Debye Lecture 8


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Figure 1  (A) Cartoon depicting the stages of nucleation and growth for the preparation of monodisperse NCs in the framework of the La Mer model. As NCs grow with time, a size series of NCs may be isolated by periodically removing aliquots from the reaction vessel. (B) Representation of the simple synthetic apparatus employed in the preparation of monodisperse NC samples.
Cobalt Nanocrystal Superlattices (T. Betley et al)

Hexagonal packing

10 nm Cobalt NCs

Cubic packing
Figure 13  TEM cross-section through a (111)-oriented island of 100 Å CdSe NCs. The sample was cleaved along the (111) axis. The top of the image shows a glassy region formed at high growth rates. The bottom shows the long-range order possible at slower growth rates. Striations seen of the (112)$_{SL}$ fcc planes.
3D Colloidal supercrystals of nanocrystals

Crystallisation at the liquid - liquid interface leads to formation of perfectly facetted colloidal crystals.

Optical micrograph of CdSe 3D colloidal crystals

Three-dimensional colloidal supercrystals of CoPt$_3$ nanocrystals

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Figure 20  (A) TEM image of a (100) projection through a three-dimensional superlattice of 40 Å CdSe NCs. (B) At high magnification, the internal lattice structure of the NC building blocks is resolved. (C) Small-angle electron diffraction pattern demonstrates the lateral perfection of the superlattice domain. (D) TEM image showing the (100) projection for a superlattice of 40 Å CdSe NCs. (E) High magnification shows lattice imaging of the individual NCs. (F) Small-angle electron diffraction demonstrates the perfection of another characteristic face orientation. (G) TEM image of an face superlattice of 64 Å CdSe NCs viewed along the (111) axis. (H) Higher magnification image showing the individual NCs in the superlattice and (I) a small-angle electron diffraction pattern showing ordering in the (111) orientation over the scanned 2 µm area.
Figure 22. (A) High resolution TEM image shows a section of a (111)\textsubscript{Ag}-oriented superlattice of 62 Å CdSe NCs. The periodic dot pattern running through the image arises from the coherent imaging of columns of Cd and Se atoms making up the NCs in the superlattice. (B) Wide-angle electron diffraction pattern from a ~2 μm area. Strong modulation of the diffraction pattern results from the preferred alignment of the individual NC axes within the superlattice. At lower flux, the small-angle electron diffraction pattern can be seen emerging from the central beam. (C) Wide-angle electron diffraction pattern from a NC glass, having an isotropic orientation of NCs, is prepared from the same NC sample.
Figure 5  (A) WAXS patterns for CdSe NC samples ranging from 17 to 90 Å in diameter.  (B) Three-dimensional representation of a CdSe NC, as developed from TEM studies, exemplifies the atomistic structure employed in SAXS and WAXS modeling (62).  (C) SAXS and WAXS pattern for an ~4500 atom (62 Å) CdSe NC samples (dots).  Simultaneous fitting, using nonlinear least squares methods, to the SAXS and WAXS patterns fits the sample average NC size to ~4500 atoms, aspect ratio to 1.2 (prolate), and size distribution to 4.2%.  
Modeling NP Shape

Modeling Stacking faults

Scattered Intensity (arbitrary units)

Equivalent Diameter ~63Å

Spherical 1:1

Prolate 1.22

(a)

(b)
Small angle X-ray Scattering SAXS

(4.8) \[ I(q) = I_0 N[(\rho - \rho_o)^2 \frac{4}{3} \pi R^3 \left[3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}\right]]^2 \]

Where \( \rho \) and \( \rho_o \) are the electron density of the particle and the dispersing medium respectively. \( I_0 \) is the incident intensity and \( N \) is the number of particles. \( F(q) \) is the material form factor (the fourier transform of the shape of the scattering object) and is the origin of the oscillations observed. Thus for a spherical particle of radius \( R \)

(4.9) \[ I(q) = I_0 N(\rho - \rho_o)^2 F^2(q) \]
(4.10) \[ F(q) = \frac{4}{3} \pi R^3 \left[3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}\right] \]
The scattered intensity, $I(q)_{\text{total}}$, from an arbitrary collection of $N$ particles is

$$I(q)_{\text{total}} = I_0 N F^2(q) S(q), \quad 5.$$ 

where the structure factor $S(q)$ is the interference introduced by the correlation between particle positions. The structure factor can be extracted from the experimental data by dividing the SAXS pattern of the NC glasses by that of the NCs dispersed in PVB. When the NCs are dilute, their positions are uncorrelated and $S(q) \sim 1$. Equation 6 expresses the structure factor in terms of an average radial distribution $\rho(r)$ of particles about an arbitrary reference particle (110).

$$S(q) = 1 + \frac{4\pi \rho_0}{q} \int_0^\infty r \left[ \frac{\rho(r)}{\rho_0} - 1 \right] \sin(qr) \, dr \quad 6.$$ 

The structure factor can be Fourier transformed to yield a pair distribution function (PDF) $g(r)$ where

$$g(r) = \frac{\rho(r)}{\rho_0} = 1 + \frac{1}{2\pi^2 \rho_0} \int_0^\infty [S(q) - 1]q \sin(qr) \, dq. \quad 7.$$
Cap exchange to modify surface:

A

Pyridine
Δ 60°C

B

Tricetylphosphate
Δ 80°C

C

TBP / TBPO
Δ 60°C

D

Tricetylphosphate
Δ 80°C

E

Vacuum
Δ 150°C

F

Pyrazene
Δ 80°C

Pyridine
Δ 60°C
Figure 11  (A) SAXS patterns for close-packed glassy solids of 32 Å NCs with (a) TOPO caps and (b) TBPO caps. Inset (B) PDFs gives inter-particle separations for (a) of 11 Å and (b) or 7 Å. (C) SAXS patterns for glassy solids of 34 Å CdSe NCs capped with (c) pyridine, (d) pyrazine, and (e) bare semiconductor surfaces. Inset (D) PDFs give inter-particle spacings of (c) 7 Å, (d) 5 Å, and (e) <2 Å.
Figure 21. (a) SANS patterns for epitaxial superlattices prepared from CdSe NCs ranging from 35 to 64 Å in diameter. The interparticle separations are indicated for the 64 Å CdSe NC superlattice. (b) SANS patterns of ordered epitaxial thin films prepared from 34 Å CdSe NCs derivatized with (a) tristylphosphine, giving a ~17 Å inter-particle spacing; with (f) the native tristylophosphine chalcogenide, giving a ~11 Å spacing; and with (g) tinbutylphosphine oxide, giving a ~7 Å spacing (45).
TEM image of a 3D superlattice formed by nanospheres with hexagonal symmetry. Inset: Wide angle electron diffraction pattern indicates directional ordering (see arrow).

TEM image of a superlattice formed by nanocubes. Inset: Electron diffraction pattern of a 3D superlattice showing directional ordering. The superlattice shows cubic symmetry.

Small angle X-ray (SAXS) reflections for a fcc superlattice formed by spheres.

SAXS of a superlattice formed by cubes.
TEM micrographs of a fcc superlattice showing the (112) projection (left) and the (100) projection (right)
TEM micrographs of a quantum cube superlattice
Quantum Dot Solids for Amplified Stimulated Emission

Fig. 4. Development of a sharp stimulated emission band as a function of pump intensity in PL spectra of films ($T = 80$ K) fabricated from (A) TOPO-capped QDs with $R = 2.1$ nm and (B) ZnS-capped QDs with $R = 1.35$ nm. (Insets) Superlinear intensity dependence of the stimulated emission (circles) showing a clear threshold compared to the sublinear dependence of the PL intensity outside the sharp stimulated emission peak (squares).

Quantum Dot Solar Cells

FePt Nanocrystals (4 nm)
Magnetic recording

Computer \( \rightarrow \) V \( \rightarrow \) I

Servo Electronics

to piezos

Sample

X-Y Piezo Scanning Stage

4 nm ferromagnetic FePt particle assembly

Reading

Writing

MR signal [mV]

x [\( \mu m \)]

500 fc/mm

1040 fc/mm

2140 fc/mm

5000 fc/mm

Reading 4 nm ferromagnetic FePt particle assembly

Writing
Spin-dependent tunneling in Nanocrystal arrays

Chuck Black, Bob Sandstrom, Chris Murray, Shouheng Sun

- shortest current path \(\sim 8\) nanocrystals

- \(G_{V=0}\) follows simple thermal-activation

- data fit by: \(\ln(G_{V=0}) = \text{const.} - \frac{E_c}{k_B T}\)

- from fit to data, measure \(E_c \approx 10\) meV

- for all devices measured, \(10\) meV \(\leq E_c \leq 14\) meV
Magnetic Nanomaterials for Functional Nanodevices

Researchers: Shouheng Sun, Hao Zeng, Min Chen

Fe(acac)₃ + ROH + RCOOH + RNH₂ + Ph₂O

Single component
Self-assembly

Self-assembled Fe₃O₄ NPs
Potential for spintronic device applications
Quantum cubes:
Cubic 12 nm PbSe nanocrystals Assembling into a superlattice.
Large terrace on PbSe Superlattice of 10 nm PbSe Nanocrystals
Self-assembled CdSe nanorod solids

Optical micrograph of self-assembled CdSe nanorods (between crossed polarizers).
Figure 3 Large-field TEM images are employed to develop statistics on NC size and shape. A collection of 48 Å CdSe NCs at (A) low magnification (scale bar = 200 Å) and (B) higher magnification (scale bar = 80 Å) (45); monolayer of 80 Å Co NCs at (C) low magnification (scale bar = 500 Å) at (D) higher magnification (scale bar = 65 Å) (32).
Figure 9  (A) Comparison of experimental SAXS patterns for CdSe NC samples, ranging from 32 to 72 Å in diameter, dispersed in PVB (dotted lines) and close-packed into glassy solids (solid line). (B) Pair distribution functions (PDFs), g(r) extracted from experimental SAXS data. TOPO/TOPSe caps maintain an average inter-particle spacing of $11 \pm 1$ Å.
Figure 14  Time-resolved SAXS studies of a Ag superlattice as it self-assembles during evaporation from toluene. The sharp peaks that develop are from the inter-planar spacings of the deposited Ag superlattice (68).

Figure 15 Time-resolved SAXS studies of melting a Ag NC superlattice as a function of temperature. The disappearance of the sharp superlattice reflection upon heating indicates an order-to-disorder transition as the Ag NC superlattice is amorphized (69).
Figure 16 HRSEM images captures the morphology of self-assembled, close-packed islands and three-dimensional colloidal crystals of CdSe NCs. (a) The initial stages of growth for an island of ~750 Å CdSe NCs. (b) Three-dimensional growth forms more extensive islands of ordered 64 Å CdSe NCs. (c) One in a crop of similar size, incomplete (111)$_{SL}$-oriented colloidal crystals of 57 Å CdSe NCs. (d) At <1% in a crop of colloidal crystals in the shape of a square pyramid may be found. (e) Slow growth rates form complete, regular colloidal crystals. Colloidal crystals of 48 Å NCs show the characteristic pyramidal shape of a (111)$_{SL}$-oriented fcc structure. Ledges and terraces have closed off, forming vicinal (100)$_{SL}$ facets. The inset shows a (100)$_{SL}$-oriented colloidal crystal from the same sample preparation (45).
Figure 4.7 Optical micrograph of three-dimensional colloidal crystals of 57 Å CdSe QDs. The triangles form spokes that extend radially outward from the center on the bottom of a glass vial. The red color of the triangles is characteristic of the size-dependent absorption for the 57 Å CdSe NC building blocks [127].
Figure 18  
(A) TEM image of a faceted colloidal crystal prepared from 60 Å CdSe NCs. A star-shaped electron channeling pattern along the (111)g1 direction demonstrates ordering in the single domain colloidal crystal. (B) TEM image of one facet of the colloidal crystal showing the 60 Å CdSe NC building block.
Figure 19 (A) HRSTEM of a three-dimensional superlattice of 64 Å CdSe NCs grown epitaxially on an amorphous carbon substrate. Ordered rows of NCs form terraces, ledges, and kinks. (B) Superlattice growth is analogous to the terrace, ledge, kink model that describes monotonic crystal growth. (C) TEM image shows an ordered assembly of 64 Å InP NCs (120).
Figure 8: a) TEM image of a single cubic superlattice built of cubic FeO nanocrystals with 11 nm edge length. b) TEM image of a larger superlattice oxidized or decomposed after storage. c) SAED of the cubic superlattice in b) showing reflections for magnetite and orientational ordering in the superlattice.
Figure 4: a) LRTEM image of a quadratic subunit of a TEM grid showing nearly cubic superlattice built up of cubic wuestite nanocrystals. b) SAED of a selected superlattice with uneven but symmetric intensity distribution caused by preferred alignment of the particles (orientational ordering). c) TEM image of aligned superlattices arising during deposition of cubic FeO nanocrystals in a magnetic field parallel to the substrate. d) TEM image of aggregated superlattices deposited without external magnetic field.
Fe$_3$O$_4$ nanoparticles

Shape induce crystal alignment

(14 nm MnFe$_2$O$_4$ nanoparticles)

H. Zeng, et al
Figure 32. (Top) Cartoon of inter-particle interactions. At large inter-particle distance ($D$), NCs are electrically isolated and the superlattice is an insulator with a Coulomb bandgap. As the inter-particle distance decreases, exchange interactions become significant and the localized electronic wavefunctions of the individual NCs spread out over multiple NCs in the superlattice. In metallic superlattice exchange interactions lead to an insulator-to-metal transition. (Bottom) (a) $dI/dV$ or normalized density of states (NDOS) versus applied $V$ for (a) decanethiol-capped Ag NCs maintaining $D \sim 1.2$ nm and (b) hexanethiol-capped Ag NCs providing $D \sim 0.5$ nm (195).
Figure 33: Magnetic susceptibility versus temperature at 400 Gauss for Pb QD assemblies separated by dodecane- (C_{12}), octane- (C_{8}), and hexane- (C_{6}) carboxylates (196).