

Surface Properties of Precipitated CdS Nanoparticles Studied by NMR

V. Ladizhansky,[†] G. Hodes,[‡] and S. Vega^{*,†}

Departments of Chemical Physics and Materials and Interfaces, Weizmann Institute of Science,
76100 Rehovot, Israel

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CdS and CdS:Mn nanoparticles were studied by ^{113}Cd and proton NMR. Nanoparticle samples were synthesized by precipitation of CdS from an aqueous solution of Na_2S and CdSO_4 . The nanoparticles were not deliberately capped by any surface-termination agent. The NMR spectra of CdS nanoparticles prepared with an excess of Cd consist of three frequency bands: a bulk line corresponding to the inner Cd atoms with full sulfur coordination, a broad band due to surface Cd atoms, and a sharp line of CdSO_4 in solution. The assignment of these lines is accomplished by experiments on S-rich samples, by the study of the temperature dependence of the spectra, and by comparing the chemical shift values of the lines with tabulated chemical shift values of different cadmium compounds. A significant amount of water was found in the samples. This water is trapped in microscopic pores resulting in a lowering of the water–ice phase transition and a significant shortening of the proton T_1 and T_2 relaxation times. The NMR spectra of CdS:Mn do not show any additional spectral structure. Mn^{2+} ions remain in the included water and/or are located at the nanocrystallite surface and do not appear to be incorporated inside the nanoparticles.

Introduction

The study of nanometer size semiconductor crystallites provides an opportunity to observe properties present neither in the bulk nor at the molecular limit.¹ As the diameter of a semiconductor crystallite approaches the exciton Bohr diameter, its electronic and optical properties change.² When the nanoparticle radius is smaller than the size of the bulk exciton, the band gap increases as the crystal size decreases resulting in a blue shift of the optical absorption spectrum. For example, for CdS this quantum size effect occurs when the crystallite diameter is comparable to or below 5–6 nm, the size of the exciton.

For particles of such a small size, a large percentage of the atoms is located on or near the surface. The existence of the vast interface between the nanoparticles or clusters and the surrounding medium can have a profound effect on the cluster properties.^{3,4}

How to control the cluster surfaces, and therefore the cluster properties, presents a major challenge in this field. Recently methods have been developed to cap the surface of the clusters with organic molecules that can prevent further growth, passivate surface electronic defects, and prevent agglomeration.^{5–7} By varying these molecules one can control the surface dynamics, the chemistry, and the degree of capping. Polyphosphates,⁵ thiols,^{6,7} and phosphine oxides⁸ are among the most commonly used capping reagents.

Another and related subject of intense research is the preparation and study of nanocrystalline thin films.⁹ Such films, consisting of nanocrystallites of a few nanometers, can easily reach a thickness of a few hundred nanometers. These films are characterized by large “internal” surfaces (“internal” in the sense that the surface atoms are for the most part not exposed to the front geometric surface of the semiconductor). A large surface area implies the possibility of a high concentration of

surface states which may act as trapping or recombination centers. It was shown that the surface state characteristics play a dominant role in the photovoltaic phenomena occurring in nanocrystalline films.¹⁰ It is expected that nanocrystalline powders, obtained by precipitation from aqueous solution, have highly imperfect surfaces that resemble the internal surface structure of thin films.

Here we investigate the use of NMR spectroscopy to characterize the surface and bulk properties of precipitated CdS nanocrystals. NMR spectroscopy is one of the techniques that can provide information about the electronic structure and environment of atoms in solids in a nondestructive manner. As a surface technique, however, NMR suffers the disadvantage of having a relatively low sensitivity and NMR of surfaces remains restricted to materials with high surface areas. Ultra-small semiconductor crystallites, with a low volume-to-surface ratio, are attractive targets for NMR spectroscopy. The surface species are expected to be directly observable, something that is impossible in normal polycrystalline materials with volume-to-surface ratios much larger than 1000. Consequently, nanocrystallites can be used as models for the study of phenomena such as the chemisorption and dynamics of organic molecules on surfaces. As was pointed out above, the surface itself plays an important role in the physics of nanocrystallites.

NMR of organic species bound to surfaces has been used to characterize the surface chemistry of nanoparticles. CdS nanocrystallites capped with thiophenol were studied by solution state ^1H NMR.¹¹ From these studies it was found that thiophenol is bound to well-defined discrete sites on the surface. These data also showed that the nanocrystallites are not completely capped by thiophenol molecules and that islands of covered regions exist which are separated by uncovered regions. It was concluded that the thiophenol molecules bind to cadmium atoms in a terminal manner and experience rotations about Cd–S and S–C bonds. The distance between binding Cd sites was estimated to be about 1 nm. The question of incomplete

[†] Department of Chemical Physics.

[‡] Department of Materials and Interfaces.

coverage was thoroughly studied by optically pumped ^{129}Xe NMR.¹² Nanocrystallites with low thiophenol coverage resulted in a xenon line shape consisting of two components, interpreted as xenon signals arising from two distinct surface domains. These results were consistent with previous studies by liquid state proton NMR.¹¹

In this study, we performed ^{113}Cd NMR experiments on samples that consist of CdS nanocrystals that are not capped by ligands. In this case the nonterminated surface cations can bind to solvent molecules, oxygen atoms or hydroxyl groups, and S^{2-} ions. It will be shown that the chemical shifts and relaxation times of the inner and surface cadmium atoms differ. The presence of large quantities of water in the sample is demonstrated, and the influence of the addition of small amounts of manganese to the sample on the NMR parameters is discussed.

Experimental Section

The nanocrystalline CdS samples were obtained by precipitation from a mixture of aqueous solutions of CdSO_4 and Na_2S . Deoxygenated aqueous solutions of Na_2S and CdSO_4 of molarity 0.1 M were prepared from $\text{Na}_2\text{S}\cdot 7\text{H}_2\text{O}$ and $3\text{CdSO}_4\cdot 8\text{H}_2\text{O}$. The reaction forming CdS occurs instantaneously. The precipitated powders were washed with water, filtered, and dried under vacuum in a desiccator. Doping with Mn^{2+} was accomplished by adding a suitable amount of $\text{MnSO}_4\cdot 6\text{H}_2\text{O}$ to the initial Cd solution. X-ray diffraction was utilized to determine the mean size and the crystal structure of the samples. The diffraction spectra were compared with known X-ray diffraction (XRD) spectra of the different crystal structures of CdS in a fingerprint manner to characterize the lattice symmetry type. The mean size of the nanoparticles was deduced from the width of the diffraction peaks and was found to be 3.5–4 nm. To define the concentration of Mn in the samples, atomic emission spectroscopy (AES) was used.

The samples consist of macroscopic clusters of CdS nanoparticles that are not dispersible in solution. Thus individual crystallites could not be observed in transmission electron microscopy (TEM) measurements.

All NMR experiments were performed on a home-built 200 MHz spectrometer with a Larmor frequency of the ^{113}Cd isotope equal to 44.366 MHz. Static NMR spectra in the temperature range of 180–400 K were acquired using a 10 mm Bruker multinuclear probe. The temperature was controlled using a variable-temperature unit W110512 of Bruker with a temperature stability of 0.2 K.

Magic angle spinning (MAS) experiments were performed using 7 mm high speed, 7 mm standard, or 5 mm high-speed probes of Doty Scientific Inc.

The echo sequence $\{\pi/2-\tau-\pi-\tau-\text{acquisition}\}$ was used for the detection of the signal. The length of the $\pi/2$ pulse varied from 3.2 to 5.5 μs . Cross-polarization experiments were done with a mixing time of 2 ms. To improve signal-to-noise ratios, the signals were accumulated from a large number of experiments with repetition times of 2, 4, 10, 40, and 200 s.

Results and Discussion

In this section our experimental ^{113}Cd NMR and ^1H NMR results of CdS nanoparticle samples are summarized. The NMR experiments were aimed to try to characterize the spectroscopic features of the bulk samples composed of these particles. According to the preparation procedure, the nanocrystalline samples can be divided into two groups: those prepared with an excess of cadmium ($\text{CdSO}_4:\text{Na}_2\text{S} = 2:1$) and those prepared

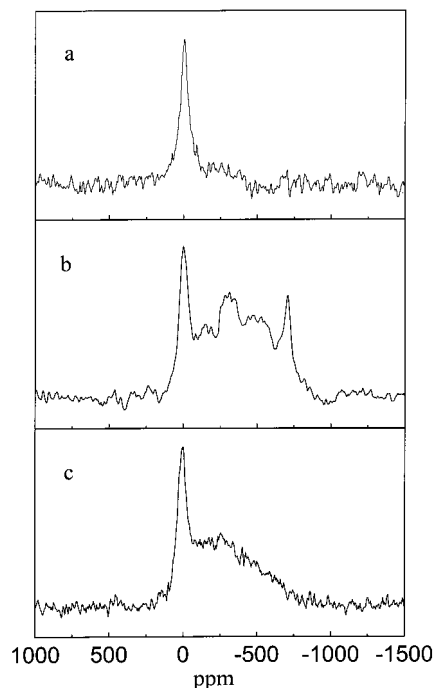


Figure 1. ^{113}Cd NMR spectra obtained from (a) a sample of S-rich CdS nanoparticles with 3.5 nm diameter and a sample of Cd-rich CdS nanoparticles, also of 3.5 nm, before (b) and after (c) washing with water during sonication. These spectra were obtained after the accumulation of 8000 echo signals, measured at a repetition time of 10 s.

with an excess of sulfur ($\text{CdSO}_4:\text{Na}_2\text{S} = 1:1.5$). The nanocrystallites in these samples are expected to have Cd-rich and S-rich surfaces, respectively. After precipitation, most of the CdSO_4 and Na_2S was removed by washing the samples in water.

CdS Nanocrystallites with S-rich Surfaces. The ^{113}Cd NMR spectrum of a polycrystalline bulk CdS sample consists of a single line of about 3 kHz width. The frequency position of this line was chosen as a reference for all cadmium spectra. The spectrum of the S-rich nanoparticle sample (Figure 1a) resembles the spectrum of the bulk material with a single inhomogeneously broadened line at the frequency of the bulk CdS.

CdS Nanocrystallites with Cd-rich Surfaces. Most experiments were performed on nanocrystallites with Cd-rich surfaces. The spectra of the Cd-rich samples differ from those of the S-rich samples. They contain a strong peak at the position of the CdS bulk line and, in addition, a broad negatively shifted band of lines between -750 and 0 ppm. The exact shape of this broad feature varied from sample to sample, but its location and overall width remained constant (Figure 1b).

The difference in spectral structure between Cd-rich and S-rich samples can be explained by the fact that the surface atoms of the Cd-rich samples are only partially coordinated by sulfur, while in the S-rich samples, most cadmium atoms are coordinated by four sulfurs. Since the bond structure on the surface is distorted, the NMR signal from the surface nuclei is expected to be shifted by different chemical shift interactions. Since the volume-to-surface ratio of our 3.5–4 nm sized samples is ca. 5 and the fully relaxed NMR line intensities are proportional to the number of contributing nuclei, the lines corresponding to the surface atoms should be detectable. Therefore it is likely that the broad component in the spectra of Cd-rich samples results from cadmium atoms in various surface conformations. Using the shell model of Lippens and Lannoo¹³ and assuming that the last shell is composed of mostly

Cd atoms, the spectral band of the surface should account for 40–45% of the signal for nanoparticles of approximately 3.5 nm. Experimentally we found that the ratio between the bulk peak and the broad line was approximately one. The T_2 relaxation time of this broad line is of the order of 300 μ s, which corresponds to the line width of about 25 ppm. Spinning the sample at the magic angle did not have any effect on the overall line width of the band. This implies that the broad line is composed of narrow inhomogeneously shifted isotropic peaks, due to cadmium atoms having different local environments. The broad peak is centered around -350 ppm, which is close to the isotropic chemical shift of ^{113}Cd in CdO .¹⁴

In most Cd-rich samples, an additional narrow peak at -760 ppm appeared that can be assigned to the Cd signal of CdSO_4 in solution (Figure 1b). This line could be removed by additional washing of the samples in water during sonication (Figure 1c). The origin of the line is furthermore evident from its isotropic shift value.¹⁴ The absence of any sideband in the MAS spectra is an indication that the line does not originate from solid CdSO_4 .

The spin–lattice relaxation times of the lines are significantly different from one another. The solution line has a T_1 value of 1.5 s, the T_1 of the surface band varies between 3 and 5 s, and the bulk line has a relaxation time of about 70 s. These differences could be attributed to the surface kinetics or the dipolar interactions with protons resulting in shortening of the spin–lattice relaxation times. One should notice that the line due to tetrahedrally coordinated cadmium atoms has a shorter relaxation time than the ^{113}Cd line in macrocrystalline samples of CdS, where it is longer than 200 s at room temperature.¹⁵

To investigate the origin of the shifts, a set of temperature-dependent NMR experiments was performed. Lowering the temperature caused a change in the relative intensities of the spectral bands in the nanocrystalline samples but did not change their shifts, indicating that they all stem from the chemical shift interactions (Figure 2).

To show that the surface cadmium atoms are responsible for the spectral structure between -750 and 0 ppm, a Cd-rich sample with a particle size of 3.5 nm was placed in a glass tube and heated to 300 $^{\circ}\text{C}$. A flow of a $\text{H}_2\text{S}/\text{H}_2/\text{N}_2$ gas mixture was applied to this sample for 10 min to create an S-rich atmosphere that removes and replaces the oxygen atoms at the surface. After this treatment, the powder contained particles of about 10 nm in size (measured by XRD) and its spectrum resembled that of the S-rich CdS sample without any additional spectral features.

These results were compared with an experiment on an annealed sample, but in the absence of H_2S . A sample was kept at 100 $^{\circ}\text{C}$ for 7 h under vacuum in a sealed ampule to preserve the Cd to S ratio. After the sample returned to room temperature, the spectrum was measured and compared with the original one. As can be seen in Figure 3, the broad band is present in the spectrum, although its intensity is reduced probably due to an increase of the volume-to-surface ratio. The solution CdSO_4 line appears in the spectrum, suggesting that on heating, some of the surface cadmium atoms are redissolved in the aqueous solution surrounding the particles. XRD measurements revealed that the average size of the nanocrystallites changed from ca. 4 nm to ca. 11 nm as a result of the heating. These two experiments provided further evidence that the broad band is due to surface species.

An additional indication for the surface cadmium atoms is their chemical shift values. They spread over the wide range of frequencies that covers chemical shift values of many Cd

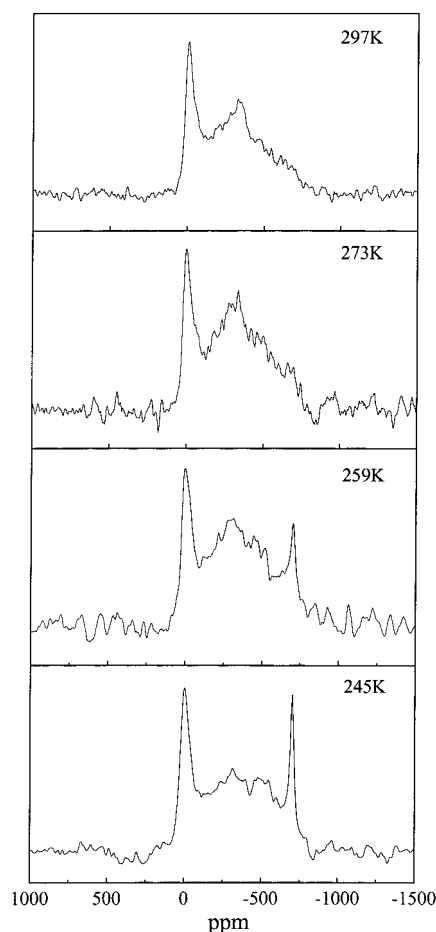


Figure 2. ^{113}Cd NMR spectra obtained from Cd-rich CdS nanoparticles of 3.5 nm at different temperatures. These spectra were obtained from 8000 accumulated echo signals, measured at a repetition time of 10 s.

compounds, in particular CdS (0 ppm), pure CdO (-259 ppm), and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (-759 ppm).¹⁴ This is consistent with our assumption that some of the cadmium surface atoms are oxidized, some are probably bound to S–O, and some are bound to hydroxyl groups. Although the chemical shift of the $\text{Cd}(\text{OH})_2$ is -958 ppm,¹⁴ which is about 200 ppm outside the spectral range, Cd atoms bound to hydroxyl groups on the surface need not necessarily have the same chemical shift as that of cadmium hydroxide. The presence of bound water or hydroxyl groups at the surface was demonstrated by cross-polarization (CP) experiments. In CP experiments, the protons having a high natural abundance of 99.985% and a high gyromagnetic ratio are excited, and their polarization is transferred via the nuclear dipole–dipole interaction to cadmium spins having a low natural abundance of 12.26% and a relatively low gyromagnetic ratio. The cadmium spins that are in a close proximity to protons will mostly be affected. The result of the CP experiment with a mixing time of 2 ms is shown in Figure 4. To remove any residual magnetization, a train of 20 $\pi/2$ pulses was applied prior to the CP pulse sequence. The bulk peak is significantly suppressed and could be due to Cd atoms that are tetrahedrally coordinated but not far from the geometric surface. The broad band is excited due to polarization transfer from protons of the hydroxyl groups or probably from water protons adsorbed on the surface to cadmium atoms. The broad band can therefore be interpreted as a surface signal. The relatively low signal-to-noise ratio of the CP spectrum was expected because a relatively short mixing time of 2 ms was chosen to prevent signal decay due to short $T_{1\rho}$ values.

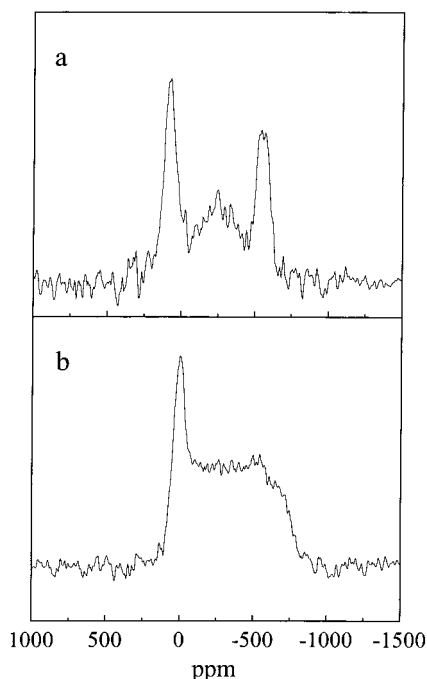


Figure 3. ^{113}Cd NMR spectra of Cd-rich sample with particles of size 3.5 nm. The sample was kept at 100 °C for 7 h in a sealed ampule. Spectrum a was obtained after cooling of the sample to room temperature, and spectrum b was obtained of the same sample before heating. The repetition time of the experiments was 10 s, and the signals were obtained after accumulation of 8000 echo signals.

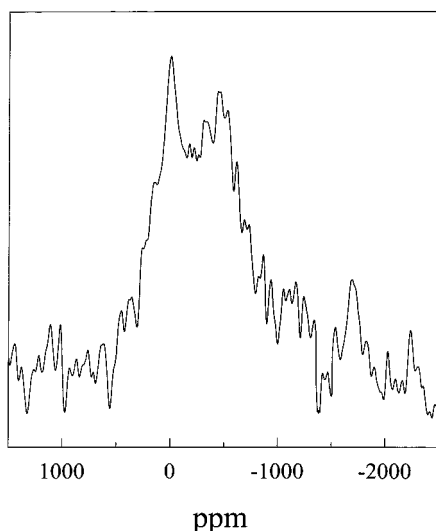


Figure 4. The cross-polarization ^{113}Cd NMR spectrum of a Cd-rich sample of nanoparticles with 3.5 nm diameter. This spectrum was obtained after 120 000 spin-echo accumulations after the CP mixing time. The repetition time of the experiment was 2 s, and the length of the mixing time 2 ms.

Water Content. To study the water content of our samples, we used proton NMR. The integrated intensity of the proton NMR lines of a 3.5 nm sample was compared with the intensity of a standard water sample. The results of these measurements showed that the sample contains approximately 75 mg of water per 1 g of powder, corresponding to a water content of about 25% in volume. Freezing of water occurs over a wide range of temperature. Cooling the sample to 142 K resulted in a reduction of the integrated intensity of the liquid water line to 10%. The disappearance of the sharp liquid-ice phase transition in microscopic pores is a well-known phenomena and was observed previously.¹⁶ The proton line is homogeneously

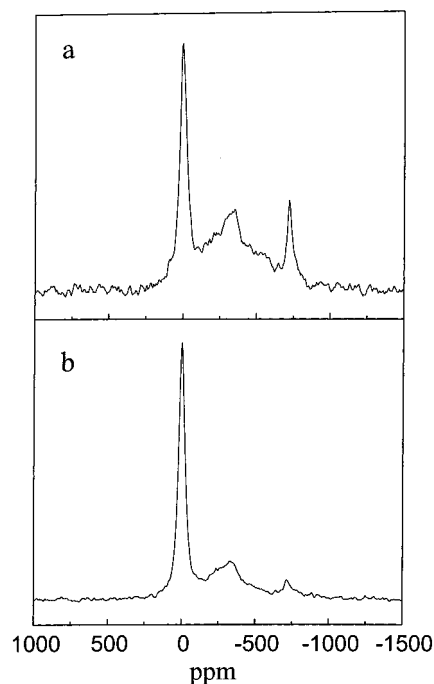


Figure 5. ^{113}Cd NMR spectra obtained from the Cd-rich CdS:Mn samples of nanoparticles, with 4 nm diameter, with atomic concentrations of paramagnetic ions equal to (a) 0.3% and (b) 0.07%. The repetition time of these experiments was 300 ms, and the spectra were obtained after 12 000 echo signal accumulations.

broadened and T_1 and T_2 relaxation times are significantly shorter than those in bulk water, indicating that the water is trapped in small pores. It was proposed¹⁷ that there are two types of water in microscopic pores: unbound, experiencing isotropic motion, and bound water, adsorbed on the crystalline surface. The exchange between these two types of water defines the relaxation times. The relatively large line width of the solution CdSO_4 line can also be due to restricted geometry: if the size of the pores is smaller than or comparable to the mean free path of the Cd ions, their correlation and therefore also their relaxation times shorten.

^1H and ^2H NMR spectra of one of the samples were measured after addition of 600 mg of powder to 150 mL of D_2O without sonication and drying for 48 h. The H_2O content of the sample did not change significantly, and only about 2 mg of D_2O was added to the sample. This suggests that water pockets are formed that are nearly closed and that do not allow easy exchange with surrounding water. Pumping the sample continuously and keeping it at 10^{-5} Torr for 72 h removed only 60% of the water.

The tenacity of the water in the samples is very significant for the interpretation of surface phenomena of these particles. It was reported that adsorption of water vapor drastically altered the photovoltaic properties of nanocrystalline CdSe thin films.¹⁰ It has yet to be seen if our findings reflect the water content of the nanocrystalline films.

NMR of the Nanocrystallites Doped by Mn^{2+} . One way to overcome the long T_1 relaxation times of the sample is to add a relaxation reagent, for example, in the form of Mn^{2+} doping of the nanoparticles. For this purpose, samples with Mn^{2+} atomic concentrations of 0.3% and 0.07% (measured by AES) were prepared. These concentrations correspond to 4 and 1 Mn^{2+} ion per particle, respectively. Figure 5 shows ^{113}Cd NMR spectra of these two samples. One can see that the Mn^{2+} ions do not induce paramagnetic shifts in the spectrum as was also observed in bulk CdSe samples.¹⁸ The spin-lattice

relaxation times of the two samples were approximately 500 ms and 3.9 s for the bulk line and 160 ms and 1 s for the surface line, respectively. These values were obtained by saturation recovery experiments. The signal intensities of these experiments could be fitted to single exponents. The primary mechanism of the relaxation is the dipolar interaction between the paramagnetic ions and the Cd nuclear spins, which rapidly decays for increasing distance. This means that Mn^{2+} ions mostly influence the relaxation of those Cd nuclei that are in their close proximity. If Mn impurities were randomly distributed in the inner part of the crystallites, there would be no difference in relaxation times between surface and the bulk peak. Moreover, after washing the samples in water and during sonication, the relaxation times approach those of the undoped samples. Thus we must assume that most Mn^{2+} ions stay in solution and/or are located on the surface (we cannot distinguish between these two options) and provide an equal relaxation time for all surface atoms, influencing the bulk atoms in a minor fashion.

Summary and Conclusions

Cd-rich nanoparticles have various chemically distinct surface sites: some surface Cd atoms are bound to hydroxyl groups and others are oxygenated, as deduced from their chemical shift values. In S-rich nanoparticles, all cadmium atoms are equivalently coordinated and only one NMR line is observed. Proton NMR shows that large amounts of water are trapped between the particles and that part of the water is bound to the nanocrystallite surface. The influence of the Mn-doping of the CdS nanoparticles was also studied. The difference between the bulk and the surface T_1 relaxation times is an indication for the fact that the Mn^{2+} ions are located outside the crystallites, either in solution or adsorbed on the surface.

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