In nanoscience, two main ambitions are the control of the structure of an extended system up to the last atom, and to establish the relationship between the assembled structure and its properties. In the field of colloidal nanocrystals, these ambitions emerge on two scales: (i) the atomic scale, in controlling the crystal structure and understanding the ensuing properties (ii) the nanocrystal scale, in growing nanocrystal superlattices and understanding the collective properties of these superlattices.

If one wish to apply nanocrystal quantum dots for opto-electrical applications both levels of control and understanding are required. For instance, many people believe that nanocrystal quantum dots will be important in new photovoltaic cells. At present, even simple, first generation quantum dot solar cells show low or moderate efficiencies due to the fact that there is not sufficient control on the atomic/nanocrystal scale as well as on the nanocrystal/superlattice scale.

In my group, we work on the chemistry and physics on both scales. We would like to control the crystallography of single-component lattices (II-VI compounds, IV-VI compounds) and binary hetero-nanocrystals such as core-shell and dumb-bell systems, such as PbSe(core)/CdSe(shell) and PbSe/CdSe dumb-bells.

In this lecture I will mainly present our progress on the second scale, i.e. the nanocrystal/superlattice scale. I will discuss (a) how and why binary nanocrystal superlattices of PbSe and CdSe are formed by spontaneous crystallization, (b) how these systems can be structurally characterized by 3-D TEM, (c) how we investigate the opto-electronic structure of such systems by local scale STM and optical measurements on assemblies, (d) the possible importance of binary lattices for photovoltaics.

(a) **Formation of binary nanocrystal superlattices.** Nanocolloid crystallization occurs as a spontaneous process on increasing the nanocrystal concentration by solvent evaporation. Hence, we prepare stable suspensions of two types of nanocrystals, e.g. PbSe and CdSe NC of given radius and relative concentration and evaporate the solvent with a tilted TEM grid present. We analyse the formed structures with TEM and 3-D TEM. Strikingly, we observe binary superlattices of stoichiometry AB, AB₂, AB₅, and AB₁₃, A=PbSe NC, B=CdSe NC. Some structures are presented in the Figure. We are currently trying to understand these results on a thermodynamic basis: the superlattices are roughly in line with the expectations of the “hard-sphere” non-interaction model. However, not all structures can be explained with this model.

(b) **Quantitative structural characterization by (3-D) TEM.** Understanding the thermodynamics and kinetics of NC superlattice-formation and also the opto-electronic properties requires a structural characterization of superlattices beyond TEM. Friedrich et al. has developed a 3-D TEM structural analysis based on acquiring TEM data over an angle of 140 degrees and quantitative reconstruction of the superlattice. In this way, the unit cell vectors of the superlattice could be determined, flawed interpretations from 2-D TEM could be avoided, intrinsic lattice defects and the order/disorder at the top and bottom surface of the superlattice studied. We observed strong contraction of the superlattice in the direction perpendicular to the substrate, with close contact between the nanocrystals. Hence, it can be anticipated that charge carrier transport will show considerable anisotropy.
Measuring and understanding the opto-electronic properties of nanocrystal superlattices.

We try to understand the relationship between the properties of single-nanocrystals and collective properties of an assembly by measuring the energy levels of single, isolated nanocrystals, and nanocrystals in an ordered 2-D array by UHV, cryogenic STM. With arrays of CdSe NC, we could not detect electronic coupling: the energy levels of the nanocrystal in the array showed the single-electron polaron states typical for isolated 0-D quantum dots. We could resolve the Fröhlich electron-phonon coupling for the S and P orbitals. In the case of PbSe QD-molecules and PbSe QD arrays, we have observed considerable effects of electronic coupling on the density of states.

Binary nanocrystal superlattices: important for photovoltaics?

Self-organization of nanocrystal superlattices is perhaps the only way to put two types of semiconductor nanocrystals in close contact in a 3-D ordered geometry. The nanostructured bulk hetero-interface has the potential of efficient charge-carrier separation, and could hence form the active layer of a QD solar cell. A solar cell based on this concept has similarities with existing organic bulk heterojunction cells, but could have significant advantages over its organic counterpart on the longer term: (1) tailoring of energy levels by use of quantum confinement, (2) a plethora of 3-D geometries of high order, (3) chemical and topological stability of inorganic semiconductors, (4) strong light absorption by semiconductor quantum dots allowing the use of thin superlattices, (5) high carrier mobility and (6) possible implementation of efficiency-enhancing concepts, such as carrier multiplication. In future work, we wish to optimize binary superlattices of semiconductor nanocrystals for efficient charge separation, transport and carrier collection.

REFERENCES


Luminescent solar concentrators - a review of recent results Optics Express 16, 21773-21792 (2008).


Scanning tunneling spectroscopy of individual PbSe quantum dots and molecular aggregates stabilized in an inert nanocrystal matrix ACS Nano 2, 600-606 (2008).


FIGURE: Binary superlattices composed of PbSe and CdSe nanocrystals: A-C: PbSe(CdSe)$_2$ with AlB$_2$ structure, D-F PbSe(CdSe)$_2$ with MgZn$_2$ structure, G-I: PbSe(CdSe)$_3$ with CaCu$_3$ structure, J-L: icosahedral PbSe(CdSe)$_{13}$ structure.