ZnSe Quantum Dots: Determination of Molar Extinction

Coefficients for UV to Blue Emitters

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Abstract

The focus on heavy metal-free visible emitters in optoelectronic devices has increased interest in ZnSe semiconductor quantum dots (QDs) over the past decade. Empirical fit equations correlating the lowest energy electron transition to their size and molar extinction coefficients (ϵ) are often used to determine the concentration of suspensions containing QDs. This is essential to the design and successful synthesis of complex semiconductor nanoparticles including core/shell and dot-in-rod heterostructures as well as consistent device fabrication. While these equations

are known and heavily used for CdSe, CdTe, CdS, PbS, etc., they are not well established for ZnSe nanocrystals; the only two reports of ϵ in the literature differ by over an order of magnitude. In this study, a series of ZnSe QDs with diameters ranging from 2 to 6 nm were characterized with small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), and UV-Vis spectroscopy. SAXS-based size analysis enabled practical inclusion of small particles in the evaluation. Elemental analysis with microwave plasma atomic emission spectroscopy (MP-AES) yields a non-stoichiometric Zn:Se ratio consistent with zinc-terminated spherical ZnSe QDs. Using these combined results, molar extinction coefficients for each QD sample were calculated. Empirical fit equations correlating QD size with its lowest energy electron transition (i.e., 1S peak position) and molar extinction coefficients for both 1S peak and high energy wavelengths are reported. These results will enable the consistent and reliable use of ZnSe core particles in complex heterostructures and devices.

The unique photophysical properties of semiconductor quantum dots (QDs) have made them the building blocks of next generation optoelectronic devices. Their color tunability, narrow emission spectra, high quantum yield (QY), and chemical and photo stability have resulted in their extensive use in quantum dot light emitting diodes (QLEDs).¹ The use of LED lights could save approximately 348 TWh (compared to no LED use) of electricity, equivalent to a total savings of more than \$30 billion and reducing CO₂ emissions by 246 cubic megatons in the United States alone.²⁻⁴ As a result, research interest in LEDs has gained steady growth over the past decade. However, a large proportion of the developed QLEDs involve the use of heavy

metals. With growing concerns regarding the toxic effects of chemicals such as cadmium, mercury, and lead to the environment and human health, and the European Union's Restriction of Hazardous Substances (RoHS) rules banning any consumer electronics containing more than trace amounts of these materials, commercialization of such LEDs faces major hurdles, necessitating the development of non-toxic alternatives.^{5,6} ZnSe-based QDs are a leading candidate for the fabrication of blue LEDs and laser diodes, making the synthetic development of these nanoparticles technologically important.⁷⁻⁹

ZnSe has a bulk bandgap of 460 nm (2.7 eV).¹⁰ As a result of the quantum confinement effect arising from a reduction in the QD diameter below its exciton Bohr radius, the optical properties of ZnSe nanoparticles can be precisely tuned by altering their size. ZnSe/ZnS core/shell heterostructures,⁷ ZnSeTe alloyed QDs¹¹, and Cu- or Mn-doped ZnSe/ZnS QDs^{12,13} have been used for the fabrication of ZnSe-based QLEDs. In order to precisely fabricate QD-containing devices or synthesize complex nanostructures, it is necessary to know the core QD size and concentration in solution. Empirical fit equations correlating the position of the lowest energy electron transition (1S peak) to the QD size and its molar extinction coefficient (ϵ_{1S}) are often used to determine QD concentrations.¹⁴ These equations are derived through the combination of sizing data obtained from TEM images and composition determination by performing elemental analysis. With known molar extinction coefficients, one can use the Beer-Lambert law to calculate the QD concentration. While these empirical fit equations are known and heavily used for semiconductors such as CdSe, CdS, CdTe, PbS, PbSe, and InP, there were no reports elaborating on the size and molar extinction coefficient relationship for ZnSe nanocrystals until recently.¹⁵⁻²⁰ Unfortunately, the sizing equation in this report is limited in range, and the published ϵ_{1S} values are an order of magnitude larger than the only other single-

point report of a ZnSe molar extinction coefficient in the literature,²¹ warranting further investigation. High energy absorption measurements that are taken at wavelengths outside the quantum confinement regime can be even more accurate for concentration determinations, as these measurements are size-independent and thus unperturbed by differences in the size dispersion of particles between samples.¹⁹ In this study, in addition to relating the 1S peak and QD size, we determined empirical equations correlating both 1S peak and high energy absorption peak measurements to ZnSe concentration.

ZnSe QDs have been synthesized using a variety of routes including arrested precipitation²², reverse micelle²³, heat up²⁴, and hot injection methods²⁵. Here, monodisperse ZnSe nanocrystals between 2 and 6 nm in diameter were synthesized by combining a hot-injection method and the extended LaMer model of growth *via* a continuous drip injection.²⁶ In this reaction, a burst of nucleation takes place due to precursor super saturation following the rapid of diethyl zinc (Et₂Zn) into a mixture of oleylamine and trioctylphosphine:selenide at 300 °C. Nanoparticle growth proceeds through a continuous drip addition of the cationic and anionic precursors at the same temperature. Control of the reaction time, and therefore the volume of precursors added into the reaction solution, results in the formation of ZnSe QDs of different sizes. Particle growth was monitored by taking absorbance measurements of diluted samples and tracking the position of the 1S peak as it shifted from 361 nm to 422 nm (**Figure 1**). For each QD sample, the reaction was ceased by removing the flask from the heating mantle and placing it on an aluminum block to rapidly cool to room temperature. Each sample was named to correspond with the resulting 1S peak position (e.g., QD361 and QD422).

Figure 1. UV-Vis spectroscopy of ZnSe cores. 1S peak-normalized absorbance spectra of ZnSe core QDs with 1S peaks between 361 and 422 nm.

Powder X-ray diffraction measurements performed on QD394 and QD423 confirmed the zinc-blende crystal structure (**Figure 2a**). The peak positions of the nanocrystals at 26.9, 44.6, and 52.9 degrees correspond to the (111), (220), and (311) crystal planes and are consistent with previously reported ZnSe nanocrystals synthesized using phosphine-selenium precursors.^{27,28} A narrowing of the XRD peaks is observed in the spectra obtained from QD422 compared with QD397, consistent with an increase in nanoparticle diameter. For the determination of average particle diameters, synthesized nanocrystals were imaged using transmission electron

microscopy (TEM), where lattice fringes are visible throughout the nanocrystals, further demonstrating their crystallinity (**Figure 2**). Average diameters were calculated by measuring the area enclosed within each nanocrystal and assuming a spherical morphology (n= 126-236 QDs per QD sample).

Figure 2. Structure and morphology of ZnSe core particles. a) XRD spectra of QD397 and QD422 along with reference peaks for zinc blende ZnSe.²⁹ Size-matched TEM images of b) QD405, c) QD419, and d) QD422. The scale bar indicates 10 nm, and the inset in each image depicts a 10 nm by 10 nm area with a scale bar of 2 nm.

While TEM is a valuable tool for obtaining essential morphological and crystallographic information, it is limited when it comes to obtaining reliable sizing information of nanocrystals. The number of nanocrystals imaged is often not representative of the entire sample: while a QD suspension contains billions of nanoparticles, usually only a few hundred QDs are imaged and

sized.³⁰ In addition, the low contrast of semiconductor QDs compared to background, especially in the case of non-heavy metal containing QDs such as ZnSe and InP, inhibits the utility of automated sizing of QDs, necessitating manual sizing of individual QDs. This adds individual errors and person to person variability to the uncertainty of the sizing results, especially for QDs in the size range of 1-4 nm. Therefore, small angle X-ray scattering (SAXS) was used as an additional tool for the accurate determination of sizing information using suspensions of as-synthesized QDs loaded into quartz capillaries, enabling ensemble sizing measurements on a significantly larger sample size.

The SAXS data were modeled using a spherical form factor and assuming a log normal size distribution (**Figure 3a**). To confirm the accuracy of SAXS as an alternative sizing method for small diameter nanoparticles, we compared sizing data obtained from SAXS and TEM; the slope of the line (SAXS diameter = slope · TEM diameter) relating the two measurements is 1.01 ± 0.03 , indicating strong agreement between the two sizing approaches (**Figure 3b**). While we observed that the standard deviations of measurements performed through SAXS were somewhat larger than those obtained via TEM, the trends in the SAXS means were more consistent with the trends seen for the optical bandgaps at small particle sizes (**Table S1**). Specifically, for the smallest particles, the TEM sizes do not increase monotonically with larger 1S peak wavelengths, whereas this subtle size differentiation is discernable in the SAXS data (**Figure S1**). Thus, we chose to use the SAXS measurements for our subsequent analysis.

Figure 3. Sizing analysis of ZnSe QDs. **a)** Experimental SAXS patterns for ZnSe QDs, fitted with a log normal size distribution to a spherical model (lines). **b)** Comparison of particle diameters obtained using SAXS and TEM. The black line denotes an empirical fit with the slope of 0.99. **c)** Relationship between the SAXS diameters and bandgap, as determined from the 1S peak position. Data from previously published ZnSe cores included for comparison,^{15,21,22,31–33} as well as a previously published theoretical equation for the relationship between ZnSe core size and bandgap energy (dashed line).³⁴ The grey shading indicates the 95 percent confidence interval for the fit equation (solid black line) to the data original to this publication (solid diamonds). The colors and sample ordering used in this figure are consistent with the colors and labels in Figure 1.

The 1S peak positions (bandgaps) are plotted against their corresponding average diameters in **Figure 3c** (filled, colored markers) and compared to literature reports (**Figure 3c**, open black markers). Our sizing data is in agreement with the theoretical work of Wang *et al.* (dashed line).³⁴ An empirical fit equation adjusts the ZnSe bandgap for the size-based quantum confinement by correlating the 1S peak (E_g , eV) with diameter (D , nm):

$$E_g(\text{eV}) = 2.70 + \frac{1}{0.0383D^2 + 0.498D + 0.0722} \quad \text{Equation 1}$$

While this equation format mirrors the inverse radius squared proportionality of bandgap and particle size seen in the particle in a box solution for an infinite quantum well, it is an unwieldy formalism for using an experimental absorbance spectrum to determine the size of particles in a solution. For this practical application, multiple fitting equations were considered to describe the relationship between the 1S peak position and the particle diameter (**Figure S2, Table S2**). While polynomials have often been used for this purpose, we find that the polynomial fit equations rapidly deviate from physical reality outside the range of the original data. Exponential and power law relationships, in contrast, maintain a monotonic increase in diameter with increasing 1S peak wavelength. The following power law equation efficiently relates the 1S peak position (λ , nm) and the particle diameter (D , nm) (**Figure 4a**):

$$D = 1.44 + 1.34 \cdot 10^{-31} \cdot \lambda^{12} \quad \text{Equation 2}$$

We note that during the preparation of this paper, another report on the size and molar extinction coefficient of ZnSe QDs with 1S peaks in the range of 400-424 nm was published, wherein a greater focus was placed on the surface properties of the QDs.¹⁵ Our experiments significantly expand this range to QDs with 1S peaks ranging from 361 nm to 422 nm, which results in empirical fit equations covering a broader range of QD diameters and optical properties. The benefit of the broader range of particles and the power law fitting function are seen in **Figure 4a**, where the previously published quadratic sizing equation (dashed line) fits our data well over the previous sample range of 400 – 424 nm, but rapidly diverges outside that range.

Figure 4. Size-dependent characterization of ZnSe particles. **a)** Diameter *versus* first exciton absorption (1S) peak position. **b)** The ZnSe QD molar extinction coefficient at the 1S peak position as a function of particle size. In both **(a)** and **(b)**, the black line indicates fit function with the 95 percent confidence interval shaded in grey. The dotted line in **(a)** is the fit function from Peng *et al.*, which was fit using data with first exciton absorption peaks ranging from 400 - 422 nm.¹⁵ The black asterisk in **(b)** represents the data point from Banin *et al.*, using their reported 3.7 nm diameter; the reported 390 nm 1S peak for this particle indicates a 3.1 nm diameter by our sizing analysis, as presented by the red asterisk.²¹ The ϵ_{1s} values reported for Zn-terminated ZnSe QDs in Peng *et al.* are an order of magnitude larger than those reported here or by Banin *et al.* and do not fit on the scale of plot **(b)**. **c)** A plot of the ratio of zinc and selenium *versus* diameter indicates that smaller particles exhibit a larger excess of zinc atoms due to their zinc-terminated surfaces but the ratio asymptotes towards unity as the particle size increases. An offset exponential function (black line) is added as a guide to the eye.

While there are several published experimental and theoretical values relating the 1S peak position to average nanocrystal diameters for ZnSe QDs, there are currently only two reports of

its molar extinction coefficient in the literature: Banin *et al.* report a molar extinction coefficient of 180,000 M⁻¹ cm⁻¹ for ZnSe QDs with a 1S peak at 390 nm and reported diameter of 3.7 nm,²¹ while Peng *et al.*¹⁵ recently reported molar extinction coefficient values for ZnSe QDs with 1S peak in the range of 400 - 424 nm. Notably the Peng values for the ϵ_{1S} are approximately an order of magnitude larger than those reported by Banin, requiring a reexamination of these values to reconcile the conflicting reports (**Figure S3**). Linear extrapolations of the Banin *et al.* value have also been used to estimate the molar extinction coefficient value for QDs of different sizes.³³ However, linear extrapolations become less effective estimates as the sizes deviate because the extinction coefficients scale with volume, not diameter.³⁵

Molar extinction coefficients can be empirically determined by carefully correlating the absorbance of a sample of QDs with known size with the concentration of its constituents using elemental analysis. To this end, each QD sample was purified through precipitation with ethanol and its absorbance in hexane carefully measured before the sample was dried under vacuum and acid-digested for analysis using microwave plasma atomic emission spectrometry (MP-AES). In a recent study, Morrison *et al.* reported that exposure of selenium to nitric acid results in the formation of the H₂Se gas, compromising the accuracy of the measurements. It was noted that pre-oxidizing the samples with hydrogen peroxide (H₂O₂), can mitigate the formation of volatile compounds upon the addition of a strong acid.³⁶ The same approach was used here to digest the ZnSe size series, whereby each QD sample was first oxidized using H₂O₂ prior to digestion with nitric acid.

The concentration of each QD suspension was calculated using sizing data obtained via SAXS measurements and the number of Zn and Se ions calculated via elemental analysis. Specifically, the molar ratios were calculated using the weight concentration of each ion (C_{Zn}

209 and C_{Se} , mg/L) and accounting for their corresponding molar masses ($M_{Zn} = 65.38$ g/mol and
 210 $M_{Se} = 78.97$ g/mol):

$$R_{Zn/Se} = \frac{C_{Zn}M_{Se}}{C_{Se}M_{Zn}} \quad \text{Equation 3}$$

211 Assuming a spherical nanocrystal, the total number of atoms in each QD is related to its diameter
 212 (D) and the ZnSe lattice constant ($a = 0.567$ nm):

$$A = \frac{4\pi}{3} \left(\frac{D}{a} \right)^3 \quad \text{Equation 4}$$

213 The QD concentration (C_{QD} , M) was calculated from the measured Zn and Se concentrations
 214 (C_{Zn} and C_{Se} , respectively) and the number of atoms in the particle:

$$C_{QD} = \frac{10^{-3}}{A} \left(\frac{C_{Zn}}{M_{Zn}} + \frac{C_{Se}}{M_{Se}} \right) \quad \text{Equation 5}$$

215 This particle concentration was combined with the carefully measured absorbance spectra from
 216 the same samples to calculate the molar extinction coefficient at the 1S peak using the Beer-
 217 Lambert law. With the 1S peak molar extinction coefficient (ϵ_{1S} , $M^{-1} \text{ cm}^{-1}$) calculated for each
 218 sample, the correlation between the nanocrystal diameter in nm and the corresponding molar
 219 extinction coefficient was determined using an empirical fit equation (**Figure 4b**):

$$\epsilon_{1S} = 35,146 \cdot D^{1.71} \quad \text{Equation 6}$$

220 **Table 1** summarizes the MP-AES data obtained for each QD sample. The Zn:Se molar ratios
 221 ($R_{Zn/Se}$) obtained by MP-AES are non-stoichiometric (**Figure 4c**), consistent with those reported
 222 for PbSe and PbS QDs.^{19,20} $R_{Zn/Se}$ decreases with increasing diameter with all samples exhibiting
 223 an excess of zinc ions, consistent with similar reports of cation-terminated spherical QDs.¹⁹
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Table 1. Summary of MP-AES data.

	Diameter	C_{Zn}	C_{Se}	No. of	Zn:Se Molar	ε_{1S}
Sample^a	(nm)^b	(mg/L)	(mg/L)	Atoms (A)	Ratio (<i>R</i>_{Zn/Se})	(10⁵ M⁻¹ cm⁻¹)
QD361	2.04 ± 0.57	33.89	30.11	195	1.37	1.19
QD364	2.21 ± 0.58	40.79	38.34	248	1.29	1.29
QD375	2.48 ± 0.67	42.70	42.27	351	1.22	1.47
QD383	2.86 ± 0.67	46.24	46.76	538	1.19	2.06
QD390	3.02 ± 0.83	41.30	42.73	633	1.17	2.04
QD397	3.46 ± 0.48	42.16	45.29	952	1.12	3.14
QD405	4.31 ± 0.69	40.43	46.92	1840	1.04	4.61
QD410	4.42 ± 0.70	41.34	46.61	1984	1.07	4.72
QD419	5.36 ± 1.00	40.66	45.62	3539	1.08	6.02
QD422	5.75 ± 0.87	41.32	47.95	4369	1.04	6.94

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^a Sample nomenclature indicates the 1S absorption peak position.

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^b Reported diameters are means ± standard deviation (SD) of SAXS measurements. SD =

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PDI/r, where PDI is the measurement polydispersity index and r is the average radius of the

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sample.

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The 1S peak-based molar extinction coefficient equation is incredibly useful from a

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pragmatic standpoint, as it enables the rapid, economical, and non-destructive determination of

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both the size and concentration of QDs in solution. One weakness in this approach, however, is

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that the 1S peak becomes wider and flatter (lower intensity at its peak) as the particle size

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dispersity increases. Thus, the concentration measurement is particularly sensitive to

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polydispersity. High energy absorption measurements, on the other hand, can be used with a

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size-independent intrinsic absorption coefficient (μ_i) or molar extinction coefficient (ε) to

calculate the total concentration of semiconductor units or particles of known diameter in a solution. These quantities have already been determined for numerous QD compositions including PbS, PbSe, InAs, and CdSe, and their relationship to bulk values demonstrated.^{19,20,37–39} Following previously published discussions⁴⁰, we have calculated the intrinsic absorption coefficient (μ_i , cm⁻¹) spectra for each of our ZnSe samples from the absorbance spectra (Abs), the volume fraction determined from MP-AES (f), and pathlength (L , cm) using

$$\mu_i = \frac{Abs \ln(10)}{fL} \quad \text{Equation 7}$$

and

$$f = C_{Zn} \frac{M_{ZnSe}}{M_{Zn}} \frac{1}{2\rho_{ZnSe}} \left(1 + \frac{1}{R_{Zn/Se}} \right) \quad \text{Equation 8}$$

where C_{Zn} and $R_{Zn/Se}$ are the zinc weight concentration and zinc-to-selenium ratio (**Table 1**), respectively, M_{ZnSe} and M_{Zn} are the molar mass of zinc selenide and zinc, respectively, and ρ_{ZnSe} is the density of ZnSe.

The theoretical $\mu_{i,th}$ is used as a comparator, as it represents the intrinsic absorption of the bulk semiconductor, and is calculated using wavelength (λ)-dependent optical constants, including the real (n) and imaginary (k) parts of the refractive index of ZnSe and the local field factor f_{LF} , as well as the refractive index of the surrounding medium (n_s):

$$\mu_{i,th} = \frac{4\pi nk |f_{LF}|^2}{n_s \lambda} \quad \text{Equation 9}$$

$$|f_{LF}|^2 = \frac{9n_s^4}{(n^2 - k^2 + 2n_s^2)^2 + 4(nk)^2} \quad \text{Equation 10}$$

254 The intrinsic absorption spectra for all 10 samples (μ_i) are plotted with $\mu_{i,th}$, calculated using
255 hexanes as the solvent ($n_s = 1.375$) (**Figure 5a**). (Note: Chloroform is often a preferred solvent
256 for this analysis because it has an index of refraction that matches that of the surface ligand
257 oleylamine ($n_{OLA} = 1.460$), ensuring that there is no optical impact from the ligand corona. In this
258 case, we chose hexane to extend the optical range of our analysis deeper into the UV.) Although
259 the two smallest particles are still exhibiting quantum confinement features in their spectra
260 around 300 nm, all of the other spectra converge nicely with each other and the bulk $\mu_{i,th}$.
261 Examination of the values at several specific wavelengths shows excellent agreement between
262 the individual experimental values, the mean of the experimental values, and the theoretical
263 value for the bulk intrinsic absorption coefficient (**Figure 5b**).

Figure 5. High energy absorption analysis of ZnSe particles. **a)** The intrinsic absorption coefficient (μ_i) spectra for 10 experimental samples (colored lines) in hexane and the theoretically calculated bulk intrinsic absorption coefficient ($\mu_{i,th}$) for ZnSe in hexane (thick black line). A zoomed in region (inset) shows where the experimental and bulk values largely coincide at high energy wavelengths. **b)** Intrinsic absorption coefficient (μ_i) at 260, 280, and 300 nm of ZnSe QDs of a range of sizes (squares, triangles, and diamonds, respectively) as well as $\mu_{i,th}$ (solid lines) and mean values, $\mu_{i,mean}$ (dashed lines) at the same wavelengths. The two smallest particles are excluded from the calculation of $\mu_{i,mean}$ because they exhibit quantum confinement effects at the relevant wavelengths, and are thus depicted with open shapes in contrast to the solid shapes used for the included values. **c)** Molar extinction coefficient (ϵ) spectra of a size series of ZnSe QDs. Inset: plot of the molar extinction coefficient at 280 nm (ϵ_{280}) versus particle diameter shows the correlation between molar extinction coefficient and particle volume. The trendline shows the best fit to a D^3 power law.

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 266 High energy molar extinction coefficients (ϵ_λ , $M^{-1}cm^{-1}$) can be calculated for QDs with known
 267 diameter (D , nm) using the intrinsic absorption coefficient at the same wavelength (μ_i and
 268 Avogadro's number (N_A , mol^{-1}) (Note: $nm^3 = 10^{-24}$ L):

$$\epsilon_\lambda = \frac{10^{-24} \pi D^3 N_A}{6 \ln(10)} \mu_{i,\lambda} \quad \text{Equation 11}$$

269 When plotted, the molar extinction coefficients clearly increase for larger particles. Examined at
 270 a single wavelength (*e.g.*, ϵ_{280}), the molar extinction coefficient scales with D^3 (**Figure 5c**). The
 271 resulting fit equation:

$$\epsilon_{280} = 23,809 D^3 \quad \text{Equation 12}$$

272 provides a simple way to use the diameter in nm (as determined by **Equation 2**) to generate the
 273 ϵ_{280} in $M^{-1} cm^{-1}$, which can be used with the absorption spectra to calculate sample concentration
 274 using the Beer-Lambert Law. We chose 280 nm as the most effective wavelength for the high
 275 energy molar extinction coefficient determination because there was congruence between the
 276 mean μ_i and $\mu_{i,th}$, it is practical to take absorbance measurements at 280 nm in a number of
 277 solvents and cuvette materials (although we have only demonstrated this fit equation using
 278 hexane), and only the smallest particles of our size series was impacted by quantum confinement
 279 effects at this wavelength, and then minimally. Scaling the ϵ_{280} to the 1S peak wavelength using
 280 the sample-specific absorption spectrum confirms the consistency of the different ways of
 281 calculating ϵ values presented here (**Figure S4**).

282
 283 In order to further investigate the optical properties of ZnSe QDs, we synthesized ZnSe/ZnS
 284 core/shell QDs using a subset of the ZnSe core size series using diethylzinc, zinc stearate, and

sulfur dissolved in oleylamine as precursors. The ZnSe/ZnS QDs demonstrated tunable emission between 365 and 431 nm with extremely small Stokes shifts of 7-10 nm and QY values as high as 47%. The photoluminescence (PL) spectra of the smallest samples indicate tails on either side of the peak. We attribute the high energy tail to fluorescence from organic ligands such as oleylamine present on the surface of the QD as a result of high energy excitation (260 nm) and the low energy tail is likely the result of unpassivated trap emission. Photoluminescence excitation spectra of the QDs were also collected and closely resemble the absorbance spectra.

Figure 6. Optical properties of ZnSe/ZnS core/shell QDs. a) Photoluminescence spectra of ZnSe/ZnS QDs following excitation at 260 nm. **b)** Normalized photoluminescence excitation spectra. **c)** QY values of ZnSe/ZnS QDs.

Conclusion:

Determination of the size and concentration of a QD sample from a simple optical measurement is a key function of any characterization or application effort using the

nanoparticles. Access to a standard set of equations to use for these size and concentration determinations is critical for consistency and repeatability in nanotechnology. In this study, we establish these foundational equations for ZnSe QDs by synthesizing and characterizing a size series of ZnSe nanocrystals with 1S peaks between 361 and 422 nm. A head-to-head comparison of average diameters obtained using TEM and SAXS demonstrated the advantage of using mean diameters determined with SAXS to include data for very small particles. Empirical fit equations correlating the QD bandgap, diameter, and molar extinction coefficient are reported, providing a standard set of equations that can be used by others in the field for the efficient and economical determination of ZnSe particle size and concentration. Further analysis of the data revealed the correlation of molar extinction coefficients with QD volume at high energy wavelengths, providing a straightforward and size distribution-independent pathway to the accurate calculation of sample concentrations.

Materials and Methods:

Materials: Tri-n-octylphosphine (TOP, 97%), selenium pellets (99.99%), 1M diethylzinc solution in hexanes, zinc stearate (ZnSt₂, purum, 10-12% Zn basis), elemental sulfur (S, 99.99%), hydrogen peroxide solution (H₂O₂, ≥30%, for trace analysis), and oleylamine (OLA, 70%, tech grade) were purchased from Sigma-Aldrich. 1-octadecene (ODE, ≥90%, technical grade) was purchased from Alfa Aesar. Anhydrous ethanol, hexanes, and nitric acid (HNO₃, trace metal grade) were purchased from Fisher Scientific. Capillary wax and a hot wax pen for sealing quartz capillaries used in SAXS measurements were purchased from Hampton Research.

Precursors: A 1 M stock solution of selenium in TOP was synthesized by stirring 10 mmol of selenium pellets and 10 mL TOP together on a hot plate heated to 80 °C until the

selenium pellets were completely dissolved. A 0.4 M stock solution of ZnSt₂ in ODE was prepared by mixing 10 mmol of ZnSt₂ and 10 mL of ODE on a hot plate at 150 °C in an argon glovebox until a clear colorless solution was obtained. To prepare a 0.2 M stock solution of sulfur in OLA, 10 mmol of elemental sulfur and 10 mL OLA in a 100 mL 3-neck round bottom flask were heated at 120 °C under vacuum for 2 hours with multiple argon backfill and evacuation cycles. The cooled solution was stored in an argon glovebox for future use.

Synthesis of ZnSe core nanocrystals: ZnSe core nanocrystals were synthesized by modifying a previously reported method.²⁵ First, 7.94 mL oleylamine were loaded into a 100 mL 4-neck round bottom flask and degassed at 85 °C for 30 minutes with multiple argon backfill and evacuation cycles. The temperature was raised to 300 °C and a mixture of 0.5 mL 1 M TOP:Se and 0.8 mL TOP was added to the flask. Once the temperature was brought back to 300 °C, a mixture of 0.5 mL Et₂Zn in hexane and 0.8 mL TOP was quickly injected into the solution. After 10 minutes, a mixture of 4 mL ODE, 4 mL TOP, 1.8 mL 1M TOP:Se, and 1.8 mL 1M Et₂Zn in hexane was injected into the reaction using a stepper motor syringe pump at a rate of 2 mL/hour. For QD422, an additional dropwise injection using the same precursor volumes was performed. Once the desired 1S peak was reached, the reaction was stopped by cooling the flask to room temperature. All samples were stored in an argon-filled glove box for future use.

Synthesis of ZnSe/ZnS core/shell heterostructures: ZnS shells were deposited on ZnSe cores using Et₂Zn, a solution of 0.4 M ZnSt₂ in ODE, and a 0.2 M solution of sulfur dissolved in OLA. The required amounts of anion and cation precursors were calculated based on the number of surface atoms needed to add three monolayers to a given size of a core nanocrystal. The required amount of the zinc precursor was divided between Et₂Zn and ZnSt₂ in a 1:1 molar ratio. 10 mL ODE was loaded into a 100 mL 3-neck round bottom flask. The flask was heated and

vacuumed at 120 °C for one hour with multiple argon backfill and evacuation cycles. The temperature was raised to 180 °C, and 200 nmoles of as-synthesized ZnSe cores were added to the flask. Upon stabilization of the temperature, Et₂Zn was quickly injected into the reaction solution. After 30 seconds, the ZnSt₂/ODE solution was quickly added to the flask, immediately followed by a dropwise injection of the S/OLA solution. Ten minutes after the final injection, the reaction was cooled to room temperature by removing the flask from the heating mantle.

QD Sample Preparation: Samples of QDs were purified through precipitation and resuspension. QDs were diluted with a 1:1 volume ratio of hexane. The QDs were centrifuged at 22,000 rcf for 3 minutes to remove any aggregates. The solution was transferred to a clean tube and ethanol added until the solution became visibly turbid. The sample was centrifuged at 22,000 rcf for 5 minutes to precipitate the QDs. The clear supernatant was decanted and the QD pellet resuspended in hexanes for characterization. QDs used for elemental analysis were precipitated and resuspended a second time.

As-synthesized ZnSe/ZnS QDs were incubated at 85 °C for 2 hours in a water bath with a 1:1 v/v ratio of QD:TOP prior to centrifugation. After the sample was centrifuged at ~22,000 rcf for 4 minutes, the supernatant was transferred into a new tube, and a 1:5 ratio of ethanol was added to the tube. The solution was then centrifuged at ~22,000 rcf for 7 minutes. The clear supernatant was discarded and the QD pellet was suspended to its original volume in 0.2 M Zn(OA)₂ in TOP and incubated at 85 °C for 2 hours.

Characterization: Absorbance spectra were taken using an NanoDrop 2000 UV-Vis spectrophotometer using cuvettes with a 1 cm path length. Photoluminescence and photoluminescence excitation spectroscopy were performed using a Horiba Jobin Yvon NanoLog spectrofluorometer outfitted with a 450 W Xenon arc lamp, double excitation and

emission monochromators, and silicon CCD detector. The collected spectra were corrected for lamp power and detector sensitivity using the supplied correction files. Absolute quantum yield values were obtained using the spectrofluorometer described above with a Quanta-phi six-inch integrating sphere. Cuvettes were loaded with hexanes in order to generate a blank reference following excitation at 260 nm. QD samples were diluted directly into the blanked cuvettes and measured under identical conditions. All measurements were performed using 5 averaged scans. The absolute quantum yield (i.e., the number of photons emitted divided by the photons absorbed) was determined using the Horiba software.

Transmission electron microscopy (TEM) images were acquired using FEI Osiris and JEOL 2100 LaB6 high-resolution microscopes operating at 200 kV. Each sample was precipitated using ethanol and resuspended in hexanes and drop-cast on a copper TEM grid, which was washed successively by hexane, ethanol, and DI water. The grid was then gently heated to evaporate any residual water. TEM images were sized manually using ImageJ by determining the area enclosed within an outline drawn around the particle and back-calculating the diameter assuming a spherical nanocrystal.

Small angle X-ray scattering (SAXS) measurements were performed on solutions of as-synthesized QDs diluted in hexanes. The samples were injected into disposable quartz capillaries with a 1.5 mm diameter and sealed using a capillary wax applied using a battery-operated hot wax pen. Once cooled, the wax provides an airtight seal. Aliquots were analyzed using a Bruker N8 Horizon, with a Cu-K-alpha radiation at 50 kV and 1000 μ A. Data analysis was performed on Bruker's DIFFRAC.SAXS software assuming a spherical particle shape with a log normal size distribution.

X-ray diffraction (XRD) measurements were performed by depositing purified QDs on a low background silicon substrate. The samples were measured on a Bruker D8 Discover system in powder diffraction mode with Cu K α radiation. Detection occurred with 0.3 second integration per step at 0.0207 - 0.0225° steps.

The QDs were prepared for elemental analysis using a digestion process modified from a previously published method.³⁶ 400 μ L of each sample was transferred to a 15 mL PTFE conical tube and the excess solvent was evaporated by pulling vacuum on the tube for 15 minutes. 200 μ L of H₂O₂ was added to the sample and the tube sealed tightly and quickly. After 3 minutes, 200 μ L of nitric acid was added to the mixture. The cap was tightly and quickly sealed, and the solution was allowed to digest for 15 minutes. The sample was diluted to a total volume of 2 mL using ultrapure water. The samples were run on an Agilent 4200 MP-AES and the concentration of both Zn and Se ions were measured. For each QD size, 2 sets of solutions were digested and measured, and each measurement was performed with 5 replicates. Reported values are the averages of the 10 measurements.

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