the larger the crystals became.

©Johan Jarnestad/The Royal Swedish Academy of Sciences

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



UV-visible spectrum and corresponding XRD pattern of CdS nanocrystals



TEM and HRTEM image of CdSe nanocrystal with an average diameter of 5.1 nm. Luminescent spectrum of 3.5 nm CdSe nanocrystals.

Murray, C. B.; Norris, D. J.; Bawendi, M. G. J Am Chem Soc 1993, 115 (19), 8706-8715.

# Technological milestones

## Quantum dots: Seeds of Nanoscience

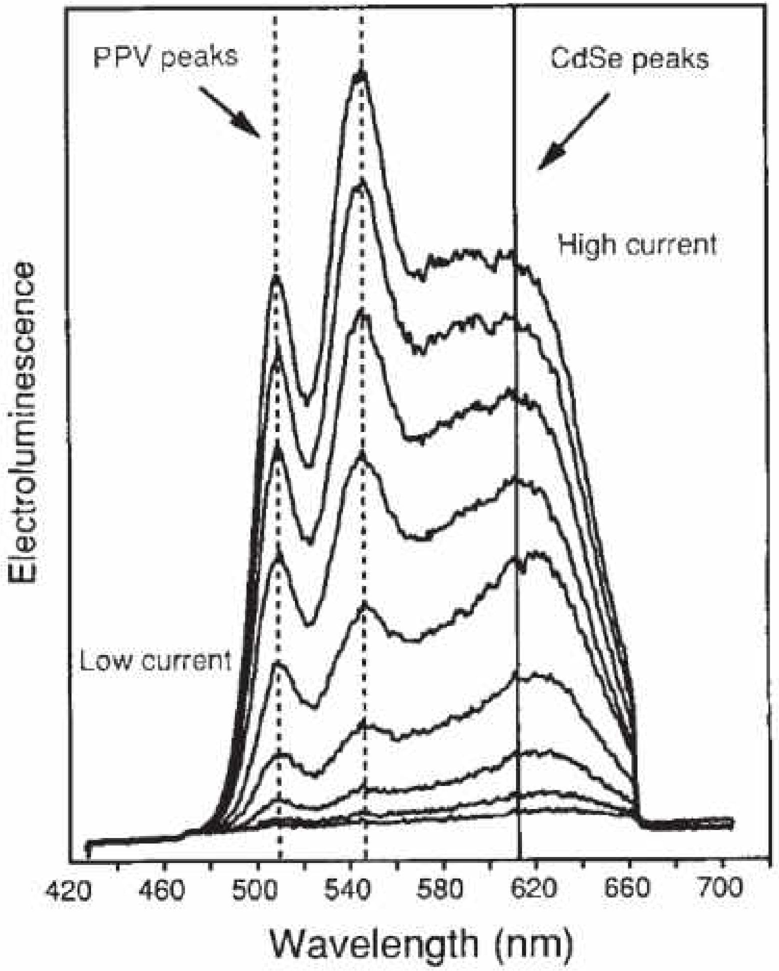
# Light-emitting diode (LED) from CdSe nanocrystals

## and a semiconducting polymer

- Light emission arises from the recombination of holes injected into a layer of semiconducting p-paraphenylene vinylene (PPV) with electrons injected into a multilayer film of cadmium selenide nanocrystals.

- Close matching of the emitting layer of nanocrystals with the work function of the metal contact leads to an operating voltage of only 4V.

- Due the quantum size effect the colour of this emission can be varied from red to yellow by changing the nanocrystal size.

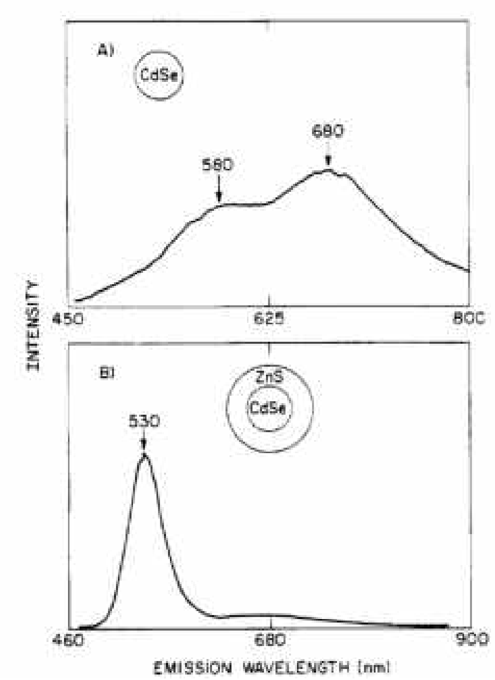


Voltage dependent color of CdSe/PPV (p-paraphenylene vinylene) samples.

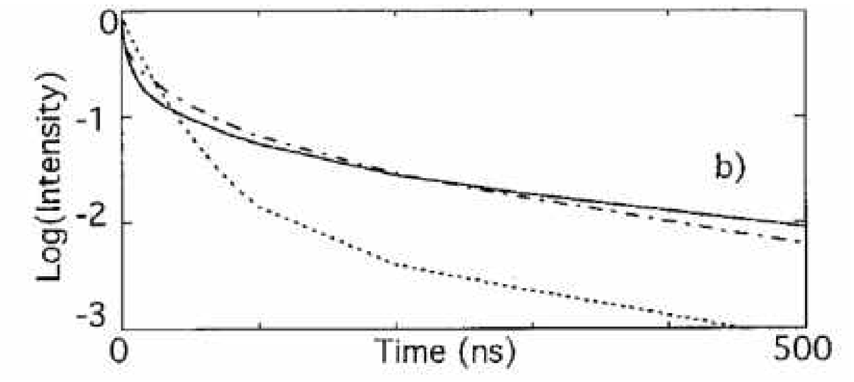
Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P. Nature 1994, 370 (6488), 354-357.

# Core-shell quantum dots

- Core-shell nanoparticles were created that consisted of a wide-bandgap shell, such as ZnS, to confine electrons and holes to a small-bandgap core (such as CdSe).
- In this way, the charge carriers in the core were separated from surface states, such as unsaturated bonds, that are detrimental to optical performance.
- The resulting CdSe/ZnS core-shell quantum dots had a luminescence quantum yield at room temperature of up to 50%, with better long-term stability and reduced bleaching.



Room temperature luminescence spectra: (A) CdSe, (B) (CdSe)ZnS. The integrated quantum yield in B is more than an order of magnitude higher than in A.



Reconstructed time decay plot: (CdSe)ZnS – solid line, (CdSe)TOPO - dashed line.

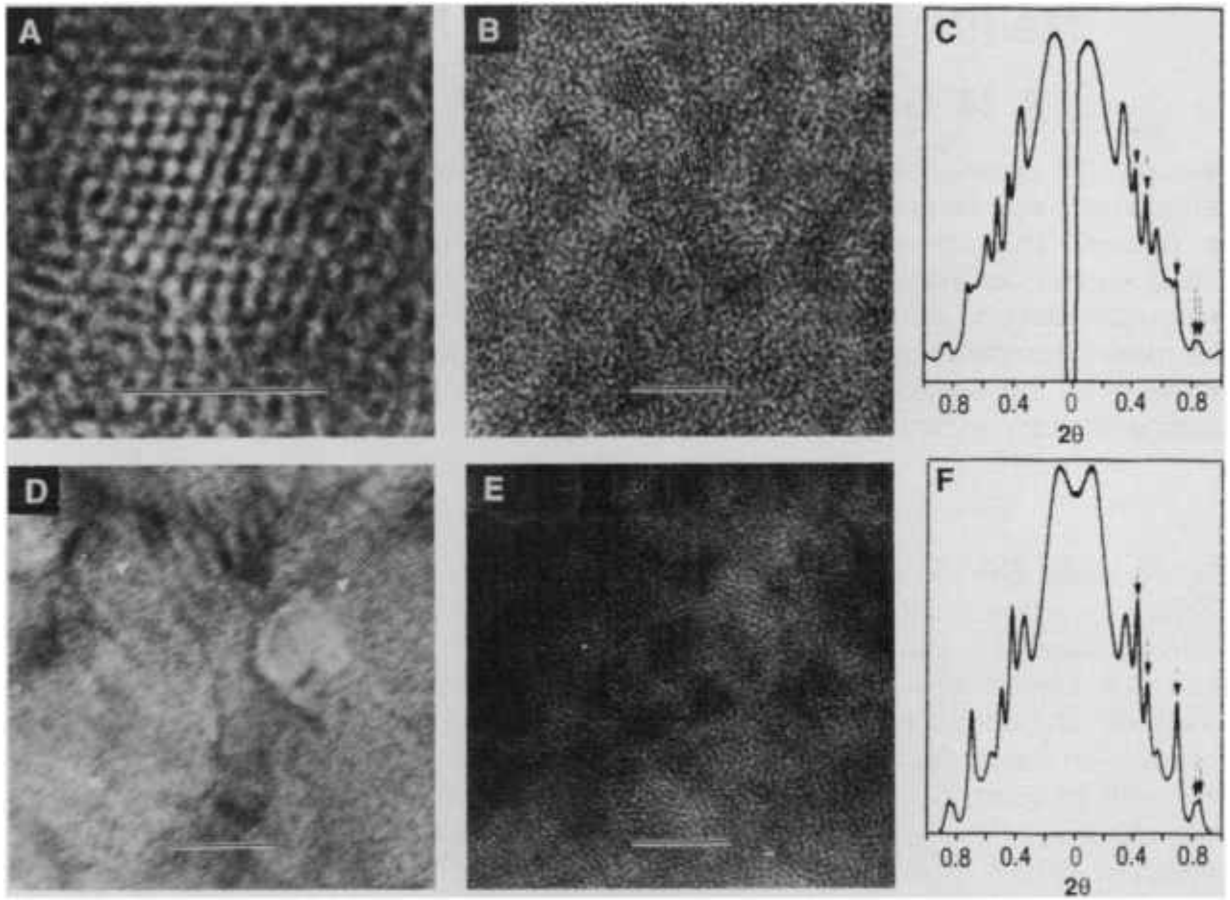
K. Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. J Am Chem Soc 1990, 112 (4), 1327-1332.
Hines, M. A.; Guyot-Sionnest, P. J Phys Chem 1996, 100 (2), 468-471.

# Melting in semiconductor nanocrystals

Temperature-dependent electron diffraction studies on nanocrystals of CdS show a large depression in the melting temperature with decreasing size, as a larger fraction of the total number of atoms is on the surface.

Implications:

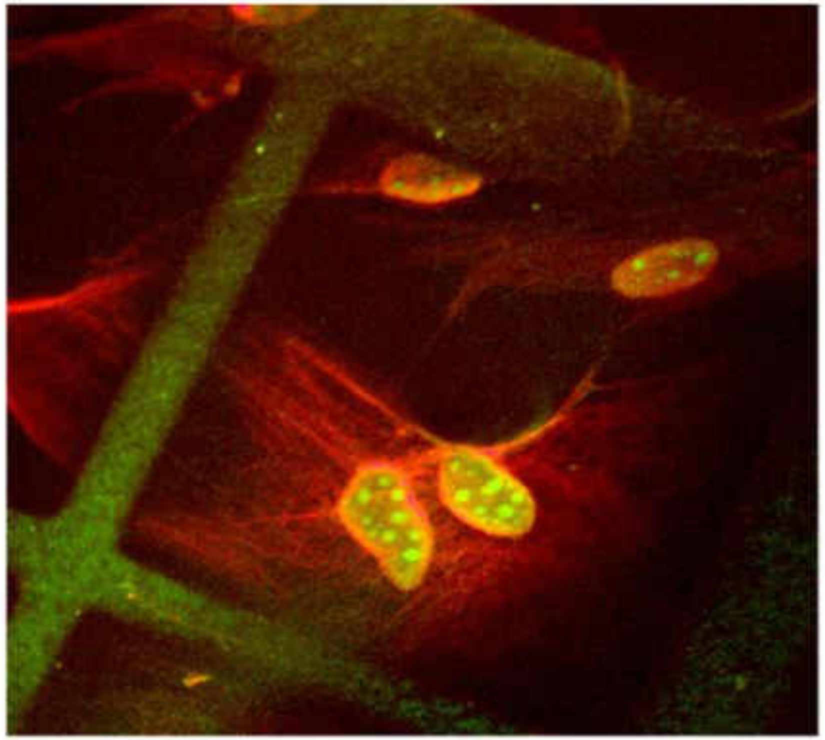
- The optimum annealing temperature for preparation of high-quality defect-free nanocrystals can be expected to be a small fraction of the bulk annealing temperature.
- The ability to fuse nanocrystals to form a film at relatively modest temperatures indicates that nanocrystals may provide a new low-temperature route to thin-film growth.



Goldstein, A. N.; Echer, C. M.; Alivisatos, A. P. Science 1992, 256 (5062), 1425-1427.

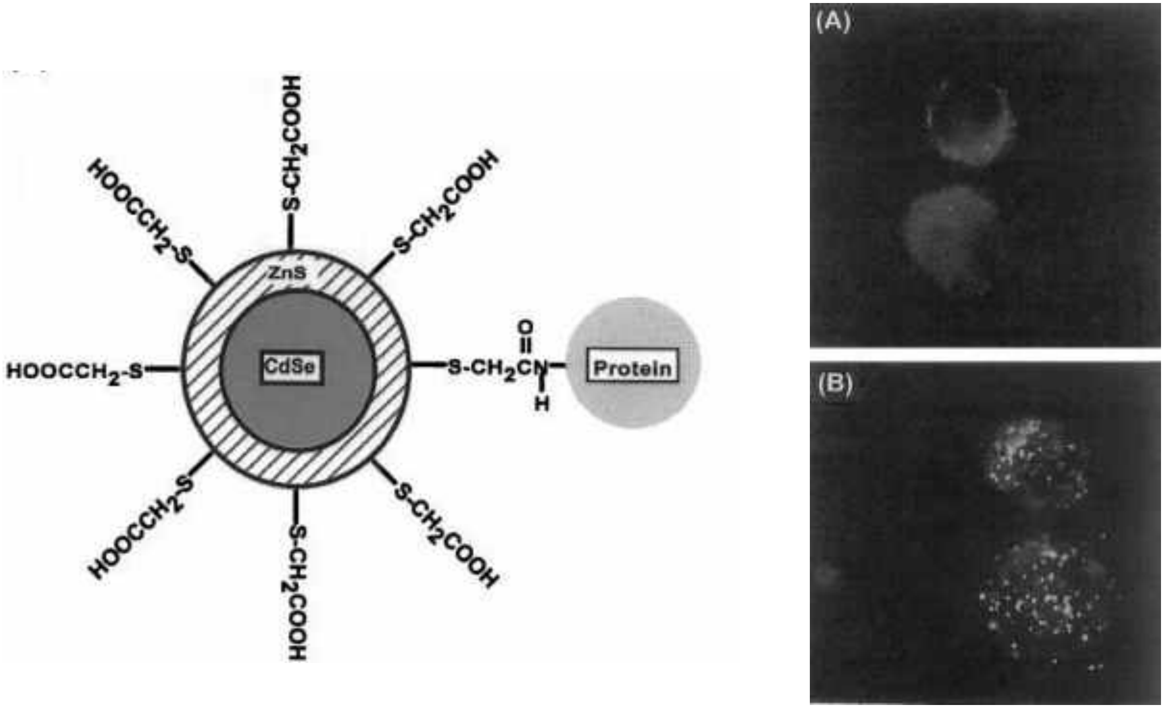
# Synthesis of water-soluble quantum dots - new tool for labelling biomolecules

## Functionalization using polysilanes



Two-color labeling of mouse 3T3 fibroblast with green and red CdSe NCs.

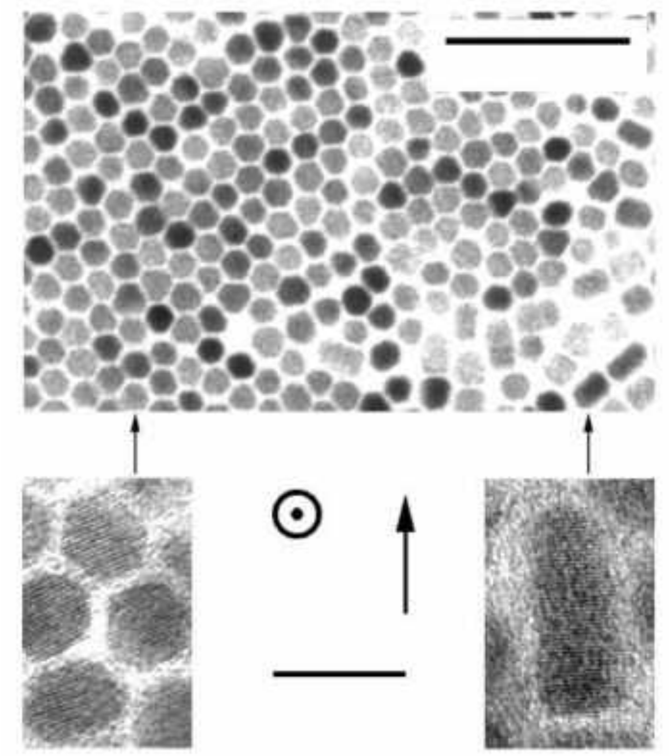
## Functionalization using thiols



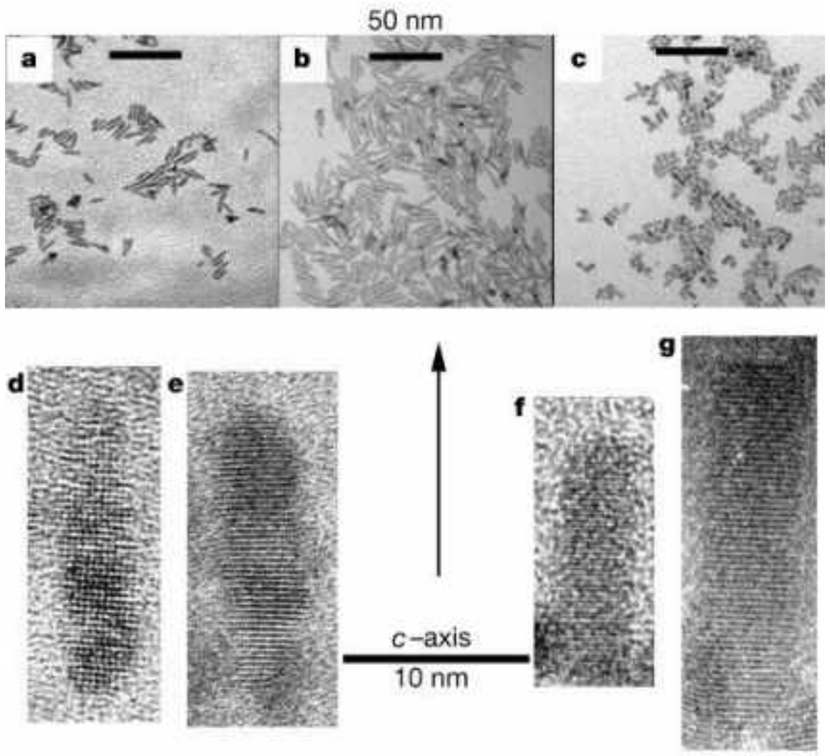
Left: Schematic of a ZnS-capped CdSe QD that is covalently coupled to a protein by mercaptoacetic acid. Right: Luminescence images of cultured HeLa cells that were incubated with (A) mercapto-QDs and (B) QD-transferrin conjugates.

Bruchez, M.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. Science 1998, 281 (5385), 2013-2016.
Chan, W. C. W.; Nie, S. M. Science 1998, 281 (5385), 2016-2018.

# Shape control of nanocrystals - nanorods



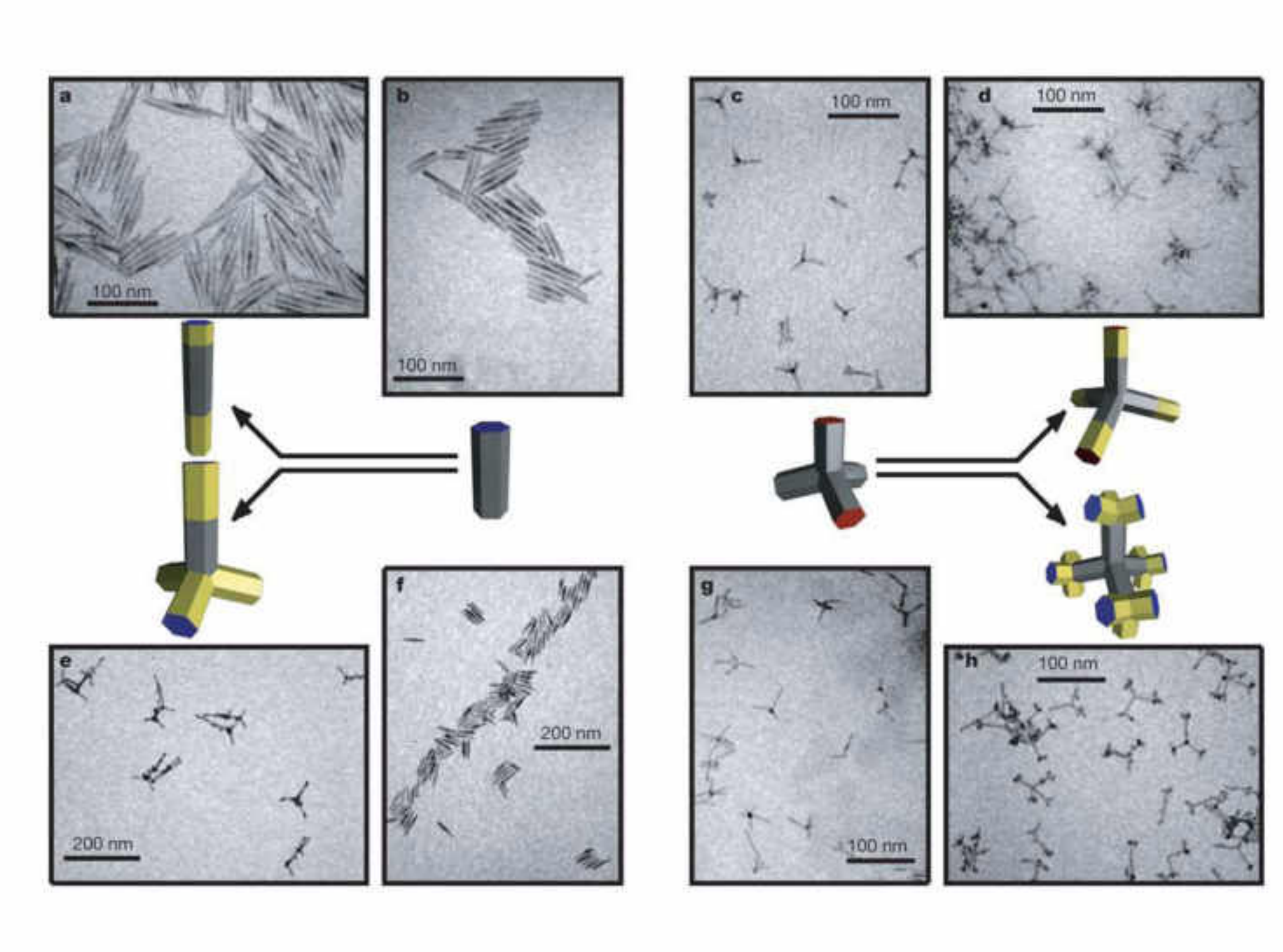
Three-dimensional orientation of CdSe quantum rods observed by TEM.

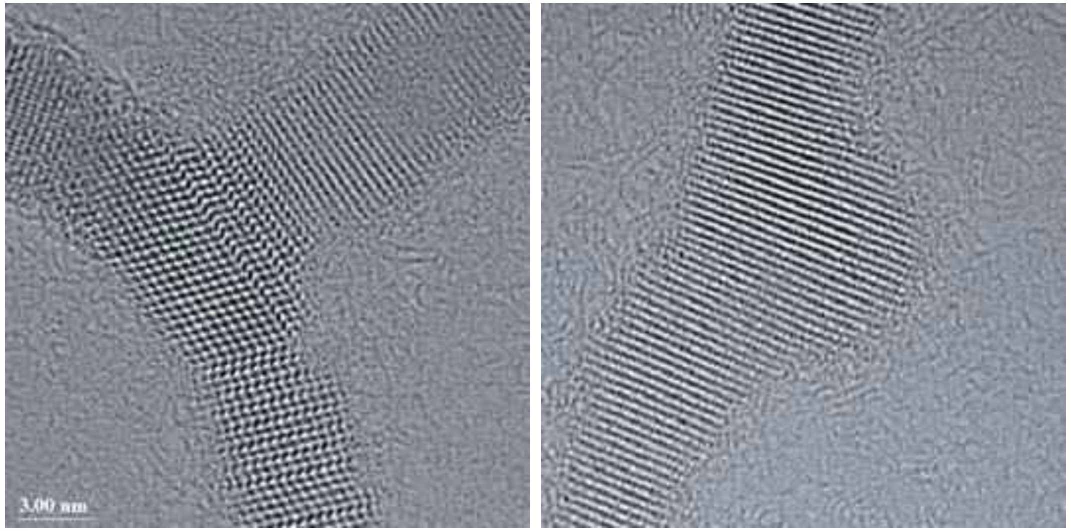


TEM images of different samples of quantum rods. A-c, Low-resolution TEM images of three quantum-rod samples with different sizes and aspect ratios. d-g, High resolution TEM images of four representative quantum rods. d and e are from the sample shown in a; f and g are from the sample shown in c.

Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. Nature 2000, 404 (6773), 59-61.

# Shape control of nanocrystals – branched rods

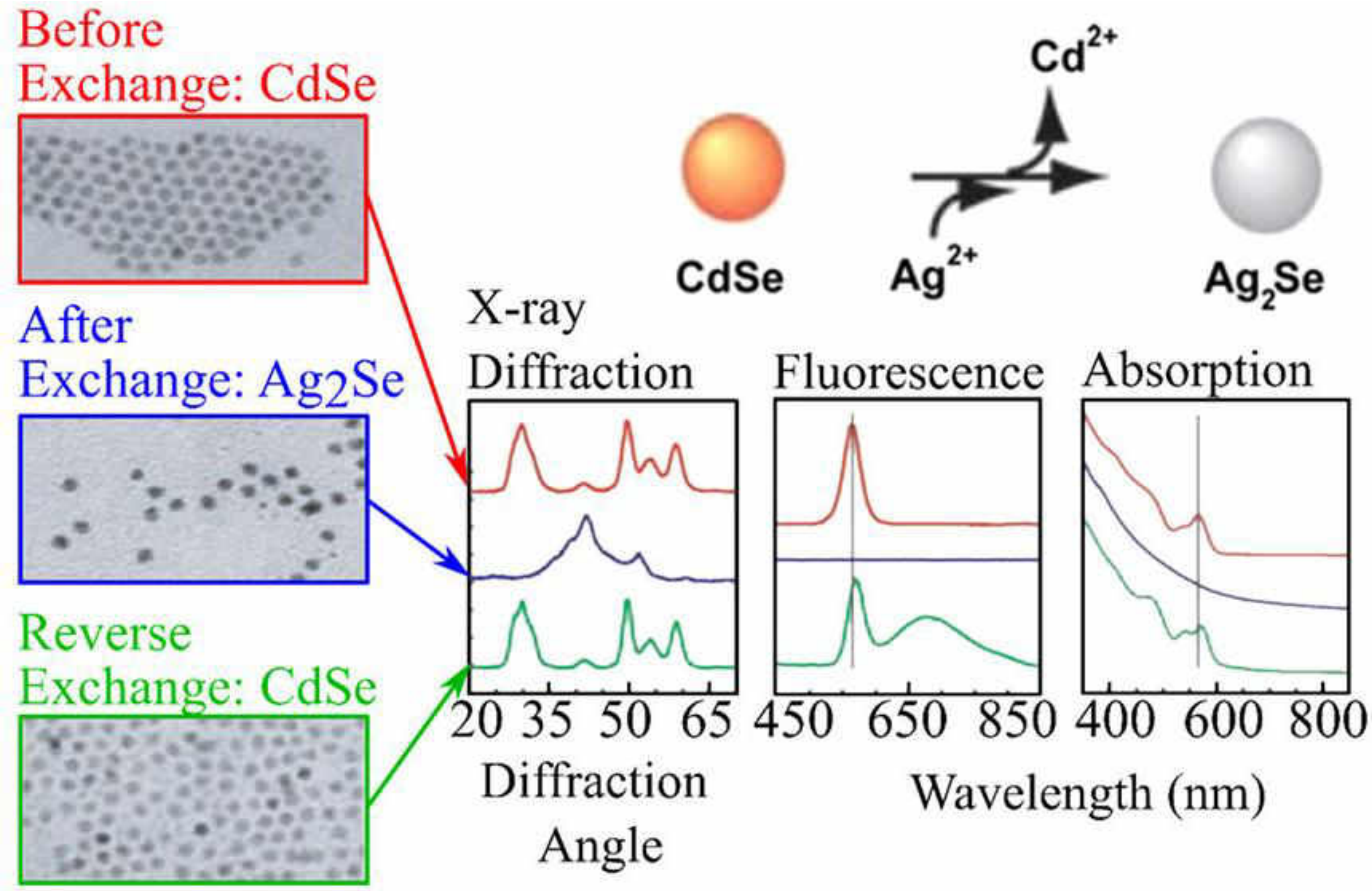




High-resolution electron microscopy of heterojunctions. a, HRTEM of a branch point shows a zincblende core and wurtzite branches of CdTe and an original wurtzite rod (upper right) of CdSe. b, Examination of a linear junction between CdSe (upper right) and CdTe reveals continuous wurtzite growth.

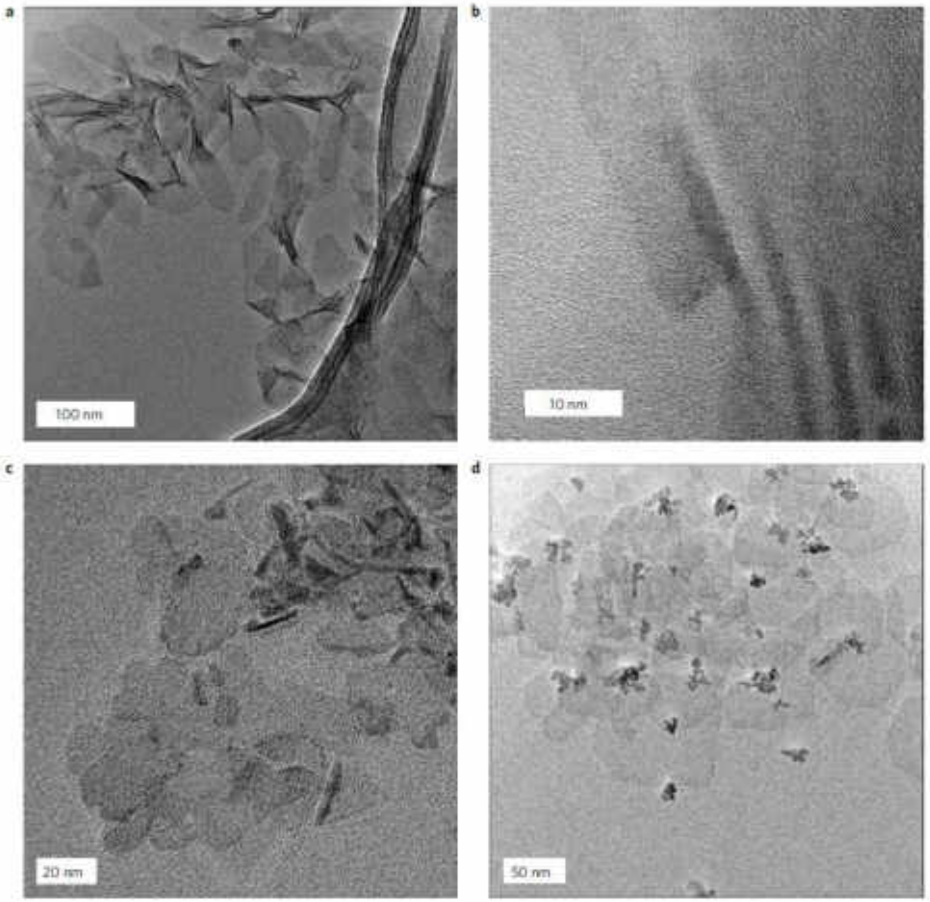
Peng, X. G.; Manna, L.; Yang, W. D.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. Nature 2000, 404 (6773), 59-61.

# Cation exchange reaction

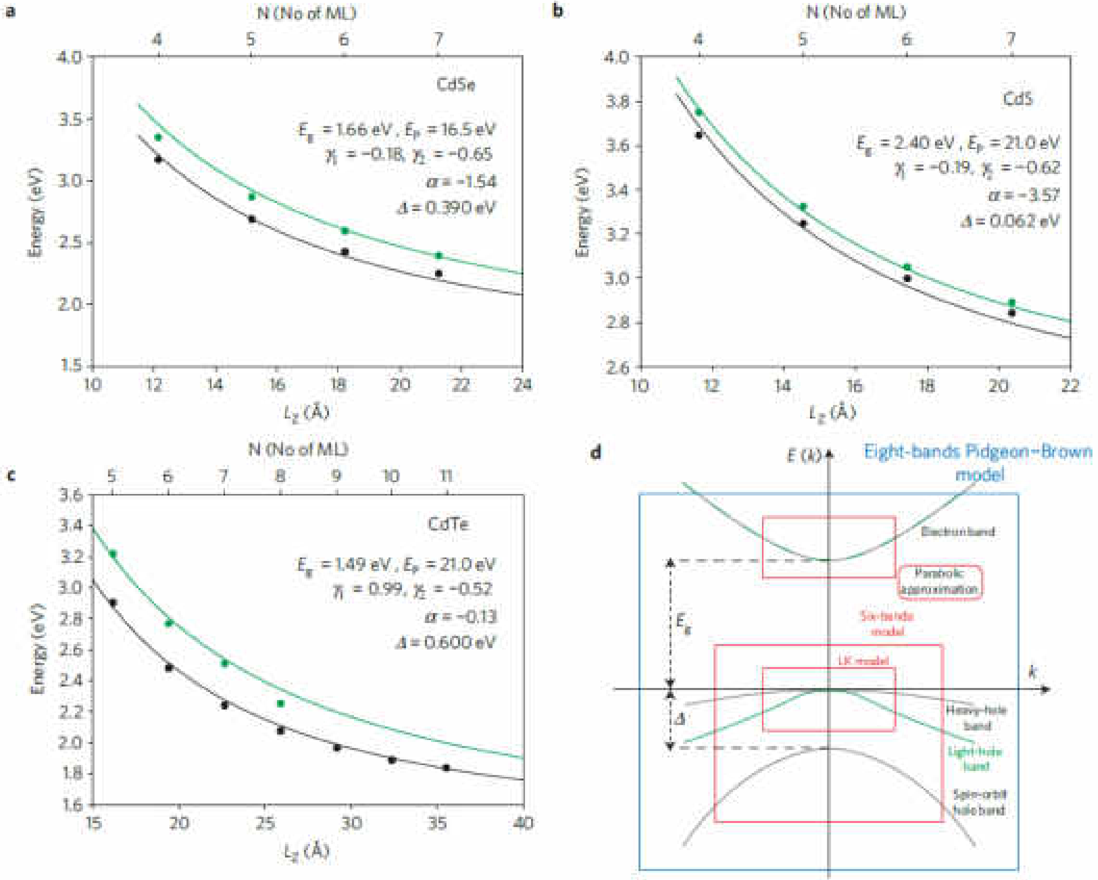


Son, D. H.; Hughes, S. M.; Yin, Y.; Alivisatos, A. P. Science 2004, 306, 1009– 1012.

# Shape control of nanocrystals – platelets with 2D electronic structure



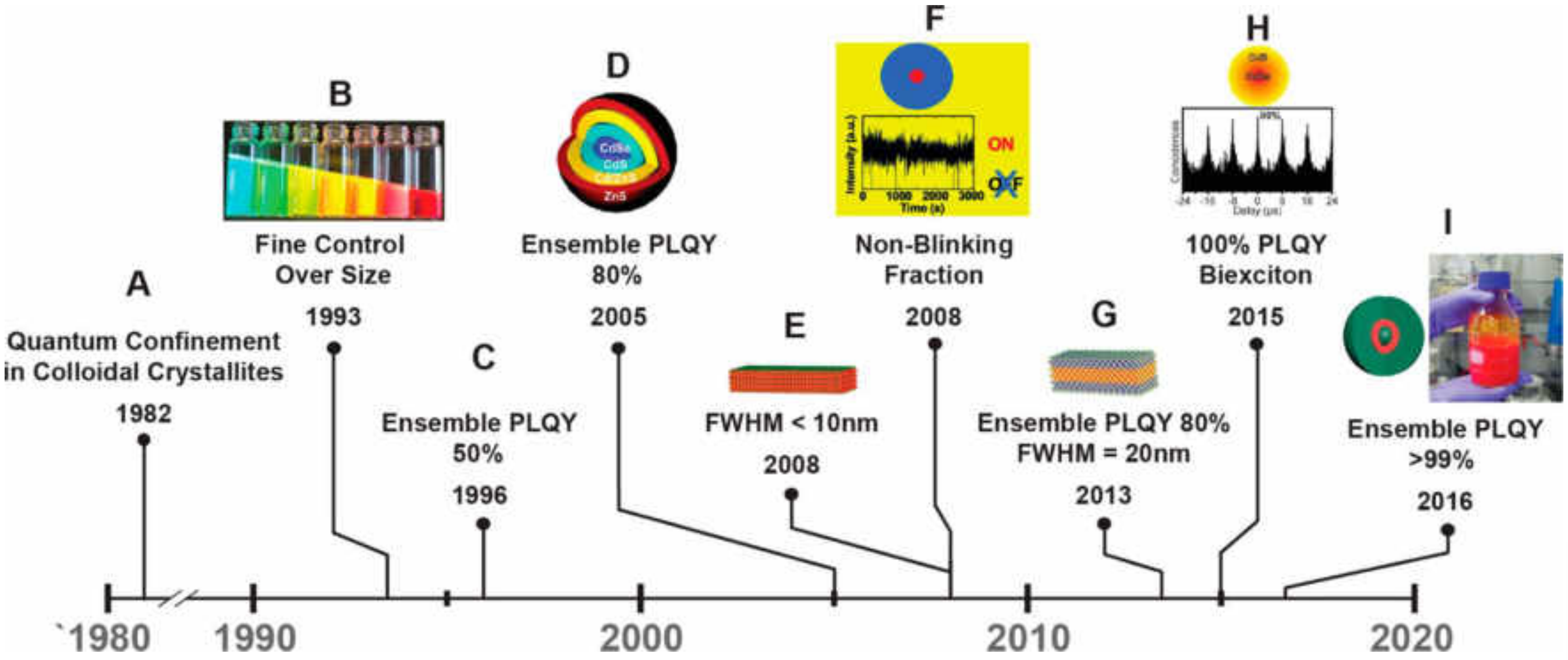
TEM images of nanoplatelets. a, Five-monolayer-thick CdSe NPLs. b, Six-monolayer-thick CdSe NPLs standing partly on their side. c, Six-monolayer-thick CdS NPLs. d, Six-monolayer-thick CdTe NPLs.



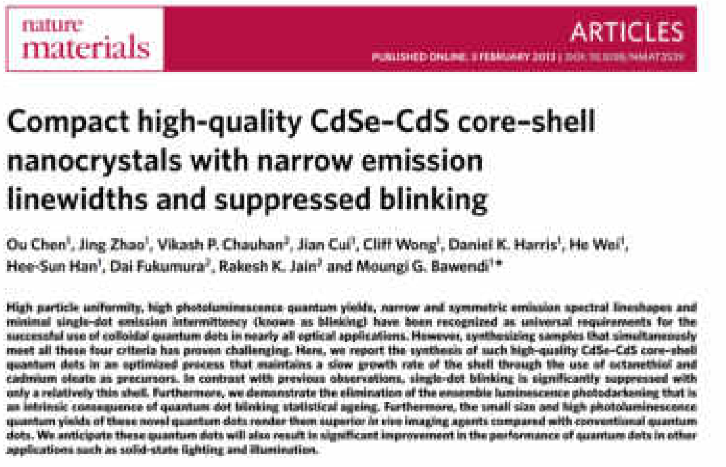
Energies of the electron/light-hole (green) and electron/heavy-hole (black) transitions versus the NPL thickness for CdSe (a), CdS (b) and CdTe (c). d, Schematic representation of the energy band structure in the vicinity of the 0-point of the Brillouin zone, as well as the validity domain of various band-structure models.

Ithurria, S.; Tessier, M. D.; Mahler, B.; Lobo, R. P. S. M.; Dubertret, B.; Efros, A. Nat Mater 2011, 10 (12), 936-941.

# Timeline of luminescence performance enhancement



Colloidal QD research timeline illustrating evolution of nanostructure and luminescence performance.



nature materials

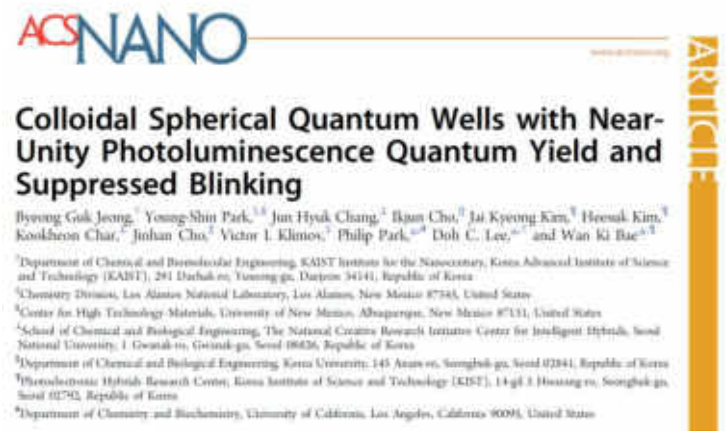
ARTICLES

PUBLISHED ONLINE: 3 FEBRUARY 2013 | DOI: 10.1038/NMAT3539

Compact high-quality CdSe–CdS core–shell nanocrystals with narrow emission linewidths and suppressed blinking

Ou Chen[1], Jing Zhao[1], Vikash P. Chauhan[2], Jian Cui[1], Cliff Wong[1], Daniel K. Harris[1], He Wei[1], Hee-Sun Han[1], Dai Fukumura[2], Rakesh K. Jain[2] and Moungi G. Bawendi[1]*

High particle uniformity, high photoluminescence quantum yields, narrow and symmetric emission spectral lineshapes and minimal single-dot emission intermittency (known as blinking) have been recognized as universal requirements for the successful use of colloidal quantum dots in nearly all optical applications. However, synthesizing samples that simultaneously meet all these four criteria has proven challenging. Here, we report the synthesis of such high-quality CdSe–CdS core–shell quantum dots in an optimized process that maintains a slow growth rate of the shell through the use of octanethiol and cadmium oleate as precursors. In contrast with previous observations, single-dot blinking is significantly suppressed with only a relatively thin shell. Furthermore, we demonstrate the elimination of the ensemble luminescence photodarkening that is an intrinsic consequence of quantum dot blinking statistical ageing. Furthermore, the small size and high photoluminescence quantum yields of these novel quantum dots render them superior in vivo imaging agents compared with conventional quantum dots. We anticipate these quantum dots will also result in significant improvement in the performance of quantum dots in other applications such as solid-state lighting and illumination.



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ARTICLE

Colloidal Spherical Quantum Wells with Near-Unity Photoluminescence Quantum Yield and Suppressed Blinking

Byeong Guk Jeong,† Young-Shin Park,‡,§ Jun Hyuk Chang,† Ikjun Cho,∥ Jai Kyeong Kim,⊥ Heesuk Kim,⊥ Kookheon Char,∥ Jinhan Cho,# Victor I. Klimov,‡ Philip Park,*,¶ Doh C. Lee,*,† and Wan Ki Bae*,⊥

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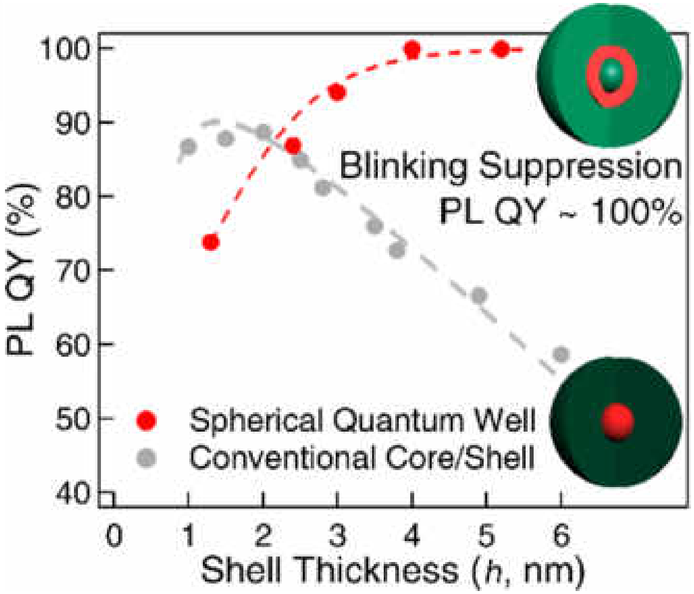
¶Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, United States



# Expanding science and lessons learnt

Catalysis

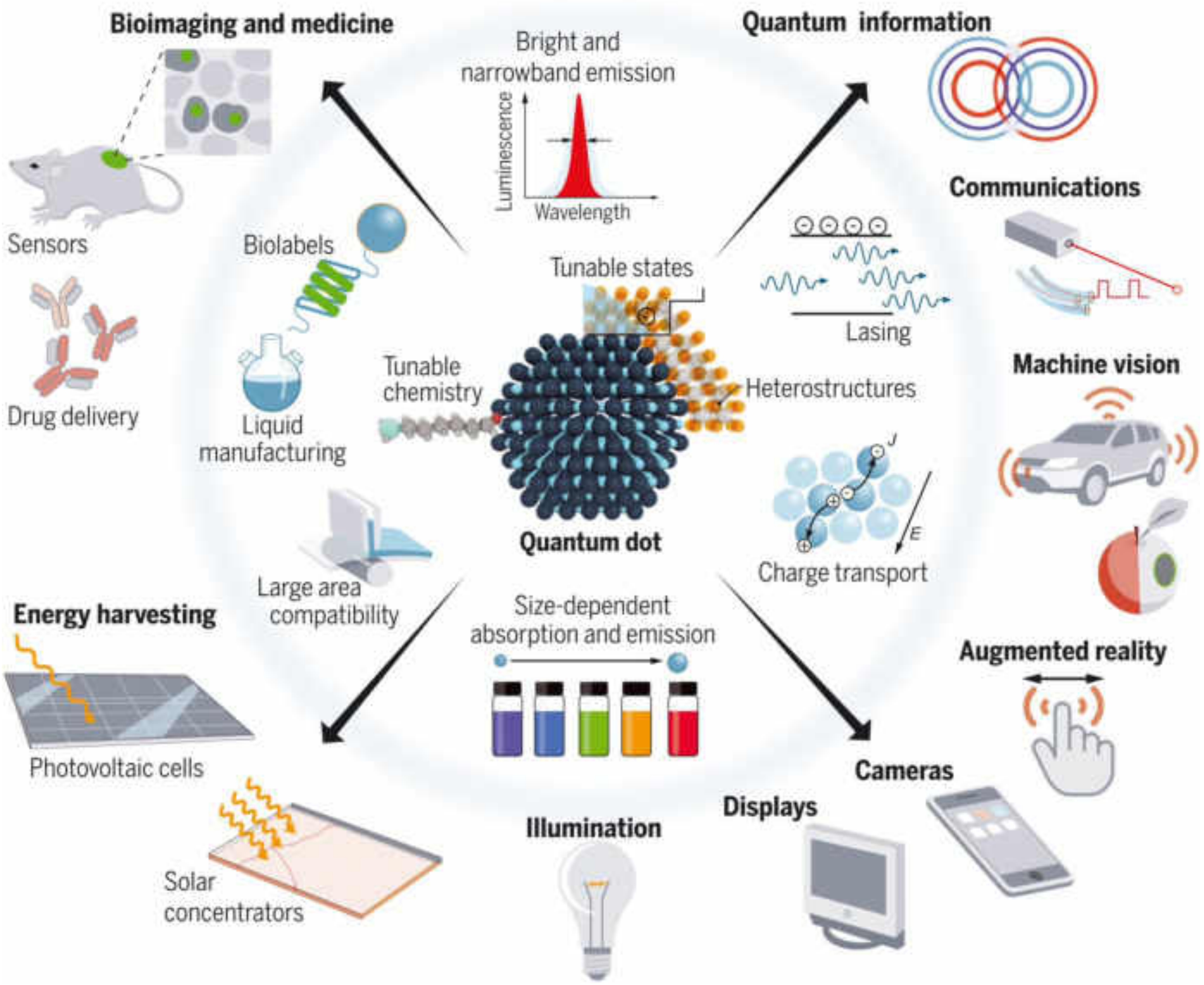
Biological applications

Simple finding, report them early

Have colleagues to work on them

One useful application

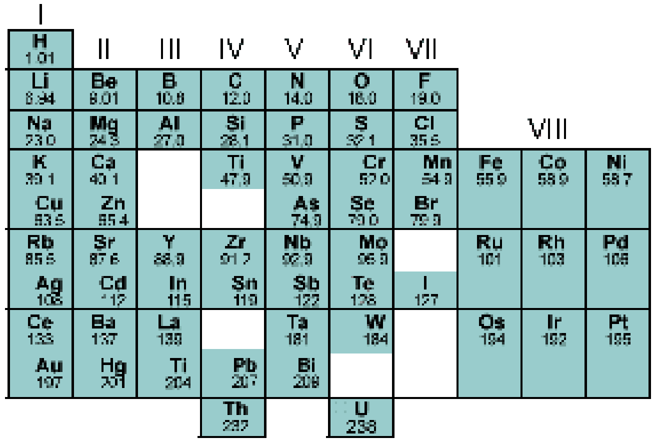
Have industry adoption



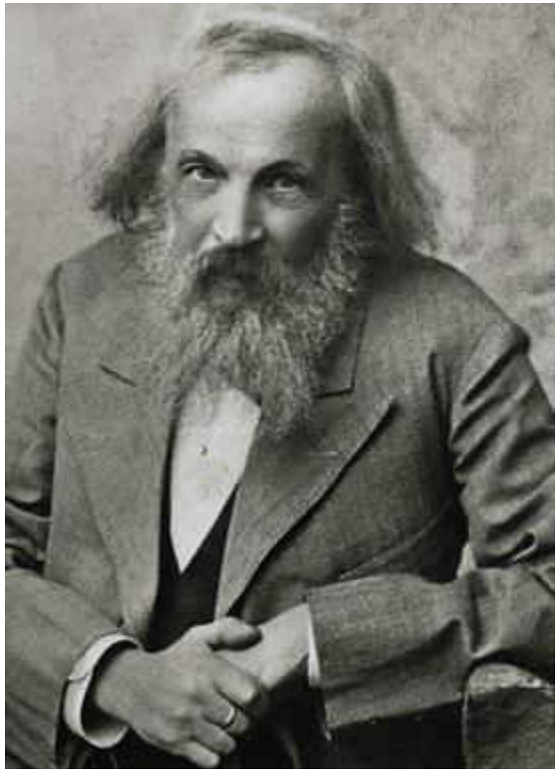
F. P. García de Arquer, D. V. Talapin, V. I. Klimov, Y. Arakawa, M. Bayer, E. H. Sargent, Science 2021, 373, eaaz8541.

# Legacy of Mendeleev continues

Mendeleev's Periodic Table



| I | II | III | IV | V | VI | VII | VIII | | |
|---|---|---|---|---|---|---|---|---|---|
| H 1.01 | | | | | | | | | |
| Li 6.94 | Be 9.01 | B 10.8 | C 12.0 | N 14.0 | O 16.0 | F 19.0 | | | |
| Na 23.0 | Mg 24.3 | Al 27.0 | Si 28.1 | P 31.0 | S 32.1 | Cl 35.5 | | | |
| K 39.1 | Ca 40.1 | | Ti 47.9 | V 50.9 | Cr 52.0 | Mn 54.9 | Fe 55.9 | Co 58.9 | Ni 58.7 |
| Cu 63.5 | Zn 65.4 | | | As 74.9 | Se 79.0 | Br 79.9 | | | |
| Rb 85.5 | Sr 87.6 | Y 88.9 | Zr 91.2 | Nb 92.9 | Mo 95.9 | | Ru 101 | Rh 103 | Pd 106 |
| Ag 108 | Cd 112 | In 115 | Sn 119 | Sb 122 | Te 128 | I 127 | | | |
| Ce 133 | Ba 137 | La 139 | | Ta 181 | W 184 | | Os 194 | Ir 192 | Pt 195 |
| Au 197 | Hg 201 | Ti 204 | Pb 207 | Bi 209 | | | | | |
| | | | Th 232 | | U 238 | | | | |



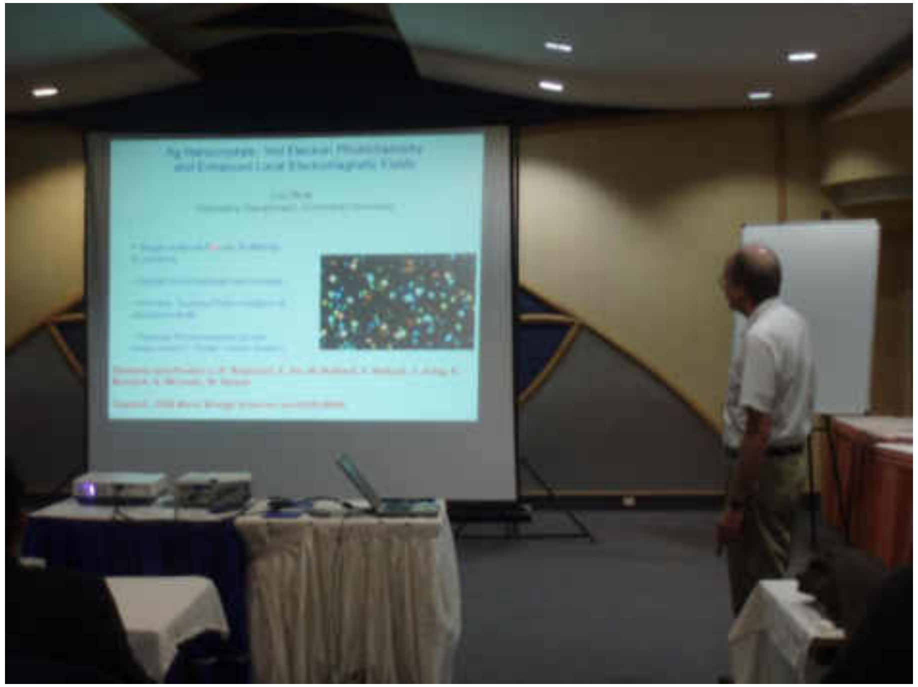
Dmitri Ivanovich Mendeleev (1834-1907)

Modern Periodic Table

ACS Publications
Most Trusted. Most Cited. Most Read.

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H | | | | | | | | | | | | | | | | | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Cn | Nh | Fl | Mc | Lv | Ts | Og |
| | | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
| | | | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |

# Prof. Brus @ IIT Madras






# With Prof. Bawendi