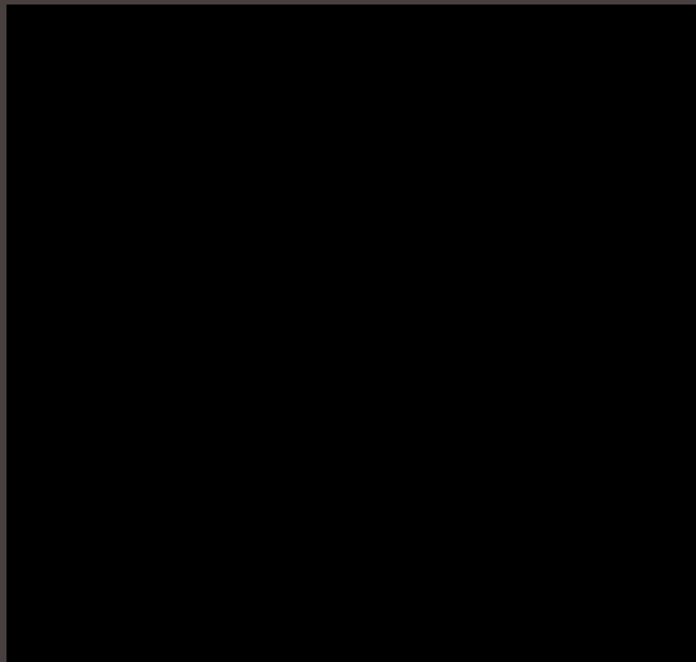
Semiconductor nanocrystals

Image of fluorescence in various sized Cadmium Selenide Quantum Dots.

(Dr. D. Talapin, University of Hamburg, http://www.chemie.uni-hamburg.de/pc/Weller/).

Applications:

? **Biology** -- fluorescent tags to measure and quantify biological phenomena
? **Precision light calibration** -- a source of precision wavelength materials
? **Semiconductors** -- "designer atoms" that allow control of the bandgap through material and composition sizes
? **LEDs** -- tunable colors for light-emitting diodes
? **Photovoltaic Solar Cells** -- low-cost, high-efficiency devices
? **Optical Transistors** -- ultra-fast switching devices under 1 picosecond



Quantum Dots and the Engineering of Low Dimensional Thermoelectric Devices

The efficiency of thermoelectric devices is controlled by a factor termed the Figure of Merit, denoted as "ZT." ZT is described in the following relationship as:

The temperature difference between T_H and T_C, which is user specified. The three remaining factors are the Seebeck coefficient a, the thermal conductivity ə, and the resistivity ɟ. Since high Figures of Merit correspond to more efficient devices, it would be ideal to develop a device with a large Seebeck coefficient, a small thermal conductivity, and a high electrical conductivity (corresponding to a low resistivity).

Fluorescent ink.
Quantum Dots and a New Generation of Anti-Counterfeiting Technology

?A size and composition dependent bandgap wh ich can be tuned atom by atom during fabrication to emit at any visible or infrared wavelength
?A broad, tunable absorption pattern with absorption peaks
?An emission intensity that depends on excitation wavelength
?Sharp, Gaussian emission peaks
?Extreme form flexibility can be incorporated into paint, inks, plastic sheaths, paper, coatings, optical gratings, etc

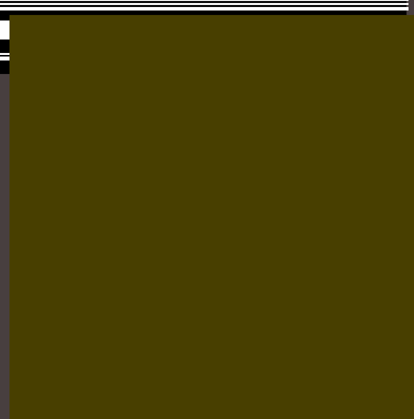
Quantum Dots Enables New Market for Night Vision Fluorescent Paints and Taggents

Quantum Dots as an Anti-Fratricide Combat Identification Paint
Quantum dots emitting in the infrared range of wavelengths are invisible to the naked eye, yet can readily be seen with the proper night vision equipment. By impregnating helmets, combat fatigues, and other gear with the proper sized quantum dots, the gear can be made to emit radiation at almost any unique infrared wavelength. Without intimate knowledge of the exact makeup of the quantum dots in question, such emission will either appear to hostile forces as noise, or will be completely undetectable, making it a powerful friend identification tool. This represents a radical improvement over the capabilities or traditional combat identification paint, which can only fluoresce at a limited number of known frequencies determined by the composition of traditional materials. Quantum dots in paint can fluoresce at any wavelength desired, making the task of mimicking or identifying the correct fluorescence signature almost impossible.

Quantum Dots Anti-Trespass Taggents - EviDust
Quantum dots can be fashioned into tiny beads of EviDust identical to naturally occurring dust, but with the additional abilities both to emit infrared radiation and adhere to passerby. Such radiation, being pre-specified and tunable to any infrared wavelength, is extremely difficult for hostile forces to mimic, identify, or detect without intimate knowledge of the quantum dot's composition or size. EviDust's natural stickiness combined with its completely unique radiation signature makes it a great tool with many uses for the intelligence community.
Along the border of hostile and sparsely populated regions with difficult terrain (caves, mountain passes, etc), EviDust would act as a superior tracking device, sticking for days to the boots and clothing of combatants that pass through a zone sprinkled with the dust. Espionage in particular would have immense uses for such a difficult to distinguish material that possesses all the advantages of a homing beacon, and is easily inserted onto another person.

Quantum Dots - Life Science Applications

? **Spectral Multiplexing**
? **FRET and Quenching Donors**
? **Microscopy and Cell Staining**
? **In vivo Imaging**
? **Immunoassays**
? **Dot Blots and other membrane based detection technologies**
? **DNA/RNA Assays & Microarrays**
? **Flow Cytometry**
? **High Throughput Screening**
? **Whole Blood and Tissue Screening**
? **Two Photon Absorption and Up-conversion Dyes**
? **Fluorescence Lifetime Applications**



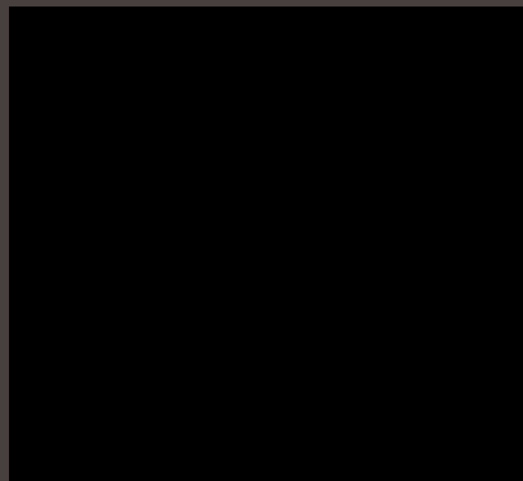
Synthesis of semiconducting nanocrystals

- $CdMe_2$ and Se dissolved in TOP
- Cold solution is injected into hot TOPO (300°C)
- Temperature drops to ca. 170°C
- Increase of temperature to higher temperature (below 300°C) for a specified time

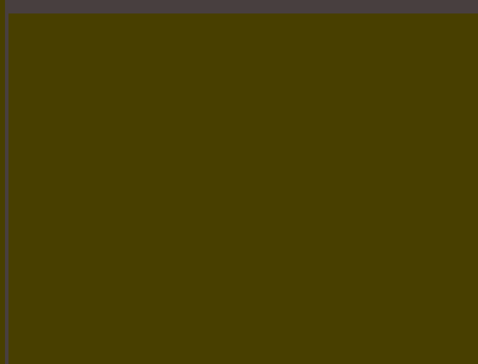
Kinetically controlled synthesis

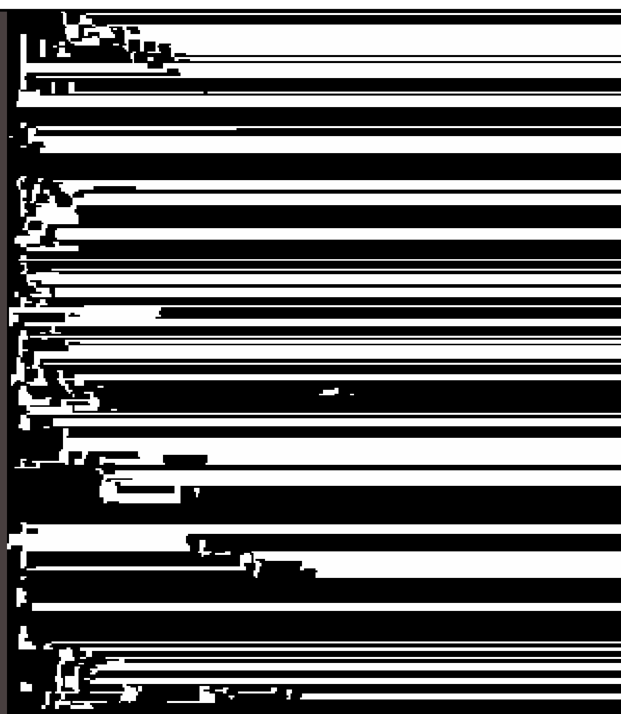
- Nucleation
- Growth
- Shape
- Composition

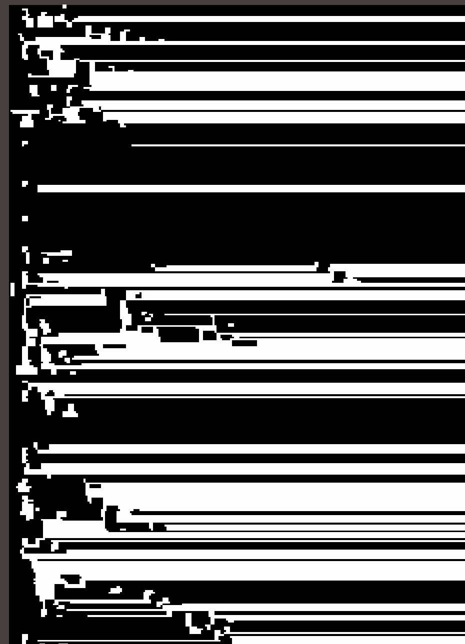
TOPO: Tri-n-octylphosphine oxide
TOP: Tri-n-octylphosphine



Monodispersity - size - shape - defects





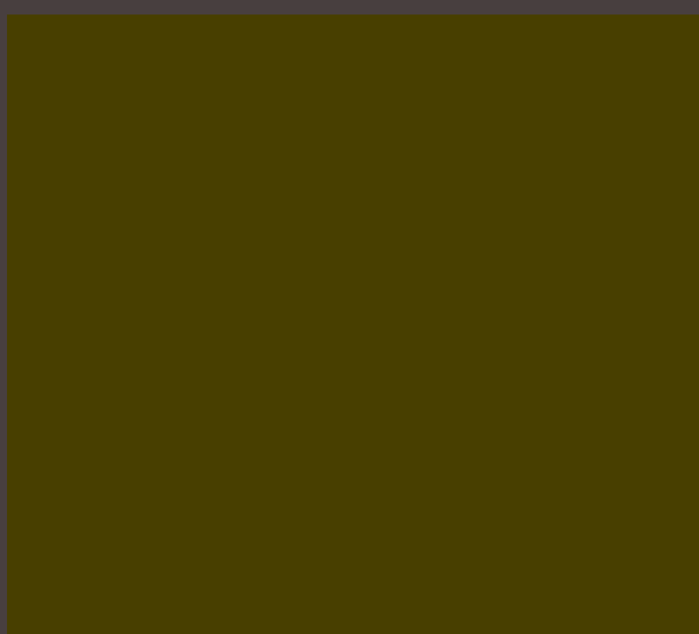


Shape, capping and core-shell materials

Core-shell materials

$CdS/Cd(OH)_2$
CdSe/ZnS
CdSe/ZnSe
CdSe/CdS/ZnS
CdSe/(Cd,Zn)S/ZnS
Silica shells
Organic shells

Improve quantum yield (Unit cell mismatch important)
Improve photostability
Decrease decay/reactions
Reduces toxicity



a) High-resolution TEM image of a typical tetrapod-shaped CdSe nanocrystal, looking down the [001] direction of one arm. The nucleus is the zincblende structure, with wurtzite arms growing out of each of the four (111) equivalent faces.
b) Low-magnification TEM image of CdTe tetrapods. Scale bar, 100 nm.
c) High-resolution TEM image of a tetrapod that has branches growing out of each arm. There are zincblende layers near the ends of the original arms, and the branches are wurtzite with some stacking faults.

d) TEM image of branched tetrapods result from nucleation of CdTe zincblende branch points on the end of each arm. Scale bar, 100 nm.

Anisotropic CdSe crystals by surface controlled growth

Impurities in TOPO are influencing (decreasing) the crystallization rate.

Anisotropic growth: Hexyl-phosphonic acid, (HPA, $C_6H_{15}PO_3$) was added to pure TOPO to `simulate' the presence of those impurities.

CdSe nanocrystals (NCs) prepared by the hot-injection solvothermal synthesis

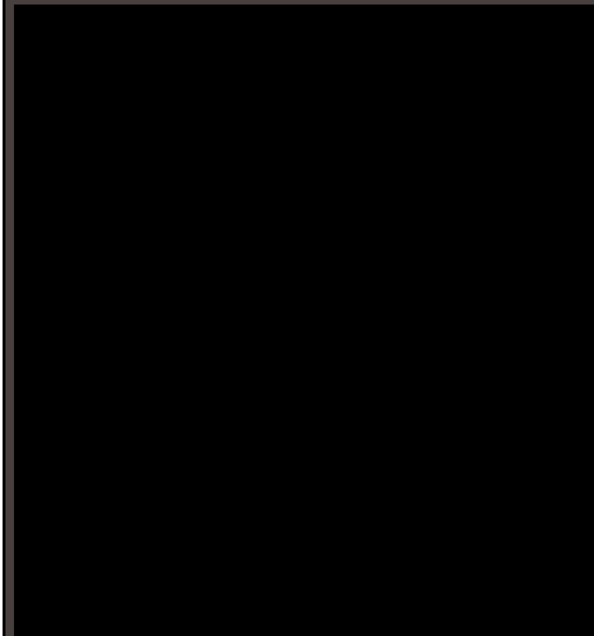
Colloidal suspensions of CdSe NCs under weak daylight (top) and under UV excitation leading to brilliant luminescence (bottom);

Left flask: CdSe(core)/ZnSe(shell)/ZnS(shell)/TOPO-HDA NCs with a CdSe core of 2.8 nm in diameter;

Right flask: CdSe/TOPO-HDA (core diameter: 4.3 nm).

CdSe/TOPO-HAD NCs (6.0 nm in diameter) self-assembled on a TEM grid; and a high-resolution TEM image of a single CdSe NC

Optical absorption spectrum showing the fundamental (i.e., HOMO→LUMO) and a few higher energy inter-band transitions of 4.3 nm CdSe/TOPO-HDA NCs, together with the exciton luminescence spectrum (in red).



sonant tunneling spectrum
tained with a single CdSe quantum
t of 4.3 nm in diameter: the
sonances at positive bias indicate
e atom-like S, P, D, and F electron
vels, the theoretical separations are
dicated with arrows, the quantum
nfinement energy is in good
reement with pseudo-potential
lculations. Some valence levels
g., HOMO, HOMO1) are seen at
gative bias.[30b]

Essential points of the synthesis of monodisperse CdSe nanocrystals with separate nucleation and growth:

a) Sketch of the free energy of formation of a cluster according to classical nucleation theory. b) Sketch of the solubility product [Cd][Se] as a function of temperature. Solid line: thermodynamic curve for the equilibrium between the monomers Cd-TOPO and Se-TOP and a macroscopic CdSe crystal. Dashed line: the solubility product for the equilibrium between the monomers and the critical nuclei $(CdSe)_c$ indicative of supersaturation. The points indicate: nucleation (1), cooling (12), and growth of the nuclei at two different temperatures (3 and 3').

Classical:

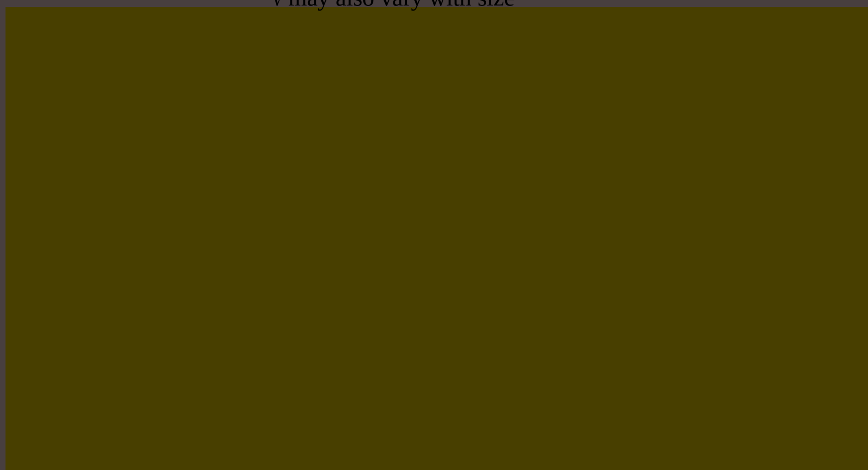
÷G (<0) : Free energy associated with crystal formation
ν (>0): Surface energy

Magic numbers?

One of the reasons why the classical approach to nucleation may fail:

÷G is not independent on size

ν may also vary with size



c) The concentration of monomer precursors and critical nuclei $(CdSe)_c$ as a function of the total precursor concentration added to the reaction flask, calculated for the equilibrium given in Equation (1); c=75 CdSe units in accordance with experimental observations, (the concentrations are given in arbitrary units). The point at which the concentration of critical nuclei rises steeply is called the critical point.[9]

d) Experimental observation of the growth evolution of nuclei into mature nanocrystals at 240?C. The diameter of the nanocrystals first increases and than becomes constant. Increase of the temperature to 260 and 280?C (full curve) leads to further growth similarly to the addition of excess precursors (dashed curve).

evident

Quantum Dot Material System	Emission Range	Quantum Dot Diameter Range	Quantum Dot Type	Standard Solvents	Qauntum Dot Example Applications
CdSe	465nm - 640nm	1.9nm - 6.7nm	Core	Toluene	Research, Solar Cells, LEDs
CdSe/Zns	490nm - 620nm	2.9nm - 6.1 nm	Core-Shell	Toluene	Visible Fluorescence Applications, Electroluminescence, LEDs
CdTe/CdS	620nm - 680nm	3.7nm - 4.8nm	Core-Shell	Toluene	Deep Red Fluorescence Apps.
PbS	850nm - 2100nm	2.3nm - 9.8nm	Core	Toluene	Near Infrared Applications, Security Inks, Solar Cells, IR LEDs
PbSe	1200nm - 2340nm	4.5nm - 9nm	Core	Toluene	Opto-electronics, Optical Switching, Non-linear Applications, Photonics, Telecommunications

Semiconductor nanocrystals for biological imaging

Aihua Fu, Weiwei Gu, Carolyn Larabell and A Paul Alivisatos

Conventional organic fluorophores suffer from poor photo stability, narrow absorption spectra and broad emission spectra. Semiconductor nanocrystals, however, are highly photo-stable with broad absorption spectra and narrow size-tunable emission spectra.

Recent advances in the synthesis of these materials have resulted in the generation of bright, sensitive, extremely photo-stable and biocompatible semiconductor fluorophores. Commercial availability facilitates their application in a variety of unprecedented biological experiments, including multiplexed cellular imaging, long-term in vitro and in vivo labeling, deep tissue structure mapping and single particle investigation of dynamic cellular processes.

Semiconductor nanocrystals are one of the first examples of nanotechnology enabling a new class of biomedical applications.

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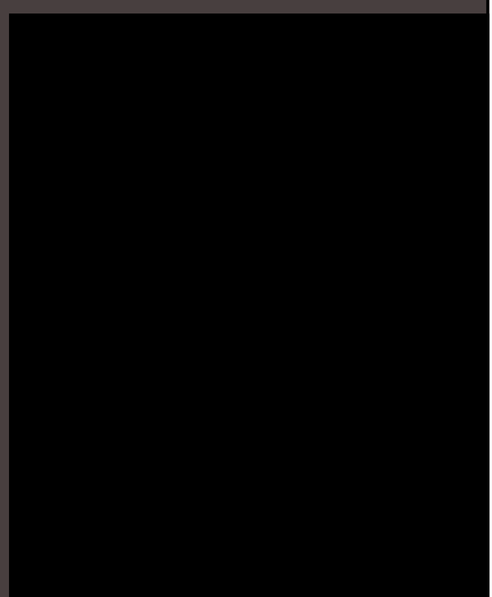

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Toxicity

Cadmium and selenium are known to be toxic [24]. Therefore, concerns have arisen about the toxicity and environmental impact of semiconductor nanocrystals. Most of the above cell and animal experiments showed that when correctly capped by both ZnS and hydrophilic shells, no obvious CdSe nanocrystal toxicity was observed under normal experimental conditions. Several groups have varied parameters such as synthesis, surface coating and incubation concentration to further investigate the potential toxicities of nanocrystals [24,43,45]. Cytotoxicity was observed when Cd^{2+} or Se^{2+} ions were released. This occurred when the nanoparticle surface coating was not stable, exposing the CdSe to oxidization by air or UV damage [24,45]. Surface molecules also have a role in QD cytotoxicity [44,45]. Although cells can tolerate PEGsilica coated QDs at concentrations up to 30 mM (QDs Cd surface atom concentrations), mercaptopropionic acid coated QDs have deleterious effect at 6 mM [45].

Cytotoxicity of Colloidal CdSe and CdSe/ZnS Nanoparticles Christian Kirchner, Tim Liedl, Stefan Kudera, et al. Nano Letters, 2005, Vol. 5, No. 2, 331-338

Probing the Cytotoxicity of Semiconductor Quantum Dots Austin M. Derfus, Warren C. W. Chan, et al. Nano Letters 2004, Vol. 4, No. 1, 11-18