

Small Is Different: Shape-, Size-, and Composition-Dependent Properties of Some Colloidal Semiconductor Nanocrystals

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ABSTRACT

As the size of material becomes equal to or falls below the nanometer length scale that characterizes the motion of its electrons and thus its properties, the latter become sensitive not only to the size but also to the shape and composition of the particles. In this Account, we describe the changes of some interesting properties in different colloidal semiconductor nanoparticles, such as the electronic relaxation rates as spherical nanoparticles change to nanorods, and the changes in the structure or size of very small nanoparticles upon adsorbing strongly bound molecules. We have also determined and explained the difference in the interfacial crossing rates of electrons and holes in a composite nanostructure.

A. Introduction

The physical and chemical properties of a material are determined by the type of motion allowed for its electrons to execute. The latter is determined by the space in which the electrons are confined. Unbound (unconfined) electrons have motion that is not quantized and can thus absorb any amount of energy given to them and use it simply to move more rapidly. Once bound in an atom, a molecule or a material, their motion becomes highly confined and quantization sets in. The allowed types of motion in atomic or molecular orbitals are found to have well-defined energies that are separated from one another. The smaller the space in which the bound motion takes place, (i.e., the stronger the confinement) the larger the energy separation between the allowed energies of the different types of motion becomes. The nuclear confinement is the strongest type of confinement of the motion of subatomic particles. The motion of the nucleons within

the atomic nucleus is confined to the femtometer scale. This is followed by electronic confinement in atoms. In the hydrogen atom, the electron is confined to a length scale of ~ 50 pm.

In a bulk semiconductor, excitation involves the formation of an electron and hole (the charge carriers), which are separated by distances that encompass a number of molecules or ions making the material. This, along with the high dielectric constant of the material, makes their binding energy relatively small. Such a distance is known as the Bohr radius and is on the nanometer length scale. The minimum amount of energy required for the formation of the charge carriers is known as the band gap energy of the semiconductor. It is the energy difference between the top of the valence band and the bottom of the conduction band. The formation of a separated electron and hole bound by weak Coulombic attraction is also called the formation of a Wannier-type exciton, which is transported through the semiconductor bulk crystal until it is trapped, annihilated if it collides with another exciton (as in the case of high-intensity laser excitation), or relaxed by radiative recombination of the electron and hole.

What happens if we reduce the physical size of the semiconductor material so it becomes comparable to or smaller than the Bohr radius? This would decrease the space in which the charge carriers (the excitons) move and thus confine their motion. Like the motion of an electron in a box, as the size of the box decreases, its kinetic energy, as well as its excitation energy, increases. Similarly, when the size of the semiconductor particles becomes smaller than their Bohr radius, their band gap energy increases. Equally important, the energy of the band gap absorption (and thus the nanoparticle color) and that of the emission increase and become sensitive to the size and shape of the particles. Thus, the optical and other physical and chemical (e.g., oxidation–reduction) properties of semiconductor nanoparticles become sensitive to the size and shape of the particles.

The size or shape control can be accomplished by adjusting the space in which the nanoparticles grow (e.g., in templates). In colloidal solution synthesis, controlling the size or shape is done by adjusting the ratio of the concentration of the chemicals making the nanoparticle to that of the selected capping material (e.g., polymers, micelles, surfactants, or dendrimers). This type of synthesis is termed the bottom-up method. In the top-down method, the bulk is “machined” down to the nanometer length scale by lithographic or laser ablation–condensation techniques.

Because of the dependence of the semiconductor nanoparticle properties on the size and shape of the nanoparticle, as well as the fact that the surface-to-volume ratio greatly increases, new properties are expected that are not possessed by either the macroscopic semiconductor material or the individual entity that makes the

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semiconductor.^{1–13} The potential of using these new properties in new technological applications has been discussed in many fields,¹⁴ such as “nanoelectronics”,^{15,16} photovoltaics,^{17–20} and optoelectronics.^{21,22} Because electrons and holes have large amplitude at the surface, they have high probability of being trapped by surface impurities. This extends their use in the field of oxidation–reduction chemistry with many expected applications in fields such as photocatalysis^{17,23,24} and photo degradation and detoxification of chemical waste and environmental pollutants.^{25,26}

Our group is involved in studying the new properties of both semiconductor and metallic nanocrystals as their size, shape, and composition change. An exposure to our work on the *metallic* nanoparticles was given in an earlier Account and in feature or review articles in different publications.²⁷ In this Account, we discuss the results of some of our work on II–VI colloidal semiconductor nanoparticles of different sizes, shapes, and composition.

B. Contrasting Electronic Excitation in Semiconductor Nanoparticles and in Conjugated Molecules

Just like in conjugated molecules, excitation of a neutral semiconductor nanoparticle creates an electron and a hole (a positive charge). In both cases, molecular orbitals can describe the electronic excitation process. However, the type of molecular orbitals formed in the two cases are quite different. In conjugated molecules, the occupied and unoccupied molecular orbitals (MO) are made of linear combinations of the same type of atomic orbitals. Furthermore, the electron and hole density in a MO is present on the same type of atoms (e.g., carbon atoms in conjugated polyenes) and are thus strongly correlated. In a semiconductor nanoparticle like CdSe or HgS, the occupied MOs are made of a linear combination of atomic orbitals (ao) on the negatively charged anions (e.g., S^{2–}, Se^{2–}, ...), while the unoccupied MOs are made of ao on the metallic cations (Cd²⁺, Hg²⁺, ...)(see Figure 1). Thus, the band gap excitation involves a charge transfer of an electron from the HOMO in the Se^{2–} or S^{2–} electronic system to the vacant LUMO of the Cd²⁺ or Hg²⁺ (the bottom of the conduction band in the bulk). This creates a hole in the HOMO (which corresponds to the top of the valence band in the bulk). Thus, the holes always occupy the anion MOs, while the excited electrons occupy the cation MOs. Because of this and the high dielectric constant of the semiconductor material, the charge carriers in a semiconductor nanoparticles are weakly coupled and thus are not strongly correlated. They can be excited, be trapped, and relax nonradiatively almost independently of one another. Furthermore, excitation of the excited electron formed in band gap absorption takes place between different MOs of the metal cation. The holes formed in the band gap absorption can be excited to other higher energy anion MOs. The excitation of either charge carrier formed in the band gap absorption is called the intraband excitation, while the band gap excitation itself

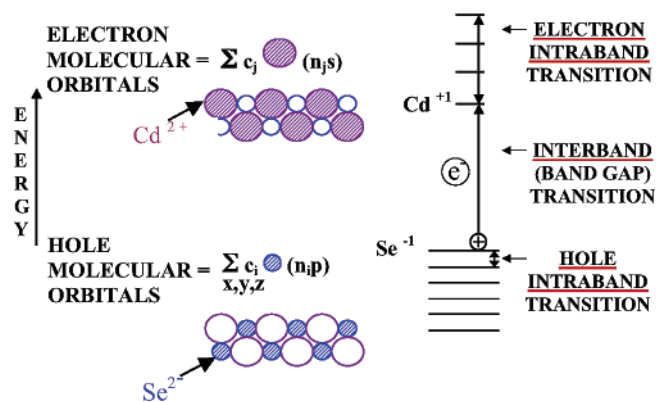


FIGURE 1. Molecular orbitals are different in a semiconductor nanoparticle than in a conducting polymer: (left) the molecular orbitals of the hole (bottom) in the Se^{2–} electronic system and the electron (top) in the Cd²⁺ electronic system in a CdSe semiconductor nanoparticle; (right) the band gap (interband or HOMO to LUMO) transition (separating the electron and hole) and the different intraband transitions of the electron (top) and hole (bottom) in a semiconductor nanoparticle. The interband transition is a charge-transfer type of transition from the Se^{2–} MOs to the Cd²⁺ MOs to form a delocalized Cd⁺ and Se[–] electronic system in the band gap state.

is termed the interband excitation (see Figure 1). In II–VI semiconductors, the different MOs made from the *n* p atomic orbitals of the negatively charged anion are much closer to one another in energy than those formed from the five s atomic orbitals on the positively charged cations. For this reason, the electron intraband absorption occurs at higher energy than the hole intraband absorption, which is observed in the infrared region.

C. Size and Shape Dependence of the Nonradiative Relaxation of Excited Electrons

The mechanism(s) of the relaxation (cooling) of hot electrons excited to higher intraband states has been a topic of active research recently. *In the bulk*, the excited electron being in the conduction band *continuum* can relax by giving the lattice phonons one phonon energy at a time as it cascades down rapidly to the band gap level without facing problems resulting from the mismatch of the hot electron energy and the phonon quantum (because the electron in the conduction band has continuous values of energy). As electronic quantization takes place due to quantum confinement, the electron in a nanoparticle acquires fixed values of energies and can thus give the lattice only fixed quantized amounts of energy at a time as it cascades down to the band gap level. These electronic excitation energies are too large (fraction of an electronvolt) compared to the phonon energies (0.02 eV). Thus, as the electron cascades from one level to the other, it gives off energies that require the excitation of 10 or so phonons *simultaneously*. Such a process is improbable and slows down the electronic relaxation leading to the phenomenon known as “phonon bottleneck.” However, the observed electronic relaxation in nanoparticles is

found to be on the subpicosecond to picosecond time scale, and therefore, other mechanism(s) must be operative.

At high laser intensities, the excitation of more than one electron–hole pair takes place. In the case of exciting two electrons and two holes, the repulsion between the two excited electrons and the attraction of one of them to the hole leads to the recombination of one of the electron–hole pairs. The energy given off in this recombination process is used to ionize the other electron. This process is known as the Auger process²⁸ and can lead to the relaxation of the two excited electrons. This mechanism is well documented²⁹ experimentally and occurs at reasonable femtosecond laser intensities.

How about at low laser intensities? Efros³⁰ proposed that the excited electron couples with the hole. As it relaxes to a lower energy state, it gives its energy to the hole, whose level structure is known to have small energy spacing (almost continuous), thus preventing energy mismatch problems in the relaxation process. This is then followed by the relaxation of the hole by the phonon bath. This mechanism was supported by the results of Nozik and his group in some III–V semiconductor nanoparticles. It is shown that in removing hole traps on the surface, the cooling time increases³¹ from a few picoseconds to 0.35–0.45 ps. Furthermore, Nozik³¹ showed that an injected extra electron into the nanocrystal has a few picoseconds (not a fraction of a picosecond) cooling time when photoexcited. Klimov³² showed that when hole traps are added to CdSe nanoparticles, the cooling time increases.

The above results suggest that the electron–hole mechanism has a decay time of 0.3–0.4 ps. In CdS, holes are found³³ to be trapped by the surface 10 times faster than the electrons. It is thus expected that unless the surface is completely free of surface traps or in semiconductors in which the hole density of states is not very high, the electron–hole mechanism will not be important. It will not compete with mechanisms involving the surface. Surface trapping is a well accepted mechanism of fluorescence quenching of semiconductor nanoparticles. Surface passivation is known to increase the fluorescence intensity of CdSe by orders of magnitudes.^{34,35}

It is very difficult to get rid of surface defects. Furthermore, bound to the surface is the capping material, which is usually large organic molecules having large vibrations that can absorb large amounts of excited electronic energies in few vibrations. They also have small vibrations that assist in matching the energies. The interaction between the excited electron density at the surface and the electrons of these large molecules could thus lead to the relaxation of an excited electron by the vibrations of the traps or the capping molecule in a time comparable to (or a bit longer than) that observed in large molecules (known to be on the subpicosecond time scale³⁶). If the coupling between the excited electron and the surface is very strong, it is liable to be trapped; that is, not only can energy be transferred to the surface, but also the excited electron itself can be transferred to the traps or to the

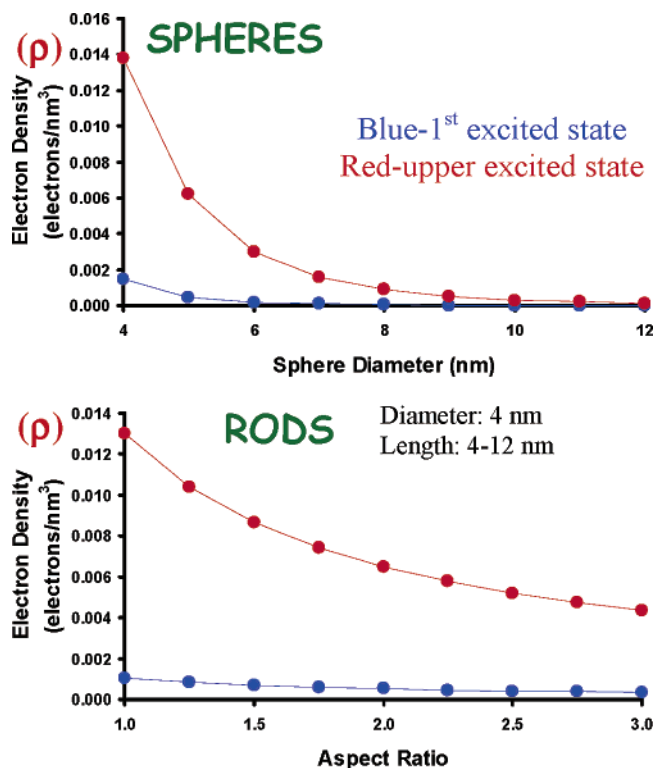


FIGURE 2. The density of excited electron on the nanoparticle surface: calculated excited electron density in a surface shell of 0.2 nm thickness around a sphere (top) and a cylinder (bottom) in which the electron is confined. This is shown as a function of the sphere (dot) radius (top) and the aspect (length to width) ratio of the cylinder (bottom) for two electronic excited states. This shows that due to the small size of the nanoparticle and the increase in the kinetic energy of its electrons, the excited electrons in nanoparticles have nonvanishing probability of being on the surface. This could lead to their energy relaxation and trapping by surface molecules or traps.

capping material on the surface. The higher the excitation energy of the excited electron, the more probable this process becomes.

In support of this mechanism is the fact that due to the small size of nanoparticles, the increase in the electron kinetic energy upon quantum size confinement, and the inhomogeneous potential on the surface, there is indeed a nonvanishing probability for the excited electron to be on the surface. Using the known wave functions of particles confined in a sphere or in a cylinder, Alex Schill³⁷ in our group calculated the electron density in a shell of 0.2 nm thickness on the surfaces of each shape. The results are shown in Figure 2 for two excited states (shown in red and blue) as a function of the sphere diameter (top) or the aspect (length to width) ratio of the rods (bottom). The interaction energy between the excited electron and the trap or the bonds connecting the capping material to the surface determines the rate of the energy exchange between the hot electron and surface species acting as the bath or as the trap. Of course, Franck–Condon factors and density of the final state are other important parameters. If one assumes that these vary little with size or shape, then the change in the excited electron density

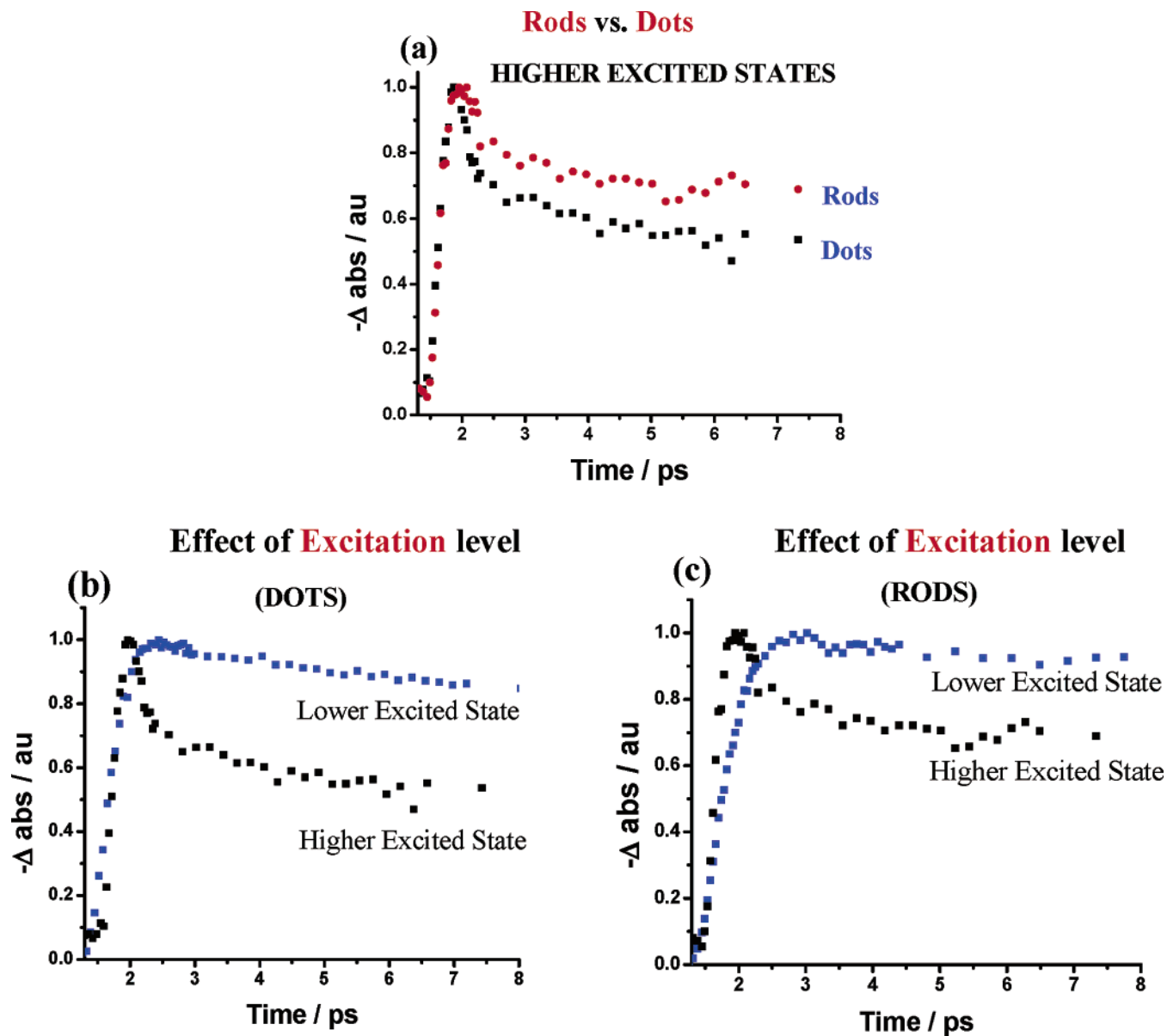


FIGURE 3. Dependence of excited electron relaxation time on size, shape, and degree of excitation: comparison of the relaxation time of excited electrons in a spherical (quantum dot of 4 nm) and rod-shaped (12 nm × 4 nm) CdSe nanoparticles in colloidal solution. Panel a shows that spherical particles relax more rapidly than the rods. Panels b and c show that the excited electrons in both dots and rods relax more rapidly in higher excited states. These results are consistent with surface mechanism of relaxing excited electrons (see ref 37).

present on the surface becomes the most important parameter that determines its relaxation rate.

From Figure 2, one can then conclude the following:³⁷

(1) For spheres (top figure), as the diameter increases, the relaxation rate decreases. (2) For the rods (bottom figure), as the aspect ratio increases, the relaxation rate decreases. From this, one concludes that as the spheres (aspect ratio = 1) change to rods of the same diameter, the relaxation rate decreases. (3) Electrons in higher excited states (hot electrons) have larger electron density on the surface and can thus relax more rapidly by this mechanism.

In a detailed study, Klimov³⁸ found previously that the $P \rightarrow S$ electronic relaxation time in CdSe nanoparticles increases (i.e., rate decreases) as the sphere (dot) diameter increases. These results can now be explained by the

surface mechanism and support the first conclusion above. In our group, Darugar et al.³⁷ tested other predictions above. Figure 3a compares the decay of the excited state of dots with that of the rods, showing slower decay for the latter, supporting the second prediction above. Figure 3b compares the decay of higher and lower excited states for the dots, and Figure 3c compares the same for the rods. These results³⁶ support the third prediction above.

It is expected that the exact mechanism of the relaxation could differ from system to system, depending on the quality of the surface and the type of capping material or trapping sites. It could involve either energy transfer to the capping material or charge transfer (i.e., trapping of the excited electron) to the capping material or to

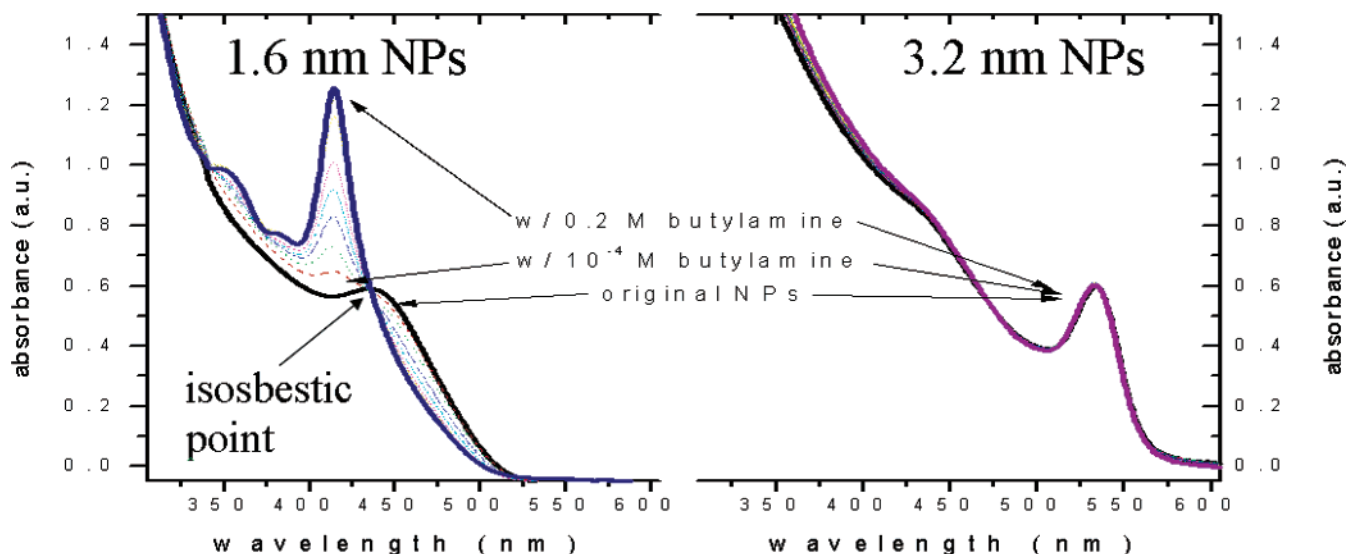


FIGURE 4. Smaller nanoparticles are even more different: the effect of adsorption of butylamine on the surface of 3.2 nm CdSe (right) and 1.6 nm CdSe (left) nanoparticles on their band gap visible absorption. While no effect is observed for the large nanoparticle, a blue shift of the absorption at 445 nm (to 414 nm) and sharpening of the spectrum is observed for the small nanoparticle. This change is found to be exothermic, activated, and size-dependent around the 1.6 nm size. See the text for a discussion of the kind of CdSe transformation occurring in the very small nanoparticles upon adsorption of the amine (see ref 39 for details).

surface defects or both energy and charge transfer. For a perfect surface (if such surface can be formed), the electron–hole coupling mechanism³⁰ could dominate.

D. More Interesting Properties for Even Smaller Nanoparticles: The Nanoparticle–Molecular Transition^{39,40}

As the size of the nanocrystal becomes very small (1.5 nm [less than 1.6 nm]), the fraction of surface atoms becomes large and their energetics determines a large fraction of the nanocrystal energy. Most of the atoms become exposed to the medium, and the adsorption of other species on their surfaces could have a large effect on the nanoparticle properties. In this section, the effect of adsorption of *n*-butylamine on the optical, kinetic, thermodynamic, and structural properties is discussed.^{39,40} CdSe nanocrystal has a metastable Wurtzite structure. As the nanocrystal becomes too small (1.6 nm), Landes³⁹ in our group found that the adsorption of butylamine to its surface changes its band gap at 445 nm (see Figure 4), which decreases in intensity as a new sharper band increases in intensity at higher energy (414 nm).⁴⁰ According to theory,⁴¹ a blue shift in the spectrum can result from either the formation of a smaller nanocrystal with a magic number of CdSe molecules or a change in the crystal from the metastable to the stable zinc blend structure.

The changes in the spectrum show a good isosbestic point, indicating that an equilibrium exists between two species (presumably the free nanoparticle and the nanoparticle with adsorbed butylamine). The equilibrium constant of this association reaction is determined as a function of temperature.⁴⁰ From this, the heat of the reaction is determined and found to be exothermic and size-dependent in the size range around 1.6 nm. The rate

of the transformation is also determined⁴⁰ as a function of temperature from which the value of the activation energy is determined, which is also found to be size-dependent. As the size of the nanoparticle increases, both the exothermicity and the value of the activation energy increase. However, the activation energy is found to increase much more rapidly with size than the exothermicity. This explains why these spectral changes are not observed³⁹ for the larger nanocrystals (e.g., the 2.2 nm or larger).

Whether the adsorption of the amine leads to the dissociation of some CdSe molecules (to attain a crystal with a magic number) or to changes in crystal phase is not yet known. In molecular language, we do not know whether the amine reacts with the CdSe to give CdSe crystals with a smaller number of CdSe molecules or whether the exothermicity of the reaction gives the CdSe crystal sufficient energy to go over the barrier and isomerize. There are two observations that might lend support to crystal structure changes. The first observation is that phase changes are observed to occur when pressure is applied to large CdSe nanocrystals.⁴² Second, the addition of butylamine to the small nanoparticles results in a decrease,⁴³ rather than an increase (as observed for the 2.2 and 3.5 nm particles), in the probability of the hyper-Rayleigh scattering. This suggests that the symmetry of the nanoparticle structure increases after the addition of the amine to the small nanoparticles but not to the large ones. The stable zinc blend phase for CdSe is indeed more symmetric.

Whether the structure or the size of CdSe nanocrystal changes upon adsorbing the amine can best be differentiated by direct structure determination. Due to the small size of the nanoparticles and the interference from the capping material and the amine, the high-resolution

transmission electron microscopy (HRTEM) method has not succeeded so far.

E. Electron and Hole Relative Rates of Crossing the Interface in a Composite Nanostructure⁴⁴ (Quantum Dot–Quantum Well Structure)

Weller⁴⁵ and his group were first to prepare and study the onion-shaped CdS·HgS·CdS quantum dot–quantum well (QDQW) nanoparticles in colloidal solution (see Figure 5). This nanoparticle has a CdS core capped with a shell of HgS, which is then covered with a shell of CdS. Upon excitation with femtosecond pulses at 400 nm, the electron and hole are separated within the CdS system. Since the band gap energy of the HgS is the lowest in this system, the electron and hole relax rapidly and cross the CdS–HgS interface into HgS well. They then radiatively recombine to give the characteristic HgS fluorescence.⁴⁶ The question that our group⁴⁴ had raised was which charge carrier, the electron or the hole, crosses the CdS–HgS interface first and why? To answer this question, we need to monitor the time of arrival of each carrier in the “HgS well” after separating them in the CdS core with a 400 nm laser pulse having 100 fs pulse width. The rise time of the fluorescence emission gives us the arrival time of the slowest carrier, since the emission requires the presence of the two carriers in the HgS well. This is only true if the recombination time of the carriers in the HgS well is very rapid. We found this to be the case. When the electron and hole are separated in the HgS well by exciting its band gap absorption, the observed fluorescence rise time is found to be <100 fs (bottom of Figure 5). This is much faster than the 1.5 ps observed for the HgS emission rise time if the carriers are separated in the CdS core and cross to the HgS well. The latter is shown on the top of Figure 5. This suggests that the crossing time of the slowest carrier (the electron or the hole) is 1.5 ps. We need now an independent measurement of the crossing time of one of the carriers. It is known that the hole in the HgS well has an absorption in the infrared region⁴⁷ at 4.7 μm. Monitoring the rise time of this absorption gives the arrival (crossing) time of the hole in the HgS well. This is found to be 150 fs. Thus, the 1.5 ps must be the crossing time of the electron.

Why does the electron transfer (cross) from the excited CdS core to the HgS well in a time that is 10 times slower than the hole? We proposed⁴⁴ the following explanation. As was discussed in the Introduction, the excited state of a semiconductor nanoparticle is a charge-transfer-type state. Thus, photoexcitation of the core produces $(\text{Cd}^+\text{S}^-)^*$, that is, an electron is transferred from S^{2-} to Cd^{2+} by light absorption. Now the relaxation of the electron and hole from the excited Cd^+S^- in the core to the $\text{Hg}^{2+}\text{S}^{2-}$ in the well can be represented by the following equation:

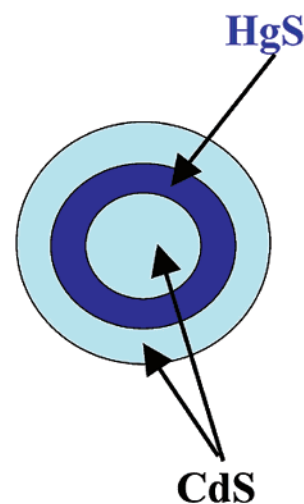
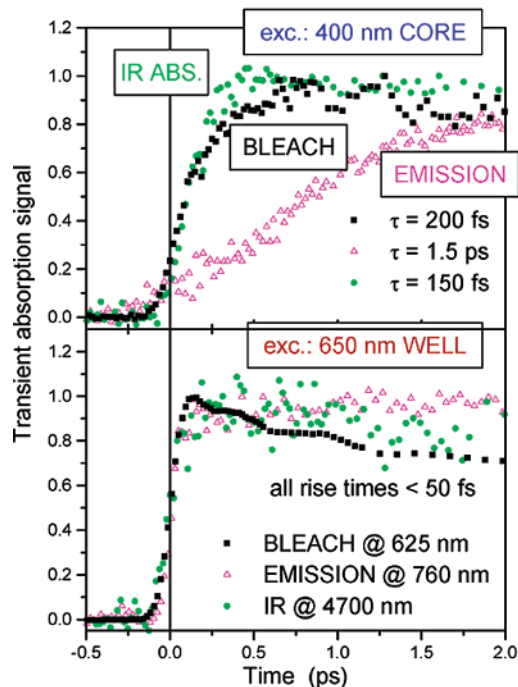
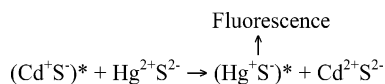


FIGURE 5. Electron crosses the interface 10 times more slowly than the hole in an electron dot–electron well nanoparticle. The transfer times of the electron and hole across the interface in a CdS/HgS/CdS quantum dot–quantum well nanoparticle are determined from the results in the top figure. The rise of the absorption shown in green is that of the hole as determined from its absorption in the HgS well. This is 10 times faster than the rise time of the emission (shown in red triangles). Since the HgS emission arises from the combination of the electron and hole in the HgS well, it is thus determined by the arrival time of the slowest carrier, which must then be the electron. This is true only if the electron and hole combine rapidly as soon as they cross CdS–HgS interface. This is supported by the results shown in the bottom part of the figure, which shows that if the electron and hole are formed in the HgS well by direct photoexcitation, they recombine very rapidly as shown from the rapid rise of the resulting emission (red triangles) (see ref 44 for details).

This change involves a double charge-transfer process. An electron is transferred from Cd^+ to Hg^{2+} to form Hg^+ in $(\text{Hg}^+\text{S}^-)^*$ and a hole (positive charge) is transferred from S^- in $(\text{Cd}^+\text{S}^-)^*$ to S^{2-} in $\text{Hg}^{2+}\text{S}^{2-}$ to form S^- in $(\text{Hg}^+\text{S}^-)^*$.

Thus, the hole is transferred from S^- to S^{2-} , that is, between the same chemical species in the two materials the MOs of which have great overlap with one another, and the Franck–Condon factors in the Marcus theory are thus large. However, the electron is transferred from Cd^+ in $(Cd^+S^-)^*$ to Hg^{2+} in $Hg^{2+}S^{2-}$, that is, between two different chemical species having orbitals of different sizes and energies. Thus, the Franck–Condon factors are expected to be small, and large amounts of energy have to be dissipated, making the rate of the electron transfer relatively slow, as observed.

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