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Comment on “Size Dependent Optical Properties and Structure of ZnS Nanocrystals Prepared from a Library of Thioureas”

Tangi Aubert, Aleksandr A. Golovatenko, Anna V. Rodina, Zeger Hens

In their recent article, Owen et al. published a new dataset for ZnS quantum dots, linking optical band gap with nanocrystal diameter[1]. Such bandgap/size datasets have been very helpful in the field of quantum dots to build calibration or sizing curves. These sizing curves are widely used to quickly determine nanocrystal sizes from absorption measurements, and they have been reported for a large variety of materials. The sizing of ZnS quantum dots, however, has always suffered from the low contrast this material provides in bright field transmission electron microscopy (TEM), which is the most common technique for measuring nanocrystal dimensions. In this regard, the work presented by Owen and coworkers is remarkable, both from a synthesis and a characterization perspective. Quasi-spherical ZnS quantum dots are formed across a broad diameter range, and sized by high-angle annular dark-field scanning transmission electron microscopy (STEM) and pair distribution function (PDF) analysis of X-ray scattering. On the other hand, the optical band gap of the nanocrystals was determined from their UV-vis absorption spectra as it is routinely done for this purpose. Finally, the authors fitted their dataset using a function that adds the inverse of a second-order polynomial to the bulk band gap energy.

Although this type of function may fit well experimental data and provide reliable size calibration within the limits of the fitted data range, we recently pointed out the limitations of this approach, which often makes use of several adjustable parameters without physical meaning[2]. To address this shortcoming, we proposed a general expression to describe size quantization in semiconductor nanocrystals, in an effort to standardize nanocrystal size determination based on optical band gap measurements[2]. We validated this expression for ten different materials, including Cd and Pb chalcogenides (CdS, CdSe, CdTe, PbS, PbSe and PbTe), a III-V semiconductor (InP), indirect (Si) and negative (HgTe) band gap materials, and non-spherical nanocrystals (cube-shaped $CsPbBr_3$). Thanks to the extensive dataset from Owen et al., we can now show that this model is in good agreement with the experimental data for ZnS as well, and we provide here a sizing curve for ZnS in line with this standardized approach.

The initial motivation to develop a general, analytical expression for a sizing function was the need for meaningful extrapolations outside of experimental data ranges. To this end, we considered the expected behavior at small and large diameters, and integrated a correction for the impact of nonparabolic energy bands on the quantum dot band gap. This ultimately led to a parameter-free model, capable of predicting the optical band gap (E_1), as a function of the nanocrystal diameter (d), based on bulk semiconductor parameters only:

$$E_1(d) = \frac{1}{2}\left[E_0 + \sqrt{E_0^2 + 8|E_0|\alpha\pi^2 \frac{R_y a_0}{\varepsilon_\infty d_0} \frac{e^{-\frac{d}{d_0}}}{\left(1-e^{-\frac{d}{d_0}}\right)^2}}\right] \tag{1}$$

Here, E_0 is the bulk optical band gap, which is the difference between the single-particle gap E_g and the exciton binding energy E_{ex}, R_y the Rydberg constant (13.606 eV), a_0 the Bohr radius of hydrogen (0.053 nm), ε_∞ the high-frequency dielectric constant of the material, and d_0 is seen as the largest diameter where strong quantization dominates. For consistency between different materials, d_0 was systematically identified with the exciton Bohr diameter, calculated using the high-frequency dielectric constant:

$$d_0 = 8\pi \frac{\varepsilon_\infty \varepsilon_0 \hbar^2}{\mu m_0 e^2} \tag{2}$$

In Eq 2, ε_0 is the vacuum permittivity, $\hbar$ the reduced Planck constant, m_0 the free electron mass, e the elementary charge, and μ the reduced effective mass of an electron-hole pair. In the process of establishing Eq 1, α was initially introduced to compensate for approximations made in the calibration procedure. Our study of the ten aforementioned materials later showed α to be material independent, and a single value α = 0.7 was determined, although the physical meaning of this factor remains unclear.

Table 1. Physical parameters and fit results for ZnS. Room temperature values of the parameters were used by default when available. When multiple values were reported, averaged or rounded values were used.

parameter	**ZnS**[a]
E_g (eV)	3.763[3]
E_{ex} (eV)	0.037[3]
E_0 (eV)	3.726
ε_∞	5.3[3]
m_e (m_0)	0.27[3]
m_h (m_0)[b]	2.0[3]
d_0 (nm)	2.3
E_{fit} (eV)	0.679
d_{fit} (nm)	2.0

[a] average between zinc blende and wurtzite values.
[b] density-of-states heavy-hole values were used for m_h.

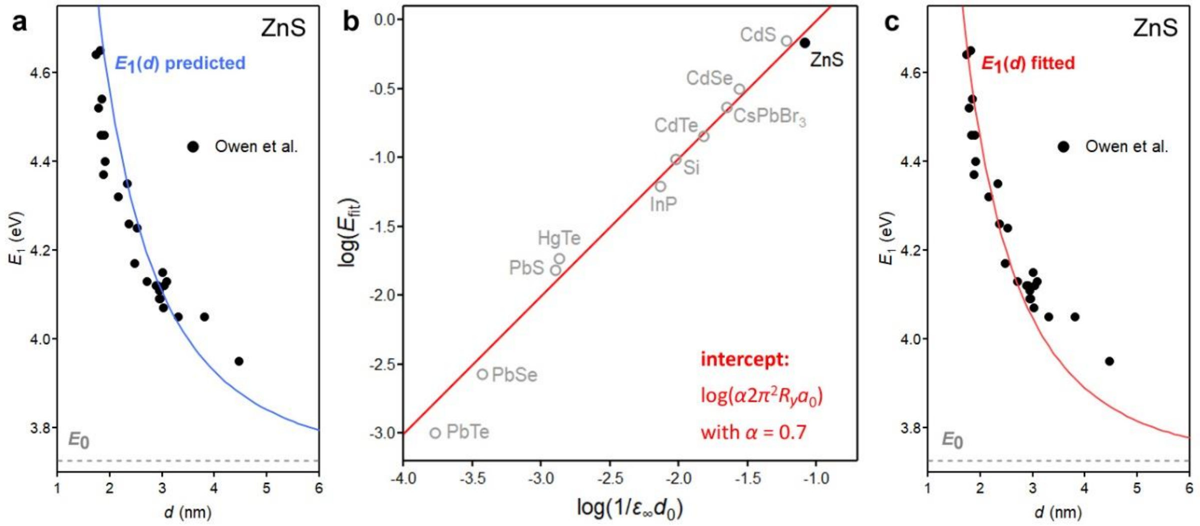

Figure 1. (a) Optical band gap energy predicted by Eq 1 for ZnS (blue continuous line), and compared to the experimental data from Owen et al.[1]. (b) Log–log representation of E_{fit} as a function of $1/\varepsilon_\infty d_0$, comparing the new value obtained for ZnS (full black marker) with the materials investigated in our previous work (open grey markers)[2]. The red line depicts the linear regression with α = 0.7. (c) Optical band gap energy obtained as best fit of Eq 4 to ZnS dataset (red continuous line), which resulted in a d_{fit} value of 2.0 nm. In (a) and (c), only the data used by Owen et al. in their sizing curve fit are shown. The bulk optical band gap is indicated with gray dashed lines.

Inspired by the work published by Owen et al, we used Eq 1 to predict the optical band gap energy of ZnS nanocrystals using the parameters listed in Table 1. As shown in Figure 1a, the results show very good agreement with the dataset from Owen et al.. For this prediction, we used averaged parameters between the zinc blende and wurtzite phases of ZnS. As for CdSe[2], these two polymorphs can be difficult to discriminate in nanocrystals and even coexist within the same sample; a point noted by Owen et al. in their PDF analyses. Thus, using parameters that can approximate both polymorphs can be more relevant in practice.

While Figure 1a is already a good confirmation for the predictive power of our model, we can also use this additional dataset to verify the α value. To this end, the experimental data were fitted to the following expression:

$$E_1(d) = \frac{1}{2}\left[E_0 + \sqrt{E_0^2 + 4E_0E_{\mathrm{fit}}\frac{e^{-\frac{d}{d_0}}}{\left(1-e^{-\frac{d}{d_0}}\right)^2}}\right] \qquad (3).$$

Here, E_{fit} is the only adjustable parameter. The resulting value (Table 1) is plotted as a function of $1/\varepsilon_\infty d_0$ and compared to the other materials in Figure 1b. Interestingly, ZnS, being at the low dielectric constant/small Bohr diameter extreme of the materials set considered, still shows good agreement with the previously observed trend. In fact, a linear fit including all the materials in Figure 1b still yields a best fit value of $\alpha = 0.7$.

Despite the good correspondence between Eq 1 and the new bandgap/size data for ZnS, some of the bulk semiconductor parameters used to calculate E_1 through Eq 1 are not always accurately known. This holds true in particular for the Bohr diameter, whose calculation involves multiple parameters that each have their own uncertainties. Thus, in order to further improve the sizing curve, d_0 is replaced by an adjustable parameter d_{fit} in our general expression:

$$E_1(d) = \frac{1}{2}\left[E_0 + \sqrt{E_0^2 + 8|E_0|\alpha\pi^2\frac{R_y a_0}{\varepsilon_\infty d_{\mathrm{fit}}}\frac{e^{-\frac{d}{d_{\mathrm{fit}}}}}{\left(1-e^{-\frac{d}{d_{\mathrm{fit}}}}\right)^2}}\right] \qquad (4).$$

Fitting the experimental data of Owen et al. to Eq 4 (Figure 1c), yielded a d_{fit} of 2.0 nm, a figure very close to the calculated d_0 of 2.3 nm (Table 1). This result neatly illustrates the advantage of a sizing function that allows assessing bulk semiconductor parameters. In this regard, our results strongly suggest that ZnS has a relatively small Bohr diameter, smaller than the value of 5 nm that is often mentioned in the literature[1]. In practice, sizing curves are mostly used to determine the nanocrystal diameter from the optical band gap. To this end, Eq 4 can be inverted to the following expression of the sizing curve:

$$d(E_1) = d_{\mathrm{fit}} ln\,\frac{x(E_1)+1}{x(E_1)-1} \quad with \quad x(E_1) = \sqrt{1 + 2\varepsilon_\infty d_{\mathrm{fit}}\frac{E_1(E_1-E_0)}{\alpha\pi^2 R_y a_0|E_0|}} \qquad (4).$$

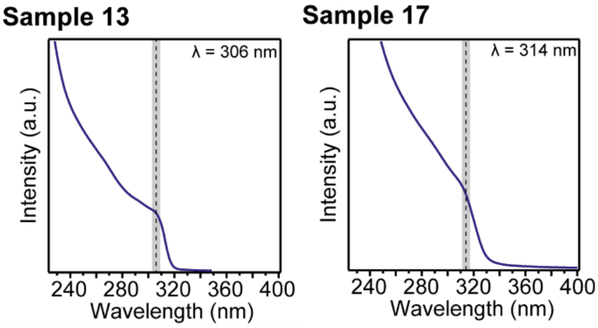

Figure 2. UV absorption spectra of the two largest samples used by Owen et al. in their fit, and the position of their extracted first optical transition (reproduced from the Supporting Information of ref. [1]).

As a final point, Figures 1a and 1c show that both in the case of the prediction with Eq 1 and the fit with Eq 4, the experimental sizes for the two largest samples deviate significantly from the predicted sizing curve. Possibly, this problem results from the way the optical band gap of quantum dots is routinely obtained from absorption spectra. To illustrate the issue, Figure 2 reproduces the UV absorption spectra of these two largest samples as provided by Owen et al. As can be seen, both spectra lack a clear feature, such as a Gaussian peak, that helps identifying the band gap. Hence, transition energies estimated from such spectra will only provide a rough estimate of the band gap. If done systematically, such energies can still be used for the purpose of size calibration, but one should take care calling such values the optical band gap. In fact Owen et al. had to treat the bulk optical band gap as an adjustable parameter in order to fit their experimental results. This point is well illustrated here for ZnS, which has a very small Bohr diameter, but the same holds true for other close-to-bulk nanocrystals of, for instance, CdSe or InP. This point hints at an intrinsic limitation of sizing curves, and could motivate the search for a more systematic approach to experimentally determine optical band gaps as well. On the other hand, one could also consider reverting the approach and use an experimentally determined nanocrystal size, e.g. by TEM, to estimate its band gap based on our model.

In conclusion, we found that the band gap/size dataset recently published by Owen et al. is in good agreement with the predictions of the parameter-free sizing curve we published recently. Best agreement is obtained for a refined Bohr diameter of 2.0 nm, a figure considerably smaller than often published values of 5.0 nm, but close to values calculated using bulk parameters in-between those of zinc blende and wurtzite ZnS. This correspondence provides additional validation of our generalized approach to quantum dot sizing curves, and we therefore believe that the optimized parameters reported here for size quantization in ZnS can be valuable to spread a standardized approach to sizing curves in quantum dot studies.

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