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Observation of Large Changes in the Band Gap Absorption Energy of Small CdSe Nanoparticles Induced by the Adsorption of a Strong Hole Acceptor

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ABSTRACT

When butylamine in relatively high concentrations (0.1−0.25 M) is added to a colloidal solution of CdSe nanoparticles (NPs) that are approximately 1.6 nm in diameter, the band gap absorption changes from a broad, relatively weak absorption centered at 445 nm to a narrow, relatively strong absorption centered at 414 nm. The effect of concentration on the observed spectrum shows an isobestic point, suggesting an equilibrium between two species. The possible mechanisms for such a transformation are discussed.

1. Introduction. Colloidal techniques such as those introduced by Murray et al.[1] are widely employed for the preparation of CdSe nanoparticles (NPs). This method is useful for preparing highly crystalline NPs that range in size from one to several nanometers in diameter with wurtzite crystal structure. Several research groups have shown experimentally that the size and/or structure can be affected by temperature, pressure, or high-intensity light.[2−4] The size and shape transformations of NPs have been shown to depend on the NP size.[5,6] These experiments have suggested that for very small NPs, solvent and capping interactions play a comparatively larger role in the NP stability because these small NPs are primarily composed of surface atoms.

When the NP size is reduced such that the particle is essentially all surface, the curvature of the surface is so high that virtually all of the surface atoms have a slightly different coordination and/or effective oxidation state. The experimental and theoretical studies of very small (1−2 nm) CdS[7,8] and CdSe[9,10] NPs are examples of such NP systems that are dominated by surface interactions.

Previous work has suggested[11] that when butylamine is added to colloidal CdSe NPs of ∼3 nm in diameter, the amine binds to the NP surface and prevents the NPs from undergoing radiative electron−hole recombination. In this way, the luminescence quantum yield was quenched but the lifetimes were not affected. A comparative study revealed[12] that similar experiments performed on smaller NPs of approximately 1.6 nm in diameter yielded increased luminescence quenching, as well as lifetime quenching. It was suggested that in smaller NPs, the deep-trap luminescence pathways that result from enhanced surface discontinuities cause electron-transfer-induced quenching to be allowed in the smaller NPs. Thus butylamine can quench the luminescence of smaller NPs in two ways: by binding to surface sites and eliminating luminescence centers, as in larger NPs, and by undergoing electron transfer with deep trap sites, as suggested by the lifetime quenching. The previous reports[11,12] illustrate the contribution of surface effects to the luminescence characteristics of CdSe NPs. Additionally, the recent results of Talapin et al. suggest the use of hexadecylamine in the enhancement of fluorescence yield by adding the amine to the reaction mixture.[13] These results clearly indicate the different results that can be achieved by introducing surface additives during or after particle formation, as well as the importance of understanding the nature of the NP surface.

The current report presents the effects of adding amine to a colloidal solution of 1.6 nm CdSe NPs. When butylamine is added, the absorption spectrum of the CdSe NPs is shifted toward an absorption feature at 414 nm. The resulting absorption spectrum, regardless of the initial maximum and line width, exhibits a narrow band gap absorption at 414 nm. Additionally, this transition is found to be exothermic. Our experimental results suggest that the amine provides a pathway for the NPs to readjust to a more thermodynamically stable structure. The energy liberated by this process can be

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thought of as a surface interaction energy induced by the butylamine.

2. Experimental Section. Trioctylphosphine oxide (TOPO) and trioctylphosphine (TOP) capped CdSe NPs were prepared from $(CH_3)_2Cd$ and Se precursors by the method developed by Murray et al.[1] with the following modifications. After the TOPO was dried at 200 °C for 20 min, the temperature was lowered to 120 °C for NP preparation. The heating mantle was removed from the reaction vessel for injection of the precursors. After injection, the heating mantle was reapplied, and the temperature was raised very slowly to ~130−140 °C to establish a very slow and controlled growth rate.

After the preparation was complete, hexane was added to the NP/TOPO solution and the samples were brought to room temperature. This cooling in hexane causes much of the excess TOPO to crystallize. The NP/hexane samples were filtered. Size selective precipitation was not used to narrow the size distribution or to eliminate excess capping material beyond the initial step. The excess capping material is removed in the methanol titration/centrifugation process of size-selective precipitation.[1] If this process is performed, the NP samples will not resuspend in the common organic solvents. The samples were stored in the dark under argon to slow the surface degradation and Ostwald ripening processes that have been reported previously. By this method, very small NPs that are slightly over a nanometer in diameter are prepared. CdSe NPs in this size range are characterized by band-edge absorption of 400−450 nm.

Stock solutions of CdSe NPs were prepared in hexane or toluene. *n*-Butylamine, isobutylamine, tributylamine, aniline, benzylamine, hexadecylamine, and nitrobutane were used as purchased from Aldrich. Solvents were obtained from Fischer. Steady-state absorption spectra were performed using a Shimadzu UV-3101PC UV-vis−NIR scanning spectrophotometer. After an additive was placed in the NP solution, the sample was vigorously mixed for several seconds, after which the UV-vis absorption spectrum was immediately obtained.

Temperature controlled experiments were performed using a water/glycerin heat bath. The constant temperature solution was flowed through a metal cuvette holder placed inside the Shimadzu spectrophotometer, in which each CdSe NP sample was placed for 15 min to equilibrate the solution temperature. A thermocouple was placed inside the metal holder to monitor the temperature throughout the experiment. Butylamine was added to the sample, the solution was stirred, and measurements were taken after 20 min to ensure that the mixture had reached equilibrium at each temperature.

3. Results and Discussion. When *n*-butylamine was added to toluene solutions of ~1.6 nm CdSe NPs having absorption features ranging from ~400−500 nm, the samples exhibited a reduction in the original absorption feature and an increase in a strong, well-defined absorption at 414 nm. Figure 1 illustrates this effect on NPs that have an absorption maximum at 445 nm. As the amount of *n*-butylamine added to the NP solution increases, the original absorption feature at 445 nm gradually decreases in intensity while a new feature at 414 nm is formed. The presence of an isobestic point clearly shows that there are two species in equilibrium in solution. The NP sample to which *n*-butylamine has been added is characterized by the new absorption feature at 414 nm. It is clear in Figure 1 that the 1S transition feature at 414 nm exhibits a narrower line width than the initial feature at 450 nm, suggesting that the resulting sample has less inhomogeneous broadening than the original sample. Furthermore, it results from an electronic excitation that is higher in energy than the original absorption at 445 nm.

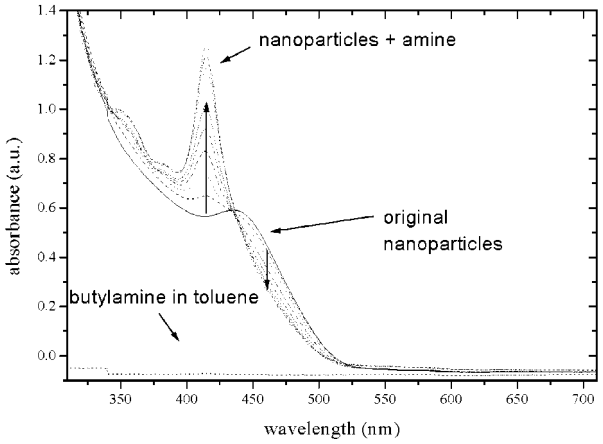

Figure 1. Absorption of the original NP solution is broad and centered at ~440 nm. As butylamine is added to the solution, the original absorption feature decreases and a new feature centered at 414 nm appears. The new feature exhibits a narrower line width than the original absorption band edge, suggesting that the transformation has involved a narrowing of the distribution of NPs.

These effects were found to depend on solvent and surface interactions, similar to the pressure-induced phase transition data from Tolbert and Alivisatos.[5] The effects of butylamine on NPs suspended in hexane were much less pronounced and not as quantifiable as in toluene solution. The importance of using butylamine as opposed to other electron donating species was also studied. Figure 2 compares the spectrum of a colloidal NP sample that exhibits a broad absorption at 445 nm with spectra of samples to which equal molar amounts of different nitrogen containing compounds have been added, e.g. isobutylamine, tributylamine, aniline, benzylamine, hexadecylamine, and nitrobutane. The results indicate that butylamine, followed by isobutylamine and benzylamine, was most effective of the compounds that were measured in causing the formation of the 414 nm peak. The important observation is that for all three amines, the band position and shape of the new band at 414 nm is very similar. This suggests that the absorption is due to electron and hole transitions in CdSe NPs that have been transformed to a smaller size with a narrower size distribution, and not due to an electronic transition in a CdSe-amine complex with the original NPs. Figure 2 also shows that the NP absorption spectra in the presence of benzyl and hexadecylamine are greatly reduced in intensity, suggesting the dissolution of the nanoparticles. We propose that butylamine possesses higher ability to both penetrate the bulky TOPO/TOP capping layer, and to use its nonbonding pair of electrons in stronger binding with the NP surface atoms to induce the observed

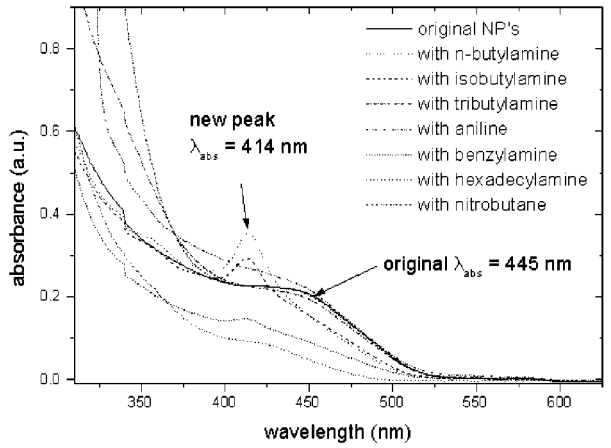

Figure 2. Comparison of the effectiveness of different types of amines on the formation of the 414 nm absorbing species illustrates the relative efficiency of these compounds in inducing a transformation to 414 nm. Isomolar amounts of each nitrogen compound were added to colloidal NP solutions. Butylamine, a monosubstituted straight chain amine, was more efficient at inducing the transformation than other amines. The nanoparticle spectra with benzyl and hexadecylamines decrease greatly in intensity, suggesting that the two amines dissolve the nanoparticles. Also, the effect of adding nitro-*n*-butane was examined as well, and in this oxidized form, the chemical adduct had no effects on the electronic structure of the NP.

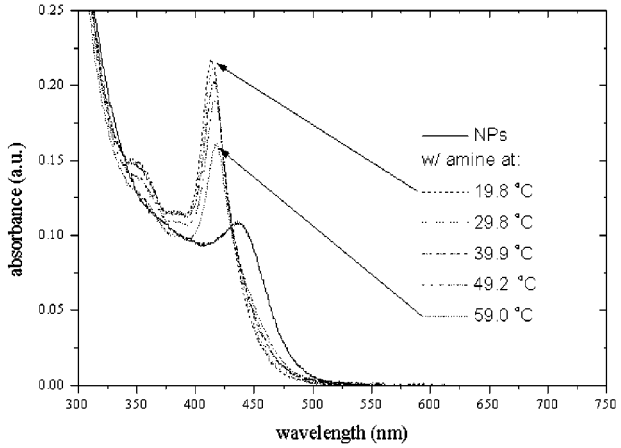

Figure 3. Temperature comparison of the transformation in the presence of butylamine shows that at higher temperatures there is less transformation, indicating that the interaction is exothermic.

changes in the electronic structure. The energy released by the binding is large enough to induce the breaking of Cd−Se bonds that are necessary for reorganization, but not so large as to destroy or dissolve the NPs. Such destruction can be observed in the spectra resulting from the addition of both hexadecylamine and benzylamine to the NPs, as seen in Figure 2. Similarly, when it was attempted to suspend NPs in neat butylamine, total destruction of the NPs resulted.

Finally, the relative transition from the 445 nm peak to the 414 nm peak as a function of temperature was studied. The absorption measurements indicate that the interaction reaches equilibrium in approximately 20 min. Figure 3 shows the results of this experiment. The most obvious results of this experiment are that the transformation is inversely related to the temperature. The highest degree of transformation occurs at the lowest temperatures, indicating that the equilibrium that is observed is exothermic.

The observed transformation is clearly dependent on the NP size, as a comparison between previous studies of 3.2 nm NPs[11] and the current study of 1.6 nm NPs reveals. Additionally, the experiment with different nitrogen-containing compounds suggests that the transformation cannot occur unless the additive can adsorb to the NP surface. Thus, surface effects are important as well.

In addition to NP size and surface, there are two other possible contributions to the relative stability of smaller NPs that may be involved in the observed transformation. First, geometrical effects can affect the stability of very small NPs. It has been known for many years in the field of cluster science that certain electronic and geometric combinations of atoms can yield stable structures at certain atomic arrangements, referred to as "magic numbers".[14] Recently, experimental confirmation of the stabilization of SiO_2 clusters into magic number formations has been reported.[15] The experimental results of Soloviev et al.[9] and the theoretical modeling by Eichkorn and Ahlrichs[10] support the discontinuity in stable CdSe NP sizes below ~2 nm in diameter and the formation of such magic number structures. The CdSe NP size associated with a band edge absorption centered at 414 nm has been observed in many reports of CdSe NP preparations and represents such a magic number structure for CdSe.[1,16]

The other factor that may contribute to small NP stability is crystal structure. In their theoretical study of small CdSe NPs, Eichkorn and Ahlrichs modeled several cluster sizes and predicted that a stable CdSe NP exists with a zinc blend conformation rather than the wurtzite structure that is most commonly observed in CdSe NPs.

4. Conclusions. The previous study revealed that the amine had no effect on the overall electronic structure of the 3.2 nm NPs, as indicated by the unchanged absorption spectra in the presence of amine.[11] In contrast, the addition of amine to a colloidal solution of 1.6 nm NPs initiates a dramatic change in the electronic structure of the NPs. NP size is clearly a factor in the transformation. Also, the amine must be able to bind to the NP surface in order to induce the transformation. Thus the surface is also important in this process. Other studies have shown[2,5,10] that crystal structure and geometry are closely related to both NP size and surface, with the relationship growing even more important at smaller NP sizes.

Based on the observations of the optical spectra in this report, as well as on the previous studies of small NP systems, the following changes are proposed. The amine binding to the NP surface is an exothermic process. The energy released by this process can induce changes in either the NP size or its crystal structure, or some combination of both. It is possible that the NP can undergo a phase transition from a wurtzite structure to a zinc blend structure. Additionally, Cd−Se bonds may be broken until the NP size can acquire a "magic number" configuration giving the particle a more thermodynamically stable structure. Alternately, both processes can occur simultaneously, leading to the appear-

ance of the 414 nm peak in the absorption spectrum and the narrowing of the distribution.

Attempts to characterize the structure changes by TEM and X-ray diffraction techniques were unsuccessful due to the small size of the particles relative to the capping material. A detailed thermodynamic and kinetic analysis of the transformation in the presence of butylamine is underway.

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