

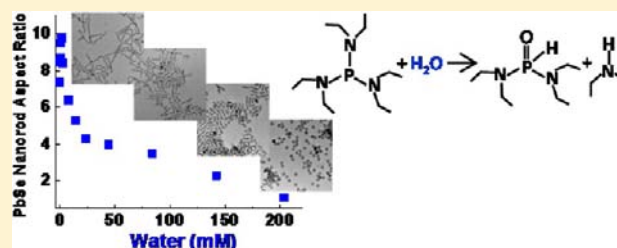
Control of PbSe Nanorod Aspect Ratio by Limiting Phosphine Hydrolysis

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S Supporting Information

ABSTRACT: The aspect ratio and yield of PbSe nanorods synthesized by the reaction of Pb-oleate with tris(diethylamino)phosphine selenide are highly sensitive to the presence of water, making it critical to control the amount of water present in the reaction. By carefully drying the reaction precursors and then intentionally adding water back into the reaction, the nanorod aspect ratio can be controlled from 1.1 to 10 and the yield from 1 to 14% by varying the water concentration from 0 to 204 mM. $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR show that water reacts with tris(diethylamino)phosphine to create bis(diethylamido)phosphorous acid. It was determined that bis(diethylamido)phosphorous acid is responsible for the observed aspect ratio and yield changes. Finally, it was found that excess oleic acid in the reaction can also react with tris(diethylamino)phosphine to create bis(diethylamido)phosphorous acid, and upon the removal of both excess oleic acid and water, highly uniform, nonbranching nanorods were formed.



INTRODUCTION

Due to their exceptional physical properties, PbSe nanorods are attractive components for use in optoelectronic devices such as photovoltaics and light emitters.^{1–3} Recently, Koh et al.⁴ synthesized single-crystal, PbSe nanorods with homogeneous size distributions (5% diameter and 20% length)⁵ using a catalyst-free, one-pot, solution chemistry method. The development of this synthesis has allowed PbSe shape-dependent optical properties to be explored which were previously unattainable due to the lack of high-quality materials. For example, it has been recently shown that PbSe nanorods have larger Stokes shifts,⁶ more efficient multiple exciton generation,^{1,2,7} higher absorption coefficients,^{1,7} and longer effective biexciton lifetimes^{3,7} than PbSe nanocrystals. Additionally, PbSe nanorods are the first material to demonstrate the splitting of the Fröhlich mode in anisotropic structures.⁵ While PbSe nanorods with aspect ratios of ~ 1.5 – 12 ,⁷ with diameters from ~ 2.8 to 5.6 nm and lengths from 6 to 47 nm,^{7,8} have been synthesized, it has been difficult for us as well as other groups to reproduce such a wide aspect ratio range.³ Therefore, there is a need for a greater understanding of the formation mechanism of PbSe nanorods such that uniform nanorods with aspect ratios over a broad range can be controllably synthesized.

In this paper, we show for the first time that the amount of water present in the reaction, either added intentionally or present as a contaminate, has a dramatic effect on both the PbSe nanorod morphology and yield. We found that if the amount of water in the reaction is not controlled, the small amount present in the nanorod precursors is sufficient to create a large irreproducibility from batch to batch. It is thus critical to control the amount of water in the reaction in order to control the nanorod morphology. If the precursors are first carefully

dried and water is intentionally added to the reaction at concentrations from 0 to 204 mM, the nanorod aspect ratio can be precisely controlled from 1.1 to 10 and the yield from 1 to 14%. This result is particularly surprising since water has little effect on the common PbSe nanocrystal synthesis reaction.^{9,10} We have found that the role of water is *indirect*; i.e., hydrolysis of tris(diethylamino)phosphine used in the reaction forms bis(diethylamido)phosphorous acid. By synthesizing this latter compound independently and adding it to the nanorod reaction, we have identified it as responsible for both the nanorod aspect ratio and yield variation. Our results add to the growing consensus^{9,10} that drying metal oleates *in situ* by simple heating under an inert atmosphere is insufficient to obtain completely anhydrous reaction conditions.

Additionally, we found that excess oleic acid in the reaction undergoes similar chemistry. Upon removal of both the excess oleic acid and water, the nanorod reaction slowed considerably, and highly uniform, nonbranching nanorods were formed. These homogeneous nanorods may allow for easier alignment of nanorods over large surface areas for devices.

MATERIALS AND METHODS

General Considerations. Standard Schlenk-line techniques were used unless otherwise noted. Lead(II) oxide (PbO, 99.999%), 1-octadecene (90%), oleic acid (90%) tris(diethylamino)phosphine (97%), selenium powder (99.5%, 100 mesh), tetrachloroethylene (99%), and diethylamine (99.5%) were purchased from Sigma-Aldrich. Hexanes (98.5%), ethanol (200 proof), and tetrahydrofuran (THF, 99.9%) were purchased from commercial sources. PbO, Se, hexanes, ethanol, THF, and tetrachloroethylene were used without further

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purification. Oleic acid and 1-octadecene were dried by heating them to 110 °C under vacuum for 2 h and then placing them over activated 3 Å molecular sieves in a glovebox. We refer to oleic acid and 1-octadecene that have not undergone this procedure as “wet”. Diethylamine was dried by placing it over activated 3 Å molecular sieves in a glovebox for several days followed by vacuum distillation. Tris(diethylamino)phosphine (**1**) was purified by first heating under Ar to 225 °C for 2–3 h to decompose minor impurities, signified by the onset of a yellow color, followed by vacuum distillation under a dynamic vacuum of ~200 mTorr at 65–77 °C. $^{31}\text{P}\{^1\text{H}\}$, ^1H , and ^{13}C nuclear magnetic resonance (NMR) spectroscopies were used to confirm the purity of **1** (see Figure S1 in the Supporting Information for spectra).

Synthesis of Pb-Oleate. Typically, 4.4 g (20 mmol) of PbO and 19 mL of oleic acid (60 mmol) were heated to 110 °C under vacuum for 2 h. Once the solution was colorless, it was placed in two vials while it was still above room temperature. The viscous solution of Pb-oleate and oleic acid was allowed to cool to room temperature overnight, and the mixture became a fluffy, sticky, white solid. The extra oleic acid was removed by washing the solid with acetone, forming a milky white suspension. Next, the solution was centrifuged at 4 krpm for 3 min, which caused the solid Pb-oleate to separate from the solution and deposit on the bottom of the vial, leaving the oleic acid in the acetone. This acetone cleaning step was repeated eight times in order to ensure that all the oleic acid was removed. The Pb-oleate was then placed in a vacuum oven at room temperature overnight in order to remove any remaining acetone and water. Finally, the vacuum oven was backfilled with Ar, and the white powdery Pb-oleate was stored in a glovebox.

PbSe Nanorod Synthesis. The PbSe nanorods were synthesized using the general method developed by Koh et al.⁴ except for the differences noted below. To prepare PbSe nanorods in the absence of water, dried Pb-oleate isolated as described above (0.77 g; 1 mmol), dried oleic acid (0.37 mL; 1.2 mmol), and 5 mL of dried 1-octadecene were mixed under Ar and heated to 150 °C. Next, 3 mL of purified **1** was mixed with Se (0.237 g; 3 mmol) and loaded into a syringe. Upon mixing **1** and Se, the solution became warm. This solution was then injected into the Pb-oleate solution, which caused the temperature to drop to ~130 °C. The reaction was allowed to continue for 2 min, during which time the temperature rose to ~135 °C. The reaction became a dark brown color after ~80 s. After 2 min, the reaction was cooled to room temperature using a liquid nitrogen bath. The nanorods were isolated from the unreacted precursors and byproducts by adding ~0.5 mL of hexanes and ~8 mL of ethanol, and centrifuging at 4 krpm for 4 min. This process was performed in air. The product formed a black solid at the bottom of the vial which was separated by decanting. This purification procedure was repeated using ~1 mL of hexanes and ~5 mL of ethanol. The nanorods were immediately transferred into an Ar-filled glovebox for storage. This reaction yielded ~5 mg of nanorods.

For some of the reactions water was intentionally added to the reaction. The same procedure described above was followed, except small amounts of water were added to the Pb-oleate, oleic acid, and 1-octadecene solution before heating. Water concentrations between 0 and 204 mM were explored. For the lower water concentrations (<84 mM), dry oleic acid was diluted with water first, and then a portion of that was added to the solution. For example, to obtain a water concentration of 23 mM, 0.01 g of water was added to 1 mL of dry oleic acid, and 0.37 mL of this solution was added to the reaction. This dilution step was necessary in order to obtain small concentrations. For higher water concentrations (>84 mM), water was directly added to the reaction solution. For example, to obtain a 142 mM water concentration, 23 μL of water was added to the reaction. Depending on the water concentration, the reaction became dark brown between 10 and 90 s and yielded between 5 and 39 mg of nanorods (Figure S5).

PbSe Nanorod Synthesis without Water or Excess Oleic Acid. PbSe nanorods without intentionally added water or excess oleic acid, i.e., an oleic acid-to-Pb ratio of 2 instead of 3.2, were also prepared. In this synthesis the volume lost as a result of removing the

excess oleic acid (0.37 mL) was made up for by adding extra 1-octadecene, such that the Pb-oleate and tris(diethylamino)phosphine selenide concentrations remained the same. Otherwise, the reaction was performed exactly as described above for the reactions without added water. Removal of water and excess oleic acid slowed the reaction considerably, turning dark brown after 2–4 min (rather than after 80 s). Therefore, the reactions were allowed to proceed for longer times (3.5–15 min). These reactions yielded between 7 and 35 mg of nanorods.

Synthesis of Bis(diethylamido)phosphorous Acid (2**).** In air, water and **1** (in a 5:1 molar ratio) were mixed in THF for ~12 h. The volatiles were then separated by vacuum distillation, and NMR was used to characterize the product. NMR indicates that the majority of the material isolated was **2**, although a small amount of unknown phosphines are present (see Figure S2). The NMR data obtained for **2** match those found previously by Vather et al.^{11,12} ^1H NMR (C_6D_6): δ 0.87 (12H, t, J_{HH} 7.0 Hz, $4\times\text{CH}_3$); δ 2.79 (8H, m, $4\times\text{CH}_2$); δ 6.66 (1H, d, J_{HP} 561.9 Hz, P–H). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 19.5.

PbSe Nanorod Characterization. Transmission electron microscopy (TEM) samples were made by making dilute nanorod chloroform solutions and drop-casting a small volume (<500 μL) onto lacey carbon TEM grids. TEM images were obtained on a JEOL 2200FS transmission electron microscope operating at 200 kV. The CCD camera on which the images were recorded was calibrated with a gold lattice magnification standard. To determine the amount of branching in the nanorod sample, at least 100 nanorods were examined and determined to be either a straight rod, an “L”, a “T”, a cross shape, or a shape with multiple 90° angles and branches. From these statistics the percentage of branching and multibranching was determined. PbSe nanorods were suspended in tetrachloroethylene to measure their room-temperature absorbance and photoluminescence. PbSe nanorod absorbance spectra were obtained using a Perkin-Elmer Lambda 750 spectrometer equipped with deuterium and tungsten lamps, and PbS and PMT detectors. The photoluminescence of the PbSe nanorods was obtained using a Bruker Vertex 80v Fourier-transformed infrared spectrometer equipped with a UV/vis/NIR CaF_2 beamsplitter and a Hamamatsu PbS/Si detector. The samples were excited with a 660 nm diode laser perpendicular to the collection axis.

NMR. All NMR samples were run on a Bruker Avance-300 instrument; ^1H , $^{31}\text{P}\{^1\text{H}\}$, and ^{13}C spectra were recorded at 300.13, 121.48, and 75.46 MHz, respectively. The solvents were used as references for the ^1H and ^{13}C spectra, and an external H_3PO_4 reference was used for the $^{31}\text{P}\{^1\text{H}\}$ samples. CDCl_3 was initially used as the solvent for **1**; however, we found that it reacted with CDCl_3 over time, so anhydrous benzene- d_6 was used instead as the solvent for both **1** and **2**. It is important to use anhydrous, as the water in standard benzene- d_6 reacts with **1** to form **2**.

RESULTS AND DISCUSSIONS

The impact of water concentration variation on the PbSe nanorod morphology is demonstrated in Figure 1. Without water present the nanorods have an aspect ratio of 8 ± 3 , Figure 1a. Upon water addition the nanorod aspect ratio initially increases to 10 ± 4 , Figure 1b, and then decreases to 1.1 ± 0.1 (nanocrystals) as the water concentration continues to increase, Figure 1c–h. The majority of the aspect ratio change with water concentration is due to the decreasing nanorod length, not the increasing nanorod diameter. The average relative standard deviations of the nanorod diameters, lengths, and aspect ratios are 15%, 34%, and 38%, respectively. The detailed dimensions of the nanorods shown in Figure 1 are given in Table S1. In addition, nanorod branching decreases as the water concentration increases. The nanorods synthesized without water present are highly branched, ~90% of the nanorods are branched, and ~57% contain multiple branches (e.g., they contain more than one ~90° junction). As the water

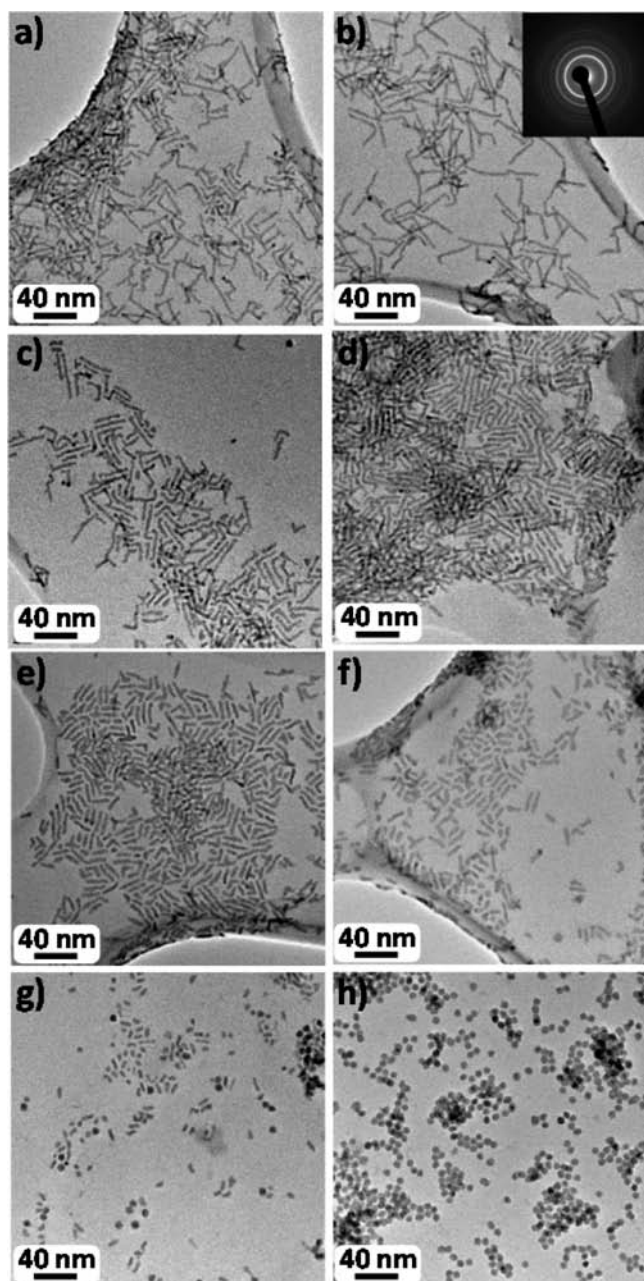


Figure 1. TEM images of PbSe nanorods synthesized with varying amounts of intentionally added water: (a) 0, (b) 0.7, (c) 8, (d) 14, (e) 23, (f) 84, (g) 142, and (h) 204 mM. The aspect ratio, diameter, and length of these nanorods are given in Table S1. Electron diffraction indicates the nanorods are rock-salt PbSe. A typical electron diffraction pattern is shown in the inset of panel b.

concentration is increased from 0.7 to 204 mM, the fraction of nanorods containing branches decreases from 60% to 0%.

The decrease in aspect ratio with the increase in water concentration is shown graphically in Figure 2a; the majority of the aspect ratio decrease occurs between 0 and 23 mM water. The reaction yield (based on Pb atoms) increases from 1% to 14% as the water concentration increases (Figure 2a). Additionally, we found that adding a large concentration of water (~1.2 M) to the reaction resulted in the uncontrolled synthesis of large (~100 nm), nonuniform PbSe particles with a 100% yield (see Figure S4). Also, as the water concentration increases, the reaction turns dark brown faster (Figure S5). If

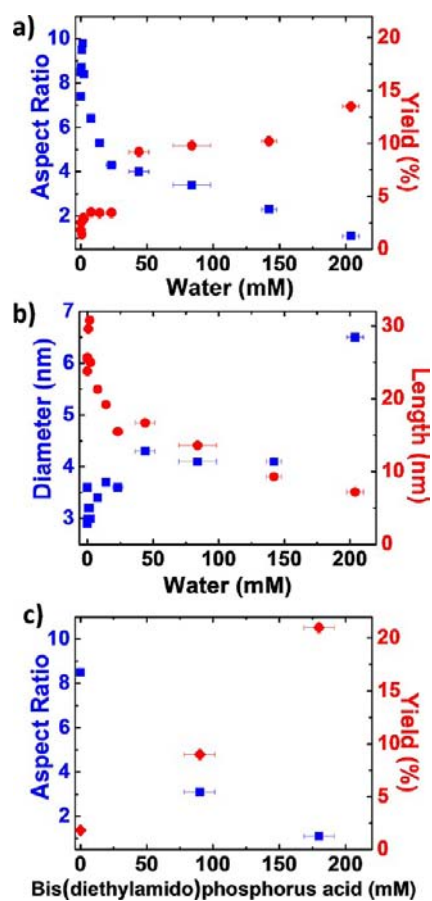


Figure 2. (a) Average PbSe nanorod aspect ratio (blue squares) and PbSe nanorod reaction yield (red circles) as a function of intentionally added water. (b) Average PbSe nanorod diameter (blue squares) and length (red circles) as a function of intentionally added water. (c) Average PbSe nanorod aspect ratio (blue triangles) and PbSe nanorod reaction yield (red diamonds) as a function of added bis-(diethylamido)phosphorous acid (2). Some of the water concentration and yield error bars are hidden by data points. The error bars on the dimensions are not shown for clarity, but can be found in Table S1.

this color change is taken as an indication of the nucleation time, then this indicates that the addition of water results in a faster reaction rate. Furthermore, since these reactions do not reach thermodynamic equilibrium by the end of the 2 min reaction (Figure S6), this increase in reaction rate is responsible for the yield increase upon water addition. It is interesting to note that when oleic acid, 1-octadecene, and Pb-oleate are not dried before the reaction, nanorods with aspect ratios between 4 and 7 are formed.^{1,3} Using Figure 2a as a guide, this implies that the water concentration in these reactions is between ~7 and ~50 mM. This water is from the “wet” oleic acid and 1-octadecene as well as from the water produced from PbO and oleic acid reacting to form Pb-oleate. When rigorously dried Pb-oleate and “wet” oleic acid and 1-octadecene are used, nanorods with aspect ratios near 9 are formed. This indicates, as previously mentioned by Baumgardner et al.,¹⁰ that the majority of the water contamination is from the water released from the Pb-oleate formation and that less than ~1 mM of the water contamination comes from the “wet” oleic acid and 1-octadecene. Nevertheless, it is clearly critical that all precursors be dry in order to gain control over the nanorod morphology.

Room-temperature absorbance and photoluminescence of the nanorods shown in Figure 1 are presented in Figure 3.

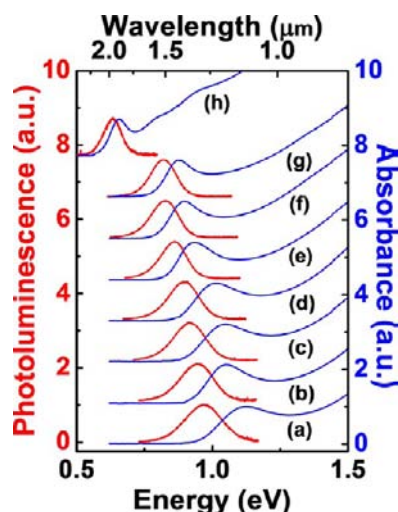
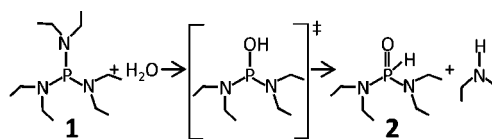


Figure 3. Room-temperature absorbance and photoluminescence of the PbSe nanorods shown in Figure 1. The letters next to each spectrum correspond to the letters in Figure 1.

While the nanorod length has some effect, the first exciton peak energy is mostly determined by the diameter.^{8,13} Since the nanorod diameter increases from 2.9 to 4.3 nm as the water concentration is increased from 0 to 142 mM and then jumps to 6.5 nm as the water concentration is increased to 204 mM (Figure 2b), the energy of the first exciton follows a similar trend, decreasing from 1.1 to 0.88 eV as the water concentration is increased to 142 mM and then jumping down to 0.66 eV as the water concentration is increased to 204 mM. The photoluminescence of the nanorods at all water concentrations has well-defined peaks with full-width at half-maxima similar to the first exciton peaks in the absorbance spectra, and consistent with the size distributions. Also, surprisingly, there is no correlation between the photoluminescence intensity and the water concentration. This indicates that there is no photoluminescence degradation, and therefore no increase in the creation of nonradiative defects, upon the addition of water to the reaction.

With the correlation between water and aspect ratio firmly established, we then focused on the question of how the water influences the reaction. Water can be doing one of two things: (1) *directly* modifying the nanorod morphology and yield, by perhaps binding to the surface of the nanorods, or (2) *indirectly* modifying the nanorod morphology, by reacting with another component in the reaction to create a third species which then goes on to modify the nanorod aspect ratio and reaction yield. Since water does not affect the PbSe nanocrystal reaction,^{9,10} which is very similar to the nanorod reaction but uses trioctylphosphine instead of tris(diethylamino)phosphine (1),¹⁴ we decided to start by examining the effect water has on 1. As mentioned in the Materials and Methods section, we found that mixing water with 1 in a 5:1 ratio at room temperature in THF converts all of 1 into bis(diethylamido)phosphorous acid (2) and a small amount of other unidentified phosphine species. This indicates that the reaction of 1 with water results in both 2 and diethylamine, as has been shown previously by Szewczyk et al.¹⁵ and illustrated in Scheme 1. It should be noted that, following hydrolysis to form diethylamine, the hydroxide group is initially bound to the phosphorus atom, followed by a rearrangement, similar to that seen in phosphonic acid,^{16,17} to create 2. This reaction suggests that it

Scheme 1. Reaction of Compound 1 with Water To Yield 2 and Diethylamine



is possible that water is acting *indirectly* by creating 2 and diethylamine, and one or both of these hydrolysis products are responsible for the nanorod aspect ratio and yield modifications. Koh et al.¹⁴ have also proposed that diethylamine is present in the nanorod reaction; however, they suggest that it comes from the decomposition of 1 at elevated temperatures.

To test if 2 and/or diethylamine are responsible for the nanorod aspect ratio and yield changes, we separately added them directly to the reaction. First, dried diethylamine was added to the solution of 1 and Se before injection. The concentration of diethylamine in the reaction was 807 mM. Since water creates diethylamine from 1 in a 1:1 ratio, this diethylamine concentration would correspond to a water concentration of 807 mM if the diethylamine had been formed by the reaction of water with 1. The addition of diethylamine to the reaction resulted in branched nanorods with an aspect ratio of 8 ± 4 and a yield of 2% (Figure S7). This is similar to the results obtained when no water is added, which indicates that diethylamine is not responsible for the aspect ratio and yield changes. This result is contrary to that found by Koh et al.,¹⁴ who suggest that diethylamine increases the nanorod reaction rate.

Next, two nanorod reactions were performed with different concentrations of 2, 90 and 180 mM. Before injection, 2 was added to the solution of 1 and Se. Compound 2 was isolated from the reaction of water with 1, which had a small amount of other phosphine impurities present (Figure S2). The addition of 2 to the reaction, at a concentration of 90 mM, results in branched nanorods with an aspect ratio of 3.1 ± 0.8 and a yield of 9%. Increasing the concentration of 2 to 180 mM creates nanocrystals with an aspect ratio of 1.1 ± 0.1 and a yield of 21%. Figure 4 shows TEM images of the nanorods synthesized with increasing amounts of 2, demonstrating the decrease in aspect ratio as the concentration of 2 is increased. This trend in morphology and yield is similar to that seen with the addition of water, as is shown by comparing panels a and c in Figure 2. Note that, since water creates 2 from 1 in a 1:1 ratio, there is a one-to-one correspondence between the *x*-axes of Figure 2a,c. From these results we can conclude that 2 is responsible for the nanorod aspect ratio and yield control, and that water acts *indirectly* to control the nanorod aspect ratio and yield by reacting with 1 to create 2.

The presence of small amounts of water has a dramatic influence on the PbSe nanorod reaction and essentially no effect on the PbSe nanocrystal reaction because the nanorod reaction utilizes 1, which is more susceptible to hydrolysis than the trioctylphosphine used in the nanocrystal synthesis. Trioctylphosphine is not prone to hydrolysis because the P–C bond is strong and not easily cleaved.¹⁷ In contrast, as we have shown above, when 1 reacts with water, one of the amine ligands is removed, creating the reactive compound 2. This occurs because the P–N bond is moderately polar and is susceptible to attack by nucleophiles such as water.^{14,17}

There is an interesting parallel between this work and that done by Evans et al.¹⁸ on the synthesis of PbSe nanocrystals

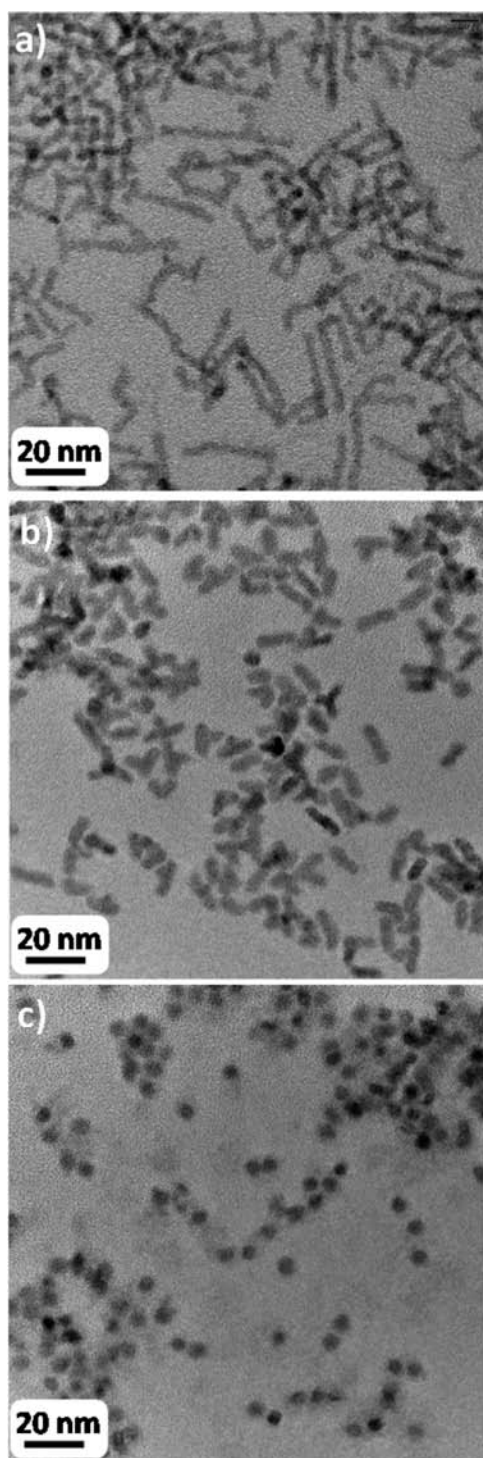


Figure 4. PbSe nanorod aspect ratio decreases with increasing amounts of bis(diethylamido)phosphorous acid (**2**): a) 0 mM, AR = 8 ± 3 , $D = 2.9 \pm 0.5$ nm, $L = 24 \pm 8$ nm; b) 90 mM, AR = 3.1 ± 0.8 , $D = 3.8 \pm 0.5$ nm, $L = 11 \pm 2$ nm; c) 180 mM, AR = 1.1 ± 0.1 , $D = 4.6 \pm 0.5$ nm, $L = 5.1 \pm 0.4$ nm. AR, D , and L are the average nanorod aspect ratio, diameter, and length, respectively.

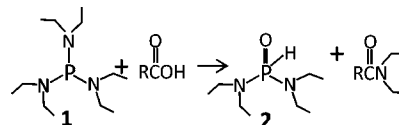
from Pb-oleate and trioctylphosphine selenide. In their work, they show that tertiary phosphine selenides do not react with Pb-oleate and that it is in fact secondary phosphines, present as impurities, which are responsible for the PbSe nanocrystal formation. They hypothesize that the secondary phosphines create PbSe by promoting the dissociation of oleate from Pb-

oleate to form a reactive Pb-phosphine complex which then reacts with Se to form PbSe. In this work we find that **2** similarly promotes the formation of PbSe. While not a secondary phosphine, **2** does contain the same P–H moiety. This suggests that **2** might play a similar role in the PbSe nanorod synthesis as secondary phosphines play in the PbSe nanocrystal synthesis (i.e., **2** may be increasing the PbSe nanorod yield by dissociating the oleate from the Pb-oleate to form a more reactive Pb-phosphine complex). Additionally, we have observed that **2** reacts with Pb-oleate, likely forming a Pb–P complex (Figures S9a and S10). However, while this parallel leads to an interesting hypothesis, a more in-depth analysis of the PbSe nanorod reaction is required to fully understand the mechanism of how **2** increases both the nanorod aspect ratio and yield. Furthermore, the mechanism by which the nanorods are formed is also not completely understood. While it has been suggested that they form by an orientated attachment mechanism,⁴ other possible mechanisms such as axial growth,¹⁹ solution–liquid–solid growth^{20,21} (if Pb or Se seeds formed during the reaction), or a combination of mechanisms cannot be ruled out.

While the trend of aspect ratio and yield can be explained by the presence of **2**, comparing Figure 1f to Figure 4b, there is clearly more branching in the nanorods made with a 90 mM **2** concentration as compared to the nanorods made with a similar concentration (84 mM) of water. In the sample made from **2**, 36% of the nanorods are branched, while in the sample made with water only 12% of the nanorods are branched. Since the main difference between adding **2** directly versus adding water to create **2** is the presence of diethylamine, this indicates that the absence of diethylamine may lead to increased branching. Furthermore, while the addition of diethylamine had no effect on the nanorod aspect ratio or yield, the nanorods made with 807 mM diethylamine were only 50% branched (Figure S7), while those made without water were 90% branched (Figure 1a). We therefore speculate that the main role of diethylamine in the reaction is influencing the branching of the resulting products. The details of the subtle role of diethylamine require further study.

Having established the importance of phosphine hydrolysis on nanorod morphology, it becomes clear that excess oleic acid can participate in similar chemistry with compound **1**. By reacting oleic acid with **1** in THF, we found that oleic acid can yield **2** under similar conditions (Figure S3). This has been shown previously by Burgada,²² who proposed the reaction shown in Scheme 2. It is therefore reasonable to conclude that

Scheme 2. Reaction of **1** with Oleic Acid Results in **2** and *N,N*-Diethyloleamide ($R = C_{17}H_{33}$)



excess oleic acid is also affecting the nanorod morphology. To demonstrate this, we removed both the excess oleic acid (i.e., an oleic acid to Pb ratio of **2**) and the water and found that the synthesis proceeded much slower. The reaction became dark brown after 2–4 min and not at ~80 s as is the case with excess oleic acid present but no water (Figure 1a). Since the reaction rate slowed significantly without excess oleic acid, we can conclude that excess oleic acid in the reaction also acts *indirectly*

to increase the reaction rate by reacting with **1** to create **2**. The resulting nanorods were highly uniform and nonbranching (~1% branched) as shown in Figure 5. Along with these

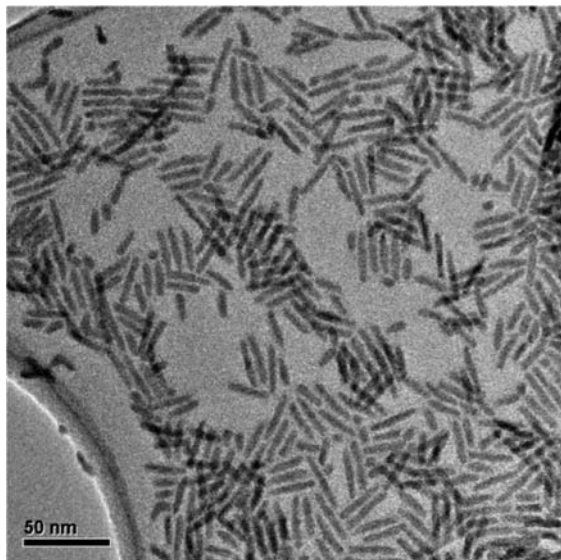


Figure 5. PbSe nanorods synthesized with no water and no excess oleic acid. These nanorods have very little branching (~1%).

nanorods, a population of nanocrystals with similar diameters was also formed. These nanocrystals were easily removed from the uniform nanorods via a size-selective precipitation with chloroform and acetone as the solvent/nonsolvent pair (Figure S8). Thus, by removing both water and excess oleic acid, the generation of compound **2** can be suppressed, revealing a slower reaction which creates far more uniform, nonbranching nanorods. Research is currently underway examining this improved reaction to see how uniform the nanorods can be made and over which aspect ratio ranges.

CONCLUSIONS

We have demonstrated that even small amounts of water in the PbSe nanorod reaction have a large effect on the PbSe nanorod aspect ratio and yield, and thus it is critical to control the amount of water in the reaction by carefully drying the reaction precursors. The nanorod aspect ratio can be controlled from 1.1 to 10 and the yield from 1 to 14% by changing the water concentration from 0 to 204 mM. This is due to the water acting *indirectly* by reacting with tris(diethylamino)phosphine (**1**) to create bis(diethylamido)phosphorous acid (**2**), which is the compound ultimately responsible for the nanorod aspect ratio and yield changes. Furthermore, we have shown that excess oleic acid also reacts with **1** to create **2**, and upon the removal of all excess oleic acid and water, the nanorod reaction slows considerably, and highly uniform, nonbranching nanorods are formed along with a population of nanocrystals. As a result of their homogeneity, these nanorods may be more easily aligned over large surface areas for devices.

ASSOCIATED CONTENT

Supporting Information

NMR, detailed nanorod dimensions as a function of added water, and additional results from nanorod reactions with various amounts of water, diethylamine, oleic acid, Pb-oleate,

TDPSe, and component **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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