Selective Microwave Absorption by Trioctyl Phosphine Selenide: Does It Play a Role in Producing Multiple Sized Quantum Dots in a Single Reaction?

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Chemical transformations carried out under MW (microwave) irradiation often produce unexpected rate enhancements because of selective MW absorption by the reactants in the solution. We demonstrate unprecedented control over nucleation, growth, and Ostwald ripening in the formation of CdSe quantum dots (QDs), the quintessential quantum dot. The selectivity of the MW reactions is demonstrated by the ability to generate multiple, different sized QDs in the same reaction, where each QD component exhibits 6−7% size dispersity. The number of QDs in solution translates to color saturation (intensity), and the size of the QD translates to color index and is completely controlled by temperature and concentration in the MW reaction. The ability to repetitively generate nucleation and growth events in which a specific color index with defined color saturation is isolated from a single reaction offers potential for preparing mixed QD compositions for applications in optical barcoding, white light emitting diodes (LEDs), and photovoltaics (PVs).

Introduction

For the past decade organic and inorganic reactions have been shown to exhibit enhanced reaction rates for molecular conversions when carried out under microwave (MW) irradiation relative to traditional convective approaches.[1−3] Extrapolation of MW irradiation methods to problems in nanomaterial synthesis has also shown rate enhancement coupled to improved material properties.[4−7] The origin of the reaction rate enhancement for chemical reactions in a MW reaction is poorly understood; however, the consensus of the field implies the rate enhancement for molecular reactions can be traced to efficient dielectric heating (super heating) of the reaction components within a solvent cage.[8−10] This is easily understood by considering that in a MW reaction, molecules with a large static dipole are selectively heated and will rapidly thermalize to the solvent.[11]

Since the rate of MW heating is described as the ratio of the real and imaginary components of the dielectric constant, the phase-lag between the applied MW field and the molecular dipole of the reaction components results in dielectric molecular heating.[8] The rate of solvent thermalization will depend on solvent viscosity and molecular volume of the heated reactant in solution.

In a set of recent studies, we explored the use of MW irradiation to selectively heat the reactive monomers for quantum dot (QD) synthesis in the presence of alkanes, which are non-MW absorbing.[11] Through the use of a non-MW absorbing solvent, the reaction rate for formation of both II−VI and III−V nanocrystals was markedly accelerated.[11−13] Interestingly in the MW, the size of the isolated QD was observed to depend on the reaction temperature and not the power while dispersity was independent of the observed temperature and power. This is counter-intuitive for lyothermal reactions where size focusing and defocusing is observed in the QD reaction driven by a diffusion controlled process because of Ostwald ripening.[14−17] The difference in growth behavior for QDs in a MW and a thermal reaction can be interpreted by delineating the independent growth regimes, namely, diffusion controlled and reaction driven.[15] Both diffusion control and reaction driven processes compete in a given reaction and can have

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substantial impact on the growth rates, observed size focus, and defect levels within a QD. The rate of reaction is dependent on both the diffusion of the monomer to the surface and the rate of reaction of the Cd and Se monomer with the growing QD. The diffusion limit is controlled by the net migration of monomers to the reaction surface; thus for a fast reaction rate and slow diffusion the growth rate of the QD is diffusion controlled. On the other hand, if the reaction rate is slow and diffusion is fast, the growth rate is governed by the addition of monomers to the QD surface, and thus the rate limiting step is reaction driven.

A lyothermal reaction is observed to follow diffusion control resulting in the observed size focusing/defocusing behavior. In the reaction driven limit the size of the QD will not rapidly defocus by Ostwald ripening if the activity of the monomer in solution (a_{solute}) is greater than the activity for the monomer generated by particle dissolution (a_{solid}). In a reaction driven regime, Ostwald ripening will give rise to QD growth, but the dispersity should remain focused if the QDs are not kinetically rough.[18] One way to achieve a reaction driven QD growth regime would be the rapid depletion of the monomer in the diffusion layer around the formed nuclei. Typically this is not achievable unless the monomer can be selectively activated. Such an effect was suggested for a MW controlled reaction in our earlier study on CdSe and CdTe.[11]

In this manuscript, we interrogate the control offered by a reaction driven growth for CdSe QDs. Although MW induced growth occurs for all the II–VI materials, CdSe is the only QD illustrated in this manuscript because of its wide usage by the broader community. The demonstration of three (and even four) independent QD sizes using the single reaction MW methodology for a decreasing reaction temperature protocol and a single larger QD if the reaction temperature is raised illustrates the control offered by a reaction driven growth process for QDs.[15] While repeated nucleation or SILAR growth can be seen in a lyothermal reaction, the excess thermal energy results in rapid evolution to a single QD size for both experiments unless very specific reaction controls are applied.[19–21] The MW QD synthetic methodology leads to highly reproducible, narrow QD color codes (QD size and dispersity) and color saturation (QD concentration) controlled by the MW conditions. The MW QD synthetic methodology is compatible with industrial processing and may simplify development of applications ranging from biology to device platforms where bar-coding, controlled color, or multiple QD sizes are important.[22–30]

Experimental Section

Chemicals. All reactants and solvents in the reactions were used as purchased without further purification. Cadmium stearate (CdSA, 90%) and Selenium powder (Se, 99.99%) were purchased from Strem Chemicals. Tri-*n*-octylphosphine (TOP, 90%) was purchased from Alfa Aesar. Decane (99%) was purchased from Acros Organics. 1-Hexyl-1-methylimidazolium chloride was purchased from Aldrich Chemical.

Characterization. The QD sizes were analyzed on raw (non-size selected) QD samples isolated by complete precipitation of the QD batch by addition of a minimum volume of toluene/butanol (1:3) followed by addition of excess MeOH. Although the samples can be size selected from solution to improve dispersity, the lack of size selection was intentional to eliminate errors in the reported size, size dispersity, and QD concentrations in the reaction batch. Isolation of the QD by centrifugation, washing with MeOH and resuspension in toluene allowed the raw QD reaction to be directly analyzed by a combination of optical (absorption, photoluminescence), X-ray diffraction (structure, size determination by Scherrer broadening), and TEM analysis (size, shape). Size dispersity for the samples was ~6–7% based on limited TEM statistics and absorption full width half-maxima (fwhm) analysis (absorption fwhm ~ 28–31 nm for the reported sizes). Absorption spectra were carried out a Cary 50 UV–vis spectrophotometer, photoluminescence measurements were performed on a Varian Cary Eclipse Florescence spectrophotometer, and powder X-ray diffraction was recorded on 10 mg samples on a Rigaku DMAX 300 Ultima 3 Powder X-ray diffractometer (using Cu Kα λ = 1.5418 Å radiation). The transmission electron micrographs (TEM) were obtained using a Philips CM 300-field emission gun with a maximum acceleration voltage of 300 keV. A Gatan 673 wide angle CCD camera (Tietz Tem-Cam F415/MP slow scan) with a field of view of 61 mm × 61 mm was used to digitize the micrographs. TEM samples were prepared as dilute solutions in toluene with an absorbance of less than 0.1 to prevent aggravation. One drop of the prepared solution was placed onto a holey carbon 400 mesh TEM grid for 30 s, and the drop was wicked away. The TEM sample was dried overnight in a desiccator prior to imaging. QD size and size dispersity were validated by TEM and cross-referenced to pXRD and absorption measurements.

Synthesis of CdSe QDs. The synthesis of CdSe is carried out by literature procedures[12] using trioctyl phosphine selenide (TOPSe) as the Se^{2-} source and cadmium stearate (CdSA) as the Cd^{2+} source for the thermal and MW reactions.[11,31] The stock cadmium solution is prepared by dispersing CdSA (1.0 mmol, 679.36 mg) into 20 mL of solvent by sonication, while a 1 molar Se stock solution is prepared under Argon using Se powder (0.01 mol) dissolved in 10 mL of TOP. The MW reactions are carried out in decane under ambient conditions, while the thermal reactions are carried out in Octadecene under Argon.

Multiple CdSe QDs in the MW were prepared in a single reaction process by sequential addition of monomers at root temperature (RT) followed by MW heating to successively

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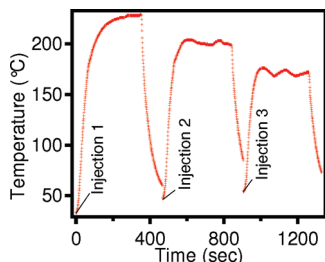
Figure 1. MW cycling protocol used for decreasing reaction temperature sequence to produce three discrete tight dispersity QD samples in the MW cavity.

lower reaction temperature set-points, as shown in Figure 1. Carrying out the same successive additions as shown in Figure 1 but ramping the reaction to successively higher set-points yields a single QD size. To maintain identical total reaction times (5 min) the specific times for the three MW regimes (heating, hold, cool down) are varied. The time for ramping to reaction temperature at 300 W applied MW power ranges from 2−3 min. The hold time for the reaction at the reaction temperature ranges for 30 s−2 min. The cool down cycle is held constant at 1 min. The same results as presented in the manuscript for CdSe growth are also obtained if the hold time is held constant. For the lyothermal reaction the identical sequence is applied; however, the reaction runs for 20 min (thermal) for each monomer addition step. The MW reactions are carried out in a single mode CEM Discover System operating at 300 W, 2.45 GHz with a pressure limit of 300 psi. The thermal reactions are carried out in a standard three-neck flask with convective heating (heating rate 5 °C/min) at identical temperature set points as the MW process.

Results and Discussion

The mechanism for growth control of QDs is well established with two critical domains, a pure diffusion controlled ($K < 0.01$) and a reaction driven ($K > 100$) limit, where $K = a_{solute}/a_{solvent}$ (a_{solute} represents the activity of the solubilized monomer in solution, while a_{solid} represents the activity of the monomer on the solid surface).[15,18] Under the diffusion limit the monomer activity in solution approaches the monomer activity of the QD surface, thus $K \leq 1$. This condition is easily met in a lyothermal reaction. In a reaction driven process, $K > 100$ indicating the activity of the monomer in solution is far higher than the activity of monomer generated by QD dissolution. This is an intriguing regime where the TOPSe in solution exhibits a higher activity resulting in rapid depletion of monomer within the diffusion shell. Since QD dissolution depends on surface roughness and time, the low a_{solid} implies low surface roughness, or fast reaction times must exist for the reaction to be described in the reaction control limit.[15,18]

Our earlier observation of a temperature dependent reaction with tight dispersity CdSe QDs out of the MW suggested a reaction driven regime for QD growth exists in the MW.[11] If this is the case, one would predict that carrying out the reaction in a stepped profile with three successively lower reaction temperatures, as shown in Figure 1, should result in the production of three independent well-defined QD sizes with the QD dispersity identical for each step. In addition, for a reaction carried out at

increasing temperatures should give rise to a single larger QD, similar to the SILAR reaction.[32]

Effect of Decreasing Temperature Set-Points. The optical data and TEM analysis for carrying out the CdSe QD growth using a decreasing reaction set-point profile (230 °C, 200 °C, 170 °C) is shown in Figure 2A and Figure 2B. In Figure 2A, each successive introduction of monomer at RT and heating to a lower temperature set-point yields a new lower energy PL feature and increasingly complex excitonic spectra at higher energy for the absorption spectral manifold. For the three monomer additions, based on the new spectral features it appears three individual QDs are formed in the solution. The complexity of the absorption spectral manifold arises from the overlapping higher lying excitons for the successively smaller QDs generated in the reaction. Conducting the MW reaction at four specific temperature points (240 °C, 210 °C, 180 °C, and 150 °C), yields four PL features consistent with four discrete CdSe QDs, as observed in the absorption and PL spectra (Supporting Information, Figure S1).

The observable narrow PL features in Figure 2 can be assigned as individual PL features with discrete fwhm at 537 nm (28 nm fwhm), 583 nm (31 nm fwhm), and 619 nm (30 nm fwhm). The PL features correlate with CdSe QDs of 3.11 nm, 3.63, and 4.92 nm, respectively. The QD sizes assigned from PL are confirmed by Scherrer analysis of the pXRD data and by inspection of the TEM of the raw sample after the third monomer addition reaction (Figure 2B). The narrow PL features (28−31 nm) imply tight distributions for the QD size dispersity following growth. Comparison of identical QD sizes prepared by a traditional lyothermal route yield a fwhm of 28−29 nm for 5% size dispersity sample, suggesting the stepped reaction profile does not increase the dispersity of the QD samples grown in the MWs.[33,11] Assuming no significant loss of dispersity in sequential reaction events, as suggested by the lack of change in PL fwhm for the largest QD during the reaction, this implies the initial dispersity established by the MW absorption of QD growth is maintained during the entire time of the reaction for all QDs in solution. TEM analysis for each individual step in the reaction confirms no size change occurs or changes in the size dispersity for each individual QD size generated during the MW cycling (Supporting Information, Figure S2). The lack of change to the QD size dispersity or QD sizes for each subsequent reaction is surprising and implies no contribution from size defocusing during the MW reaction. The observation of no size defocusing implies Ostwald ripening is a minor contributor, which is somewhat surprising. One possible explanation is the time scale of the reaction is short, or the QDs in the solution lack of kinetic roughness because of annealing of surface defects potentially by direct MW absorption by the QD following monomer depletion.[18]

Effect of Increasing Temperature Set-Points. Assuming a reaction driven growth regime in the MW, carrying out

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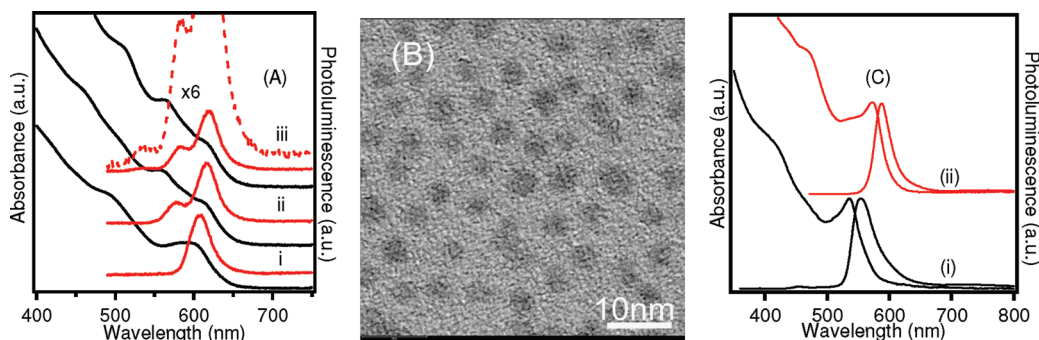(33) Reiss, P.; Bleuse, J.; Pron, A. *Nano Lett.* **2002**, *2*(7), 781–784.

Figure 2. (A) Absorption and PL spectra for CdSe QDs prepared at sequentially lower reaction set-points (i) 230 °C, (ii) 200 °C, (iii) 170 °C. (B) TEM of CdSe QDs (A iii) grown after three monomer additions at sequentially lower temperature. (C) The absorption and PL spectra of CdSe QDs grown using an increasing temperature set-point protocol. (i) 180 °C and (ii) at 240 °C

the reactor at increasing temperature set-points is expected to increase the QD size and narrow the size-dispersity, rather than produce individual QDs. In effect a size focusing reaction arising from the lower energy for a monomer to add to a pre-existing QD if the reaction to a larger QD size is thermodynamically favorable.[32] In Figure 2C, the absorption and PL data are shown for a two monomer addition carried out at 180 °C (first monomer addition) and 240 °C (second monomer addition). It is evident from the absorption profile that the initial 180 °C step produces a QD of 3.6 nm in size (λ_{abs} = 536 nm, λ_{em} = 554 nm). The second 220 °C produces a larger CdSe QD of 4.5 nm in size (λ_{abs} = 573 nm, λ_{em} = 588 nm), nearly identical to the size expected for a reaction carried out at 240 °C. A narrowing of the absorption excitonic features and the PL fwhm (56 nm → 32 nm) is also observed following the second monomer addition for the data in Figure 2C. The narrowing of the spectral features implies narrower size dispersity following the two step MW heating at increasing temperature set-points similar to a SILAR reaction. Inspection of the absorbance intensity, which correlates to the number of QDs in solution (when corrected for ε) shows no increase in the number of QDs in the reaction mixture following the second monomer addition implying the monomer reacts with the QDs in solution and does not form a renucleation event. These results support that CdSe QD growth in the MW is well-described by the reaction-driven regime ($K > 100$).[15,18]

Influence of Selective Absorption by TOPSe. While it is clear that the reaction temperature controls the observed QD size, it is unclear whether or not the growth behavior is traceable to selective activation into TOPSe in solution leading to the observation of an enhanced reaction rate. As suggested previously,[11,12] TOPSe has the largest MW cross-section, implying that TOPSe absorption accounts for the rate acceleration in the MW and subsequent growth behavior of the QDs. To confirm the MW growth behavior is attributable to selective absorption into TOPSe generating a highly activated Se monomer in the solute, a set of experimental controls were conducted to compare the results from a lyothermal method, a MW reaction carried out in the presence of a strong MW absorber, and a MW reaction carried out without additional monomer. The reactions are conducted with identical reaction set-points (220 °C, 180 °C) via addition of monomer at

RT and subsequent heating. The lyothermal reaction requires longer reaction times because of the slower heating rates.

Lyothermal Reaction. The absorption and PL spectra for the lyothermal reaction carried out with monomer addition and temperature ramping to 220 °C followed by monomer addition at RT and reaction at 180 °C are shown in Figure 3A. The initial absorption and PL for the 220 °C growth can be assigned to the formation of a 4.42 nm CdSe QD (580 nm PL, 29 fwhm) (Figure 3A (i)). Following addition of fresh monomer and heating to 180 °C (3 h) yields an absorption and PL feature consistent with a 4.57 nm QD (593 nm PL, 38 fwhm) (Figure 3A (ii)). Notably the absorption and PL data in Figure 3A for the lyothermal reaction do not exhibit two discrete PLs, exhibit PL broadening, and exhibit QD growth to a larger size following the second monomer addition, even though the reaction is carried out at a lower temperature set-point. Upon introduction of fresh monomer, the absorption fwhm broadens from 28 → 43 nm for absorption, and the PL spectra broadens from 30 → 38 nm implying loss of size focus in the reaction. The temperature dependent growth behavior for a lyothermal growth reaction is consistent with repeated results.[16,34,35]

The time dependent changes in the absorption and PL features following the second monomer addition for the lyothermal reaction are telling (Supporting Information, Figure S3). Inspection of the absorption and PL spectra following the second monomer addition at RT and subsequent heating to 180 °C indicates an appearance of a second nucleation/growth event at short experimental times, 30−60 min. After 60 min, the second absorption feature is lost, and the lowest energy exciton broadens. In conjunction with the absorption spectral changes, a small PL shoulder is observed, which is lost at longer reaction times. The observed time dependent growth and broadening observed in the spectral data can be attributed to classical Ostwald Ripening processes in a diffusion controlled reaction limit.[15,18] It is worth noting that lyothermal reactions do show size focusing (SILAR method), as well as separate nucleation events, if the monomer addition is added slowly at the same reaction temperature.[32]

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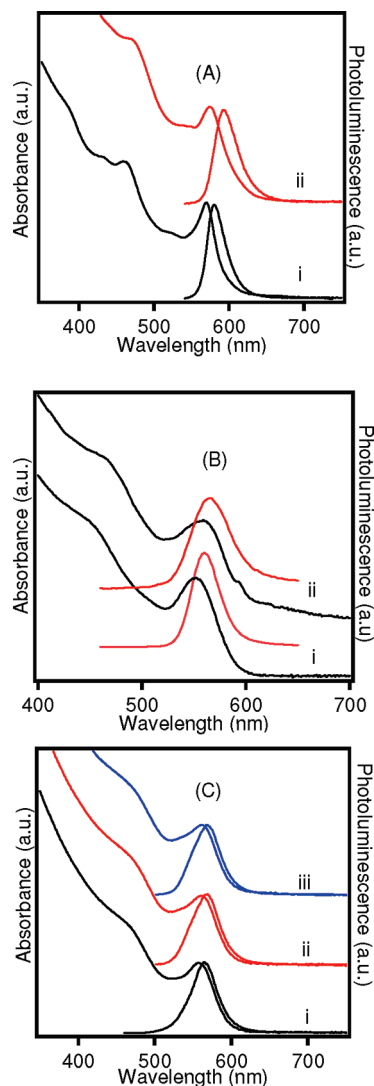
Figure 3. Absorption and PL spectra for (A) lyothermal reaction carried out at (i) 220 °C and (ii) 180 °C. (B) growth of QD in the MW in the presence of 0.2 mmol ImCl at (i) 220 °C and (ii) 180 °C. (C) MW reaction in the absence of monomer addition at (i) 220 °C, (ii) 200 °C, and (iii) 180 °C.

Reaction in the Presence of a Strong MW Absorber. In the MW, it is well-known that the strongest MW absorber will selectively absorb the MW energy.[36] Since the selectivity of MW absorption by molecules in solution should follow the magnitude of the molecular dipole and thus the dielectric constant of the material, carrying out the reaction in the presence of 1-hexyl-3-methyl imidazolium chloride (ImCl), an ionic liquid with a known large static dipole and large dielectric constant should increase the heating rate of the solution.[37,38] The experimental control was carried out by adding 0.2 mmol (0.0492 g) ImCl to the reaction components, where ImCl is in a 1:5 mol ratio of TOPSe to ImCl. The assumption that the MW energy is more efficiently absorbed by ImCl rather than TOPSe is evidenced by the increased heating rate to reach reaction

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temperature which exhibits a 2.47 °C/s in the absence of ImCl and a value of 3.02 °C/s in the presence of 0.2 mmol ImCl in the reaction mixture.

MW absorption into TOPSe may lead either to activation of TOPSe (a_{solute}) consistent with a reaction driven growth regime or to rapid solvent heating by thermalization. If the observed reaction properties arise from TOPSe activation via selective absorption into TOPSe, then one would predict addition of a stronger MW absorbing molecule (larger dipole moment) to the reaction should have a large impact on the observed QD growth behavior by suppressing the fractional contribution of MW energy absorbed directly into TOPSe. On the other hand, if TOPSe only enhances reaching the reaction temperature and thus accelerates the reaction rate via thermally triggered nucleation, the addition of a strong MW absorber should further enhance the reaction rate.

The results for a two monomer addition protocol at 220 and 180 °C are shown in Figure 3B. For the same reaction temperature, the size of the QDs grown in the presence of ImCl is larger than the QDs isolated in the absence of ImCl. In the presence of ImCl, the QD grown at 220 °C has a PL feature at 545 nm (fwhm 28 nm) corresponding to a 3.96 nm QD. For the reaction at 180 °C, the PL shifts to 560 nm and broadens (PL fwhm 28 → 44 nm). The size of the QD grows from 3.96 to 4.23 nm during the second reaction step. The broader PL feature for the samples grown in the presence of ImCl implies a loss of the QD size dispersity. Although it is difficult to distinguish between a reactant and a solvent heating effect, the competition for MW absorption when ImCl is added appears to eliminate the observed discrete QD formation and impacts the temperature dependent growth behavior. This suggests that a simple rate enhancement arising from accelerated solvent heating cannot be used to completely explain the observed reaction observations.

Reaction in the Absence of Monomer Addition. To further interrogate the impact of selective MW absorption by TOPSe, the affect of carrying out the identical reaction in the absence of fresh monomer are shown in Figure 3C. The reaction was carried out as shown in Figure 1; however, no fresh monomer is added prior to heating to the next temperature point. The absorption and PL spectra in Figure 3 C show no observable shift in the spectral profile or spectral broadening for the reaction heated to 220 °C, 200 °C, and 180 °C, sequentially. This indicates the growth behavior in the MW cannot be attributed to lowering the reaction temperature alone. The lack of a new PL feature, a PL spectral shift, or PL broadening for the exact same reaction without additional monomer being added implies the monomer is consumed during the initial MW ramping and thus does not contribute to changes in the QD size or dispersity unless fresh monomer is added. By comparison to the lyothermal reaction, one would have expected a loss of size focus because of Ostwald ripening, unless the QD distribution is tight and the surface of the QDs is smooth because of the lack of kinetic roughening.[15] Although the assumption of QD surface roughness being low contributing to the lack of apparent Ostwald ripening cannot be

easily proven, it is reasonable to assume the MW energy is absorbed into the QD and may result in a continuous annealing effect of the QD surface within the MW cavity. The assumption is supported by the fact that a QD has a MW absorption cross section (approximately 1/3 of TOPSe) coupled to the fact that the monomer is depleted and the number of QDs (as well as size) increase as the reaction progresses, resulting in an increased fraction of the MW energy being absorbed by the QD.

Influence of Monomer Concentration on QD Growth. The three results from the MW reaction controls, namely, lyothermal growth, addition of fresh monomer in the presence of ImCl, and growth in the absence of fresh monomer, implies the QD nucleation/growth is coupled to the absorption of MW energy by the TOPSe. While it is clearly indicated that TOPSe absorption must be important, the temperature dependent growth is yet unexplained, and the influence of monomer concentration on the number of nuclei generated in a solution following MW irradiation must be investigated. To investigate the number of nuclei formed at each step of the reaction and thus whether there is a change in the number of QDs in solution after the final heating cycle, the number of QDs generated at each reaction step was analyzed.

Number of QDs in Solution. Inspection of Figure 2A shows that for addition of equimolar concentrations of fresh monomer when corrected for the absorption cross-section, the CdSe PL intensity is not equivalent for each QD formation. While this might imply a lower number of QDs for each step, this is misleading as the extinction coefficient for a QD is size dependent.[39] Assuming the PL intensity will reflect the product of the probability for the absorption (ε) multiplied by the absorption cross section if the quantum yields are similar, then the observed PL can be correlated to the number of nuclei in solution.

In Figure 2A, the PL intensity ratio is 100 (537 nm, 3.11 nm): 41 (583 nm, 3.63 nm): 15 (619 nm, 4.92 nm). To be understood, the ratio in PL intensity must be corrected. A correction in PL intensity can be made by multiplying the observed intensity by a scalar generated from the ratio of the extinction coefficient for a given QD pair since I_{PL} is proportional to ε^*QY. The PL intensity ratio in Figure 2A for the 4.92 and 3.63 nm QD is 2.7 and is in good agreement with the ratio of extinction coefficients ($\varepsilon_{3.63}/\varepsilon_{4.92} = 2.3$) between a 4.92 and 3.63 nm QD ($\varepsilon_{4.92} = 382{,}466$ M L^{-1} cm^{-1} and $\varepsilon_{3.63} = 167{,}466$ M L^{-1} cm^{-1}). The experimentally observed ratio of PL intensities between the 3.11 and 3.63 nm QD is 2.4 in Figure 2A, which is in good agreement with the ratio of extinction coefficients of 2.1 for the two QDs ($\varepsilon_{3.63} = 167{,}466.7$ M L^{-1} cm^{-1} and $\varepsilon_{3.11} = 80{,}800$ M L^{-1} cm^{-1}). The observed changes PL intensities are within the experimental limit of this calculation, suggesting the number of QDs formed in the MW reaction is constant at constant molarity of monomer. The observation of no change in the number of initially formed QDs or QD size evolution during the second heating cycle is
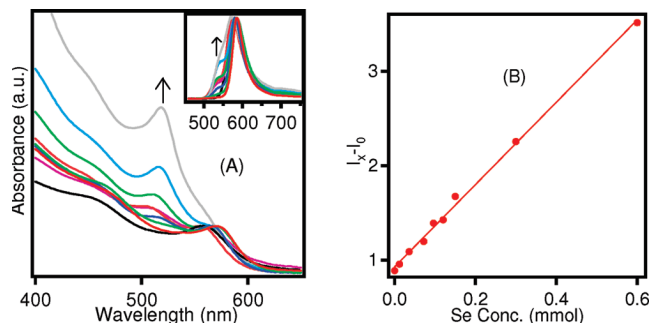

Figure 4. (A) Absorption and emission (inset) spectra for reaction with increasing concentration of fresh monomers affect during the second step. (B) Plot of the relative intensity of the absorption contributions for the two independent QDs generated in the two step reaction as a function of added TOPSe monomer in a 1:3 CdSA to TOPSe mole ratio.

consistent with the suggestion that all of the initial monomer from a prior monomer addition is consumed and does not contribute to further QD size evolution. If the MW absorption into TOPSe was screened by the presence of the larger QD, one might expect that the number of nuclei would decrease for each subsequent reaction. Likewise, if the monomer was not consumed, then the number of nuclei would be expected to vary as the monomer concentration would effectively increase for each subsequent reaction event. The lack of changes in the number of QDs in solution and the size of the QD for the largest size after three reaction cycles indicates that the monomer does not react with a previously formed QD.

Monomer Concentration Dependence for Number of QDs. In an attempt to probe the relationship between the monomer concentration, number of nucleation events, and the formation of CdSe QDs in the MW for a two monomer addition protocol, a series of reactions were carried out at various concentrations for the second monomer addition (0.1–3.0 mmol) at fixed volume and monomer ion mole ratio (1:3 CdSA to TOPSe). The absorption and the PL spectra (Figure 4A) exhibit an increase in the intensity of the higher energy feature with increasing monomer concentration. By spectral deconvolution, the red shift in the PL can be attributed to the overlapping PL features and not a shift in the size. Spectral deconvolution and fitting the width, frequency, and area using a Gaussian profile for each concentration indicates no change in the exciton absorption wavelength, no change in fwhm, and only a change in the area for the smaller QD over the entire concentration range (0.1–3.0 mmol). A plot of the difference in absorption intensity (I_x (0.6 mmol TOPSe) $- I^o$ (0 mmol TOPSe)) for the smaller QD at 520 nm as a function of the TOPSe concentration indicates the number of QDs generated is dependent on the concentration of monomer (Figure 4B). A linear increase in the absorption for the second QD with a slope of 4.23 is observed which indicates the reaction is Se limited.

The observation that the number of QDs is linearly dependent on the TOPSe concentration is not surprising, as this is expected if the nucleation and growth occur instantaneously upon absorption of the MW energy into TOPSe. The constant number of the initial QD coupled to the concentration dependence for the smaller QD strongly

(39) Protasenko, V.; Bacinello, D.; Kuno, M. *J. Phys. Chem. B.* **2006**, *110*(50), 25322–25331.
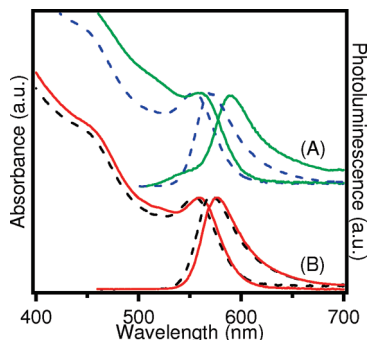
Figure 5. Absorption and PL spectra of CdSe reactions before (dashed line) and after (solid line) only a single monomer is added following an initial MW cycling event. (A) 0.3 mmol TOPSe. (B) 0.04 mmol CdSA/ decane. All samples were heated at 220 °C for 30s and 190 °C for 30s.

implies the growth events are independent for each QD in solution and only relates to TOPSe absorption.

Influence of Addition of Only a Single Monomer. To analyze the contribution ascribable to TOPSe, the reaction was carried out for a two-step reaction (220 and 180 °C) where only one of the monomers is added (CdSA or TOPSe). The optical data is shown for addition of 0.3 mmol TOPSe in Figure 5A, while the change in the optical data for addition of TOPSe between 0.072 mmol → 0.3 mmol, is shown in Supporting Information, Figure S4. Upon addition of 0.3 mmol TOPSe in the absence of CdSA, a shift in the absorption exciton of 7 nm is observed, while a shift of 19 nm in the PL occurs. In addition a weak, new PL feature appears at higher energy. The spectral shift corresponds to a change in QD size from 4.18 to 4.42 nm. The observed spectral shift and weak PL feature that appears and the observed growth in the absence of CdSA supports the suggestion that the monomer is effectively and TOPSe is the limiting reagent.

Upon addition of 0.4 mmol CdSA in the absence of TOPSe, no new PL feature or significant growth is observed in the reaction although the reaction reaches the desired reaction temperature albeit at a slower rate (Figure 5B). The results support the analysis that the TOPSe is the critical reaction component in the MW reaction and suggests strongly that the QDs in solution absorb the MW energy as the TOPSe is depleted.

Conclusion

The ability to systematically control nucleation and growth within a MW via reaction driven processes, allows an unprecedented control over QD growth allowing multiple tight dispersity CdSe QDs to be isolated within a single reaction. Using a MW therefore allows the generation of controlled QD bar codes from a single MW reaction, where color saturation and color index is completely controlled by the reaction conditions. It is believed the ability to create tight dispersity nuclei repetitively in the single reaction reflects the ability of the MW to selectively heat the TOPSe precursor, thus triggering instantaneous nucleation and rapid reduction in the monomer concentration within the solvent cage of the reaction. The selective absorption of MW energy into TOPSe leads to a large K value, zero growth conditions in solution, and the limit of the participation of Ostwald ripening during the time scale of the reaction. The lack of Ostwald ripening participation is surprising and suggests a smooth (defect-free) surface leading to zero growth rate must also contribute to reaction driven process, as suggested by Talapin.[15,18] We believe the zero-growth rate reflects reconstruction of the QD because of direct MW absorption of the QD, which will scale with QD size, providing the necessary energy for surface reconstruction and thus the minimization of kinetic roughness.[15]

Supporting Information Available: Figure S1 illustrates the ability to create up four discrete QDs in one reaction. Figure S2 provides TEM images of the QDs at each monomer addition step. Figure S3 shows the complete evolution for a lyothermal reaction over a period of 3 h. Figure S4 illustrates the effect of addition of only one monomer. This material is available free of charge via the Internet at http://pubs.acs.org.