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Role of Crystal Structure and Chalcogenide Redox Properties on the Oxidative Assembly of Cadmium Chalcogenide Nanocrystals

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Abstract

Oxidative assembly of metal chalcogenide nanocrystals (NCs) enables the formation of 2-D (dense) and 3-D porous structures without the presence of intervening ligands between particles that can moderate transport properties. This route has been demonstrated to be successful for a range of single-component structures including CdQ, PbQ, and ZnQ (Q = S, Se, Te). En route to the controllable assembly of multicomponent nanostructures, the roles of Q redox properties ($2Q^{2-} \rightarrow Q_2^{2-} + 2e$) responsible for particle cross-linking and the native structure (cubic zinc blende vs hexagonal wurtzite) in the kinetics of assembly in single-component CdQ NCs are evaluated using time-resolved dynamic light scattering (TR-DLS). For wurtzite CdQ, the rates follow the ease of oxidation, with telluride as the fastest, followed by selenide and sulfide. However, when comparing CdS wurtzite (*w*) and zinc blende (*zb*), the cubic NCs exhibit surprisingly slow kinetics. NMR studies reveal the *zb* structure to have lower ligand coverage (by a factor of 4) relative to that of *w*, and the formation of free disulfide (the product of ligand oxidation) is slow. This is attributed to differences in the surface energies of *w* and *zb* facets, with *w* having polar (0001) facets of high energy compared to the neutral facets of the *zb* structure. The *zb*-CdS NCs prepared by low-temperature synthesis methods are likely to suffer from surface defects that may moderate reactivity. EPR studies suggest that *zb*-CdS has paramagnetic sulfur vacancies not present in *w*-CdS. These data suggest that structure plays an unexpectedly large role in the kinetics of CdQ NC oxidative assembly, providing a useful lever to moderate activities in multicomponent assemblies.

Graphical abstract

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Notes

The authors declare no competing financial interest.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01118. TEM micrographs; PXRD patterns; ^1H NMR, ^{19}F NMR, and IR spectra; and particle size analysis (PDF)

1.0. INTRODUCTION

Semiconducting nanocrystals (NC) based on metal chalcogenides exhibit significant promise in technical applications because of the easily tunable band gap throughout much of the visible spectrum, controlled by the size and shape of the nanocrystals, as well as their ease of synthesis. Accordingly, this class of semiconducting quantum dots (QDs) is of considerable interest for optoelectronic device applications such as field-effect transistors (FETs),^{1,2} photodetectors,^{3,4} light-emitting diodes (LEDs),^{5–7} solar cells,^{8,9} and radiation detectors.^{10–12} However, to realize applications based on facile carrier transport, metal chalcogenide NCs need to be interfaced together. Thus, considerable focus has been placed on exchanging the long-chain insulating ligands typically employed in NC synthesis with shorter and more labile passivating ligands for the improvement of charge transport in devices^{13,14} as well as other passivation techniques such as the use of molecular metal chalcogenide complexes as ligands for colloidal NCs or halide passivation on the NC surface for solution-based passivation.^{15–17}

A second consideration is the need for multiple components acting in harmony. Core-shell heterostructured spherical NCs can be designed to improve photoluminescence yields by the reduction of trap states,^{18–22} whereas heterostructured nanorods enable charge separation.²³ Other heterostructured nanomaterials such as carbon nanotubes dispersed with gold nanoparticles allow for strong electronic coupling in the material. In catalysis, heterogeneous materials, for example, MoS₂ grown on graphene, have demonstrated an improvement in catalytic hydrogen evolution.^{24,25}

A sol-gel assembly method has been developed in our laboratory to provide a reproducible and robust approach to linking metal chalcogenide NCs into three-dimensional architectures (i.e., gels, xerogels, and aerogels) or thin films. The absence of intervening ligands leads to facile charge extraction while maintaining the quantum confinement effects of the individual NCs.^{26–30} Gelation is achieved by a two-step sol-gel process: (1) irreversible ligand removal (deprotection) by the oxidation of surface thiolate ligands ($2RS^- \rightarrow RS-SR + 2e^-$) and (2) oxidative assembly by the formation of di- or polychalcogenide cross-linkages between NCs (Figure 1).³¹ The generality of this approach enables the assembly of a diverse group of chalcogenide nanoparticles including CdQ, PbQ, ZnQ, and Bi₂Q₃ (Q = S, Se, Te) into single-component gels.^{26–40} By employing core@shell nanocrystals, such as CdSe@ZnS,

we can make homogeneous multicomponent gels in which the second component is uniformly distributed at the interfaces between particles.³⁸ Presently, we seek to create multicomponent gels comprising two distinct nanocrystal compositions with a rational control of heterogeneity. To do so, we need to have a better understanding of the kinetic factors that govern NC assembly.

Previous work in our group has shown that the kinetics of aggregation of CdSe@ZnS NCs are directly affected by the NC concentration, NC size, and oxidant concentration.^{38,40} Qualitatively, we noted that the rates of CdQ gelation also depend on Q, with tellurides gelling rapidly relative to sulfides.³⁶ We hypothesize that differences in the rate of aggregation and gelation will be governed by the redox characteristics of Q (S = 0.48 V, Se = 0.92 V, and Te = 1.14 V), leading to heterogeneity in multicomponent systems comprising different chalcogenides.⁴¹ Here, we seek to quantify this effect as a means to rationally control heterogeneity in multicomponent composites. In doing so, we have revealed a new and unexpected contributor to the kinetics of assembly, finding that the crystal structure adopted by CdQ (cubic zinc blende vs hexagonal wurtzite) has a profound effect on the rate of gelation.

2.0. EXPERIMENTAL SECTION

2.1. Synthesis

2.1.1. Materials—Bis(trimethylsilyl)sulfide (TMS), trioctylphosphine oxide (TOPO, 90%), tetranitromethane (TNM), 4-fluorothiophenol, 16-mercaptohexadecanoic acid (MHA), tetramethylammonium hydroxide, selenium, tellurium, 1-tetradecylphosphonic acid (TDPA), hexafluorobenzene, and triethylamine were purchased from Sigma-Aldrich. Trioctylphosphine, cadmium oxide (99.999%), cadmium chloride, and sodium sulfide were purchased from Strem. *d*₆-Acetone was purchased from Cambridge Isotopes Laboratory Inc. All solvents were used as received except for trioctylphosphine oxide, which was distilled prior to use.

2.1.2. 4-Fluorothiophenolate-Capped Cubic (zinc blende, zb) CdS Nanocrystal (NC) Synthesis—*zb*-CdS NCs were synthesized following a modified literature procedure.⁴² CdCl₂ (0.086 g, 0.5 mmol) was stirred in methanol under Ar gas flow until a clear solution was formed. A solution of 0.125 g of Na₂S (0.5 mmol) in methanol was injected, followed by a solution of 4-fluorothiophenol and triethylamine (Cd/S molar ratio 1:10, based on the starting Cd concentration). NCs were dispersed in acetone and isolated by precipitation with *n*-heptane and centrifugation, and this process was repeated one time.

2.1.3. Hexagonal (Wurtzite, w) CdS Nanocrystal (NC) Synthesis—*w*-CdS NCs were synthesized by modifications of literature procedures.^{43–45} CdO (0.060 g, 0.47 mmol), TDPA (0.23 g), and TOPO (3.0 g) were heated to 320 °C (with the thermocouple placed in the heating mantle adjacent to the flask exterior) under a flow of argon. Once a clear and colorless solution was produced, the sample was injected with 2 mL of TOP, the temperature was increased to 370 °C, and a solution containing 86 μL (0.41 mmol) of TMS in 2.4 mL of TOP was injected. The temperature was held at 370 °C for 10 min before being cooled to

75 °C and annealing for 24 h. Four milliliters of toluene was injected, followed by precipitation with ethanol and isolation by centrifugation. This process was repeated twice.

2.1.4. 4-Fluorothiophenolate Capping of *w*-CdS NCs—A solution of 4-fluorothiophenol and triethylamine in acetone was added to solid *w*-CdS NCs (Cd/S ratio of 1:10 based on original moles of Cd employed in the synthesis) and sonicated. The resulting 4-fluorothiophenolate-capped CdS NCs were precipitated with *n*-heptane and dispersed in acetone to form the nanocrystalline sol.²⁶

2.1.5. *zb*- and *w*-CdSe NC Synthesis—CdSe NCs were synthesized by a modified literature preparation.^{43–48} CdO (0.050 g, 0.4 mmol) was combined with tetradecylphosphonic acid (0.200 g) and trioctylphosphine oxide (4.0 g) in a round-bottomed flask under Ar. The mixture was heated to 320 °C until a clear solution was produced, and then the temperature was reduced to 150 °C. A solution containing 0.032 g (0.4 mmol) of Se in 2.4 mL of TOP was injected into the Cd solution, and the temperature was slowly increased to 220–260 °C depending on the desired crystal structure (lower temperature for *zb* and higher temperature for *w*). Finally, the solution temperature was reduced to 75 °C, and 4 mL of toluene was injected. CdSe NCs were isolated as described for *w*-CdS NCs.

2.1.6. *w*-CdTe NC Synthesis—CdTe NCs were synthesized following a literature procedure with a slight modification.³⁶ In a typical synthesis, 0.050 g (0.4 mmol) of CdO was combined with 0.200 g of tetradecylphosphonic acid and 3.75 g of trioctylphosphine oxide in a round-bottomed flask under Ar. The mixture was heated to 320 °C until a clear solution was produced, and then the temperature of the solution was reduced to 150 °C. A solution containing 0.060 g (0.4 mmol) of Te in 2.4 mL of TOP was injected into the Cd solution, and the temperature was slowly increased to 270 °C and then quickly cooled. Finally, the solution temperature was reduced to 75 °C. CdTe NCs were isolated as described for *w*-CdS NCs.

2.1.7. 16-Mercaptohexadecanoic Acid Ligand (MHA) Exchange—A solution of MHA and tetramethylammonium hydroxide in methanol was added to solid CdQ NCs (Cd/thiol ratio of 1:4 based on the original number of moles of Cd employed in the synthesis) and shaken vigorously. The resulting MHA-capped CdQ NCs were precipitated with ethyl acetate and finally dispersed in methanol to form the nanocrystalline sol. Mercaptoundecanoic acid-capped *w*-CdSe NCs were prepared by the same procedure.

2.2. Characterization

2.2.1. Transmission Electron Microscopy (TEM)—TEM and energy-dispersive spectroscopy (EDS) studies 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.). Bright-field images were taken with Amtv 600 software. TEM samples were prepared by the dispersion of nanoparticles in solvent (methanol or toluene) and the deposition of a drop of sol on a Formvar carbon-coated 200 mesh Cu grid, followed by drying in air. The particle sizes were analyzed by NIS-Elements D3.10 software. To obtain the histograms, the particle sizes were categorized into 0.5 nm bin sizes.

2.2.2. Powder X-ray Diffraction (PXRD)—The structural properties of CdQ NCs were studied by PXRD performed on a Bruker D2 Phaser using the $K\alpha$ line of a Cu anode source (30 kV, 10 mA). Samples were deposited on a zero background quartz holder, and data were collected over the 2θ range of 20–60°. Data were compared to powder diffraction patterns (pdf's) in the ICDD database, release 2000. The particle size was determined using the Scherrer equation (eq 1), with K set to 0.9.

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

2.2.3. Optical Spectroscopy—UV–visible spectra were obtained on CdQ sols using a Shimadzu UV-1800 spectrometer in a quartz cuvette. On the basis of these data, the NC concentration was calculated using the first absorption peak in the UV–visible spectrum to determine the size-dependent extinction coefficients, as published by Yu et al.⁴⁹

2.2.4. Nuclear Magnetic Resonance Spectroscopy (NMR)—4-Fluorothiophenolate-capped CdS NC sols were characterized with ^1H and ^{19}F NMR spectroscopy measurements. These were performed on a Varian Mercury 400 NMR spectrometer in d_6 -acetone at room temperature. Chemical shifts were reported in parts per million. The solvent volume in the NMR tubes was held constant (750 μL) for each sample, and 9 mg of solid NCs was dispersed. For mechanistic studies of the sol–gel process, 20 μL of a 10% oxidant (TNM) solution was injected into the NMR tubes. Prior to the acquisition of final spectra on gels, samples were allowed to age at room temperature for several days following visual observation of gelation.

To quantify ligand loss from *zb*- and *w*-CdS NCs, a common standard for ^{19}F NMR spectroscopy, hexafluorobenzene with a known concentration of 0.447 M was added to each test tube containing the CdS samples (*zb*- and *w*-) that had been overoxidized using excess TNM oxidant to remove all of the thiolates as disulfide from the NC surface. The concentration of disulfide byproduct was determined on the basis of the standard hexafluorobenzene concentration; other reaction byproducts were minimal and could not accurately be accounted for in the determination because of noise.

2.2.5. Electron Paramagnetic Resonance (EPR) Spectroscopy—EPR spectroscopy was performed on a Bruker EMX X-band spectrometer equipped with an Oxford variable-temperature cryostat. Data were acquired at a temperature of 110 K with a microwave frequency of 9.4 GHz, a microwave power of 1.99 mW, a modulation frequency of 100 kHz, a receiver gain of 30 dB, and a modulation amplitude of 1.0 G (with 10 points per modulation amplitude). The sample was prepared by dispersing NCs or aerogels in acetone in a Suprasil quartz capillary tube with a 4 mm outer diameter and was frozen in liquid nitrogen prior to being placed in the instrument.

2.2.6. Time-Resolved Dynamic Light Scattering (TR-DLS)—TR-DLS measurements were performed with a Zetasizer Nano ZS instrument (Malvern Instruments,

Westborough, MA) with a 633 nm He–Ne laser and a detector positioned at 173°. The Z -average hydrodynamic radius (R_H) was determined using the Zetasizer software (version 6.2) provided by Malvern. By monitoring the change in the hydrodynamic radius upon the addition of the oxidizing agent, the onset and kinetics of aggregation were determined. For all of the TR-DLS measurements, the CdQ sol volumes were held constant (3 mL) and the sol was pipetted into a disposable cuvette. After adding TNM, the disposable cuvette was vigorously shaken and immediately placed in the DLS instrument. The average hydrodynamic radius (R_h) was calculated as described previously.³⁸

2.2.7. X-ray Photoelectron Spectroscopy—X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra XPS in spectrum mode at 10 mA and 15 kV with a monochromatic Al K α X-ray source. A low-energy electron flood gun was employed for charge neutralization of the nonconducting samples. The pressure in the analytical chamber during spectral acquisition was approximately 1×10^{-9} Torr. The pass energy for survey spectra was 160 eV, and the pass energy for high-resolution scans was 20 eV. The binding energy scales were calibrated on the basis of the most intense C 1s high-resolution peak binding energy.

3.0. RESULTS AND DISCUSSION

3.1. Initial Evaluation of Gelation Kinetics: CdQ (Q = S, Se, Te)

To assess the role of chalcogenide Q (S, Se, Te) in gelation kinetics, CdS, CdSe, and CdTe NCs were synthesized and capped with 16-mercaptohexadecanoic acid, and the time-dependent aggregation was evaluated by time-resolved dynamic light scattering (TR-DLS) upon introduction of oxidant. Earlier work in our group demonstrated that for constant NC and oxidant concentration smaller NCs aggregate faster than the larger NCs (CdSe). Likewise, increasing oxidant concentration decreases the time required to achieve a gel, resulting in larger aggregate sizes at the gel point, thus affecting the transparency of the final macroscopic gel.³⁸ Accordingly, to evaluate the effect of Q, CdQ NCs of similar size were generated by modifying existing literature preparations, as described in the Experimental Section, and a constant volume of oxidant was employed. The average NC size and standard deviation were determined from histograms of >100 particles acquired by TEM imaging (Figure S1): 4.5 ± 0.6 nm (CdS), 4.7 ± 0.5 nm (CdSe), and 4.6 ± 0.8 nm (CdTe). The kinetics of aggregation of sols of CdS, CdSe, and CdTe capped with 16-mercaptohexadecanoic acid (MHA) at an NC concentration of 3×10^{-7} M (as determined from optical spectroscopy) and treated with 20 μ L of the oxidizing agent (3% TNM) were studied using TR-DLS.

The TR-DLS plot of the hydrodynamic radius, $\bar{R}_h$, as a function of time after the addition of the oxidizing agent is shown in Figure 2. As indicated previously, we hypothesized that the kinetics of aggregation would follow the redox characteristics of Q^{2-} , with $Te > Se > S$. As expected, the $\bar{R}_h$ for CdTe NCs grows rapidly, achieving a value of ca. 1 μ m after 10 min, indicative of rapid aggregation, whereas CdS NCs are slower, taking nearly 20 min to achieve a similar aggregate size. However, instead of the CdSe demonstrating intermediate kinetics, these NCs were found to react much slower than CdS, with little upturn in the

hydrodynamic radius prior to 20 min. An evaluation of PXRD patterns for the three samples reveals a possible explanation (Figure S2). The CdSe pattern is indicative of cubic (*zb*) as the major structure type, whereas CdS and CdTe are distinctively hexagonal (*w*).

CdSe is known to suffer from polytypism between the *zb* and *w* crystal structures, which differ only by the close-packed layer stacking patterns (ABCABC for *zb* and ABAB for *w*). There is a very low energy difference between the two crystal structure types, within a few millielectronvolts per atom, making interconversion and intergrowth between the two crystals a common occurrence.^{50,51} To test the hypothesis that structure plays a role in the kinetic differences, we sought to compare *w*-CdS to *zb*-CdS. The sulfide system was chosen over the selenide because the energy difference between cubic and hexagonal CdS is greater than for CdSe, which is expected to reduce the occurrence of intergrowth structures or byproduct formation of the secondary phase at synthesis temperatures chosen to target the primary phase.⁵²

3.2. Probing Structure Effects, *zb*- vs *w*-CdS

3.2.1. Effect of Structure on Kinetics—Cubic (*zb*-CdS) and hexagonal (*w*-CdS) NCs were prepared by modifying literature procedures, employing a room-temperature inverse micelle route for the metastable *zb* and a high-temperature arrested precipitation route for *w*.^{42,43} In this instance, 4-fluorothiophenolate was used as the capping agent, trapping the *zb*-CdS as it is prepared or being exchanged with the native trioctylphosphine oxide ligands of *w*-CdS. The success of the exchange for *w*-CdS is evident in the ¹H NMR spectrum (Figure S3). As shown in Figure 3c, the structural data for the two is distinct, with the low-temperature synthesized phase adopting the cubic structure and the high-temperature, the hexagonal. The absence of the (102) reflection at ca. 35° 2θ in the room-temperature prepared material is a strong indicator that *zb* is the dominant phase. As shown in Figure 3a,b and Figure S4, the sizes are similar: 4.1 ± 0.4 nm for *zb*-CdS and 4.5 ± 0.6 nm for *w*-CdS NCs, consistent with crystallite size values obtained by the application of the Scherrer equation to PXRD data (Table S1). Figure S5 shows the UV–visible absorption spectra for both the 4-fluorothiophenolate-capped *w*-CdS NCs and the *zb*-CdS NCs; the spectra are distinct, with *zb*-CdS having an onset near 500 nm and *w*-CdS, at 450 nm, consistent with the formation of distinct structures in the two samples. (Note that on the basis of size alone, *zb*-CdS would be expected to have a higher energy transition because it is slightly smaller than *w*-CdS.)

Figure 4 displays the aggregation kinetics of the *zb*- and *w*-CdS NCs over time using the TR-DLS measurements. It is clear that for *w*-CdS the aggregation is so rapid that it occurs within several minutes of the introduction of the TNM oxidant. To verify that the aggregation is induced by the oxidant and not primarily a consequence of photooxidation (which can also occur, albeit at a much slower time scale), the TR-DLS of mercaptoundecanoic acid-capped *w*-CdS in the absence of oxidant was probed; no apparent increase in scattering is observed on the time scale of the experiment (Figure S6). Oxidation-induced assembly of *zb*-CdS NCs occurs by slower aggregation kinetics than for *w*-CdS, over several hours (Figure 4). Morphologically, the gels appear similar with clearly evident porous networks, but visually the gels formed from *zb*-CdS are much more compact (Figure

S7). Thus, the thermodynamics of Q^{2-} oxidation are not sufficient to describe the reactivity; structure appears to be playing an important role.

In contrast to *zb*-CdS, the *w*-CdS lattice lacks inversion symmetry about the *c* axis, rendering the (0001) and (000 $\bar{1}$) surfaces crystallographically nonequivalent, with one facet being cation-terminated (and therefore positively charged) and the opposing facet being anion-terminated.^{44,53–56} This difference results in an overall polarity in *w*-CdS that is not present in the *zb* counterpart, where the facet polarities essentially cancel, and may be responsible for the difference in the rate of loss of the surface capping ligands despite the fact that *w* and *zb*-CdS are otherwise structurally similar.⁵⁷ Indeed, such facet energy differences have been invoked in the formation of heterodimers of

w- CdS (0001)//*zb*- CdTe ($\bar{1}\bar{1}\bar{1}$) over *w*-CdS(000 $\bar{1}$)/*zb*-CdTe(111) by ion-exchange treatment of *w*-CdS with trioctylphosphine telluride. The observation that heterodimers arise only between Cd²⁺-terminated *w*-CdS and Te²⁻-terminated CdTe is attributed to the passivation of the resultant exposed CdTe(111) facet (cation-terminated) by protecting ligands, which reduces the surface energy.⁵⁸ Another recent study exploiting this phenomenon employs site-specific (facet-specific) ligand coverage to make amphiphilic *w*-CdQ nanorods that can then be arranged using end-to-end attachment.⁵⁹

Gacoin and co-workers employed the 4-fluorothiophenolate capping ligand to monitor the aggregation and gelation using ¹H and ¹⁹F NMR spectroscopy.^{28,30} Assuming a two-step process for colloidal aggregation starting with (1) the oxidative loss of the surface thiolate capping agent followed by (2) the formation of surface chalcogenide linkages between NCs, monitoring this process in situ with ¹H and ¹⁹F NMR would enable us to learn whether a contributing factor in the kinetics of colloidal aggregation was the loss of the surface thiolate ligand, possibly due to the differences in the surface facets between the two crystal structures.

3.2.2. Ligand Loss Kinetics in *zb*- vs *w*-CdS—NMR spectra were monitored over time for *w*-CdS and *zb*-CdS NCs capped with 4-fluorothiophenolate following treatment with 20 μ L of 10% TNM solution in *d*₆-acetone at room temperature. Figure 5 shows the ¹⁹F NMR spectra for the *w*-CdS NCs before and after the addition of the oxidizing agent, with a broad peak at –125 ppm indicative of the 4-fluorothiophenolate ligand on the surface of the CdS NC clearly evident before addition. There is also a peak corresponding to the disulfide that is centered at –115 ppm and already evident prior to the addition of the oxidant, presumably because of CdS-mediated photooxidation of some of the surface 4-fluorothiophenolate ligand.^{28,30} Upon the addition of the TNM (oxidant), there is a decrease in the intensity of the peak located at –125 ppm, which also shifts downfield and splits into two peaks, –124 and –122 ppm, with a simultaneous increase in the disulfide peak at –115 ppm indicative of the oxidative elimination of surface thiolates by the formation of free disulfide, as shown in eqs 2 and 3. The small shifts in peak positions observed upon the addition of the oxidant are likely due to changes in the electrostatic charges at the surface of the particle and possibly the formation of the aggregates in solution,¹³ whereas the peak splitting is attributed to the formation of bridging thiolates (–122 ppm) from terminal thiolates (–124 ppm) as the surface becomes depopulated by oxidative removal of

thiolates.⁶⁰ Other smaller peaks between –110 and –115 ppm are likely due to byproducts formed from reactions of sulphenylnitrite, formed from isomerization of the thionitrate as shown in eq 4, including sulfinite, sulfonate, and sulfonic acid derivatives of the 4-fluorothiophenol.⁶¹

(3)

At the gel stage, no peak due to bound 4-fluorothiophenolate is apparent. Although this might be interpreted as complete oxidation of the bound ligand, prior studies indicate that residual ligands remain under the conditions employed.²⁶ More likely, the viscosity of the gel prevents the tumbling of bound thiolates, and the peak broadens into the background. Similar chemical transformations are evident in the ¹H NMR spectra (Figure S8).

Figure 6 shows the ¹⁹F NMR spectra of the *zb*-CdS NCs sol and gel after the addition of the oxidizing agent. In contrast to *w*-CdS, before the addition of oxidant, the peak ascribed to bound thiolate (–123 ppm) is exceptionally broad, and peaks ascribed to products from photooxidation are weak (–116 ppm, disulfide; –112 ppm, sulfonate). Intriguingly, the addition of oxidant has little effect on the spectrum; the peaks at –112 and –116 grow somewhat but remain small compared to the peak corresponding to bound thiolate, which is still clearly evident after gelation. The NMR studies suggest that the surface ligand loss for the *zb*-CdS NCs after the addition of the oxidant is slower than for the *w*-CdS, which correlates with the TR-DLS studies, consistent with one of the factors in the slower kinetics of aggregation of *zb*-CdS being slower surface thiolate ligand oxidative elimination. Indeed, the prominence of the sulfonate peak at –112 ppm, which is of similar intensity to the disulfide at –116 ppm, suggests that the thionitrate is not being immediately trapped by bound thiolates to form disulfide but instead has time to isomerize to the sulphenyl nitrite. This may be ascribed to the lower reactivity of thiolates surface-bound to *zb*-CdS (due to facet binding energies), a lower concentration of available surface thiolates, or both. Intriguingly, the oxidation products are sufficiently low in concentration that they are not observed at all by ¹H NMR (Figure S9).

3.2.3. Quantifying Surface Ligation in *zb*- vs *w*-CdS—To evaluate whether differences in the extent of surface ligand capping may be playing a role in the slow kinetics of thiolate loss and gelation in *zb*-CdS, we quantified the number of capping groups in each

case by treatment with excess TNM and an evaluation of the concentration of product disulfide by ^{19}F NMR calibrated against an internal standard (Figure S10). To verify that all of the organothiulates were removed, we acquired FT-IR spectra before and after the oxidative treatment (Figure S11). Characteristic peaks of 4-fluorothiophenolate present in as-prepared NCs were absent after oxidative stripping. For the *zb*-CdS NCs, there were an average of 75 4-fluorothiophenolate ligands per particle (5.68 ligands/nm²), whereas the *w*-CdS NCs had much higher surface ligand coverage, with an average of 300 4-fluorothiophenolate ligands per particle (18.9 ligands/nm²).

The observation of fewer ligands on *zb*-CdS vs *w*-CdS is surprising because the thiulates are presumed to act as protecting groups that act to limit the oxidative assembly of nanoparticles. Loss of thiulates leads to exposure of bound chalcogenide and consequent oxidative assembly. By this rationale, one would expect aggregation rates in *zb*-CdS to be faster, not slower, than in *w*-CdS. However, if the uncapped portions are deactivated, perhaps due to surface oxidation, such deactivation may actually be a cause, and not an effect, of a low extent of ligand capping.

3.2.4. Quantifying Surface Oxidation *zb*- vs *w*-CdS—A recent paper by Thomas et al. discussed the role of the surface composition of CdSe QDs on the luminescence properties between *zb*-CdSe and *w*-CdSe, indicating that *zb*-CdSe NCs with a surface layer of CdO showed improvement in the PL emission.⁶² To determine if our *zb*-CdS QDs might have an oxide layer not present in *w*-CdS, which could prevent the formation of dichalcogenide linkages responsible for oxidative assembly, XPS studies were conducted. The binding energies of cadmium 3d_{5/2} and 3d_{3/2} electrons for CdS bulk are reported to be 405 and 412 eV, respectively.⁶³ The Cd spectra for *zb*- and *w*-CdS NCs are presented in Figure 7. In addition to the expected peaks for CdS, both spectra have peaks at ca. 2 eV higher energy corresponding to Cd–O. However, quantification of the oxide suggests that the extent of oxidation is similar in the two materials. This suggests that bulk oxidation is not responsible for the differences in reactivity, although it remains possible that the regions of oxidation in the two materials are distinct and contribute to the reactivity differences.

3.2.5. Assessment of Surface Defects in *zb*- vs *w*-CdS—Finally, we considered the possible role of surface defects resulting in the deactivation of the *zb*-CdS surface relative to *w*-CdS. The exceptional peak broadening observed for bound thiolate in the ^{19}F NMR spectra of *zb*-CdS suggested the possibility of a paramagnetic center in these materials not present in *w*-CdS. The most common paramagnetic centers relate to cation or anion vacancies that, if surface bound, may moderate the activity of the NCs toward oxidative assembly. To verify the presence of a paramagnetic impurity, electron paramagnetic resonance spectroscopy (EPR) was performed on samples of uncapped *zb*-CdS, isolated without the addition of the 4-fluorothiophenolate capping ligand (Figure 8a), *zb*-CdS synthesized with the 4-fluorothiophenolate capping ligand (Figure 8b), and *w*-CdS capped with 4-fluorothiophenolate (Figure 8c). Uncapped *zb*-CdS NCs show a clear EPR signal with a *g* value of 2.004 that matches the known values for sulfur vacancies in similar *zb*-CdS NCs.⁶⁴ The specific anionic vacancy for CdS crystals behaves as a double donor, with a paramagnetic singly occupied state.^{64–67} Upon capping with 4-fluorothiophenolate, the *zb*-

CdS NCs exhibit the same $g = 2.004$ signal, along with a new signal in the EPR spectrum that we could not identify but seems to be a result of the 4-fluorothiophenolate addition. In contrast, 4-fluorothiophenolate-capped w -CdS is EPR silent. It is not surprising that the zb -CdS should be defective because it is prepared at room temperature and there is insufficient energy to anneal out defects; however, it is surprising that 4-fluorothiophenolate should give rise to a new signal in zb -CdS but not in w -CdS, which is another indication that these two materials have distinctive surface features. The presence of anionic vacancies at or near the surface of the zb -CdS nanocrystals could explain at least a trivial amount of the slower onset and kinetics of aggregation. If there was a decrease in the quantity of surface chalcogenides, then there would be a decrease in the sticking probability of these nanocrystals in solution. Finally, Figure 8d is the EPR spectrum for zb -CdS upon gelation (following the addition of oxidizing agent TNM), which showed no peak in the EPR spectrum, indicating that paramagnetic centers are no longer present. We surmise that the oxidative gelation process eventually leads to passivation.

3.3. Discussion: Differences in Reactivity between w -CdS and zb -CdS

For oxidative assembly to occur, we must have active sites (surface chalcogenides available for oxidative cross-linking). These sites typically arise from deprotection by oxidation of surface thiolates and assembly occurs by oxidative dichalcogenide interparticle cross-linking (Figure 1). Assuming the thermodynamics of bound chalcogen oxidation are similar in zb and w -CdS, and noting the quantity of surface oxide is similar in the two materials, the kinetic differences can be ascribed to differences in (1) deprotection rates, (2) the number of active sites, and (3) surface facet activity. If the number of active sites correlates to the ligand surface coverage (i.e., ligand binding affinity is a good descriptor of activity), then the lower rate of zb -CdS makes sense. The more symmetrical crystal structure of the zb -CdS NCs results in facets of similar surface energies, whereas in w -CdS the polar (0001) surface facets have considerably higher surface energy, requiring more ligands to achieve passivation.⁶⁸ The high activity may result in more facile oxidative removal of ligands (i.e., faster rate), and once exposed, the (0001) facets of w -CdS would be expected to be quite reactive. Indeed, catalytic H_2 evolution using CdS occurs at a greater rate for w - vs zb -CdS NCs.⁶⁹ The poor reactivity of zb -CdS may also be exacerbated by the formation of surface anion vacancies, as suggested by EPR studies. In any case, when it comes to the oxidative assembly of cadmium chalcogenide NCs, it is clear that structure dominates chalcogen redox properties in the reaction kinetics.

3.4. Effect of Q on Gelation in w -CdQ

To evaluate the intrinsic role of chalcogenide redox characteristics on the rate of oxidative assembly, sols of CdS, CdSe, and CdTe NCs, all adopting the wurtzite structure type and capped with 16-mercaptohexadecanoic acid (MHA), were evaluated. NC PXRD data shown in Figure S12 is consistent with all three samples adopting the wurtzite structure, and TEM data in Figures S13 and S14 show the particles to all be of a similar size (ca. 4.5 nm). Figure 9 shows the time evolution of R_h as a function of chalcogenide in w -CdQ (Q = S, Se, and Te) NCs from TR-DLS data after the addition of 20 μ L 3% TNM solution (oxidant). Once the crystal structure effects are accounted for, the onset of gelation follows the relative redox

properties of the Cd-chalcogenides. Specifically, *w*-CdTe has the fastest onset and aggregation kinetics in solution, followed by CdSe NCs and finally CdS.

4.0. CONCLUSIONS

Through TR-DLS studies, NMR spectroscopy, and EPR spectroscopy, we show that in addition to the redox characteristics of the chalcogenide in CdQ NCs the crystal structure (wurtzite vs zinc blende) has a profound effect on the kinetics of oxidative assembly (gelation). The differences in surface ligand loss between the *w*-CdS and the *zb*-CdS NCs are a likely contributor to the extreme differences in the kinetics of colloidal aggregation, with the larger concentration of surface ligand coverage possibly reflecting the higher surface reactivity of *w*-CdS, which has polar (0001) facets. The presence of paramagnetic sulfur vacancies in *zb*-CdS may also contribute to the lower reactivity of this structure. For identical structures and sizes, the gelation kinetics followed the thermodynamic trend with respect to the redox properties of Q^{2-} for Q = S, Se, and Te. The ability to tune the kinetics of colloidal aggregation through the crystal structure is expected to enable property tuning of the final macroscopic gels and allow the development of multicomponent assemblies with defined heterostructures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Sol-gel formation of metal chalcogenide (MQ) nanocrystals into a 3D matrix.

Figure 2. Time evolution of $\bar{R}_h$ for MHA-capped CdQ NCs as a function of Q. CdS and CdTe adopt the hexagonal wurtzite structure, whereas CdSe adopts the cubic zinc blende structure.

Figure 3.

(a) TEM micrograph for the 4-fluorothiophenolate-capped *w*-CdS and (b) TEM micrograph of the 4-fluorothiophenolate-capped *zb*-CdS. (c) PXRD spectra for the *w*- and *zb*-CdS NCs and associated powder diffraction pattern (pdf) stick diagrams.

Figure 4.

Time evolution of $\bar{R}_h$ as a function of crystal structure for *zb*-CdS and *w*-CdS. Inset: $\bar{R}_h$ over time for *w*-CdS NCs at short time intervals.

Figure 5. Time evolution of the ^{19}F NMR spectra for *w*-CdS NCs upon the addition of TNM (oxidant).

Figure 6. Time evolution of the ^{19}F NMR spectrum for *zb*-CdS NCs upon the addition of TNM (oxidant).

Figure 7.

XPS elemental analysis of two CdS QD samples capped with 4-fluorothiophenolate ligand (a) *zb*-CdS; the peak corresponding to the Cd atom bound to S is represented by the pink trace, and the peak bound to O is represented by the red trace; (b) *wz*-CdS; the peak corresponding to the Cd atoms bound to S is represented by the blue trace, and the peak corresponding to the Cd bound to O is represented by the black trace. The red star indicates the oxidized Cd peaks, which are blue-shifted from the peaks seen for the CdS signals for both 3d_{3/2} and 3d_{5/2}.

Figure 8. EPR spectrum for the (a) uncapped *zb*-CdS NCs, (b) 4-fluorothiophenolate-capped *zb*-CdS NCs, (c) *w*-CdS NCs capped with the 4-fluorothiophenolate ligand, and (d) *zb*-CdS gels prepared from the oxidative assembly of 4-fluorothiophenolate-capped *zb*-CdS NCs.

Figure 9.
Time evolution as a function of chalcogenide for $\bar{R}_h$ in w-CdQ NCs.