Photochemical Instability of CdSe Nanocrystals Coated by Hydrophilic Thiols

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Abstract: The photochemical instability of CdSe nanocrystals coated by hydrophilic thiols was studied nondestructively and systematically in water. The results revealed that the photochemical instability of the nanocrystals actually included three distinguishable processes, namely the photocatalytic oxidation of the thiol ligands on the surface of nanocrystals, the photooxidation of the nanocrystals, and the precipitation of the nanocrystals. At first, the thiol ligands on the surface of a nanocrystal were gradually photocatalytically oxidized using the CdSe nanocrystal core as the photocatalyst. This photocatalytic oxidation process was observed as a zero-order reaction in terms of the concentration of the free thiols in the solution. The photogenerated holes in a nanocrystal were trapped onto the thiol ligands bound on the surface of the nanocrystal, which initiated the photooxidation of the ligands and protected the nanocrystal from any photooxidation. After nearly all of the thiol ligands on the surface of the nanocrystals were converted into disulfides, the system underwent several different pathways. If the disulfides were soluble in water, then all of the disulfides fell into the solution at the end of this initial process, and the nanocrystals precipitated out of the solution without much variation over their size and size distribution. When the disulfides were insoluble in water, they likely formed a micelle-like structure around the nanocrystal core and kept it soluble in the solution. In this case, the nanocrystals only precipitated after severe oxidation, which took a long period of time. If the system contained excess free thiol ligands, they replaced the photochemically generated disulfides and maintained the stability and solubility of the nanocrystals. The initiation stage of the photooxidation of CdSe nanocrystals themselves increased as the thickness and packing density of the ligand shell increased. This was explained by considering the ligand shell on the surface of a nanocrystal as the diffusion barrier of the oxygen species from the bulk solution into the interface between the nanocrystal and the surface ligands. Experimental results clearly indicated that the initiation stage of the photooxidation was not caused by the chemical oxidation of the system kept in air under dark conditions or the hydrolysis of the cadmium−thiol bonds on the surface of the nanocrystals, both of which were magnitudes slower than the photocatalytic oxidation of the surface ligands if they occurred at all. The results described in this contribution have already been applied for designing new types of thiol ligands which dramatically improved the photochemical stability of CdSe nanocrystals with a ligand shell that is as thin as ∼1 nm.

Introduction

Colloidal inorganic nanocrystals have been of great interest for fundamental research and industrial development in recent years due to their flexible processibility and unique properties.[1,2] Colloidal nanocrystals are metastable species in comparison to the corresponding bulk crystals/solids and have to be kinetically stabilized. The most common method to keep them stable is chemically attaching a monolayer of organic molecules to the atoms on the surface of nanocrystals. These organic molecules are often called surfactants, capping groups, or ligands. In addition to the protection function, this monolayer of ligands on the surface of a nanocrystal provides the necessary chemical accessibility for the nanocrystals by varying the terminal groups of the ligands pointing to the outside environment. For both of the functions, the stability of the ligands on the surface of nanocrystals is the key concern, which ultimately determines the stability of the entire nanocrystal/ligands complex.

Not much is known regarding the nature and chemical properties of the binding between nanocrystals and their ligands. When people look for ligands for nanocrystals, a general practice is to borrow knowledge from traditional solution-coordination chemistry and surface chemistry on bulk materials.[3,4] This approach has been successful qualitatively in many cases, although there are some obvious structural and chemical distinctions between solution ions, atoms on flat bulk surfaces, and atoms on the surface of nanocrystals. For example, cadmium ions in solution absorb minute amounts of UV and visible light. In contrast, cadmium ions on the surface of CdSe nanocrystals play a very active role in the strong absorption of nanocrystals.[2] This may result in strong photochemical activities of the cadmium−ligand bonds formed on the surface of the nanocrystals. In fact, thiol-coated CdSe nanocrystals have shown very profound photochemical instability in solution. Compared to atoms on the flat surface of bulk substrates, the binding abilities

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of the atoms on the curved surfaces may be affected by their diverse structural environments (curvature, shape, etc.) and size-dependent electron configurations.

It is very important to understand the photochemical instability of the thiol-stabilized nanocrystals. Thiols are probably the most utilized ligands for stabilizing semiconductor[3,5−8] and noble metal[4,9−12] nanocrystals. They have been used almost exclusively in the biomedical-related studies based on nanocrystals. Unfortunately, the stability of the thiol-stabilized nanocrystals used, especially in the case of semiconductor nanocrystals, is not satisfactory mainly due to the photooxidation of the nanocrystal/ligands complex. The unstable nature of these nanocrystals makes it hard to reproducibly apply chemical and biochemical procedures to them. Knowledge regarding the photochemical instability of the thiol-coated nanocrystal complex will certainly help to discover an optimal solution for the photochemical instability of these nanocrystals. Furthermore, methods established and knowledge gained by studying the photochemical instability of thiol-coated nanocrystals may provide a starting point to investigate other chemical and photochemical processes occurring on the surface of nanocrystals.

Experimentally, colloidal semiconductor nanocrystals have an intrinsic advantage over their metal counterparts. Their strong size-dependent optical properties can be used as the probes for the photooxidation processes.[2] In addition, the exceptional control over their size, size distribution, and shape in the synthesis of cadmium chalcogenides nanocrystals[13,14] provides good samples for some delicate studies, such as exploring any size/shape-dependent chemical and photochemical properties of nanocrystals.

The results described below will reveal that the photochemical instability of thiol-coated CdSe nanocrystals actually includes three different processes. When the photooxidation started, the ligands were catalytically oxidized under radiation of UV light (254 nm) to form disulfides with CdSe nanocrystals acting as the photocatalysts. After this step, the nanocrystal/ligand complex may undergo several different processes upon the solubility of the disulfides and the availability of excess free thiol ligands. The results indicate that dithiols, which have a strong tendency to form intramolecular disulfides and cannot pack as densely as the mono-thiols, are not a good choice for improving the photochemical stability of nanocrystal/ligand complexes. The photochemical instability of the thiol ligands is also independent of the acidity of the thiols. The diffusion of oxygen was the rate-determining step in the photooxidation of the nanocrystal/ligand complexes. In comparison to the photochemical instability, the instability of CdSe nanocrystals under dark conditions caused by the chemical oxidation or the hydrolysis of the cadmium−ligand bonds on the surface of nanocrystals is negligible.

The experimental results indicate that the photochemical processes on the surface of colloidal nanocrystals may be assessed more accurately and conveniently in comparison to the same types of studies applied to self-assembled monolayers (SAMs) on the flat surfaces of bulk materials.[15,16] This is so because colloidal nanocrystals possess a much larger surface-to-volume ratio, and they can be dispersed readily in a variety of solvents. The experimental results have been used for the design and development of a series of exceptionally stable nanocrystal/ligand complexes, which are nanocrystals stabilized by dendron ligands.[17]

Experimental Section

Chemicals. Technical grade (90%) trioctylphosphine oxide (TOPO), technical grade (90%) trioctylphosphine (TOP), cadmium acetate hydrate (99.99+%), selenium powder (−100 mesh, 95%), anhydrous toluene (99.8%), mercaptoacetic acid (MAA, 97+%), 4-mercaptobenzoic acid (MBA, 97%), 3-mercaptopropionic acid (MPA, 99+%), 11-mercaptoundecanoic acid (MUA, 95%), 16-mercaptohexadecanoic acid (MHDA, 95%) and deuterium oxide (99.9% atom D) were purchased from Aldrich. Dihydrolipoic acid (DHLA) was prepared following a published method using thioctic acid purchased from Aldrich.[18] 1,4-dithio-D,L-threitol (DTT) was purchased from Alfa. Anhydrous ethyl ether, toluene, acetone, ethyl acetate, and methanol were purchased from EM Science. Both the ethyl acetate and methanol were of HPLC grade.

Synthesis of CdSe Nanocrystals.[13] A selenium stock solution was prepared in a drybox under a nitrogen atmosphere. The solution was made by mixing 0.8 g of selenium, 20 g of TOP, and 0.35 g of anhydrous toluene (99.8%). The solution was stored in a glass vial and sealed with a rubber septum. Forty grams of TOPO were weighed in a reaction vessel, and 0.5 g of cadmium acetate were added. The vessel was placed under argon flow and heated to 330 °C. At this temperature the selenium stock solution was swiftly injected into the reaction vessel in a single step. The reaction temperature was adjusted to 270 °C immediately after the injection. Small aliquots of the reaction mixture were taken at 1-min intervals to assess the reaction progress with a UV spectrometer. The reaction was stopped 5 min after the injection, and heat was immediately removed. The reaction mixture was allowed to cool to ∼30−50 °C, and methanol and acetone were added to precipitate the nanocrystals. The vessel was covered to protect it from light and was left standing for ∼2 h to allow the nanocrystals to settle. The supernatant was decanted, and the precipitate was centrifuged to remove remaining solvent. The remaining nanocrystals were then stored under dark conditions without drying. The size of the nanocrystals synthesized by the above procedure was about 3.2 nm with the first exciton absorption peak at about 555 nm.

Typical Synthesis of Thiol-Coated Nanocrystals.[3] Twenty milligrams of MUA were placed in a reaction vessel. Fifteen mililiters of methanol (11.85 g) were added and the pH was adjusted to >10 with tetramethylammonium hydroxide pentahydrate. Under dark conditions, 20 mg of CdSe nanocrystals were dissolved in the mixture, and the vessel was placed under argon flow. The mixture was heated under reflux at 65 °C overnight. The reaction was stopped and allowed to cool to ∼28 °C, removed from argon, and kept out of the light. Nanocrystals in 2-mL aliquots were precipitated with ethyl acetate and ether. The aliquots were centrifuged, and the supernatant was decanted. Methanol was added to dissolve the precipitate, and ethyl acetate was added to reprecipitate the nanocrystals. The mixture was centrifuged, and the supernatant was removed. The precipitate was redissolved in methanol and precipitated with ethyl acetate once more. The final purified nanocrystals were dried 5 min in a vacuum oven (>30 inHg) and dissolved in 400 μL of water or deuterium oxide (for NMR studies). This same method was used in the synthesis of the other types of thiol-coated CdSe nanocrystals.

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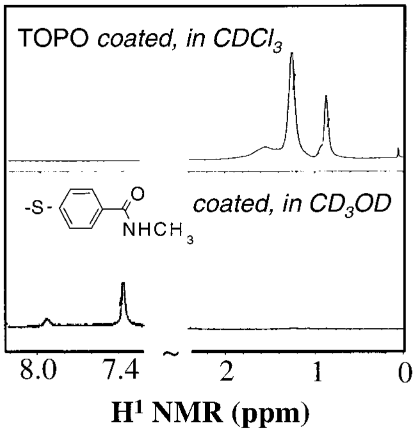

Figure 1. H^1 NMR spectra of CdSe nanocrystals before (top) and after the replacement of the TOPO ligands by an aromatic hydrophilic thiol (see ref 3 for synthesis of this compound). The peaks in the aliphatic protons region of TOPO were completely replaced by the two broad peaks, one at 7.38 ppm for the aromatic protons and the other at 7.93 ppm for the amide proton of the thiol.

Photooxidation Studied with a UV−Vis Spectrophotometer. All photooxidation experiments were performed in a photooxidation chamber under constant airflow with a UVP model UVGL-25 multiband ultraviolet lamp. The lamp was set to 254 nm (short wavelength) and was placed ~4 cm directly above the samples. The samples were placed in 1-cm polypropylene cells, and the sample volume was ~2 mL. The samples were prepared by adjusting the absorbance (optical density, OD) of the purified nanocrystals at the first exciton absorption peak to 0.1−0.3. The UV−vis absorption spectra were recorded at certain time intervals. The temporal evolution of the optical density at the original exciton absorption peak was calculated from the spectra. The original concentrations of CdSe nanocrystals were calculated using the molar absorption coefficient reported by Mews group.[19]

NMR Experiments. Two milliliters of D_2O and 2 mg of free MPA were added into two cells each, and 2 mL of water was added into another cell. Fifty microliters of purified MPA-coated nanocrystals were added to the water cell and one of the D_2O cells, respectively. All three samples were placed in the photooxidation chamber. The two samples containing CdSe nanocrystals were monitored by UV−vis measurements, and the two samples with free MPA were periodically measured with a JEOL 270 MHz NMR spectrophotometer.

Results

The Surface Ligands Replacement of TOPO by hydrophilic thiols followed a procedure modified from the one reported by Peng et al.[3] Proven by NMR measurements (see Figure 1 as an example), the replacement and purification were both complete. The broad peaks that appeared in the spectra are a result of the close-packing feature of the ligands on the surface of the nanocrystals. The lack of sharp peaks at the corresponding positions of the free ligands in Figure 1 implies that the free ligands, thiols, and TOPO, were removed by the purification procedures. The resulting nanocrystals were all extremely soluble in water. We noticed that, in addition to the requirements of protic solvents and basic conditions, reaction temperature was a crucial factor for this reaction. Without refluxing in methanol, the thiol-coated CdSe nanocrystals were very fragile and often could not withstand the following purification procedure. If the temperature reached about 100 °C, nanocrystals coated by the ligands with short chain lengths underwent Ostwald ripening, indicated by the red-shift of the absorption peak of CdSe nanocrystals. For these reasons, all of the results discussed below are based on the samples prepared by refluxing in methanol overnight.

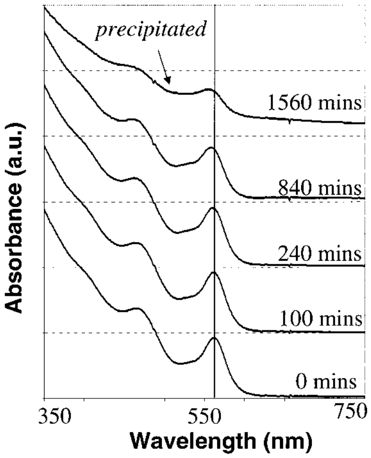

Figure 2. Temporal evolution of the absorption spectra of MUA-coated CdSe nanocrystals in water under the photooxidation conditions. The time progression follows the photooxidation of the nanocrystals from the start of the experiment to the precipitation of nanocrystals.

It was observed that the stability of thiol-coated nanocrystals was often related to the original TOPO-coated nanocrystals. Freshly synthesized TOPO-coated nanocrystals, instead of dried and aged ones, normally yield more stable thiol-coated nanocrystals. For this reason, samples for any parallel experiments were prepared with the same batch of TOPO-coated nanocrystals on the same day, and worked out as parallel as the conditions allowed. Key experiments were repeated with different batches of nanocrystals.

UV−Vis Absorption. The photochemical instability of thiol-coated CdSe nanocrstyals can be readily monitored by recording the UV−vis spectra of the samples dissolved in water at different reaction times. The size-dependent absorption of CdSe nanocrystals provides a sensitive and convenient detection probe of the photooxidation of the nanocrystals themselves. As shown in Figure 2, upon the photooxidation of CdSe nanocrystals, the size of nanocrystals became smaller, and the peak position due to the first exciton absorption of nanocrystals shifted to blue. At the same time, the absorbance or optical density (OD) at the original absorption peak decreased also due to the shrinkage of the nanocrystals. The precipitation of the nanocrystals caused the obvious nonzero baseline for the last spectrum in Figure 2. Thiols with a low molecular mass sometimes precipitated out of the solution by showing none or very few nanometers of peak shift. Therefore, the temporal evolution of the optical density was a more accurate indicator for the photooxidation processes in most cases.

Influences of the Hydrocarbon Chain Length of Aliphatic Thiols. Figure 3 illustrates the temporal evolution of the optical density at the original peak of CdSe nanocrystals coated by mercapto-fatty acids with different chain lengths. It clearly indicates that the longer the chain was, the longer the initiation stage was. MAA-coated CdSe nanocrystals were even more fragile than MPA-coated nanocrystals, and the related experimental results were not easy to reproduce.

In Figure 3, all of the experiments were stopped shortly after the observation of the precipitation of nanocrystals by plain sight. For clarity, the precipitation of MHDA-coated nanocrystals is not shown because it took more than 120 h. It is worth mentioning that the precipitation of nanocrystals was weakly associated with their own photooxidation (Figure 3). For thiols with a short chain, nanocrystals precipitated very closely to the

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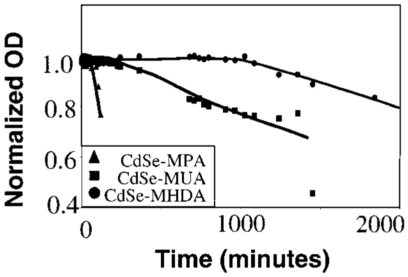

Figure 3. Temporal variation of the normalized optical density (OD) at the original absorption peak of thiol-coated CdSe nanocrystals during the photooxidation. All of the three experiments were stopped shortly after the precipitation of the nanocrystals. The precipitation of MHDA-coated nanocrystals occurred at about 120 h, which is not shown in the plot.

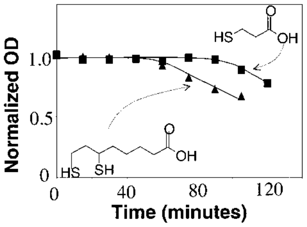

Figure 4. Effect of monothiols (MPA) versus dithiols (DHLA) on the photochemical instability of the nanocrystals.

starting point of the photooxidation of the nanocrystals. For thiols with longer chains, the precipitation took much longer than the initial photooxidation indicated by UV−vis study. For instance, MHDA took more than 120 h to precipitate although the initiation of the photooxidation of the nanocrystals occurred at about 15 h.

Chelating Dithiols versus Monothiols. To improve the stability of thiol-coated semiconductor nanocrystals in water and a more controllable coupling scheme, several groups started to use chelating dithiols, instead of common monothiols.[5,6] However, the experimental results obtained by us indicate that chelating dithiols, such as DTT and DHLA, cannot improve the photochemical stability of the nanocrystals. Figure 4 reveals that both the initiation of the photooxidation and the precipitation of DHLA-coated nanocrystals occurred earlier than MPA-coated nanocrystals did. Similar to MAA, CdSe nanocrystals coated by DTT were extremely unstable.

Aromatic Thiols versus Aliphatic Thiols. In comparison to aliphatic thiols, aromatic thiols have a smaller pK_a, which makes them easier to convert into thiolates at a given pH value. As a result, aromatic thiols can replace TOPO on the surface of nanocrystals in methanol with triethylamine used as the base. Under the same conditions, aliphatic thiols cannot make those nanocrystals soluble in methanol. This motivated Peng et al. to choose aromatic thiols to modify the surface of CdSe nanocrystals in hopes of a better photochemical stability.[3] However, the photochemical stability of nanocrystals coated by aromatic thiols is actually worse than the stability of nanocrystals coated by aliphatic thiols with a similar length dimension (Figure 5).

Due to the above results, efforts focused on the study of aliphatic monothiols. Unless specified below, "thiols" or "thiol ligands" will refer to aliphatic monothiols with single hydrocarbon chains.

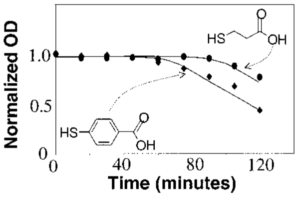

Figure 5. Effect of aliphatic versus aromatic thiol ligands on the photochemical instability of CdSe nanocrystals.

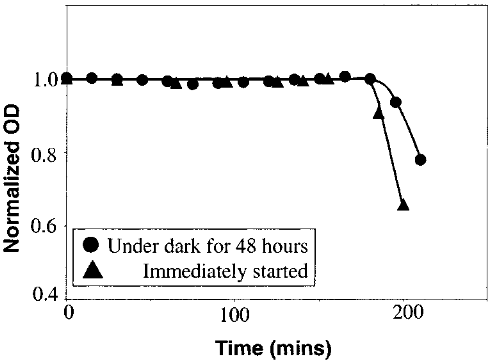

Figure 6. Chemical oxidation of the nanocrystal/ligand complexes in air under dark conditions or the hydrolysis of the cadmium−thiol bonds on the surface of the nanocrystals did not change the initiation stage of the photooxidation of the CdSe nanocrystals themselves. The normalized temporal optical density decay is shown for a sample kept under dark conditions for 48 h and one immediately placed under UV light. See more details in the text.

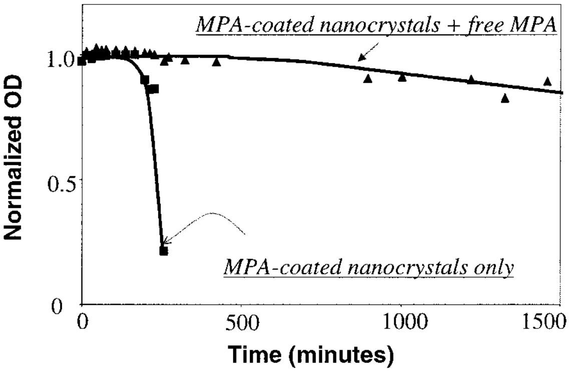

Figure 7. Effect of excess free ligands on the photochemical stability of CdSe nanocrystals. Ten milligrams of excess free MPA were added to one of the sample cells with CdSe−MPA nanocrystals.

Chemical Oxidation, Hydrolysis versus Photochemical Oxidation. The existence of the initiation stage of the photooxidation of the nanocrystal's cores is not caused by the chemical oxidation of thiols or the hydrolysis of the cadmium−thiol bonds formed at the surface of the nanocrsytals, although such processes may result in some pinholes in the ligand monolayer and accelerate the photooxidation of the complex. This point was proven by a simple experiment. An aqueous solution of MPA-coated CdSe nanocrystals after purification was separated into two equal parts. The first part was immediately placed into the photooxidation chamber, and the second part was kept in air under dark conditions for 48 h before it was placed into the chamber. The results shown in Figure 6 clearly indicate that the initiation stage of both parts was more or less identical.

Excess Free Ligands. The photooxidation of nanocrystals coated by hydrophilic thiols showed improved stability with excess free thiols in the solution. For instance, an aqueous solution of MPA-coated CdSe nanocrystals with OD = 0.2 and a volume of 2 mL stayed soluble for more than 50 h when 10 mg of free MPA was added into the solution, with the initiation stage prolonged to 8.5 h (Figure 7). It was observed that the lifetime of these nanocrystals increases with the increase of the concentration of free thiols.

H^1 NMR Coupled with UV−Vis Absorption. The photooxidation data detected by UV−vis measurements are mostly related to the photooxidation of the nanocrstyals themselves, although the precipitation of nanocrystals can be associated with the photooxidation of the ligands. The direct evidence of the photooxidation of the ligands was obtained from the H^1 NMR experiments. Usually, the features of the NMR spectra of ligands on the surface of nanocrystals are broad (Figure 1), which makes it hard to perform accurate and sensitive measurements. In addition, very high concentrations of nanocrystals are required, and such solutions are generally not suited for parallel UV−vis measurements. To solve this problem, we designed a new type of experiment, for which a certain amount of free MPA was added into a diluted D_2O solution of MPA-coated nanocrystals. This special solution along with two control solutions, a D_2O solution containing the pure free ligands without any nanocrystals and an aqueous solution of the pure thiol-coated CdSe nanocrystals without any free ligands, were placed into the photooxidation chamber. The UV−vis spectra of the two solutions with nanocrystals (same initial OD at the absorption peak position) were recorded during the photooxidation, and the two solutions with free ligands (same initial free thiol concentration) were monitored by NMR spectroscopy at certain time intervals. The NMR results are illustrated in Figure 8. The NMR spectra before the photooxidation process (top row) were identical to the standard spectrum of free MPA, and the new peaks that resulted from the photooxidation match very well with the corresponding disulfide molecule of MPA, $COOH-(CH_2)_2-SS-(CH_2)_2-COOH$.[20,21] We did not detect any signs of the corresponding sulfonates which were repeatedly observed in the mass spectroscopy studies of the photooxidation of the thiol SAMs on the flat surface of gold.[15,16] The control experiment with pure MPA revealed that the oxidation of the free thiols without nanocrystals was significantly slower, and the experimental values were used to eliminate the effect of the oxidation of the free ligands themselves in solution. This allowed us to see how much photooxidation was due to the presence of nanocrystals in the special solution. The calibrated concentrations of the remaining thiols along with the normalized OD at the original absorption peak of CdSe nanocrystals at the different reaction time intervals are plotted in Figure 9.

Interestingly, before the nanocrystals themselves in both solutions (with or without free ligands) showed any sign of photooxidation, the formation of the disulfide had already started. In fact, the results reveal that the formation of the disulfide started immediately after the sample was placed into the photooxidation chamber. Thiols were quickly turned into disulfides, and CdSe nanocrystals acted very much like photocatalysts. On average, the turnover number of the thiols to the disulfides for each nanocrystal was about 3 molecules/min. Since the free MPA was in great excess, it is not surprising to see a linear temporal dependence of the concentration of the free MPA in the solution (Figure 9). The photocatalytic oxidation was very likely limited by the availability of the surface area of the nanocrystals.

Discussion

Three distinguishable processes are involved in the photochemical instability of thiol-coated CdSe nanocrystals, which are the photocatalytic oxidation of the thiol ligands, the photooxidation of CdSe nanocrystals, and the precipitation of the nanocrystals. The third process is a result of the first two processes. The precipitation caused by the chemical oxidation in air under dark conditions or the hydrolysis of the chemical bonds between the surface cadmium atoms and the ligands has a much longer time scale if they occurred at all (see Figure 6 and related text).

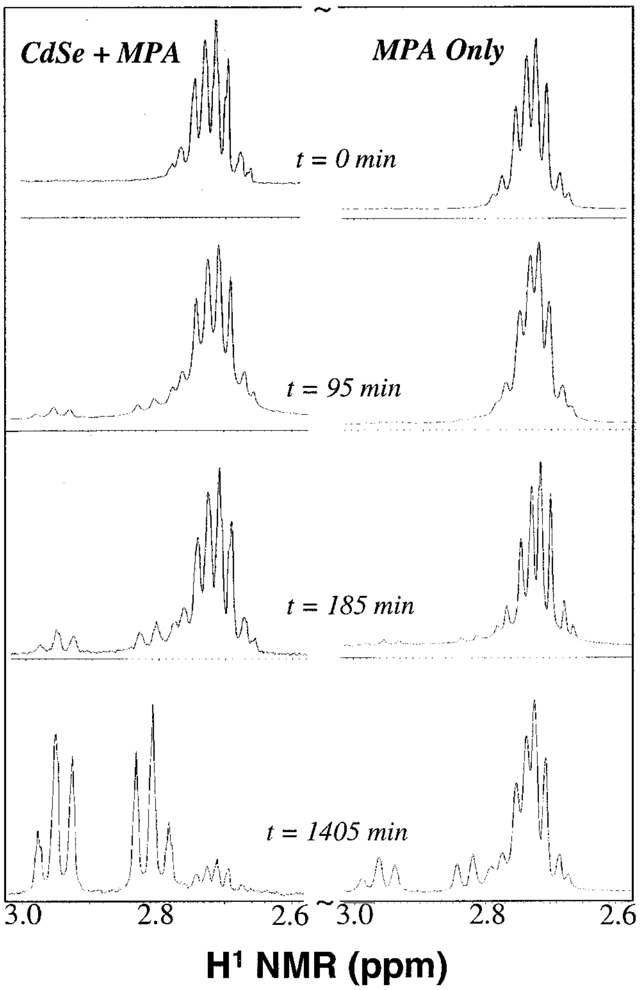

Figure 8. Photocatalytic oxidation of thiol ligands on the surface of CdSe nanocrystals. NMR spectra are shown for a D_2O solution of CdSe−MPA nanocrystals with 2 mg of free MPA initially and a D_2O solution of free MPA only. The volume of both samples was 2 mL. At $t = 185$ min (corresponding to the third row of the NMR spectra), another control sample containing only MPA-coated CdSe nanocrystals with the same concentration as the one mentioned above started to be photooxidized and precipitated out of the solution (See Figure 9). The last row corresponds to the precipitation point of the CdSe−MPA + free MPA solution.

Apparently, the photooxidation of the surface thiols occurred before the photooxidation of CdSe nanocrystals themselves (Figures 7, 8 and 9). Nanocrystals acted as photochemical catalysts for the oxidation of the surface ligands, and the surface ligands acted as the photooxidation scavengers for the nanocrystals. The results for MPA-coated nanocrystals indicate that the photooxidation of the surface ligands occurred immediately after the solution was placed into the photooxidation chamber (Figure 9). The turnover number was determined as 3 MPA/minute for each particle in the experiment using MPA-coated nanocrystals mixed with large excess free MPA (Figures 8 and 9). In the control experiment with pure MPA-coated nanocrystals, it took about 170 min for the nanocrystals to start their

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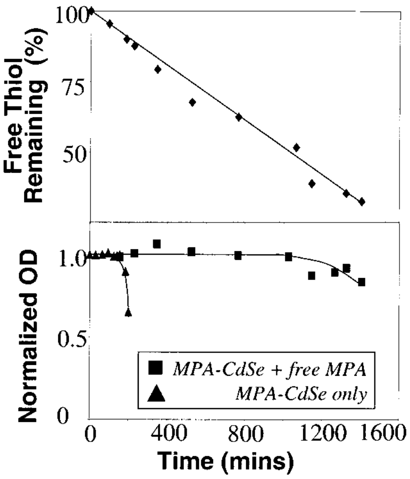

Figure 9. Temporal relationship between the photocatalytic oxidation of the thiol ligands on the surface of the nanocrystals and the photooxidation of the nanocrystals themselves. The calibrated concentrations of the remaining free MPA shown on top were determined by the NMR experiments, and the influence of the oxidation of free MPA in solution without nanocrystals was deducted (see text).

photooxidation. In 170 min, each nanocrystal in the mixture solution converted about 510 MPA molecules into the disulfides. For the 3.2-nm CdSe nanocrystals used in the experiment, a full monolayer of thiol ligands should contain no more than 110 ligands (assuming 50% atoms on the surface of the nanocrystals being cadmium and those surface cadmium atoms being completely coated by the thiol ligands). By comparing these two numbers, it is reasonable to conclude that nearly all of the thiol ligands were oxidized when the MPA-coated nanocrystals started to precipitate out of the solution in the absence of free ligands. In addition to this conclusion, it should be safe to say that the resulting disulfides were quickly "pushed away" from the ligand shell by the free ligands in the solution. Without the free ligands, disulfides may stay around inside the ligand shell with the remaining thiol ligands. When nearly all of the ligands were converted into the disulfides, the entire ligand shell was not attached to the surface of nanocrystals any more and fell into the solution. This caused the precipitation of the nanocrystals. If there was a sufficient amount of free ligands inside the solution, the free ligands took the empty spots on the surface of the nanocrystals, and the nanocrystals stayed soluble in the solution until only a limited amount of the free ligands was available in the solution.

The resulting disulfides related to MPA are moderately soluble in water. The solubility of disulfides decreases as the length of the hydrocarbon chain increases. This is probably why it took much longer for the nanocrystals coated by the thiols with long hydrocarbon chains to precipitate out of the solution, especially for MHDA-coated nanocrystals. Since they were insoluble in the solution, the disulfides likely formed a micelle-like structure around each particle and kept the nanocrystal soluble at the early stage of the photooxidation of the CdSe nanocrystals themselves. Gradually, the nanocrystals became severely oxidized and the inorganic core became smaller because of the oxidation product diffusing out of the micelle-like structures. At a critical point, the small inorganic core could not support the micelle-like structure any longer, and the whole system collapsed to form precipitates. Apparently, the size distribution of the nanocrystals became less uniform as the photooxidation developed (Figure 1), which indicates that smaller nanocrystals were oxidized more rapidly than the larger ones. This may be considered as evidence that the oxidation products diffused out of the ligand shell, instead of staying inside the shell and surrounding the remaining CdSe core.

There is an alternative explanation for the final precipitation of MUA- or MHDA-coated nanocrystals. When the nanocrystals were severely oxidized, the resulting cadmium ions may diffuse out of the ligand shell, which may act as bridges between carboxylate groups on the outer surface of the ligand shell, causing the precipitation of the nanocrystals. Using other types of terminal groups for the thiol ligands, these two different mechanisms for the precipitation of the nanocrystals may be distinguished.

The existence of the initiation stage of the photooxidation of the CdSe nanocrystals coated by thiols is very likely due to the selective oxidation of the ligands prior to that of the nanocrystals themselves. This point is strongly supported by the parallel experiments using nanocrystal solutions with and without excess free ligands (Figures 7 and 9). This conclusion is also consistent with the strong quenching of photoluminescence of CdSe nanocrystals by thiol ligands. Likely, the photogenerated holes are quickly trapped by the deprotonated thiols on the surface of the nanocrystals, which quenches the photoluminescence of the nanocrystals and initiates the photooxidation of the surface ligands. It is well-known that the photogenerated holes rather than the electrons play the vital role for photooxidation.[22]

The time scale of the initiation stage is strongly dependent on the chain length of the thiol ligands (Figure 3). As shown by Figure 6, this temporal variation was not caused by the chemical oxidation under dark conditions or the hydrolysis of the thiol-cadmium bonds on the surface of the nanocrystals. A reasonable explanation for this chain-length dependence is that the thicker ligand layer slowed the diffusion of oxygen species from the bulk solution onto the interface between a nanocrystal and its ligand layer where catalytic photooxidation occurrs. As a result, it took more time to completely oxidize the thiols with a longer hydrocarbon chain on the surface of the nanocrystals. We noticed that such a diffusion-controlled model was also proposed to explain the chain-length dependence of the photooxidation of the thiol-based SAMs on gold substrates.[23]

If the diffusion of oxygen from the bulk aqueous solution to the interface between a nanocrystal and its ligand shell was the controlling step, the initiation stage should be able to fit Fick's first law of diffusion.

Fick's first law of diffusion is given by

$$J_{\mathrm{A}} = -D_{\mathrm{A}}(\mathrm{d}[\mathrm{A}]/\mathrm{d}x)$$

where J_{A} is the rate of passage of species A per unit area. D_{A} is the diffusion coefficient of A, and d[A]/dx is the concentration gradient of A. The negative sign in the law implies that a substance will diffuse in the direction that eliminates the concentration gradient. The experimental data is fitted by taking several simple assumptions. It is reasonable to assume that the same amount of oxygen was required to oxidize the thiol ligands with different chain lengths if the size of the nanocrystals was the same. The second assumption is that the concentrations of oxygen species at the interface between a nanocrystal and its ligand shell and in the bulk aqueous solution were independent of the chain length of the ligands. The last assumption is that the diffusion coefficient of oxygen through the ligand shell did not depend on the chain length of the ligands. With these three conditions, the experimental data was fitted to Fick's first law by normalizing the fit to the experimental point of MPA-coated

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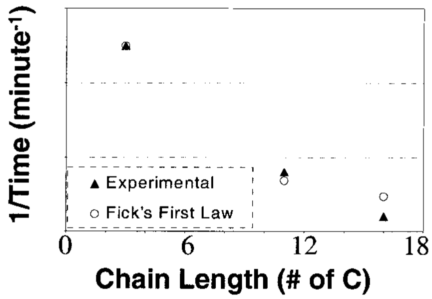

Figure 10. Fitting of the time scale of the initiation stage of the thiol-coated CdSe nanocrystals with different chain lengths to Fick's first law of diffusion. The fitting was normalized to the first experimental point (MPA-coated nanocrystals).

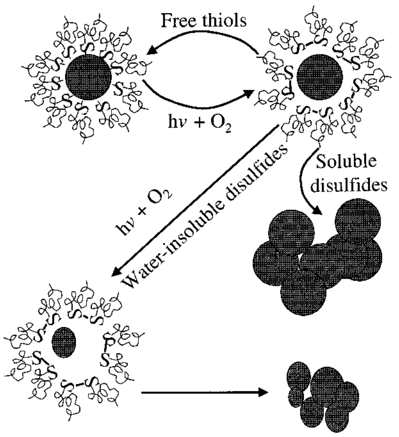

Figure 11. Scheme of the proposed mechanisms for the photochemical instability of thiol-coated CdSe nanocrystals.

nanocrystals. The experimental results shown in Figure 10 fit the law reasonably well. Currently, a more detailed and quantitative study regarding this issue is an active subject in our laboratory.

The diffusion-controlled model can explain the instability of the dithiols and aromatic thiols versus MPA. In this model, the diffusion of oxygen through the ligand shell on the surface of nanocrystals determines the time scale of the initiation stage. Compared to MPA, dithiols and aromatic thiols cannot pack as densely, and the diffusion of oxygen is much easier through the loosely packed ligand shell.

The overall mechanisms of the photochemical instability of thiol-coated CdSe nanocrystals are complicated. Experimental results indicate that the system may proceed differently by varying the availability of free thiols in the solution and the solubility of the resulting disulfides. Many issues, such as the size and shape of the nanocrystals, the power and the wavelength of the radiation, the temperature when the photooxidation takes place, the terminal groups of the ligands, etc., need to be studied. However, on the basis of the experimental results presented above, we can deduce a reasonably clear but qualitative mechanism for the photooxidation of thiol-coated CdSe nanocrystals (Figure 11).

The above mechanisms provided a basis for us to design a series of dendron ligands for stabilizing semiconductor and noble metal nanocrystals in aqueous solutions. The experimental results of CdSe nanocrystals coated by the new dendron ligands showed significant improvement over the photochemical stability in comparison to those coated by the thiol ligands with a single chain even if their molecular masses were similar. Presumably, this was so because the hyper-branched structural feature and possible complex secondary and tertiary structures of the dendron ligands provide a more efficient barrier for the diffusion of oxygen.[17]

The mechanisms proposed in Figure 11 may explain why some sophisticated biochemical coupling procedures performed using semiconductor nanocrystals coated by MAA,[7] DTT,[5] and DHLA[6] are possible but not easy to repeat. Likely, all of the original published procedures were based on samples with some excess thiols in the solution. After the bulky molecules were coupled to the surface of the thiol-coated nanocrystals, the nanocrystal conjugates became very stable against photooxidation because of the additional diffusion barrier provided by the conjugation reactions. Presumably, the amount of free thiols in the solution needed to be controlled quite precisely to make the process reproducible. If there were insufficient free thiols in the solution, the nanocrystals could not survive the whole process. If there was a great excess of free thiols in the solution, the coupling reactions may occur mainly for the solution species.

The results reported in this paper indicate that the photochemical processes that occurred on the surface of colloidal nanocrystals are somewhat like those taking place on the flat surface of bulk substrates. However, the former can be characterized and studied using standard solution methods in a convenient, nondestructive, and versatile manner, which is often not easy to be carried out for the related studies of the SAMs on the flat surface of bulk substrates.

Conclusions

The photochemical instability of thiol-coated CdSe nanocrystals was studied. As the first example of this type of study, the results demonstrate that photochemical processes on the surface of colloidal nanocrystals can be assessed more conveniently and precisely compared to those related to the SAMs on the flat surface of bulk materials. It is possible to study photochemical and chemical processes on the surface of nanocrystals quantitatively by the use of conventional solution-phase methods. This work distinguished three different processes for the photochemical instability of thiol-coated CdSe nanocrystals in water. The system started with the photocatalytic oxidation of the surface thiol ligands to form the disulfides using CdSe nanocrystals as the photocatalysts. This photocatalytic process prevented the photooxidation of nanocrystals themselves. If the disulfides were soluble in water, nanocrystals precipitated out of the solution by losing their surface ligands. If excess free thiol ligands existed in the solution, they replaced the oxidized disulfides and kept the nanocrystals in solution for a longer period of time. The photocatalytic process was determined as a zero-order reaction in terms of the concentration of the free thiols in the solution. If the disulfides were insoluble in water, the photooxidation of the nanocrystals occurred after the first step, and the disulfides presumably formed a micelle-like structure around the surface of nanocrystals. Nanocrystals eventually precipitated out of the solution probably because the size of the nanocrystal's core became too small to support the micelle-like structure. The diffusion of oxygen was found as the rate-determining step for the photooxidation processes because the closely packed ligand monolayer acted as a barrier for the diffusion process. As a result, the photochemical stability of CdSe nanocrystals was closely related to the thickness and packing of the respective ligand monolayer.

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