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Nanoassembly

Reversible Gelation of II–VI Nanocrystals: The Nature of Interparticle Bonding and the Origin of Nanocrystal Photochemical Instability**

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Semiconducting nanocrystals (NCs) with dimensions smaller than the bulk exciton Bohr radius exhibit unique, size-tunable opto-electronic properties due to quantum confinement effects. Accordingly, there has been tremendous interest in the synthesis and characterization of colloidal semiconductor NCs, and they have been investigated for a variety of applications ranging from biological labeling and diagnostics[1] to photovoltaics,[2–5] photodetectors,[6] sensors,[7–9] and catalysts.[10] However, the stability of colloidal NCs is a major issue in many of these applications. The most common method of stabilization is by chemically attaching ligands to the surface atoms of the NCs. Consequently, semiconducting NCs are generally synthesized in the presence of coordinating surfactant ligands, for example, trioctylphosphine oxide, which confers dispersibility in non-polar media. For biological applications, dispersibility in polar media (i.e. water) is needed and this is often achieved by substitution of non-polar surfactant ligands with carboxylate-terminated thiolates by treatment with mercaptoundecanoic acid, mercaptoacetic acid, dihydrolipoic acid, etc., in base.[11] However, the stability of thiolate coated II–VI semiconductor NCs, such as CdSe, is typically poor, often leading to precipitation.

In 2001, Peng and co-workers reported a detailed study of the photochemical instability of thiolate-capped CdSe NCs.[12] The photooxidation of the thiolate ligands on the NCs can be catalyzed by the CdSe NCs in the presence of light and O_2, producing disulfides and thus, effectively decomplexing the particle en route to aggregation.[12] However, if free thiols are present in the solution, they can replace the thiolates lost as disulfide, dispersing aggregates as they form and prolonging the stability of the sol. We and others have exploited oxidative removal of the thiolates as a means to link particles together into three-dimensional architectures (gels), in which metal chalcogenide NCs are assembled into porous network structures.[13–22] Importantly, analyses of oxidized CdS sols have shown that the thiols and their oxidized products (disulfides and sulfonates) can be completely removed from the gel network, and are therefore not participating in interparticle bonding, which leads to the conclusion that CdS NCs are physically connected to each other without any organic linkers.[13–16] The extent of particle interaction in the network (and the related extent of quantum confinement) is found to be a direct function of the dimensionality of the network, itself controlled by the density.[18,23] Such architectures are of interest for applications requiring maximal transport of charge (through the gel network) and small molecules (through the interconnected pore network), such as sensing and photocatalysis. Here we show that, analogous to the work of Peng et al., thiolates can be employed to break up the gel network into its constituent NCs. Additionally, for the first time, we probe the properties of the interparticle bonding in CdSe gels and aggregates.

Dispersion studies were performed principally with CdSe gels, aerogels and xerogels prepared from oxidation of high temperature prepared NCs that were capped with 11-mercaptoundecanoic acid (MUA) in the presence of base (tetramethylammonium hydroxide (TMAH)).[20] Treatment of CdSe wet gels with fresh methanolic solutions of MUA and TMAH (pH 12.0) results in formation of a sol that is visually identical to the precursor NCs (Figure 1) in 2–3 min. Likewise, basic MUA solutions can disperse CdSe aerogels (2–3 min) and xerogels (10–15 min) into sols. Thiols (i.e., MUA without TMAH) also disperse gels, but at a lower rate than thiolates. Interestingly, the treatment of a dispersed sol with an oxidant (a methanolic tetranitromethane (TNM) solution or H_2O_2) leads once more to the formation of a gel network (Figure 1), suggesting the process of gelation and dispersion is cyclable.

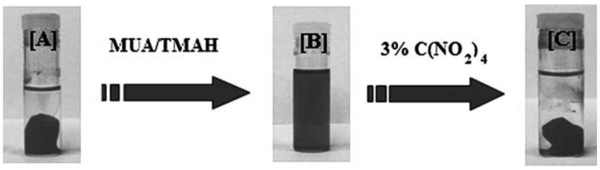

Figure 1. Photographs of a CdSe wet gel [A], the dispersed solution that results upon addition of MUA in methanol/TMAH (pH 12) [B], and the wet gel network that forms after re-oxidation with TNM [C].

Our initial hypothesis, identical to Peng's,[12] was that the NCs are held together in the porous gel network by dative bonds. Therefore, Lewis bases, such as thiolates, can bind to particle surfaces and replace interparticle dative bonds with

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particle–ligand bonds, leading to the dispersion. However, we have found that the introduction of other Lewis bases such as pyridine, amines or tetrahydrofuran, does not result in the break up of the gel network.

In order to understand why certain Lewis bases, such as thiolates, can disperse CdSe gels, whereas bases such as pyridine can not, we evaluated how the NCs change chemically during the gelation process by employing Raman spectroscopy. To do so, we chose to study the systems prepared from room temperature synthesized NCs, since they are poorly luminescent, and therefore CdSe fluorescence is less likely to obscure the chemical signals. Raman spectra of the 4-fluorobenzenethiolate (FPhSH) capped CdSe NCs prepared by the inverse micellar route, and the corresponding aerogels and xerogels, are shown in Figure 2. The CdSe NCs exhibit the characteristic Cd–Se optical phonon mode at 207 cm^{-1} (Figure 2a).[24] The peaks at 344 cm^{-1}, 381 cm^{-1}, 502 cm^{-1}, 632 cm^{-1} and 814 cm^{-1} are assigned to the FPhSH capping group and/or its oxidized product (4-fluorobenzenesulfonate).[25] The relatively less intense peak at 695 cm^{-1} and the shoulder at 830 cm^{-1} can be assigned to residual bis-(2-ethylhexyl) sulfosuccinate sodium salt (AOT) surfactant from the inverse micelle synthesis.[26]

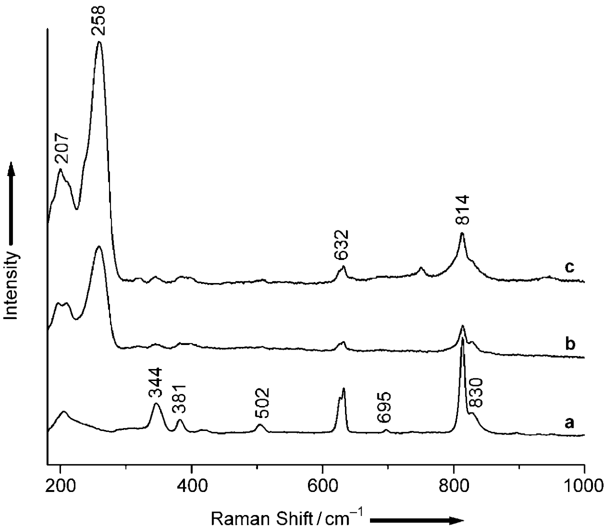


Figure 2. Raman spectra of CdSe precursor NCs capped with a) FPhSH, b) the corresponding aerogel, and c) xerogel.

Raman spectra of the corresponding CdSe aerogels and xerogels also exhibit the Cd–Se optical phonon mode at 207 cm^{-1} (Figure 2b and c). The decrease in relative intensity of the other peaks is consistent with the oxidative removal of the thiolate ligands upon gelation and washing. However, the main difference between the Raman spectra of precursor NCs and aerogels/xerogels is the presence of a moderately broad, intense peak at 258 cm^{-1}, which can be assigned to Se–Se bonds in the as-prepared nanostructures.[27,28] The breadth indicates significant disorder in the Se–Se bond arrangements; presumably, Se^{2-} is being oxidized and undergoing catenation, leading to Se_n^{2-} species.

To confirm the formation of Se_n^{2-} in the gelation process, we evaluated the surface speciation of CdSe NCs and aerogels, prepared using the standard high-temperature synthesis route, using X-ray photoelectron spectroscopy (XPS). Typical survey spectra are shown in Figure S1 in Supporting Information. Higher-resolution spectra were taken of the Cd (Figure S2) and Se regions of the samples. While no change is seen in the Cd spectra, the Se 3d peak shifts by 1.2 eV from 53.7 eV in the NCs to 54.9 eV in the aerogel (Figure 3). This shift is intermediate between the maximum shift expected for Se^{2-} to Se_2^{2-} (0.9 eV)[29] and Se^{2-} to Se^0 (1.9 eV),[29] consistent with formation of Se_n^{2-} species (a combination of Se^0 and Se^-). Importantly, while we have observed the formation of an SeO_2 peak at 59.4 eV[29] in samples that were kept in air for long periods of time (a few months, Figure S3), there is no evidence of oxygen incorporation in freshly prepared CdSe gels. This confirms that surface oxygen-containing species are not formed during gelation and therefore do not participate in the interparticle bonding.

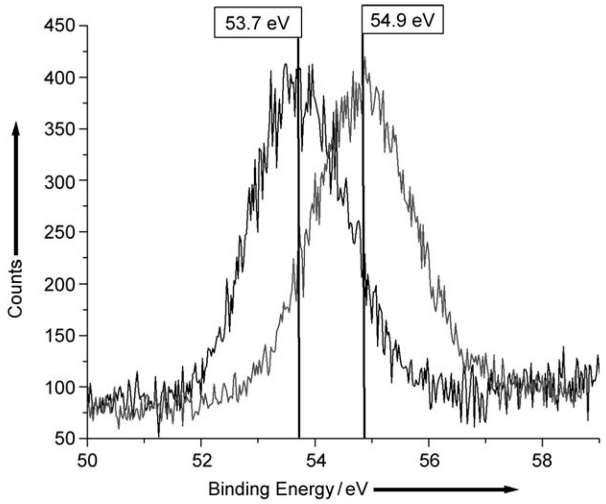
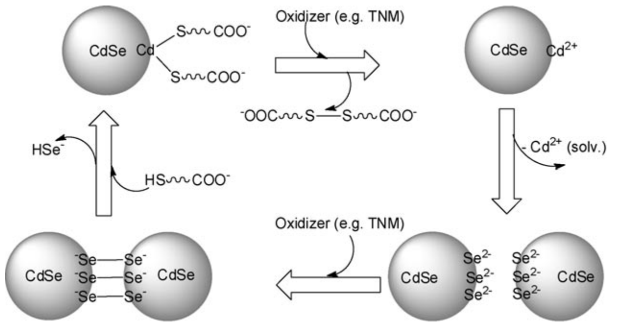


Figure 3. XPS spectra of the Se 3d area of MUA capped CdSe NCs (peak at 53.7 eV) and aerogels (peak at 54.9 eV). The escape depth of the photoelectrons in this energy range is 5–10 Å.[32]

Based on these data, we surmise that Se–Se bond formation, arising from the oxidation of the exposed CdSe NCs, is responsible for the linkage between particles in the gel networks. To confirm that oxidation of Se^{2-} leads to Se–Se bond formation, we treated Na_2Se with a methanolic solution of TNM. Even with Na_2Se:TNM mole ratios as high as 10:1, crystalline Se is readily formed (Figure S4). Because CdSe NCs have unpassivated Se^{2-} species on their surface,[30,31] formation of polyselenide species can be expected in the presence of an oxidizing agent, analogous to the Na_2Se to Se transformation. This, then, would explain the observation of reversible gelation in the present case: thiols and thiolates can act as reducing agents to cleave the Se–Se bonds in these nanostructures. However, other common Lewis bases, such as pyridine, are not reducing; hence, they do not disperse the CdSe gels.

A proposed mechanism for gelation and dispersion based on the formation of diselenide is shown in Scheme 1. During gelation, oxidation of thiolate leads to the formation of disulfides or sulfonates, producing decomplexed Cd^{2+} ions on the particle surface. The Cd^{2+} ions can then be solvated by the carboxylate species and/or solvent (methanol is known to bind strongly to binary metal cations[33]), leaving a selenide-rich NC surface. In the presence of excess oxidizing agent, surface selenide groups can oxidize and form diselenide (or polyselenide) species, linking the particles together. Finally, the addition of a reducing agent, such as a thiol, will result in the cleavage of the Se–Se bonds and the liberation of HSe^- (or a more reduced Se species), forming individual NCs that are again surface-complexed with thiolate ligands.



Scheme 1. Proposed mechanism of CdSe NC gelation/dispersion.

Based on the proposed mechanism, the following can be predicted: 1) Cd^{2+} and oxidized thiolates will be liberated during the oxidative gelation, 2) gel dispersion can be effected with any reducing agent of suitable potential to cleave Se–Se bonds, and 3) particle etching will occur upon cycling of gelation and dispersion. The loss of Cd^{2+} and sulfur during the oxidative removal of thiolates (point 1) has been confirmed by energy dispersive X-ray analyses. Spectra of the residual from evaporating the supernatant of a CdSe wet gel show the presence of Cd and S, and the absence of selenium. The atomic ratio of Cd:S is found to be 1:2.1, consistent with an average of two thiolates binding to one surface Cd^{2+} ion.

In order to verify that the dispersion process is driven by reduction (point 2) we have investigated other common reducing agents such as tris(2-carboxyethyl)phosphine hydrochloride (TCEP), D,L-1,4-dithiothreitol (DTT) and 2-mercaptoethanol (ME). Consistent with our hypothesis, addition of the above reducing agents to wet gel structures results in a disperse solution of CdSe NCs. We also tested whether a "pure" (non-coordinating) reducing agent can break up the gel. To this effect, we stirred a CdSe aerogel with $NaBH_4$ in ethanol, in an ice-bath. As a control, we simultaneously stirred the same amount of CdSe aerogel in ethanol only (no reducing agent). After stirring overnight, both monoliths have been transformed to a powder. However, TEM images (Figure S5) show that the $NaBH_4$ treated sample is broken into particles, while the control sample still maintains the gel structure, consistent with the proposed mechanism. The absence of a dispersed sol in the $NaBH_4$ case is attributed to the lack of suitable solubilizing functionalities.

To further differentiate the roles of reducing or ligating character on gel dispersion, we attempted to disperse ZnS wet gels using N-containing ligands (pyridine and ethylenediamine), both of which are known to have a stronger Lewis basic affinity for the harder Zn^{2+} ion than the softer Cd^{2+} ion. However, even after 1 year, the ethylenediamine and pyridine treated samples have not dispersed. On the other hand, the gels disperse within a minute when thiols are introduced (Figure S6). This supports our hypothesis that chemical reduction is a crucial step in gel dispersion.

Finally, in order to probe the effect of oxidation and reduction cycles on the particle size (point 3), powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), and UV/Vis spectroscopic studies were employed. PXRD of the recovered NCs from dispersed aerogels and xerogels show that the recovered NCs retain the hexagonal crystal structure of the precursor NCs (Figure S7). Consistent with the irreversible loss of Cd^{2+} and reduced Se species during the assembly and disassembly, a slight decrease in average crystallite size (2.8 nm) is observed for the NCs recovered from aerogels and xerogels compared to the precursor NCs (3.0 nm) after one cycle of oxidation and reduction.[34] The primary particle size calculations using TEM images (Figure S8) also reveal a slight decrease in particle size for the dispersed NCs (3.5 ± 0.5 nm) compared to the precursor NCs (3.8 ± 0.5 nm). The fact that the particle size determinations by TEM give slightly larger values than the crystallite size determinations by PXRD may be due to the presence of an amorphous coating around the CdSe NCs. Alternatively, the discrepancy could be due to strain broadening contributions in the PXRD, or the presence of multiple domains within individual particles. A more detailed discussion of these points is presented in the Supporting Information.

Because the size changes suggested by TEM and PXRD are small and within the standard deviation of our measurements, we have employed UV/Vis absorption spectroscopy to confirm the etching of the NCs during the assembly and disassembly process. UV/Vis absorption spectra of the CdSe precursor NCs and the NCs recovered after dispersion of the corresponding wet gels are shown in Figure 4 and the data is tabulated in the Supporting Information. Absorption spectra of thiolate-capped CdSe NCs exhibit a sharp onset at 550 nm with maximum at 515 nm (Figure 4a). Upon reduction of the corresponding wet gel with MUA/methanol/TMAH, the recovered NCs showed a blue shift in the absorption onset to 545 nm (maximum at 508 nm; Figure 4b), consistent with a higher degree of quantum confinement due to a decrease in particle size. These recovered NCs were used to make fresh gels by treatment with TNM. Then, the resulting monolithic gels were re-dispersed in the thiolate solution a second time to recover the NCs. Recovered NCs exhibit a further blue shift in absorption onset to 535 nm (maximum at 504 nm; Figure 4c). Repeating this process a third time resulted in a shift in the onset to 531 nm (maximum at 492 nm; Figure 4d) for the recovered NCs, confirming a continuous decrease in the optical chromophore size.

The same trend is observed in another II–VI system, CdS. CdS wet gels can also be dispersed using MUA/MeOH/

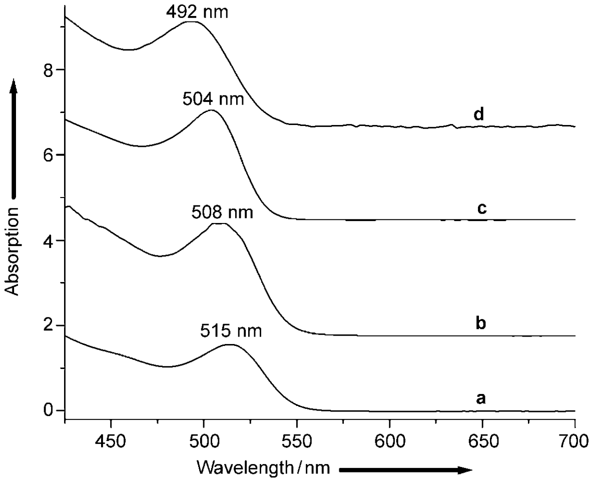


Figure 4. Visible absorption spectra of a) the CdSe precursor NCs and b) NCs isolated from the dispersed wet gels. c,d) NCs isolated after a second (c) and third (d) cycle of re-gelation and re-dispersion.

TMAH solutions under the same conditions as CdSe. Upon successive gelation–dispersion cycles, the UV/Vis absorption maximum and onset position show a blue shift (Figure S9), just like CdSe, indicating that the same etching of the surface occurs. Moreover, the size reduction can be monitored using TEM analysis (Figure 5). The size of the CdS NCs decreases from 4.4 ± 0.5 nm for the original sol to 3.8 ± 0.4 nm, 3.7 ± 0.5 nm and 3.1 ± 0.5 nm for NCs isolated after one, two and three dispersions, respectively. Thus, it appears that a similar oxidation–reduction mechanism is responsible for the gelation–dispersion of the CdS NCs and gels.

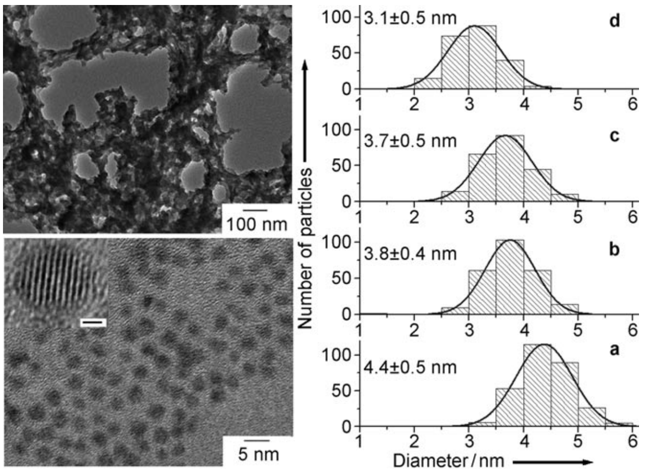


Figure 5. Left: TEM image of the CdS aerogel (top) and NCs after one dispersion (bottom). The inset shows the HRTEM image of one CdS particle (inset scale bar is 1 nm). Right: the size distribution analysis of a) the CdS precursor NCs and b–d) NCs isolated after one (b), two (c), and three (d) dispersion–gelation cycles.

In conclusion, Raman and XPS studies suggest that the bonding between particles in as-prepared CdSe gels is largely due to covalent Se–Se bonds. Hence thiols, thiolates and a variety of other common reducing agents have the ability to disperse CdSe gels, whereas pure Lewis bases (e.g., pyridine) do not. Repeated oxidation of thiolate coated NCs and reduction of wet gels leads to a continuous decrease in primary particle size, as suggested from UV/Vis spectroscopy, TEM and PXRD analyses. Hence, the programmed assembly and disassembly of CdSe quantum dots provides a method of making smaller NCs by selective etching of the nanoparticle surface. Furthermore, the same mechanism applies to CdS, and presumably for sol–gel reactions of other metal chalcogenide NCs (e.g. ZnS, PbS). Overall, these data suggest that the well-known photochemical instability of chalcogenide semiconductor NCs can be attributed to photo-oxidation and subsequent interparticle linkage of surface chalcogenide species, not simply to aggregation of decomplexed particles, as originally proposed.[12]

Experimental Section

Synthesis of CdSe gels, aerogels and xerogels: Colloidal CdSe nanocrystals (NCs) were prepared by inverse micellar[13,14,16] or high-temperature[35] synthetic routes using coordinating surfactant ligands. Surfactants were exchanged with 4-fluorophenylthiol (FPhSH, inverse micellar route) or mercaptoundecanoic acid (MUA, high temperature route) in the presence of tetramethylammonium hydroxide (TMAH) as reported in the literature.[12,20] Colloidal CdSe wet gels were prepared by oxidative aggregation of the thiolate capped CdSe NCs using a methanolic tetranitromethane (TNM) solution. The resulting wet gels were transformed into monolithic aerogels and xerogels by CO_2 supercritical drying and bench top drying, respectively.[18–20]

Dispersion studies: Thiolate solutions containing MUA were prepared by dissolving 0.1092 g of MUA (0.5 mmol) in methanol (5 mL) and titrating to pH 12 with TMAH. CdSe wet gels, aerogels and xerogels prepared from a 4 mL sol of high-temperature synthesized NCs (dried gel weight ca. 2 mg) were dispersed in the above solution. Ethyl acetate was added to precipitate the particles, which were isolated using centrifugation. The NCs were then washed two times with ethyl acetate to remove the residual MUA and dispersed in 12 mL of methanol to form a sol. Re-gelation was achieved by adding 0.05 mL of 3% TNM to 4 mL aliquots of the resultant CdSe sol. Dispersion studies of CdSe gels with D,L-1,4-dithiothreitol and 2-mercaptoethanol were conducted similarly. Dispersion by tris(2-carboxyethyl)phosphine hydrochloride (TCEP) was performed by adding 3–5 mL of a 0.1 M methanolic solution of TCEP to CdSe wet gels.

Further details on the synthesis, characterization and dispersion of chalcogenide gels, including CdS and ZnS, can be found in the Supporting Information.

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Keywords: chalcogenides · gels · nanomaterials · raman spectroscopy · reaction mechanisms

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