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Precursor and oxygen dependence of the unidirectional, seeded growth of CdSe nanorods

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Abstract

It was recently shown that, by controlling the O₂ concentration, the seeded-growth of CdSe nanocrystals (NC) can be manipulated to proceed either unidirectionally (from the (0001) facet) or three-dimensionally. In this contribution, we investigate two new Se precursors (*i.e.* SeO₂ and NaHSe) and compare them with Se obtained from etching of smaller NC seeds. Under anaerobic conditions, both precursors led to successful 3-dimensional (3D) NC growth. At high O₂ concentrations, the seeded growth of rods was enhanced by the NaHSe precursor, while impeded by the use of SeO₂. Mechanistic studies showed that the reduction of SeO₂ to Se²⁻ produces an excessive amount of O₂. This leads to rod fragmentation due to etching as well as the production of deep traps that quench their luminescence. These new precursors, along with a heightened understanding of oxygen's role, expand the synthetic repertoire of the redox-assisted, seeded-growth of CdSe and better position this low temperature (125 °C) methodology towards realizing advanced NC heterostructures.

Keywords

quantum rods; unidirectional; seeded growth; nanocrystals; oxygen

INTRODUCTION

Semiconducting nanocrystals (NCs) have attracted significant attention because of their broad absorbance and narrow emission, as well as their resistance towards photobleaching.¹⁻³ This has led to their incorporation in various device configurations, including biosensors,^{2,3} photodetectors,⁴ photovoltaics,⁵ and LEDs.⁶ One of their most intriguing properties of semiconducting NCs is their strong quantum confinement, allowing their band gap to vary over a broad energy range (*i.e.* from UV to NIR) based on composition and diameter.^{2,7,8} NC morphology also plays an important role in determining the properties of NCs. For example, one-dimensional (1-D) NCs, known as quantum rods (QRs) differ from zero-dimensional quantum dots (QDs), in that they exhibit linearly polarized emission,⁹ a higher Stokes shift¹⁰ and switchability in electric fields.¹¹ Although QRs are not confined in one dimension (*i.e.* length), they still exhibit quantum confinement, which is determined mainly by their diameter.¹² To these ends, there has been an intense

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Supporting Information. Histograms of the NC size distributions for all samples and additional HRTEM of notched nanorods are available. Supporting Information is available free of charge via the internet at <http://pubs.acs.org>.

research focus on devising synthetic methods that produce NCs that have both monodisperse size and shape distributions.¹³⁻¹⁵

Most NC synthetic methods involve a one-pot, hot injection approach in which the NC precursors are injected into a high-temperature (150-300 °C) mixture of surfactants and coordinating solvents.^{7,8,13} For such growth both the nature of the precursors and the coordinating ligands that stabilize the NC suspension determines the morphology of the resulting NCs.^{9,13,16} In some cases, such coordination agents can be the actual solvent (*i.e.* 3-amino-1-propanol (APOL)) in which synthesis takes place.^{14,15,17,18} Consequently, the main factor controlling the morphology stems from differences in the surface chemistry of the distinct NC facets and their interactions with the coordinating ligands and various passivating agents (*i.e.* oxygen).^{14,15,19,20} Strong interactions between the NC facet and the coordinating ligand typically leads to slower growth-rates from those facets.^{15,20} More recent synthetic approaches involve the use of a QD seed from which new NC morphologies are realized.^{15,21-23} This class of regrowth is useful for its potential to realize heterojunctions,^{15,21-24} with important applications for nanostructured devices.²⁵

Most types of seeded growth of CdSe involve dispersing QD seeds in a hot (>200 °C) surfactant mixture, followed by the fast addition of growth precursors.²¹⁻²³ Although such a method is effective, there is often polydispersity in the rod diameter, which can lead to varying properties.²⁴ Another type of seeded growth is the so-called “oriented attachment” mechanism, where QD seeds align along their natural *c*-axis dipole and fuse to form nanowires (NWs).²⁶ This method produces high aspect ratio NWs at the expense of challenging length-control.

Recently, our group has pioneered a new approach to seeded growth that exploits the redox chemistry of selenium within 9:1 3-amino-1-propanol (APOL):water mixtures.^{17,18} At 125 to 135 °C, and in the presence of oxygen, CdSe QDs were shown to grow asymmetrically along their *c*-axis.^{14,15} Such seeded growth is based on the availability of Cd²⁺ and Se²⁻ precursors originating from the addition of CdCl₂ and a redox-assisted Ostwald ripening process, respectively (*vide infra*).^{14,15} More importantly, 1-D and 3-D growth are controlled by the amount of dissolved O₂ in the growth medium. At high oxygen concentrations, the nonpolar CdSe facets (*i.e.* (10 $\bar{1}$ 0), (01 $\bar{1}$ 0) and (11 $\bar{2}$ 0)), as well as one of the polar facets (*i.e.* (000 $\bar{1}$)) become passivated, which results in the unidirectional growth along the 0001 direction.¹⁵ When oxygen is removed three-dimensional growth occurs due to the absence of a passivating oxide layer.¹⁵

A potential drawback of redox-assisted growth is that the Se-source is produced from the oxidative etching of the smaller QDs in the seed sample, which leads to growth saturation.¹⁵ The addition of an external Se-source could potentially lead to a more controllable growth, albeit the choice of Se-precursor needs to be carefully considered along the narrow design space of the APOL/water growth medium.

In this contribution, we investigate two new Se precursors (*i.e.* SeO₂ and NaHSe) that do not rely on the oxidative etching of the smaller NCs. Furthermore, we elucidate the interplay of oxygen concentration on the redox-assisted seeded-growth mechanism and show that the aforementioned precursors behave differently depending on the oxygen concentration. Unlike NaHSe that contains the Se precursor in its proper oxidation state (Se²⁻) for growth, the SeO₂ precursor requires a reduction step that also produces oxygen. This SeO₂-generated oxygen, if not taken into account, accelerates etching and competes with seeded growth, leading to rod fragmentation and deep trap formation. These two precursors expand the synthetic repertoire of the redox-assisted seeded-growth mechanism and provide the

necessary tools and understanding for subsequent use of this method for low-temperature growth of various NC heterostructures.¹⁵

EXPERIMENTAL SECTION

Chemicals

Trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, 90%), and 3-amino-1-propanol (APOL, 99%, water content, <0.4%), Se shot (99.999+%), CdO (99.99+%), *n*-octylamine (99%), SeO₂ (99.999%) and NaBH₄ (98%) and CdCl₂ (99.99%) were purchased from Aldrich and used without further purification. Hexylphosphonic (HPA) was purchased from Alfa Aesar and was used without further purification.

Synthesis of CdSe seeds

CdSe QDs were synthesized at high temperatures using a CdO precursor as reported elsewhere (Ref. 27). Briefly, a mixture of TOPO (4 g), HPA (0.25 g) and CdO (50 mg) were degassed in a three-neck flask equipped with a condenser, a thermometer and a rubber septum and heated under vacuum at 160 °C for 30 min until a clear solution was formed. The reaction vessel was purged with nitrogen and the temperature was increased to ~300 °C. Subsequently a solution of Se (50 mg) in TOP (3.0 mL) was quickly injected into the reaction vessel while the heating mantle was removed. This causes the temperature of the reaction mixture to rapidly drop to ~250 °C and show a characteristic color change that is indicative of CdSe nanocrystal formation. Subsequently, the heating was restored to a temperature between 260 and 300 °C in order to grow CdSe QDs of desired size. The reaction was stopped by decreasing the temperature and exposing to air.

Seeded growth of CdSe using SeO₂ precursor

CdSe nanocrystals were purified by precipitation with methanol, followed by centrifugation and decantation of the supernatant. APOL (2 mL) was added to the precipitated CdSe nanocrystals and heated at ~70 °C for one hour until a clear solution was formed. Acetone was added to precipitate the APOL-capped QDs and remove the TOP, TOPO and HPA. Following centrifugation and decantation, the QDs were redispersed in APOL (1 mL) to form a stock solution of CdSe NCs.

Aliquots of the stock CdSe seeds were diluted in APOL such that the OD at the first absorption maximum was 4.0. 1 M solutions of CdCl₂ and SeO₂ were added such that the final Cd and Se concentrations were 10 μM in order to provide a Cd- and Se-source for growth, respectively. Water was then added to bring the final APOL:water ratio to 9:1 v/v, which was found to be important for growth.^{14,15,17,18} Four samples were prepared as follows: the first was left open to the atmosphere giving it steady-state oxygen concentration; the second was sealed under atmospheric conditions, making the oxygen concentration equivalent to that present in the ampoule; the third and fourth had three and five freeze-pump-thaw (FPT) cycles, respectively, prior to being sealed under vacuum. These four samples were then annealed for four days at 125 °C. Subsequently, APOL was removed and the CdSe nanocrystals were surface exchanged back to TOPO/TOP/*n*-octylamine by mixing the growth solution with a solution of TOPO/TOP/*n*-octylamine (10/20/70 wt%). This was followed by precipitation with methanol, centrifugation and decantation to isolate the pellet of CdSe NCs, which was then redispersed in chloroform to form a clear solution, on which UV/Vis, PL and HRTEM characterization was carried out.

Kinetic Study of CdSe-seeded growth using the SeO₂ precursor

CdSe solutions on 9:1 APOL:H₂O were prepared as described above. The first sample was left open to air, while the remaining solution was made and divided into 1 mL aliquots,

exposed to 3 FPT cycles each and sealed into ampoules of *ca.* 4 mL in volume, which contained 1 mL of reaction mixture. Samples were annealed at 125 °C and 1 mL aliquots were removed every 24 hours for a total of 96 hours. Samples were redispersed in chloroform and characterized by HRTEM analysis.

Seeded growth of CdSe rods using NaHSe precursor

Elemental Se (1.0 mmol) was added to MilliQ water (2 mL) and chilled in an ice bath. While chilled, NaBH₄ (2.0 mmol) was slowly added to the mixture and the flask was sealed with a septum and vented with a needle to allow H₂ gas to escape. After several hours, the dark elemental Se has been converted to water soluble NaHSe, along with the formation of a white borate precipitate.²⁸⁻³⁰ The white precipitate was then centrifuged out and the aqueous NaHSe (0.5 M) solution was used without further purification. The aqueous Se precursor solution was added to the CdSe seed suspension in a 9:1 (v/v) APOL:H₂O mixture having 10 μM CdCl₂ so that the final concentration of Se was 10 μM. In the case where no Se precursor was used, condition similar to those reported in ref. 15 were used. All samples were grown at 125 °C for four days and transferred to chloroform prior to HRTEM analysis.

Growth of CdSe NCs under elevated oxygen concentrations

CdSe QDs were dispersed in 9:1 APOL:H₂O as described above. CdCl₂ was added to yield a 10 μM final concentration in the reaction mixture. One sample was allowed to grow in air, and the other sample was bubbled with oxygen for the duration of the growth period. Growth was carried out at 125 °C for 24 hours. Aliquots were removed from the two samples after 1, 3, 6, 12 and 24 hours and re-dispersed in chloroform using the method that was described earlier. These samples were characterized using UV/Vis absorption, PL spectroscopy and HRTEM.

Determination of oxygen concentration in 9:1 v/v APOL:H₂O mixtures

All oxygen measurements were made using a Mettler-Toledo O₂ 4100 oxygen sensor. The standing concentration of oxygen in APOL:H₂O was determined by degassing a sealed beaker containing water (50 mL) by bubbling N₂ gas under moderate stirring. When the concentration of oxygen reached a minimum value, the N₂ purge line was removed from the water and APOL:H₂O (1 mL) was quickly injected. The oxygen concentration was monitored until the value became constant. This was repeated three times. For Samples (3) and (4) of APOL:H₂O (1 mL) was degassed for three and five freeze-pump-thaw cycles, respectively and sealed into glass ampoules. Correspondingly, the glass ampoule was placed into a sealed beaker containing H₂O (50 mL) and bubbled with N₂ gas under moderate stirring. When the concentration of oxygen reached a minimum, the N₂ purge line was removed, the ampoule was broken, and the oxygen concentration was measured.

Nanocrystal Characterization

UV/Vis absorption measurements were made using a Varian Cary 5000. Photoluminescence (PL) measurements were collected using a Jobin-Yvon Spex Fluorolog 3-211 spectrofluorometer. The dimensions and size distribution of CdSe NCs were measured using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a Tecnai T12 TEM operating at 120 kV and a JEOL 1010 FasTEM operating at 200 kV, respectively. The HRTEM was equipped with a high-resolution objective lens pole-piece (spherical aberration coefficient Cs=0.5 mm) providing a point-to-point resolution of <0.19 nm in phase contrast images. HRTEM specimens were prepared by depositing a dilute solution of chloroform dispersed TOPO/TOP/*n*-octylamine capped NCs onto an ultra thin (~10 nm) amorphous carbon film supported on a mesh copper grid.

RESULTS AND DISCUSSION

The first step for both the redox-assisted etching (85 °C) and seeded-growth (125 °C) of CdSe NCs in 9:1 APOL:H₂O is the surface oxidation of the seed QD by dissolved oxygen via equation (1) ^{17,18,31-36}

Oxygen adsorption is followed by the faceted etching of the surface oxides via reactions 2, 3 and 4.

Equation (2), which details the conversion of surface SeO₂ to acidic H₂SeO₃, occurs rapidly in aqueous solution. This is quickly followed by the neutralization of the acidic H₂SeO₃ surface functionalities by basic APOL solution (equation (3)), resulting in an accelerated dissolution of the Se-sites on the NC surface. Through complexation with APOL, the CdO sites will also etch (albeit more slowly) from the surface of the NC (equation (4)), a process which can be slowed via the addition of a Cd-source such as CdCl₂.¹⁷ At low temperatures (85 °C), equations 1-4 result in the faceted etching of CdSe NCs to produce QDs with a Cd-rich surface.¹⁷

When the temperature is raised to 125 °C two new reactions, accounting for the reduction of Se⁴⁺ to Se²⁻, take place. Reaction (5) shows the reduction of H₂SeO₃ to Se⁰,¹⁴ which is accompanied by the release of water and O₂. Figure S1 in the Supplementary Information (SI) Section illustrates that O₂ generation is proportional to the amount of SeO₂ precursor and annealing duration. In the presence of amines, Se⁰ disproportionation has been reported by four groups,^{37-39,14} takes place to yield Se²⁻, SeO₃²⁻ and the release of six protons (reaction (6)) the latter of which are quickly neutralized in the basic APOL solution, which provides the driving force for reactions 5 and 6 to occur. This is in agreement with the results of Figure S1 (inset), where O₂ generation increases for smaller amounts of SeO₂, *via* a lesser APOL/H₂O neutralization by the acidic SeO₂. The combination of these two reactions provides the Se²⁻ source needed for NC growth. In the presence of CdSe NC seeds, the production of NCs with larger sizes and absorption cross-section indicates seeded-growth takes as opposed to Ostwald ripening (Figure S2a).^{14,15} In the absence of seed, uncontrollable growth takes place that produces CdSe NCs with various sizes (Figure S2b).

As explained in the Introduction, the presence of oxygen causes unidirectional growth of CdSe rods from the (0001) facet due to the selective oxygen passivation (reaction (1)) of the nonpolar [(10 $\bar{1}$ 0), (01 $\bar{1}$ 0) and (11 $\bar{2}$ 0)] and polar (000 $\bar{1}$) facets. If oxygen is removed, growth on all of the facets occurs, leading to three-dimensional growth.¹⁵ These studies,

however, were performed without the addition of an external Se source, relying on the oxidative etching of smaller NCs (reactions 1-4) to provide the needed Se^{2-} ions for growth. Such oxidative etching is undesirable for the production of Se^{2-} , since it alters the concentration of the starting seeds. A more favorable situation is to utilize an external Se-precursor, that by controlling its concentration, the desired growth can be obtained. In accordance to reactions (1-4), the logical choice is to investigate the addition of SeO_2 as a model precursor for growth (based on the reduction/diproportionation reactions (5) and (6)).

Seeded Growth in the presence of SeO_2

To test the effects of adding SeO_2 on growth, four samples were grown using a seed CdSe QD sample, with an optical density of 4.0 at the first absorption maximum, in 9:1 (v/v) APOL: H_2O . To each of the samples, CdCl_2 and SeO_2 were added so that their concentration in the growth medium was 10 μM each. Sample 1 was grown in open air such that a constant O_2 concentration of 8.1 ppm was maintained over the entire growth period; Sample 2 was sealed in a glass ampoule in air with a starting oxygen concentration of 8.1 ppm, and Samples 3 and 4 were sealed after 3 or 5 freeze-pump-thaw (FPT) cycles prior to growth, with initial oxygen concentrations of 4.2 ppm and 0.2 ppm, respectively. Here it is important to stress that the O_2 generated from reaction 5 is significantly lesser than the initial O_2 concentration. This is because the starting SeO_2 precursor concentration is relatively small (*ca.* 10 μM) and the generated O_2 is expected to preferentially diffuse towards the vacuously sealed, overlaying space that is *ca.* 75% of the total ampoule volume. Unless otherwise stated, all samples were grown over four days at 125 $^\circ\text{C}$, before surface exchange with TOPO/TOP/ODA and redispersed in chloroform to render them amenable for further characterization (HRTEM, UV/Vis and PL spectroscopy).

Figure 1a illustrates the absorbance and photoluminescence (PL) spectra as a function of oxygen concentration of both the seed and resulting NCs after growth. Figure 1b depicts the λ_{max} and full-width at half-maximum (FWHM) values of the PL emission that are respectively related to NC size and polydispersity. Peak deconvolutions were carried out on all PL spectra and listed in Table S1 in the SI Section. With the exception of Sample 1, all other PL spectra can be readily fitted with a single Gaussian-shaped peak, indicative of sample homogeneity for both the seed and Samples 2-4, albeit a slight broadening of the latter.⁴⁰ On the other hand, the PL of Sample 1 necessitates a minimum of three Gaussians (shown in dashed lines underneath the main peak in Figure 1a) to achieve an optimum fit.

In order to gain a more thorough understanding of the UV/Vis and PL results of Figure 1, a detailed HRTEM study of the initial and final NC size and size variation was conducted. Figure 2 shows the length, width, aspect ratio and volume for the initial CdSe seed as well as Samples 1-4. Representative HRTEM images of the various samples, as well as histograms of the length, width, aspect ratio, and volume distributions can be found in Figures S3-S7 of the SI Section. As expected, progressive oxygen restriction for Samples 2-4 results in a gradual increase in their width, which is also registered by both absorbance and PL red-shifts shown in Figure 1. Length-wise, an increase is registered for Samples 2 and 3 and begins to plateau for Sample 4. These results are in accordance with the slight decrease of the aspect ratio (length/width) in Figure 2b, while the overall volume ($\text{width}^2 \times \text{length}$) of the NCs appears to steadily increase. Moreover, the decrease of both the PL FWHM and NC aspect ratio for Samples 2-4 suggests that spherical, as opposed to unidirectional, growth is favored as the oxygen concentration is reduced, in accordance with our previous studies.¹⁵

In contrast to Se^{2-} originating from seed-etching,¹⁵ these results indicate that the addition of SeO_2 enhances NC growth at oxygen deficient conditions. This increase is most pronounced for Samples 3 and 4, where the addition of 9.7 ppm SeO_2 leads to a volume growth of 31% and 134%, with respect to the results from Ref. 15. Such growth acceleration

can be explained by the fact that O_2 is in the right side (*i.e.* products) of equation 5. In accordance to the Le Chatelier's principle, the speed of SeO_2 (H_2SeO_3) reduction is enhanced by lower O_2 concentrations, therefore more Se^{2-} source is formed according to equations 5 and 6 for Samples 3 and 4. However, when O_2 is abundant, the addition of SeO_2 impedes growth (*i.e.* the volume for Sample 1 and 2 decreases by 60% and 5%, respectively), when compared to the growth with no SeO_2 added (from Ref. 15). This is demonstrated by the increase in NC length to 5.5 nm for Sample 1 as opposed to 16 nm when the Se-precursor originated from the etching of NC seeds.¹⁵

Seeded growth for different Se precursors

The unexpected results from the SeO_2 precursor at high O_2 concentration (Sample 1) indicates that oxygen-containing reagents can strongly interfere with the unidirectional seeded-growth of CdSe rods. This has forced us to consider alternative, non-oxygenated Se precursors that are compatible with the basic APOL/ H_2O growth medium. Hydroselenic acid (H_2Se) is a possible choice, however its weak acidic nature ($pK_{a,1} = 3.89$ and $pK_{a,2} = 11.01$ at $25^\circ C$) and its toxicity forced us to consider the more basic NaHSe alternative. NaHSe is readily prepared in aqueous solutions by the quantitative reduction of Se^0 to Se^{2-} by carefully adding $NaBH_4$.²² The use of NaHSe precursor is expected to bypass reactions 5 and 6, as the Se-source is already in the proper oxidation state (*i.e.* Se^{2-}).

Figure 3a shows the UV/Vis and PL spectra for samples grown using different Se-precursors in the presence of O_2 (open to air). The corresponding experimental and peak-deconvoluted values for the aforementioned spectra as well as the absorbance-normalized PL spectra are shown in Table S2 and Figure S8 in the SI section, respectively. Samples A (Se from seed etching) and C (Se from NaHSe) exhibit a blue-shifted PL (indicative of partial etching) that can be fitted with a single Gaussian peak. On the other hand, NCs grown with the SeO_2 precursor (Sample B) display the broadest PL emission and is best fitted with two Gaussian peaks. Comparing the PL FWHM among the three precursors showed that the use of the NaHSe precursor (Sample C) resulted in a near identical values to that of the seed. In terms of NC brightness (Figure S8), it appears that more oxygenated precursors lead to higher PL intensity (Sample B > Sample A > Sample C). This is in accordance with our earlier results¹⁷ and will be the topic of a future publication. Figure 4 illustrates representative TEM and HRTEM images of Samples A-C and the initial seed CdSe. Compared to the initial dot-like seed, Samples A and C consist of rod-like NCs, whereas Sample B contains a mixture of both dots and rods.

In order to quantify the average NC width, length, aspect ratio and volume of Samples A-C and the CdSe seed, a HRTEM analysis was performed and is shown in Figure 5. Histograms for the width, length aspect ratio and volume distributions can be found in Figures S9-S12 in the SI section. For Samples A and B, the results for the average growth in the width, length, aspect ratio, and volume are in accordance with Ref. 15 and Figure 2, respectively. In the case of Sample C (NaHSe precursor) the unidirectional growth of CdSe at high O_2 concentration is not only maintained, but also enhanced (*i.e.* length increases from 4 to 14 nm and aspect ratio from 1.3 to 4.7). This indicates that NaHSe is a suitable replacement for SeO_2 as Se-precursor for rod growth in the presence of O_2 . One thing that needs to be taken into account is that the addition of NaHSe causes some etching with regards to the width of the NR (*c.a.* 0.4 nm), which is in agreement with the spectroscopic result of Figure 3. This is believed to originate from a partial etching of the surface oxide that is quickly replaced by the ample O_2 in the growth media (samples open to air).

Time-dependant growth as a function of oxygen and SeO₂ precursor

One aspect of the seeded growth that remains unclear is the exact mechanism that leads to the disruption of unidirectional growth in the presence of SeO₂ and oxygen. For this we conducted a study of the time-lapsed seeded growth in the absence and presence of SeO₂ (Figure 6 and 7, respectively) for two oxygen concentrations. Histograms of the size distributions can be found in Figures S13-16 in the SI section. Open to air and deoxygenated conditions from three freeze-pump-thaw cycles (4.6 ppm O₂) were chosen to stimulate 1- and 3-D growth, respectively. Aliquots were removed every 24 hours for a total of 96 hours and the width, length, aspect ratio and volume were measured via HRTEM and plotted as a function of growth time. In the absence of a SeO₂ precursor (Figure 6), a rapid increase in both the width and length is witnessed in the first 24 hrs. This is most likely due to the rapid production of Se precursor from the oxidative etching of small NCs (eq. 1-6). After the first 24 hours, the growth reaches a plateau in terms of volume (Figure 6d), which remains constant for the remainder of this experiment. This signifies a switch from interparticle to intraparticle ripening. The latter is supported by the decreasing width (Figure 6a) and increasing length and aspect ratio (Figure 6b and c) with a rate proportional to the O₂ concentration.

In the case where SeO₂ precursor is added (Figure 7), the growth characteristics become strongly dependant on O₂ concentration. For low O₂ concentration (4.2 ppm), the increase in width, length and volume indicates a monotonic three-dimensional growth as supported by the nearly constant aspect ratio. At high O₂ concentrations, the growth appears to be arrested after 48 hours, as witnessed by the changes incurred in width, length and volumes of the NCs. This suggests the presence of a competing process that retards rod growth as witnessed in the absence of SeO₂ precursor (Figure 6). Upon closer HRTEM investigation of the longest rods in the sample after 96 hrs incubation with SeO₂ precursor at open air, the appearance of notching along the rod becomes evident (see inset in Figure 7b). More images of notched nanorods collected from all samples grown in the presence of air and the SeO₂ precursor are shown in Figure S17 of the SI section. This explains the presence of small dots along with rods in Figure 4c, along with the broad PL spectrum of Samples 1 and B and in Figure 1, 2 and 3, respectively, as well as their corresponding peak deconvolutions. On the other hand, no notches were observed for nanorods grown with the NaHSe precursor (shown in Figure 4d).

To further investigate rod fragmentation, the UV/Vis absorbance and PL emission spectra of the time-resolved growth study in Figures 6 and 7 were also measured. Figure S18 in the SI section shows the two sets of spectra for NCs grown when oxygen is abundant (*i.e.* open to air) in the absence and presence of the SeO₂ precursor. With no SeO₂ added (Figure S18a), both the absorption and PL spectra follow the expected trends for the NC sizes reported in Figure 6a. This indicates that, despite PL broadening, all samples maintain their excitonic behavior. On the other hand, the addition of the SeO₂ precursor (Figure S18b) causes a severe PL divergence in terms of blue-shifting when contrasted to the absorption edge. This agrees with rod fragmentation and suggests that excitonic luminescence originates from the low diameter NCs, especially after 72 hours. Moreover, the emergence of deep trap luminescence after 48 hours (marked by asterisks in Figure S18b), indicates that the resulting NCs contain a large amount of defects.⁴¹ This suggests that the excessive release of O₂ during SeO₂ reduction (eq. 5 and Figure S1) causes uncontrollable etching and surface passivation, and is responsible for both rod notching and deep trap formation. If this hypothesis is true, then the similar behavior should be observed for NC grown under elevated O₂ concentrations in the absence of SeO₂.

To test this, CdSe seeds were subjected to similar growth conditions (*i.e.* 125 °C in 9:1 v/v APOL:H₂O) while continuously bubbling with pure O₂. Figure 8b illustrates the UV/Vis

absorbance and PL emission spectra for NCs after O₂ bubbling as compared to the control (seeded growth while open to air; Figure 8a), as a function of growth time. NCs grown in air (Figure 8a) show little change in their UV/Vis and PL spectra albeit with broadening due to rod growth, as reported before.¹⁴ On the other hand, growth while bubbling with O₂ displays the emergence of deep trap luminescence after 12 hours (see broad feature marked with an asterisk in Figure 8b). Additional bubbling completely quenches the excitonic PL, as shown by the PL spectra taken after 24 hours. Figure S19 in the SI section illustrates the length and aspect ratio distributions for the initial seed and the samples grown for 24 hours while open to air or bubbled with oxygen. These results indicate that excessive amounts of O₂ limits one-dimensional growth by reducing the change in length from 7 to 5 nm and aspect ratio from 2.4 to 1.8, respectively (Figure S19). This verifies that one-dimensional seeded growth can be stunted by excessive O₂ concentration, and explains the utility of an oxygen free precursor such as NaHSe.

Seeded growth at different SeO₂ concentration

Last but not least, a control experiment was carried out to verify that morphology control is not affected by the precursor concentration but rather the O₂ concentration in the reaction mixture as suggested in Refs. 14 & 15, and data herein. Figure S20 illustrates the effect of SeO₂ precursor concentration in O₂ rich (open to air) and O₂ poor (0.2 ppm) conditions. As expected, in O₂ poor environment, a monotonic redshift is observed in accordance with 3D seeded-growth to produce larger dots. Similarly, in O₂ rich environment, the 1D seeded-growth was retained irrespective of SeO₂ concentration. Interestingly, in O₂ rich environment, a faster lateral etching rate (producing smaller diameter nanorods) was witnessed at lower SeO₂ precursor concentrations. This can be explained by equation (2), in light of the fact that the lateral selenium oxide passivating the sidewalls of NCs or NRs etches faster in an APOL environment with lower SeO₂ concentrations. This has been experimentally witnessed in Ref. 17, where the etching rate of CdSe NCs slows down as the surrounding APOL/H₂O mixture is slowly saturated with dissolved SeO₂ in the form of APOL salt (*i.e.* [HO(CH₂)₃NH₃⁺]₂SeO₃²⁻). Moreover, the similar decrease in the etching rate was observed as the CdCl₂ concentration was also increased.¹⁷

CONCLUSIONS

In this study we investigate two Se precursors (*i.e.* SeO₂ and NaHSe) on the redox-assisted seeded-growth of CdSe NCs. Their different redox states and oxygen content has minimal effect when seeded-growth occurs under anaerobic conditions, leading to three-dimensional growth. At elevated O₂ concentration, the behavior of these two precursors diverges. While NaHSe follows the expected unidirectional rod-growth due to lateral oxide-surface passivation, SeO₂ produces excessive amount of O₂ that results in enhanced etching and rod fragmentation. Kinetic studies confirm that the excess O₂, produced by the reduction of SeO₂ to Se²⁻, is responsible for the aforementioned behavior and also leads to the formation of deep traps at the surface of these NCs. These findings enhance our mechanistic understanding of the low-temperature, redox-assisted, seeded-growth of CdSe and open up new possibilities for the realization of complex NC heterostructures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) Normalized UV/Vis absorbance and photoluminescence (PL) spectra of the initial CdSe seed and resulting NCs grown after 4 days of growth at 125 °C and in the presence of 10 μM SeO_2 . Sample 1 was open to air while Samples 2-4 were sealed in ampoules at 8.1 ppm, 4.9 ppm and 0.2 ppm starting O_2 concentrations, respectively. (b) Plot of the PL λ_{max} and PL full-width at half-maximum (FWHM) as a function of starting oxygen concentration. Interpolating lines are to guide the eye. Excitation wavelength was 360 nm.

Figure 2. Average length, width (a), aspect ratio and volume (b) dependence of the initial CdSe seed after 4 days of growth at 125 °C under different starting oxygen concentrations and in the presence of 10 μ M of SeO₂. Interpolating lines are to guide the eye.

Figure 3.

(a) UV/Vis absorbance and photoluminescence (PL) spectra of the initial CdSe seed and resulting NCs grown with no added Se-source (Sample A), SeO_2 (Sample B) and NaHSe (Sample C). (b) Plot of the PL λ_{max} and FWHM for the aforementioned samples. Interpolating lines are to guide the eye. Excitation wavelength was 360 nm.

Figure 4. Representative low magnification TEM and HRTEM images of CdSe NCs grown at 125 °C for four days in air and in the presence of different Se-precursors: (a) Initial seed QDs, (b) CdSe NCs grown without adding a Se-precursor (Sample A), (c) CdSe NCs grown using SeO₂ (Sample B) and (d) CdSe NCs grown using NaHSe (Sample C). Sample B shows a mixture of QDs and QRs, while Samples A and C are mostly populated with long rods.

Figure 5.

Average width and length (a) as well as aspect ratio and volume (b) for the initial NC seed and those grown in 9:1 v/v APOL:H₂O, in the presence of oxygen (open to air) for four days at 125 °C. Sample A relies on seed NC etching as its Se-source, while in Samples B and C, 10 μM of SeO₂ and NaHSe were added, respectfully. Interpolating lines are to guide the eye.

Figure 6.

Variation in the width (a), length (b), aspect ratio (c), and volume (d) of CdSe NCs as a function of growth duration, for seeded growth at 125 °C in 9:1 v/v APOL:H₂O media with no added SeO₂ precursor under oxygen-rich (solid line) and oxygen-poor (dashed line) conditions. Interpolating lines are to guide the eye.

Figure 7.

Variation in the width (a), length (b), aspect ratio (c), and volume (d) of CdSe NCs as a function of growth duration for seeded growth at 125 °C in 9:1 v/v APOL:H₂O with 10 μM SeO₂ under oxygen-rich (solid line) and oxygen poor (dashed line) conditions. The inset in (b) shows a CdSe NR after 96 hours seeded growth in air that displays characteristic notches along the side walls as indicated by the two arrows and the white outline for ease of viewing. Interpolating lines are to guide the eye.

Figure 8.

UV/Vis Absorbance and PL spectra for 24 hours of seeded growth at 125 °C in 9:1 v/v APOL:H₂O with no SeO₂ added for samples grown in (a) air and (b) bubbled with O₂. Excitation wavelength was 360 nm for all but the 12 and 24 hour spectra in (b), which were excited at 380 nm. Asterisks (*) indicate deep trap emission.