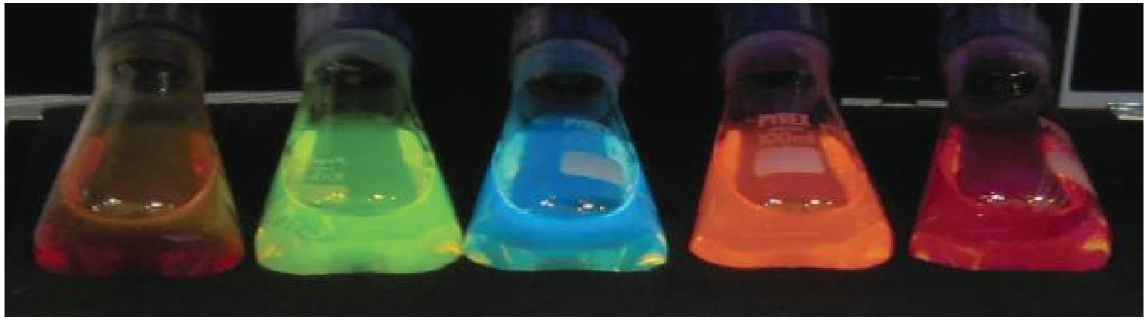
Making and Using Nanoparticles - the Marketplace Potential

2006 Expert Lecture Series Leaders in Nanotechnology



Paul O'Brien

The School of Chemistry

and The Manchester Materials Science Centre

Unilever R&D Port Sunlight
Tuesday 9th May
4.00-5.00 pm Room CR1

The University of Manchester

Structure of Talk

- Why now ?
  - Looking at some nanodimensional objects by way of introduction
- Synthetic approaches semiconductors
- How nanoparticles grow and rods and tetrapods
- Other materials a rogues gallery
- What are some of the opportunities
  - The Nanoco Technologies Ltd perspective
- Closing remarks

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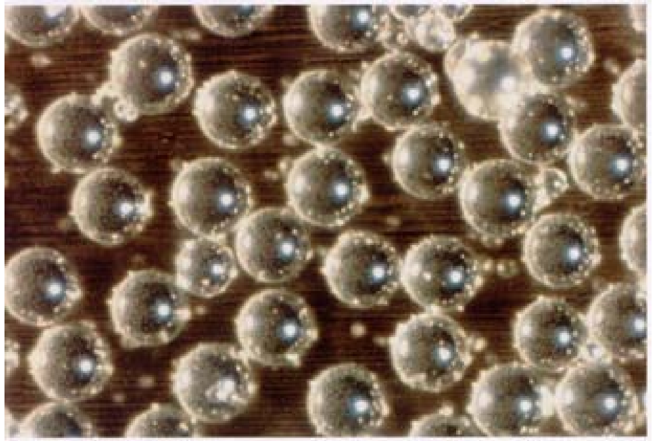
What are lost dimensions?

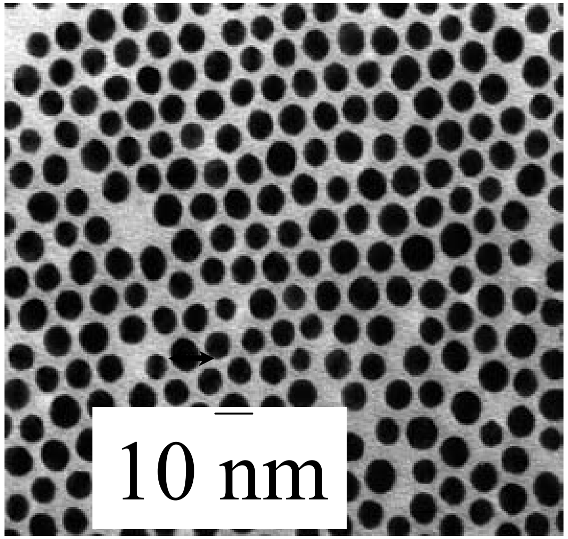
Industrial Development and a History of Precise Size Control

1850

1980

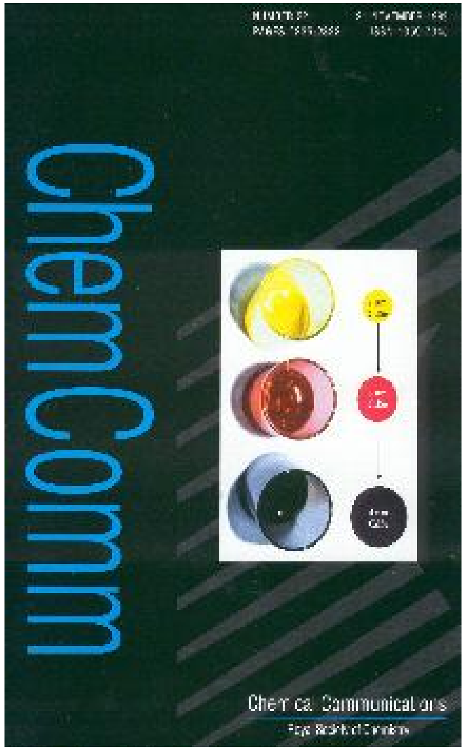


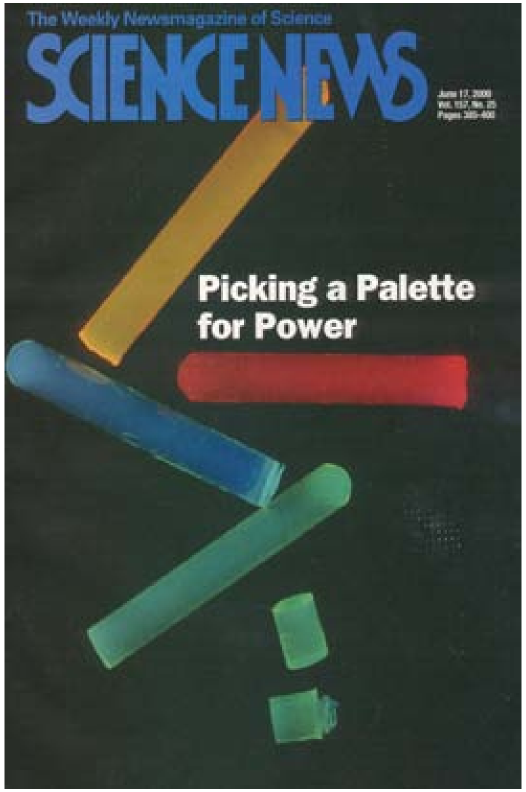
2004



Ball Bearings for the 21st Century!

Why Now?

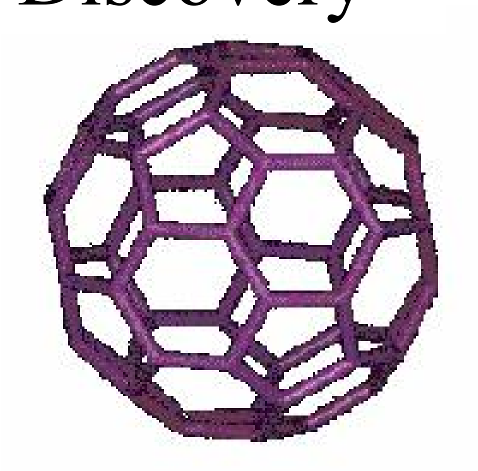

ChemComm
Chemical Communications

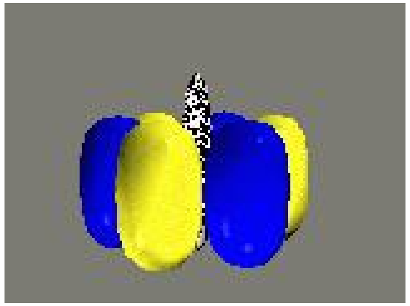

The Weekly Newsmagazine of Science
SCIENCE NEWS
Picking a Palette
for Power

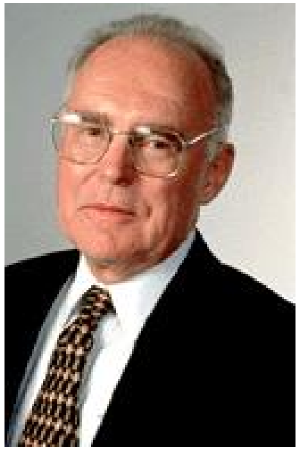

IPO REVIEW (ALAS)
CHIPS
RED HERRING
THIS
COULD
CHANGE
EVERYTHING

DART

Discovery







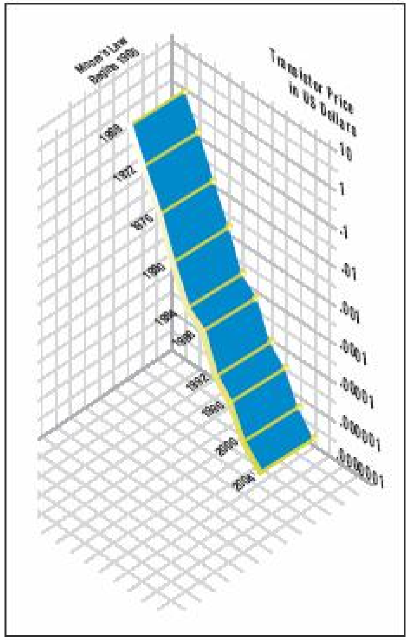
Access

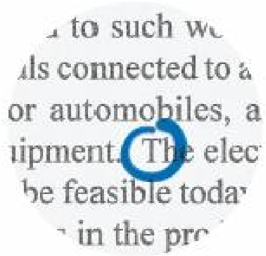
Reason

Scanning Tunneling Electron Microscopy

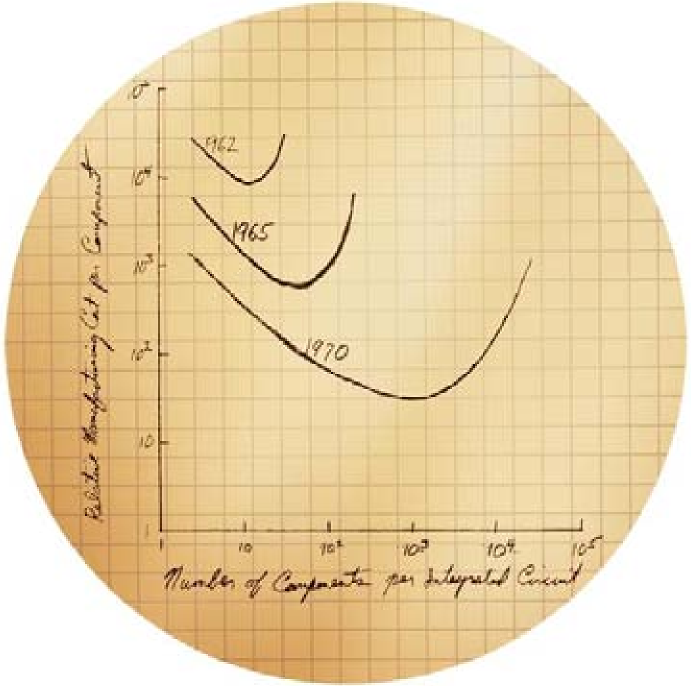
Gerd Binnig and Heinrich Rohrer

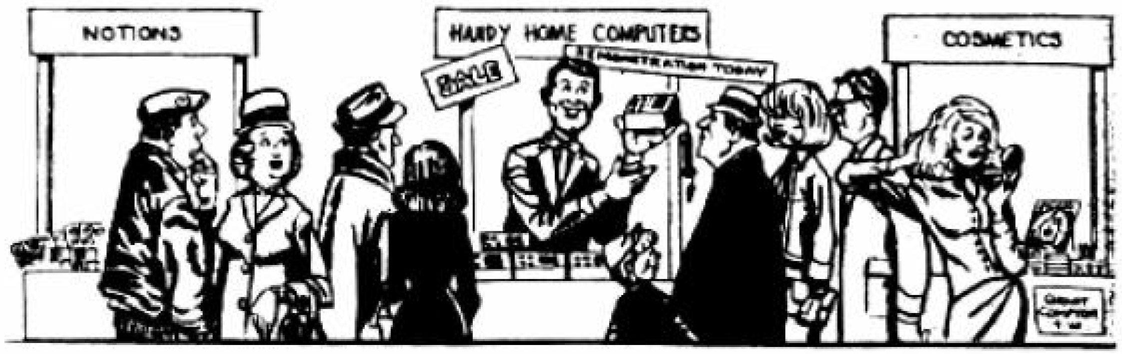
Technology





The price per transistor
on a chip has dropped dramatically since Intel was founded in 1968. Some people estimate that the price of a transistor is now about the same as that of one printed newspaper character.





Electronics, Volume 38, Number 8, April 19, 1965

Microprocessor	Year of Introduction	Transistors
4004	1971	2,300
8008	1972	2,500
8080	1974	4,500
8086	1978	29,000
Intel286	1982	134,000
Intel386™ processor	1985	275,000
Intel486™ processor	1989	1,200,000
Intel® Pentium® processor	1993	3,100,000
Intel® Pentium® II processor	1997	7,500,000
Intel® Pentium® III processor	1999	9,500,000
Intel® Pentium® 4 processor	2000	42,000,000
Intel® Itanium® processor	2001	25,000,000
Intel® Itanium® 2 processor	2003	220,000,000
Intel® Itanium® 2 processor (9MB cache)	2004	592,000,000

350 nm

250 nm

180 nm

10 things we'll know by this time next year

What will be the big scientific hits and misses of the next 12 months? Alok Jha looks ahead

Thursday January 8, 2004

The Guardian

Guardian Unlimited

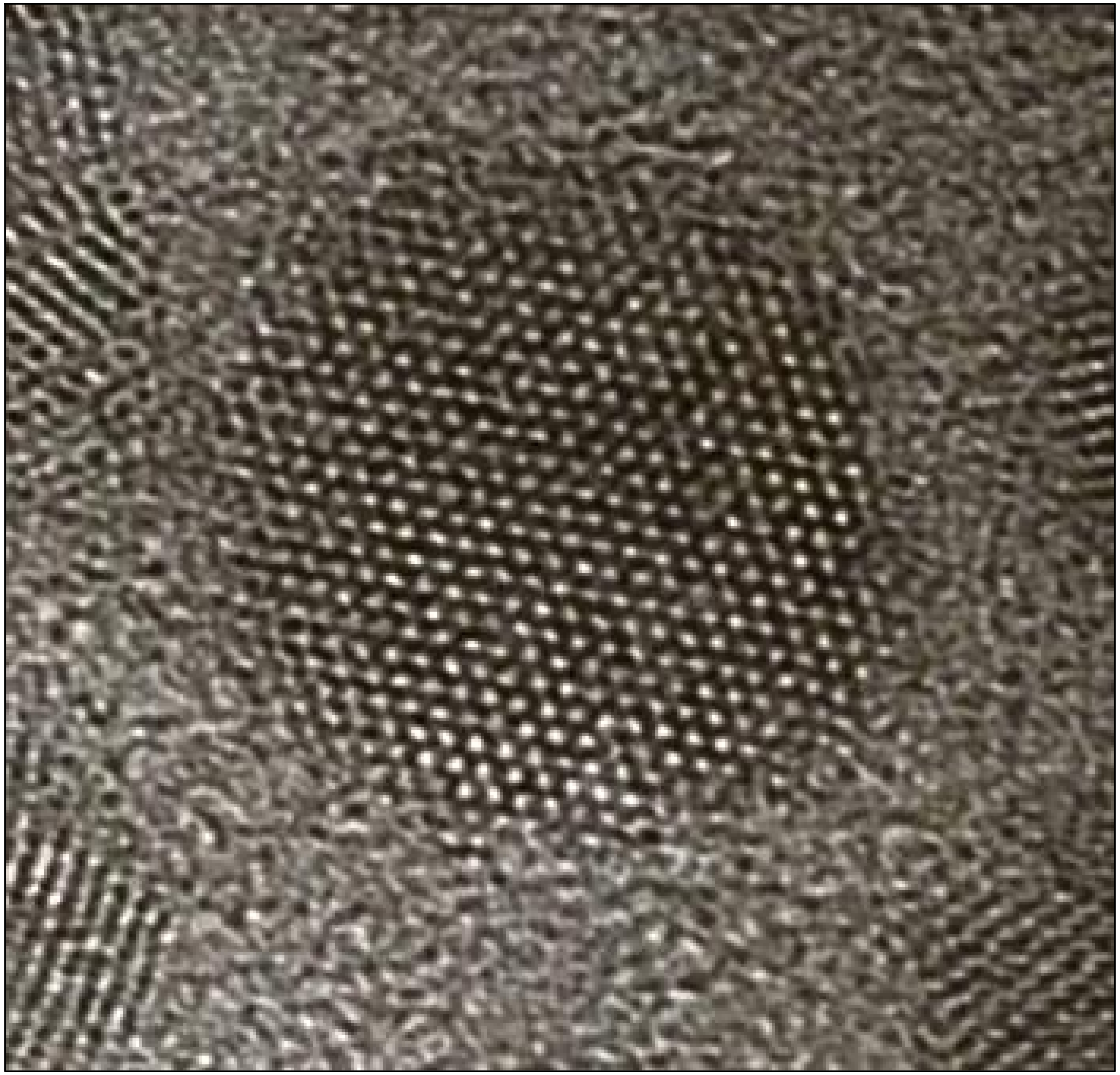
1. How to make better cancer drugs

2. All about quantum dots

It may not sound like much, but these miniscule particles have not been nicknamed the ball bearings of the 21st century for nothing; before ball bearings were invented, there was no use for them and now they're everywhere. Scientists say it will be the same with quantam dots.

Paul O'Brien, a chemist at Manchester University who helped to set up NanoCo, says the dots could replace inks or dyes in biological screening programmes. And further down the line, they could be used in security - bank notes could have barcodes made from the dots that would be very difficult to copy.

Until now the dots could only be produced in small batches and then only using dangerous chemicals. But this year NanoCo, a company spun out of the university, hopes to produce large quantities of them without using toxic materials.



Chem Commun., 1999, 1573-1574

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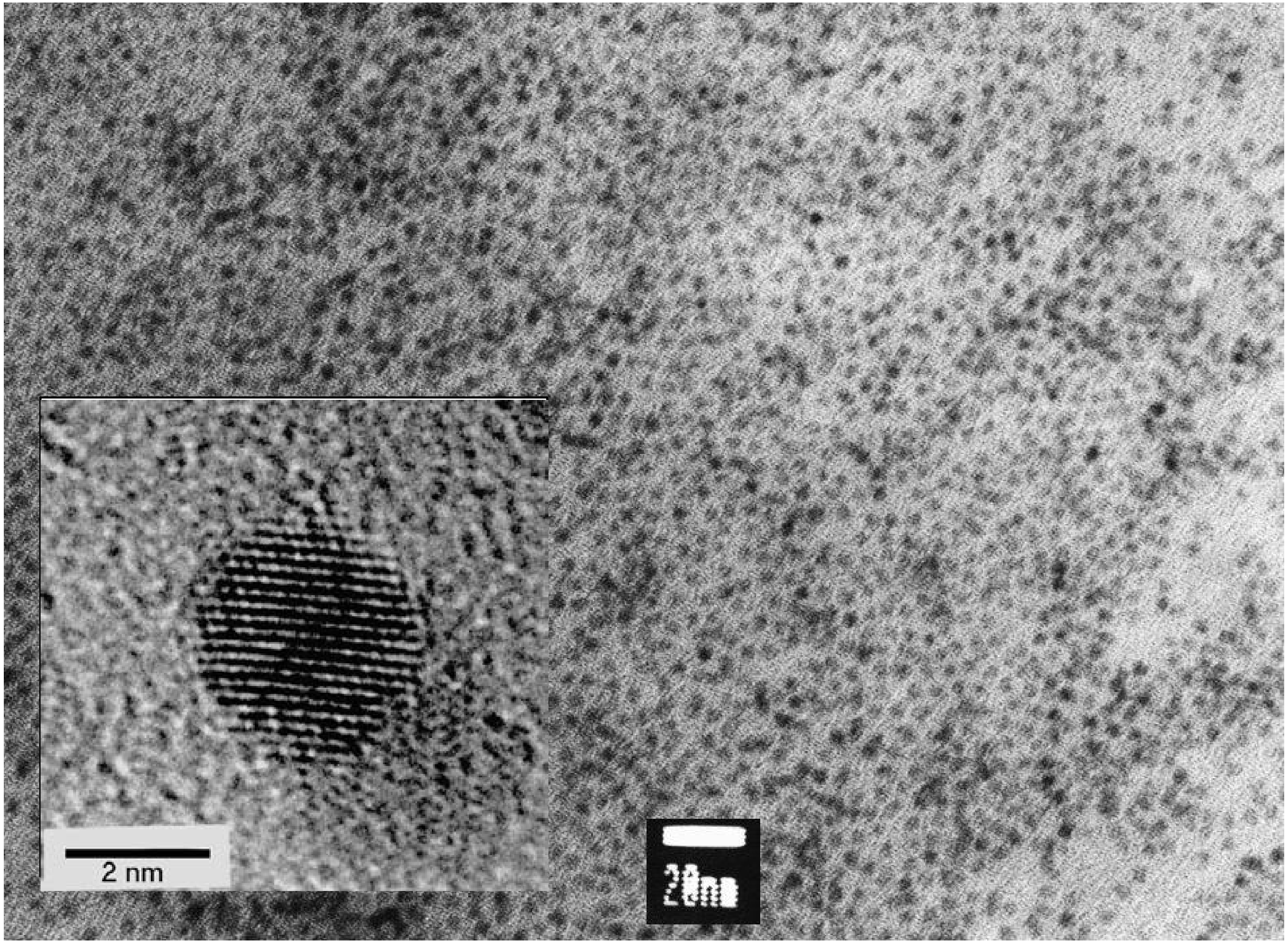
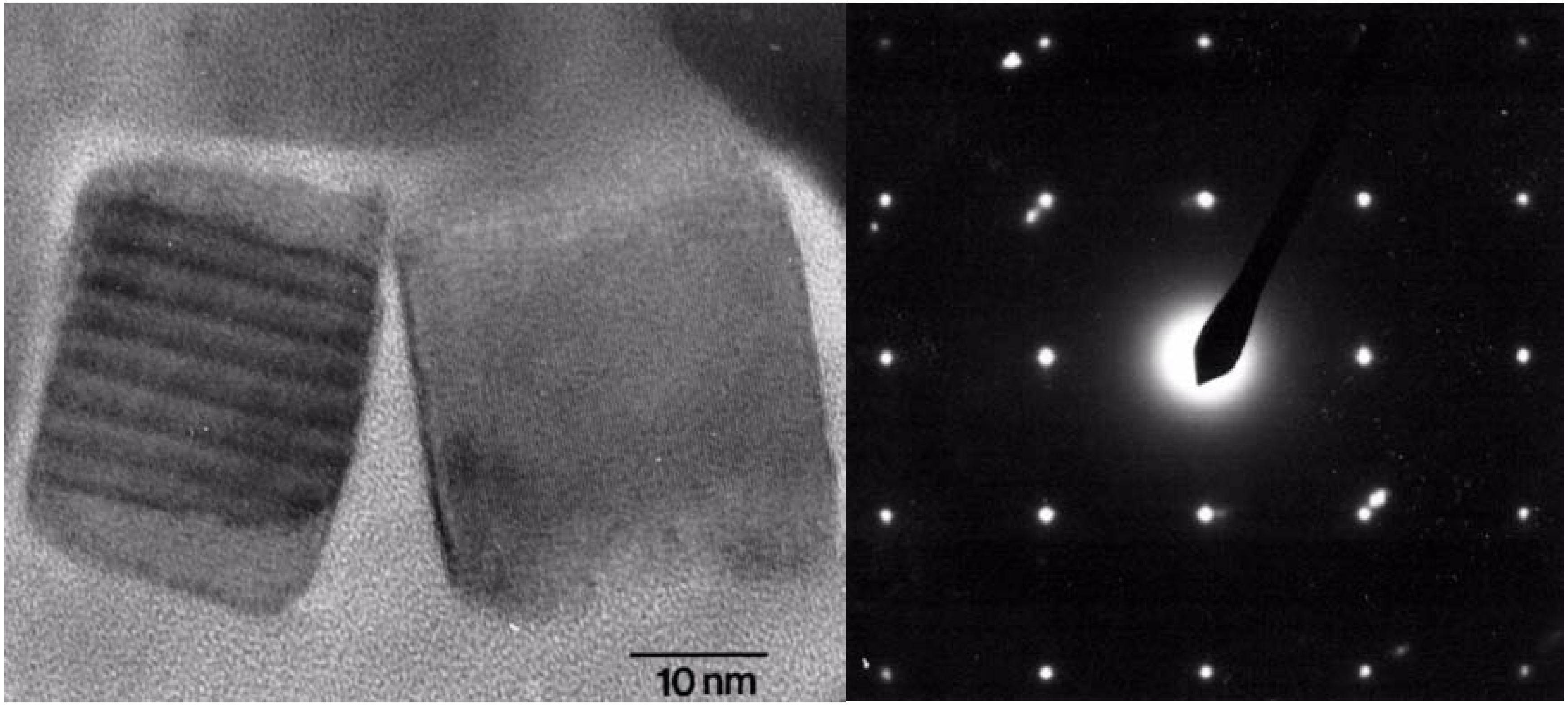
More CdSe





Sample of PbS Coated with TOPO

J. Materials Chemistry, 1997, 7, 1011

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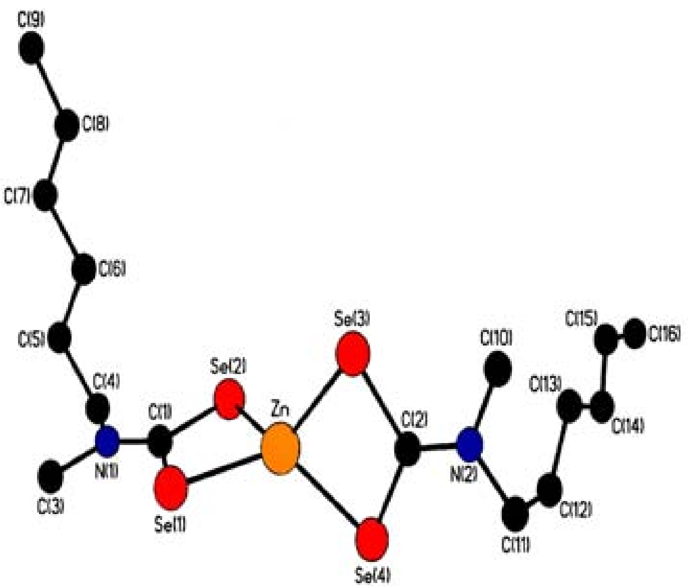
$. Cd(Se_2CNRR')_2 \longrightarrow CdSe$

O'Brien et al Chem Comm, 1998 1849, ibid 1999, 1573.



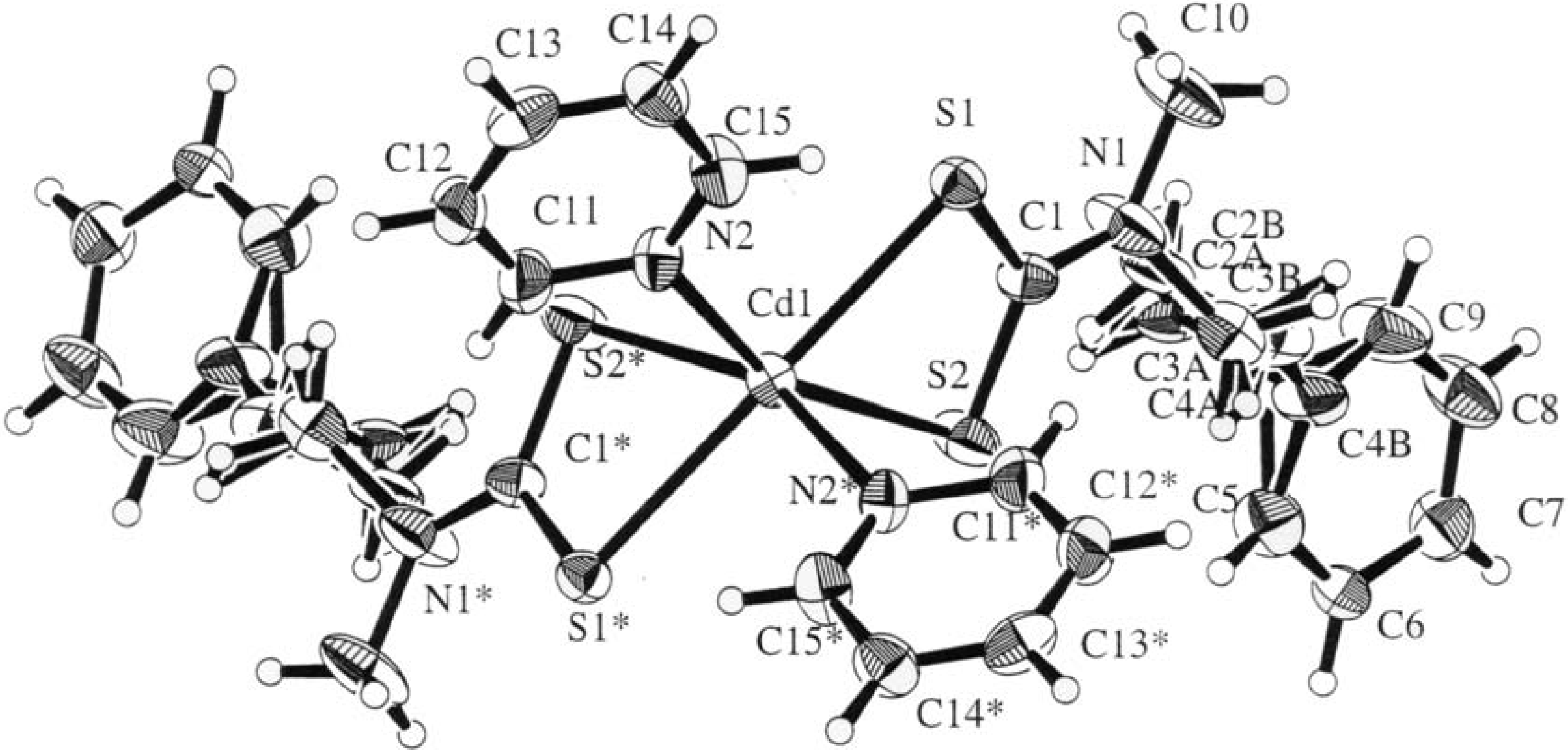
Patent Family
UK patent application No. 9518910.6
PCT application WO 97/10175.
US patent No. 09/043,258 (Granted)
EP patent application No. 96927134.5

$Me_2Cd + TOPSe \longrightarrow CdSe$

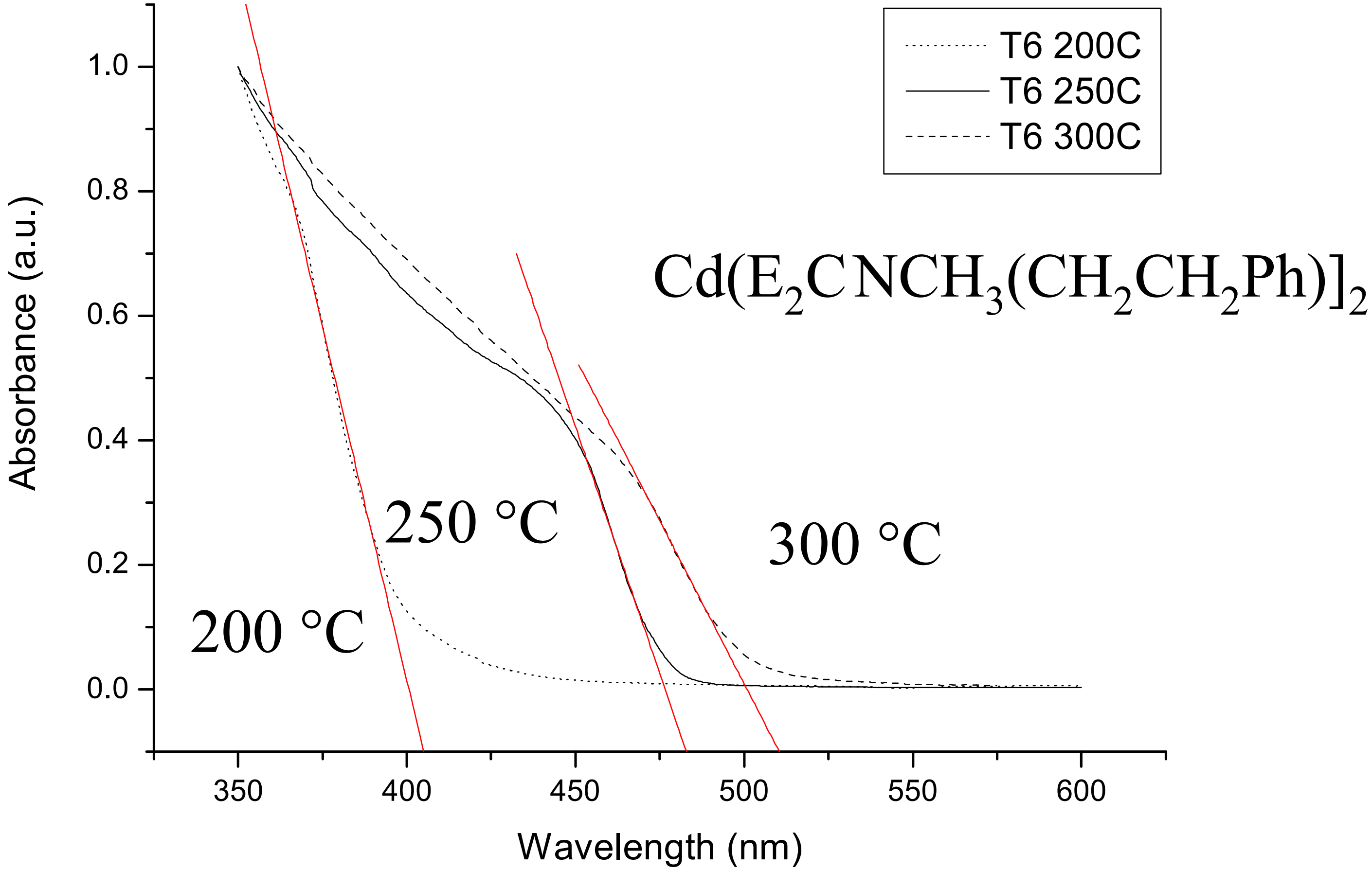
The NanoCo Process

Combining the strengths of UMIST and
The Victoria University of Manchester

New strategies for the synthesis of nanoparticulates



X-Ray single crystal structure of $Cd(E_2CNCH_3(CH_2CH_2Ph)]_2$



UV-Vis spectra of aliquots T6 (20 min), of runs CdS 200℃, CdS 250℃ and CdS 300℃ fitted to a direct transition.

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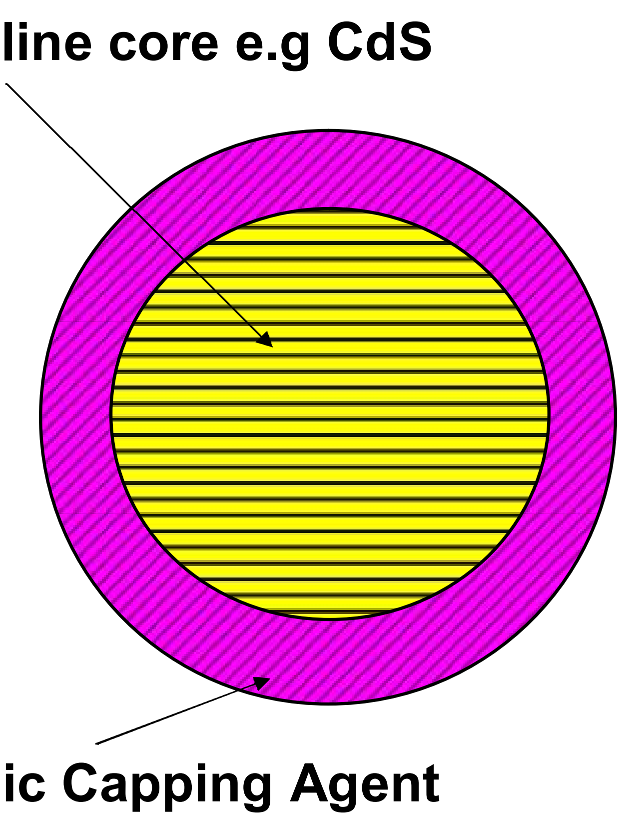
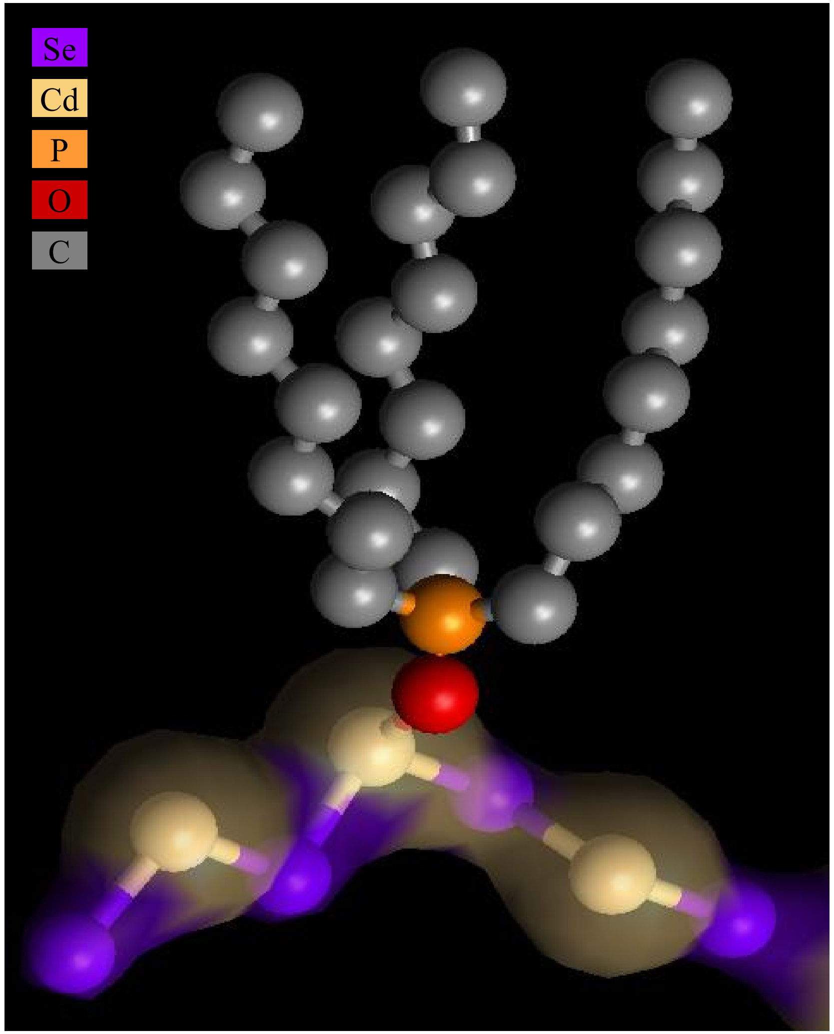
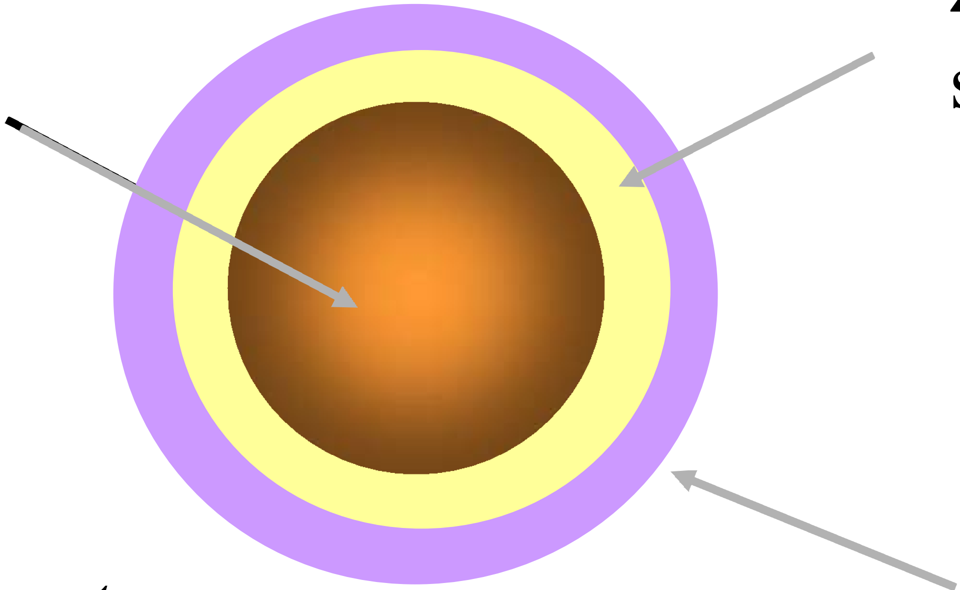
Quantum Dot Structures I





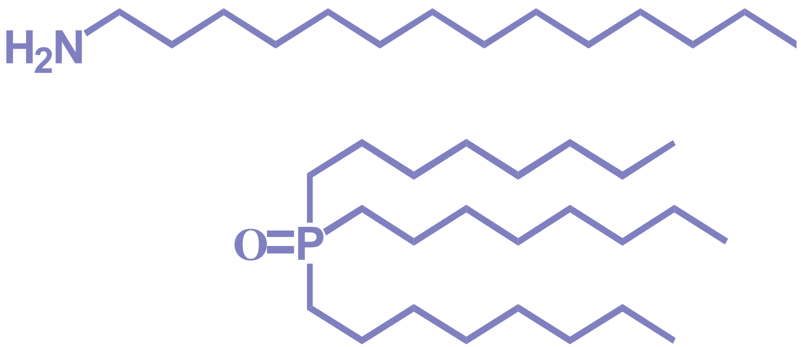
'Metal Organic Dot'

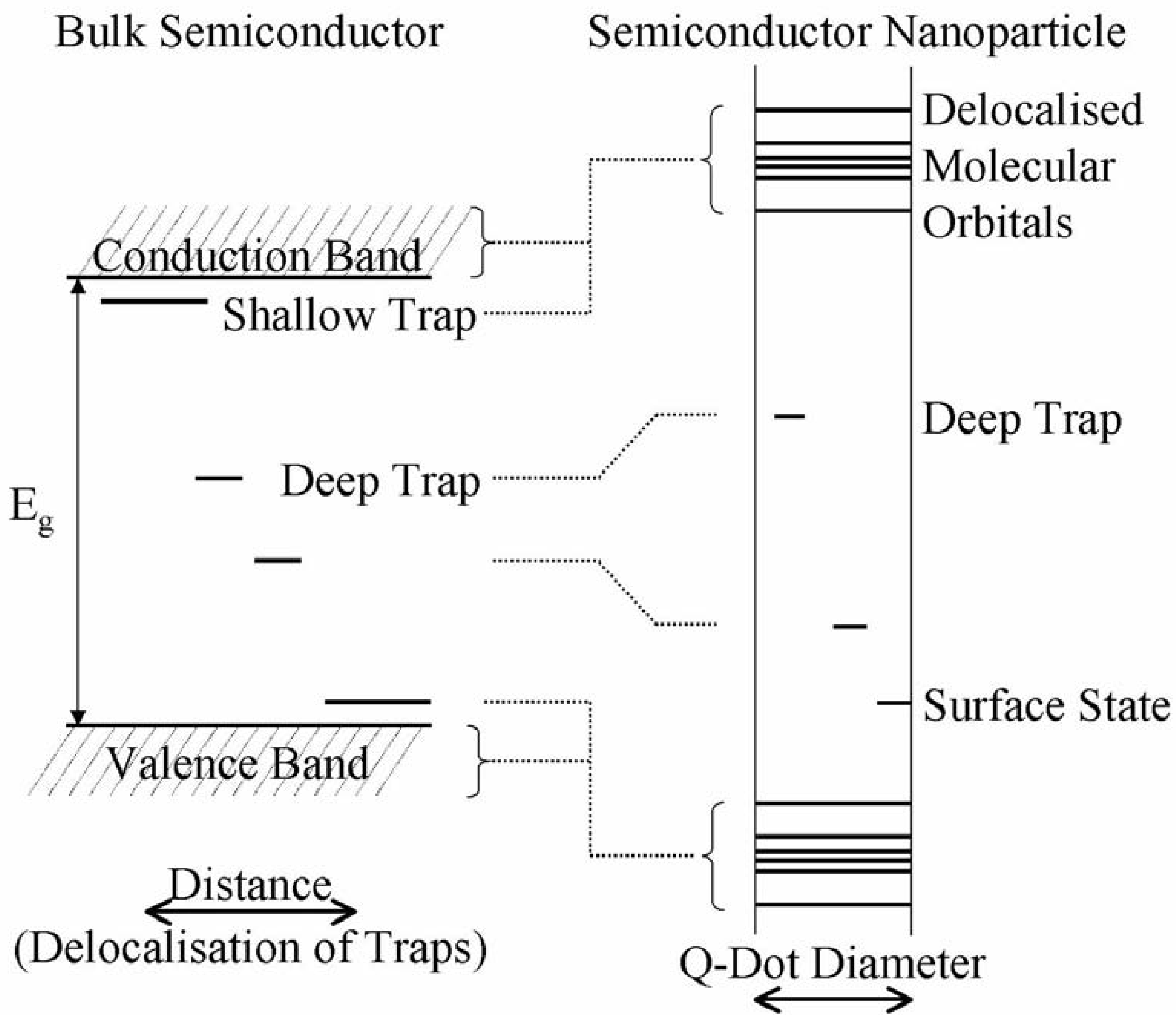
Quantum Dots II

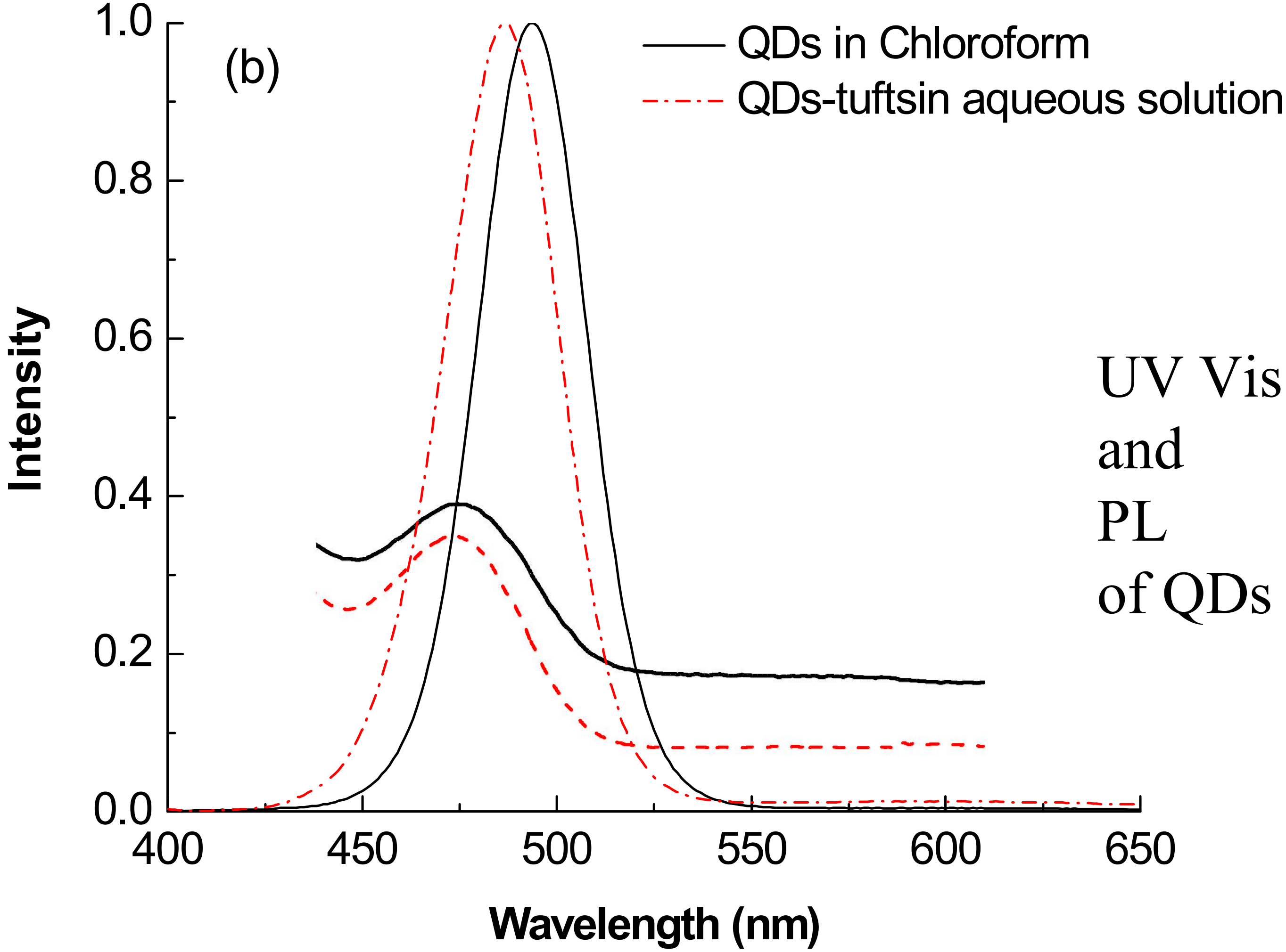


Core Shell Structures

- Broadband excitation
- Narrow bandwidth emission
- Emit light of high intensity
- Available in many colours
- Resistant to quenching
- Photochemically stable




Bulk Semiconductor
Semiconductor Nanoparticle
Delocalised
Molecular
Orbitals
Conduction Band
Shallow Trap
Deep Trap
E_g
Deep Trap
Surface State
Valence Band
Distance
(Delocalisation of Traps)
Q-Dot Diameter


(b)
QDs in Chloroform
QDs-tuftsin aqueous solution
Intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650
UV Vis
and
PL
of QDs

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JOURNAL
Materials
CHE

Controlled synthesis of CdS nanorods and hexagonal nanocrystals

Yunchao Li,† Xiaohong Li,† Chunhe Yang and Yongfang Li*

Key Laboratory of Organic Solids, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China 100080. E-mail: liyf@iccas.ac.cn

Received 3rd July 2003, Accepted 27th August 2003
First published as an Advance Article on the web 3rd September 2003

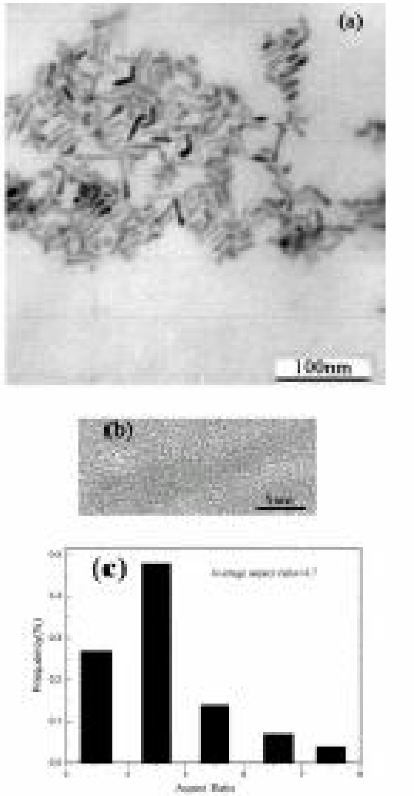


Fig. 7 (a) TEM image of CdS nanorods synthesized at 180 °C for 3 I with a reaction solution of 0.8 g $Cd(C_2H_5OCS_2)_2$ in 4 g HDA. (b) Higl resolution TEM image of a representative nanorod. (c) Aspect ratio histogram of the nanocrystals.

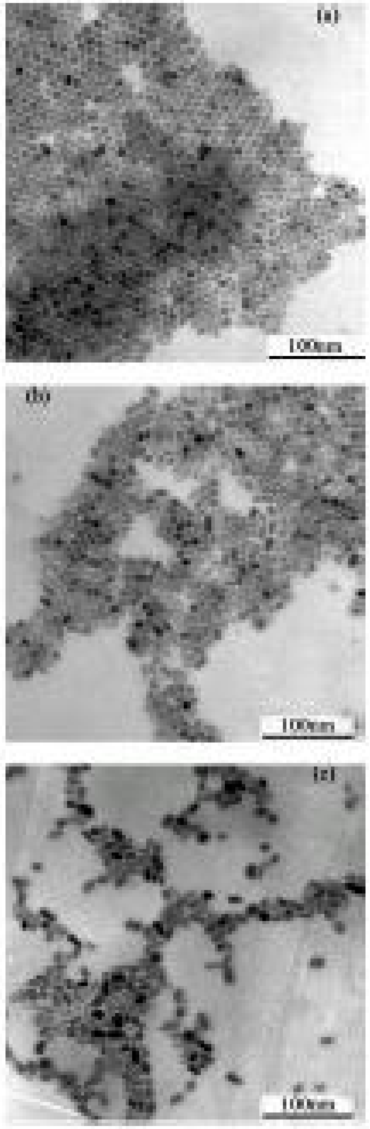
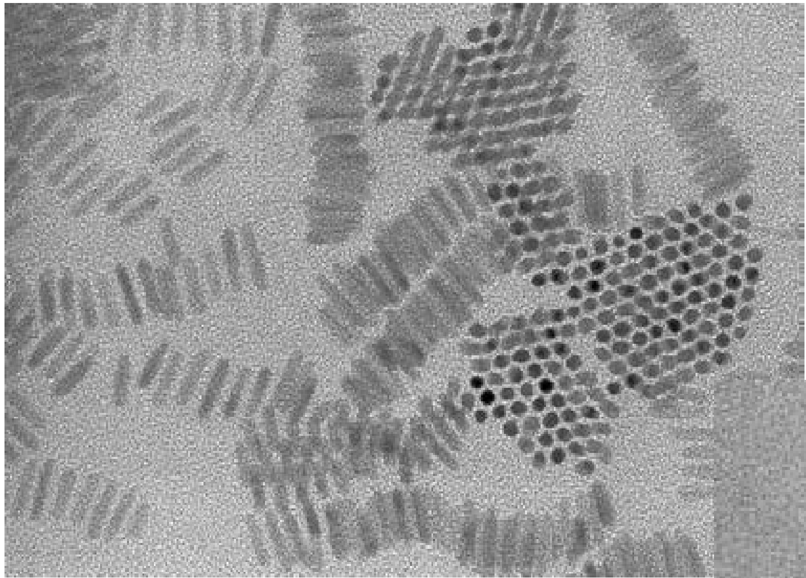
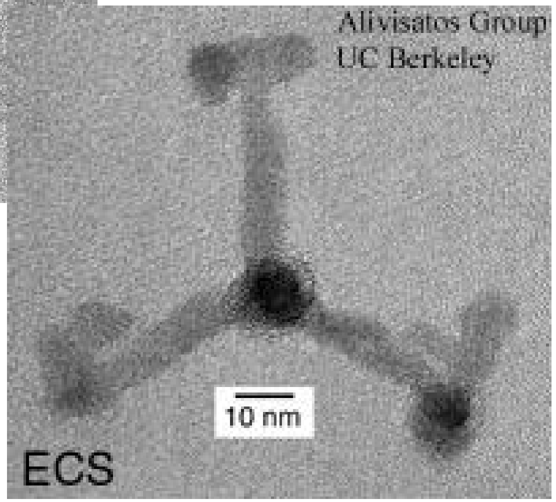
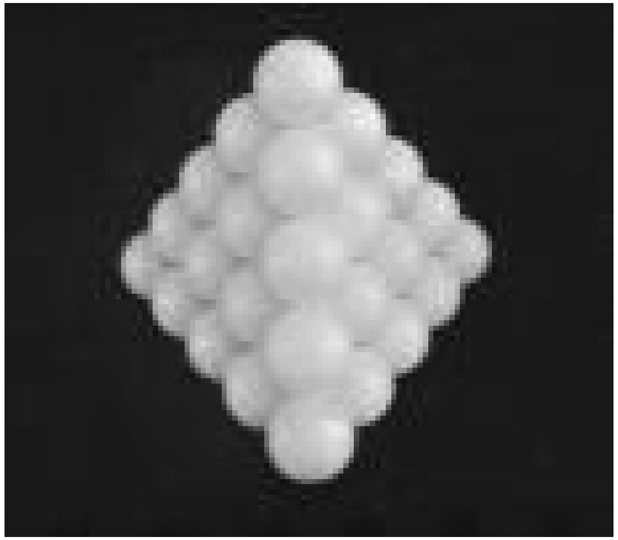
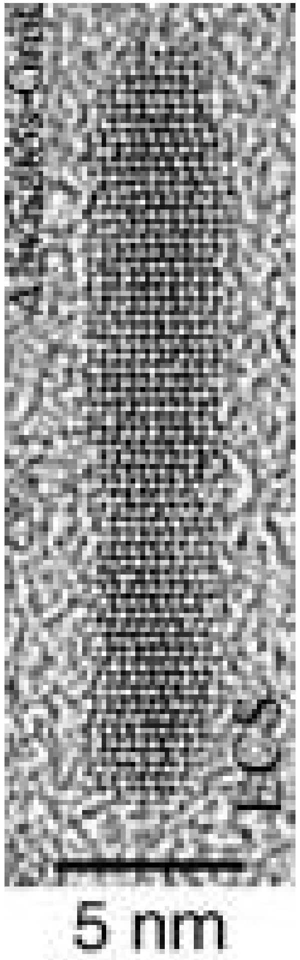


Fig. 4 TEM images of CdS nanocrystals prepared at 260 °C for 3 h, from solutions of (a) 0.1 g, (b) 0.2 g, (c) 0.4 g $Cd(C_2H_5OCS_2)_2$ in 4 g HDA and 2 ml TOP.



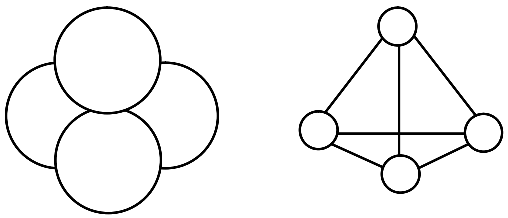

Alivisatos Group
UC Berkeley
10 nm
ECS




ECS
5 nm

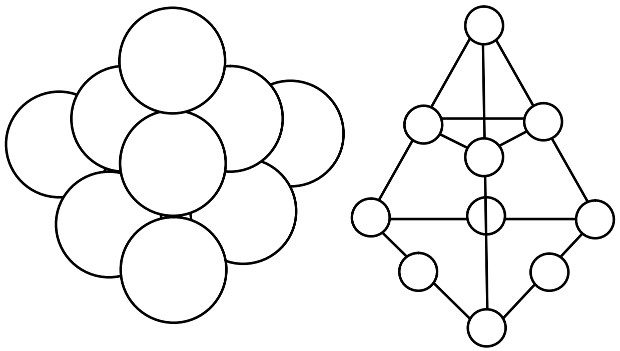
Tetrahedron

N = 2



Total atoms = 4
Surface atoms = 4

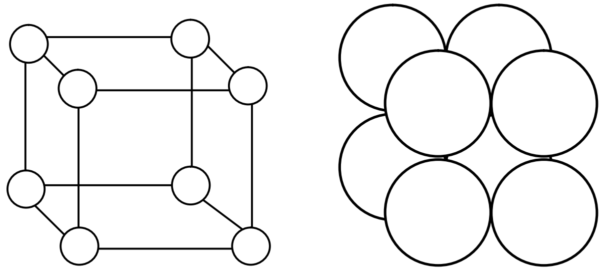
N = 3



Total atoms = 10
Surface atoms = 10

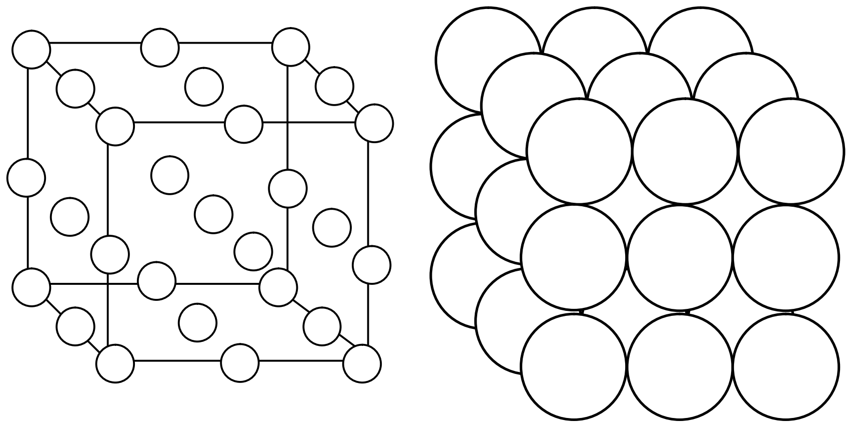
Cube

N = 2



Total atoms = 8
Surface atoms = 8

N = 3

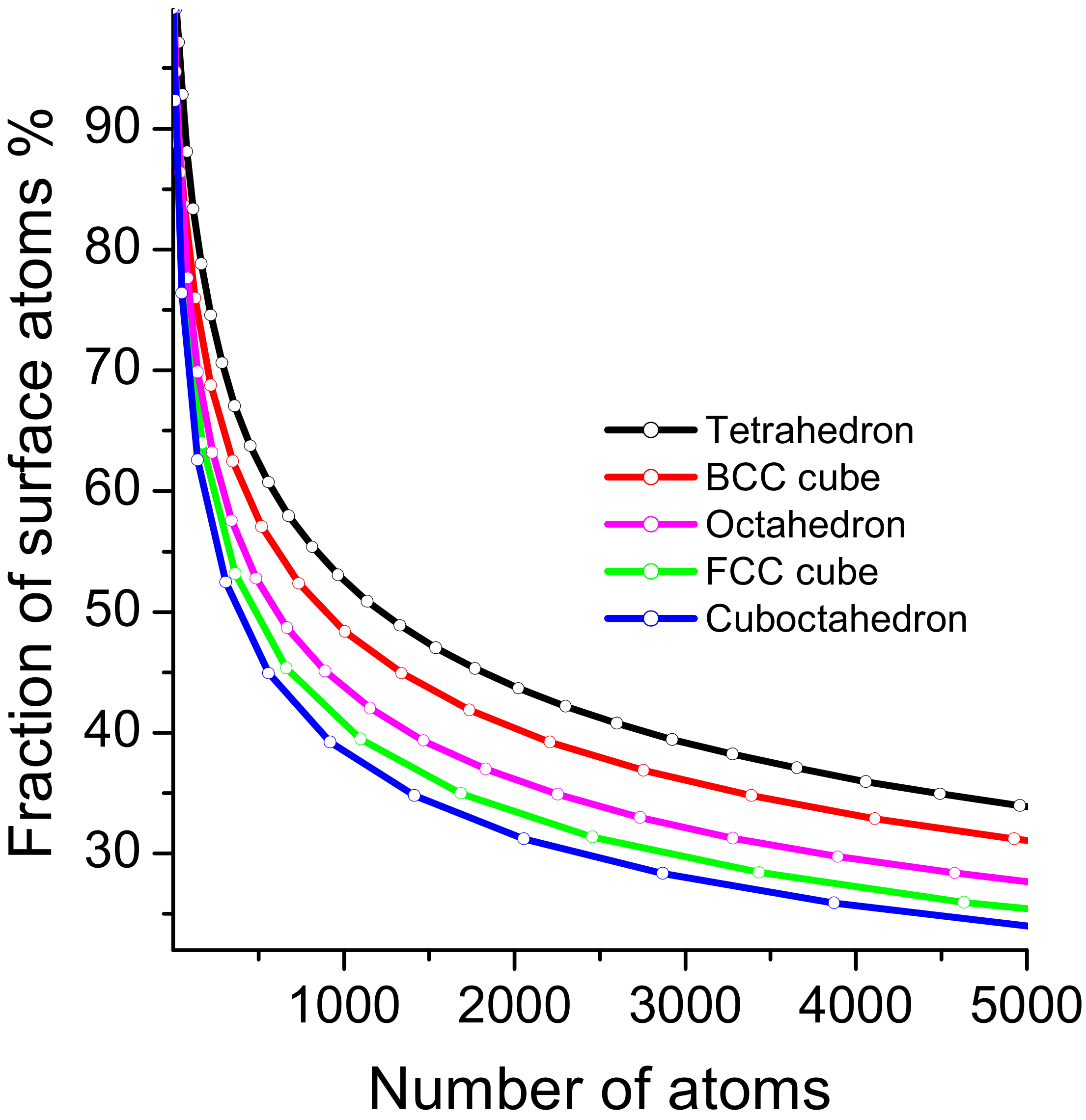


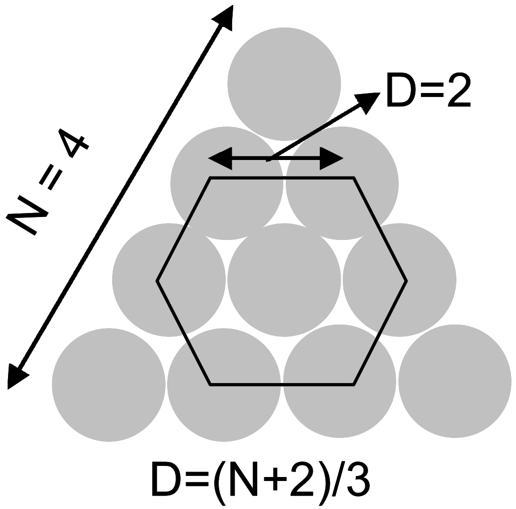
Total atoms = 27
Surface atoms = 26

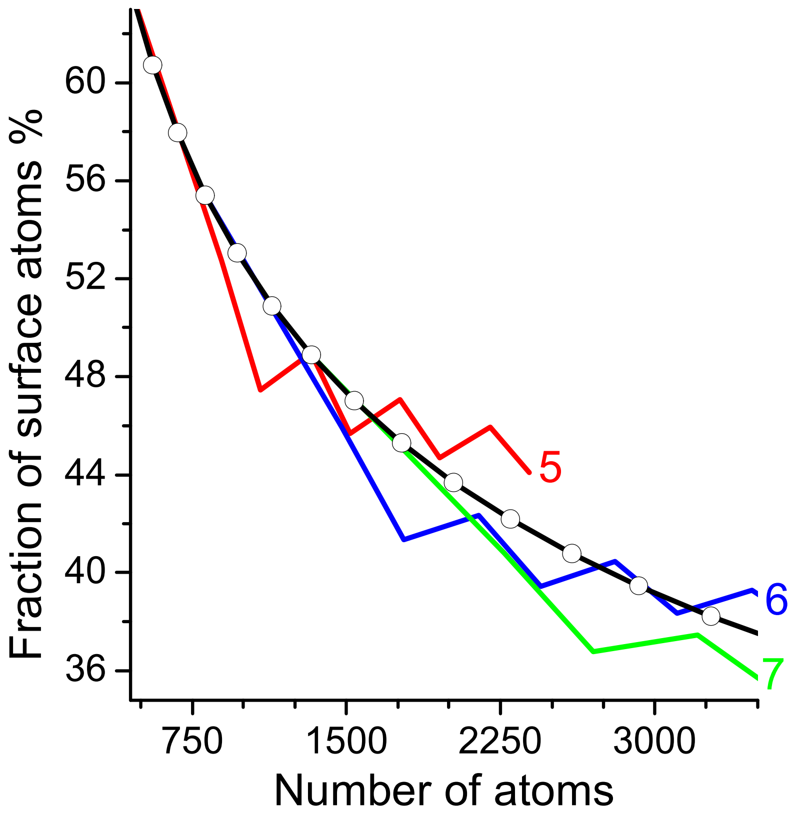
Shape	**Total atoms**	**Surface atoms**
Cube Bcc packing	$(N+1)^3+N^3$	$6N^2+2$
Cube Fcc packing	$4N^3+6N^2+3N+1$	$12N^2+2$
Octahedron Fcc packing	$\frac{2N^3}{3}+\frac{N}{3}$	$4N^2-8N+6$
Tetrahedron Fcc packing	$\frac{N^3}{6}+\frac{N^2}{2}+\frac{N}{3}$	$2N^2-4N+4$
Cuboctahedron triangular faces, fcc packing	$\frac{10N^3}{3}-5N^2+\frac{11N}{3}-1$	$10N^2-20N+12$

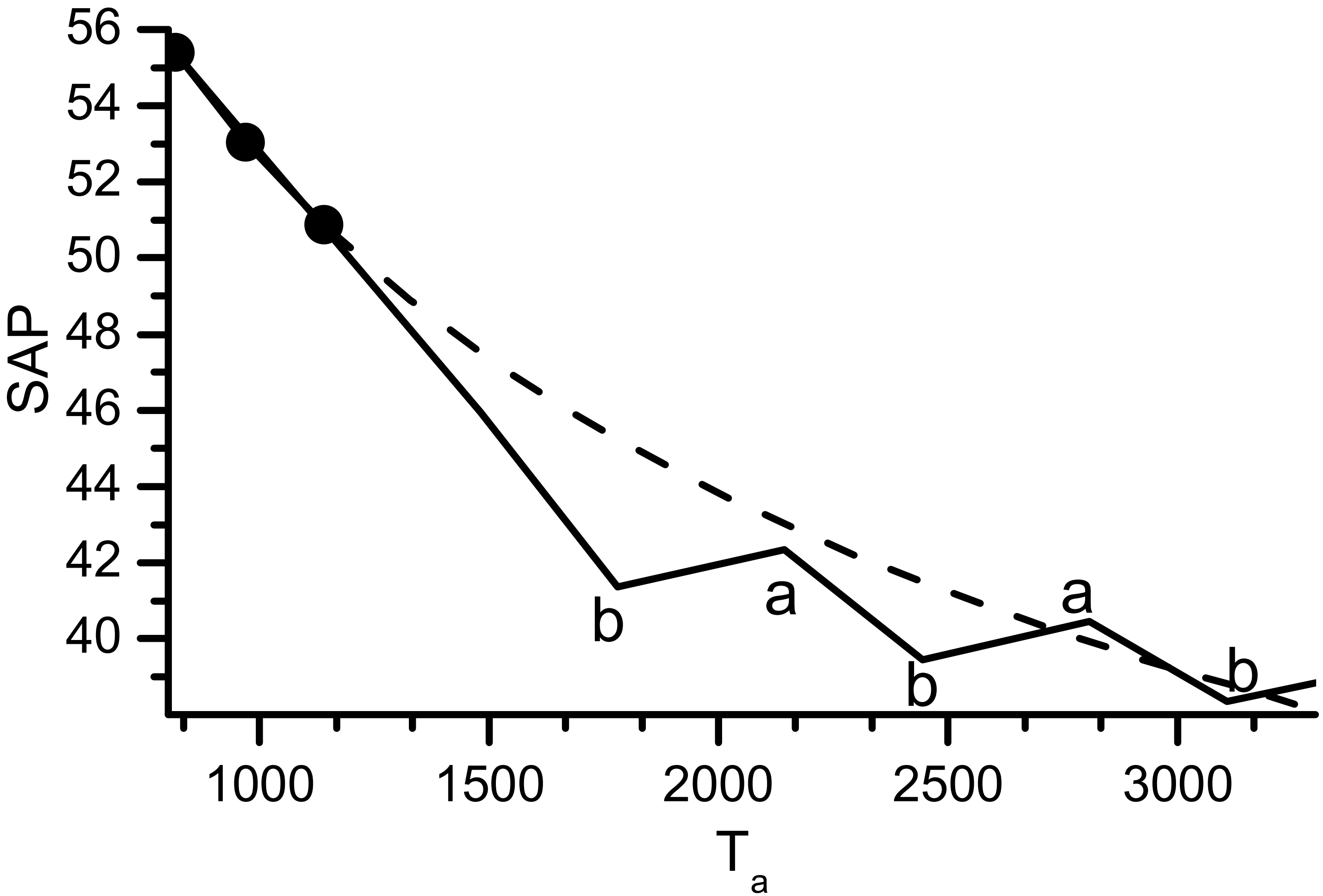
Relationship between the number of shells N and the total number of atoms and surface atoms for different shapes

P. John Thomas and P. O'Brien
J. Amer. Chem. Soc., 128, 2006 5615-5615

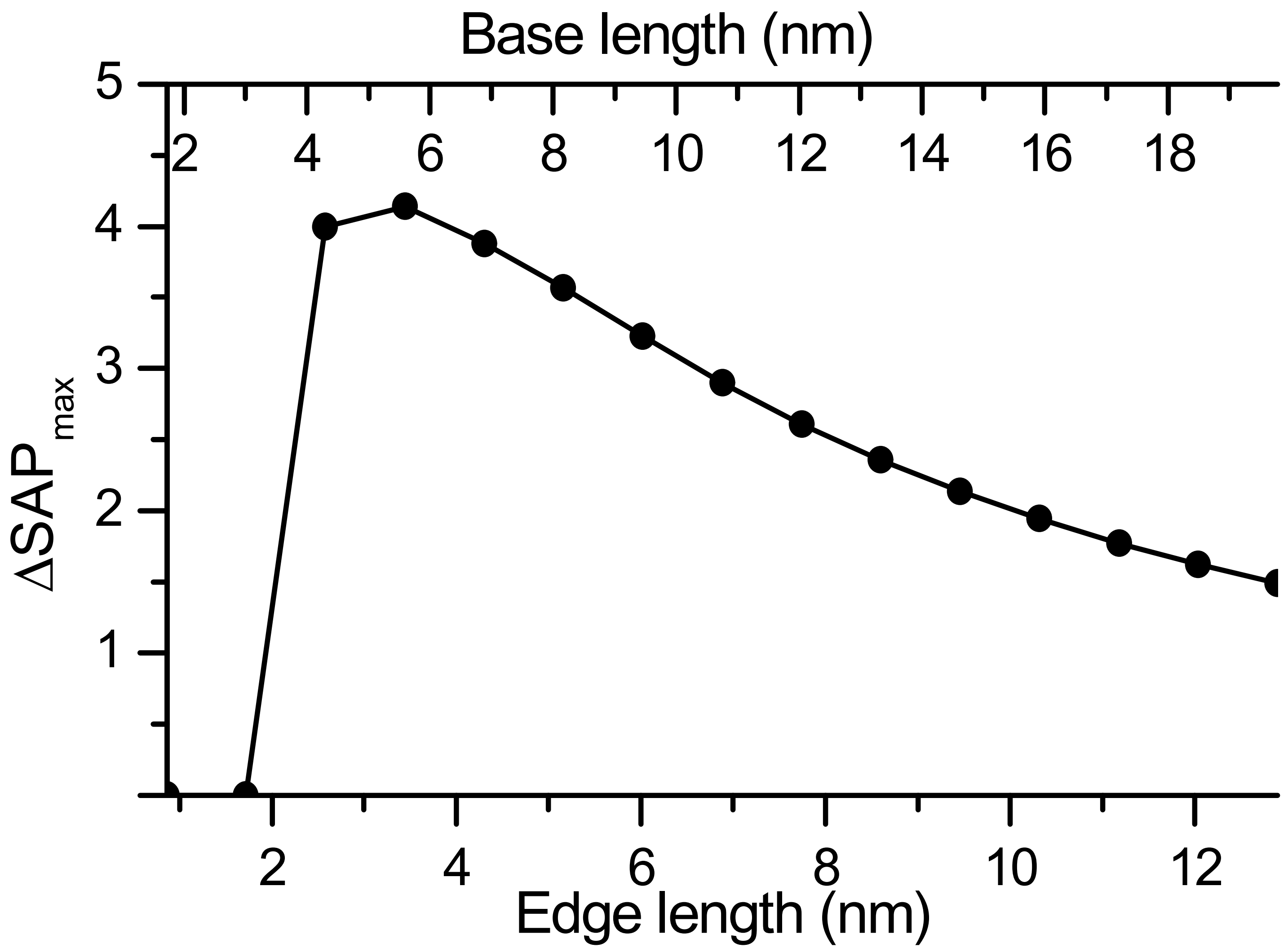

Fraction of surface atoms %
90
80
70
60
50
40
30
1000
2000
3000
4000
5000
Number of atoms
Tetrahedron
BCC cube
Octahedron
FCC cube
Cuboctahedron


N = 4
D=2
D=(N+2)/3


Fraction of surface atoms %
60
56
52
48
44
40
36
750
1500
2250
3000
Number of atoms
5
6
7



Plot showing the changes in the surface atom percentage (SAP) accompanying the growth of four hexagonal branches. The dotted line represents the SAP profile that the seed would have adopted if branching had not taken place.



:Plot showing changes in the maximum difference in the surface atom percentage (ΔSAPmax) between the tetrahedron and the corresponding structures with four hexagonal branches grown from a CdSe seed.

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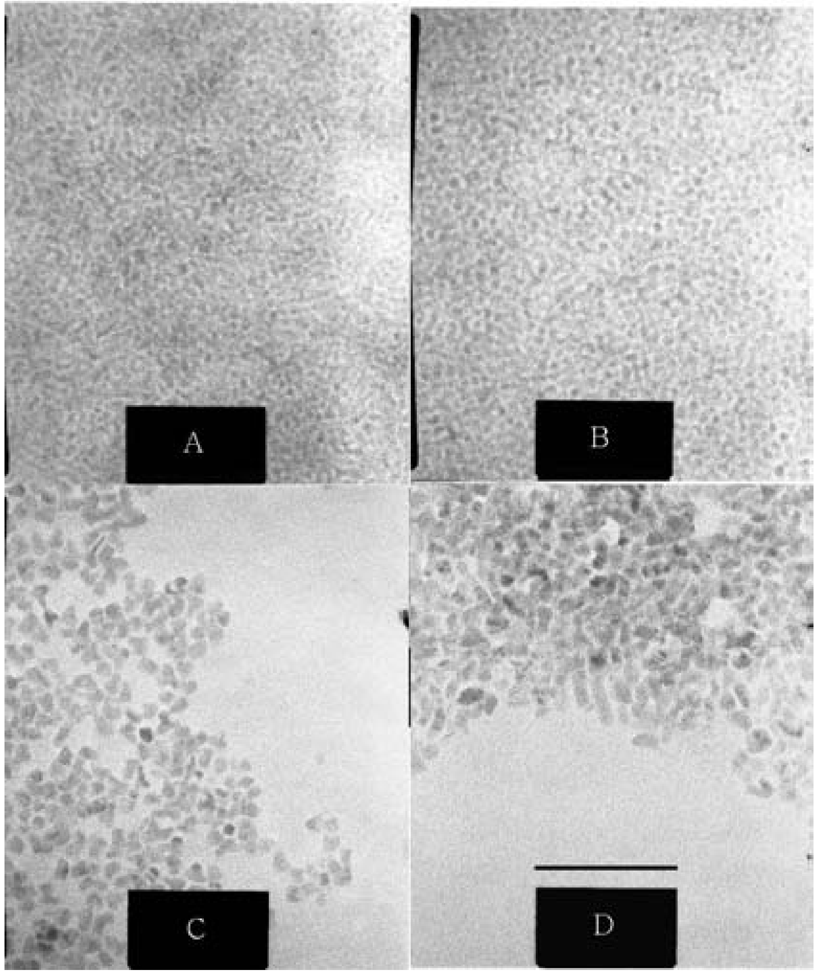
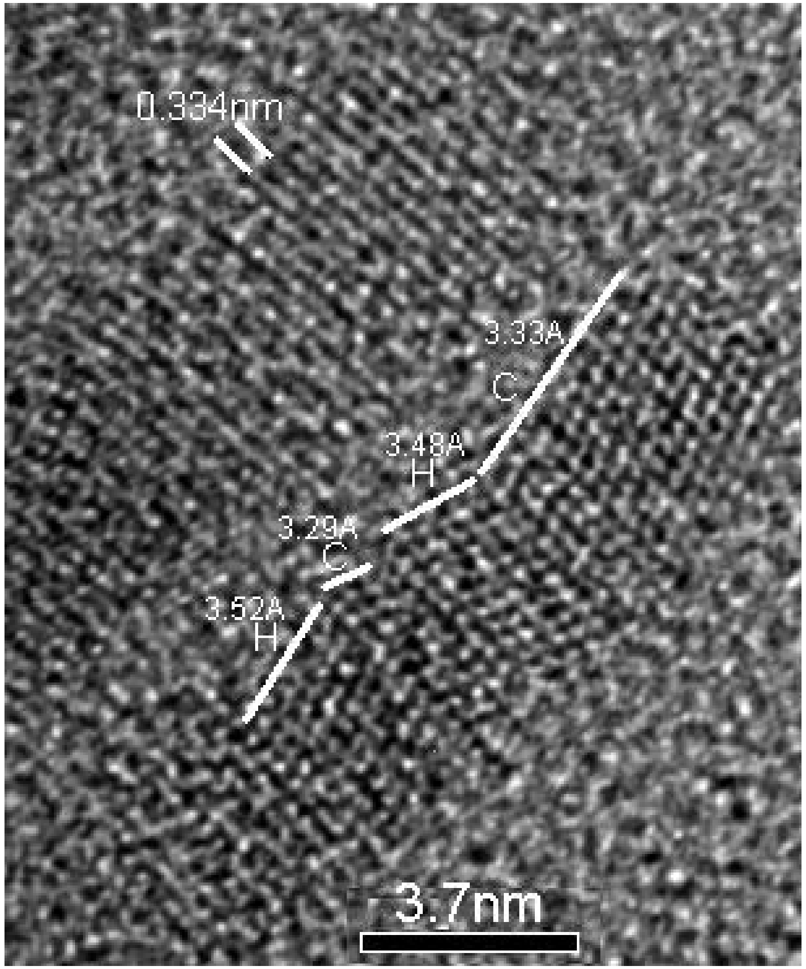
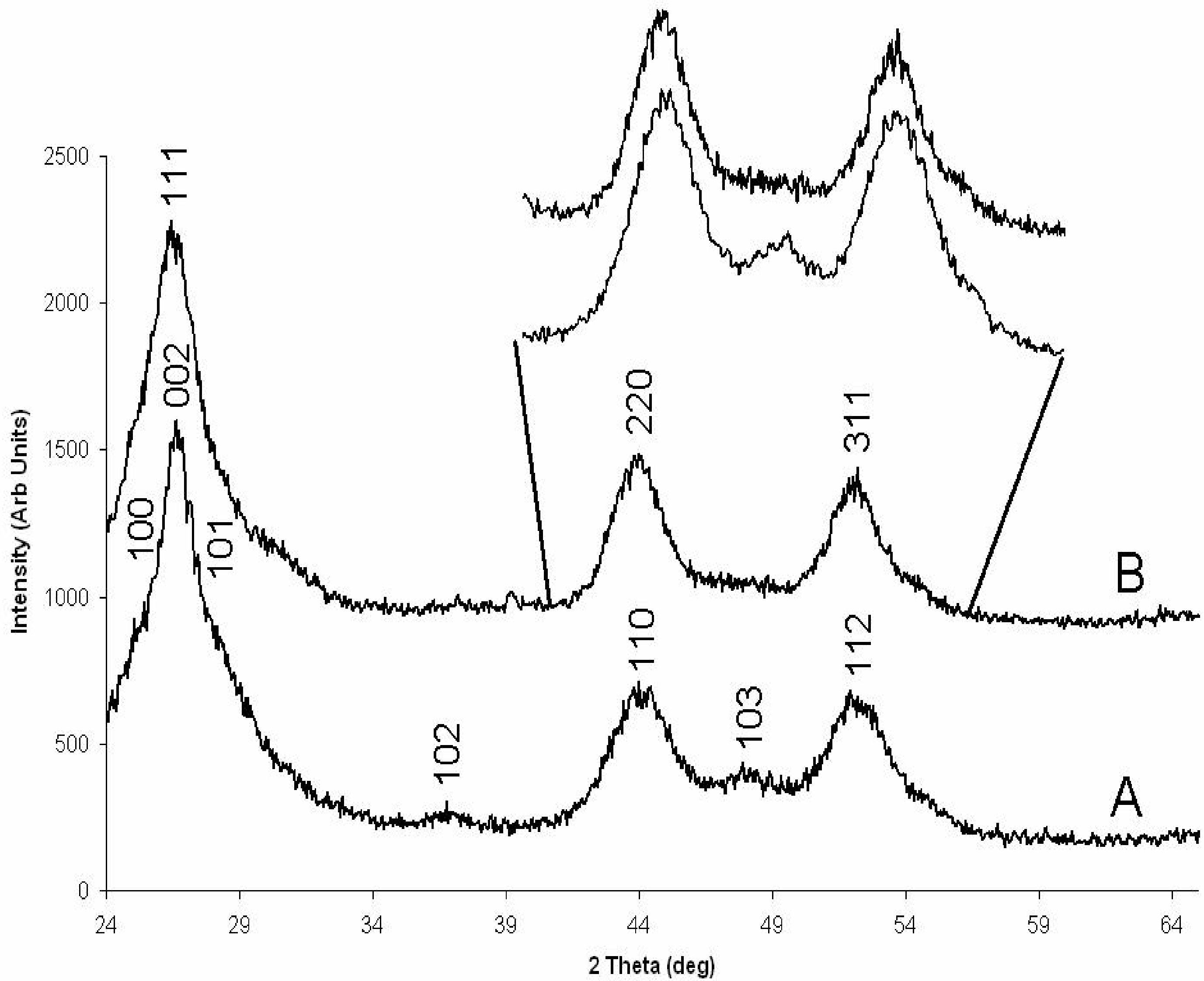




Chem. Comm. 2005 2817-2819

Sample	mmol $CdAc_2$	Final Molarity	λ_{em} (nm)	% rods	Diam** (nm) (std)
A	1.3	0.011	465	<5	3.5 (0.7)
B	2.2	0.018	489	<5	4.0 (1)
C	21.7	0.181	499	~15	6.5 (1)
D	31.6*	0.198	504	72	7.0 (1)



Powder XRD showing hexagonal phase of A and the cubic phase of B. Inset at higher resolution.

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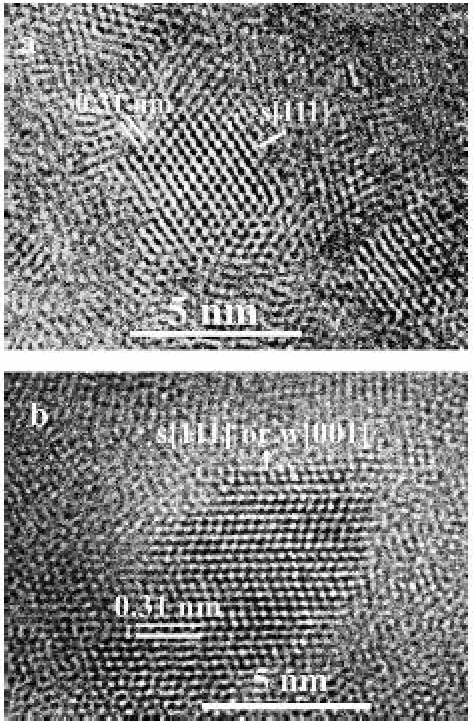
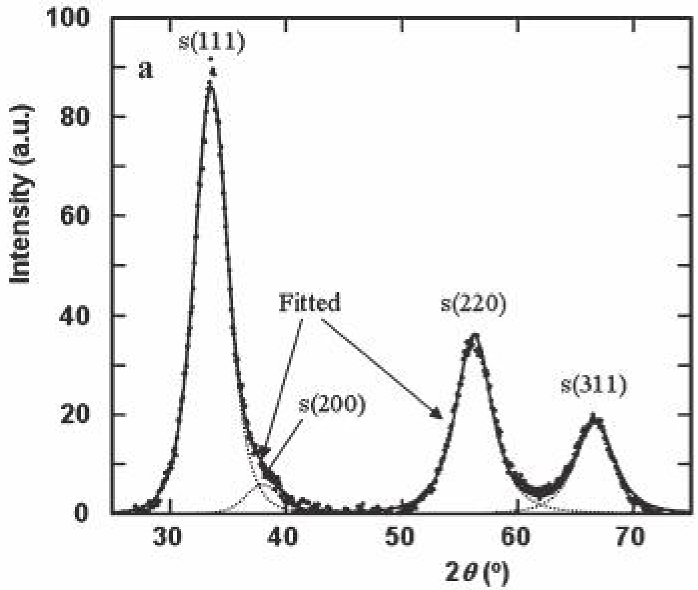
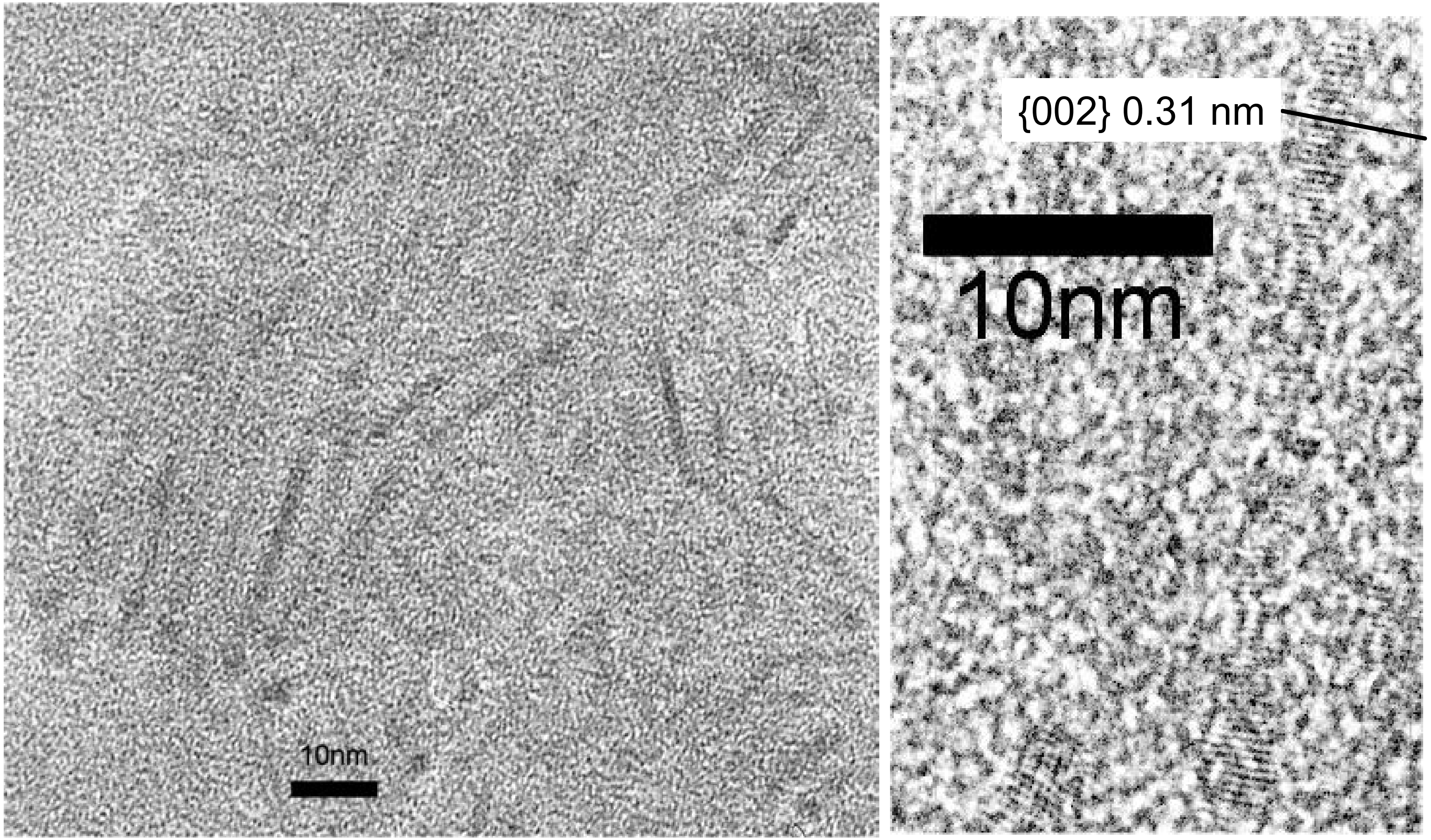




Kinetically controlled formation of a novel nanoparticulate ZnS with mixed cubic and hexagonal stacking†

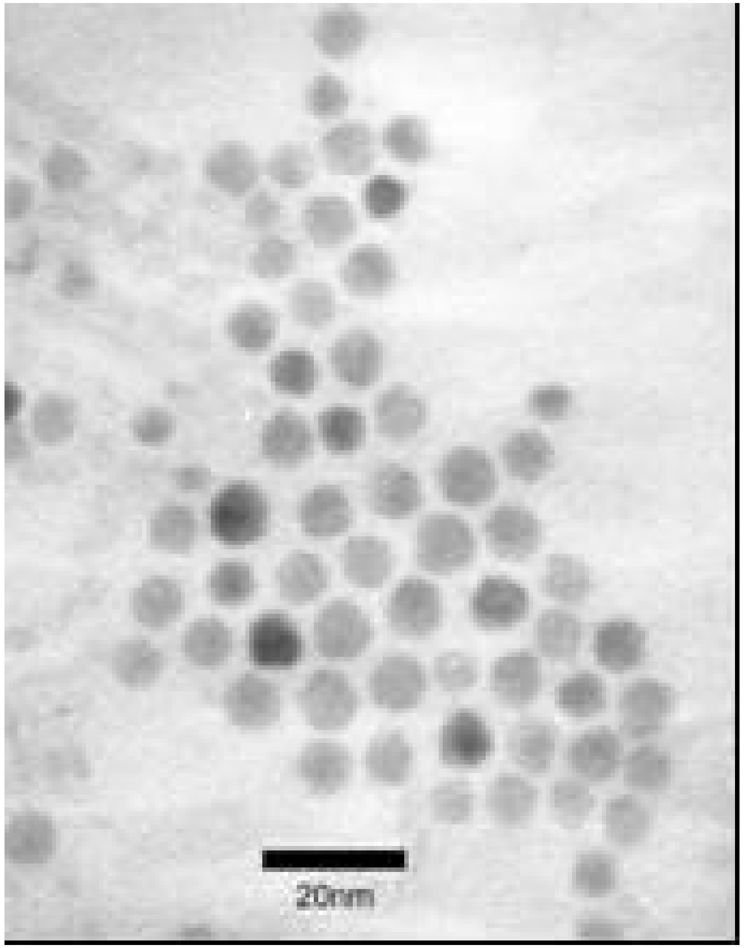
Hengzhong Zhang,*[a] Bin Chen,[a] Benjamin Gilbert[b] and Jillian F. Banfield[ab]

J. Mater. Chem., 2006, 16, 249–254 | 249

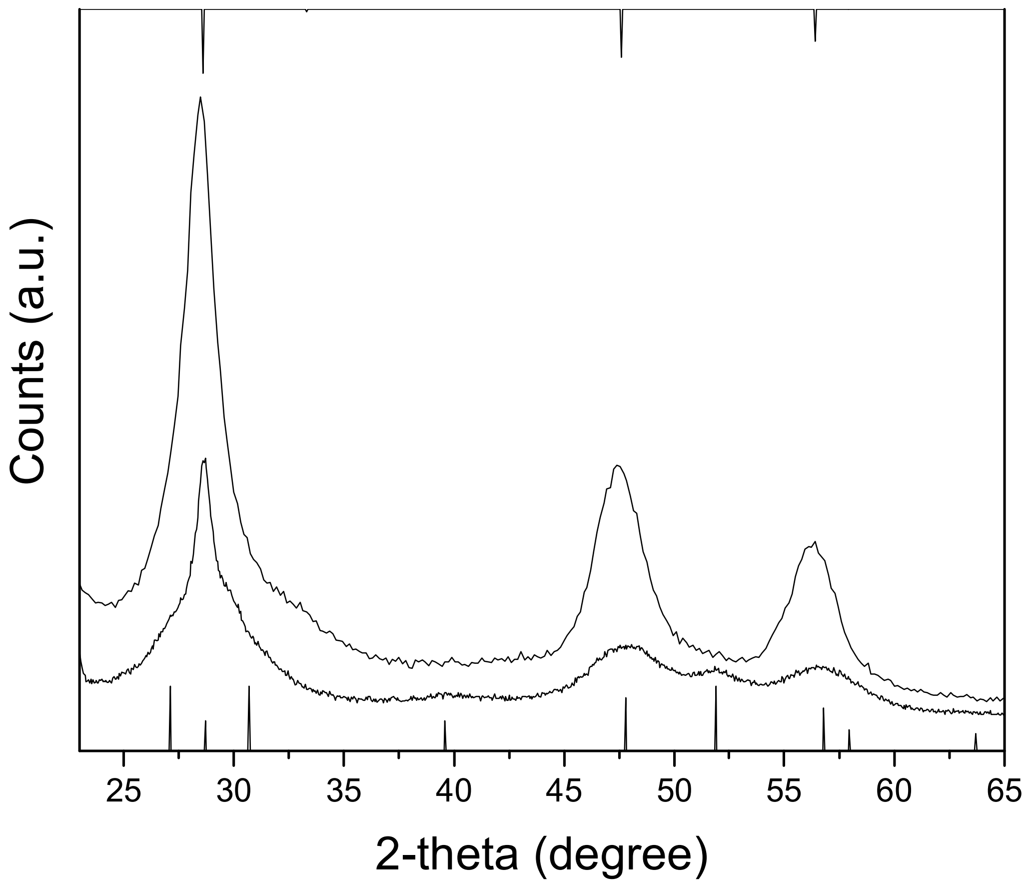


The low temperature (140 ºC) growth of hexagonal ZnS nanorods in a mixture of hexadecylamine and octylamine from sulfur and zinc acetate

J. Experimental Nanoscience 2006, in press.



ZnS as before but at 180 º C



XRPD of ZnS (a) rods grown at 140^{o}C and (b)dots grown at 180^{o}C. Also shown are the bulk indices for hexagonal (below) and cubic (top).

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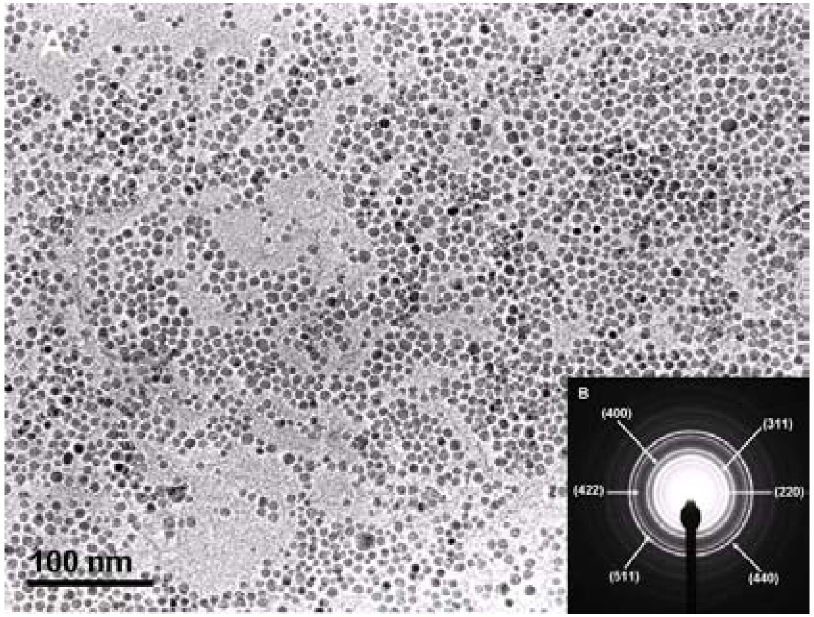
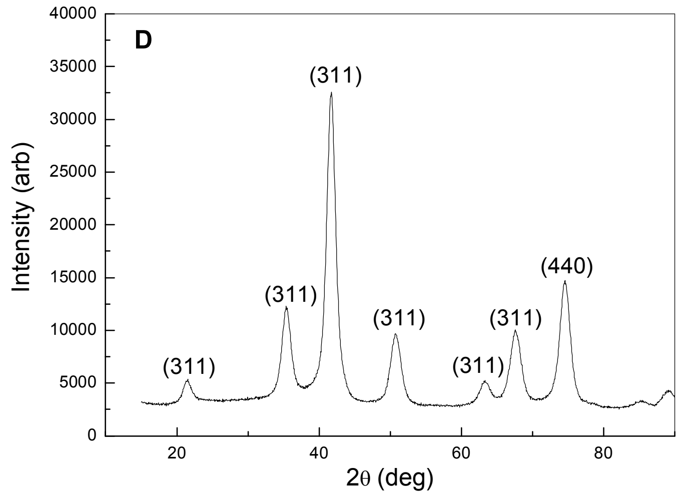
Some Oxides…………..

Precursor	Solvent	Reaction T_m	Time (hour)	Product and Size
$Fe(acac)_3$	HDA	250 °C	2	Fe_3O_4 10.5 nm
$Mn(acac)_2$	HDA	270 °C	1	MnO 17.5 nm
$Co(acac)_2$	HDA	240 °C	3.5	CoO 20.0 nm
$Ni(acac)_2$	HDA+TOPO (2:1 w/w)	220 °C	2	NiO 14.0 nm
$Cr(acac)_3$	HDA	340 °C	3	No Reaction

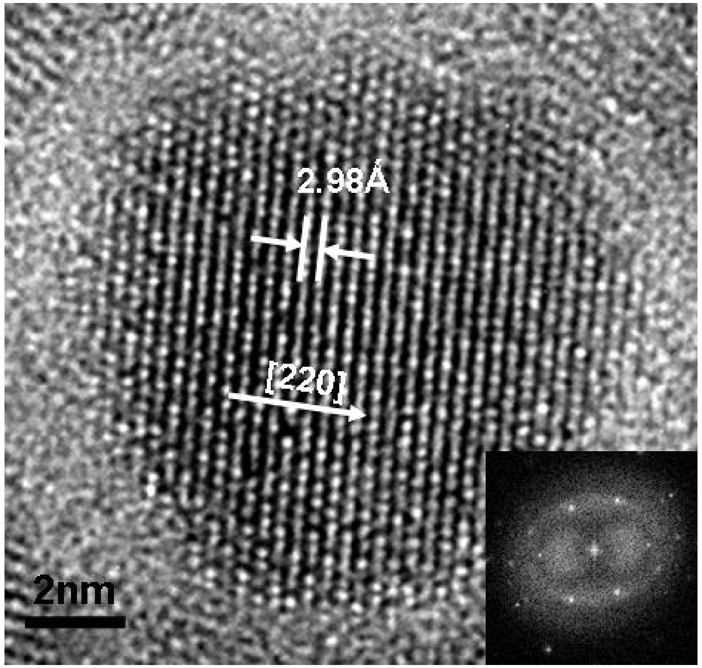
Generic routes to metal oxides

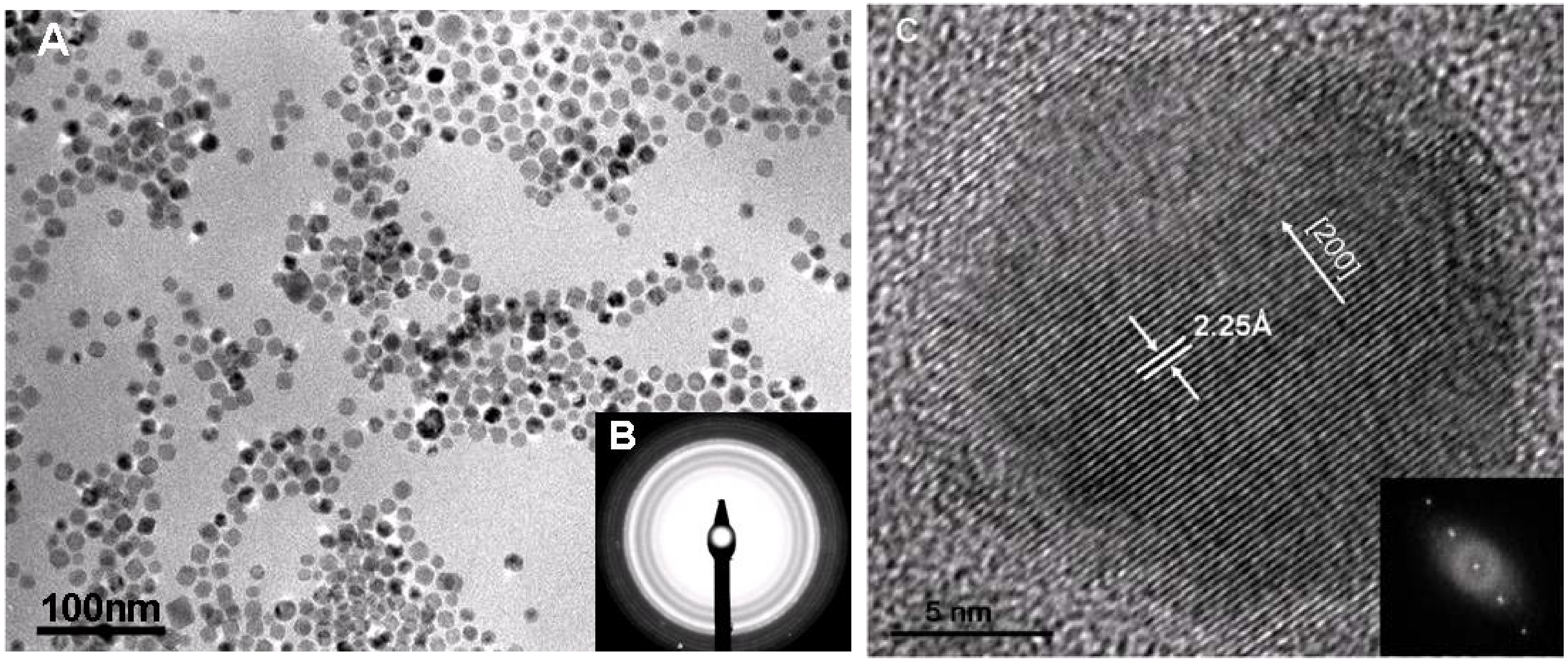
J. Mater Chem in press 2006





(A) TEM image, (B) Selected area electron diffraction (SAED) pattern acquired from the corresponding Fe_3O_4 nanoparticles,
(C) HRTEM image of a 10 nm diameter of Fe_3O_4 nanoparticle, (insert) FFT of the HRTEM,
(D) XRD pattern of Fe_3O_4





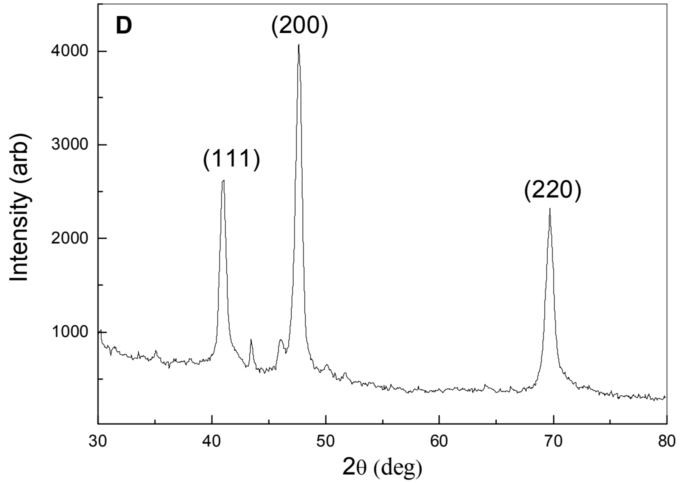
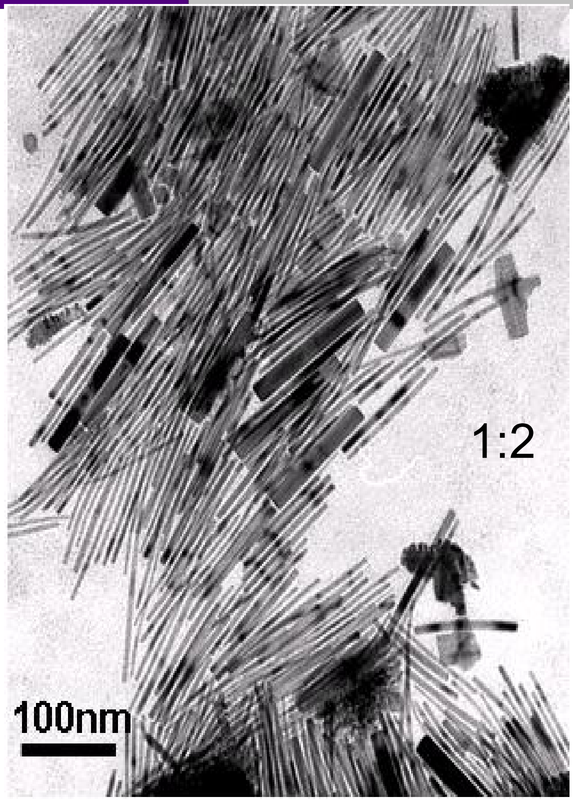


Fig. 3 (A) TEM image, (B) SAED pattern acquired from the corresponding MnO nanoparticles, (C)HRTEM image of a 18 nm diameter of MnO nanoparticle, (insert) FFT of the HRTEM, (D) XRD pattern of MnO

Some Cobalt Phosphide………..



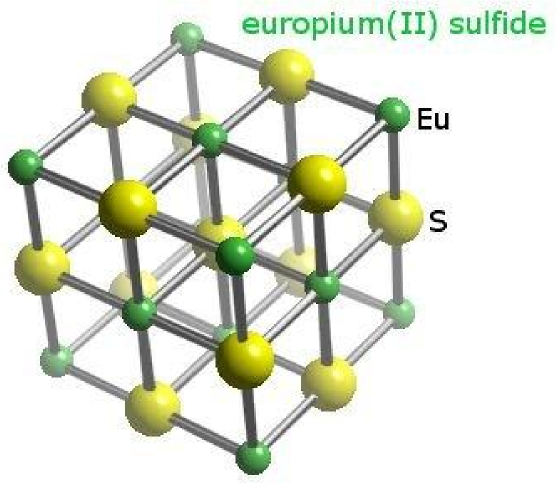
TEM images of CoP nanowires prepared with different weight ratios of HDA to TOPO:

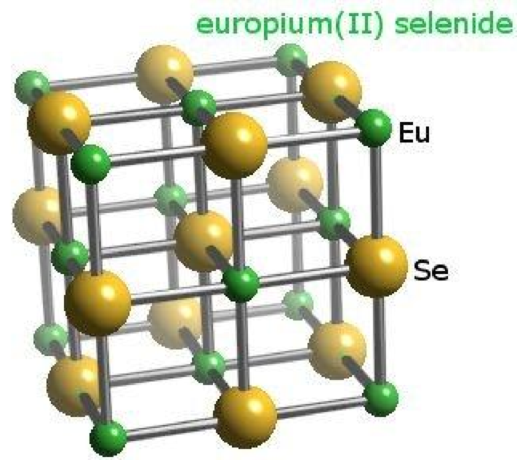
However, the reaction of [Co(acac)$_2$]with TOPO as the only solvent did not give any wires of CoP even at 360 ^oC over three hours. Similar experiment in HDA alone gave only CoO nanoparticles.

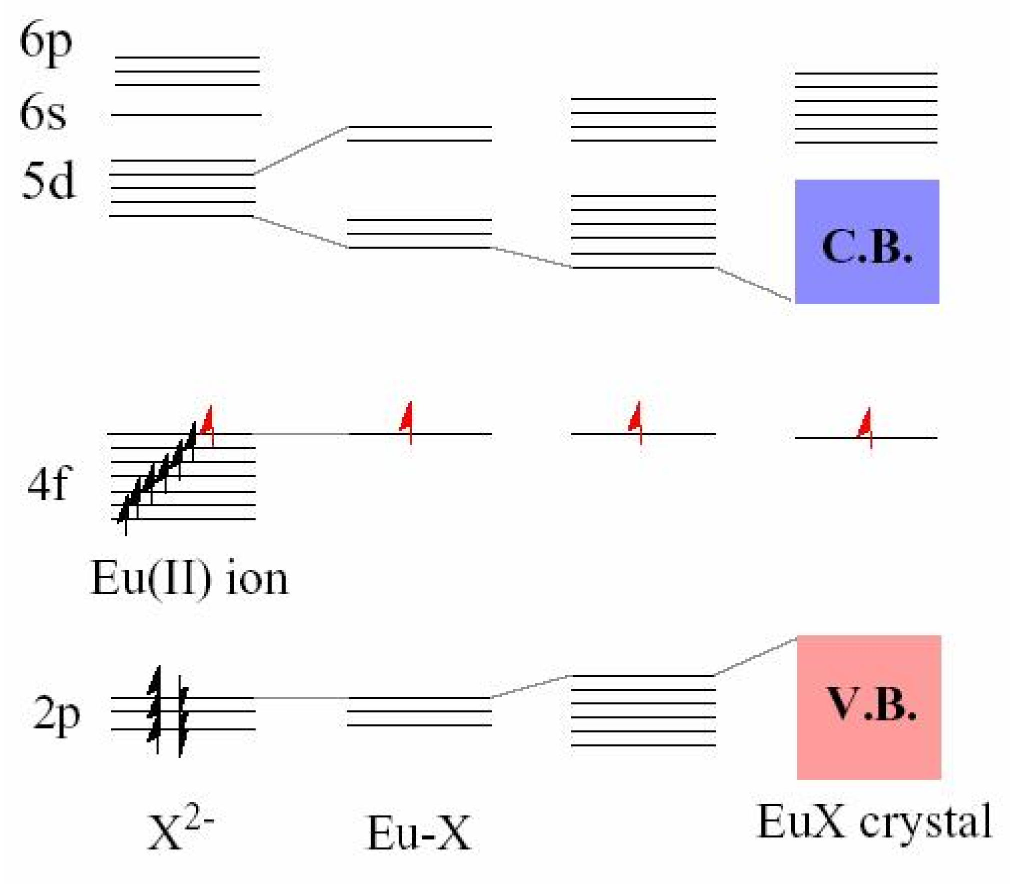
J. Amer. Chem. Soc., 2005, 127, 16020-16021

EuS and EuSe…………..

Eu(II) chalcogenide nanocrystals





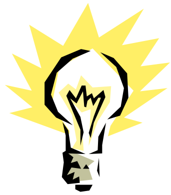


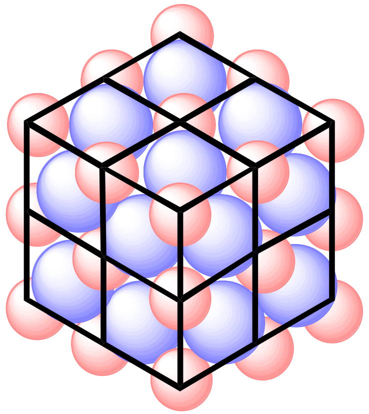
NaCl type structures

Preparation of EuS using photo-irradiation

$[Eu(dtc)_4]^-$

Photo-reduction

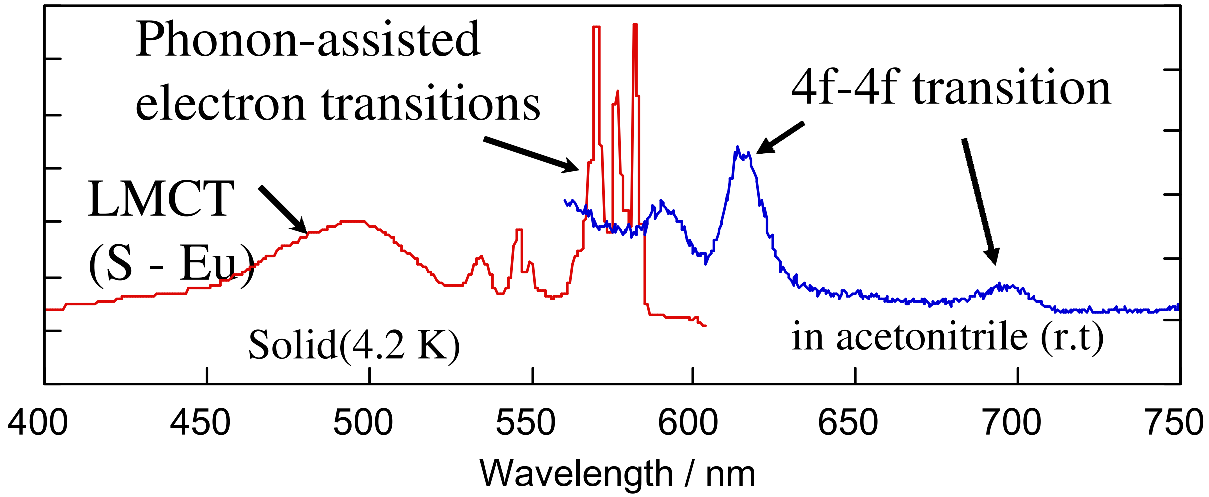




Eu(III) complex

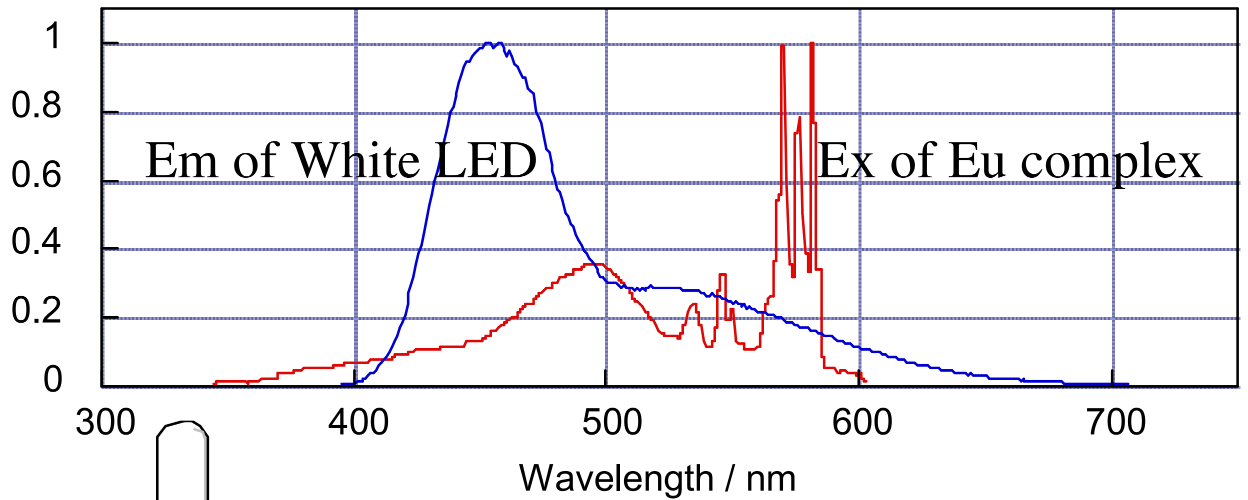
Eu(II)S

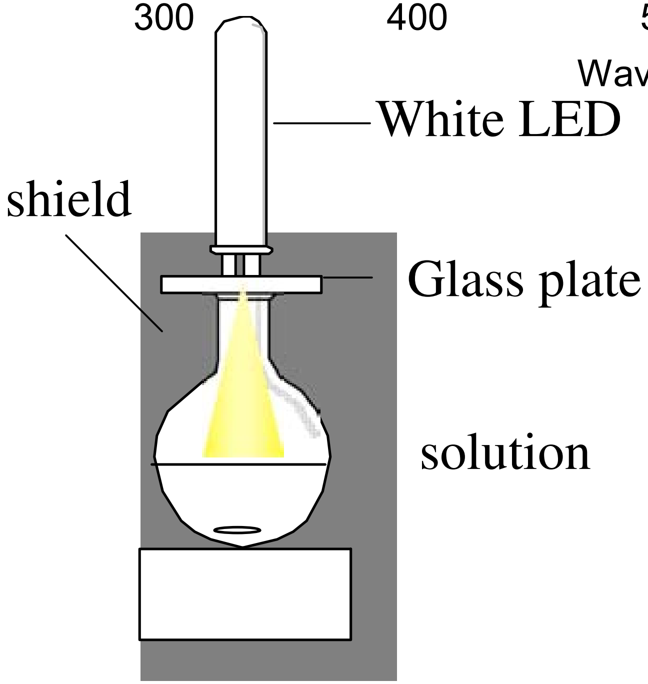
Energy levels of EuS-complex



Excitation spectrum from ‘T. Yamase et al, *Chem. Lett.*, 907 (1997)

White LED for excitation light source

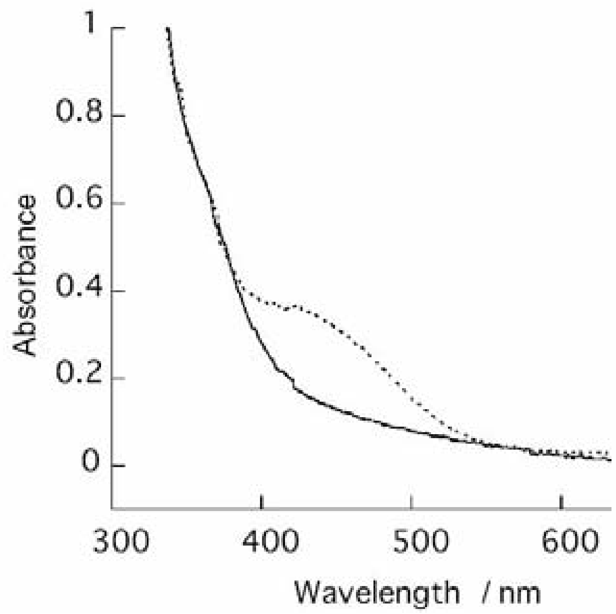




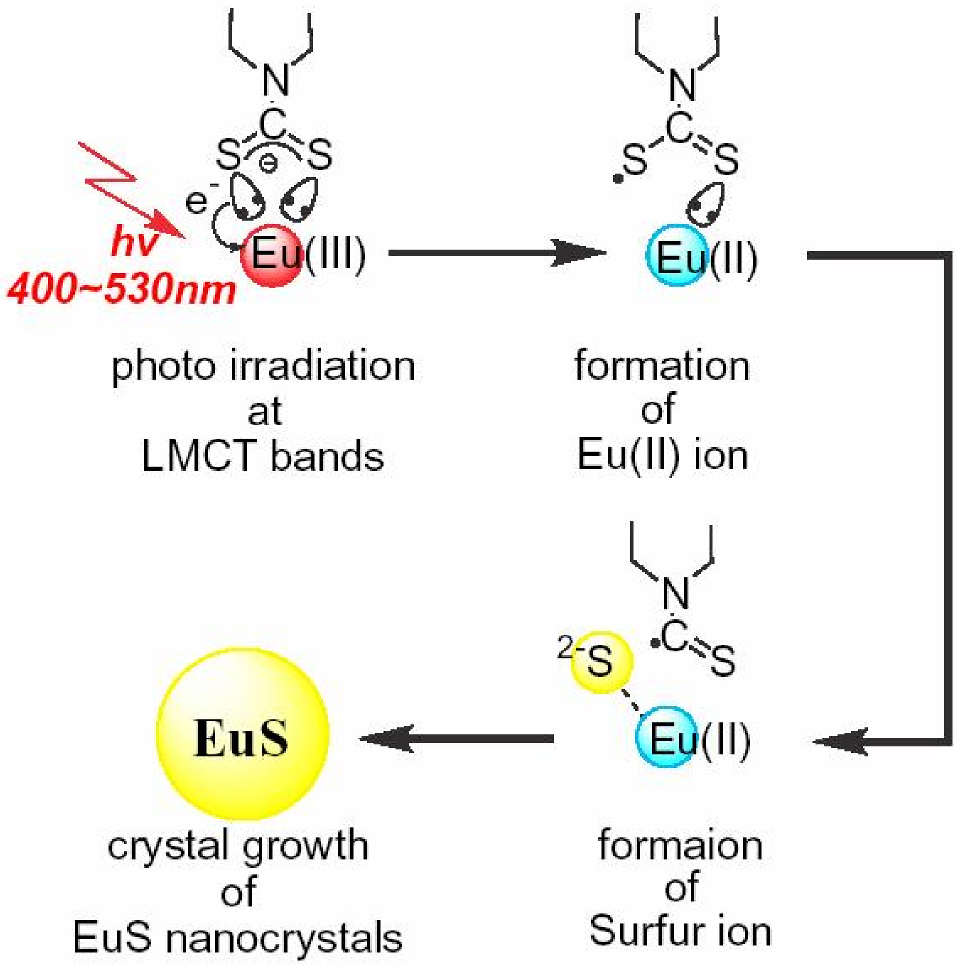
$Na[Eu(S_2CEt_2)_4]\cdot 5H_2O$
in acetonitrile (1 mM)
Absorbance ~ 0.4 / cm (440 nm)
for 3 days

EuS nanoparticles from single-source precursor

a

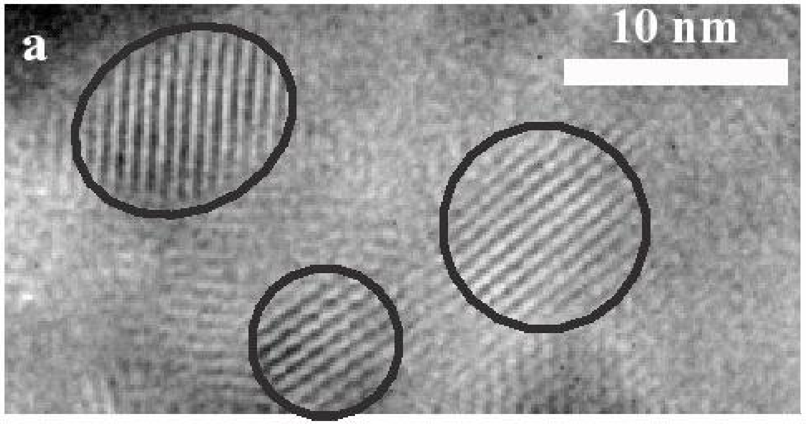


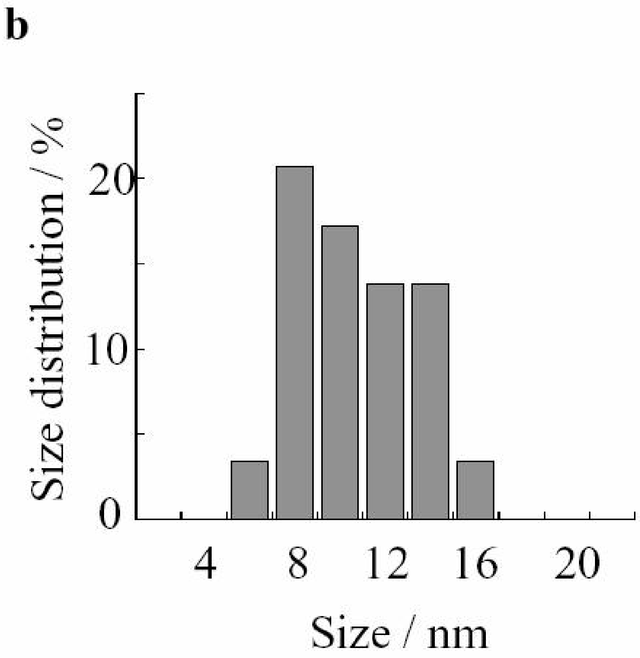
b

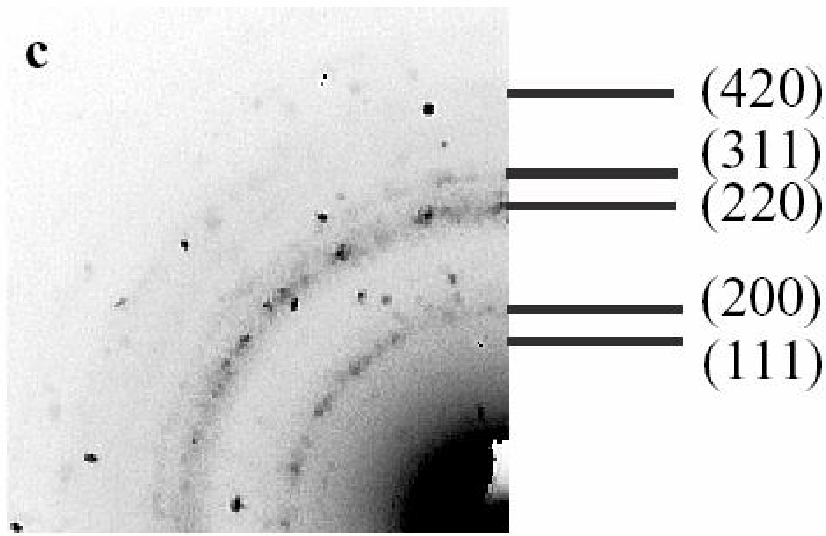


Y. Hasegawa, M. Afzaal, P. O'Brien, Y. Wada, S. Yanagida, Chem. Commm., 2005 242-244

TEM observations







Sulfides by CVD...........

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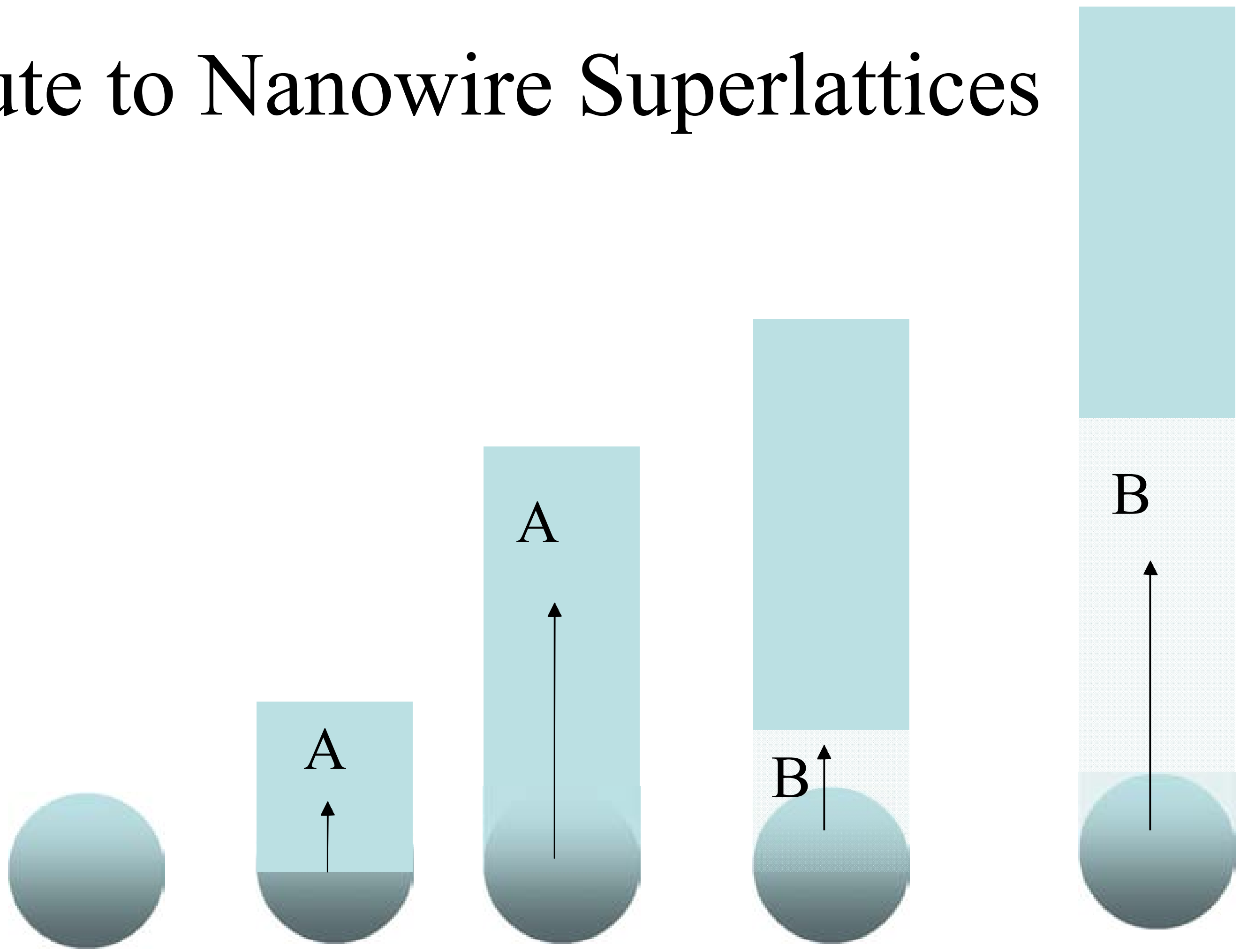
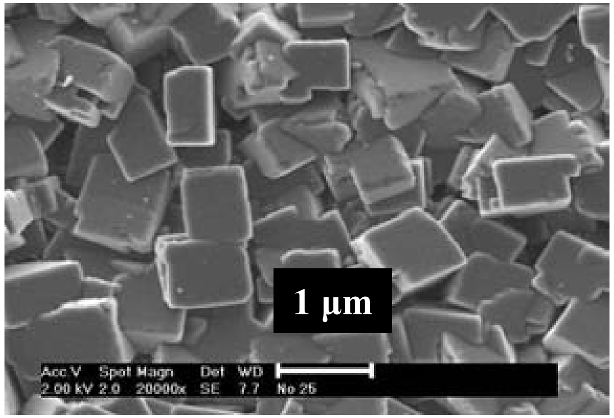
A Route to Nanowire Superlattices



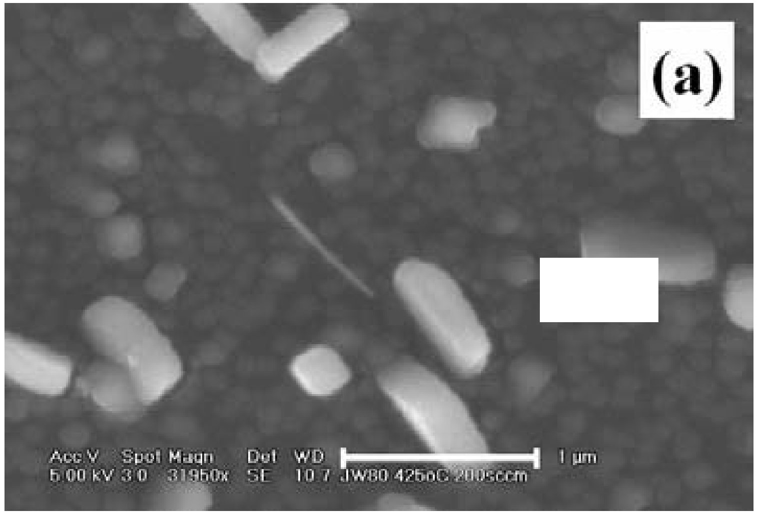
Growth of nanowire superlattice structures for nanoscale photonics and electronics: M.S.Gudiksen, L.J.Lauhon, J. Wang, D.C. Smith and C.F.Lieber, Nature 415, 2002, 617-620

- Our previous studies on the growth of PbS thin films by AA and LP-MOCVD on glass and Si substrates, have lead to films comprising large (*ca.* 1 μm) cubic crystallites (Figure 2).



PbS films deposited on glass.

- Our present study, using Si substrates seeded with Au nanoclusters, *via* a custom made AP-MOCVD kit, has yielded films of radically different morphology
- (Figure 3).



SEM images of PbS deposited at
(a) T_{prec} = 325 °C, T_{subs} = 350 °C,

M. Afzaal, K. Ellwood, N. L. Pickett, P.O'Brien, J.Raftery, J.Waters J. Mater. Chem., 2004, 14, 1310

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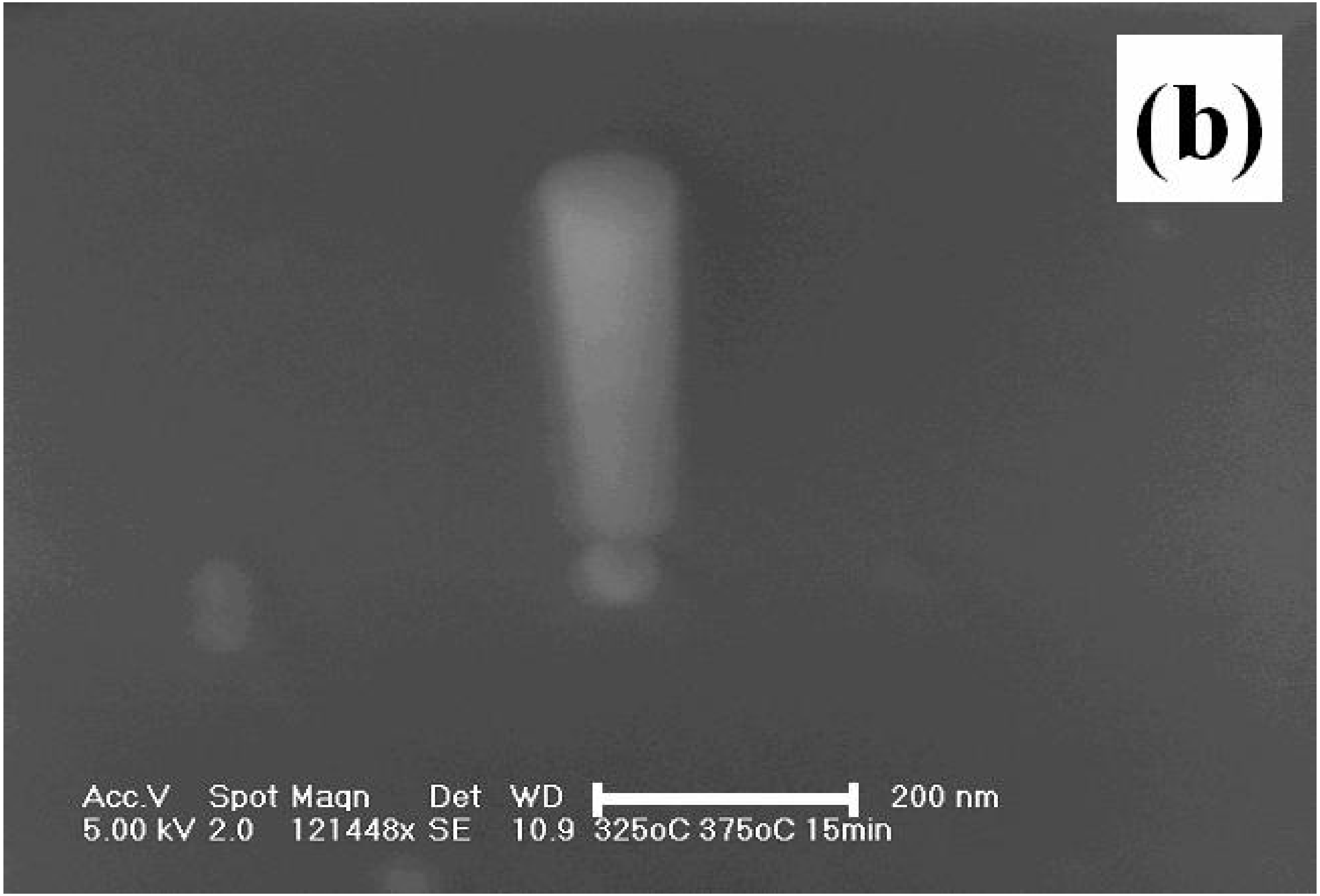
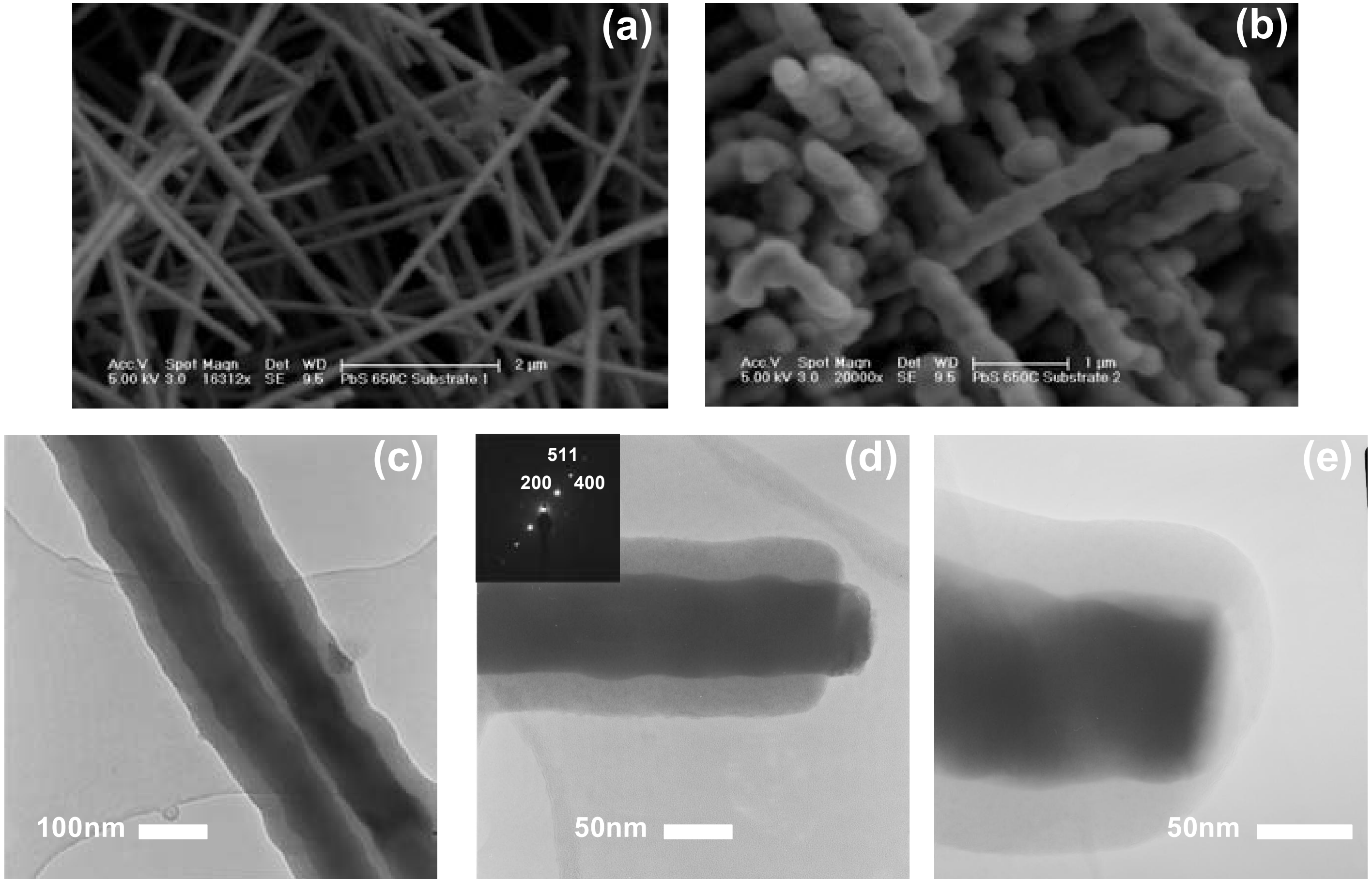


Chemical Route to Punctuation

? 



Silica coated PbS nanowires M. Afzaal and P.O'Brien

Journal of Materials Chemistry 2006 16, 113-115.

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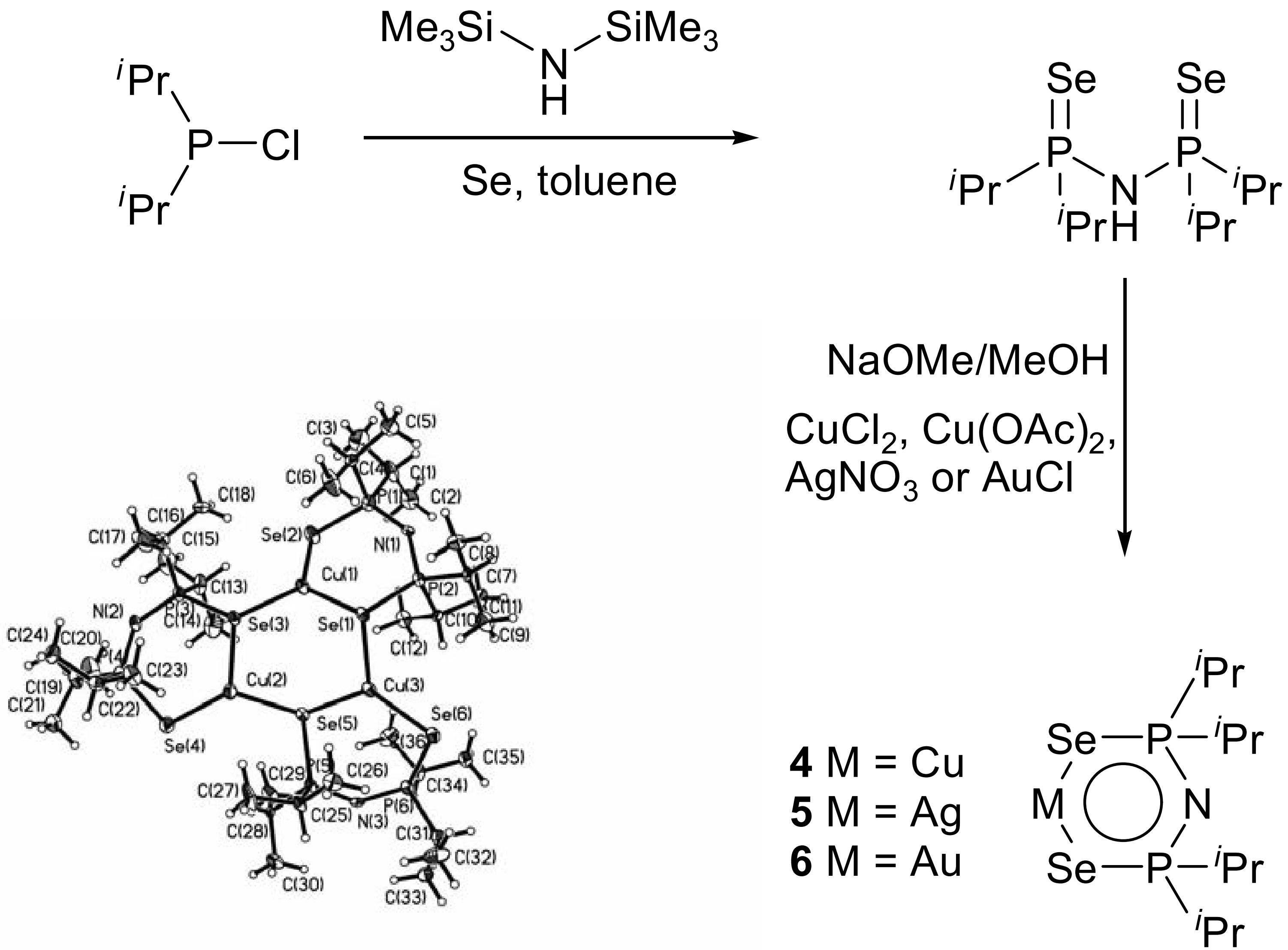
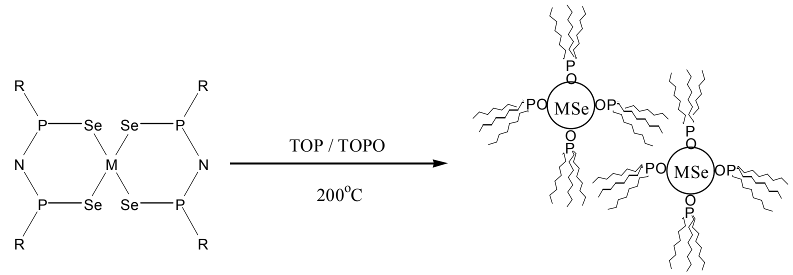
New Ways to Tellurides……..

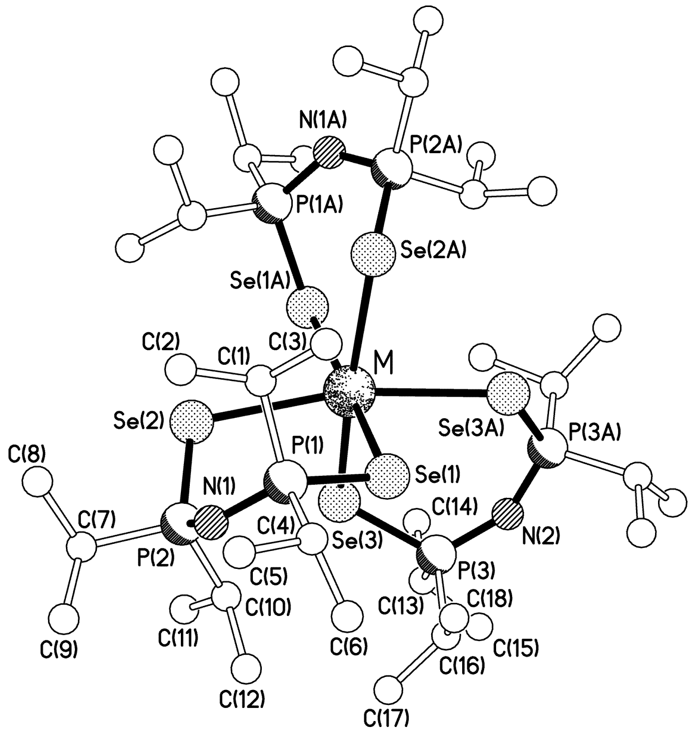


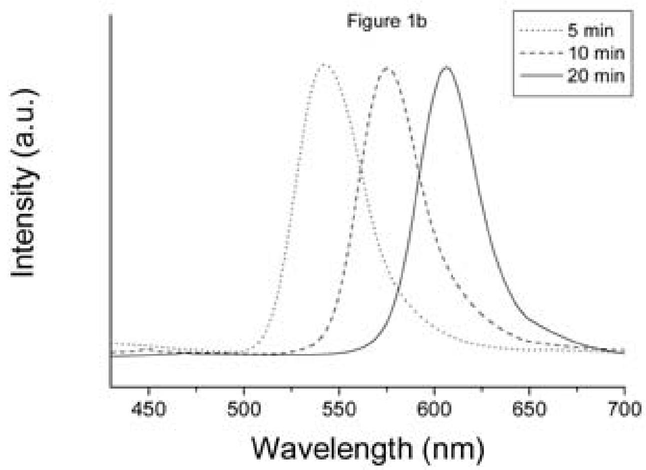
Imino-*bis*(diisopropylphosphine chalcogenide)



where R = ^{i}Pr or Ph and M = Cd, Zn or Hg

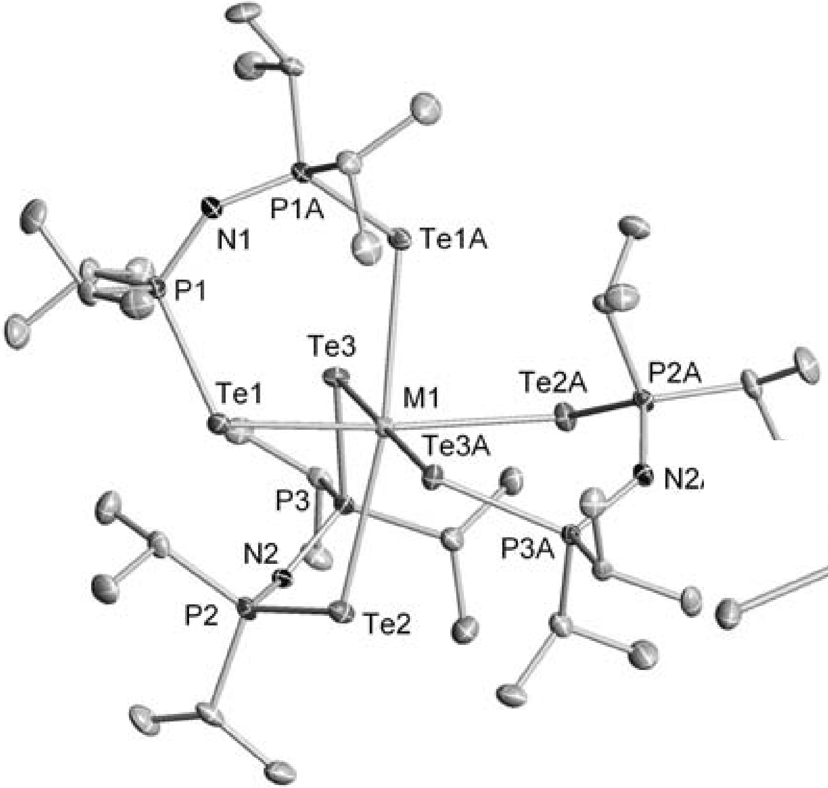
- Efficient synthesis of *"air-stable"* M $[N(SePR_2)_2]_2$ (yields 95-99%).
- Reaction can be scaled up (~25g) without loss to quality/yield.
- *"Dot"* synthesis is convenient and efficient.

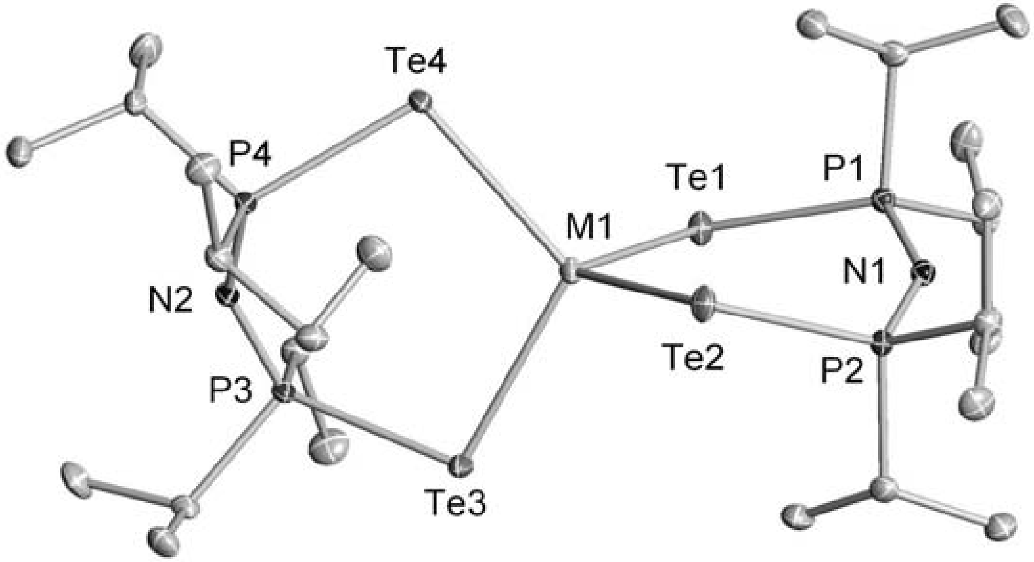




PL of CdSe by Thermolysis of $Cd[N(SeP^{i}Pr_2)_2]_2$

D.J.Crouch, P. O'Brien, M.A.Malik, P.J.Skabara and S.P. Wright, Chem. Commm., 2003 1454.





T. Chivers, DJ. Eisler, JS Ritch, Dalton Trans. 2005, 2675.

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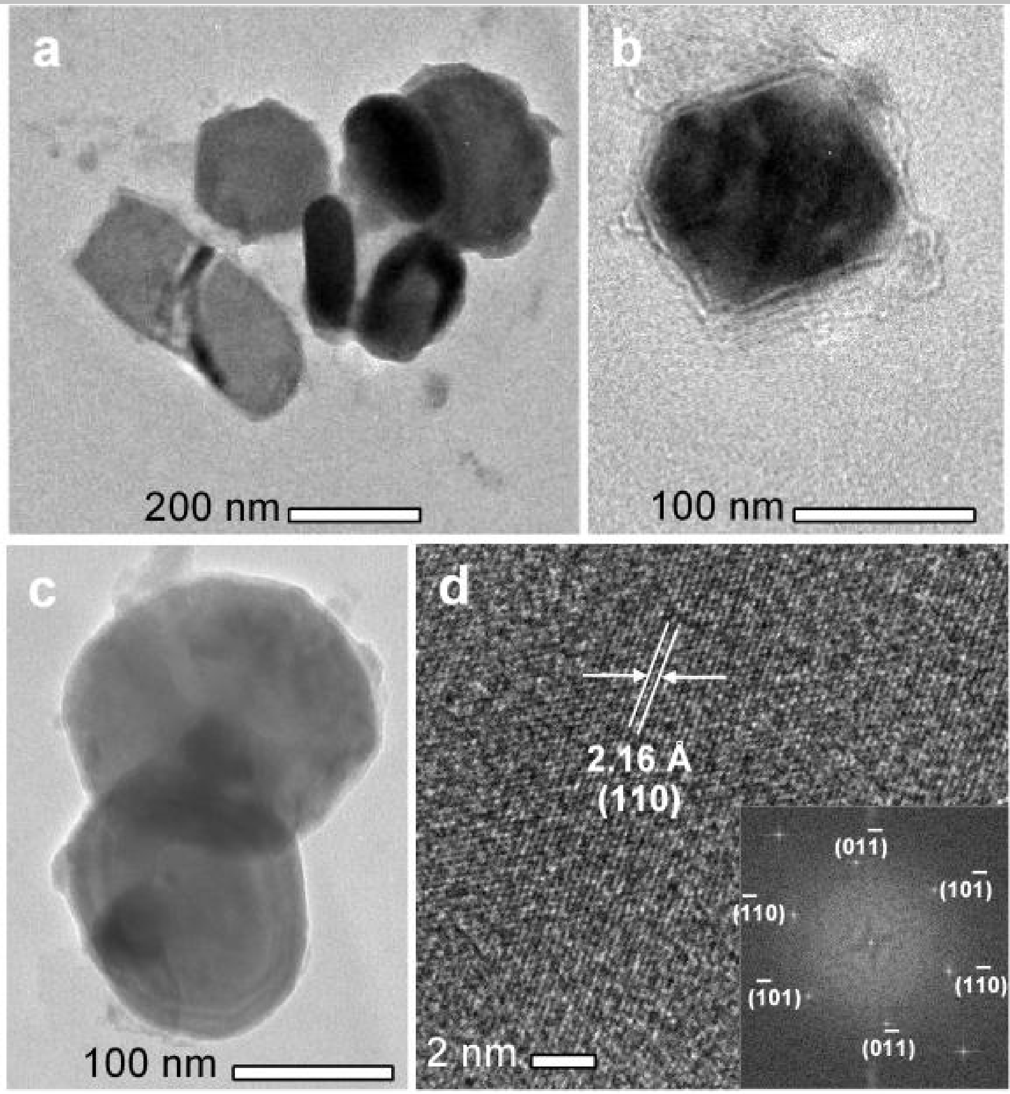
TEM Pictures of Sb_2Te_3



HRTEM and FFT (inset) of the films grown at 475 ºC

J. Amer. Chem.Soc. 2006, 128, 3121-3122

Structure of Talk

- Why now ?
  - Looking at some nanodimensional objects by way of introduction
- Synthetic approaches semiconductors
- How nanoparticles grow and rods and tetrapods
- Other materials a rogues gallery
- What are some of the opportunities
  - The Nanoco Technologies Ltd perspective
- Closing remarks

NANOCO TECHNOLOGIES

***illuminating* the future**

Company overview

- **World leading technology company**
  - Produce fluorescent semiconductor nanoparticles "quantum dot“ and quantum dot products
- **Patented technology solves problem of producing high quality quantum Dots on a large scale**
- **Strategic partnerships with Application Developers**
  - **Tailored solutions to incorporate quantum dots into commercial applications**
- **Quantum Dots are a “platform technology” with many applications in different industry sectors**
- **Developed a range of quantum dots acceptable for commercial use**
- **Nanotechnology Spin-out company from University of Manchester, UK**

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The University of Manchester

A True Platform Technology

What are Quantum Dots?

- Semiconductor material 100,000 x smaller than the width of a human hair
- Size gives unique electronic and optical properties
- Platform technology with many applications across different industry sectors

Why use them?

- Replacement for luminescent dyes and inorganic materials
- Better optical and electronic efficiencies
  - More stable
  - More versatile
- True platform technology which can be utilized in a range of applications across different industries

Nanoco Solves “Scale up” Problem

The Problem

The existing quantum dot ‘manufacturers’ processes are

- Complex
  - Hazardous and used banned substances
- Costly
- Low manufacturing yield
  - No-one can produce a 1g batch

Without stable, cost effective supply of larger quantities of quality QD, developers are unable to bring there applications to market

The Solution

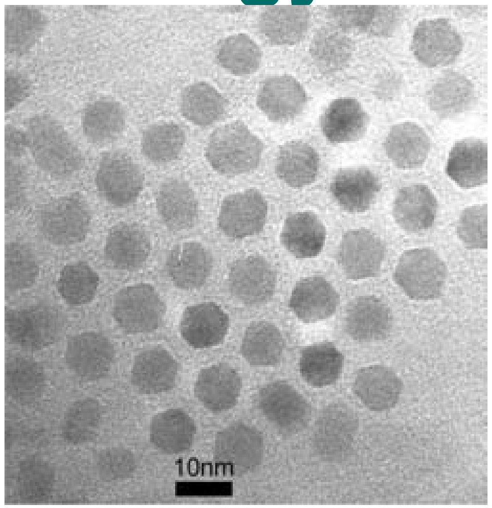
Nanoco’s patented technology can

- Using a ‘simple’ and controlled process
- At a low cost
- Now regularly produce r+d batches of 100g

Nanoco also has world leading patent technology to unlock the market

Nanoco's Technology

High resolution electron microscope
Image of single QD (5nm across)

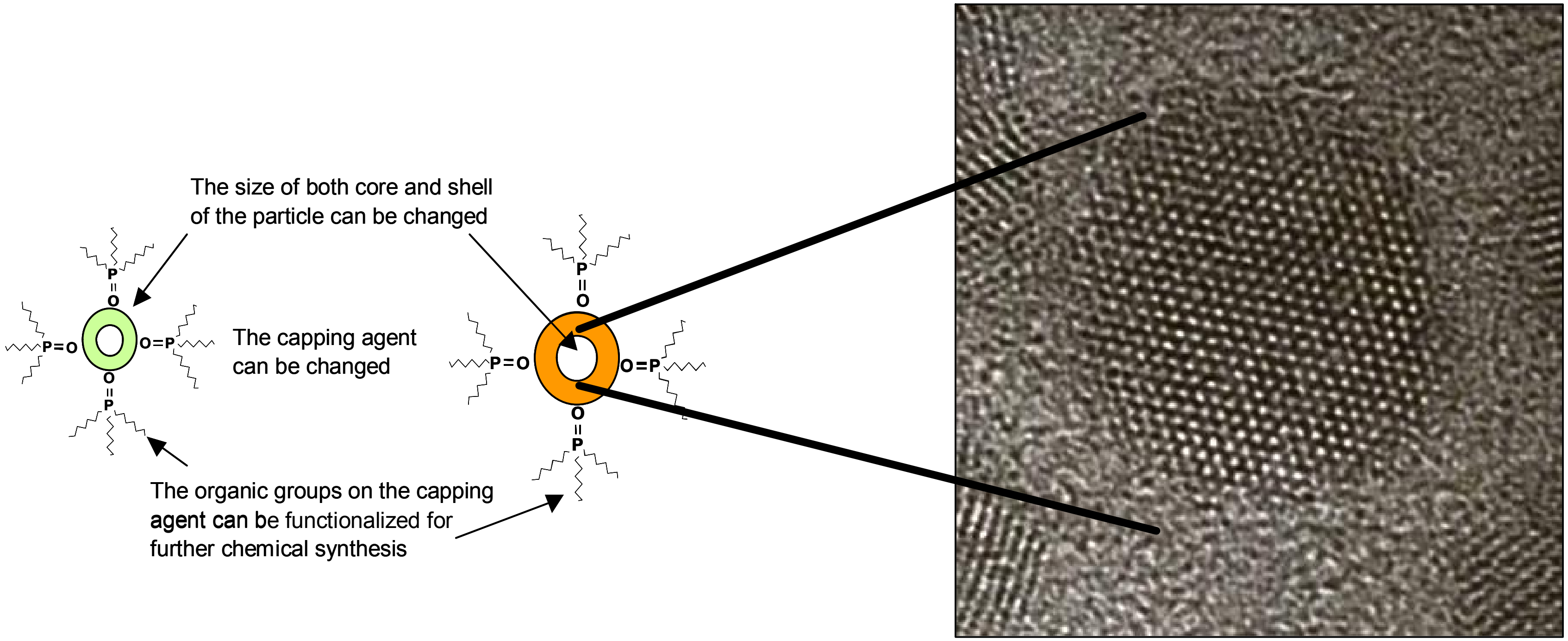


Electron microscope image showing QD
In very ordered patern

Dilute solution QD excited by UV light

30 grams of 560nm QD. No other company in the world can produce this quantity. Market value in today's bio applications greater than $10Million. Competitors can only produce 100 milligrams, 300X less material per batch. Nanoco will soon be producing 1 kilo batches

What are Quantum Dots?



High-resolution transmission electron microscopy image showing the lattice plans of a nano-crystalline Quantum Dot, measuring 5nm across (80,000 times smaller than the width of a human hair)

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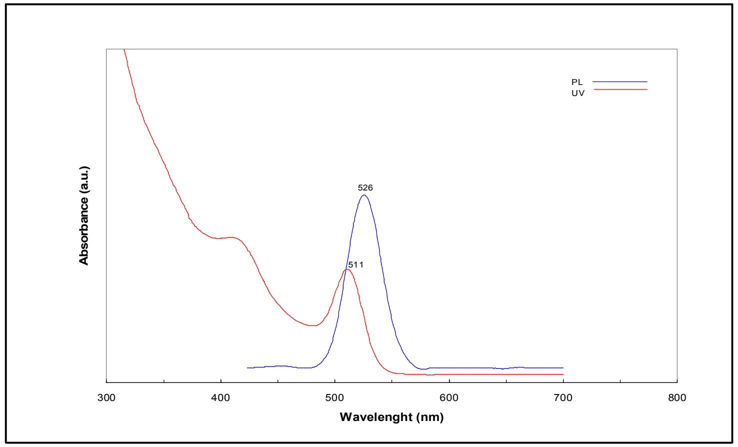
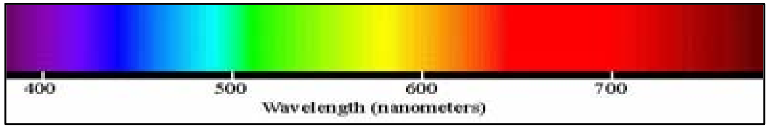
What are Quantum Dots?



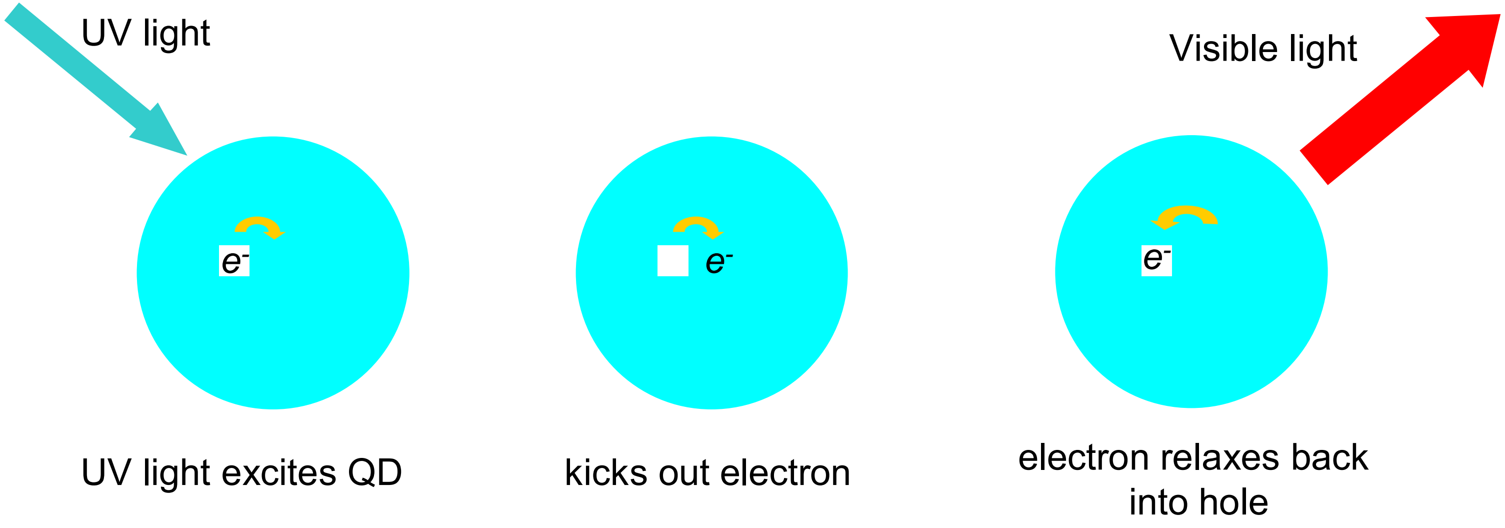


- **Quantum dots absorb light over a wide wavelength range but have narrow emission spectra.**

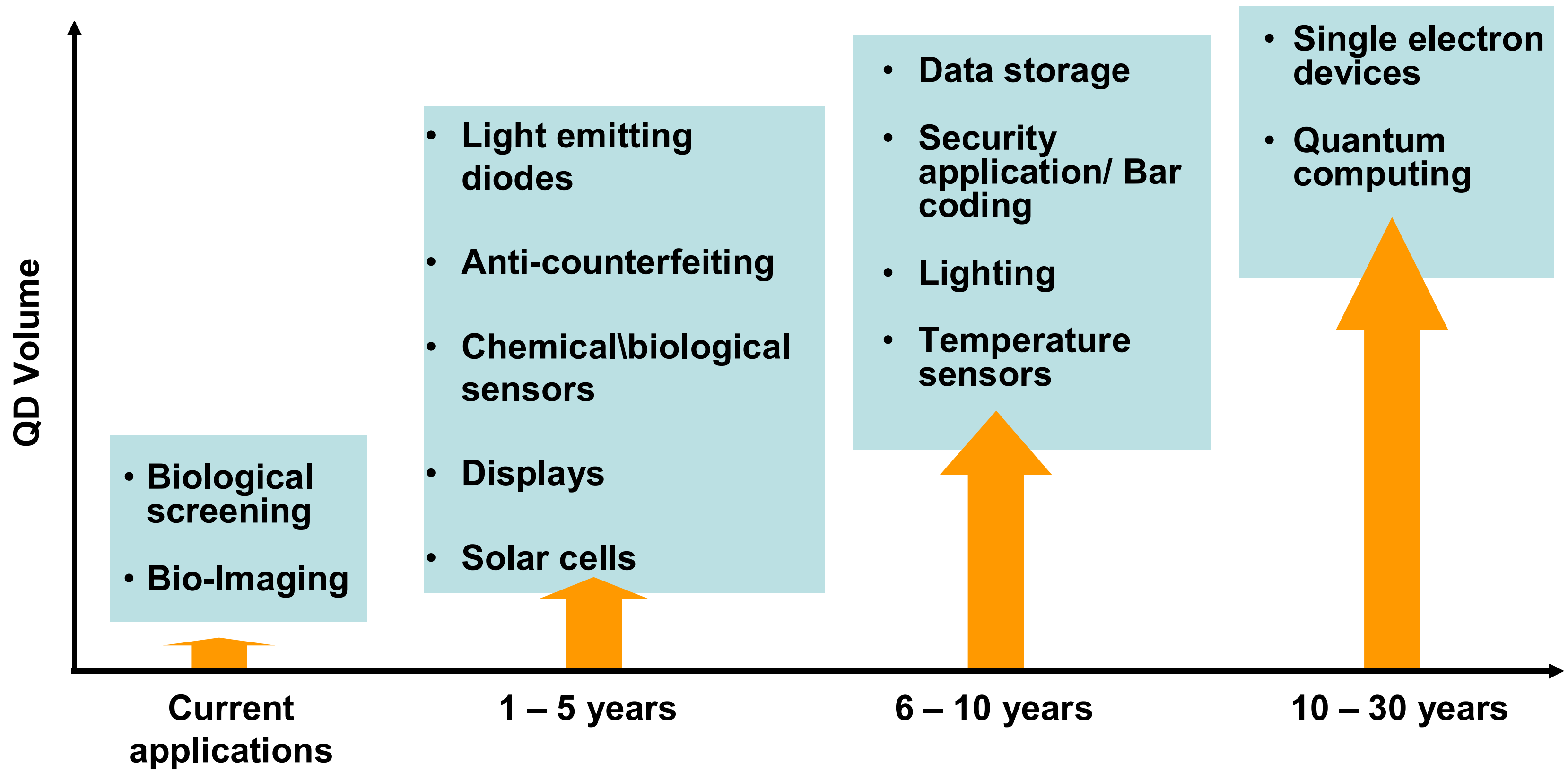
- **The solutions, all contain the same semiconductor material (CdSe) but are different colours because unlike bulk CdSe, when below a certain size limit, we can control the electrical properties of the particles, by simply changing their size.**

How Quantum Dots Work

- UV light excites QD and kicks out electron creating electron and a vacant hole
- As electron relaxes back into the hole a photon is emitted (visible light)
- Size quantization effect – wavelength emitted depends on physical size of the quantum dot



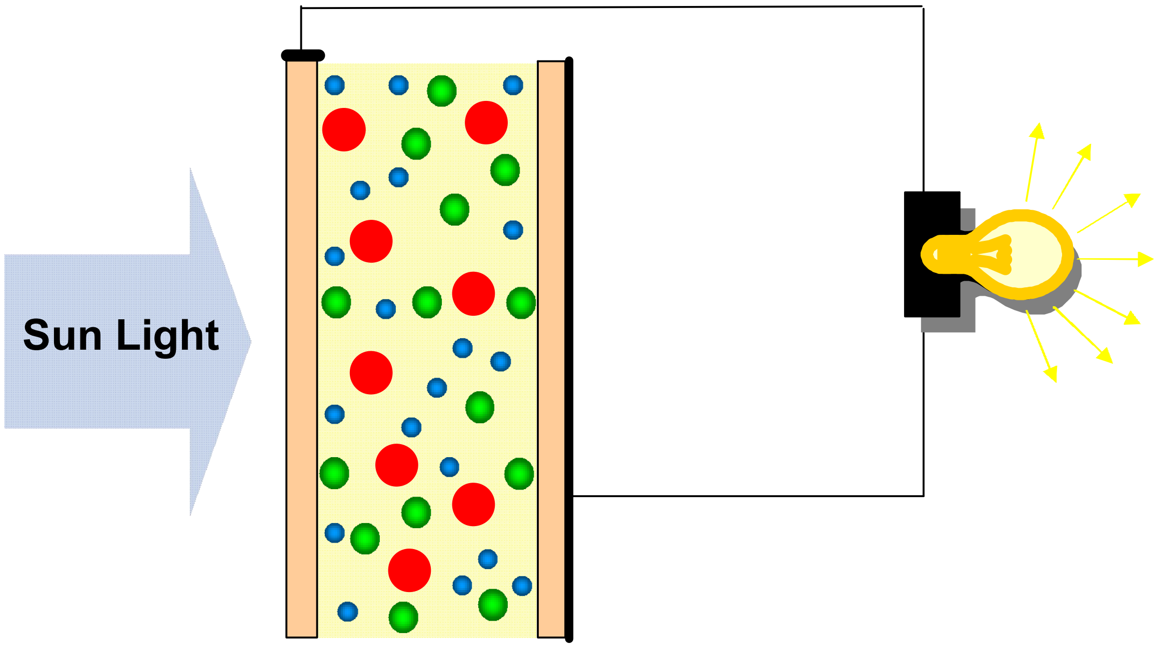
Quantum Dot Applications



Nanoco's technology is allowing the QD market to grow rapidly

QD Solar Cell Devices

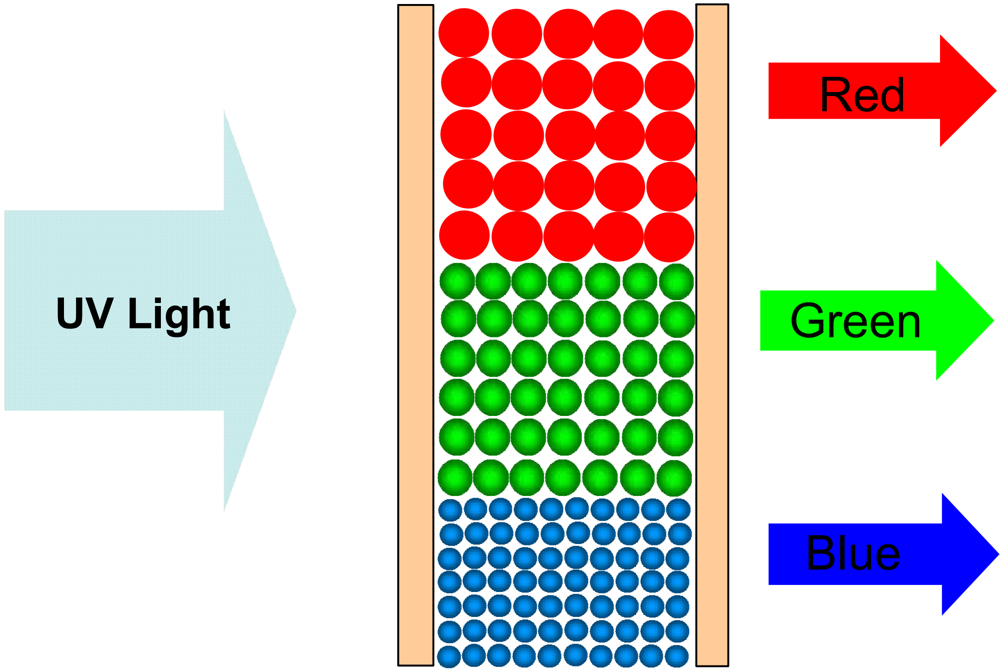
- Capture full spectrum of radiation
- Quantum dots can be processed into inks
- High efficiency of quantum dots
- Tune the quantum dots to the radiation that you want to capture



Applications: Plastic solar cells, Gratzel cells, Solar roof tiles

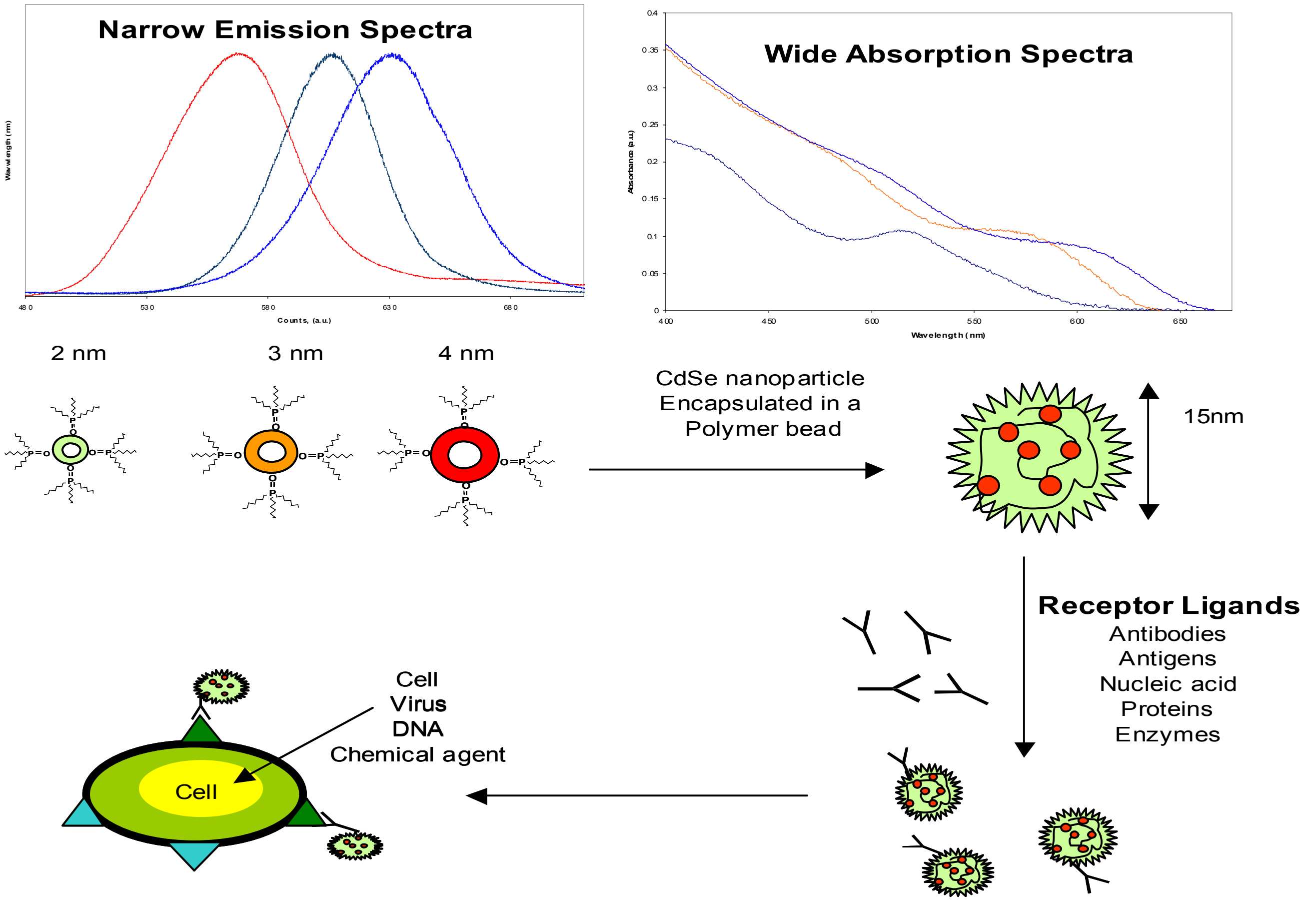
Displays and QD-LED's

- Low energy consumption,
- Same material for all colours,
- High efficiency

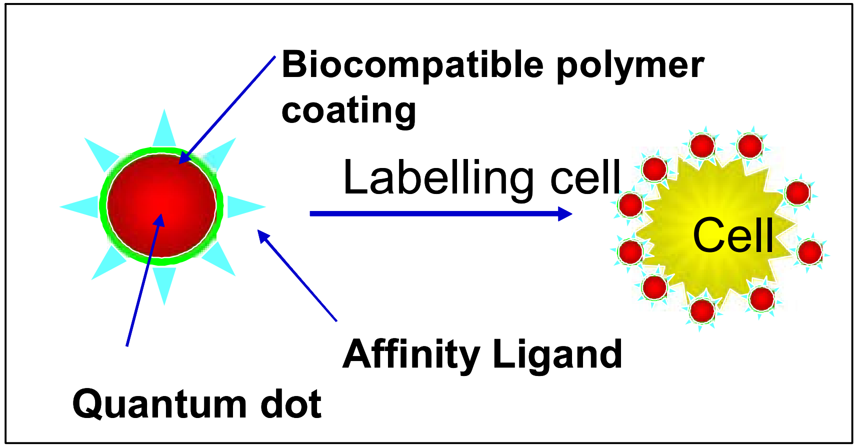


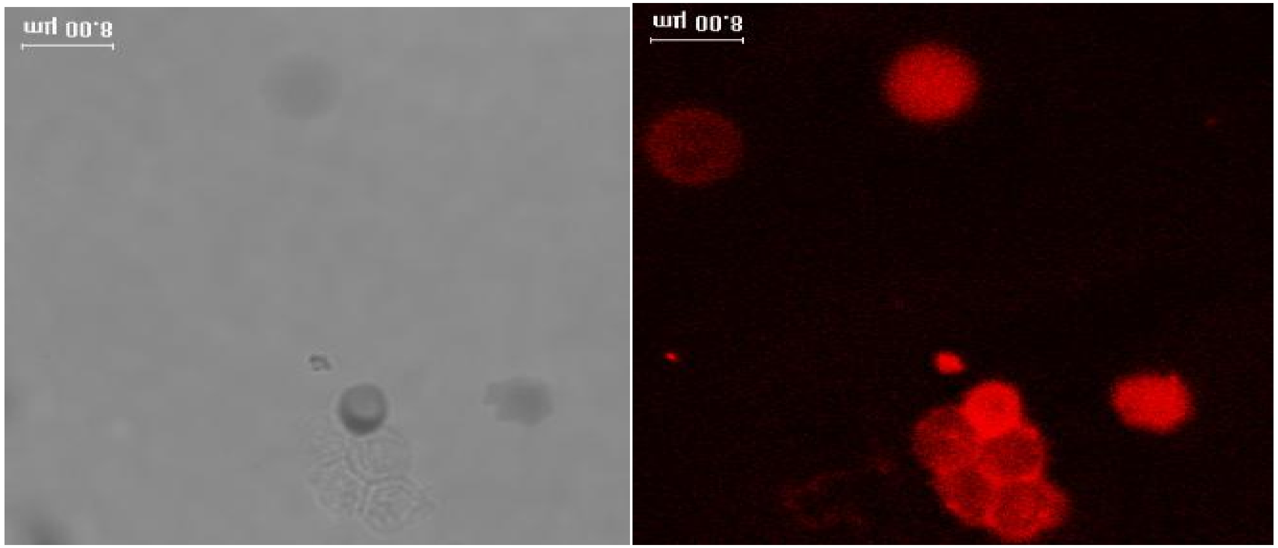
Make full colour displays made by using quantum dots for each primary colour

QD Biological Applications



Healthcare and Life Sciences Luminescent component in biological probes



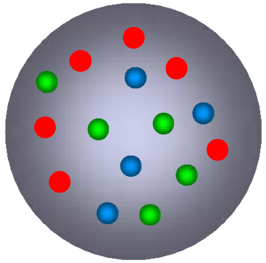


Confocal pictures of different size (A) 615nm,
(B) 489nmCdSe/ZnS QDs labeling Lymphocyte Cells

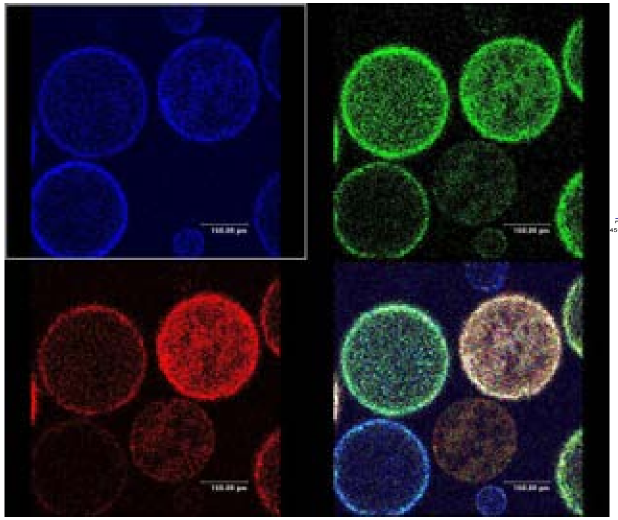
Quantum Dot Contain Beads

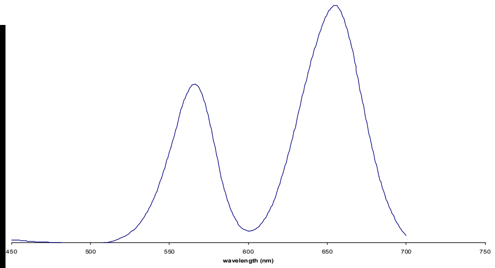
Quantum dot-containing polymer beads encoded beads

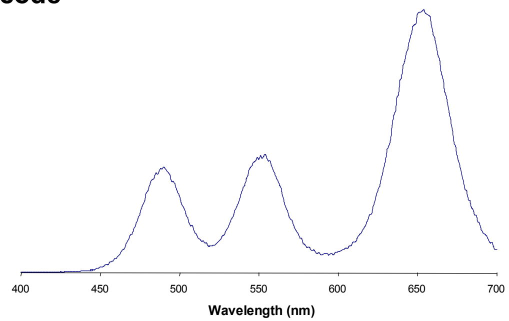
- High throughput screening
- Anti-counterfeiting
- Phosphors
- Monitoring flow systems

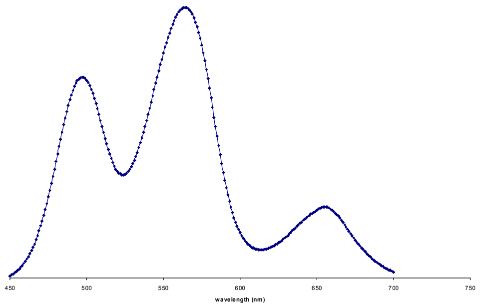


Schematic of a polymer bead containing three different colours of quantum dots to give an optical barcode





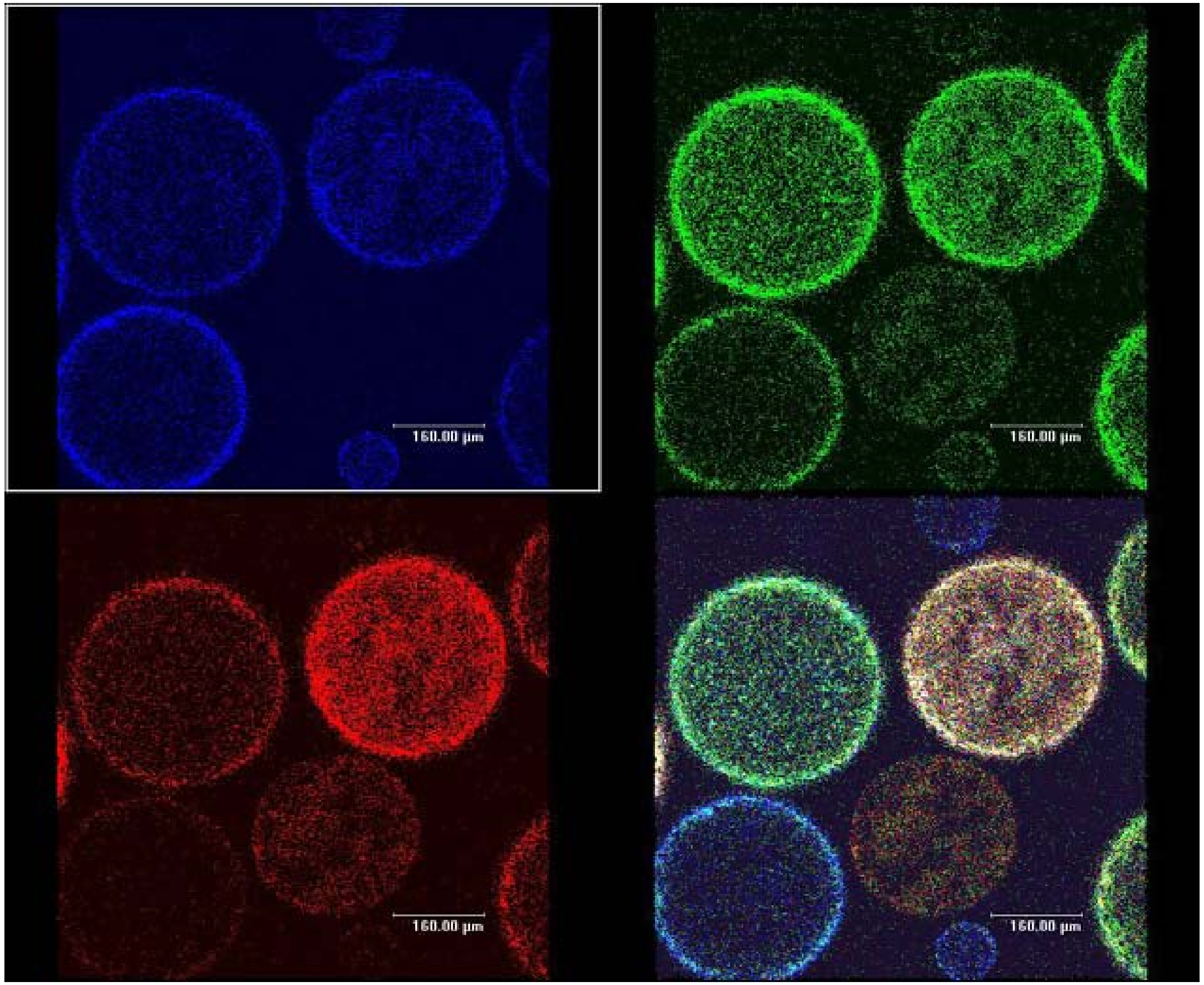




Nº of colours	Nº of intensities	Nº of combinations
2	2	4
3	3	27
4	4	256
5	5	3125

Microscope image of a polymer bead containing three different sizes of quantum dots and the photoluminescent emission spectrum of 3 different bead encodings

Identification of Beads by Fluorescence Profiles



4 types beads, 3 types QDs (532nm, 572nm & 628nm)

Chem. Commun, 2003, 2532 , J.Mater Chem., 2005,15,1238.

Summary

- World leading technology solution to existing problem – Scale up
- Nanoco is *de facto* partner of choice to QD application developers
- Large emerging market for QD based applications
- World leading technology and management team

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www.nanocotechnologies.com

Nanoco Technologies Limited

48 Grafton Street

Manchester

M13 9XX

United Kingdom

Tel: +44 161 275 4606

info@nanocotechnologies.com

Structure of Talk

- Why now ?
  - Looking at some nanodimensional objects by way of introduction
- Synthetic approaches semiconductors
- How nanoparticles grow and rods and tetrapods
- Other materials a rogues gallery
- What are some of the opportunities
  - The Nanoco Technologies Ltd perspective
- Closing remarks

A New University for the 21st Century

- Established on 1st October 2004
- Royal Charter granted on 22nd October 2004
- 34 000 students from over 150 countries (1/3 postgraduate)
- 2000 academic staff & 1200 research staff
- £504M turnover (2004-5)
- £300M capital investment programme
- Manchester 2015 Agenda launched

Milestones in Chemistry

1824 Mechanics Institute chemistry a foundation subject

1851 Frankland appointed start of chemistry Owen's

1867 Roscoe isolates elemental vanadium

1887 BA Meeting with Mendeleev.

1915 Weizmann works on starch into butyl alcohol

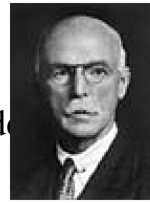
1903 Faculty of Technology

1907 Pope works on chiral nitrogen and sulfur

1937 Hawo Prize

1933 M.Polanyi arrives in Manchester

1929 Hard Prize



1947 Robinso Prize

1957 Todd ze

1952 John Polanyi Ph.D.

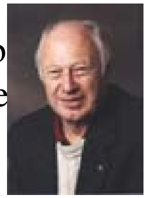
1964 New Chemistry Building Jack Lewis 61-67

1961 Calvi ize

1966 Faraday uilding

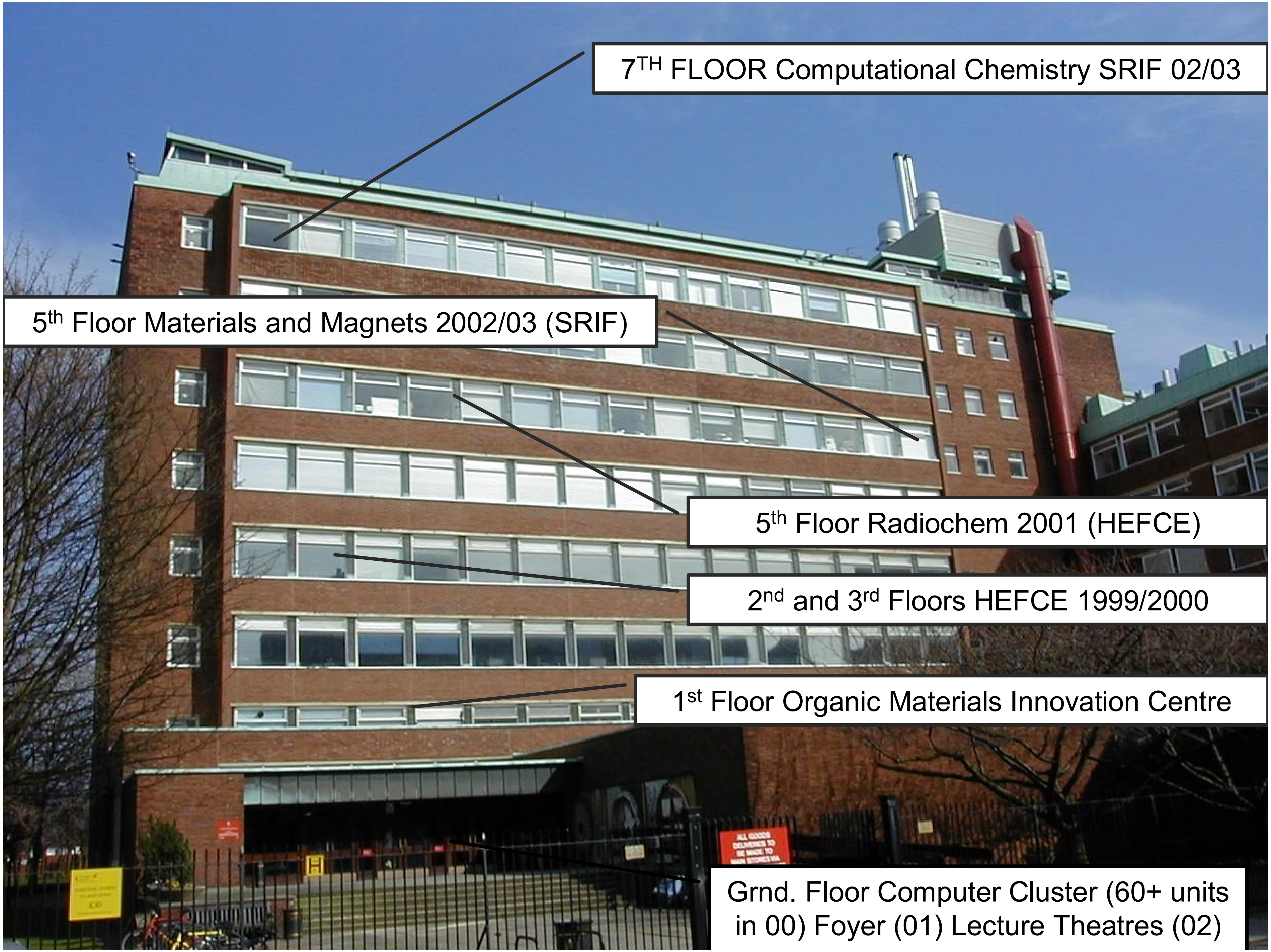
1986 Polanyi Nobel Prize

1993 Nob to Michae

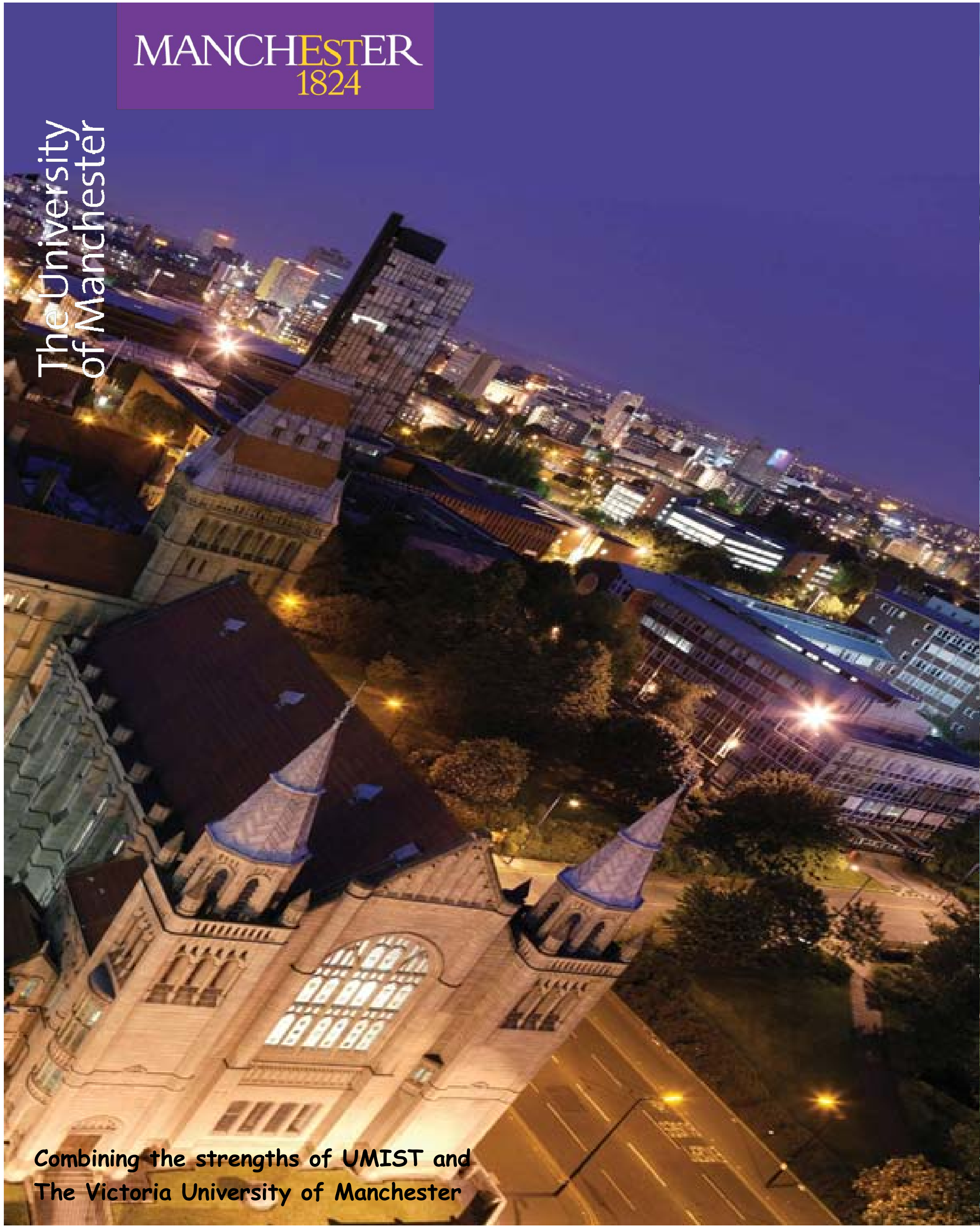


2004 New School in the University of Manchester

1998 Major refurbishment programmes started



7TH FLOOR Computational Chemistry SRIF 02/03
5th Floor Materials and Magnets 2002/03 (SRIF)
5th Floor Radiochem 2001 (HEFCE)
2nd and 3rd Floors HEFCE 1999/2000
1st Floor Organic Materials Innovation Centre
Grnd. Floor Computer Cluster (60+ units in 00) Foyer (01) Lecture Theatres (02)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