Interactions between nanocrystal quantum dots in the weak and strong coupling regime.

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It is believed by many that quantum dots may form the basis for third-generation solar cells, with an efficiency that might exceed the mono-gap limit of a device with one-type of semiconductor (maximal 31 %). A prerequisite is that a third-generation principle is at hand in order to avoid photon losses or charge-carrier thermalization; i.e. photon up- or down conversion, absorption of sub-band gap light by an intermediate level, collection of hot carriers. In each of these processes, the energy levels of the individual quantum dot components and their mutual quantum mechanical interaction is of importance.

We have studied several aspects of the self organization of quantum dots into ordered superlattices with TEM, cryogenic TEM and scanning probe methods . Using cryo-TEM, we observed string formation in quantum colloids of CdSe and PbSe, pointing to pair interactions of several kT and considerable dipole moments in the crystal (Figure 1). The microscopic origin of these dipole moments is under discussion. Crystal dipole moments strongly affect self-assembly of quantum dots into a superlattice. For instance, the atomic planes of the PbSe nanocrystal superlattice presented in Figure 1(top-right) are all oriented in the same way, due to the presence of well-defined dipole moments.

The degree of electron and hole delocalization in quantum dot superlattices has been studied in a local way, by scanning tunneling microscopy and spectroscopy on each quantum-dot site in the superlattice. The local density of states is then compared to that of an individual isolated quantum dot. For superlattices of PbSe quantum dots (Figure 2) we found that there is a considerable coupling between the energy levels of neighboring quantum dots; electron delocalization is stronger than hole delocalization. In addition, the quantum mechanical coupling varies from place to place in the lattice, without a clear relationship to the lattice structure. This means that small atomic variations may lead to electronic disorder.

Finally, we studied the electronic properties of nanocrystal heterojunctions with atomic epitaxy. The optical results point to charge-separated excitons and a strong electronic coupling between the two phases. The importance of these results for future photovoltaics will be highlighted in the lecture.

(1) Dipolar Structures in Colloidal Dispersions of PbSe and CdSe quantum dots. *M. Klokkenburg et al., Nano Letters* 7, 2931 (2007).

(2) Frequency-dependent spontaneous emission rate from CdSe and CdTe nanocrystals: Influence of dark states. *A. F. van Driel et al., Physical Review Letters 95, 236804 (2005).*

Electronic coupling and exciton energy transfer in CdTe quantum-dot molecules. *R. Koole et al., Journal of the American Chemical Society* 128, 10436-10441 (2006).

(3) Highly luminescent CdSe/CdTe colloidal hetero-nanocrystals with temperature-dependent emission color. *P. Chin et al., Journal of the American Chemical Society* , in press.

(4) Variable orbital coupling in a two-dimensional quantum-dot solid probed on a local scale. *P. Liljeroth et al. Physical Review Letters 97, 096803 (2006).*

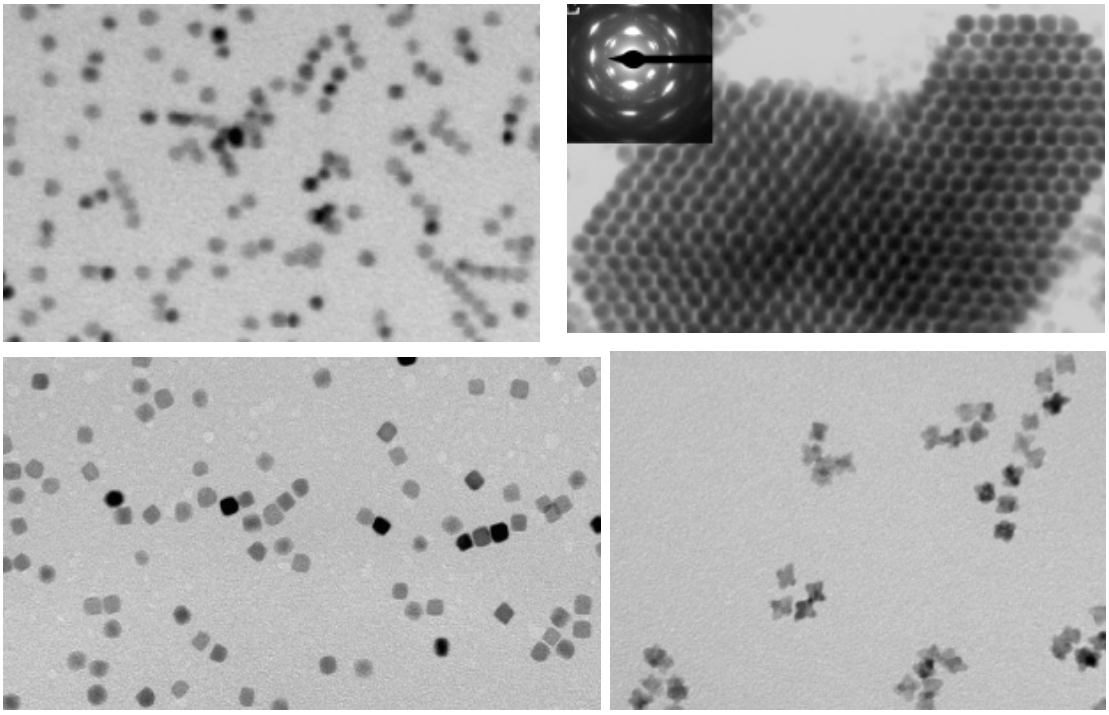

Figure 1: Quantum dot self-organization: Cryogenic TEM pictures of PbSe quantum dots of different shapes: reversible string formation points to strong dipolar interactions (pair potential is about 8 kT). In the quantum dot solid (upper right) the atomic lattices planes are also oriented!

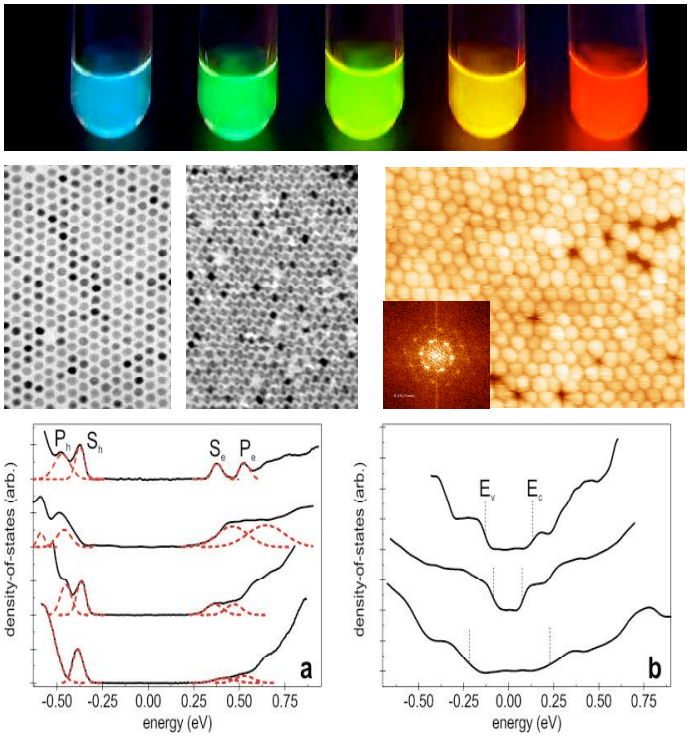

Figure 2 Quantum confinement and self-assembly of colloidal semiconductor quantum dots

Top: Suspensions of colloidal CdSe nanocrystals of diameter between 2 nm emitting in the blue to 6 nm emitting in the red.

Central row: TEM pictures of a self-assembled monolayers of spherical PbSe nanocrystals (7 nm in diameter) and star-shaped PbSe nanocrystals with hexagonal ordering. Right: STM picture of a self-assembled monolayer of spherical PbSe nanocrystals (7 nm)

Below: Cryogenic tunneling spectra acquired at PbSe quantum-dot sites in a 2-D array showing electron delocalization (left) and electron and hole delocalization (right) due to quantum mechanical coupling. The spectrum of an isolated quantum dot showing strong quantum confinement is presented top-left for comparison