The absorption coefficient of PbSe/CdSe core/shell colloidal quantum dots

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PbSe/CdSe core/shell colloidal quantum dots (QDs) are used as a model system to study the absorption coefficient of colloidal QD heterostructures, consisting of at least two semiconductor materials. We show that at energies far above the band gap (3.1 and 3.5 eV) the experimental intrinsic absorption coefficient is in excellent agreement with the Maxwell–Garnett effective medium theory for core/shell heterostructures and bulk values for the dielectric function. This allows for a straightforward measurement of the QD concentration from the absorbance spectrum. It also implies that basic optical measurements on core/shell heterostructures, such as measurements of the oscillator strength and photoluminescence lifetime, can be corrected for the local field reduction in QD heterostructures. © *2010 American Institute of Physics*. [doi:10.1063/1.3499754]

Colloidal quantum dot (QD) research is driven by the combination of tunable electronic and optical properties, depending on the size and shape of the QDs, and an easy, solution-based fabrication and processing. While QDs consisting of a single semiconductor with an organic ligand capping, show promising properties for applications in lasers, detectors, and solar cells,[1] their drawbacks, such as oxidation and fast Auger recombination, shifted the focus of the research field to QD heterostructures, combining at least two semiconductors in a core/shell nanocrystal.

Since colloidal QDs are made in a wet chemical synthesis, the basic characterization is mostly done on QDs suspended in an organic solvent. Because of their small size, the macroscopic optical properties of suspended QDs are determined both by the intrinsic optical properties and by the surrounding medium. This effect is typically described by the Maxwell–Garnett effective medium theory. The importance of this effect can hardly be underestimated, as it will alter the absorbance, the photoluminescence (PL) peak position and emission rate and the PL quantum yield,[2] depending on the surrounding medium or solvent. For example, Moreels *et al.*[3] used this theory to calculate the dielectric function of PbSe, PbS, and PbTe colloidal QDs and study the effect of quantum confinement on these elementary material properties. This effect is typically described by the local field factor f_{LF}, which is the ratio of the field inside the QD and the field in the surrounding medium.

Here, we analyze the effect of the effective medium on the absorbance (A) of core/shell PbSe/CdSe QDs, where not only the solvent but also the inorganic core/shell structure determines the local field factor. To quantify the spectrum of the absorbance (A), it is converted to the spectrum of the intrinsic absorption coefficient μ_i. For this, the QD volume fraction f and the cuvette length L are needed as follows:

$$\mu_i = \frac{\ln 10 \times A}{fL}. \tag{1}$$

The intrinsic absorption coefficient μ_i provides the characteristic decay length of the light intensity in a hypothetical medium with a QD volume fraction of one.

For PbSe,[4] PbS,[5] wurtzite and zinc blende CdSe,[6–8] InAs,[9] and ZnO[10] QDs, it was shown that at high energies (3.1 eV for PbSe and PbS, 3.54 eV for CdSe, 2.76 eV for InAs, and 5.0 eV for ZnO), μ_i is independent of the QD size. Moreover, it generally coincides with the theoretical value calculated using bulk optical constants and the Maxwell–Garnett effective medium theory as follows:[11,12]

$$\mu_i = \frac{2\pi}{\lambda n_s} Im(\epsilon_c) |f_{\mathrm{LF}}|^2. \tag{2}$$

Here, n_s is the solvent refractive index, ϵ_c and ϵ_s the complex dielectric function of the QD material and the solvent, respectively, and λ the wavelength. For spherical particles, the local field factor reads as follows:

$$f_{\mathrm{LF}} = \frac{3\epsilon_s}{\epsilon_c + 2\epsilon_s}. \tag{3}$$

The fact, that at short wavelengths a bulklike absorption coefficient is found, means that the electronic states at high energies are not quantum confined but form a continuum in these QDs. Hence the QD concentration [QD], an essential quantity to assess synthesis quality and to control deposition, can be determined as follows from the absorbance at high energies, irrespective of size dispersion, using the Beer–Lambert law and μ_i as calculated above:

$$[\mathrm{QD}] = \frac{A}{\epsilon L} = \frac{A \ln 10}{\mu_i N_A V_{\mathrm{QD}} L}. \tag{4}$$

Here N_A is Avogadro's constant and V_{QD} the volume of the QD.

For core/shell QDs, the formulas above cannot be applied directly, since the shell will alter the dielectric screening. An expression for the absorption coefficient of core/shell particles was proposed by Neeves *et al.*[13,14] If the volume fraction of core/shell particles in solution is small, it reads as follows:

$$\mu_i = \frac{2\pi}{\lambda n_s} Im(3\epsilon_s \beta),$$

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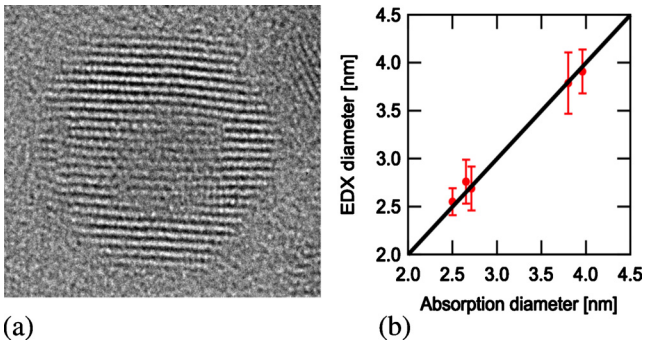

FIG. 1. (Color online) (a) HR-TEM image of a PbSe/CdSe core/shell QD, clearly showing the PbSe core and the CdSe shell. (b) Diameter determined from EDX vs diameter determined from the position of the first absorption peak, using the PbSe sizing curve. The black line indicates a 1-to-1 relationship (Ref. 4).

$$\text{with} \quad \beta = \left(\frac{\epsilon_{\text{sh}}\epsilon_a - \epsilon_s\epsilon_b}{\epsilon_{\text{sh}}\epsilon_a + 2\epsilon_s\epsilon_b} \right),$$

$$\epsilon_a = \epsilon_c \left(3 - 2\frac{V_{\text{sh}}}{V_{\text{QD}}} \right) + 2\epsilon_{\text{sh}}\frac{V_{\text{sh}}}{V_{\text{QD}}},$$

$$\epsilon_b = \epsilon_c \frac{V_{\text{sh}}}{V_{QD}} + \epsilon_{\text{sh}} \left(3 - \frac{V_{\text{sh}}}{V_{QD}} \right). \tag{5}$$

Here, ϵ_{sh} denotes the complex dielectric function of the shell. Importantly, μ_i becomes dependent on the ratio between the shell and the total QD volume for core/shell heterostructures. This is purely an effect of the change in the effective medium and not an effect of quantum confinement. Hence, to compare theory with experiment, a precise knowledge of the core diameter and shell thickness is essential for QD heterostructures.

We take the example of PbSe/CdSe QDs, made by cation exchange on PbSe QDs,[15] to study the absorption coefficient of QD heterostructures. They offer an ideal test case, since the total QD diameter and the concentration remains constant throughout the exchange procedure. Indeed, as Pb atoms in the PbSe lattice are gradually replaced by Cd atoms, a CdSe shell with increasing thickness is formed for prolonged exchange times. This is confirmed by high-resolution transmission electron microscope (HR-TEM) images [see Fig. 1(a)], which clearly show the CdSe shell around the PbSe core. HR-TEM however is not suitable for high-throughput measurements of the core diameter and shell thickness. Hence we use TEM-based energy dispersive x-ray spectroscopy (EDX) to determine the Pb/Se ratio of the original PbSe QDs and of the derived PbSe/CdSe QDs. Since the Se-content remains constant throughout the exchange process, we can calculate the PbSe core diameter from the reduction in the Pb/Se ratio and the parent PbSe QD diameter. These values are in good agreement with the core diameters obtained using the location of the first absorption peak and the PbSe QD sizing curve[4] [see Fig. 1(b)]. Recent work by Zhang *et al.*[16] using a similar approach for the CdSe growth confirm this result. They observe a shift of only 32 nm in the absorption spectra upon growth of three CdSe monolayers (~1 nm shell thickness), which corresponds to a shift in the diameter of just 0.17 nm, less than a Cd or Se monolayer. This illustrates that we can use the PbSe QD sizing curve to determine the core diameter and shell thickness of PbSe/CdSe QDs, provided that the parent PbSe QD diameter is known.

Under the assumption that the initial, known QD volume fraction does not change during the cation exchange process, the spectrum of μ_i [see Fig. 2(a)] is readily obtained from the absorption spectrum of a PbSe/CdSe suspension [see Eq. (1)]. In Fig. 2(a), spectra for several differently sized PbSe QDs clearly coincide at energies far above the band gap, whereas the spectra for PbSe/CdSe QDs show a broad band of values due to the influence of the CdSe shell. Figure 2(c) shows a set of experimentally determined intrinsic absorption coefficients at 3.1 eV ($\mu_{3.1\ \text{eV}}$) and 3.5 eV ($\mu_{3.5\ \text{eV}}$) for PbSe/CdSe QDs with different total diameter, core diameter and shell thickness as a function of the shell/QD volume ratio $V_{\text{sh}}/V_{\text{QD}}$. For small shells μ_i slightly increases, reaching a maximum value. For larger shells, μ_i decreases rapidly. The full lines represent $\mu_{i,th}$ values calculated with bulk PbSe and CdSe optical constants at 3.1 eV (400 nm) and 3.5 eV (355 nm).[17,18] Clearly, we find an excellent agreement between these theoretical values and the experimental results for $\mu_{3.1\ \text{eV}}$ and $\mu_{3.5\ \text{eV}}$ [see Fig. 2(c)].

Following Neeves *et al.*,[13] the local field factor in the core of a core/shell QD reads as follows:

$$f_{\text{LF}} = \frac{9\epsilon_{\text{sh}}\epsilon_s}{\epsilon_{\text{sh}}\epsilon_a + 2\epsilon_s\epsilon_b}. \tag{6}$$

At 3.1 eV, $|f_{\text{LF}}|^2$ gradually increases from the value of PbSe core QDs to that of CdSe core QDs, which accounts for the initial rise of the intrinsic absorption coefficient of PbSe/CdSe core/shell QDs for small shells [see Fig. 2(b)]. With thicker shells, μ_i decreases, because the contribution of the CdSe shell, which absorbs less than the PbSe core, becomes

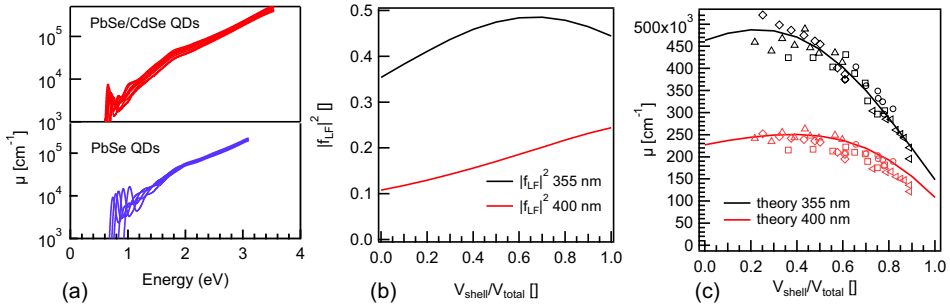

FIG. 2. (Color online) (a) Spectra of μ_i for PbSe/CdSe QDs with constant V_{QD} and increasing V_{sh} and PbSe QDs with varying diameters. (b) Local field factor calculated for PbSe/CdSe core/shell QDs at 355 nm and 400 nm. In the limiting case it becomes the local field factor for PbSe QDs (V_{sh}=0) or CdSe QDs (V_{sh}=V_{total}). (c) Intrinsic absorption coefficient $\mu_{3.5\ eV}$ at 355 nm and $\mu_{3.1\ eV}$ at 400 nm for PbSe/CdSe core/shell QDs as predicted by theory (line) and as measured (with total diameter of circles=5.2 nm, squares=5.8 nm, triangles=7.8 nm, left arrows=4.5 nm, and diamonds=7.5 nm).

more important. The great correspondence between the experimental and theoretical values for μ_i proves that the Maxwell–Garnett effective medium theory can adequately describe the absorption of QD heterostructures at high energies. At these energies, the energy levels of both the PbSe core and the CdSe shell form a continuum, allowing us to treat the absorption of these QD heterostructures using bulk values.

Calculating μ_i using the Maxwell–Garnett effective medium theory and bulk values for the dielectric function offers an elegant and reliable way to determine the QD concentration of suspensions of QD heterostructures [see Eq. (4)], based on a straightforward absorbance measurement and knowledge of the core and shell size. This is essential for the successful integration of these QDs in applications such as light-emitting diodes and lasers. In typical synthesis schemes for core/shell growth, where the concentration remains constant, it also allows for direct monitoring of the dynamics of shell growth. For studies on the intrinsic carrier dynamics in QD heterostructures, the contribution of the change in the local field can be taken into account, using this effective medium theory.

In summary, we used PbSe/CdSe QDs as a model system to test the validity of the Maxwell–Garnett model for colloidal core/shell QDs. These QDs have a well-defined concentric core/shell structure and both size and concentration can be determined easily. We have shown that their intrinsic absorption coefficient at energies well above the band edge can be predicted using the Maxwell–Garnett effective medium theory and bulk values for the dielectric function. The validity of this model has important implications for colloidal QD heterostructure research, since the local field influences all optical characterization methods. It changes, for example, the magnitude of the absorption spectrum and the PL decay rate. Hence this model not only offers an easy way to determine concentrations of QD suspensions but has to be taken into account when extracting the intrinsic physics of colloidal QD heterostructures from standard optical measurements.

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