

Conformation of Ethylhexanoate Stabilizer on the Surface of CdS Nanoparticles

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CdS nanoparticles (NP), 22 Å, have been synthesized from cadmium 2-ethylhexanoate in DMSO as a uniformly sized dispersion. After ripening, CdS exhibits a sharp excitonic emission peak at 402 nm, while in freshly prepared dispersions a broad trapped emission at 510 nm dominates. By using one- and two-dimensional NMR spectroscopy, the conformation of the stabilizer adsorbed to the NP has been determined. The long hexyl chain of 2-ethylhexanoate ions spreads over the surface of NP, whereas the short ethyl end is primarily surrounded by DMSO. Surface modification of CdS with nucleophiles such as 4,4-bipyridine, thiophene, trimethylamine, and thiomolybdate anion results in a partial replacement of the stabilizer and reorientation of the hexyl chain away from the surface. The difference in the degree of replacement and/or conformational changes of 2-ethylhexanoate ion depends on the electron donor activity of the modifier.

Introduction

The investigation of nanoparticle-based materials has witnessed a period of intense growth over the past decade. This field has attracted the attention of numerous research groups of diverse research backgrounds. Recent advances in this area have been reviewed by several authors.^{1–7} One of the most significant aspects of these studies is the surface modification of nanoparticles (NP) which can be utilized as a method of variation of their optical properties and as a tool for their spatial organization.^{6–9} Theoretical and experimental study of the interactions between the electronic systems of the NP core and that of the modifier is expected to be one of the most interesting areas of research in this field.

Surface structure of NP is being studied by a variety of spectroscopic techniques including nuclear magnetic resonance spectroscopy (NMR). The latter has been applied to the investigation of nanoclusters quite extensively with the emphasis on the determination of surface density of stabilizer molecules and their chemical bonding with the cluster.^{10–19} Although NMR signals allow for registration of even small changes in both electronic interactions of various components and in their structure, the major concern for the broader application of this technique to NP research is the necessity to have relatively large quantities of NMR-active nuclei in the specimen. In this respect, a high particle per volume ratio in powders favors the application of the solid-state NMR for NP studies in order to achieve suitable signal intensity. The tradeoff for that is peak broadening and limited selectivity characteristic for the solid-state NMR. Conversely, various techniques of NMR in liquids afford determination of fine details of the structure of large molecular assemblies such as proteins and polymers.²⁰ A similar level of

structural description would be quite desirable for NP, too. However, low molar concentration of NP in solutions, their partial agglomeration, and line broadening due to long relaxation times¹⁴ create problems for the acquisition and analysis of the NMR data.

The purpose of this publication is twofold: (1) to suggest a synthesis of NP with surface properties convenient for the competitive modification by a large variety of organic substances and (2) to investigate the potential of the liquid-state NMR for elucidating the structure of the NP surface. The produced NP are stabilized by the 2-ethylhexanoate anion (ethex) and DMSO held in an adsorbed state by relatively weak noncovalent interactions. This affords facile displacement of the stabilizers by a variety of organic molecules. Along with apparent limitations, the weakly stabilized particles can also be used as a convenient model system for the description of electronic processes on the NP surface discussed in the subsequent publication. Relatively high mobility of ethex ions electrostatically adsorbed to the CdS surface alleviates relaxation time line broadening and allows for the accurate assignment and analysis of the NMR spectra. It is also demonstrated that NMR can be used to determine atomic groups residing in the vicinity of the semiconductor surface and to establish the conformation of ethex moieties.

Experimental Section

Cadmium 2-ethylhexanoate, Cd(ethex)₂, (Strem Chemicals), sodium sulfide (Ultra puris Fluka), (NH₄)₂MoS₄ (Strem, Aldrich), dimethyl sulfoxide (DMSO, Aldrich), DMSO-*d*₆ (Aldrich), polyethylene powder (spectral grade, Aldrich), polyvinyl spectroscopic grade (Aldrich), high-purity fused quartz plates (Monsanto), DMF (Fisher), MeCN (Aldrich), 99.999%, and argon gas were used in their commercial form. Ultrapure water (18 MΩ) was obtained from a Barnsted E-pure deionization system.

CdS nanoparticles were synthesized according to the follow-

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ing procedure. Typically, Cd(ethex)₂, 0.004 g, was dissolved in 49.9 mL of DMSO previously purged with nitrogen for at least 30 min in order to remove trace amounts of oxygen and hydrogen sulfide. Following sonication for 15–30 min, 0.10 mL of a stock Na₂S solution was rapidly injected into the vigorously stirred Cd²⁺ solution. The sodium sulfide solution was prepared fresh every time from 0.6 g of Na₂S·9H₂O dissolved in 25 mL of deoxygenated water (Ar bubbling for 30 min). Synthesis and subsequent ripening required about 6 h for completion. If stored in the dark, UV–vis absorption characteristics of thus-prepared CdS dispersions did not change for several months, whereas emission parameters did as described in the Results and Discussion section. Upon exposure to the ambient light, the peak at 365 nm became broader and gradually disappeared over a period of 1 week. A short exposure, for example, during the preparation of UV and NMR samples, did not cause any apparent change of its UV–vis spectrum. High-purity Na₂S and a low concentration of cadmium ions were important factors in producing CdS crystallites with a narrow size distribution. Cd²⁺ ions were taken in a 5% excess compared to S²⁻ ions to promote adsorption of the negatively charged 2-ethylhexanoate anion and, therefore, stabilization of the NP.

UV–vis absorption spectra were taken by using a HP 8453 and HP 8452A diode array Hewlett-Packard spectrophotometers. Fluorescence spectra were taken on a modular Fluorolog 3 SPEX spectrofluorometer.

Nuclear magnetic resonance (NMR) spectra were taken by using Varian Inova 400 and 600 MHz instruments operating at ¹H frequencies of 399.96 and 599.98 MHz, respectively. NP samples were dissolved in 99.9% DMSO-*d*₆ (Aldrich), with 1% v/v TMS as an internal standard. Presaturation of the residual solvent line was used to improve the dynamic range of the spectrum. The synthetic procedure described above was found to be essential for obtaining a well-resolved NMR spectrum.

Powder X-ray diffraction (XRD) spectra were collected by using a Siemens D5000 instrument. Samples for X-ray study were prepared by spreading a dispersion of NP in DMSO over fused quartz plates and evaporating the solvent at 10⁻⁵ mmHg in a Mag III Cook vacuum system.

High-resolution transmission electron micrographs (HR-TEM) were obtained by using a JEOL 4000 Ex instrument operating at 400 kV. A 200 mesh copper grid was coated with a layer of carbon. A drop of DMSO dispersion was deposited onto Cu grids, and then the solvent was evaporated under vacuum.

Results and Discussion

Structural Properties. Instead of covalently bound organic molecules, two relatively labile stabilizers have been employed: 2-ethylhexanoate anion (ethex) and DMSO. They are expected to be in a constant dynamic exchange between adsorbed and dissolved state and, therefore, can be easily replaced with other molecules. This property can be utilized for surface modification of NP with organic groups with moderate affinity to the CdS surface.

At sufficiently low concentrations of CdS, these stabilizers allow for the crystallization of narrow-sized NP with sharp absorption and emission peaks. After ripening, ethex/DMSO-stabilized CdS reveals a maximum of absorption at 365 ± 5 nm (3.4 ± 0.06 eV) (Figure 1) characteristic of the first excitonic state. A weak shoulder corresponding to the second excitonic transition, located in the valley of the absorption edge, can be observed around 335 nm. According to the experimental correlations between the position of the first absorption feature and the nanoparticle diameter for CdS,²¹ the 365 nm absorption

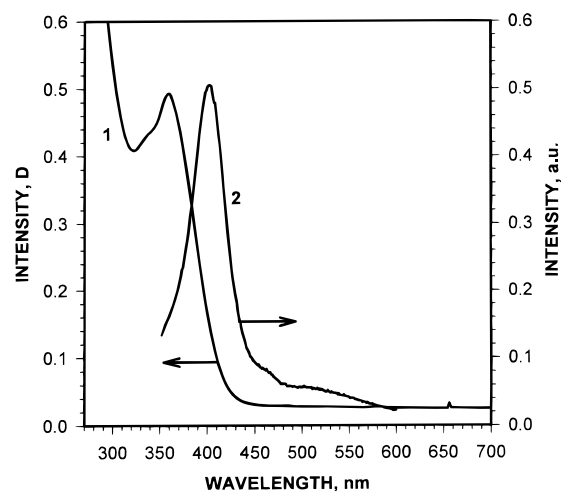


Figure 1. UV–vis absorption (1) and excitonic emission (2) spectra of CdS nanoparticles after storing in a light-protected environment for 3 weeks.

maximum corresponds to NP with a diameter of 22.5 Å, with the error in determination of the average particle size being 1.5 Å. The kinetics of CdS growth is found to be quite slow, which, in general, simplifies the synthesis of uniformly sized nanoparticles.^{22,23} Typically, it takes about 6 h until the UV–vis absorption spectrum ceases changing. The sluggishness of the process can be attributed to the low concentration of the precursors as well as to the surface activity of 2-ethylhexanoate anion adsorbing on CdS.

As-synthesized NP display a broad luminescence peak at $\lambda_{\max} = 510$ nm, $\Delta\lambda_{1/2} = 100$ nm, which is commonly attributed to the recombination of charge carriers trapped in the surface states. Within a period of 3 weeks, a sharp peak at $\lambda_{\max} = 402$ nm, $\Delta\lambda_{1/2} = 40$ nm, develops, while the intensity of the trapped emission significantly decreases (Figure 1). After that period of time, the emission characteristics do not change if the solution is stored in the dark. Annealing of the starting dispersion at 70 °C for 10 h only broadens and shifts the absorption peak to 400 nm.

HR-TEM images give a visual representation of ethex/DMSO-stabilized CdS (Figure 2). As expected, CdS NP are monocrystals with an average diameter close to that determined from UV data. Interatomic distances match lattice spacings for zinc blende structure with $d_{200} = 2.35$ Å, $d_{220} = 2.43$ Å, and $d_{111} = 3.30$ Å, as determined from TEM images and electron diffraction. X-ray diffraction peaks (Figure 3) are observed at $2\theta = 26.8^\circ$ ($d = 3.32$ Å), 28.7° ($d = 3.11$ Å), 31.0° ($d = 2.88$ Å), and 44.3° ($d = 2.04$ Å). The signals at $2\theta = 26.8^\circ$, 31.0° , and 44.3° correspond to the [111], [200], and [220] planes of cubic CdS, while the satellite peak at $2\theta = 28.7^\circ$ can be attributed to [101] plane in hexagonally packed CdS of larger particles formed during the vacuum concentration of CdS dispersions for XRD measurements. The cubic-to-hexagonal phase transition of CdS is quite facile due to low activation energy of this process, with cubic phase being metastable.²¹ Note that a size distribution of as-synthesized nanoparticle dispersions used in this study cannot be estimated on the basis of TEM or XRD data because the evaporation of DMSO and concentration of the sample (XRD) result in the destabilization of the colloid and subsequent growth of the particles. In particular, the absorption peak in reconstituted CdS colloids obtained after partial removal of DMSO undergoes a significant red shift while acquiring a steplike profile.

¹H NMR. For ethex/DMSO-*d*₆-stabilized CdS, ¹H NMR peaks observed are those arising from aliphatic protons in the

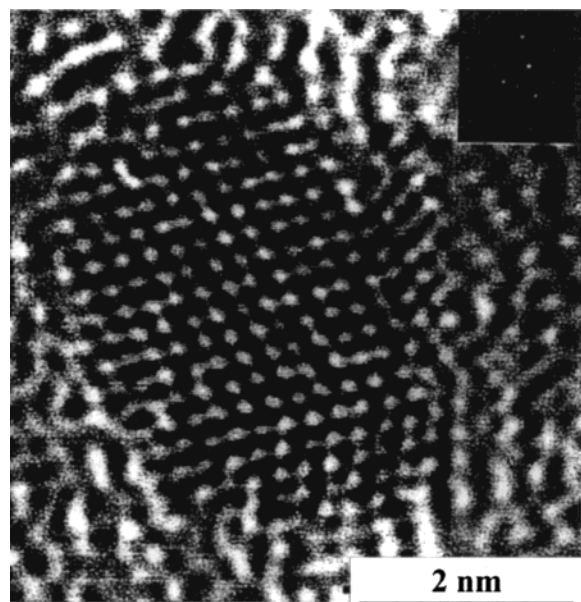


Figure 2. Transmission electron microscopy image of a selected CdS nanoparticle. During the TEM specimen preparation, the extensive agglomeration occurs due to removal of DMSO serving as one of the stabilizers. The image was selected from one of those of separately lying single nanoparticles, on which the effect of solvent removal is believed to be minimal.

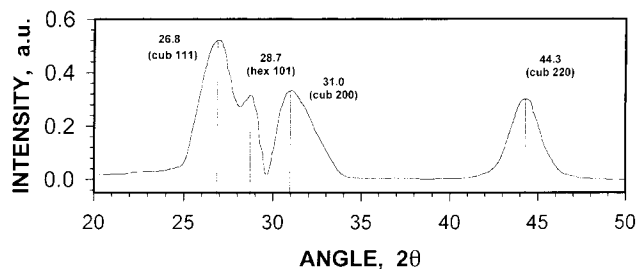


Figure 3. X-ray diffraction of nanoparticles obtained after vacuum evaporation of the solvent. The numbers by the peaks indicate the position of their maxima (in degrees) and atomic plane assignments. Asymmetric contour of the $2\theta = 31.0$ peak is likely to be attributed to the overlap with a broadened [102] peak from hexagonal CdS formed in some amount during the concentration of the sample, which is also evident from the presence of $2\theta = 28.7$ peak.

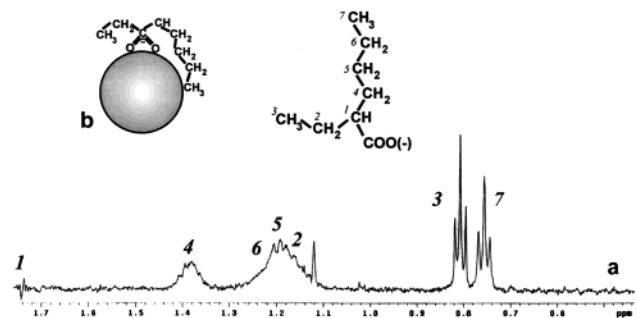


Figure 4. (a) Proton nuclear magnetic resonance spectra of CdS nanoparticles stabilized by DMSO- d_6 /ethex. (b) Conformation of ethex molecules on CdS nanoparticles. The numbers by the peaks indicate their assignments to corresponding protons of the ethex group.

2-ethylhexanoate moiety. They are organized in four groups of signals located in the region between 0.4 and 1.8 ppm (Figure 4). From the TOCSY (total correlation spectroscopy) spectrum of a sample of CdS NP bonded with ethex (Figure 5), it is possible to obtain the corresponding resonance assignments. The most downfield peak at 1.74 ppm corresponds to the α -CH

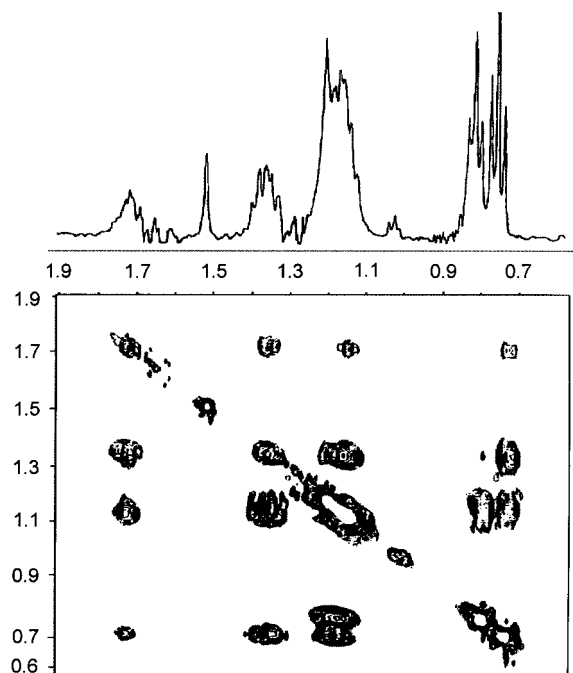


Figure 5. TOCSY nuclear magnetic resonance spectrum of ethex groups adsorbed on CdS. The standard, one-dimensional NMR spectrum is stretched along the top-left to bottom-right diagonal of the TOCSY spectrum. The 2D peaks located on the both sides of the diagonal are the mirror images of each other. Their presence reflects the fact that the protons corresponding to the signals located on the point of intersection of the diagonal with horizontal and vertical lines drawn from the 2D peak are cross-polarized, which indicates their spatial closeness.

group (hydrogen-1), which is attached to the electron-withdrawing carboxylate group. Particularly informative are the two well-resolved triplets at 0.81 and 0.75 ppm. Of these two triplets, the one resonating at 0.81 ppm is assigned to methyl-3, located on the ethyl chain. This assignment is based on the fact that this methyl group shows a scalar correlation (TOCSY cross-peaks) only to methylene-2, which in turn shows a correlation to the α -CH group (Figure 5). On the other hand, methyl-7, located on the hexyl chain, resonates at 0.75 ppm and displays short- and long-range scalar correlations, e.g., to methylene-4, at 1.38 ppm, to methylene-6 and -5, and to the α -CH group at 1.74 ppm, thus clearly identifying this resonance as originating from a methyl group associated with the hexyl chain. Assignments of other signals are indicated in Figure 4.

By comparison, in sodium 2-ethylhexanoate solution, the peaks from both $-\text{CH}_3$ groups of sodium 2-ethylhexanoate dissolved in DMSO- d_6 are magnetically equivalent (superimposable chemical shifts) and produce a triplet centered at 0.81 ppm. In sharp contrast, the signal from the $-\text{CH}_3$ group in the hexyl chain shifts upfield to 0.75 ppm, when ethex is attached to nanoparticle, and back to 0.81 ppm, when the ethex moiety is replaced by the modifier (Figure 6). Consequently, it is concluded that the adsorption of ethex to NP changes the environment around the methyl-7, which indicates that this methyl group appears to be in close proximity to the semiconductor core. Thus, ethex assumes a conformation presented in Figure 4b, where the long hexyl chain spreads over the CdS surface, being attracted to it presumably by van der Waals forces. The ethyl side chain resides mainly in the solution. Note that in the previous NMR studies covalently bound stabilizers in hydrophobic solvents were shown to be oriented perpendicularly to the CdS surface.^{14,16–19}

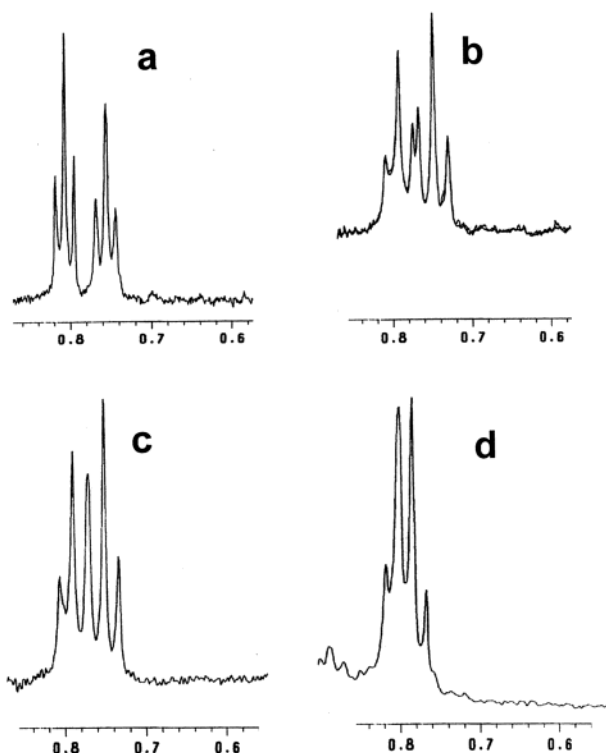


Figure 6. Proton nuclear magnetic resonance spectra of methyl protons in ethex for CdS nanoparticles progressively modified with MoS_4^{2-} in a molecular ratio of 0:1 ((a), naked CdS), 10:1 (b) 50:1 (c), and 150:1 (d) thiomolybdate groups per nanoparticle

The NMR spectra of NP are likely to undergo a transformation upon surface modification with nucleophiles such as thiols and heterocycles. Indeed, the progressive modification of CdS with thiomolybdate anion, MoS_4^{2-} , causes the CH_3 triplets at 0.75 and 0.81 ppm to collapse gradually into a multiplet at 0.80 ppm (Figure 6). Upon the modification of the NP surface, both CH_3 groups become magnetically equivalent, hence eliminating the shift in NMR lines corresponding to the methyl-7 group in NP-bonded ethex situated in close proximity to the CdS surface. Such behavior describes the partial replacement of ethex moieties from the CdS surface by potent nucleophilic molecules such as thiomolybdate and a concomitant change in the conformation of the CdS-adsorbed stabilizer. Within the degree of precision of NMR, one can conclude that the conformation change of ethex anion upon attachment of MoS_4^{2-} on the surface of NP is virtually complete. This includes both completely displaced molecules as well as the ones remaining in adsorbed state with the perpendicular orientation of the hexyl chains with respect to the CdS surface. It is necessary to point out that the modification with thiomolybdate strongly influences the electronic density of the NP surface. This factor must also affect the NMR line position. This effect is somewhat camouflaged by the straightening of the hydrocarbon chain, and it should be more pronounced for carbon and hydrogen atoms in close vicinity to CdS. However, their NMR signals overlap with those from other atoms (Figures 4 and 5) and are difficult to analyze.

The conformational character of the observed NMR line shifts can also be seen from the similarity of the spectral changes for structurally different surface modifiers. Besides thiomolybdate, several other compounds have been tested, which are expected to strongly bind to the CdS surface: 4,4'-bipyridine, 2-carboxythiophene, and trimethylamine. Notably, the nature of the observed changes in NMR signals for the CH_3 triplets at 0.75 and 0.81 ppm was identical for all these compounds (Figure 7). The difference between these modifiers was only in the

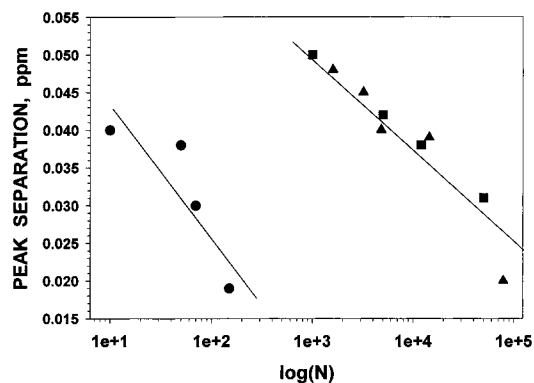


Figure 7. Dependence of the center-to-center peak separation between two terminal methyl groups on the concentration of the surface modifier: thiomolybdate (●), 4,4'-bipyridine (▲), and trimethylamine (■).

concentrations of a particular additive causing comparable NMR line shifts (Figure 7). As such, to reach 0.04 ppm separation between the peaks, the modifier per nanocluster ratio, N , for 4,4'-bipyridine should be about 100 times greater than for the thiomolybdate anion. This should be attributed to the difference in strength of the modifiers as nucleophiles: a large negative charge of sulfur atoms in MoS_4^{2-} results in much greater affinity to the electrophilic cadmium sites on the CdS surface than that of 4,4'-bipyridine. Interestingly, the data points corresponding to surface modification with trimethylamine and 4,4'-bipyridine fall on approximately the same line in Figure 7, whereas one may expect to see a stronger effect from the heterocycle. While being different as nucleophiles, other factors such as steric interactions with the protective shell of ethex molecules should also be considered, which may result in partial compensation of their nucleophilic strength.

Conclusion

CdS nanoparticles with narrow size distribution stabilized by 2-ethylhexanoate and DMSO were synthesized and characterized. The emphasis here was made on the ^1H NMR description of the conformation of the stabilizer molecule in the liquid state. The assignment of the observed signals was accomplished by using TOCSY 2D NMR spectra. One of the important features of the prepared dispersions is the observation of two separate triplets corresponding to the terminal methyl groups located on the ethyl and hexyl chains. This is indicative of a "wrap-around" conformation of the ethex molecules, which differs from the geometry of other stabilizers being perpendicularly oriented to the surface of NP. Packing of the hydrocarbon chains can be perturbed by the surface modification with various nucleophiles. This results in the detachment of hexyl chains from the surface of CdS. This study demonstrates the potential of ^1H NMR for elucidation of fine details of the surface structure of the protective organic shell around semiconductor NP.

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References and Notes

- (1) Alivisatos, A. P. *J. Phys. Chem.* **1996**, *100*, 13226. Alivisatos, A. P. *Endeavour* **1997**, *21*, 56–60.
- (2) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302–1317. Collier, C. P.; Vossmeier, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371–404.
- (3) Henglein, A. *Chem. Rev.* **1989**, *89*, 1861.
- (4) Weller, H. *Angew. Chem.* **1993**, *32*, 41. Weller, H.; Eychmuller, A.; Vogel, R.; Katsikas, L.; Hasselbarth, A.; Giersig, M. *Isr. J. Chem.* **1993**, *33*, 107.
- (5) Empedocles, S.; Bawendi, M. *Acc. of Chem. Res.* **1999**, *32*, 389–396. Norris, D. J.; Bawendi, M. G.; Brus, L. E. *Mol. Electron.* **1997**, 281–323.
- (6) Herron, N.; Thorn, D. L. *Adv. Mater.* **1998**, *10*, 1173–1184.
- (7) Woggon, U. *Optical Properties of Semiconductor Quantum Dots*; Springer-Verlag: Berlin, 1997.
- (8) Peng, X.; Wilson, T.; Alivisatos, P.; Schultz, P. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*(1/2), 145–147. Vossmeier, T.; Jia, S.; Delonno, E.; Diehl, M. R.; Kim, S. H.; Peng, X.; Alivisatos, A. P.; Heath, J. R. *J. Appl. Phys.* **1998**, *84*, 3664–3670.
- (9) Shiang, J. J.; Heath, J. R.; Collier, C. P.; Saykally, R. J. *J. Phys. Chem. B* **1998**, *102*, 3425–3430.
- (10) Badia, A.; Cuccia, L.; Demers, L.; Morin, F.; Lennox, R. B. *J. Am. Chem. Soc.* **1997**, *119*, 2682–2692.
- (11) Becerra, L. R.; Murray, C. B.; Griffin, R. G.; Bawendi, M. G. *J. Chem. Phys.* **1994**, *100*, 3297.
- (12) Lee, J. K.; Kuno, M.; Bawendi, M. G. *Mater. Res. Soc. Symp. Proc.* **1997**, *452*, 323–328.
- (13) Moran, K. L.; Harrison, W. T.; Kamber, I.; Gier, T. E.; Bu, X. H.; Herren, D.; Behrens, P.; Eckert, H.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1930–1943.
- (14) Sachleben, J. R.; Wooten, E. W.; Emsley, L.; Pines, A.; Colvin, V. L.; Alivisatos, A. P. *Chem. Phys. Lett.* **1992**, *198*, 431–436. Sachleben, J. R.; Colvin, V.; Emsley, L.; Wooten, E.; Alivisatos, A. P. *J. Phys. Chem. B* **1998**, *102*, 10117–10128.
- (15) Veinot, J. G.; Ginzburg, M.; Pietro, W. J. *Chem. Mater.* **1997**, *9*, 2117–2122.
- (16) Thayer, A. M.; Steigerwald, M. L.; Duncan, T. M.; Douglass, D. C. *Phys. Rev. Lett.* **1988**, *60*, 2673–2676.
- (17) Nosaka, Y.; Shigeno, H.; Ikeuchi, T. *J. Phys. Chem.* **1995**, *99*, 8317–8322.
- (18) Nosaka, Y.; Shigeno, H.; Ikeuchi, T. *Surf. Rev. Lett.* **1996**, *3*, 1209–1213.
- (19) Majetich, S. A.; Carter, A. C.; Belot, J. A.; McCullough, R. J. *J. Phys. Chem.* **1994**, *98*, 13705–13710.
- (20) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: New York, 1987.
- (21) Vossmeier, T.; Katsikas, L.; Giersig, M.; Popovic, I. G.; Diesner, K.; Chemseddine, A.; Eychmuller, A.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 7665–7673.
- (22) Peng, X.; Wickham, J.; Alivisatos, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 5343–5344.
- (23) Petrovski, J. M.; Wang, Z. L.; Green, T.; El-Sayed, M. A. *J. Phys. Chem. B* **1998**, *102*, 3316–3320.
- (24) The kinetic constant of growth implies that (1) the initial stage of nucleation and formation of CdS primary clusters has been completed, (2) the concentration of cadmium and sulfur ions is determined by the solubility product of CdS, and (3) CdS nanoparticles interact primarily with each other, molecules of solvent, and stabilizer(s).
- (25) The initial concentration of NP, 2×10^{-6} mol/dm³, is calculated by using the density of cubic CdS, 4.50 kg/dm³. Particles with $d = 22$ Å contain 104–100 CdS units per crystallite. The calculated rate constant takes into account an overlap of absorption spectra between starting and final CdS clusters.