

Reply to “Comment on ‘Size-Dependent Composition and Molar Extinction Coefficient of PbSe Semiconductor Nanocrystals’”

■ We acknowledge (as we did in our above-entitled paper¹) that Moreels *et al.*² have done an excellent job in determining the nonstoichiometric composition of PbSe quantum dots (QDs). Starting from that point, the contributions in our paper¹ were as follows:

1. We confirmed the nonstoichiometric compositions of PbSe QDs, using three different synthesis methods from different laboratories.
2. We found that such nonstoichiometric compositions were strongly size-dependent.
3. In order to calculate the exact numbers of Pb and Se atoms for any size of PbSe QDs, we introduced a model (Figure 3 and eqs 3–6 in ref 1), which has the fewest theoretical assumptions. Through this model, we found that there was almost a monolayer of Pb atoms on each QD surface, but that this was not closely packed.
4. On the basis of the above results (especially the calculation of the exact numbers of Pb and Se atoms in one particle), we calculated the molar extinction coefficients of PbSe QDs strictly following the Lambert–Beer law using the data from the peak value of the first exciton absorption, which was found to be strongly size-dependent with a power law with exponent of ~ 2.54 .
5. We tested the accuracy of this power law through controlled particle etching. Such experiments are direct and decisive.³

One of the reasons to investigate the molar extinction coefficients of PbSe QDs is that we believe one should use n (the numbers of Pb and Se atoms in one particle based on a nonstoichiometric model)¹ rather than A (the numbers of Pb and Se atoms based on a stoichiometric model)² to count the atom numbers in a particle, which is the prerequisite to finding QD particle concentration in solution and subsequently the molar extinction coefficient for that particle size. This is an important difference between our paper¹ and the paper by Moreels *et al.*² The final values of the exponent vary from 1.6 (extracted from ref 2 by us), 2.07 (presented in the Letter from Moreels *et al.*), and 2.54 (our paper¹). From a chemical point of view, we think these are significantly different.⁴

Using the absorption coefficient for short wavelengths (*e.g.*, 400 nm in ref 2) may be theoretically possible for very pure samples, but the resulting calculated particle concentrations can be greatly affected by the absorbance contributions from organic ligands and/or unexpected impurities including other organic components and some small or different types of particles in practical systems at such short wavelengths.⁵ For this reason, we recommend using the molar extinction coefficient at the band gap which involves minimal or no contributions from unwanted scattering/absorption.

Moreels *et al.* also commented that we used “integration or normalization on a wavelength scale”. We want to clarify that we used the data from the peak values of the first exciton absorption peaks. This is what the Lambert–Beer law requires. Similar treatments have also been adopted in determining the molar extinction coefficients of CdS, CdSe, CdTe,³ and PbS⁶ QDs. The integration is necessary when we need

to consider the size distribution contributions since not all syntheses produce monodisperse size distributions. This is done through the comparison of the half-width at half-maximum (hwhm) to the long wavelength side of the first exciton absorption peak.¹ Integration from the peak wavelength to the long wavelength side generally gives similar or the same results as the one using hwhm. The reason we do not integrate the shorter wavelength side (from the peak wavelength) stems from the same consideration of eliminating any unwanted/unknown absorption from impurities; this not only simplifies the concentration calculation but also makes it more accurate. For absorption measurements, wavelength is widely used in chemistry, providing data on a wavelength scale is easily recognized by researchers in the field.

In conclusion, we found strong size-dependent compositions for PbSe QDs. Based on that and the model with the fewest assumptions, we obtained a series of size-dependent molar extinction coefficient data for PbSe QDs. Our work¹ goes beyond a simple reproduction of previously published results. Instead, we followed the requirements of the Lambert–Beer law and the strict error control of analytical chemistry and, especially, used n but not A for calculating the number of atoms in one particle, even though such changes may not lead to significant differences in the final results.

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