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Aggregation Kinetics of Metal Chalcogenide Nanocrystals: Generation of Transparent CdSe(ZnS) Core(shell) Gels

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Abstract

Transparent CdSe(ZnS) sol-gel materials have potential uses in optoelectronic applications such as light emitting diodes (LEDs) due to their strong luminescence properties and the potential for charge transport through the prewired nanocrystal (NC) network of the gel. However, typical syntheses of metal chalcogenide gels yield materials with poor transparency. In this work, the mechanism and kinetics of aggregation of two sizes of CdSe(ZnS) core(shell) NCs, initiated by removal of surface thiolate ligands using tetranitromethane (TNM) as an oxidant, were studied by means of time-resolved dynamic light scattering (TRDLS); the characteristics of the resultant gels were probed by optical absorption, transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). At low concentrations of NCs (ca. 4×10^{-7} M), the smaller, green-emitting NCs aggregate faster than the larger, orange-emitting NCs, for a specific oxidant concentration. The kinetics of aggregation have a significant impact on the macroscopic properties (i.e. transparency) of the resultant gels, with the transparency of the gels decreasing with the increase of oxidant concentration due the formation of larger clusters at the gel point and a shift away from a reaction limited cluster aggregation (RLCA) mechanism. This is further confirmed by the analyses of the gel structures by SAXS and TEM. Likewise, the larger orange-emitting particles also produce larger aggregates at the gel point, leading to lower transparency. The ability to control the transparency of chalcogenide gels will enable their properties to be tuned in order to address application-specific needs in optoelectronics.

Keywords

Reaction-limited colloidal aggregation; diffusion-limited colloidal aggregation; quantum dots; dynamic light scattering; small angle X-ray scattering

Introduction

The assembly of nanocrystals (NCs) into functional materials remains a key hurdle in the development of NC based devices. Sol-gel methods provide a tried and true approach for linking NCs into three dimensional architectures (i.e. gels, xerogels and aerogels) while preserving the properties of individual NCs.^{1,2} Thus, CdSe(ZnS) gel materials³ retain the NC band gap tunability, which arises due to the dominance of quantum size effects in the

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Supporting Information

Time evolution of $\bar{R}_h$ for concentrated green-emitting CdSe(ZnS) sols and orange-emitting sols oxidized by different amounts of 3% TNM; SAXS spectrum of an orange-emitting gel formed from 4 μ L of TNM. This information is available free of charge via the Internet at <http://pubs.acs.org>.

electronic structure of CdSe NCs, and the intense NC band-edge luminescence, due to the shutdown of non-radiative recombination pathways by over-coating the CdSe NC core with the ZnS shell. Moreover, removal of surface ligands and formation of a network of NCs connected to each other during the gelation process is expected to provide better electronic communication between NCs. However, the lack of transparency of the sol-gel CdSe(ZnS) materials produced to date remains a barrier to their use in optoelectronic applications, such as in light emitting diodes (LEDs).

Gacoin and co-workers have extensively studied the sol-gel transition of CdS NCs and showed the possibility of formation of transparent CdS gel materials when the sizes of the fractal clusters in the gel are below the wavelength of visible light.⁴ Furthermore, they demonstrated that the structure of the CdS gel materials depends on the nature and concentration of the oxidant. Therefore, it can be assumed that controlling the ligand and surface oxidation, and thus the aggregation and gelation kinetics, is key to achieving transparency in CdSe(ZnS) gel materials. In this study, by means of time resolved dynamic light scattering (TRDLS) and small-angle X-ray scattering (SAXS), we evaluated the kinetics of the sol-gel process for CdSe(ZnS) NCs as a function of oxidant concentration, NC concentration, and NC size. Based on the TRDLS and SAXS analysis, we correlated the kinetics of aggregation and gelation of CdSe(ZnS) NCs to the structural properties of the resulting gel materials and the degree of transparency.

Experimental Section

Materials

Selenium powder (99.5%), stearic acid (95%), diethylzinc (1M, in hexane), bis(trimethylsilyl)sulfide, trioctylphosphine oxide (TOPO, 90%), tetranitromethane (TNM), and 11-mercaptoundecanoic acid (MUA, 95%) were purchased from Aldrich. Trioctylphosphine (TOP, 97%) and cadmium oxide (99.999%) were purchased from Strem Chemicals. 1-tetradecylphosphonic acid (TDPA, 98%) was purchased from Alfa-Aesar and tetramethylammonium hydroxide pentahydrate (TMAH, 97%) was purchased from ACROS. Toluene, methanol and ethyl acetate were purchased from Mallinckrodt. TOPO was distilled before use; all other chemicals were used as received.

Synthesis of CdSe(ZnS) core(shell) nanocrystals (NCs)

Highly luminescent CdSe(ZnS) core(shell) NCs were synthesized according to literature methods with slight modifications.^{5,6,7} In a typical synthesis of green-emitting NCs, a mixture of 0.0127 g (0.1 mmol) of cadmium oxide, 0.04 g (0.14 mmol) of TDPA and 2.0 g (5.17 mmol) of TOPO were heated to 330 °C under argon flow to generate a homogeneous colorless solution. The temperature of the solution was reduced to 150 °C and a solution of selenium containing 0.01 g (0.13 mmol) of selenium powder in 2.4 mL of TOP was injected. The temperature of the mixture was then increased up to 250 °C at a rate of 10 °C per 10 minutes and aged for four hours. In a typical synthesis of orange-emitting NCs, 0.15g (0.53 mmol) of stearic acid was used instead of TDPA, the selenium solution was injected at 320°C, and NCs were grown for two hours at 300°C. After aging the green and orange NC solutions, a small aliquot was taken for their characterization.

In order to make the ZnS shell, a mixture of 0.15 mL of 1M diethyl zinc in hexane, 0.03 mL of bis(trimethylsilyl)sulfide (0.14 mmol) and 2 ml of TOP was slowly injected over a time period of 15 minutes (the total molar ratio of the injection solution was CdSe:ZnS 1:1.4, based on the number of moles used in the synthesis) using a syringe pump at 180 °C and followed by annealing at 75 °C overnight. As-prepared CdSe(ZnS) core(shell) NCs were purified by two cycles of dispersion in toluene and precipitation with methanol.

MUA exchange

0.1 g (0.43 mmol) of MUA was dissolved in 10 mL of methanol and the pH increased up to ~10 using TMAH. The MUA solution was added to the purified CdSe(ZnS) core(shell) NCs and shaken vigorously to achieve complete ligand exchange (Cd:MUA molar ratio of 1: 4, based on original moles of Cd employed in the synthesis). The resulting MUA capped NCs were washed with ethyl acetate two times and then dispersed in methanol to make the NC sol.

NC characterization

Structural properties of CdSe(ZnS) core(shell) NCs were studied by powder X-ray diffraction (PXRD) performed on a Rigaku Diffractometer (RU200B) using the $K\alpha$ line of a Cu rotating anode source (40 kV, 150 mA). Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were carried out on a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV with a coupled EDS detector (EDAX inc.). Photoluminescence spectra were obtained with a Cary Eclipse (Varian, inc.) fluorescence spectrometer and a Cary 50 (Varian, inc.) spectrophotometer was employed to obtain UV-vis spectra. The size of the CdSe core NCs (prior to ZnS overcoating) was determined by TEM.

Time resolved dynamic light scattering (TRDLS)

TRDLS measurements were performed using a Zetasizer Nano ZS instrument (Malvern Instruments, Westborough, MA) with a He-Ne laser beam at 633 nm and the detector positioned at 173°. Autocorrelation functions were accumulated for at least 15 s over different time periods, depending on the oxidant concentration, and the size distribution and the Z-average hydrodynamic radius ($\bar{R}_H$) were determined using the Zetasizer software (version 6.2) provided by Malvern. To determine the effect of oxidant concentration on the kinetics of aggregation and gelation at room temperature, sols of CdSe(ZnS) core(shell) NCs with two different nominal sizes (referred to by their color of emission: green or orange emitting) and of two different NC concentrations (3.86×10^{-7} and 3.86×10^{-8} M, green emitting only) were used. NC concentration was determined by UV-vis spectroscopic measurements using size dependent extinction coefficients published by Yu et. al.⁸ The average NC sizes were determined by high resolution TEM measurements. In all DLS measurements, sol volumes were constant (3 mL) and the sol was pipetted into a disposable cuvette. After adding varying amounts of 3% TNM, the cuvette was vigorously shaken and immediately placed in the DLS instrument.

Because of the Brownian motion of the particles and aggregates, the intensity of the scattered light fluctuates with time and the normalized second-order intensity correlation function $g^{(2)}(\tau)$ can be obtained with the digital correlator in the DLS instrument by autocorrelation of these intensity fluctuations over a very short time interval (Equation 1)

$$g^{(2)}(\tau) = \frac{\langle I(0)I(\tau) \rangle}{\langle I(0) \rangle^2} \quad (1)$$

where $I(\tau)$ is the scattering intensity and τ is the decay time. $g^{(2)}(\tau)$ can be related to the normalized first-order electric field correlation function $g^{(1)}(\tau)$ by the Siegert relation (Equation 2)^{9,10}

$$g^{(2)}(\tau) = B(1 + \beta |g^{(1)}(\tau)|^2) \quad (2)$$

where B is the base line of the correlation function and β is the coherence factor. For monodisperse solutions, $g^{(1)}(\tau)$ decays exponentially (Equation 3),

$$g^{(1)}(\tau) = \exp(-\Gamma\tau) \quad (3)$$

where Γ is the decay rate. However, for polydisperse solutions, $g^{(1)}$ must be represented as a sum or distribution of exponentials (Equation 4)

$$g^{(1)}(\tau) = \int G(\Gamma) \exp(-\Gamma\tau) d\Gamma ; \int G(\Gamma) d\Gamma = 1 \quad (4)$$

where $G(\Gamma)$ is the distribution function of Γ .¹¹ Analysis of autocorrelation functions using the method of cumulants yields the mean decay rate $\bar{\Gamma}$ which is equal to $\bar{D}q^2$ where $\bar{D}$ is the average translational diffusion coefficient and q is the scattering vector (Equation 5)

$$q = 4\pi n / \lambda \sin\theta / 2 \quad (5)$$

where n is the refractive index of the solvent and θ is the scattering angle. The average hydrodynamic radius $\bar{R}_h$ can be calculated from the Stokes-Einstein relationship (Equation 6)

$$\bar{R}_h = (k_B T) / 6\pi\eta\bar{D} \quad (6)$$

where T is the absolute temperature, k_B is the Boltzmann constant and η is the viscosity of the solvent. Additionally, the aggregate size distribution can also be obtained by analysis of intensity autocorrelation functions using a non-negatively constrained least squares (NNLS) algorithm that is part of the Zetasizer software. The average is reported for the peak corresponding to the largest aggregate size.

Small-angle X-ray scattering (SAXS)

SAXS measurements were carried out using a Rigaku Smartlab X-ray diffractometer (40 kV, 44 mA) with Cu K α radiation. Sol volumes (3 mL) were pipetted into disposable cuvettes and varying amounts of 3% TNM were introduced, as was the case for TRDLS, then a portion was transferred to 2.0 mm boron-rich capillary tubes and allowed to gel. Scattering intensities were recorded from 0 to 8° 2 θ . The parasitic scattering produced by the sample holder, slits and air is subtracted from the experimental scattering intensity.

Results and discussion

Synthesis and Characterization of CdSe(ZnS) Core(shell) NCs

Highly luminescent green- and orange-emitting CdSe(ZnS) core(shell) NCs were synthesized according to literature methods with slight modifications.^{5,6,7} As-prepared CdSe(ZnS) core(shell) NCs were purified by two cycles of dispersion in toluene and precipitation with methanol and then exchanged with 11-mercaptopundecanoic acid (MUA). Figure 1 shows a high resolution transmission electron microscope (HRTEM) image of the as-synthesized green- and orange-emitting CdSe core NCs along with UV-vis and photoluminescence (PL) spectra of MUA-capped core(shell) NCs. Core sizes (determined by HRTEM measurements) and optical properties of CdSe(ZnS) core(shell) NCs are listed in Table 1.

As expected, orange-emitting NCs have larger cores than the green-emitting NCs, and this is also reflected in the lower energy of absorption onset and band edge emission maxima, consistent with less quantum confinement in the orange-emitting NCs. The full width at half-maximum (FWHM) values of the band-edge emission peaks of CdSe(ZnS) in the PL spectra are between 31–34 nm, suggesting the presence of fairly monodisperse NCs. Gelation is achieved by oxidative ligand removal and formation of oxidized chalcogenide linkages between NCs.¹² Importantly, tetranitromethane is a non-oxygen transferring oxidant and does not actively participate in bonding; NC-NC bonding occurs via purely inorganic di- or poly-chalcogenide linkages.¹²

Probing the effect of kinetics of the aggregation and gelation on gel transparency by time resolved dynamic light scattering (TRDLS)

Aggregation kinetics can be considered in the context of two limiting regimes. Fast, diffusion-limited colloidal aggregation (DLCA), in which growth of the average cluster size has a power law behavior; and slow, reaction-limited colloidal aggregation (RLCA), in which exponential growth of the average cluster size occurs.¹³ In the DLCA regime, power law behavior of the growth in the average radius of gyration $\bar{R}_g$ of the aggregates can be shown by solution of the Smoluchowski equation (Equation 7)¹⁴

$$\bar{R}_g(t) = \bar{R}_g(0) [1 + \alpha t / \tau]^{z/D_f} \quad (7)$$

In the RLCA regime, exponential scaling of $\bar{R}_g$ is expected with a dependence represented by Equation 8.

$$\bar{R}_g(t) = \bar{R}_g(0) \exp(\alpha t / \tau) \quad (8)$$

In these equations z is the dynamic exponent, D_f is the fractal dimension, α is the sticking probability and τ is the reciprocal Smoluchowski rate (Equation 9)

$$\tau = 3\eta / (4k_B T) N_0 \quad (9)$$

where η is the viscosity of the solvent, k_B is the Boltzmann constant, T is the absolute temperature and N_0 is the primary particle concentration. In the DLCA regime, there are no repulsive forces between colloidal particles, and therefore every collision results in sticking, and aggregation kinetics depend solely on diffusion. In the RLCA regime, aggregation kinetics depend on the sticking probability of colloidal particles upon collision, due to the presence of inter-particle repulsive forces.

TRDLS is a powerful tool to study the kinetics of colloidal aggregation and gelation. We monitored the sol-gel transition of CdSe(ZnS) core(shell) NCs by TRDLS, and Z-average hydrodynamic radii, $\bar{R}_h$, of the aggregates were obtained as a function of time. Because $\bar{R}_h$ is proportional to $\bar{R}_g$ when $q\bar{R}_h$ values are not equal to unity, we employed $\bar{R}_h$ to study the kinetics of aggregation of CdSe(ZnS) core(shell) NCs.^{15,16} To determine the effect of oxidant concentration on the kinetics of aggregation and gelation at room temperature, sols of CdSe(ZnS) core(shell) NCs with the same NC concentration (3.86×10^{-7} M) and of two sizes (green and orange emitting) were used. Additionally, in order to explore the concentration effect, DLS measurements were done for green-emitting NC sols at a 10-fold increase in concentration. In all TRDLS measurements, sol volumes were constant (3 mL) and the sol was pipetted into a disposable cuvette. After adding varying amounts of 3%

tetranitromethane (TNM, oxidant), the disposable cuvette was vigorously shaken, and immediately placed in the DLS instrument.

Figure 2a shows the time evolution of $\bar{R}_h$ as a function of oxidant concentration in the aggregation of green- and orange-emitting NCs (N.B. the aggregation time period was selected over ranges where $q\bar{R}_h$ is not equal to unity). Aggregation is initiated by the removal of thiolate ligands by oxidation, consequently reducing the energy barrier for aggregation. Thus, increasing the oxidant concentration increases the aggregation rate due to the rapid removal of thiolate ligands from the NC surface, thus reducing the repulsive forces and increasing the sticking probability.

For green-emitting NCs treated with 4–10 μL of TNM, aggregation follows RLCA kinetics as indicated in Figure 2b by the linear behavior on the semi logarithmic scale. Attempts to use the DLCA kinetic models resulted in poorer fits in each case. All the green-emitting wet gels are transparent (Figure 3a), although there is a decrease in transparency with the increase of oxidant, which is quantified by optical transmittance as shown in Figure 3b. The gel formed by 50 μL of TNM (Figure 3a) is poorly transparent, perhaps due to deviation of aggregation kinetics from the RLCA model. However, we were unable to collect enough data by DLS to probe the kinetics due to the very fast aggregation and gelation (within a few seconds) that occurs at this high concentration of oxidant. Likewise, a 10-fold increase of NC concentration caused rapid aggregation even at the lowest ratio of oxidant to NC concentration used in the above study (4 μL TNM in the prior study corresponds to 40 μL TNM for a 10-fold NC concentration), and this may be due to a significant increase of the collision frequency in the concentrated sols.¹⁷ The decrease of the TNM amount (from 40 to 10 μL TNM) drastically slows down the aggregation and gelation from a few seconds to several days for the high concentration of NCs. This may be due to the very low sticking probability, because of the large repulsive energy barrier for aggregation that arises from the surface ligands, which are being removed at much slower rates at low TNM concentrations. Furthermore, we did not observe any correlation between the aggregation kinetics of NCs and theoretical kinetic models (RLCA or DLCA) at this high NC concentration from TRDLS data (supporting information Figure S1) and all of the resultant gels are opaque (Figure 3d). These observations indicate that the control of aggregation kinetics of green-emitting CdSe(ZnS) core(shell) NCs can be utilized to alter the macroscopic properties of the resulting gels when the concentration of NCs is rather low (ca 4×10^{-7} M). At low NC and oxidant concentrations, aggregation follows RLCA kinetics and leads to formation of transparent gel structures.

Aggregation kinetics clearly depend on the overall NC size, as orange-emitting NCs showed slower aggregation kinetics compared to the green-emitting NCs for the same oxidant and NC concentrations. This may be due to the slower diffusion rate of larger NCs and the presence of a larger number of surface ligands on the NC surface compared to that of the green-emitting NCs for the same particle concentration. For orange emitting NCs, it is difficult to describe the aggregation kinetics using theoretical models since we weren't able to distinguish RLCA or DLCA kinetics by means of aggregation plots (supporting information Figure S2). The resulting wet gels have poor transparency and opacity increases with the amount of oxidizing agent used to form the wet gels (Figure 3c).

TRDLS has also been used to study the sol-gel transition of various systems.^{18,19} We extended this study to the metal chalcogenide system in order to understand the effect of aggregation and gelation kinetics on the macroscopic properties of the resultant gels. The sol-gel transition can be described as a divergence-of-connectivity correlation.²⁰ At the gelation point, aggregates resulting from nonequilibrium cluster-cluster aggregation processes overlap and form a network to fill the total volume of the solution.²¹ Hence, the

approximate largest aggregate size near the gel point resulting from the cluster growth can be employed to explain the macroscopic properties (i.e. transparency) of the gel structure resulting from different kinetics.²²

Martin and coworkers probed the silica sol-gel transition by TRDLS. According to their observations, the intensity correlation function $g^2(\tau)$ shows a stretch exponential decay during the pre-gelation period (Equation 10) and a transition from a stretch exponential decay to a power-law decay at the gel point (Equation 11)^{21,19}

$$g^2(\tau)-1 \approx \sigma_1^2 \{A \exp(-Dq^2\tau) + (1-A) \exp \left[-\left(\frac{\tau}{\tau_c}\right)^\beta \right] \}^2 \quad (10)$$

$$g^2(\tau)-1 \approx \sigma_1^2 \{A \exp(-Dq^2\tau) + (1-A) \left[1 + \left(\frac{\tau}{\tau^*}\right)^{\frac{n-1}{2}} \right] \}^2 \quad (11)$$

where σ_1^2 is the initial amplitude of the intensity correlation function, A is the fraction of the translational diffusion mode, D is the translational diffusion coefficient, τ_c is the characteristic time for the stretch exponential mode ($0 < A < 1$), β is the stretch exponent ($0 < \beta < 1$), τ^* is the time at which power-law behavior begins and n is the fractal dimension of the scattered photons ($0 < n < 1$). For the sol state, the first exponential function relates to the translational diffusion of the clusters or aggregates, which follows a stretched exponential decay; whereas at the gel point, the initial exponential function follows a power-law decay.

Figure 4 shows the time evolution of intensity correlation functions, $g^2(\tau)$, for the green- and orange-emitting CdSe(ZnS) core(shell) NC sols oxidized by 4 μ L of TNM. Solid and dashed curves represent the fitted curves using Equation 10 and 11, respectively. In both cases, the decay time, τ , for the intensity correlation function, $g^2(\tau)$, increases with time, indicative of an aggregation process. Equation 10 was used to fit successfully to the initial intensity correlation functions that show a stretch exponential decay of $g^2(\tau)$, suggesting that the samples remain in the sol state. At the gel point, the power law behavior of the intensity correlation function $g^2(\tau)$ is evident by the successful fitting to the experimental curve using Equation 11, as indicated by the dashed lines in Figure 4. Near the gel point t_{gel} , the approximate largest aggregate size of the resulting gel can be determined from NNLS analysis, and these data are summarized in Table 2. For the green-emitting CdSe(ZnS) core(shell) gels, the approximate maximum aggregate sizes near the gel point are below the wavelength of visible light at low oxidant concentrations, explaining the transparency. The maximum aggregate size near the gel point increases with the oxidant concentration, and it can be assumed that rapid aggregation at relatively high oxidant concentrations (e.g. 50 μ L of TNM) results in comparatively larger aggregates,¹⁷ consequently increasing the scattering of light and resulting in opaque gels. For the orange-emitting gels, the comparatively larger aggregates near the gel point significantly increase the scattering of visible light photons, making them less transparent than green-emitting gels for the same amount of TNM added. The aggregation of colloidal particles depends on both the collision frequency and sticking probability. The slower aggregation inherent in the larger particles, due to the slower diffusion and larger number of surface ligands that need to be removed from the surface, delay the gel point, but the fact that the aggregates present near the gelation point are larger than those for green-emitting sols suggests a higher sticking probability is occurring for the de-protected orange-emitting NCs.

Probing the effect of the kinetics of aggregation and gelation on structural characteristics of the resultant gels by small-angle X-ray scattering (SAXS)

As we pointed out earlier, aggregation of colloidal particles results in disordered fractal clusters that are connected to form the wet gel structure at the gel point. The SAXS technique can be employed to study the structure of the wet gels and this allows correlation of the structural characteristics of the wet gels to the aggregation process, and ultimately to the macroscopic properties of the gels. Furthermore, this allows the structural characteristics of green-emitting gels that result from relatively high amounts of oxidizing agent, where the kinetics are too fast to resolve by DLS, to be probed.

Figure 5 shows scattering intensity, $I(q)$, of wet gels formed by introduction of different concentrations of TNM to green-emitting sols, as a function of the scattering vector, $q = (4\pi/\lambda) \sin(\theta)$. In a typical scattering curve of a mass fractal aggregate, the power law behavior of $I(q)$ within the mass fractal region occurs in the q range $1/\xi \gg q \gg 1/a$, where ξ is the correlation length and a is the average particle size. $I(q)$ deviates from power law behavior for q above $1/\xi$, which is called Guinier region.²³ The $I(q)$ of Guinier and fractal regions, and the crossover between the Guinier and fractal regions, can be fit by Equation 12,

$$I(q) = A \frac{\Gamma(D+1)}{(1+q^2\xi^2)^{(D-1)/2}} \frac{\sin[(D-1)\arctan(q\xi)]}{(D-1)q\xi} \quad (12)$$

where A is a constant for a given D and ξ , and Γ is the gamma function.²⁴

Fitting the above equation for the low and medium q regions of the experimental curves, the fractal dimension D and correlation length ξ of the wet gels formed by different amounts of TNM can be obtained (Table 3).

Fractal dimension values estimated from the fitting process are in the range between ~1.8 and ~2.0, except for the gel formed by 50 μL of TNM. According to Gacoin et al., transparent CdS gels resulting from the RLCA mechanism have a fractal dimension of 1.9.⁴ From our observations, the fractal dimension decreases with the increase of oxidant concentration and there is a significant decrease at 50 μL of TNM. The fractal dimension also explains the change of cluster mass, which is related to the correlation length and fractal dimension, according to Equation 13.^{23, 25}

$$m \propto \xi^D \quad (13)$$

As we confirmed by TRDLS, fast removal of ligands from the NC surface with the increase of oxidant concentration increases the probability of NC sticking and leads to larger aggregates before they form the gel network, and this can be further confirmed by the increase of the correlation length with the increase of oxidant concentration, as it is associated with the average cluster size.^{4,26} Furthermore, the increase of sticking probability prevents the small clusters from permeating the large clusters, and so they are rapidly attached at the edge of the large clusters, resulting in more open and less dense aggregates and a lower fractal dimensionality of the final gel structure (Table 2).^{13a} A dramatic change is observed between 10–50 μL , consistent with a shift toward DLCA. Relative cluster-mass values are consistent with this phenomena, since the relative cluster mass, m , decreases between 10 and 50 μL of TNM, although there is a significant increase of the cluster size according to the correlation length values (Table 3). TEM images of the gel structures formed by 8 and 50 μL of TNM reveal this difference. As shown in Figure 6a and b, the resulting gel structure is more dense at a low concentration of oxidant, where aggregation

follows RLCA kinetics. At high concentration of oxidant, faster kinetics resulted in a more open and less dense gel structure as indicated in Figure 6c and d. Because these are disordered fractal materials, no symmetry is apparent in the TEM images.

The trend towards DLCA (i.e., increased sticking probability) observed for the larger, orange-emitting particles in the TRDLS is also reflected in the SAXS data. Orange-emitting gels formed from addition of 4 μ L of TNM exhibit lower fractal dimension ($D = 1.76$) and higher correlation length values ($\xi = 8.49$, supporting information Figure S3) than the green-emitting gels formed under the same conditions.

Conclusions

The mechanism and kinetics of aggregation of green- and orange-emitting CdSe(ZnS) core(shell) NCs, initiated by removal of surface thiolate ligands using TNM as an oxidant, was studied by means of TRDLS and the characteristics of the resultant gels were probed by optical absorption, TEM and SAXS. Analysis of the sol-gel transition process clearly indicates that the degree of transparency of the resultant gels depends on the structural characteristics of the gels, which are in turn governed by the kinetics of aggregation and gelation of NCs. For small, green-emitting NCs, aggregation follows RLCA kinetics at low concentrations of NCs and oxidant, and the resulting gel structures are transparent due to the formation of aggregates that, at the gel point, have sizes below the wavelength of visible light. As the particle concentration, size or oxidant concentration is increased, there is a shift away from RLCA kinetics and the resultant aggregates trapped at the gel point are larger, scattering visible light and increasing opacity. These trends correlate with the fractal dimensionality of the gel networks, in which decreasing dimensionality correlates with larger, lower density aggregates arising from increased sticking coefficients (i.e., a shift towards a DLCA mechanism) and decreased transparency. As a next step towards exploitation of these sol-gel materials in optoelectronic applications, we are using the gelation conditions established here to fabricate transparent semiconducting CdSe(ZnS) core(shell) sol-gel films.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Gaponik N, Herrmann AK, Eychmüller A. *J Phys Chem Lett*. 2012; 3(1):8–17.
2. Mohanan JL, Arachchige IU, Brock SL. *Science*. 2005; 307(5708):397–400. [PubMed: 15662006]
3. Arachchige IU, Brock SL. *J Am Chem Soc*. 2007; 129(7):1840–1841. [PubMed: 17256934]
4. Gacoin T, Lahlil K, Larregaray P, Boilot JP. *J Phys Chem B*. 2001; 105(42):10228–10235.
5. Peng ZA, Peng X. *J Am Chem Soc*. 2000; 123(1):183–184. [PubMed: 11273619]
6. Hines MA, Guyot-Sionnest P. *J Phys Chem*. 1996; 100(2):468–471.
7. Qu L, Peng X. *J Am Chem Soc*. 2002; 124(9):2049–2055. [PubMed: 11866620]
8. Yu WW, Qu L, Guo W, Peng X. *Chem Mater*. 2003; 15(14):2854–2860.

9. Berne, BJ.; Pecora, R. Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics. Dover Publications; Mineola, NY: 2000.
10. Brown, W. Dynamic light scattering: the method and some applications. Clarendon press; NY: 1993.
11. Koppel DE. J Chem Phys. 1972; 57(11):4814–4820.
12. Pala I, Arachchige I, Georgiev D, Brock S. Angew Chem, Int Ed. 2010; 49(21):3661–3665.
13. (a) Lin MY, Lindsay HM, Weitz DA, Ball RC, Klein R, Meakin P. Nature. 1989; 339(6223):360–362. (b) Lin MY, Lindsay HM, Weitz DA, Ball RC, Klein R, Meakin P. Phys Rev A. 1990; 41(4): 2005–2020. [PubMed: 9903311] (c) Lin MY, Lindsay HM, Weitz DA, Klein R, Ball RC, Meakin P. J Phys: Condens Matter. 1990; 2:3093–3113.
14. Umbach P, Georgalis Y, Saenger W. J Am Chem Soc. 1998; 120(10):2382–2390.
15. Hanus LH, Sooklal K, Murphy CJ, Ploehn HJ. Langmuir. 2000; 16(6):2621–2626.
16. Jasmine MJ, Prasad E. J Phys Chem B. 2010; 114(23):7735–7742. [PubMed: 20496918]
17. Burns JL, Yan Y-d, Jameson GJ, Biggs S. Langmuir. 1997; 13(24):6413–6420.
18. Shibayama M. Bull Chem Soc Jpn. 2006; 79(12):1799–1819.
19. Shibayama M, Norisuye T. Bull Chem Soc Jpn. 2002; 75(4):641–659.
20. Martin JE, Wilcoxon JP. Phys Rev Lett. 1988; 61(3):373. [PubMed: 10039314]
21. Martin JE, Wilcoxon J, Odinek J. Phys Rev A. 1991; 43(2):858. [PubMed: 9905103]
22. Miyazaki S, Endo H, Karino T, Haraguchi K, Shibayama M. Macromolecules. 2007; 40(12):4287–4295.
23. Schaefer DW, Keefer KD. Phys Rev Lett. 1984; 53(14):1383.
24. Vacher R, Woignier T, Pelous J, Courtens E. Phys Rev B. 1988; 37(11):6500–6503.
25. Emmerling A, Petricevic R, Beck A, Wang P, Scheller H, Fricke J. J Non-Cryst Solids. 1995; 185(3):240–248.
26. Beurroies I, Duffours L, Delord P, Woignier T, Phalippou J. J Non-Cryst Solids. 1998; 241(1):38–44.

Figure 1.
(a) HRTEM images of green- (a) and orange- (b) emitting CdSe core NCs. The inset shows absorption and emission spectra of MUA-capped core (shell) NCs.

Figure 2.

(a) Time evolution, as a function of the amount of TNM, of $\bar{R}_h$ for green- and orange-emitting CdSe(ZnS) NCs; and (b) $\log \bar{R}_h$ vs time for green-emitting CdSe(ZnS) core(shell) NCs.

Figure 3. Photographs, and (b) transmittance of green-emitting wet gels formed from different TNM concentrations; (c) Photographs of orange-emitting wet gels formed from different TNM concentrations; (d) Photographs of green-emitting wet gels (10-fold increase in concentration) formed by different TNM concentrations. Note: 40 μL of TNM in (d) corresponds to the same NC:TNM ratio as 4 μL in Figure 3a and c.

Figure 4.

Intensity correlation functions, $g^2(\tau) - 1$ of the (a) green-, and (b) orange-emitting CdSe(ZnS) core(shell) NC sols oxidized by 4 μL of TNM as a function of time.

Figure 5. SAXS spectra of green-emitting wet gels formed by different amounts of TNM. Lines composed of open circles represent the fitting of Equation 12 to the experimental curves.

Figure 6.
TEM images of gel clusters formed by (a), (b) 8 μL , and (c), (d) 50 μL of TNM.

Table 1

Core size and optical properties of CdSe(ZnS) core (shell) NCs

	Core size (nm)	Absorption onset (eV)	Band edge emission maxima (eV)	FWHM (nm)
Green-emitting NCs	4.6 ± 0.3	2.17	2.19	31.3
Orange-emitting NCs	5.3 ± 0.4	2.00	2.03	33.5

Table 2

Gel point, t_{gel} , and average cluster size near the gel point for green- and orange-emitting gels formed from different amounts of TNM

Amount of TNM (μ L)		4	6	8	10
Green-emitting gels	t_{gel} (min)	16	6	4.5	3
	Average cluster size (nm)	230	320	390	470
Orange-emitting gels	t_{gel} (min)	43	25	15	7.5
	Average cluster size (nm)	480	510	540	670

Table 3

Fractal dimension, D , correlation length, ξ , and relative cluster mass, m , values of the green-emitting gels formed from different amounts of TNM.

Amount of TNM (μL)	4	6	8	10	50
D	1.96	1.95	1.84	1.83	1.30
ξ (nm)	4.5	5.1	6.1	7.5	14.8
$m \propto \xi^D$	19	24	28	40	33