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Synthesis of Magic-Sized CdSe and CdTe Nanocrystals with Diisooctylphosphinic Acid

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We report the observation of quantized growth in magic-sized CdSe and CdTe nanocrystals that utilize diisooctylphosphinic acid as the surface passivating ligand. The interaction between the diisooctylphosphinic acid and the coordinating solvent, hexadecylamine, results in the growth of only certain allowed sizes of nanocrystals. Magic-sized CdSe nanocrystals were synthesized with band edge absorption peaks at 414, 446, and 490 nm. Magic-sized CdTe nanocrystals were synthesized with band edge absorption peaks at 445 and 483 nm. The synthesis detailed here allows for the isolation of larger magic-sized nanocrystals than has been previously reported. The emission of diisooctylphosphinic acid-capped magic-sized nanocrystals is low, with a quantum yield of less than 1%. Photoluminescence excitation scans revealed a significantly reduced emission from absorption at the band edge. The diameter for the smallest CdSe magic-size was 1.7 nm, and the diameter for the smallest CdTe magic-size was 1.8 nm, as determined by transmission electron microscopy.

Introduction

Magic-sized nanocrystals are composed of a well-defined number of atoms and only exist at certain stable sizes.[1−3] This allows the synthesis of large quantities of nanocrystals, all with identical properties, which cannot be achieved in traditional nanocrystal synthesis. The unique stability of magic-sized nanocrystals also differentiates them from traditional nanocrystals. Traditional CdSe nanocrystals have either wurtzite or zinc blende structure, while the stability of magic-sized nanocrystals is thought to arise from a cluster-cage structure.[4] The cluster-cage structure has yet to be reported for bulk semiconductors. This unique structure has only been accessible by a bottom up synthetic approach.

On the basis of the result of mass spectrometry experiments, powder X-ray diffraction measurements, and theoretical modeling, Kasuya et al. have proposed that this cluster-cage structure is composed of alternating four- and six-membered rings, which allows for only certain sizes of nanocrystals.[4] They were able to synthesize several different sizes of the cluster-cage structure by using a reverse micelle synthesis, corresponding to $(CdSe)_{13}$, $(CdSe)_{33}$, and $(CdSe)_{34}$. The $(CdSe)_{33}$ and $(CdSe)_{34}$ have band edge absorption at 414 nm.[4] No other sizes were synthesized because only these sizes result in a closed cage structure. The largest size synthesized by Kasuya et al. corresponds to an external cage of $(CdSe)_{28}$ that is stabilized by an internal structure of $(CdSe)_6$. To grow the next larger allowed size, it is thought that a new layer must be grown around the existing cage. This process would be observable by the appearance of a new peak in the UV−visible absorption spectrum that is red-shifted from the previous band edge absorption. Such a unique redshift has been observed.[1,5,6] It is this quantized growth of the absorption spectrum that is the hallmark of true magic-sized nanocrystals.

Kudera et al. previously demonstrated quantized growth of CdSe nanocrystals.[1] Their synthesis utilized nonanoic acid to decompose CdO into a reactive precursor in an amine solvent, with an injection of Se dissolved in trioctylphosphine to begin the nanocrystal synthesis. The nanocrystals in the reaction solution were allowed to grow at 80 °C for up to 2500 min. The specific sizes of nanocrystals obtained from the quantized growth were those with band edge absorption peaks at 384, 406, and 431 nm. Their magic-size CdSe nanocrystals had a Cd:Se ratio between 1.1 and 1.3:1.[1] The fluorescence spectrum of these nanocrystals was broad and featureless, the result of trap-state emission. Kudera et al. observed band edge recombination only after passivating the surface with

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a ZnS shell. When growth of the 431 nm absorbing nanocrystals was allowed to continue, the nanocrystals no longer displayed quantized growth, but rather a continuous red-shift in the absorption spectrum.

A recent study by Zanella et al. has investigated the optical properties of magic-sized II−VI nanocrystals.[6] Magic-sized nanocrystals were prepared by decomposing CdO with a carboxylic acid in the presence of a primary amine, followed by an injection of the anion (S, Se, or Te) dissolved in phosphines. The magic-sized CdTe nanocrystals with band edge absorption at 445 nm (2.4 nm diameter, CdTe I) and band edge absorption at 487 nm (3.1 nm is diameter, CdTe II) synthesized in their study displayed an intense, sharp emission spectrum. This was surprising because the other II−VI nanocrystals of similar size had a broad emission spectrum that was dominated by trap states.[1,7,8] Zanella et al. also determined that the Cd:Te ratio for the magic-size nanocrystals was 1.2:1. This is the same cation:anion ratio that has been measured in traditional II−VI nanocrystals.[9]

In this study, we demonstrate an alternative synthesis of magic-sized CdSe and CdTe nanocrystals and report on their optical properties. Magic-sized CdSe nanocrystals are synthesized with band edge absorption peaks corresponding to 414 nm ($CdSe_{414\ nm}$), 446 nm ($CdSe_{446\ nm}$), and 490 nm ($CdSe_{490\ nm}$). The $CdSe_{414\ nm}$ synthesized in this study have a nearly identical absorption spectrum to the $(CdSe)_{33}$ and $(CdSe)_{34}$ synthesized by Kasuya et al.[4] Magic-sized CdTe nanocrystals with band edge absorption peaks of 445 nm ($CdTe_{445\ nm}$) and 483 nm ($CdTe_{483\ nm}$) were also synthesized. The $CdTe_{445\ nm}$ and $CdTe_{483\ nm}$ have a similar absorption spectrum to the CdTe I and CdTe II samples studied by Zanella et al.[6]

The magic-sized CdSe nanocrystals have a weak, broad band fluorescence, whereas the magic-sized CdTe nanocrystals do not emit. Transmission electron micrographs did not provide a definitive crystal structure, but the images do show that the $CdSe_{414\ nm}$ magic-sized nanocrystals have a diameter of 1.7 nm and that $CdTe_{445\ nm}$ magic-sized nanocrystals have a diameter of 1.8 nm. The larger magic-sized $CdSe_{446\ nm}$ and $CdTe_{483\ nm}$ form ribbon structures with a diameter of 2.2 and 2 nm respectively. The synthesis described in this study allows for the isolation of larger sizes of magic-sized nanocrystals than have been previously reported. Additionally, we demonstrate that the interaction between the diisooctylphosphinic acid surface ligand and the coordinating solvent hexadecylamine is responsible for the quantized growth of the magic-sized nanocrystals in this study.

Experimental Section

CdSe Synthesis. CdSe nanocrystals were synthesized as previously reported,[8] with the exception that diisooctylphosphinic acid was used as the capping ligand, instead of a phosphonic acid. Briefly, 1 mmol of CdO (99.99%, Strem) and 10 g of hexadecylamine (HDA, 98%, Aldrich) were combined in a three-necked flask that was fitted with a temperature probe, bump trap, and rubber septum. The reaction mixture was stirred and purged with argon until the mixture reached 150 °C. Then 2 mmol of diisooctylphosphinic acid (90%, Aldrich) was injected and the temperature was then raised to 310 °C. Once the solution was colorless, 5 mL of 0.2 M Se:tributylphosphine solution (Se 200 mesh, Strem; TBP, tech grade 97−99%, Aldrich) was injected, initiating the formation of CdSe nanocrystals. As soon as a yellow color was observed, the reaction was halted with a 20 mL injection of butanol, followed by cooling with compressed air until the temperature dropped below 100 °C.

CdTe Synthesis. CdTe nanocrystals were synthesized under the same reaction conditions as the CdSe nanocrystals. Briefly, 1 mmol of CdO and 10 g of HDA were combined in a three-neck flask that was fitted with a temperature probe, bump trap, and rubber septum. The reaction mixture was stirred and purged with argon until the mixture reached 150 °C. Then 2 mmol of diisooctylphosphinic acid was injected and the temperature was raised to 310 °C. Once the solution was colorless, 5 mL of 0.2 M Te:TBP solution (Te 200 mesh, Acros) was injected, initiating the formation of CdTe nanocrystals. The reaction was halted with a 20 mL injection of butanol, followed by cooling with compressed air until the temperature dropped below 100 °C. While the reaction for the magic-sized CdSe nanocrystals was quenched at the first sign of the solution turning yellow, this was not possible for the CdTe nanocrystal reaction because the Te:TBP solution is naturally yellow. Instead the reaction mixture was allowed to react for 3 s before it was quenched with the butanol injection.

Nanocrystal Growth and Isolation. Zero minutes of growth represents the time at which the reaction solution had cooled below 100 °C, the initial aliquot (0.3 mL nanocrystals solution diluted with 3 mL of toluene) was withdrawn from the solution, and the absorption spectrum was measured. The heating mantle was then reapplied to the flask, and the temperature was raised to 150 °C. We began measuring the growth time as soon as the heating mantle was reapplied. The growth was monitored by UV−vis absorption spectroscopy on a Cary Bio 50 UV−visible spectrometer. When the nanocrystals reached the desired size, growth was halted by cooling the flask with compressed air and adding hexanes to dissolve the nanocrystals. The nanocrystals were cleaned by first precipitating them via the addition of methanol and collecting them by centrifugation. The nanocrystals were then redissolved in hexanes, and all undissolved material was collected by centrifugation. The nanocrystals remained dispersed in hexanes for analysis and electron microscopy. All photoluminescence measurements were made on an ISS PC1 single photon counting fluorimeter. Transmission electron microscopy (TEM) was performed on a Phillips CM20 operating at 200 kV.

Ligand Exchange of Dodecylphosphonic Acid for Diisooctylphosphinic Acid. CdSe nanocrystals capped with dodecylphosphonic acid were synthesized with a band edge absorption of 541 nm as described previously.[10] Diisooctylphosphinic acid was diluted with toluene to a concentration of 1 M. The dodecylphosphonic acid capped nanocrystals were diluted to a concentration of 15 mM by the addition of toluene. A 4 mL aliquot of these nanocrystals was added to 4 mL of the 1 M diisooctylphosphinic acid ligand in a glass vial. The resulting solution was stirred and heated to 80 °C to drive the ligand exchange. The solution was heated for 24 h.

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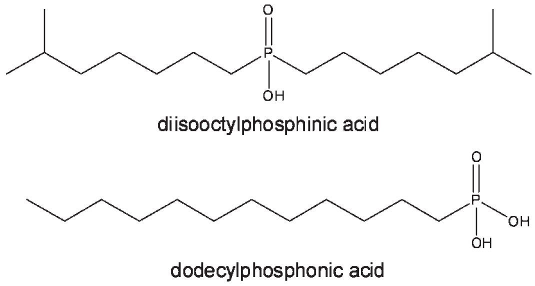

Figure 1. Dodecylphosphonic acid, shown above, is a traditional ligand used to passivate the surface of CdSe nanocrystals. Diisooctylphosphinic acid is a liquid analog shown below. It is used to generate the reactive cadmium precursor and is used as the surface ligand for CdSe and CdTe nanocrystals in this study.

Results and Discussion

Optical Properties. Alkylphosphonic acids, such as dodecylphosphonic acid (Figure 1), have been employed in the synthesis of CdSe to achieve greater control over nanocrystal shape.[11] By varying the amount or type of phosphonic acid used in the synthesis, one can preferentially grow rods, dots, or tetrapods.[11,12] Nanocrystals that have been synthesized with alkylphosphonic acid surface ligands display a continuous redshift in their absorption spectrum as the nanocrystals grow to larger sizes.[8,13] Diisooctylphosphinic acid (Figure 1) is a liquid analog of an alkylphosphonic acid that is not widely used in II−VI nanocrystal synthesis. CdSe and CdTe nanocrystals were synthesized with diisooctylphosphinic acid as the surface ligand in an alkylamine coordinating solvent as already described. When the reaction was arrested with the butanol injection, magic-sized CdSe nanocrystals, characterized by an extremly sharp (±0.16 nm particle diameter as determined from the absorption spectrum)[13] band edge absorption at 414 nm, were synthesized as shown in Figure 2A (0 min of post injection heating).[1,4] The magic-sized $\mathrm{CdSe}_{414\ \mathrm{nm}}$ nanocrystals have an additional feature in the absorption spectrum located at 383 nm, which is not usually observed in CdSe nanocrystals of this size.[7,8,14] It is possible that the 383 nm peak represents a smaller magic-size CdSe nanocrystal. While we were unable to isolate the 383 nm peak by itself, the location of this peak matches well with a previous report of magic-sized CdSe nanocrystals by Zanella et al., which have a band edge absorption at 384 nm.[6]

When the reaction flask was reheated to grow larger nanocrystals, the diisooctylphosphinic acid-capped magic-sized CdSe nanocrystals did not continuously grow. Instead, the diisooctylphosphinic acid-capped nanocrystals displayed a discontinuous redshift in their absorption spectrum. This is characteristic of magic-sized nanocrystals.[5]

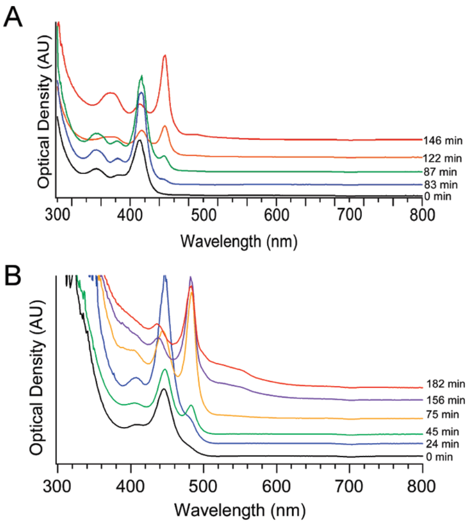

Figure 2. (A) Absorption spectrum of magic-sized CdSe nanocrystals, which have quantized growth, is shown above with the growth time for each measurement shown. Magic sizes were observed corresponging to band edge absorption peaks at 414, 446, and 490 nm. (B) Absorption spectrum of magic-sized CdTe nanocrystals, which have quantized growth, is shown above with growth time for each measurement shown. Magic sizes were observed corresponding to band edge absorption peaks at 445 and 483 nm. The peak observed to grow in at 540 nm marks the beginning of a continuous redshift, and is not a magic-size.

As the magic-sized CdSe nanocrystals were heated, the band edge absorption peak was observed to increase in intensity at 414 nm (Figure 2A). After 83 min of heating the magic-sized $\mathrm{CdSe}_{414\ \mathrm{nm}}$ nanocrystals, we observed a new peak in the absorption spectrum at 446 nm, while the peak at 414 nm persisted. As growth continued, the 446 nm peak increased in intensity without redshifting. After 146 min of growth a low intensity peak was observed at 490 nm. The peak intensity and position of the 490 nm peak remained unchanged even after heating overnight. The lack of growth to larger sizes is likely the result of insufficient precursors remaining in the reaction solution.

CdTe nanocrystals were also observed to undergo quantized growth with diisooctylphosphinic acid as the surface ligand. When the reaction was quenched, as shown in Figure 2B (0 min of post injection heating), a sharp peak in the absorption spectrum was observed at 445 nm, characteristic of magic-sized CdTe nanocrystals.[5,6] After 24 min of growth, a peak at 483 nm was observed to grow in while the peak at 445 nm remained. The peak at 483 nm continued to increase in intensity over time. The next peak to appear in the absorption spectrum was very weak and centered around 540 nm. This peak began to continually redshift with heating. Thus, these could not be considered to be magic-sized CdTe nanocrystals. Two distinct sizes of magic-sized CdTe nanocrystals were able to be grown, corresponding to band edge absorption peaks at 445 and 483 nm.

Our smallest magic-sized CdSe nanocrystal, $\mathrm{CdSe}_{414\ \mathrm{nm}}$ has a similar band edge absorption to the 406 nm previously observed by Kudera et al.[1] CdSe nanocrystals with band edge absorption at 446 nm were reported to be in the continuous growth size regime in Kudera's study. However, the results presented in this study indicate that it is possible to have stable magic-sized nanocrystals with

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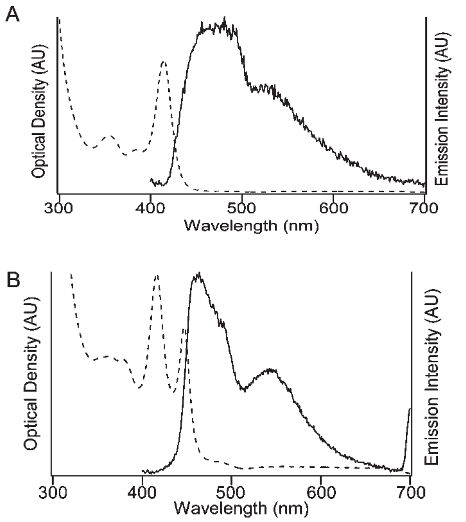

Figure 3. Absorption (dashed lines) and emission (solid lines) are shown for (A) $CdSe_{414\ nm}$, and (B) $CdSe_{446\ nm}$. The $CdSe_{414\ nm}$ nanocrystals have a broad emission similar to that of the alkylphosphonic acid capped nanocrystals.[7] Growth to the next larger sizes results in a narrowed emission spectrum with the persistence of deep-trap emission.

band edge absorption at 446 nm (Figure 2A). The main difference between the nanocrystals synthesized in this study and those synthesized by Kudera is the surface-passivating ligand. Where Kudera used nonanoic acid, this study utilized diisooctylphosphinic acid as the surface ligand. The diisooctylphosphinic acid ligand binds tighter to the nanocrystal surface[15] and allows for the growth of larger magic-sized CdSe nanocrystals.

The smallest magic-sized CdTe nanocrystals, $CdTe_{445\ nm}$, synthesized in this study match those of Zanella et al. with a band edge absorption peak at 445 nm.[6] We observed a larger size of magic-sized CdTe nanocrystals similar to the CdTe II reported by Zanella (band edge absorption of 483 nm compared to 487 nm). The difference arises in the fact that the magic-sized CdTe nanocrystals synthesized in this study have an increased selectivity over previous work. Zanella was unable to grow the 487 nm absorbing magic size (CdTe II), without also growing the 506 nm absorbing magic-size (CdTe III) simultaneously. By choosing diisooctylphosphinic acid as the surface capping ligand, we were able to grow magic-sized $CdTe_{483\ nm}$ nanocrystals in the absence of any larger sizes.

The magic-sized CdTe synthesized by Zanella et al. had an intense and narrow emission spectrum.[6] The CdTe nanocrystals synthesized in this study do not emit. The emission spectrum of $CdSe_{414\ nm}$, shown in Figure 3A has a similar broad-band emission that has been previously observed in ultrasmall CdSe nanocrystals capped with dodecylphosphonic acid.[7,8,14,16] The broad emission is spread over most of the visible spectrum and has a quantum yield of 0.8%. The measured quantum yield is an order of magnitude lower than the 8% quantum yield of white-light-emitting CdSe nanocrystals that are of similar size and capped with dodecylphosphonic acid.[17] The $CdSe_{446\ nm}$ still have significant trap state emission (Figure 3B).

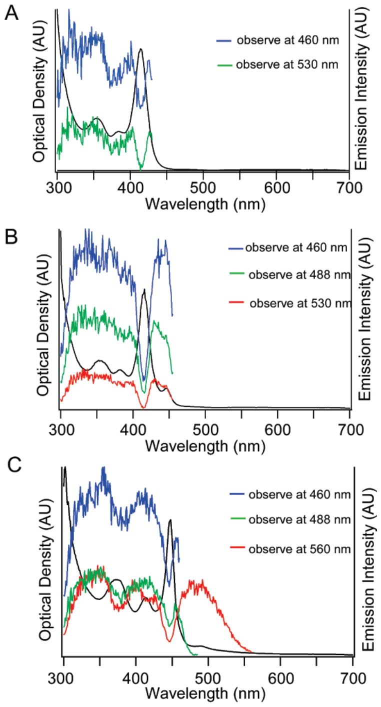

Figure 4. Photoluminescence excitation scans (colored lines) reveal the absorbing states that are responsible for each emission peak. The absorption spectrum of each sample is shown in the black curves. PLE scans for (A) $CdSe_{414\ nm}$ nanocrystals, (B) mixture of $CdSe_{414\ nm}$ and $CdSe_{446\ nm}$ nanocrystals, (C) $CdSe_{446\ nm}$ nanocrystals. In each sample, the PLE scans showed significantly reduced emission intensity for the absorption peaks corresponding to band edge absorption.

Photoluminescence excitation (PLE) measurements were performed on the magic-sized CdSe nanocrystals to determine the reason for the low quantum efficiency observed. As shown in Figure 4, absorption events at the band edge of the magic-sized CdSe nanocrystals do not lead to radiative recombination. Previous studies of the excitation spectrum of CdSe nanocrystals have shown that absorption at the band edge leads to the most efficient radiative recombination.[18] The weak emission that was observed is likely due to trap-state emission occurring at surface defects. Further, the PLE spectra show that these trap states, which relax radiatively, are populated as a result of absorption events in the continuum. Previous studies have shown that an electron from a surface Se atom can relax to fill the vacancy left in the valence band by the photogenerated electron, resulting in trap state emission.[19,20]

There are three possibilities as to why the magic-sized diisooctylphosphinic acid-capped nanocrystals do not emit via band edge absorption. The first possibility is that they have a unique crystal structure that could alter their optical properties. The second possibility is that the steric effects of the secondary phosphinic acid lower the

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quantum yield. The third possibility is that the magic-sized CdSe nanocrystals have an internal atomic defect (an extra atom or a missing atom) that creates a nonradiative trap state. A sample of dodecylphosphonic acid-capped CdSe nanocrystals were synthesized and used in a ligand exchange as already described. The initial quantum yield of the CdSe nanocrystals was 6.4%. After the ligand exchange to diisooctylphosphinic acid, the CdSe nanocrystals had a quantum yield of 0.3%. The almost complete quenching of the emission in the nanocrystals is therefore likely the result of the steric effect of the secondary phosphonic acid replacing the alkylphosphonic acid.[21] The secondary ligand would be expected to leave some surface sites unpassivated,[21] resulting in the weak trap state emission observed in the $CdSe_{414\ nm}$ nanocrystals.

Synthetic Conditions. The synthesis of the magic-sized CdSe nanocrystals was repeated using various solvents to determine if the quantized growth resulted solely from the diisooctylphosphinic acid, or if the coordinating solvent also affected the growth. In all of the reactions summarized in Table 1, the 2:1 molar ratio of diisooctylphosphinic acid to CdO was maintained, and the 1:1 molar ratio of Cd:Se was maintained unless otherwise noted. When the reaction was conducted in tri-n-octylphosphine oxide (TOPO), quantized growth in the absorption spectrum was not observed. When the reaction was performed with 1-octadecene as the noncoordinating solvent, quantized growth of the absorption spectrum was also not observed.

The synthesis was also carried out in a mixed solvent system of 5 g TOPO and 5 g HDA. When the reaction was arrested with the butanol injection, the absorption spectrum showed a peak at 414 nm that was identical to previous amine-only synthesis, which yielded magic-sized CdSe nanocrystals. When the reaction solution was reheated to 150 °C for growth, a new peak was observed (see the Supporting Information) in the absorption spectrum. With continued heating, this new peak was observed to continuously redshift. However, the main peak at 414 nm remained and became more intense. This was indicative of two distinct populations of nanocrystals in the reaction solution.

After 72 min of growth in the mixed TOPO/HDA solvent, a new peak was observed in the absorption spectrum at 446 nm (see Figure S3 in the Supporting Informatio). This is the same location that the $CdSe_{446\ nm}$ nanocrystals were previously observed. The largest magic-sized CdSe nanocrystals ($CdSe_{490\ nm}$) were not observed in the mixed solvent system. This was likely the result of the signal from the continuous growth population overwhelming the weak signal that was previously observed for this magic size. The continuous growth observed in this reaction was due to the presence of TOPO in the solvent system, and the quantized growth was due to the combination of the hexadecylamine and the diisooctylphosphinic acid. Previous studies on magic-sized CdTe and CdSe nanocrystals have involved a synthesis that employs an alkylamine as a coordinating solvent.[1,5,6] None of these previous studies reported on attempts to synthesize magic-sized II−VI nanocrystals without an alkylamine as the coordinating solvent. In this study, quantized growth is only observed when the alkylamine solvent is present with the diisooctylphosphinic acid. This indicates diisooctylphosphinic acid alone is not responsible for the quantized growth. Rather, the surface-passivating ligand and the alkylamine act together, producing the quantized growth in magic-sized nanocrystals.

Table 1. Summary of the Solvent and Reaction Conditions with Diisooctylphosphinic Acid Is Shown[a]

reaction conditions	observation of quantized growth
10 g of 99% TOPO	not observed
10 g of 90% TOPO	not observed
10 mL of 1-octadecene	not observed
5:1 Cd:Se molar ratio in 10 g of HDA	not observed
10 g HDA and 2 mmol dodecylphosphonic acid	not observed
1:5 Cd:Se molar ratio in HDA	quantized growth observed
5 g of TOPO (90%), 5 g of HDA	quantized & continuous growth observed

[a] All reactions are carried out with a 2:1 molar ratio of diisooctylphosphinic acid to CdO unless otherwise noted.

The previously published cluster-cage model for magic-sized CdSe nanocrystals may explain the quantized growth observed in our nanocrystals.[4] The cluster-cage model proposes a structure that is composed of only mixed surfaces, unlike the wurtzite structure that has both polar and mixed surfaces. Surface ligands have been shown to inhibit crystal growth on the more thermodynamically stable mixed surfaces.[15] Additionally, phosphinic acids and amines bind tighter to the mixed surface than other surface ligands such as phosphine oxides.[15] When TOPO was used as a coordinating solvent, continuous growth was observed (see Figure S2 in the Supporting Information) because the mixed surface is more available to react with the Cd and Se in the reaction solution. The phosphinic acid ligand also binds to the mixed surface in the same location as a CdSe molecule would bind.[15] If the surface ligand is occupying the same site that the Cd or Se need to access in order to bind, then growth of successive layers will be severely inhibited. Theoretical calculations have shown that branched ligands, like diisooctylphosphinic acid, will bind less tightly to the nanocrystal surface than primary ligands of the same functionality because of steric hindrance.[22] This reduction in binding energy due to steric effects is likely sufficient to allow the Cd and Se to displace some surface ligands, resulting in the slow nanocrystal growth observed. Modeling of the cluster-cage structure by Kasuya et al. has shown that cage configurations are more stable with a certain number of atoms, which maximizes the Cd to Se binding energy in the nanocrystal.[4] It is likely that the addition of several Cd and Se atoms during a short time is necessary to achieve a larger, stable structure. The addition of several atoms at once would manifest as a discrete red-shift in the absorption spectrum. This is similar to the quantized growth we and others have observed. This result confirms previous findings that a strongly binding

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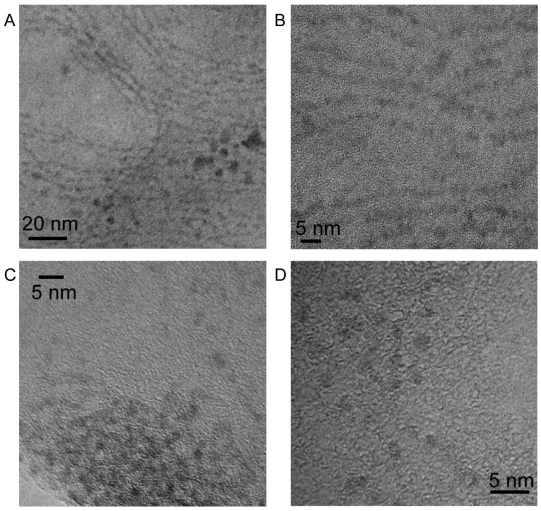

Figure 5. (A, B) TEM images of $\mathrm{CdSe_{446\ nm}}$ magic-sized nanocrystals. (C, D) TEM images of $\mathrm{CdSe_{414\ nm}}$.

surface ligand and coordinating solvent are necessary for the growth of magic-sized nanocrystals.[5]

Structural Properties. The $\mathrm{CdSe_{414\ nm}}$ nanocrystals have an absorption spectrum that is remarkably similar to the 414 nm absorbing nanocrystals previously synthesized by Kasuya et al.[4] The absorption spectrum of Kasuya's nanocrystals is interesting because it has a higher energy transition that is not observed in CdSe nanocrystals synthesized with an alkyl phosphonic acid.[7,8] The $\mathrm{CdSe_{414\ nm}}$ synthesized in this study have the same high-energy transitions observed by Kasuya et al., which leads to the conclusion that they likely possess the same structure. X-ray diffraction measurements were performed on the magic-sized nanocrystals with no peaks observed, which is likely due to the small diameter of the nanocrystals.

Magic-sized $\mathrm{CdSe_{446\ nm}}$ nanocrystals were dispersed on few-layer graphene using previously published methods.[23] The samples were imaged immediately after the cleaning procedure because the magic-sized nanocrystals photooxidize after several hours, resulting in sample degradation. The images show that the $\mathrm{CdSe_{446\ nm}}$ arrange together to form long ribbon structures (Figure 5 A, B). The ribbons have a diameter of 2.2 nm, which is in good agreement with the sizing equations developed by Yu et al., which predicts a diameter of 2.19 nm.[13] The smaller $\mathrm{CdSe_{414\ nm}}$ magic-sized nanocrystals were also imaged on few-layer graphene and are shown in Figure 5 C, D. At the smallest sizes, the magic-sized CdSe nanocrystals appear spherical. The magic-sized $\mathrm{CdSe_{414\ nm}}$ nanocrystals have a diameter of 1.7 nm, which is again in good agreement with the sizing equations of Yu et al., which predicts a diameter of 1.67 nm.

A morphological change is apparent between the $\mathrm{CdSe_{446\ nm}}$ nanocrystals shown in images A and B in Figure 5 and the$\mathrm{CdSe_{414\ nm}}$ shown in images C and D in Figure 5. The ribbon structures observed for the $\mathrm{CdSe_{446\ nm}}$ nanocrystals are similar to previously observed nanoribbons.[24−26] Further, the absorption spectrum of the $\mathrm{CdSe_{446\ nm}}$ as shown in Figure 3B is consistent with the values of previous reports for nanoribbions. Previous work by Joo et al. reported absorption peaks at 449 and 423 nm, whereas Liu et al. reported absorption peaks at 447 and 420 nm.[25,26] It appears that the $\mathrm{CdSe_{414\ nm}}$ magic-sized nanocrystals form nanoribbon structures as they grow into the $\mathrm{CdSe_{446\ nm}}$ magic-sized nanocrystals. As the $\mathrm{CdSe_{446\ nm}}$ magic-sized nanocrystals continue to grow their absorption spectrum deviates from the previously published absorption spectrum of nanoribbons.[25,26] It is possible that this represents another morphological change in the magic-sized CdSe nanocrystals; however, no change was observed in the TEM.

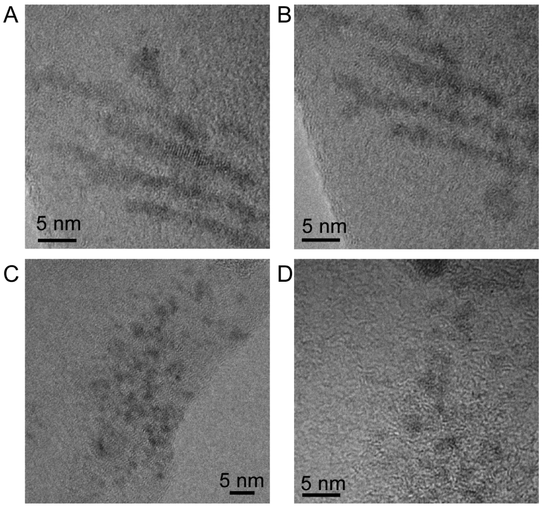

Figure 6. (A, B) TEM images of $\mathrm{CdTe_{483\ nm}}$ magic-sized nanocrystals. (C, D) TEM images of $\mathrm{CdTe_{445\ nm}}$.

Magic-sized $\mathrm{CdTe_{483\ nm}}$ nanocrystals were dispersed on few-layer graphene. The larger magic-size of CdTe nanocrystals also forms ribbon structures (Figure 6 A, B) with a similar appearance to the ribbon structures formed by $\mathrm{CdSe_{445\ nm}}$. The $\mathrm{CdTe_{483\ nm}}$ has a diameter of 2 nm. A diameter for the CdTe magic-sized nanocrystals was not able to be estimated from the sizing equations of Yu et al. $\mathrm{CdTe_{445\ nm}}$, shown in images C and D in Figure 6, have a diameter of 1.8 nm. Some larger nanocrystals were present in the CdTe samples. They may be the result of nanocrystals aggregating as the solvent evaporates from the TEM grid because there was no peak corresponding to these aggregates in the absorption spectrum.

Although the magic-sized nanocrystals that are reported here are the correct size, we cannot conclusively determine if they match the cluster-cage structure predicted by Kasuya et al. Lattice resolved images on CdSe nanocrystals have been obtained previously on nanocrystals of similar diameter, that were synthesized using an alkylphosphonic acid as the surface ligand.[23] Although the lack of lattice resolution in these images appears consistent with the cluster-cage model proposed by Kasuya, alternating 4

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and 6 member rings in a 3D structure would not be expected to produce the regular columns of atoms needed for a lattice-resolved image. It is possible that the clean up procedure utilized in this study did not completely remove excess surfactants. The methanol-hexanol-methanol wash cycle employed to clean up the ultrasmall CdSe nanocrystals by McBride et al.[23] resulted in the degradation of the absorption spectrum when used on magic-sized CdSe and CdTe nanocrystals in this study. The presence of excess surfactants could result in lower resolution images than previously observed in cleaner samples.

A recent study by Nguyen et al. calculated several different possible structures for magic-sized CdSe nanocrystals.[27] The $CdSe_{445\ nm}$ nanocrystals synthesized in this study have the same band edge absorption (2.78 eV) to the $(CdSe)_{30}$ tube with S_6 geometry proposed by Nguyen (2.78 eV).[27] The predicted diameter of 2.06 nm for $(CdSe)_{30}$ differs from the measured diameter for $CdSe_{445\ nm}$. The calculated $(CdSe)_{24}$ tube diameter of 1.65 nm is a closer match to $CdSe_{414\ nm}$. However, the energy of the band edge transition (2.83 eV) does not match well with $CdSe_{414\ nm}$.[27] A possible source of the differences could be the ligand passivation. The study by Nguyen et al. used an amine as the surface ligand where we have utilized a phosphinic acid.

Conclusion

Magic-sized CdSe and CdTe nanocrystals were synthesized with diisooctylphosphinic acid as the surface ligand. The magic-sized nanocrystals have a quantized growth mechanism which only allows for distinct sizes of nanocrystals to be synthesized. The observed trap state recombination in the fluorescence spectrum is the result of absorption from the continuum states above the band edge. The steric effects of the secondary phosphinic acid ligand result in very little emission from band edge absorption. TEM measurements showed that the magic-sized $CdSe_{414\ nm}$ nanocrystals have a diameter of 1.7 nm, and the magic-sized $CdTe_{445\ nm}$ nanocrystals have a diameter of 1.8 nm. The magic-sized nanocrystals also undergo a morphological change and are shown to form nanoribbons at larger sizes. The synthesis described here results in larger magic-sized nanocrystals than have been previously reported. The work also emphasizes the critical role that surface ligands play in the formation of nanostructures. The synthesis of larger magic-sizes provides an opportunity for detailed structural study utilizing scanning transmission electron microscopy (STEM). The superior resolution provided by STEM has been used to study nanocrystals of similar size previously,[14] and could provide insight to the origin of the stability of magic-sized nanocrystals.

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Supporting Information Available: Additional TEM images of magic-sized CdSe and magic-sized CdTe nanocrystals, absorption spectra for the nanocrystals synthesized in different solvent conditions, as well as the synthesis conditions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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