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High Activity Phosphine-Free Selenium Precursor Solution for Semiconductor Nanocrystal Growth

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A phosphine-free selenium nanocrystal precursor solution has been synthesized by heating elemental selenium powder in 1-octadecene (ODE). This mixture was characterized by UV−vis absorption, photoluminescence excitation (PLE), nuclear magnetic resonance (NMR), Se X-ray absorption spectroscopy (Se-XAS), electron impact mass spectrometry (EIMS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) to establish identifiable spectroscopic and chemical signatures that can be correlated to the chemical efficacy of the precursor for the growth of metal selenide nanocrystals. Highly temperature dependent rates of selenium dissolution and deactivation of the resultant precursor are demonstrated and optimal preparation times for the most reactive precursor are determined. Distinctive features in the PLE spectrum provide a rapid estimate of the reactivity of the as-prepared Se-ODE precursor. NMR and XAS data strongly indicate both Se−Se and Se−C bonding are present in the precursor solution, suggesting that simple selenium dissolution. This is also confirmed by (EI) mass spectra where (ODE+2Se) and (2ODE+2Se) were only found in the most active Se-ODE solutions. Se-ODE is not only chemically more benign than the traditionally employed trioctylphosphine selenide (TOPSe), but it is also demonstrated that optimized Se-ODE has nearly twice the reactivity of TOPSe for Se deposition onto CdSe core particles at 220 °C.

Introduction

The syntheses of II−VI semiconductor nanocrystals are now based on more stable precursors that are considerably less hazardous than the seminal systems involving dimethylcadmium, diethylzinc, and trioctylphosphine.[1−8] Many greener metal-fatty acid precursors have been investigated within the past decade,[4,7,9] yet there are far fewer proven chalcogen precursors. Trialkylphosphine selenides have been almost exclusively used for the production of high quality metal selenide nanocrystals[1,4,6,10−14] with detailed reaction mechanisms having been proposed based on NMR data.[5,8,15] The passivation of surface Se atoms by the phosphine moiety is advantageous where surface recombination sites need to be minimized.[16,17] However, for the application of metal selenides as active materials in photovoltaics or sensors, the presence of bulky, surface-bound organic species may be an impediment to device performance.[18,19] Furthermore, trialkylphosphines are toxic, expensive, and oxidize easily. It is therefore of ongoing interest to investigate the development of stable selenium precursors in the absence of strongly bound phosphines.

The use of a stable phosphine-free solution prepared by the dissolution of elemental selenium in 1-octadecene

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(ODE) has been explored as a viable selenium precursor for CdSe nanocrystal synthesis.[20-27] This mixture, abbreviated hereafter as Se-ODE, is suitable for fine control in CdSe nanocrystal syntheses including control of crystal structure,[21] and by virtue of there being no Se-passivant in Se-ODE, it has been used to demonstrate the importance of surface stoichiometry in binary semiconductor nanocrystals.[16] Shen et al. recently reported high quality ZnSe nanocrystals are also viable using Se-ODE,[24] and shape control of zinc-blende CdSe was achieved by Liu and co-workers.[27]

Despite the proven utility of Se-ODE,[20-27] a thorough account of the preparation and properties of this simple binary mixture has not yet been reported. Herein, we report a detailed study of the Se-ODE system. We assess the efficacy of Se-ODE as a reagent for nanocrystal growth as a function of preparation conditions and compare its reactivity to that of the conventional trioctylphosphine selenide reagent. We establish that the efficacy of Se-ODE is highly dependent on preparation temperature and time. A straightforward luminescence measurement is presented that can semiquantitatively assess the quality of preparation and reactivity of this air-stable precursor. Beyond demonstrating Se-ODE as an effective precursor for selenium deposition onto CdSe nanocrystals, the Se-ODE solutions have been characterized by NMR (^{1}H, ^{77}Se, and ^{13}C), mass spectrometry, and Se K-edge X-ray absorption spectroscopy (XAS), to provide some insight into speciation in the Se-ODE solution.

Experimental Section

Technical grade (90%) and higher purity (99.5%) 1-octadecene, selenium powder (99.99%), tri-*n*-octylphosphine (90%), oleic acid (90%), seleno-L-cystine (98%), phenyl ether (99%), cyclohexane (>99%), and CdO (99%) were obtained from Aldrich. Octadecylamine (95%) was procured from Merck. Acetone and chloroform were of analytical grade and were purchased form Univar Pty. Ltd. All chemicals and solvents were used as received without further purification.

UV−visible absorbance spectra were acquired using a Shimadzu 1601 spectrophotometer. Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were made with a Varian Eclipse Fluorimeter. All PLE measurement were performed with the following parameters: excitation slit = 5 nm, emission slit = 5 nm, and emission wavelength = 450 nm. Raw Se-ODE solutions were diluted into cyclohexane for all spectroscopic studies; however, similar results were also obtained using chloroform as a solvent.

For a typical preparation of Se/ODE solution (0.100 M), 0.553 g (0.007 mol) of selenium powder was transferred to a 100 mL two-necked round-bottom flask, and 70 mL of ODE was added. The mixture of selenium and ODE was stirred strongly with a magnetic stirring bar. The system was placed under nitrogen and then heated to the appropriate temperature. The temperature was controlled and monitored using a J-KEM Gemini temperature controller and a thermocouple. Aliquots were taken periodically for optical analysis.

CdSe core nanocrystals were prepared by a previously reported procedure and purified by solvent extraction prior to Se deposition experiments.[9] In a typical reaction, a solution of ODE/octadecylamine (2.5:1 w/w) containing 40 μM CdSe core nanocrystals (107 nmol) was heated to 100 °C and degassed for 20 min, then heated to 220 °C for growth. At this time, the surface was made Cd-rich by a previously published method.[16] To assess the efficacy of the Se-ODE solution, an adapted SILAR technique was used to deposit CdSe.[8] Specifically, 410 μL of the Se-ODE solution was injected into the solution containing the CdSe cores. UV−visible spectra were obtained at regular intervals until particle growth had ceased (shifts in the band-edge transition $\ll$1 nm/min). The number of Se atoms deposited (and hence the reaction yield) was estimated using the concentric shell model (the average volume increase of the spherical core particles) as a function of the total amount of selenium injected.[28]

Se-XAS studies were made at the Australian National Beamline Facility in Tsukuba, Japan. Solution samples were sealed with Kapton tape in windows in stainless steel sample mounts and snap frozen in liquid nitrogen before cooling to 10 K. A Si(111) double crystal monochromator was used to select the beam energy at the Se K-edge with XAS spectra obtained in transmission mode. The K-edge XAS spectra were collected for samples with edge jumps (%T) between 12.5% and 33%; with spectra collected up to $k = 15$ in each case. Raw XAS data was processed with the FEFFIT 1.2.11 suite of software, and experimental spectra were compared to those of reference standards whose XAS spectra were obtained under the same conditions. Determination of the XAS data for calculated model structures were performed with the ATOMS/Artemis software package using the FEFF 6.0 code.

ICP-AES was performed on an ICAP 6000 Series ICP Spectrometer from Thermo Scientific. Samples were diluted in phenylether, and the concentrations determined by comparison to a calibration curve produced using standard TOPSe solutions diluted in phenylether. Measurements were performed in duplicate.

^{1}H NMR and ^{1}H−^{13}C HSQC were performed on a Bruker Av400 spectrometer while the ^{77}Se NMR experiments were conducted on a Bruker DRX500 NMR spectrometer. The samples for all NMR experiments were prepared in an analogous manner to that for the conventional Se-ODE precursor with the exception that a significantly higher selenium concentration was used. In a typical preparation we used a 1:1 molar ratio of ODE/Se powder. Aliquots were obtained periodically, then passed through a 0.2 μm filter ready for NMR experiments. All experiments were performed in $CDCl_3$. For ^{77}Se NMR a saturated solution of triphenylphosphine selenide in $CDCl_3$ was used as an external secondary standard as it exhibits a doublet centered at −266.2 ppm with respect to the conventional standard Me_2Se which has a resonance at 0 ppm.[29]

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Positive ion electron impact (EI) mass spectra were run on a ThermoQuest MAT95XL mass spectrometer using an ionization energy of 70 eV.

Results and Discussion

Various conditions have been reported for preparing Se-ODE to date. Specifically, heating the mixture for 2 h at 200 °C,[21] heating the mixture at 220 °C for 3 h,[23] heating for approximately 5 min after adding Se powder to 220 °C ODE,[30] and recently Liu et al. reacted Se and ODE for 30 min at 280 °C.[27] All these methods produce optically clear, stable solutions containing selenium species that are available for reaction at elevated temperatures, but there is currently no reference frame to quantitatively compare the absolute performance of these different preparations. To investigate the effect of these reaction conditions, 0.1 M Se-ODE solutions were prepared at temperatures between 150 and 210 °C. This temperature range was investigated as selenium powder melts at 217 °C while at lower temperatures (below 150 °C) dissolution was found to be extremely slow, with virtually no apparent dissolution achieved even with extensive heating ($t > 72$ h), leaving the black undissolved Se and colorless ODE. This is in stark contrast with the related and widely used sulfur analogue (S-ODE) that forms a homogeneous solution readily with mild heating (temperatures less than 100 °C).

Optical Characterization. A representative series of UV−visible spectra taken at various times during the preparation of 0.1 M Se-ODE heated at 180 °C is presented in Figure 1. For clarity the absorbance spectra have been normalized to the small transition peak at 317 nm. Upon inspection of Figure 1 we see that the absorbance intensity between 320 and 500 nm systematically decreases with time. When heated at 180 °C the strongest coloration was observed for heating times around 3−4 h (Figure 1-top). However, at this temperature it was found that a minimum of 5 h was required to achieve complete Se dissolution. Samples heated for longer than 5 h at 180 °C became increasingly colorless over time.

Next, we investigated the effect of temperature on the dissolution rate as well as on the optical properties of the final samples. The dissolution time was taken to be the point at which no black solid selenium was observed in solution. Preparation temperatures of 150, 180, 200, and 210 °C were investigated. Photoluminescence spectra of these four solutions at the point of dissolution revealed a broad symmetrical emission band centered at ~430 nm. Photoluminescence excitation spectra (PLE) of these solutions exhibited a series of sharp features between 280 nm and 400 nm as shown in Figure 2A. As there was negligible emission from the 1-octadecene and cyclohexane solvents, the various transitions observed originate from the selenium precursor(s) in solution. The similarity of Se-ODE PLE spectra obtained at the point of dissolution indicates that similar (or identical) species are obtained for all preparations in the 150 °C−210 °C temperature range. This suggests that the physical/chemical dissolution process remains constant across the entire temperature range appropriate to selenium dissolution in 1-octadecene.

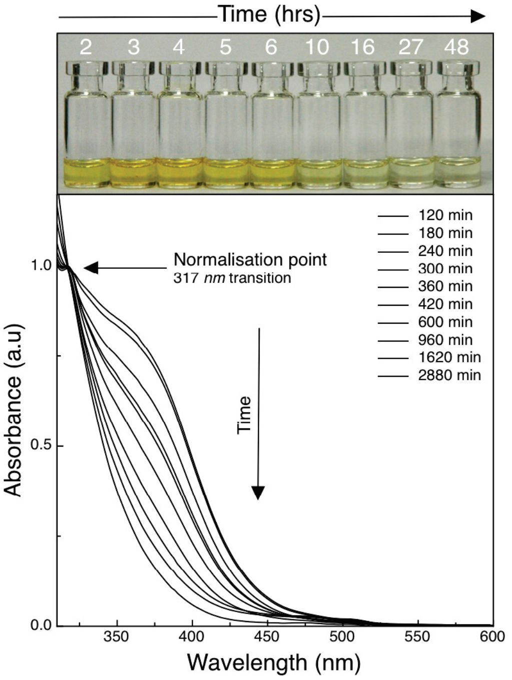

Figure 1. Top: Photo of the Se-ODE solutions as a function of heating time. Bottom: Normalized optical absorbance spectra for Se-ODE solutions as a function of heating time at 180 °C.

The dissolution time was found to decrease sharply with only small temperature increases. Specifically, it took 48 h at 150 °C, 5 h at 180 °C, 1 h at 200 °C, and only 36 min at 210 °C. The temperature dependence of the dissolution rate is shown inset in Figure 2A; where the natural log of the reciprocal of the time for dissolution ($1/t_{\mathrm{diss}}$ in s^{-1}) has been plotted against the reciprocal temperature (K^{-1}). If the dissolution of the selenium powder is assumed to be a simple first order process, then a straight line is expected from which the activation energy for the dissolution process can be estimated. From fitting the data a significant energy barrier to "dissolution" of 126 ± 13 kJ/mol was determined.

To deepen our understanding of the dissolution process, spectral changes to the solutions were investigated during heating. Figure 2B shows a series of PLE spectra taken at various time intervals during the dissolution of selenium in ODE at 180 °C. At early times three sharp PLE features dominate the spectra below 330 nm, but after prolonged heating these give way to a broad transition centered near 340 nm (indicated by the arrows). The data presented in Figure 2B show that these spectral changes occur over the course of 48 h. Clearly, changes to the selenium species in solution continue to occur after complete dissolution of the solid selenium. Furthermore, similar to the actual dissolution process, these additional changes were also found to be highly temperature sensitive (see Supporting Information).

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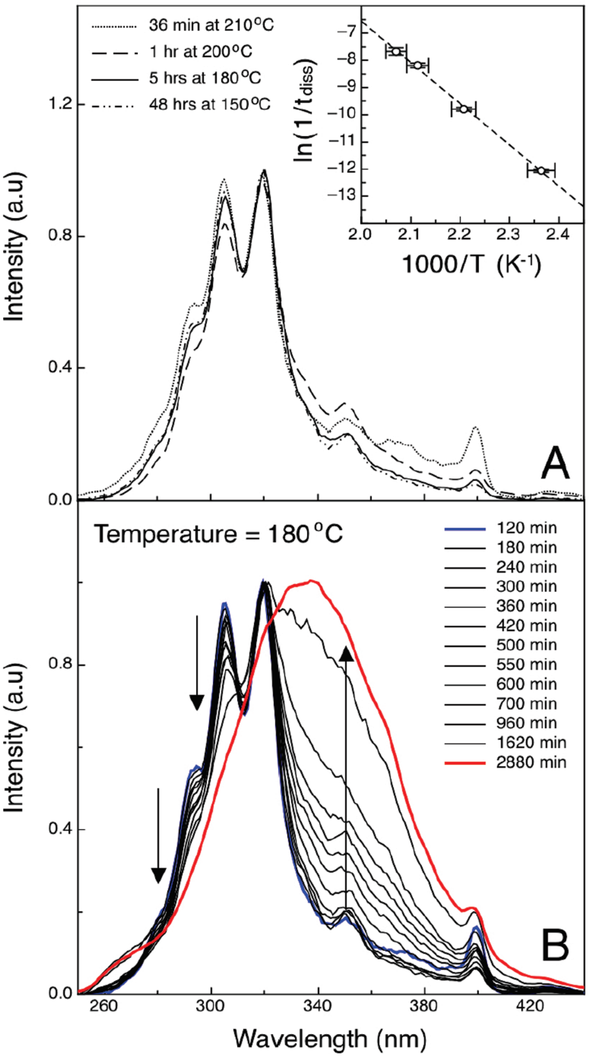

Figure 2. (A) Photoluminescence excitation spectra (λ_{emm} = 450 nm) of Se-ODE solutions at the point of full dissolution after heating at 150 °C (48 h), 180 °C (5 h), 200 °C (60 min), and 210 °C (36 min). Inset: the natural log of reciprocal dissolution time is plotted against $1/T$ showing the strong temperature dependence of the dissolution process. (B) Temporal evolution of the PLE at an emission wavelength of 450 nm for Se-ODE during heating at 180 °C.

Reactivity of Se-ODE. In an earlier study, the efficacy of Se-ODE for the nucleation and growth of high quality nanocrystals was reported.[21] During this investigation it was found that Se-ODE efficacy was highly dependent on its method of preparation. Typically, a homogeneous yellow solution was prepared by heating a mixture of selenium in ODE at 200 °C for 2 h, producing stock 0.1–0.2 M Se solutions. Prolonged heating at 200 °C produced a solution that was found to no longer nucleate nanocrystals when reacted with cadmium oleate at temperatures near 300 °C. Data from this report strongly suggested that changes to the selenium species from an active to an inactive form occur upon prolonged heating. In this section we systematically monitor changes in the reactivity of the Se-ODE solutions prepared at different temperatures by directly measuring the reaction yields for a model growth reaction of nearly monodisperse, cadmium-rich CdSe core nanocrystals. The PLE spectra for the Se-ODE samples used in this study are shown in Figure 3A. These are samples heated at 180 °C for 5 h, 17 h, and 48 h; as well as 90 min at 200 °C. Figure 3B displays the absorbance spectra for CdSe cores before and after the growth of a single selenium monolayer using the various Se-ODE solutions. The absorbance spectrum for the reaction involving the use of Se-ODE heated at 200 °C is omitted for clarity. The reactions are compared to a control reaction using TOPSe as the active selenium source.

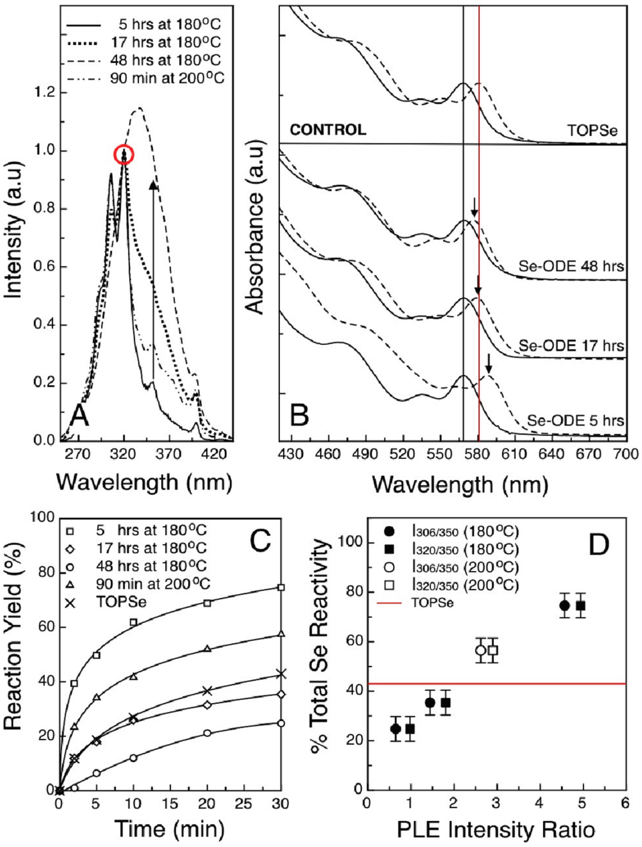

Figure 3. Growth of CdSe nanocrystals with TOPSe and Se-ODE. (A) PLE (λ_{emm} = 450 nm) of Se-ODE samples normalized at point indicated by circle; (B) absorbance spectra of initially Cd-rich CdSe particles before and after growth with Se solutions indicated. (C) Temporal changes in Se deposition calculated from absorbance spectra. (D) Se deposition yield at 30 min plotted against the $I(306\ \mathrm{nm})/I(350\ \mathrm{nm})$ and $I(320\ \mathrm{nm})/I(350\ \mathrm{nm})$ PLE ratios for Se-ODE samples prepared at 180 and 200 °C.

The band-edge absorbance peak of the CdSe is strongly correlated to particle size and has been shown to provide reliable information about growth processes in uniform systems.[9,21,31] In all reactions a significant red-shift of the band-edge transition peak was observed after injection of the Se precursor. The red shifts at the end of growth were as follows: Se-ODE(180 °C, 5 h) = 18.5 nm; Se-ODE(180 °C, 17 h) = 9.5 nm; Se-ODE(180 °C, 48 h) = 7 nm; Se-ODE(200 °C, 90 min) = 15 nm; TOPSe = 11.5 nm. We note that in this experiment all the initial particles possessed a band-edge transition at 569 nm. No significant broadening of the absorbance was observed in this optimized growth system, and the red-shift can be confidently attributed to homogeneous particle growth and not aggregation or Ostwald ripening.

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Using the empirical relationship between band-edge absorbance and particle size,[32,33] it is possible to extract particle size versus time data for each reaction, and an estimate of reaction yield can be made (Figure 3C). For the first time it is possible to compare the reaction yield of the conventional TOPSe precursor and Se-ODE in a typical SILAR-type reaction system. In the case of the optimal Se-ODE sample (prepared by heating at 180 °C for 5 h) a Se deposition yield of ~75% was obtained. This compares very favorably with the ~42% yield obtained for TOPSe. These observations can be understood by considering that an optimized phosphine-free selenium source should be more reactive toward particle growth than TOPSe, given the absence of strongly binding selenium additives in the growth medium. This hypothesis is qualitatively supported by comparing the phosphorus selenide bond dissociation enthalpy ($D°(\mathrm{Se{=}P}) = 364$ kJ/mol) to selenium−selenium bond dissociation enthalpies ($D°(\mathrm{Se{-}Se}) = 172$ kJ/mol and $D°(\mathrm{Se{=}Se}) = 272$ kJ/mol),[34] which are known to be present within Se-ODE (see discussion below). In addition, TOP is known to stabilize Se-rich molecular sized "magic clusters", which can form in competition with the growth of existing particles, reducing the observed growth yield.[14,35] Overall, these findings suggest that for high-yielding growth of epitaxial metal selenide monolayers, Se-ODE is superior to TOPSe.

The growth experiments clearly demonstrate a drastic reduction in the efficacy of Se-ODE during heating at 180 °C. The reaction yield for 5 h Se-ODE (180 °C) was determined to be 75% while the 48 h sample activity was found to be only 22% (see Figure 3C and 3D). Recently Deng,[20] and Yordanov,[22] have shown that H_2Y ($Y = S$, Se) is generated through a hydrocarbon dehydrogenation reaction at elevated temperatures when Se-ODE is heated in a range of organic solvents, including ODE. For selenium in paraffin, the yield of H_2Se after just 1 h at 280 °C was close to 50%. Thus, at most, a 50% decrease in reactivity may be expected from heating selenium under these conditions. On the basis of the 50% decrease in reactivity observed in this report, one would expect that if H_2Se generation was the major deactivation pathway during Se-ODE formation, then the concentration of Se in solution would correspondingly fall from 0.1 M to approximately 0.05 M. To ensure that H_2Se generation and release did not account for the reduced reactivity in our growth system, ICP-AES was performed on the Se-ODE to analyze its selenium content. Specifically, the concentration of Se in the 5 h (180 °C) and 48 h (180 °C) reactions were determined. From these measurements the 48 h sample was found to have 12% less Se than the 5 h sample, confirming that some Se loss had occurred. While a proportion of the reduced reactivity of the Se-ODE can therefore likely be attributed to H_2Se release, the drastically reduced yellow color and 50% reduced reaction yield of the 48 h solution compared to the 5 h sample in the most part must originate from a Se speciation change to some less active form. This is direct evidence that observed deactivation of the Se-ODE is predominantly due to a structural change of the Se-ODE species in solution. An optimized protocol for Se-ODE preparation therefore results from a balance between time taken to dissolve and the time taken to deactivate the precursor.

The reactivity of the Se-ODE is clearly highly dependent on preparation conditions. A simple spectroscopic method to estimate the precursor efficacy would therefore be extremely useful. A comparison between the changes in reaction yield for CdSe growth and the systematic changes in the PLE spectra are presented in Figure 3D, where the % Se reactivity (deposition yields) are plotted against the ratio of PLE intensities (I) at the transition peaks, with the 306 nm and 320 nm peaks intensities of the active form divided by the intensity at 350 nm (chosen as it is away from the 320 nm peak and can be attributed more to the inactive species). The PLE ratios calculated were for the $I(306\ \mathrm{nm})/I(350\ \mathrm{nm})$ (circles) and $I(320\ \mathrm{nm})/I(350\ \mathrm{nm})$ (squares) intensities of Se-ODE samples prepared at 180 °C with 5, 17, and 48 h heating, and one heated at 200 °C for 90 min. These four samples were chosen because they exhibit different ratios of the PLE intensities at different stages during heating. A linear relationship exists between the PLE ratios and the % Se reactivity. The good correlation between the PLE data and Se-ODE reactivity indicate that PLE is a good indicator of precursor efficacy, *independent* of the temperature of preparation. As such, using Figure 3D, the percent reactivity of Se-ODE (to within approximately 10%) can be quickly obtained simply by taking a PLE spectrum. The authors recommend using the $I(320\ \mathrm{nm})/I(350\ \mathrm{nm})$ PLE ratio for such calculations.

Stability of the Optimized Se-ODE Precursor. Finally, the chemical stability of the Se-ODE samples with aging was considered, again using PLE spectroscopy. In Figure 4 the PLE spectra of optimized Se-ODE samples (180 °C, 5 h) stored and aged at room temperature in air or under nitrogen for up to 1 month after preparation are presented. The data of Figure 4 show that there is no significant change in the PLE over time, and test reactions indicated the aged solutions remained viable for metal-selenide growth. These results, in combination with the correlation between PLE and Se deposition yields, consolidate Se-ODE as a highly reactive air stable selenium source.

Se-ODE Characterization. In spite of the existing reports on Se-ODE,[20−26] the issue of the structure of the Se-ODE products has not been resolved. In this section we present structural data for Se-ODE. Some possible candidate species that were initially considered include: Se_n rings; polymeric selenium; dissolved fragments of rings/chains; and alkene addition products. The study of metallic and amorphous selenium dissolved in n-alkanes was made by Perov and Moshchenskaya.[14] Using solubility and

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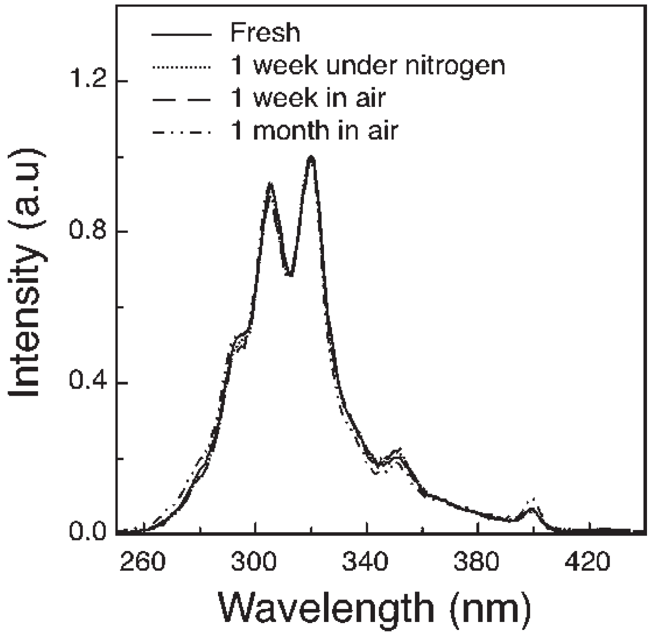

Figure 4. Photoluminescence excitation of Se-ODE prepared at 180 °C diluted in cyclohexane. Four spectra are presented: freshly prepared Se-ODE; Se-ODE after storage in air for 1 week; Se-ODE after storage under nitrogen for 1 week; and a sample stored in air for 1 month.

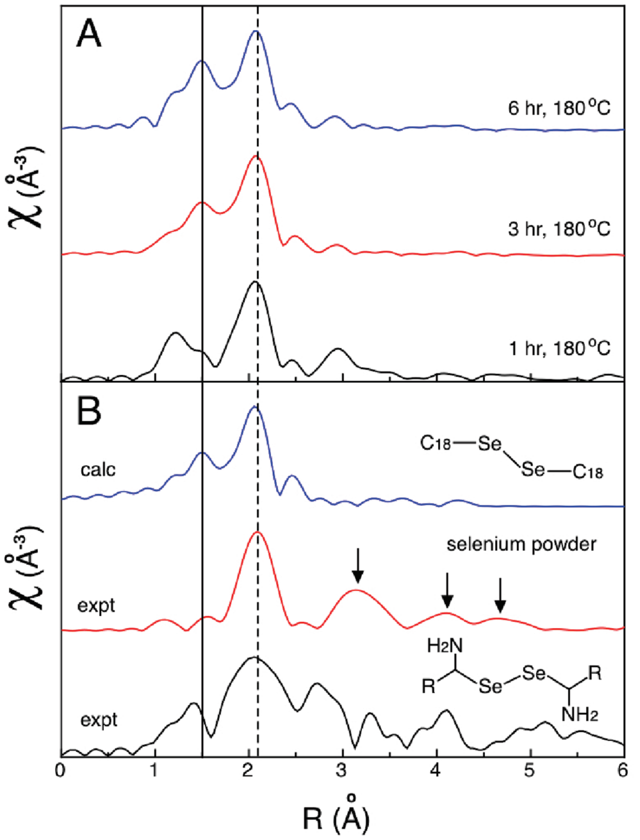

Figure 5. Se K-edge X-ray absorption data: (A) Se-ODE experimental samples corresponding to different times during the heating of elemental selenium powder in ODE at 180 °C to achieve dissolution; (B) Se-XAS data for reference materials seleno-L-cystine (R = COOH) and elemental selenium powder as well as the calculated radial distribution for a representative Se/ODE reaction product.

ebullioscopic data they concluded that heating and dissolution of elemental Se in alkanes is associated with the breaking up of cyclooctaselenium rings or Se_n chains to fragments with an average chain length of 2−3 Se atoms, although exactly how these clusters are solubilized was not mentioned. In the present study involving ODE, possible reactions between the selenium and the terminal alkene of ODE were considered as the reaction pathway. Recently Shen et al.[24] identified a peak in a mass spectrum indicating a simple 1:1 Se:ODE adduct could form in Se-ODE after 3 h heating at 220 °C. In the present study we have used Se K-edge XAS and NMR techniques to investigate the crude Se-ODE solutions.

XAS Characterization. K-edge selenium X-ray absorption spectroscopy was used to characterize the structural changes that occur when elemental selenium is heated in a solution of 1-octadecene. Figure 5 shows that a relative decrease in the peak intensity at 2.1 Å angstroms (dashed line) is coincident with a relative increase in the first-nearest neighbor peak at 1.5 Å (solid line) with increased heating time. The peak in the radial distribution function located at 2.1 Å (found for all Se-ODE samples) matches well to the Se−Se distance in the reference elemental selenium and the seleno-L-cystine samples. This is clear evidence that there are species with Se−Se bonds in Se-ODE, which is consistent with Se_n species existing in the solution. Importantly, comparison of the XAS spectrum of fully dissolved Se-ODE (6 h) with that of Se powder highlights the absence of long-range Se−Se interactions in the Se-ODE (reference arrows). This indicates that predominantly short chain Se species exist in solution, an observation that is consistent with the data of Perov and Moshchenskaya.[14]

The other prominent feature in the Se-ODE XAS data is the peak near 1.5 Å. This is much shorter than a typical Se−Se bond distance. The possible candidates include Se−C, Se−H, and selenium oxidation products. The oxidation of Se-ODE is a possibility, although the samples were vacuum-sealed after removal from the system and exposed to air only for the 15−20 min required for XAS sample preparation and mounting. Systematically varying the input structures (Se_n oligomers bound to one or more ODE chains) for FEFF calculations through the ATOMS software has indicated that a wide range of compounds can give rise to the observed XAS outcome. The calculated radial distributions for one possible structure (C_{18}−Se−Se-C_{18}), which matches well with the fully dissolved 6 h sample is presented in Figure 5B. Given the close proximity to the Se−C bond length obtained for seleno-L-cystine, as well as the excellent agreement to the calculated spectrum (Figure 5B-top) direct Se−C bonding seems highly likely.

NMR Characterization. To better appreciate the chemistry occurring in the Se-ODE system ^{1}H NMR and $^{1}H-^{13}C$ HSQC, and ^{77}Se NMR in $CDCl_3$ were performed. For the NMR experiments, a higher Se content was used to facilitate detection of the species of interest. Although this could have changed the rate of dissolution we expect that the chemistry involved in the dissolution process would not have differed greatly.

While both high purity and technical grade ODE were studied, only data for the high purity ODE are shown

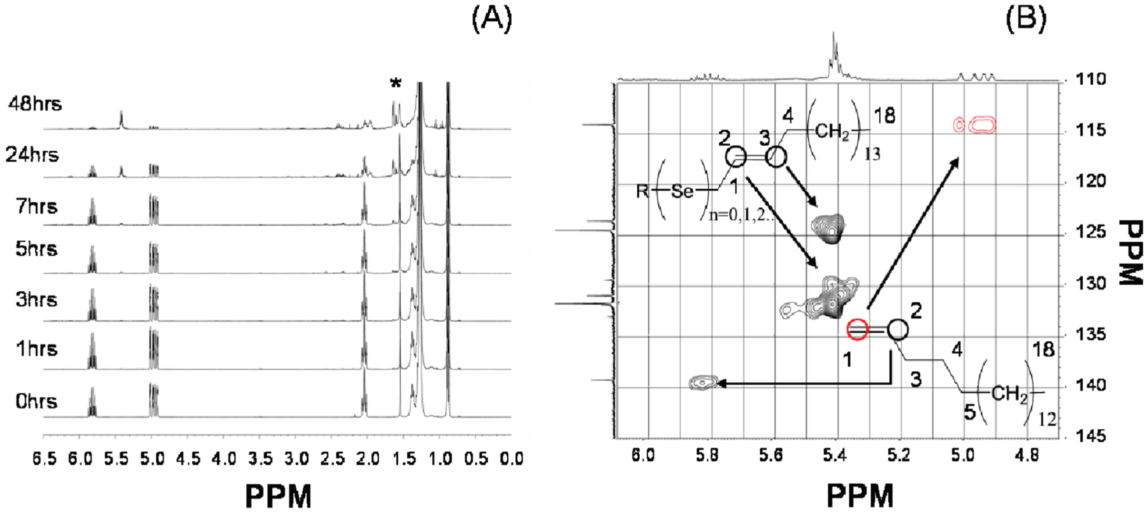

Figure 6. (A) ^{1}H NMR spectra at different temporal points during the formation of Se-ODE at 180 °C. Residual water in $CDCl_3$ solvent is indicated by *. (B) ^{1}H$-$^{13}C HSQC spectrum of the alkene region for 48 h sample. The assignment of the different species is shown by the inset model structure. Analogous assignments would occur for a range of different selenium species bound to 1-carbon.

here. A major difference between these two grades is that technical grade ODE possesses inhibitors that prevent polymerization of the alkene groups at elevated temperatures. In this respect, we note that the literature has only described the use of technical grade ODE for the fabrication of high quality nanocrystals. Importantly, dissolution of Se species in high purity ODE visibly reduces the extent of polymerization reactions observed when high purity ODE is heated by itself. This observation is consistent with Se being a free radical scavenger, and indicates that attack on/by elemental Se through thermally generated radicals is likely to be a significant reaction pathway.

In Figure 6A we show the temporal evolution of the dissolution process involving Se in high purity ODE as measured by ^{1}H NMR over a 48 h time span. Broadening of the aliphatic hydrogen signals during the heating process is consistent with a polymerization mechanism that is occurring in the presence of Se. In addition to residual 1-ODE peaks, ^{1}H NMR reveals the evolution of a number of new species in the methyl/methylene and alkene regions. Of interest is the definitive trend for the alkene hydrogen peaks centered at 5.82 and 4.96 ppm to be converted to a multiplet centered at 5.41 ppm after prolonged heating.

The ^{1}H$-$^{13}C HSQC spectrum of the alkene region for high purity ODE heated in the presence of Se for 48 h is shown in Figure 6B. It is evident that the residual alkene peaks from the ODE are still observed in this sample (see Supporting Information for the ^{1}H$-$^{13}C HSQC spectrum of unheated high purity ODE). The multiplet centered at 5.41 ppm in the ^{1}H NMR spectrum, which appears *after* selenium dissolution can be seen as arising from two chemically distinct carbon atoms. In addition, on the basis of the signal phase, each of these carbons is correlated with a single hydrogen atom. Overall, these findings show that during the dissolution process isomerization of the alkene from the 1$-$2 to the 2$-$3 position occurs. This process only occurs when selenium is present (see Supporting Information), indicating that selenium interactions are necessary for this mechanism to be activated. The slightly varied frequency response of the 2-carbon within the ^{1}H$-$^{13}C HSQC spectrum is indicative of a varied chemical environment on the 1-carbon. On the basis of this observation it is likely that Se is bonding to the 1-carbon, and is doing so in a variety of ways. If no selenium was bonded to the 1-carbon, the ^{1}H$-$^{13}C HSQC spectrum would show a relatively uniform chemical environment for both carbon species, which is not the case. While the isomerization process can be identified from the NMR, it only accounts for ~30% of the NMR signal. Other reactions must therefore be concurrently occurring. In their recent study, Shen et al. produced Se-ODE by heating at 220 °C and reported a 5.4 ppm resonance similar to the one we have found for the (relatively inactive) 180 °C samples heated for a prolonged period beyond dissolution.[24] Shen found mass spectrometry (ms) evidence (signal at 331.2 *m*/*z*) for a 1:1 Se-ODE complex in their samples. Our HSQC data would indicate that rather than the heterocyclic addition product proposed by Shen et al. the species may have a terminal SeH moiety.

It is well-known that when monoolefins are heated in the presence of sulfur or selenium, bridging chalcogenide chains form between the monoolefins by the vulcanization process. This process is found to result in three main products, and these have been depicted schematically in the Supporting Information, Figure S5A.[36] As the vulcanization reaction proceeds, it is well documented that the length of the chalcogenide chains is gradually reduced, and the concurrent formation of cyclic monochalcogenides as well as other byproducts results.[36] We cannot disregard any of these reaction products based on the present findings; however, these processes could account for the numerous chemical species that are additionally observed in the alkane region of the ^{1}H NMR spectrum.

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(36) Zaicky, J. *The Chemistry of Alkenes*; John Wiley & Sons Ltd.: New York, 1970; Vol. *2*.

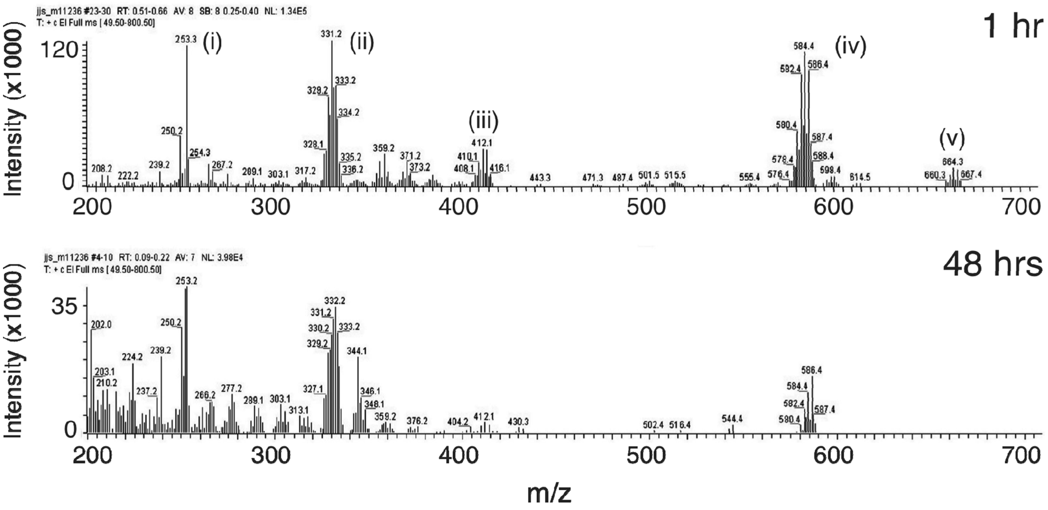

Figure 7. Positive ion EI mass spectra of active (1 h @ 200 °C) and inactive Se-ODE (48 h @ 200 °C) samples, with signals labeled corresponding to (i) ODE; (ii) ODE+Se;(iii) ODE+2Se; (iv) 2ODE+Se; and (v) 2ODE+2Se. Note that (iii) and (v) only appear in the more active sample.

Other potential products of the Se-ODE system are selenium addition products of the olefinic C1, C2 atoms of ODE (S5B); including heterocyclic selenium compounds.

To ascertain the nature and diversity of the selenium species that evolve within the reaction, we performed mass spectrometry and ^{77}Se NMR (see Supporting Information). The selenium NMR spectrum contains numerous species evolving during the dissolution process, with over 14 unique Se environments observed after 48 h of heating. The wide chemical shift range in which these resonances occur (−100 to 900 ppm) is consistent with both Se−Se and Se−C bonding in the system.[37] These results are therefore in qualitative support of the ^{1}H NMR results and the Se-XAS data.

More substantive evidence was found in the EI mass spectra of active and inactive Se-ODE samples that are presented in Figure 7. In the available detection range (up to 800 m/z) there were five singly charged species identified for the active sample (1 h). The signals from these species have been labeled (i)−(v) and are attributed to ODE (m/z = 252); ODE+Se (m/z = 331); ODE+2Se (m/z =410); 2ODE+Se (m/z = 586); and 2ODE+2Se (m/z = 664). Importantly, the two peaks (iii) and (v) were not present in the inactive sample. This strongly indicates that prolonged heating leads to a reduction in Se−Se bridging, which is consistent with the proposed vulcanization scheme. To ensure that the individual contributions to the mass spectra were not arising purely from fragmentation, gel permeation chromatography of the samples confirmed multiple oligomeric contributions below ~1000 Da (not shown). In this light, the 1:1 Se-ODE adduct recently found by Shen et al. in Se-ODE prepared by strong heating (3 h, 220 °C) is probably a less active Se-precursor.

We now have a broad physical picture of the dissolution products that are generated, but we currently cannot identify unambiguously the key structural differences between the reactive and unreactive selenium species, although the presence of Se−Se bonding seems to be important for high efficacy. One of the contributing factors is that both reactive and unreactive species are concurrently produced during the dissolution process. In this regard we note that the reactivity of bridging monoselenides (*D*°(Se−C) = 210 kJ/mol) should be significantly different from ODE molecules cross-linked through Se chains (*D*°(Se−Se) = 172 kJ/mol)[34] The question of whether such monoselenide species form the unreactive precursors remains to be confirmed by future studies, where isolation or synthesis of the individual species can be made. While the scope of the present study has been to elucidate the properties of the crude Se-ODE mixture, future work to isolate the critical components in the system is expected to lead to tailored, high purity selenium precursors with tailored reactivity.

Conclusion

A detailed study of the development of a selenium precursor solution based on a simple mixture of selenium powder dissolved in 1-octadecene has been made. The chemical reactivity of the Se-ODE system is found to be highly dependent on heating temperature and time. Structural characterization of the Se-ODE precursor attained through NMR and X-ray absorption spectroscopies, as well as positive ion impact mass spectrometry, suggests that the dissolution of the elemental selenium within 1-ODE proceeds through the fragmentation of the cyclooctaselenium rings or selenium chains to form short chain selenium bridges between alkane and/or alkene solubilizing molecules. This form of the precursor solution constitutes a highly reactive selenium source. Following prolonged heating, the short Se chains further break up to form single selenium atom bridges. The resulting monoselenides have a drastically lower chemical reactivity.

We have established a simple PLE spectroscopic check, which is directly correlated to the chemical reactivity of

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the precursor. A comparison of the chemical reactivity for an optimized Se-ODE precursor to the traditionally employed trioctylphophine selenide showed that the Se-ODE was nearly twice as reactive for nanocrystal growth. This finding highlights that this easily prepared, cheap, and air-stable Se-ODE precursor is a highly viable selenium source for the synthesis of semiconductor nanocrystals.

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Supporting Information Available: PLE spectra, plots of high purity ODE ^{1}H$-$^{13}C HSQC results, ^{1}H NMR spectral comparison of heated and unheated ODE with the Se-ODE precursors and ^{77}Se NMR spectra of Se-ODE samples. This material is available free of charge via the Internet at http://pubs.acs.org.