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Particle–Particle Interactions in Semiconductor Nanocrystal Assemblies

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ABSTRACT

To study possible interactions between semiconductor nanocrystals, crystalline superstructures of $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ have been studied spectroscopically. Interactions between the particles have been detected which are discussed with simple models including electronic and dipole–dipole interactions.

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Over the past two decades, research on structures in the size regime of a few nanometers has proven to be one of the most rapidly growing fields in modern science. This sector is being investigated by solid state physicists, inorganic chemists, physical chemists, colloid chemists, material scientists, and recently even biological scientists, medics, and engineers. Phase transition pressures, melting points, optical and optoelectronic, catalytic, magnetic, and electric properties of nanomaterials differ from those of the solid as well as from those of the molecular species of which they consist.[1−7]

The monodisperse particles become useful as building blocks of big supramolecular units.[4−6] Reports on the self-organization into quantum dot solids built from semiconductor[8−10] and metal particles[11−14] already exist.

Up to now only very little is known about the properties of these solids made from nanoparticles. Some work has been published by Heath et al. on collective properties of interacting metal nanoparticles.[15−17] Depending on the interparticle distance, those solids reflect dipole−dipole interaction followed by pure electronic coupling when the particles come into closest contact. Recently, Remacle and Levine studied theoretically electron-transfer processes in arrays of quantum dots.[18] A shift of the first electronic absorption of small cadmium sulfide clusters to lower energies compared to their solutions was first published by Vossmeyer et al.[19] for closely packed layers of cadmium sulfide nanocrystals. The layers were built up from solutions of the clusters by a spin-coating technique and were examined by absorption spectroscopy. Further investigations have been performed on such kind of closely packed layers and will be presented in a forthcoming paper.[20] Besides some further studies on Förster energy transfer in semiconductor quantum solids consisting of particles of different sizes,[21,22] little is known about the interaction between identical semiconductor nanoparticles. For this purpose cluster crystals are ideal candidates.

For our preliminary studies presented in this letter, we choose the cluster crystal compound $Cd_{17}S_4(SCH_2CH_2OH)_{26}$, which has been prepared according to the literature.[23] The structure of this thiol-stabilized molecule-like cadmium sulfide nanocrystal is known from single-crystal X-ray diffraction. In Figure 1 the internal structure of the cluster is shown. It represents a tetrahedral cutout from the bulk cubic structure consisting of four adamantane-like cages capped with barrelane-like cages at the four tips of the tetrahedron. This tetrahedron has an edge length of 1.4 nm. It is also seen from Figure 1 that neighboring clusters are bound covalently via a bridging sulfur atom from the ligand at each tip of the tetrahedra. A 3D network is formed in this manner in a cubic diamond-like superstructure. Single crystals with sizes in the millimeter range are obtained via this preparation route. Because of absorption coefficients of the clusters as high as 84 000 L/mol·cm, it is impossible to perform absorption spectroscopy on this kind of solid. To study the optical properties of this material reflection spectroscopy has been performed. For this, we milled the crystals down to grain sizes of about two μm and measured the diffuse reflection in an integrating sphere. In Figure 2 the UV−vis absorption spectrum of this compound in solution is shown together with the reflection spectrum of the crystalline material. It is clearly seen that in the spectra of the crystalline material the first electronic transition is shifted to lower energies by about 150 meV. Additionally, the transition is broadened from a full width at half-maximum of about 390 meV to about 520 meV.

For explaining the observed energetic shifting of the first electronic transition, surface and solvation effects of a surrounding polar environment were considered. Recently, Brus and co-workers presented theoretical studies on cad-

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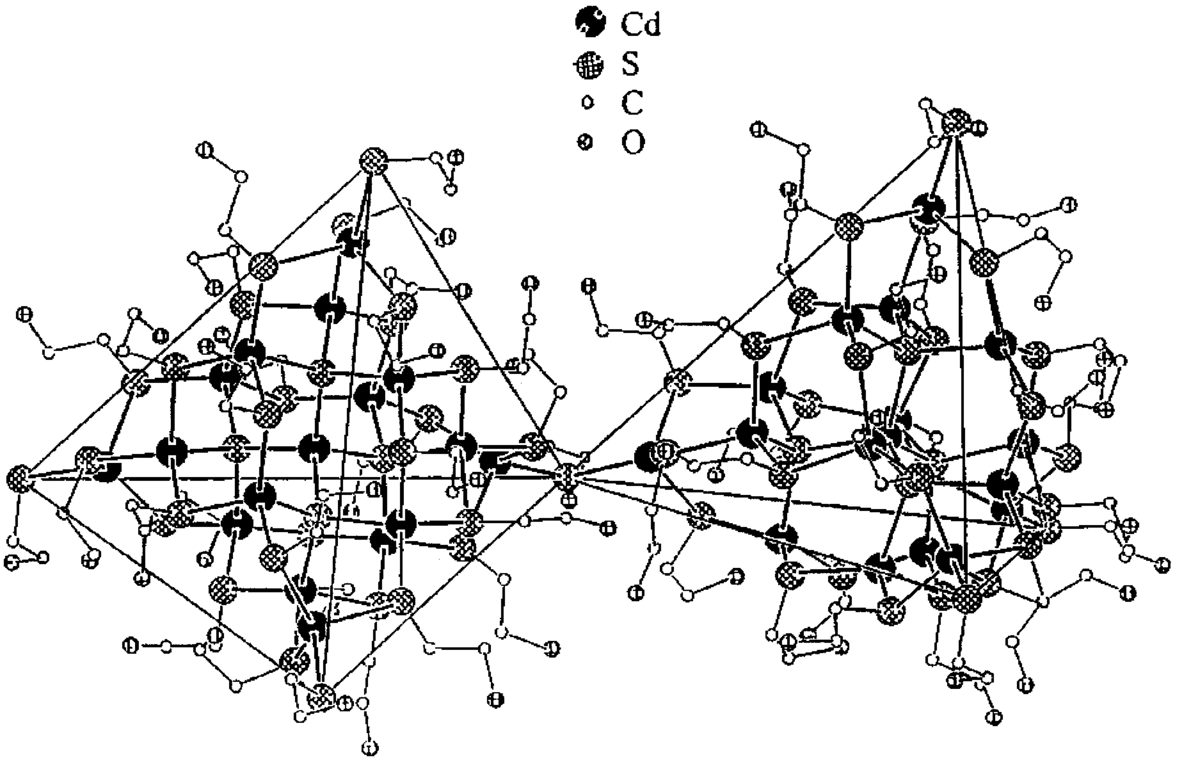

Figure 1. Crystal structure of superstructures of $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ nanocrystals. Two clusters are shown that are bound covalently at the tip of each tetrahedron via a bridging sulfur atom from the ligand. For a better understanding, the hydrogen atoms are not shown in this figure.

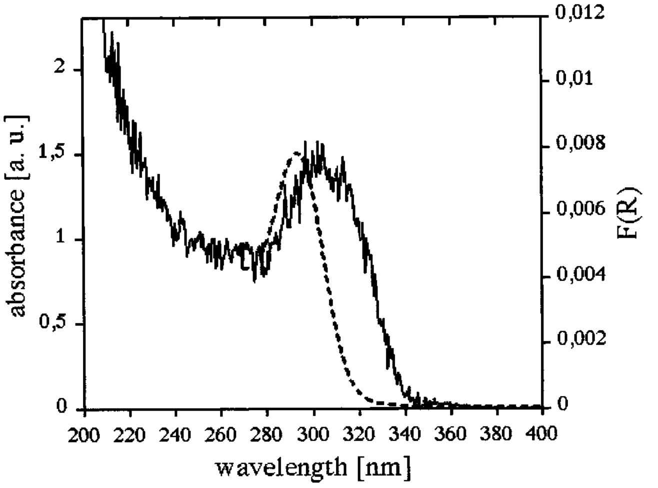

Figure 2. Absorption spectrum of $Cd_{17}S_4(SCH_2CH_2OH)_{26}$ nanocrystals dispersed in solution (dotted line) and reflection spectrum of micron-sized crystals of the same compound (solid line).

mium selenide nanoparticles[24] based on a modified pseudopotential method. Their calculations yield large dipole moments of the nanocrystals resulting from the anisotropy of the crystal structure of hexagonal cadmium selenide particles. Those moments are clearly affected by a polar environment. However, the authors propose only weak interactions with a polar environment for particles from materials with isotropic crystal structure such as cubic cadmium sulfide.

In another attempt to explain the observed red shift, we considered an electronic interaction by quantum mechanical coupling of the respective states of the individual particles. A red shift of the first electronic transition would be expected when the electronic system is enlarged. For calculating the dependence of the electronic interaction on the distance between the coupling systems, we used a periodical box potential according to Kronig and Penney[25] for simulating both the crystalline arrangement of the particles with very small distances between them and the situation in solution with large distances between the particles. In this model, the boxes representing the particles (size 1.4 nm) are separated by potential walls. The height of these energy barriers was chosen to be 3 eV, and the separation of the boxes (i.e., the interparticle distance) was varied between 20 nm reflecting large distances and 0.7 nm modeling the situation with neighboring clusters. The effective masses of the charge carriers were taken from the literature (0.2 and 0.7 for electrons and holes, respectively[26]). The 3D arrangement of the particles is taken into account by multiplying the 1D results by three. According to Brus,[27] the transition energy then is calculated by addition of the bulk band gap and the Coulomb interaction. For large distances between the clusters, a transition energy of 3.92 eV was obtained, which is in fair agreement with the experimental value (4.24 eV). For the clusters with small distances between the inorganic cores, we obtained the formation of a subband for the electron states that spans about 75 meV at a separation of 0.7 nm. Due to the higher effective mass of the holes, a narrower subband (1.5 meV) was observed for this charge carrier. The centers of the subbands remained exactly at the same energetic positions as the discrete levels in the solution case. Thus, it turns out that for the electronic interaction of semiconductor particles in close contact, a broadening of the transition band would be expected without significant energetic shifting.

Another possible explanation would be the interaction of the dipoles of the clusters. The transition dipole moment of the absorbing particle may induce dipole moments in the neighboring clusters in their ground state. Analogous to the additional coulomb term in Brus formula,[27] this interaction between the dipoles could lower the initial transition energy. For our calculations we obtained the oscillator strength of the transition from spectroscopic data and evaluated the transition dipole moment using textbook equations. Supposed that the formula of Clausius and Mossotti is appropriate in this case, the polarizability of the clusters was calculated from the bulk high-frequency dielectric constant ($\epsilon = 5.5$). Although this value could be altered for small particles, it is quite common to use the bulk value for a first rough estimate (see, e.g., ref 27). For the oscillator strength we obtained a value of close to one that is expected for this kind of molecular species having nearly perfect overlap of the wave functions of the charge carriers. The resulting transition dipole moment was 7.9 D, which fits very well in the linear dependence of the dipole moments on the cluster sizes found by others.[28−33] The resulting polarizabilities depend strongly on the assumed particle shapes and volumes. Assuming a spherical shape with a diameter of 1.4 nm, we obtained a polarizability volume of 205.8 Å^3. For a distance between the particles (center to center) of 1.4 nm, this yields a potential energy of −51.2 meV for the interaction between the dipole of the absorbing cluster and the induced dipoles in adjacted clusters. If we take the polarizability volume of the in fact tetrahedrally shaped particles (57.0 Å^3), a shift of −14.2 meV to lower energies is calculated. Comparing these results with the experimental value of −29 meV for a closely packed layer (details will be published in a forthcoming paper[20]), these calculations explain quite well the red shift of the absorption band of the clusters in the compact layer in comparison to the isolated clusters in solution. The calculated values are clearly smaller than the experimental value for the crystalline material (150 meV). Probably the covalently linked inorganic cores in the crystalline superstructure feel a closer contact than the assumed distance of 7 Å. This would result in a stronger dipolar coupling of the clusters.

Most probably, a complete description of the interaction of semiconductor nanocrystals in crystalline superstructures includes now both the electronic and the dipole−dipole interactions. The electronic coupling may be introduced by the covalent bridging of the nanocrystals in the crystalline superstructure as shown by single-crystal X-ray spectroscopy. Clearly, the models presented are rough estimates for our experimental results, and detailed theoretical studies would help form a more quantitative picture.

Results from experiments on other cluster crystals, on the concentration dependence of the transition energy of the clusters in solution, and on the dependence of this quantity on further experimental conditions will be published in a forthcoming paper.[20]

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