Size-Dependent Composition and Molar Extinction Coefficient of PbSe Semiconductor Nanocrystals

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ABSTRACT Atomic compositions and molar extinction coefficients of PbSe semiconductor nanocrystals were determined by atomic absorption spectrometry, UV−vis−NIR spectrophotometry, and transmission electron microscopy. The Pb/Se atomic ratio was found to be size-dependent with a systematic excess of Pb atoms in the PbSe nanocrystal system. Experimental results indicated that the individual PbSe nanocrystal was nonstoichiometric, consisting of a PbSe core and an extra layer of Pb atoms. For these nonstoichiometric PbSe semiconductor nanocrystals, we proposed a new computational approach to calculate the total number of Pb and Se atoms in different sized particles. This calculation played a key role on the accurate determination of the strongly size-dependent extinction coefficient, which followed a power law with an exponent of ∼2.5.

KEYWORDS: semiconductor nanocrystal · PbSe · size dependence · molar extinction coefficient · composition

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Recently, size-dependent infrared-emitting semiconductor nanocrystals have been extensively studied for potential applications such as telecommunication,[1] photodetectors,[2] solar cells,[3−9] and biomedical labeling.[10,11] Most of these applications require high electronic or optical quality of nanocrystals with proper particle concentrations. Accurate particle concentration of nanocrystals is also an essential parameter in the fundamental studies of nanocrystal nucleation and growth mechanism and oscillator strengths of the crystal interband transitions,[12] the synthesis of core−shell nanostructures,[13−15] and the self-assembly of nanocrystal superlattices.[16] The most convenient way to determine the particle concentration of a semiconductor nanocrystal solution, as demonstrated by our previous work,[17] is to measure the solution's absorbance and then calculate the particle concentration through Lambert−Beer's law. In order to use this method, the nanocrystal molar extinction coefficient must be known.

Although the nanocrystal molar extinction coefficient appears significantly important in practical application and theoretical study, experimental complications and difficulties cause its reports to be much fewer in comparison to the exponentially increased publications of nanocrystal syntheses. These reports include the molar extinction coefficients of CdE (E = S, Se, and Te),[17−22] InAs,[23] PbS,[24] and PbSe.[25] Taking the well-developed CdSe nanocrystal as an example, inconsistent molar extinction coefficients are reported by different groups. Schmelz *et al.*[18] and Striolo *et al.*[19] reported the CdSe nanocrystal molar extinction coefficient followed a cubic function of the nanocrystal diameters, while Leatherdale *et al.*[20] concluded an implied linear function. A function between a square and cubic power was determined by Yu *et al.* and confirmed by nanoparticle controlled etching experiments.[17] These inconsistencies might be mainly due to some initially small errors on sample preparation, including nanocrystal purification, and size and composition analyses.[14] It has been demonstrated that tiny differences on the particle sizes can generate large errors on the final values of the molar extinction coefficient, making the entire work invalid.[24] Therefore, the experimental errors should be minimized to get the precise molar extinction coefficient.

Generally, in order to obtain molar extinction coefficient, we need to synthesize a series of monodisperse semiconductor nanocrystals with different sizes (standard samples). In Lambert−Beer's law, $A = \varepsilon CL$, A is the absorbance at the first excitonic absorption peak position of the standard semiconductor nanocrystal solution, which

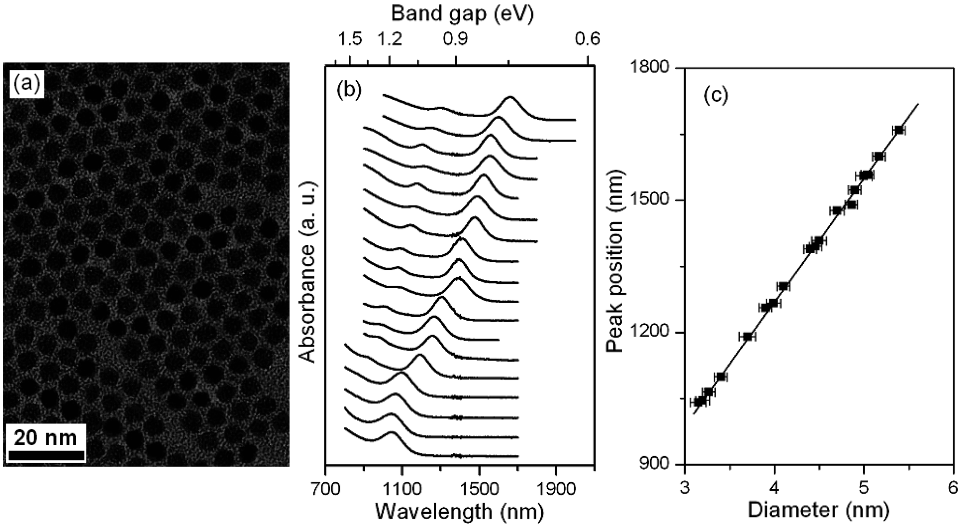

Figure 1. (a) Typical TEM image of PbSe nanocrystals with an average diameter of 5.0 nm. (b) Absorption spectra of the as-prepared 18 PbSe nanocrystal samples. (c) First absorption peak position of the 18 PbSe nanocrystal samples *versus* the nanocrystal diameter.

can be obtained from the nanocrystal absorption spectrum; L is the length ofthe light pathway, which is known from the used cuvette; ε is the unknown molar extinction coefficient; and C is the nanocrystal particle molar concentration. So if we know the particle concentration C of the standard sample, then ε can be obtained. The way to get C is to first measure the total atomic concentrations of the components in the nanocrystal standard sample (*e.g.*, the concentrations of Pb and Se in PbSe semiconductor nanocrystals) and then find the total atom number (of Pb and Se) in one PbSe particle (n) based on some theoretical models. Now the particle concentration C can be achieved by the total atomic concentration divided by n.

In this sense, the PbSe nanocrystal molar extinction coefficient reported recently by Moreels *et al.*[25] should be mentioned. They found that the studied five PbSe nanocrystal samples had a Pb/Se atomic ratio of ~1.4. To explain this observation, a model was proposed, in which the nonstoichiometric PbSe nanoparticle consisted of a stoichiometric PbSe core and a surface shell of Pb atoms. From this model, it is obvious that the lattice constant of bulk PbSe could not be simply used to calculate the total Pb and Se atom numbers in an individual nanoparticle because this bulk crystal model implies that the atom number of Pb equals that of Se. However, this calculation approach was still utilized in their work, which would bring in experimental errors. Additional inaccuracy was derived from the fact that only five PbSe standard nanocrystal samples were used in their work, and a large quantity of other size data was collected from the literature. A comparison of these literature data[26−30] has shown that the PbSe nanocrystal sizes reported by different groups are remarkably different (Figure S1a in the Supporting Information). On the basis of such great size difference, it is not realistic to fit an appropriate sizing curve, which was also illustrated in our previous publication.[26] The reason that Moreels *et al.*[25] could fit a sizing curve is that they used nanocrystal band gap energy instead of wavelength, diminishing the size difference in vision (Figure S1b in the Supporting Information).

In this article, we focus on the accurate determination of the molar extinction coefficient of PbSe semiconductor nanocrystals. To minimize the experimental errors on particle sizes, an Image-Pro Plus 6.0 software was used to analyze a large amount of PbSe nanoparticles (10 000−20 000 individual particles from several calibrated TEM images for each sample), yielding a statistically satisfied sizing curve. Additionally, a new model was proposed to determine the total Pb and Se atom number of a given nonstoichiometric PbSe nanoparticle. We found that the Pb/Se atomic ratio was size-dependent with excessive Pb atoms on the nanoparticle surface. The proposed analysis finally determined that the size-dependent molar extinction coefficient of PbSe nanocrystals was well fitted as a power law with an exponent of ~2.5. This dependency was further experimentally confirmed through effectively shrinking the nanoparticles under controlled oxidation: the nanoparticles exhibited a decrease in their effective diameter when exposed to air, but the particle concentration kept constant. We found that the absorbance of the PbSe nanocrystal solution decreased with particle shrinking, which followed exactly our determined size-dependent molar extinction coefficient curve. In comparison, a discrepancy existed between this work and the recent article by Moreels *et al.*,[25] where the molar extinction coefficient could be fitted with an exponent of ~1.6 based on their reported data.

RESULTS AND DISCUSSION

Particle Size of PbSe Nanocrystals. In comparison to the cadmium chalcogenide (CdE, E = S, Se, or Te) nanocrystals, PbSe semiconductor nanocrystals exhibit much stronger size-dependent properties because of the large Bohr radius (46 nm),[1] allowing their optical properties to be evaluated in the regime of extremely strong quantum confinement. Our recently introduced synthetic scheme with octadecene as a noncoordinating solvent[31,32] can provide high-quality PbSe nanocrystals with monodisperse size distributions (5−9%) and spherical shapes (Figure 1a).[26] The monodispersity can

TABLE 1. The 18 PbSe Semiconductor Nanocrystal Samples Used in This Paper

particle size[a] (D, nm)	concentration of Pb[b] (C_{Pb}, ppm)	concentration of Se[b] (C_{Se}, ppm)	atomic ratio of Pb/Se[c] (R)	total atom number of Pb and Se[d] (n)
3.19	10.57	2.04	1.97	440 (591)
3.20	20.19	3.62	2.12	467 (597)
3.27	10.26	1.94	2.02	490 (637)
3.40	11.27	2.20	1.95	554 (716)
3.72	14.75	2.99	1.88	751 (938)
3.95	11.95	2.60	1.75	890 (1123)
3.99	22.53	5.22	1.64	886 (1157)
4.12	14.51	3.34	1.66	1001 (1274)
4.43	17.74	4.76	1.42	1176 (1584)
4.45	15.94	3.88	1.57	1269 (1606)
4.49	15.76	3.90	1.54	1294 (1649)
4.74	9.74	2.47	1.50	1538 (1940)
4.79	17.86	4.82	1.41	1537 (2002)
4.90	14.49	3.66	1.51	1732 (2144)
5.02	17.93	4.91	1.39	1792 (2305)
5.03	16.29	4.27	1.45	1850 (2319)
5.17	20.57	5.66	1.38	1975 (2518)
5.39	21.14	5.94	1.35	2248 (2853)

[a] Analyzed by Image-Pro Plus 6.0 (Media Cybernetics Inc.) on several TEM images for each sample. [b] Measured by the AA spectrometer. [c] Calculated by $R = (C_{Pb}M_{Se})/(C_{Se}M_{Pb})$. [d] Calculated using our established function eq 6. The numbers in parentheses are the total Pb and Se atom numbers calculated using the traditional function eq 2. It is obvious that there are great differences in the total atom number within one particle based on two different models, which will finally lead to the difference in molar extinction coefficients.

be also disclosed from the absorption spectra (Figure 1b), where the half-width at half-maximum (hwhm) to the long wavelength side of the first absorption peak position is 55−65 nm (0.03−0.07 eV). In comparison, the hwhm values of PbSe nanocrystals reported by other approaches are often larger than 70 nm.[27−30] While hwhm is used as a convenient index of monodispersity (a smaller hwhm corresponds to higher monodispersity), the first absorption peak position links to the nanocrystal size. To determine the relationship between the first absorption peak position and the particle size of PbSe nanocrystals, we have measured both the absorption spectrum and TEM image of each sample. Peak positions can be precisely obtained from the absorbance measurement; an Image-Pro Plus 6.0 software was used to analyze the particle size and size distribution from the TEM images (about 10 000−20 000 individual PbSe nanoparticles from several calibrated TEM images were counted for each sample). The results in Figure 1c show that the particle size bares a linear relationship with the first absorption peak position eq 1:

$$D = (\lambda - 143.75)/281.25 \qquad (1)$$

where D (nm) is the average particle diameter of the PbSe nanocrystal sample, and λ (nm) is the first absorption peak position of the corresponding sample. It should be noted that different researchers reported very different particle sizes *versus* the first excitonic absorption peak positions for PbSe semiconductor nanocrystals. We have done repeated measurements to get this result, which is the same as the one reported in our previously published paper.[26]

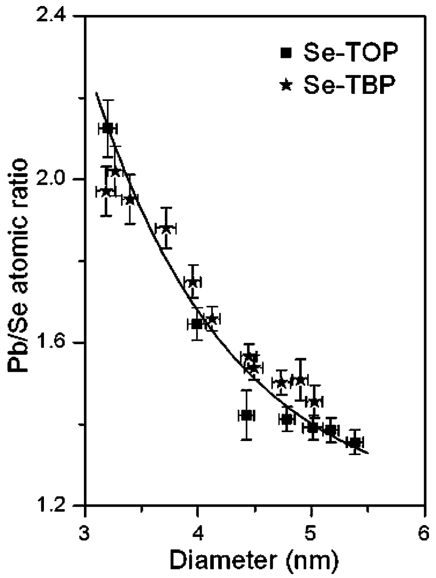

Figure 2. Pb/Se atomic ratios of PbSe nanocrystals as a function of particle diameters.

Composition of PbSe Nanocrystals. Previously reported molar extinction coefficients of binary semiconductor nanocrystals are often based on the assumption of stoichiometric nanoparticles,[17,18,23,24] where the cation and anion numbers are regarded to be identical. However, it was found that the number of Pb cations was not equal to the number of Se anions in a given PbSe nanoparticle.[25,33,34] Sapra *et al.*[34] introduced a Se-rich PbSe structure through a variable-energy synchrotron radiation photoelectron spectroscopy. The PbSe core was surrounded by a nonstoichiometric $Pb_{1-x}Se$ layer and a subsequent surface Se shell; this Se shell was capped by the trioctylphosphine (TOP) ligand. This result, however, contradicts to the recent experimental data of Moreels *et al.*,[25] although the PbSe samples of these two studies were synthesized using the same approach of Murray *et al.*[27] Moreels *et al.*[25] observed that the PbSe nanoparticle consisted of a PbSe core terminated by only one surface shell (a shell of Pb atoms), on the basis of the inductively coupled plasma mass spectrometry (ICP-MS) measurement. They further confirmed their observation using the nuclear magnetic resonance spectroscopy (NMR).[33] The NMR results clearly showed that the terminated surface Pb layer was attached to the OA ligand, where almost no TOP molecule existed. Our present elemental analysis of 18 PbSe nanoparticle samples (Table 1) through different solvents and even different synthetic approaches from Murray *et al.*[27] supported Moreels *et al.*'s model.

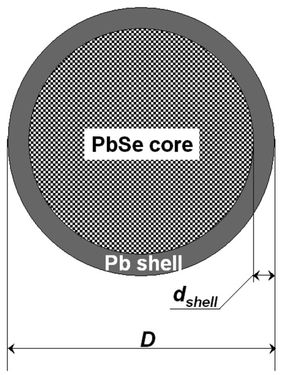

Figure 3. Schematic model of a PbSe nanoparticle. It is composed of a PbSe core and a Pb-terminated surface shell. *D* is the particle size (diameter) obtained from TEM; d_{shell} is the thickness of the Pb shell.

As shown in Figure 2, the Pb/Se atomic ratios are larger than 1.0 and exhibit a size-dependent relationship, though excessive amounts of Se as a starting material were used in our synthesis (8.0 mmol of Se and 4.0 mmol of PbO). It indicates that Pb cations terminated on the PbSe nanocrystal surface. This is in general consistent with Moreels *et al.*'s model and their experimental results of PbSe nanocrystals,[25,33] which consisted of a stoichiometric PbSe core and a Pb-terminated surface shell. The Pb termination was further found to be independent of the Se-TOP and Se-TBP precursors (Figure 2) and synthetic approaches (Figure S2 in the Supporting Information). It was also found that the Pb termination is actually also independent of reaction solvents, no matter the PbSe semiconductor nanocrystals were produced in diphenyl ether,[25,33] or in octadecene in this work. The fact that there are extra Pb atoms on the particle surface has a significant effect on the total number (n) of Pb and Se atoms in a PbSe nanoparticle; this n is later used to calculate the nanocrystal particle concentration.

Conventionally, n is calculated using the traditional function eq 2 based on the bulk crystal structure

$$n = 4\pi(D/a)^3/3 \qquad (2)$$

where a is the bulk lattice constant, which is 0.612 nm for bulk PbSe crystal.[25] Obviously, eq 2 represents the total atom number of a stoichiometric PbSe nanoparticle in which the number of Pb atom is identical to that of Se atom. Therefore, this equation cannot be simply utilized to analyze the actually nonstoichiometric PbSe nanoparticles. Considering both the PbSe core and Pb-terminated shell, we propose a new model here to calculate the actual total number of both Pb and Se atoms in a single PbSe nanoparticle (see Figure 3). First

$$n_{Se}{:}n_{Pb,shell} = 1{:}(R - 1) \qquad (3)$$

where n_{Se} is the total number of Se atom in an individual PbSe nanoparticle, $n_{Pb,shell}$ is the number of Pb atom on the surface (shell) of the corresponding nanoparticle, and R is the corresponding Pb/Se atomic ratio which can be obtained from the atomic absorption (AA) measurement (see Table 1); n_{Se} and $n_{Pb,shell}$ can be described as

$$n_{Se} = \frac{m_{core}}{M_{PbSe}} \times 6.023 \times 10^{23} = \frac{\frac{4\pi}{3} \times \left(\frac{D}{2} - d_{shell}\right)^3 \times \rho_{PbSe}}{M_{PbSe}} \times 6.023 \times 10^{23} \qquad (4)$$

$$n_{Pb,shell} = \frac{m_{shell}}{M_{Pb}} \times 6.023 \times 10^{23} = \frac{\left[\frac{4\pi}{3} \times \left(\frac{D}{2}\right)^3 - \frac{4\pi}{3} \times \left(\frac{D}{2} - d_{shell}\right)^3\right] \times \rho_{shell}}{M_{Pb}} \times 6.023 \times 10^{23} \qquad (5)$$

In the above equations, m_{core} and m_{shell} are the masses of the PbSe core and the Pb shell, respectively; M_{PbSe} (286.2 g/mol) and M_{Pb} (207.2 g/mol) are the molar masses of PbSe and Pb, respectively; ρ_{PbSe} is the density of the PbSe core (using the bulk PbSe crystal density of 8.10 g/cm^3), 6.023×10^{23} is Avogadro's constant, and ρ_{shell} and d_{shell} are the nominal density and thickness of the Pb shell, respectively. Combining eqs 3−5 and the data provided in Table 1, the unknown variants of m_{core}, m_{shell}, ρ_{shell}, and d_{shell} can be calculated. Here, d_{shell} is calculated to be 0.32 nm, which is close to the covalent diameter (0.294 nm) of Pb. It indicates that a nearly single extra atomic layer of Pb atoms is on the nanocrystal surface (shell) for all the 18 samples. On the basis of this calculated d_{shell} and the measured R, the total Pb and Se atom number ($n = n_{Se} + n_{Pb}$) in any given PbSe nanoparticles can be calculated as

$$n = n_{Se} + n_{Pb} = n_{Se} + n_{Se} \times R = \frac{\frac{4\pi}{3} \times \left(\frac{D}{2} - d_{shell}\right)^3 \times \rho_{PbSe}}{M_{PbSe}} \times 6.023 \times 10^{23} + \frac{\frac{4\pi}{3} \times \left(\frac{D}{2} - d_{shell}\right)^3 \times \rho_{PbSe}}{M_{PbSe}} \times 6.023 \times 10^{23} \times R \qquad (6)$$

The calculated n values of different sized particles shown in Table 1 (the fifth column) are further utilized to calculate the nanocrystal particle concentration (C_{PbSe} in a unit of μM) as follows:

$$C_{PbSe} = \frac{10^3}{n} \times \left(\frac{C_{Pb}}{M_{Pb}} + \frac{C_{Se}}{M_{Se}}\right) \qquad (7)$$

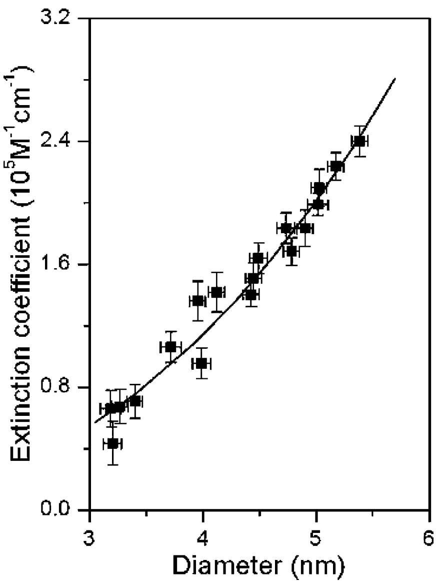

Figure 4. Size-dependent molar extinction coefficients of PbSe nanocrystals as a function of particle diameters.

where C_{Pb} (ppm) and C_{Se} (ppm) are the weight concentrations of the respective atoms measured from AA, and M_{Se} (78.96 g/mol) is the molar mass of Se. (C_{Pb}/M_{Pb} + C_{Se}/M_{Se}) is the total atom concentration of Pb and Se in a given PbSe nanocrystal standard sample, which is divided by n, the atom number of Pb and Se in one particle, to give the particle concentration (C_{PbSe}) of this given sample.

Molar Extinction Coefficient of PbSe Nanocrystals. The Lambert–Beer's law was used to calculate the molar extinction coefficient of PbSe nanocrystals (eq 8)

$$A = \varepsilon CL \qquad (8)$$

where C is the nanocrystal particle molar concentration, which is the same as C_{PbSe} in eq 7; L is the length of the light pathway, which is 1 cm in this work. On the basis of the obtained nanocrystal absorbance and particle concentration, the molar extinction coefficient of PbSe nanocrystals can be finally determined. Similar to CdE nanocrystals, PbSe nanocrystals also exhibit strongly size-dependent molar extinction coefficients, which can be fitted into a power function of the nanocrystal size (D, diameter) as below

$$\varepsilon = 0.03389D^{2.53801} \qquad (9)$$

where the unit of ε is 10^5 M$^{-1}\cdot$cm^{-1}, and that of D is nm (Figure 4).

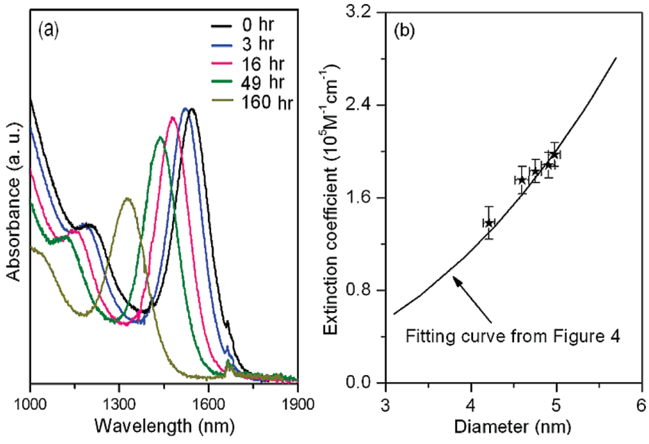

Figure 5. (a) Temporal evolution of the absorption spectra of 5.0 nm PbSe nanocrystals exposed to UV light in air (effective shrinking). (b) Molar extinction coefficients derived from panel a. They are consistent with the fitted curve obtained in Figure 4.

It should be noted that the accuracy of those experimentally achieved molar extinction coefficients can be greatly affected by the nanocrystal size distribution. Broader size distributions of nanocrystals correspond to absorption spectra with both lower absorbance and wider absorption peaks. Therefore, the measured absorbance of an actual nanocrystal sample should be calibrated with

$$A = A_m W_{hwhm}/K \qquad (10)$$

where A and A_m are the calibrated and measured absorbance, respectively, W_{hwhm} (nm) is the measured hwhm, and K is the average hwhm value, which is 60 nm. The nanocrystal molar extinction coefficient is of significant importance because many researches require a convenient determination of the nanoparticle concentration. Once the molar extinction coefficients are known (Figure 4), one can readily take an absorbance measurement to determine the nanocrystal particle concentration (eq 8), avoiding other lengthy measurements or uncertain approximations.

PbSe semiconductor nanocrystals have been found to be oxidized and decomposed when they are exposed to air.[34,35] Therefore, inert gas was required to protect the nanocrystal samples. The purification and measurements should be swiftly completed after the samples were taken from the reaction flask. On the other hand, the instable property of PbSe nanocrystals stored in air could be applied to confirm the relationship between the molar extinction coefficient and the particle size. Each individual PbSe nanocrystal particle gradually decomposed in air, while the nanocrystal particle concentration did not change (0.88 μM in this experiment). This was similar to the previously used controlled etching.[17] During this process, we found the absorbance decreased when the particle's effective size shrank (Figure 5a). As shown in Figure 5b, all the relative ε values are in nice agreement with the fitting curve of eq 9. It clearly confirms that the molar extinction coefficient values and the fitting are correctly achieved in this work.

It is worth noting that experimental errors, such as broad size distributions of the samples and inefficient purification procedures, can cause great differences in final values of the molar extinction coefficient.[17] For nonstoichiometric nanoparticles like PbSe, precise calculation of the total atom number in a nanocrystal particle is an additional key factor for reliable determination of the molar extinction coefficients. In the fifth column of Table 1, it shows that the total atom number in one PbSe nanoparticle has very different values considering the Pb-terminated surface atoms or not. Although Pb termination on the nanocrystal surface has been observed by Moreels *et al.*,[25] they still used the conventional eq 2 to calculate the total atom number of Pb and Se and reported different molar extinction coefficients for PbSe semiconductor nanocrystals from this work.

CONCLUSIONS

The molar extinction coefficients of PbSe nanocrystals at the first excitonic absorption peak have been determined by utilizing TEM, AA spectrometry, and UV−vis−NIR spectrophotometry. The large number particle statistics and our proposed calculation approach have allowed us to precisely find out the particle size and the total atom number for each standard PbSe nanocrystal sample, respectively. The experimental results have demonstrated that the individual PbSe nanoparticle is composed of a PbSe core terminated by an extra layer of Pb atoms. This property leads to a size-dependent Pb/Se atomic ratio in these nonstoichiometric PbSe nanocrystals. By taking account of the surface-terminated Pb atoms, the size-dependent PbSe nanocrystal molar extinction coefficient is proportional to ~2.5 orders of the nanocrystal diameter.

METHODS

Chemicals. Lead(II) oxide (99.99%) was purchased from Alfa Aesar. Oleic acid (OA; 90%), 1-octadecene (ODE; 90%), trioctylphosphine (TOP; 90%), tributylphosphine (TBP; 97%), and selenium (100 mesh, 99.99%) were obtained from Aldrich. Acetone, chloroform, methanol, tetrachloroethylene, toluene, concentrated HCl, and concentrated HNO_3 were purchased from VWR.

Synthesis 1. PbSe nanocrystals were synthesized on the basis of our previously reported approach.[26] In detail, 0.892 g (4.00 mmol) of PbO, 2.260 g (8.00 mmol) of OA, and 12.848 g of ODE were loaded into a three-neck flask and heated to 180 °C to dissolve PbO powder under N_2 flow. The temperature was then set to 170 °C, and 6.400 g of 10% Se-TOP solution (prepared in a glovebox) was swiftly injected into the vigorously stirred solution. After the injection, the temperature quickly dropped and was then kept at 140 °C for the growth of PbSe nanocrystals. At different reaction times, aliquots were taken as samples for the postsynthetic measurement.

Synthesis 2. Se-TBP solution could be also used as Se stock solution to produce PbSe nanocrystals. The only difference between this synthesis and Synthesis 1 is that 6.400 g of 10% Se-TBP solution was used instead of the Se-TOP solution.

Synthesis 3. Highly monodisperse PbSe nanocrystals were also synthesized in a Teflon-lined autoclave.[36] A mixture of PbO, OA, and ODE was heated until the yellow PbO powder dissolved. Then, the mixture was cooled to room temperature and mixed with a Se-TOP solution. The total mixture was further transferred into a Teflon-lined autoclave. The sealed autoclave was put into a 220 °C furnace, and the reaction was kept for 50 min. The purpose for performing Syntheses 2 and 3 was to check if the precursor or the synthesis method would affect the molar extinction efficient of the nanocrystals.

Purification. Before measuring any physical data, excessive reaction precursors and reaction solvents have to be removed. We previously introduced a purification way, which could completely remove the unreacted precursors and solvents.[26,31,32] After the original nanocrystal sample was quickly taken from the reaction flask and quenched by room-temperature toluene, an equal volume of methanol was added for extraction. The extracted PbSe nanocrystals were redispersed in chloroform and then precipitated with excess acetone. The purified PbSe semiconductor nanocrystals were finally dispersed in tetrachloroethylene for measurements. All these operations were performed under N_2 protection, and the following measurements were immediately done after purification to minimize any possible nanoparticle change.

Measurements. Transmission electron microscope (TEM) specimens were made in nitrogen atmosphere by evaporating two drops of the diluted sample solution onto carbon-coated copper grids. A JEOL FasTEM-2010 transmission electron microscope operating at 100 kV was used to take the TEM images on different areas of one grid specimen, which could eliminate the error caused by any possible nonuniform drying. On the basis of the TEM images, about 10 000−20 000 individual PbSe nanocrystalline particles were analyzed by Image-Pro Plus 6.0 (Media Cybernetics Inc.) for nanocrystal sizes. A Perkin-Elmer Lambda 9 UV−vis−NIR spectrophotometer was used to take the nanocrystal absorption spectra with an absorbance between 0.10 and 0.20.

For the atomic absorption (AA) measurements, a Perkin-Elmer AAnalyst 300 spectrometer was employed. AA samples were prepared as follows (no N_2 protection needed): 1 mL of purified PbSe nanocrystal solution with a known absorbance (A) was put into a vial. After this solution was dried by gentle heating, about 1 mL of aqua regia (a mixture of concentrated HCl and HNO_3 with a HCl/HNO_3 volume ratio of 3:1) was added to digest the dried PbSe samples. The digested sample was then mixed with a certain amount of distilled water; the total solution was made equal to 10 mL for AA measurements. From AA, the Pb and Se weight concentrations of each PbSe nanoparticle sample were obtained. The weight concentrations were first converted to molar concentrations (atom concentrations) by divided by the molar masses, respectively. The molar concentrations were then divided by the total Pb and Se atom number (n) in one particle of the corresponding nanocrystal sample to get the nanocrystal particle concentration (C or C_{PbSe}). Combining the nanoparticle concentration and the measured absorbance, the room-temperature molar extinction coefficient of PbSe nanocrystals could be finally calculated using the Lambert−Beer's law.

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Supporting Information Available: PbSe particle sizes collected from the literature versus either the first absorption peak positions or the optical band gaps, and an energy-dispersive spectrum of the PbSe nanocrystal sample produced in Synthesis 3. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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