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Composition and Size-Dependent Extinction Coefficient of Colloidal PbSe Quantum Dots

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Inductively coupled plasma mass spectrometry (ICP-MS) was combined with UV–vis−NIR spectrophotometry and transmission electron microscopy to determine the nanocrystal composition and molar extinction coefficient ϵ of colloidal PbSe quantum dot (Q-PbSe) suspensions. The ICP-MS results show a nonstoichiometric Pb/Se ratio, with a systematic excess of lead for all samples studied. The observed ratio is consistent with a faceted spherical Q-PbSe model, composed of a quasi stoichiometric Q-PbSe core terminated by a Pb surface shell. At high photon energies, we find that ϵ scales with the nanocrystal volume, irrespective of the Q-PbSe size. From ϵ, we calculated a size-independent absorption coefficient. Its value is in good agreement with the theoretical value for bulk PbSe. At the band gap, ϵ is size-dependent. The resulting absorption coefficient increases quadratically with decreasing Q-PbSe size. Calculations of the oscillator strength of the first optical transition are in good agreement with theoretical tight binding calculations, showing that the oscillator strength increases linearly with Q-PbSe size.

Introduction

Over the last 25 years, colloidal quantum dots have become one of the frontier materials in nanoscience and nanotechnology. Their exceptional physical properties, caused by quantum confinement, have initiated a vast amount of experimental and theoretical work. An important quantity in colloidal nanocrystal research is the molar extinction coefficient ϵ. In combination with the absorbance spectrum and the Beer–Lambert law, it provides the most convenient way to determine the concentration of dispersed quantum dots. Theoretically, ϵ gives insight in the spectral position and the oscillator strength of the interband transitions of colloidal quantum dots, and their evolution with size.

The dependence of the spectral position of the first exciton (or band gap) transition in the absorption spectrum on the nanocrystal size is by now well understood, and excellent agreement between experiment and theory has been demonstrated for many different materials. In contrast, the results of experimental studies on extinction coefficients and oscillator strengths of electronic transitions in colloidal quantum dots are less clear. On the basis of the maximum value of the band gap absorption, an increase of ϵ with increasing particle size has been reported for materials such as CdTe,[1] CdS,[1] CdSe,[1,2] InAs,[3] and PbS.[4] Very often, this size dependence takes the form of a power law, but the exponents vary widely from material to material and, in the case of CdTe, even for the same material (Yu et al.[1] report a cubic dependence, while Rajh et al.[5] found that ϵ is size-independent). The fact that the maximum of the band gap absorption depends on the size dispersion of the sample is anticipated in more recent reports, in which calibrated[1] or integrated[4,6] absorbances are used. For comparison with theory, the oscillator strength is a more attractive quantity because it only depends on intrinsic quantum dot properties (ϵ, for instance, also depends on the local field factor). However, literature does not yield a standard procedure to calculate the oscillator strength of the band gap transition from the absorbance spectrum. Many authors work with relative oscillator strengths, assuming that the oscillator strength has the same size-dependence as the extinction coefficient per particle[5] or the wavelength integrated extinction coefficient.[4,6] Only in the case of InAs quantum dots,[3] the oscillator strength is quantified starting from the frequency integrated absorption cross section. None of these reports establish a quantitative agreement between the experimental oscillator strength and theoretical calculations.

Here, we present a study on the extinction coefficient of spherical PbSe quantum dots (Q-PbSe) at energies far above the band gap and at the first exciton transition. Q-PbSe has been studied intensely since the development of high quality

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synthesis routes (producing either Q-PbSe doped glasses[7] or a colloidal suspension[8]), but no report on its molar extinction coefficient has been published yet. At high energy, we find that ϵ scales with the nanocrystal volume. Therefore, the absorbance at high energies provides a convenient way to determine nanocrystal concentrations irrespective of size dispersion. From the energy integrated extinction coefficient at the band gap, we can calculate the oscillator strength of the first exciton transition. The resulting quantitative values and their approximately linear increase with size correspond well with theoretical values obtained by tight-binding calculations. We have based the calculations of the nanocrystal concentration on absolute Pb and Se concentrations of digested Q-PbSe suspensions, as determined by inductively coupled plasma mass spectrometry (ICP-MS). The absorption spectrum of the suspensions was measured by UV–vis−NIR spectrophotometry, and the nanocrystal size was determined with transmission electron microscopy (TEM). The ICP-MS measurements show that colloidal PbSe quantum dots exhibit a systematic excess of lead. We demonstrate that this Pb excess quantitatively agrees with a nanocrystal model featuring a stoichiometric core and a Pb surface termination.

Experimental Section

Materials. Lead acetate trihydrate (99.999%), carbon tetrachloride (99.9%, CCl4), and dibromomethane (99+%, CH_2Br_2) were purchased from Sigma-Aldrich. Selenium powder (−200 mesh, 99.999%) was purchased from Alfa-Aeasar. Tri-*n*-octyl phosphine (97%, TOP) was purchased from STREM Chemicals. Oleic acid (>98%, OA) was purchased from Fluka. Diphenyl ether (DPE), methanol, butanol, and toluene were all of quality “for synthesis”; concentrated (65%) nitric acid (HNO_3) was of quality “normatom ultrapure”. These products were ordered from VWR. Deuterated toluene (99.96% deuterated, toluene-d_8) was purchased from CortecNet.

Q-PbSe Synthesis. Monodisperse colloidal PbSe nanocrystal suspensions with mean sizes from 3 to 8 nm were synthesized using an optimized version of the synthesis described by Murray et al.[8] The entire procedure was performed in a nitrogen filled glovebox. Two precursor solutions were prepared: 0.19 g of lead acetate trihydrate was dissolved in a mixture of 5 mL of DPE and 640 μL of OA (flask 1); 0.11 g of selenium was dissolved in 1.43 mL of TOP (flask 2). Both flasks were left stirring at 130 °C to form lead oleate (Pb|OA) and TOPSe, respectively, and were cooled down to room temperature after 1 h. Afterward, they were thoroughly mixed and subsequently injected into 5 mL of DPE at 160 °C. After injection, the temperature dropped to 120 °C, at which the reaction was allowed to continue for 0.5–10 min (a longer growth time leads to larger particles). The reaction was quenched with an excess of butanol and methanol. After centrifugation and redispersing the precipitated nanocrystals, the suspension was washed again with an excess of methanol to completely remove unreacted Pb or Se. The nanocrystals were finally dissolved in toluene.

Assessment of the Sample Purity. The absence of unreacted precursors was demonstrated by proton and phosphorus nuclear magnetic resonance spectroscopy (^{1}H and ^{31}P NMR). A Q-PbSe suspension in toluene was dried under a strong nitrogen flow, after which the dry precipitate was suspended in 750 μL of toluene-d_8. To identify unreacted Pb and Se in the Q-PbSe suspension, a solution of lead oleate in toluene-d_8 and a solution of TOPSe in toluene-d_8 were also prepared. The NMR spectra were measured at 295 K using a Bruker DRX 500 spectrometer equipped with a TBI Z-gradient probe head. Absolute concentrations of all organic species were determined by adding a known amount (2 μL) of CH_2Br_2 to the Q-PbSe suspension. To ensure that the area under each resonance in the spectrum corresponds exactly to the concentration of the respective protons in the sample, we applied a sufficiently long delay d_1 between scans in the experiment (the sum of d_1 and the acquisition time AQ has to be as long as five times the T_1 relaxation rate for a 99% signal recovery). We measured the T_1 relaxation rates of all species of interest (lead oleate, TOPSe, CH_2Br_2, and the resonances in the Q-PbSe suspension) using the “T_1 inversion–recovery” sequence and chose $d_1 =$ 45 s to fulfill the condition $d_1 + \mathrm{AQ} > 5T_{1,\max}$, with $T_{1,\max}$ being the maximal relaxation rate measured over all samples and resonances. To assess the TOP/TOPSe ratio in the Q-PbSe suspension, ^{31}P NMR spectra were measured.

Q-PbSe Size Determination. The mean size of the Q-PbSe suspensions was determined with a JEOL JEM-2200FS transmission electron microscope with Cs corrector for the objective lens. Samples were prepared by briefly dipping a TEM-grid in a 0.5 μM Q-PbSe suspension and letting it dry under ambient conditions. A Z-filter was used to obtain images with a higher contrast for the size determination. Depending on the sample, the size of 130–400 nanocrystals was determined by measuring the nanocrystal area and assuming a spherical particle. The average size of each set then represents the mean size of the Q-PbSe suspension.

Determination of the Q-PbSe Composition and Concentration. ICP-MS samples were prepared by drying a known amount of Q-PbSe under a strong nitrogen flow and digesting them in 10 mL of HNO_3. ICP-MS measurements were performed with a PerkinElmer SCIEX Elan 5000 inductively coupled plasma mass spectrometer. We determined both the Pb and the Se concentrations in our samples, from which the Pb/Se ratio was calculated. By combining the ICP-MS results with detailed modeling of the nanocrystals, the Q-PbSe composition was determined. The concentration of the samples was determined from the mean size and composition of the nanocrystals and the Pb and Se concentration, as measured with ICP-MS.

Absorbance Measurements. Identical amounts of Q-PbSe as used for the ICP-MS measurements were dried under a strong nitrogen flow, after which the dry powder was dissolved in 1 mL of CCl_4. The absorbance spectra were measured with a Varian Cary 5000 UV–vis−NIR spectrophotometer. We used a black walled self-masking microcell with a path length of 1 cm. These cells ensure a linear relation between the absorbance and the concentration, even at high absorbances. From the combination of the Q-PbSe concentration, determined with ICP-MS, and the absorbance, the molar extinction coefficient ϵ was determined.

Results and Discussion

X-ray diffraction and high resolution TEM images confirmed the formation of facetted quasi-spherical, crystalline particles (Figure 1a) with low size dispersion. The lattice constant $a = 6.126$ Å proved to be identical to that of bulk PbSe. By relating the TEM diameter to the energy E_0 (eV) of the first exciton transition measured with absorbance

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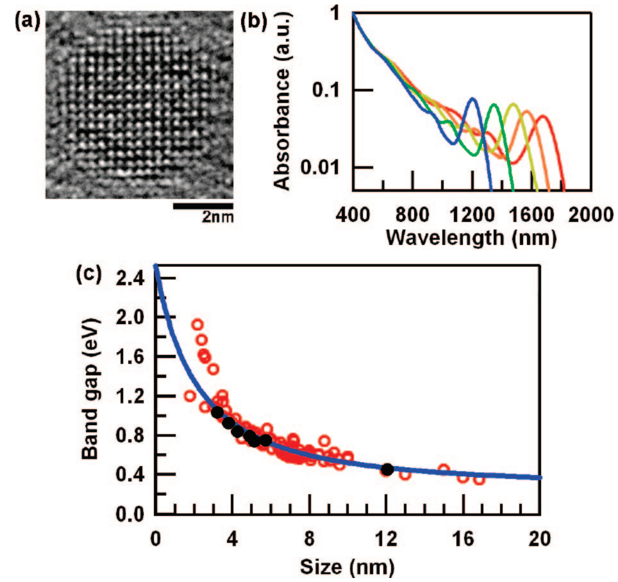

Figure 1. (a) High resolution TEM image of a quasi-spherical, facetted PbSe nanocrystal. (b) Normalized absorbance spectra of the five samples used for the determination of the Q-PbSe concentration. At low wavelengths, all spectra coincide, while a strong blue shift with decreasing size is observed for the first optical transition. (c) The sizing curve relates the optical band gap E_0 to the Q-PbSe diameter d as measured with TEM (dots, our data; open circles, literature data). An empirical fit allows us to determine the size from the spectral position of the first optical transition.

spectroscopy (Figure 1b), we constructed a sizing curve based on our data and data from literature.[7–14] This curve is used for the determination of the mean particle size d (nm) in our experiments. Considering that the band gap E_0 can be determined very precisely from absorbance measurements, using the size obtained from the sizing curve is more accurate than using the size from our TEM measurements. The fit yielded the following result (valid in the range 2–20 nm, Figure 1c):

$$E_0 = 0.278 + \frac{1}{0.016d^2 + 0.209d + 0.45}$$

In accordance with theoretical calculations,[15] E_0 varies mainly with $1/d$.

Prior to the ICP-MS measurements, the purity of a typical Q-PbSe sample was assessed. The maximal relaxation rate $T_{1,\max}$ measured (9.5 s) corresponded to the CH_2Br_2 resonance, and a ^1H NMR spectrum under quantitative conditions (d_1 + AQ = $5T_{1,\max}$) was measured for TOPSe, lead oleate, and a Q-PbSe suspension. Figure 2 compares the three spectra. The sharp multiplet at 5.46 ppm in the lead oleate NMR spectrum, corresponding to the olefinic protons of OA, is not observed in the Q-PbSe NMR spectrum. We observe a broad signal at 5.67 ppm lacking any fine structure, but this resonance corresponds to the OA ligands attached to the nanocrystals. The absence of the olefinic signal allows us to conclude that we have no free lead oleate (and therefore no unreacted Pb atoms) in our sample. The NMR spectrum of TOPSe and the Q-PbSe both show a sharp triplet at 0.92 ppm, corresponding to the methyl protons of TOPSe. As we cannot distinguish between TOP and TOPSe in a ^1H spectrum, we measured the ^{31}P spectrum of the Q-PbSe suspension. TOP has a ^{31}P resonance at −20 ppm, while TOPSe has a resonance around 35 ppm.[16] We observed a single resonance at 35.3 ppm, allowing us to conclude that we have only free TOPSe in our Q-PbSe suspension and no TOP. From the ratio of the area under the 0.92 ppm resonance in the ^1H spectrum and the area under the 3.93 ppm resonance, corresponding to CH_2Br_2, we then calculated a TOPSe concentration of 168 μM. We know from our own experience and the report of Steckel et al.[16] that the reaction yield of the Q-PbSe synthesis is rather low. Estimating a reaction yield of 2%, we calculated that for the NMR sample, the concentration of Se atoms incorporated in the nanocrystals corresponds to 38.4 mM. Comparing this value with the measured TOPSe concentration, we conclude that the fraction of unreacted Se does not exceed 0.44% of the total Se concentration in the sample. As this value falls well below the 5% uncertainty on the determination of the Se concentration with ICP-MS, the concentration of residual Se in our samples can be safely neglected.

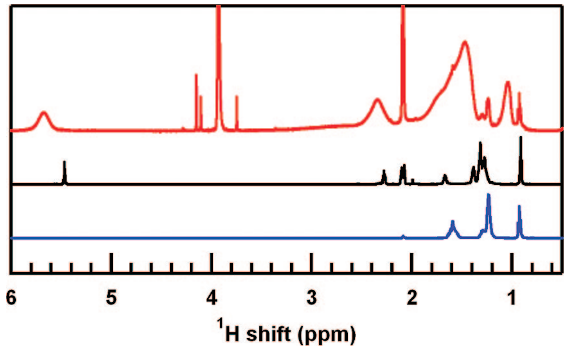

Figure 2. ^1H NMR spectra of a Q-PbSe suspension (top), lead oleate (middle), and TOPSe (bottom) in toluene-d_8, measured under quantitative conditions (d_1 = 45 s). Comparison of the different spectra allows us to conclude we have no unreacted lead in our Q-PbSe suspension (the sharp multiplet at 5.46 ppm in the lead oleate spectrum is not observed in the Q-PbSe spectrum), while the concentration of unreacted Se does not exceed 0.44% of the total Se concentration.

To determine nanocrystal concentrations, a nanocrystal suspension is often digested using a strong acid, after which the anion or cation concentration is obtained by quantitative elemental analysis. So far, reported results on binary semiconductor nanocrystals have been based on the measurement of a single compound, under the assumption of a stoichiometric nanocrystal.[1–4] Recent experiments however have shown that colloidal nanocrystals can be nonstoichiometric. Jasieniak et al.[17] have manipulated the CdSe nano-

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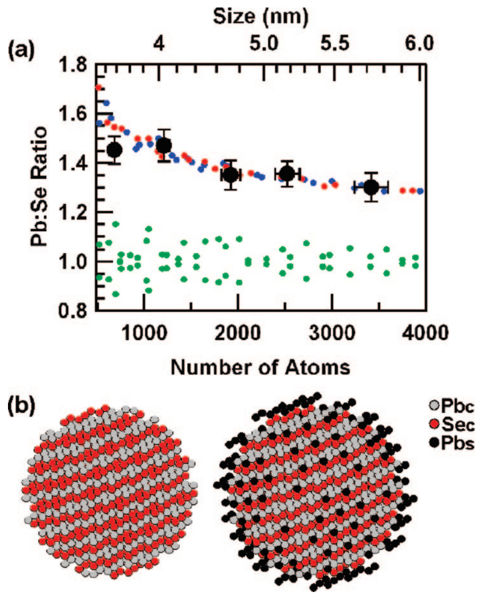

Figure 3. (a) The experimental Pb/Se ratio (black dots) can be calculated using a faceted spherical, "Pb terminated" nanocrystal model. Q-PbSe with a central Se atom (blue dots) and a central Pb atom (red dots) yields similar results. Before Pb termination, nanocrystals show a stoichiometry which is scattered around 1 (green dots). (b) Schematic representation of the quasi-spherical Q-PbSe quantum dot model, before (left) and after (right) Pb termination of the nanocrystal surface.

Table 1. Q-PbSe size d, Pb and Se weight concentrations C_{Pb} and C_{Se} (as obtained by ICP-MS measurements), calculated nanocrystal concentration $C_{\text{Q-PbSe}}$ and corresponding absorbance at 400 nm A_{400} of the suspensions used.

d (nm)	C_{Pb} (mg/l)	C_{Se} (mg/L)	$C_{\text{Q-PbSe}}$ (μM)	A_{400} (cm^{-1})
3.3	6.00	1.57	0.072	0.766
4.1	4.90	1.27	0.033	0.663
4.7	8.94	2.52	0.039	1.093
5.2	9.53	2.68	0.032	1.246
5.7	13.2	3.88	0.033	1.688

crystal surface, yielding nonstoichiometric quantum dots with a surface enriched in Cd or Se. Using X-ray photoelectron spectroscopy, Guzelian et al.[18] have determined an In/P ratio of 0.86:1 for InP nanocrystals. ICP-MS measurements performed on colloidal InAs nanocrystals[3] have shown a systematic In excess present in the samples. This was however not attributed to the nanocrystals but rather regarded as a result of the incomplete removal of the In precursor. To study the nanocrystal stoichiometry and accurately calculate the Q-PbSe concentration, we consequently relied on both the selenium and the lead concentration. From the absolute weight concentrations obtained by ICP-MS, the Pb/Se ratio can be determined as

$$R = \frac{C_{\text{Pb}}M_{\text{Se}}}{C_{\text{Se}}M_{\text{Pb}}}$$

with C_{Pb} and C_{Se} being the weight concentration of the respective atoms and M_{Pb} (207.2 g/mol) and M_{Se} (78.96 g/mol) being the molar mass. Table 1 summarizes the ICP-MS data obtained for five different Q-PbSe suspensions. The nanocrystals did not show a 1:1 Pb/Se ratio (Figure 3a, black dots). A systematic excess of lead was observed, scaling with the Q-PbSe surface area. To interpret our results, we counted the number of Pb and Se atoms in faceted spherical quantum dot models (Figure 3b). Starting from a central Pb or Se atom, we added subsequent shells of neighboring atoms until a desired size was reached. The total number of atoms A is related to the Q-PbSe size through (assuming a spherical particle):

$$A = \frac{4\pi}{3}\left(\frac{d}{a}\right)^3$$

Although not exactly stoichiometric, the Pb/Se ratio was scattered around 1 (Figure 3a, green dots) over the entire size range studied. In a second step, we added Pb atoms until each surface Se atom of a given nanocrystal was bonded to six Pb neighbors. For these "Pb terminated" nanocrystals (Figure 3b), the stoichiometry of the Q-PbSe models corresponded to the observed Pb/Se ratio (Figure 3a, blue and red dots). We conclude that a realistic model for colloidal Q-PbSe consists of a faceted spherical nanocrystal, with a central Pb or Se atom and composed of a quasi-stoichiometric PbSe core terminated by a Pb surface shell.

Combining size, shape, and composition of the Q-PbSe with the measured Pb and Se concentration, the nanocrystal concentration $C_{\text{Q-PbSe}}$ (10^{-6} mol·L^{-1}, μM) of the ICP-MS samples is given by (Table 1)

$$C_{\text{Q-PbSe}} = \frac{10^3}{A}\left(\frac{C_{\text{Pb}}}{M_{\text{Pb}}} + \frac{C_{\text{Se}}}{M_{\text{Se}}}\right)$$

When measuring the absorbance of an identical amount of Q-PbSe as for the ICP-MS measurements, the molar extinction coefficient ϵ can be determined from the Beer–Lambert law. At photon energies far above the band gap, ϵ scales with the volume of the nanocrystals. At 3.1 eV (λ = 400 nm), it is given by

$$\epsilon_{3.1\text{eV}} = (0.0277 \pm 0.0005)d^3 \text{ cm}^{-1}/\mu\text{M}$$

with d in nm (Figure 4a). This relation allows for the convenient determination of the nanocrystal concentration of a suspension with a known absorbance spectrum (the Q-PbSe size can be obtained from the same absorbance spectrum through the sizing curve). Dividing $\epsilon_{3.1\text{eV}}$ by Avogadro's constant and the nanocrystal volume yields a size independent absorption coefficient $\mu_{3.1\text{eV}} = 2.062 \times 10^5$ cm^{-1} (Figure 4d, bottom trace). This shows that only the number of PbSe units present, and not the size of the nanocrystals, determines the extinction coefficient of a Q-PbSe suspension at these photon energies. This result was already apparent in Figure 1b, where at low wavelengths (high photon energies), the normalized absorbance spectra all coincide. This suggests that the Q-PbSe optical properties are size-independent at these wavelengths. Hence, using $\epsilon_{3.1\text{eV}}$, Q-PbSe concentrations can be determined irrespective of size dispersion.

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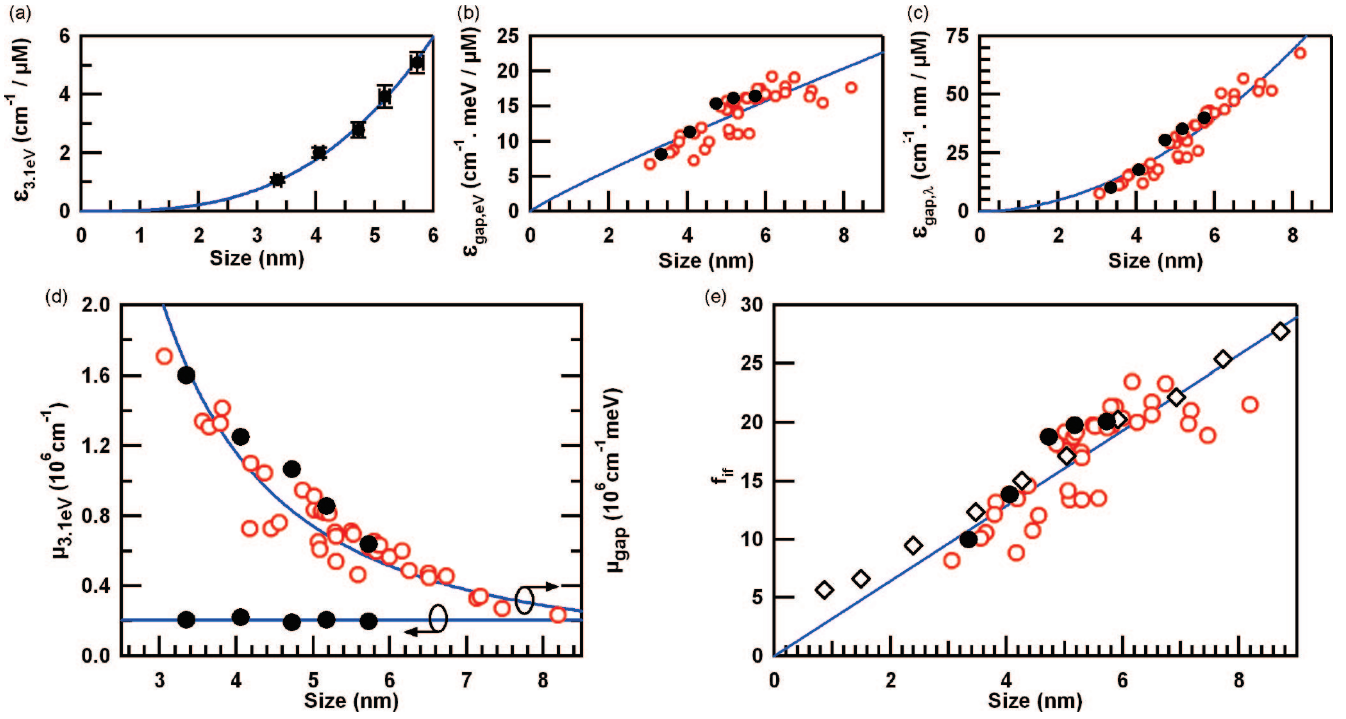

Figure 4. (a) At high photon energies, the molar extinction coefficient scales with the nanocrystal volume. (b, c) At the band gap, one can calculate an energy integrated molar extinction coefficient which scales linearly with the Q-PbSe size (b) or a wavelength integrated molar extinction coefficient which varies quadratically with the Q-PbSe size (c). Consequently, depending on the method used, a different size dependence can be found. (d) The absorption coefficient is independent of nanocrystal size at high photon energies (bottom dots), while an inverse quadratic dependence on the size is observed for the energy integrated absorption coefficient at the band gap (top dots and open circles). (e) The oscillator strength f_{if} increases linearly with nanocrystal size (dots and open circles), in close agreement with theoretical tight binding calculations (open diamonds).

Ricard et al.[19] derived an expression for the absorption cross section C_{th} of small spherical particles in a dielectric host (at a wavelength λ):

$$C_{th} = \frac{2\pi}{n_s\lambda}|f_{LF}|^2 2nk\frac{\pi d^3}{6}$$

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

f_{LF} denotes the local field factor. From the absorption cross section, the absorption coefficient μ_{th} is calculated by dividing C_{th} by the nanocrystal volume. Using bulk PbSe optical constants[20] (refractive index $n = 2.55$ and extinction coefficient $k = 4.11$) and the refractive index for CCl_4 $n_s = 1.46$, we calculated a theoretical absorption coefficient $\mu_{th} = 1.934 \times 10^5$ cm^{-1}, a value only 6% smaller than the experimentally observed one. The good agreement with the experimental value again indicates that high energy photon probe transitions between states that are essentially unaffected by quantum confinement. Our results are in line with data for InAs[3] and CdSe[6] nanocrystals, where measured absorption cross sections at high photon energy were also in good agreement with bulk values.

Literature data[1–6,21] are less consistent with respect to the molar extinction coefficient at the band gap. Expanding the procedure used by Cademartiri et al.,[4] we calculated an energy integrated molar extinction coefficient $\epsilon_{gap,eV}$ for the first exciton transition by doubling the integrated low energy half of the first absorption peak. By using the integrated value instead of the peak absorbance, we avoid the need to calibrate the absorbance for samples with markedly different size dispersions.[1] Furthermore, for the calculation of the oscillator strength, we can rely on the total Q-PbSe concentration when using an integrated molar extinction coefficient (see Supporting Information). Figure 4b shows the size-dependence of the energy integrated molar extinction coefficient, for the ICP-MS samples (dots) and samples for which we calculated the concentration using the molar extinction coefficient $\epsilon_{3.1eV}$ (open circles). Fitting a power law through the experimental data yields (d in nm)

$$\epsilon_{gap,eV} = 3.1d^{0.9}\ (\text{cm}^{-1}\ \text{meV})$$

As the error on the exponent is equal to 0.1, we can conclude that an approximately linear increase of $\epsilon_{gap,eV}$ with size is found. As an alternative, one could take the wavelength as the variable of integration. Because the absorbance peak is narrow, the resulting wavelength integrated extinction coefficient, $\epsilon_{gap,\lambda}$ is related to $\epsilon_{gap,eV}$ through the sizing curve E_0:

$$\epsilon_{gap,\lambda} = \frac{hc}{eE_0(d)^2}\epsilon_{gap,eV}$$

As confirmed by Figure 4c, the above relation implies that $\epsilon_{gap,\lambda}$ and $\epsilon_{gap,eV}$ have a different size dependence. This shows that the different results on the size dependence of the molar extinction coefficient reported in the literature[1–6,21] may be due to the method used to calculate it. From $\epsilon_{gap,eV}$, the (energy) integrated absorption coefficient μ_{gap} was derived

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in a similar way as $\mu_{3.1\mathrm{eV}}$. The top trace of Figure 4d shows μ_{gap} as a function of size. In contrast with the absorption coefficient at high energy, μ_{gap} is not size-independent. A one-parameter fit yields

$$\mu_{\mathrm{gap}} = 1.85 \times 10^7/d^2\ (\mathrm{cm}^{-1}\ \mathrm{meV})$$

with d in nm. As μ_{gap} increases with decreasing size, it follows that smaller particles are more efficient (resonant) absorbers. From the energy integrated absorption coefficient μ_{gap}, the oscillator strength per particle f_{if} of the first optical transition can be calculated as (Figure 4e, dots and open circles)

$$f_{\mathrm{if}} = \frac{2\epsilon_0 n_{\mathrm{s}} c m_{\mathrm{e}}}{e\pi\hbar} \frac{1}{|f_{\mathrm{LF}}|^2} \frac{\pi d^3}{6} \mu_{\mathrm{gap}}$$

ϵ_0 denotes the electric constant and m_{e} the electron mass. We estimated f_{LF} using $n = 5.2$ and $k \ll n$ and found values in the range 8–25, depending on quantum dot size. The fact that f_{LF} exceeds 1 for Q-PbSe does not violate the Thomas−Reiche−Kuhn sum rule. First, the upper valence band level of Q-PbSe is 8-fold degenerate, which means that summing the oscillator strength over all final one-electron states should give a value of 8. Second, the upper valence band level is not the lowest energy one electron state. As a consequence, the Thomas−Reiche−Kuhn sum contains negative terms as well, and the value of an individual oscillator strength may exceed the sum of all oscillator strengths. The experimental results show a good agreement with tight binding calculations of the oscillator strength[15] (Figure 4e, open diamonds). While the effective mass approximation predicts a size-independent oscillator strength per particle,[22,23] we find that f_{if} scales linearly with nanocrystal size.

Conclusions

In conclusion, we determined the molar extinction coefficient, corresponding absorption coefficient, and oscillator strength of colloidal PbSe quantum dots by combining ICP-MS, TEM, and UV–vis−NIR spectrophotometry. Our results show that PbSe quantum dots are nonstoichiometric, consisting of a quasi-stoichiometric core terminated by a Pb surface shell. This nonstoichiometry of Q-PbSe is of interest for theorists, who rely on realistic structural quantum dot models for opto-electronic properties calculations. At photon energies well above the first exciton transition, we find a size-independent absorption coefficient. This implies that the molar extinction coefficient at high energies enables a straightforward determination of quantum dot concentrations from the absorbance spectrum, irrespective of size distribution. At the first exciton transition, the energy integrated absorption coefficient increases quadratically with decreasing particle size. This leads to an oscillator strength that increases approximately linearly with size, in quantitative agreement with tight binding calculations.

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Supporting Information Available: Detailed calculation of the oscillator strength f_{if} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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