Absorption Cross-Section and Related Optical Properties of Colloidal InAs Quantum Dots

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We report the absorption cross-section of colloidal InAs quantum dots of mean radii from 1.6 to 3.45 nm. We find excellent agreement between the measured results and calculated values based on a model of small-particle light absorption. The absorption cross-section per dot is $6.2 \times 10^{-16}R^3$ cm^2 at 2.76 eV and $3.15 \times 10^{-16}R^{1.28}$ cm^2 at the first-exciton absorption peak, with the dot radius R in nm. We find that the per-quantum-dot particle oscillator strength of the first-exciton transition is constant for all sizes studied. The radiative lifetime of the first exciton calculated from the oscillator strength increases with dot size and ranges from 4 ns for the smallest dots to 14 ns for the largest ones.

Introduction

Semiconductor quantum dots (QDs) have been a subject of intense study over the past two decades due to the unique effects of quantum confinement.[1,2] A critical optical parameter for colloidal QDs is the absorption cross-section, σ_a, which in turn provides a relationship between the sample optical density (OD) and the QD concentration. Knowledge of QD concentration is necessary for many scientific studies and very useful for QD applications such as bio-labeling.[3] The absorption cross-section also determines the per-QD photoexcitation density at a given photon fluence, which is a crucial parameter for both spectroscopic studies[4,5] and QD optoelectronic device design. An upper limit of the QD first-exciton radiative lifetime can be calculated from σ_a, because a material's absorption and emission properties can be described within the same set of related Einstein coefficients. The calculated radiative lifetime serves as a benchmark to understand effects such as modifying the surface chemistry of QDs and to manipulate photoluminescence (PL) quantum yields.

The size dependence of σ_a and the related oscillator strength (OS) per particle at given transitions are also of great scientific interest. Theoretically, σ_a for QDs is related to the corresponding bulk parameters. For example, it has been shown that a simple small-particle absorption model derived by Ricard et al.[6] offers excellent predictions of σ_a for CdSe QDs at high photon energies.[7] σ_a deviates from bulk behavior near the band edge when quantum confinement effects dominate. Theory predicts a size-independent OS per QD of the first-exciton transition for QDs in the strong confinement regime,[2,8] because the decrease of OS due to the decrease in particle volume is canceled by the increase of OS resulting from quantum confinement with decreasing QD size. However, there are results in the literature that both support and oppose the theoretical prediction of OS in QDs. Some discrepancies may be due to the difficulty of determining the concentrations of QDs.[9] It has been demonstrated that the OS (or extinction coefficient) per QD is a constant and independent of size in both CdTe[10] and CdS,[11] while several groups have shown that it increases with QD size for CdSe.[4,7,12]

To the best of our knowledge, we have conducted the first inductively coupled plasma mass spectrometry (ICP-MS) study on different sizes of InAs QDs. In addition to measuring σ_a as a function of size, we have addressed issues such as obtaining σ_a for QDs from the corresponding bulk parameters and the dependence of σ_a on particle size. Our experimental results agree well with the calculated σ_a results based on the Ricard model. A constant OS at the first-exciton transition for all QD sizes was also obtained. As can be seen in the Results and Discussions section, the constant OS predicts that the first-exciton radiative lifetime increases with increasing QD size.

Theory

At high photon energy, the absorption spectrum of colloidal QDs becomes featureless and corresponds to that of the bulk material. Thus, the extinction coefficient of a QD sample at photon energy well above the first-exciton absorption is equivalent to that of a bulk film containing the same amount of material along the optical path. However, because the QDs are embedded in a solvent, we should consider a local-field correction factor $|f(\omega)|^2$, based on the Bruggeman effective media theory.[13,14] The σ_a per dot for the high-energy regime is found to be[6,7]

$$\sigma_a(\omega) = \frac{4}{3}\pi R^3 \frac{n_1}{n_2} |f(\omega)|^2 \alpha_b(\omega) \quad (1)$$

where n_1 and n_2 are the real parts of the semiconductor and the solvent refractive index, respectively, and $\alpha_b(\omega)$ is the bulk absorption coefficient at frequency ω, obtained from literature values.[15] The local-field correction factor $|f(\omega)|^2$ is given by

$$f(\omega) = \frac{3m_2^2}{m_1^2 + 2m_2^2} \quad (2)$$

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where m_1 and m_2 are the complex refractive index of the semiconductor and the solvent, respectively.[7] At 450 nm (2.76 eV) and in tetrachloroethylene (TCE, $m_2 = n_2 = 1.5$), σ_a of InAs QDs is calculated to be $6.2 \times 10^{-16}R^3$ cm^2.

Experimental Section

Unless otherwise noted, all chemicals were obtained from Aldrich and used without further purification. InAs nanocrystalline QDs were prepared from $InCl_3$ (Alfa Aesar) and tris(trimethylsilyl)arsine (As[TMS]$_3$), according to the method of Cao and Banin.[16] All manipulations were done in a helium atmosphere glovebox or on a Schlenk vacuum line. A precursor of InAs was prepared by mixing As[TMS]$_3$ with $InCl_3$ in trioctylphosphine (TOP) at room temperature. The solution was typically 0.76 M As[TMS]$_3$ and 1.1 M $InCl_3$ and also contained 0.20% by weight of trioctylphosphine oxide (TOPO). The InAs precursor was injected into hot (300 °C) TOP under an inert atmosphere. Dot size was controlled by growth time and number of subsequent injections after the initial nucleation. Generally, longer growth times and increased precursor injections resulted in larger dots. This method gives a broad distribution of QD sizes, and size selective precipitation with toluene/methanol was performed to obtain narrower size distributions.

To measure the concentration of QDs, all samples were digested with nitric acid and analyzed on a Varian Ultra-Mass 700 ICP-MS. The detection limits for the elements of interest are 0.002 ppm for In and 0.1 ppm for As. The measured concentration of ions C (in g/cm^3) is then used to calculate the number of QDs per cubic centimeter, N, by

$$N = \frac{C}{\frac{4}{3}\pi R^3 d} \tag{3}$$

where d is the material density ($d_{InAs} = 5.68$ g/cm^3). By combining the OD obtained from the absorbance spectra, σ_a is

$$\sigma_a = \frac{2.303(\mathrm{OD})}{Nl} \tag{4}$$

where l is the optical path length.

Results and Discussion

Figure 1A displays the absorbance spectra of the samples used in this study. To determine the relationship between the first-exciton transition peak energy and particle size (Figure 1B), we fit the following function to data from Guzelian et al.[17]

$$E\ (\mathrm{eV}) = 0.29 - 0.56/R^2 + 2.48/R \tag{5}$$

From this relationship, we determined the mean QD radius of each sample shown in Figure 1A.

We determined σ_a for each sample based on In and As concentrations separately, assuming in each case an equivalent counterion molar concentration. The ICP-MS results indicate an In excess in all samples. This could be understood from two reasons: First, the In precursor was in excess during the synthesis; second, the cleaning process using toluene/methanol to dissolve/crash QDs works less efficiently on In than As, because the In precursor does not dissolve in the washing solvents well. As a result, the As content should provide the more reliable measurement in determining σ_a. Figure 2A shows that the measured and calculated σ_a values at 450 nm (2.76 eV) for a range of sizes of InAs QDs agree quite well, within experimental uncertainty. The σ_a value per dot is determined

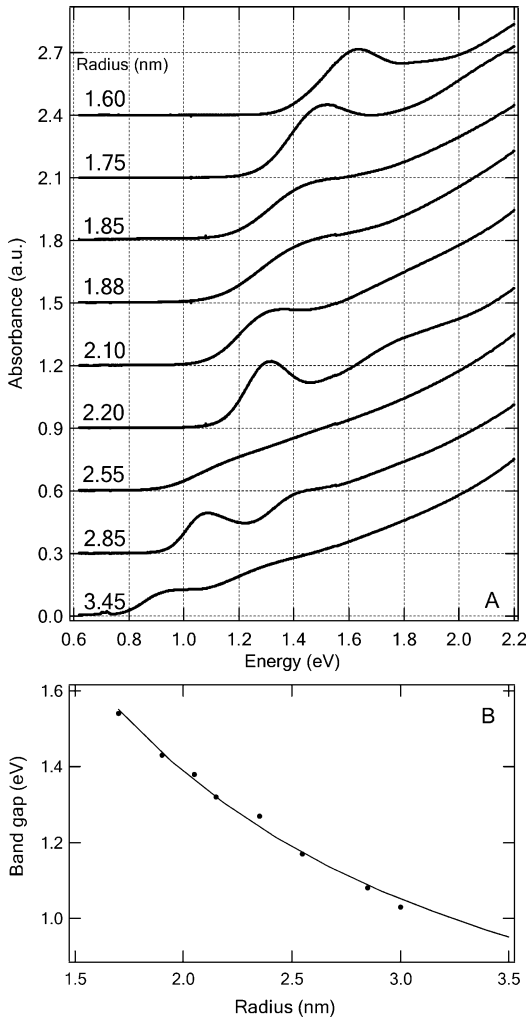

Figure 1. (A) Absorbance spectra of the different sizes of InAs QDs. Plots are vertically displaced and rescaled for clarity. (B) Band-gap energy vs radius of InAs QDs. See text for details.

experimentally to be $6.2 \times 10^{-16}R^3$ cm^2 for 2.76 eV. This confirms that σ_a's of QDs are obtainable from the corresponding bulk parameters with a simple small-particle absorption model. Note, however, this model and expression for σ_a is applicable only at high energy, where the QD absorption is equivalent to that of bulk material.

Once σ_a at one wavelength is obtained, one can extract σ_a for any other wavelength by appropriately scaling σ_a by the ratio of the ODs at the two wavelengths, because σ_a is proportional to OD. Figure 2B shows σ_a at the first-exciton peak of the InAs samples. We fit the measured values to the following relationship, $\sigma_a = 3.15 \times 10^{-16}R^{1.28}$ cm^2, indicating only a slight nonlinearity in the dependence on R. However, this result is complicated by the size dispersion of the dot samples.

The oscillator strength f at the first exciton and the Einstein spontaneous emission coefficient A_i can be calculated by integrating σ_a over the transition band[18,19]

$$f = \frac{4m\epsilon_0 c}{e^2}\int_{\nu_1}^{\nu_2}\sigma_a(\nu)\,\mathrm{d}\nu \tag{6}$$

$$A_i = \frac{8\pi}{\lambda^2}\int_{\nu_1}^{\nu_2}\sigma_a(\nu)\,\mathrm{d}\nu \tag{7}$$

where ν_1 and ν_2 are the start and end frequencies of the first-exciton absorption band in hertz, m is the mass of an electron,

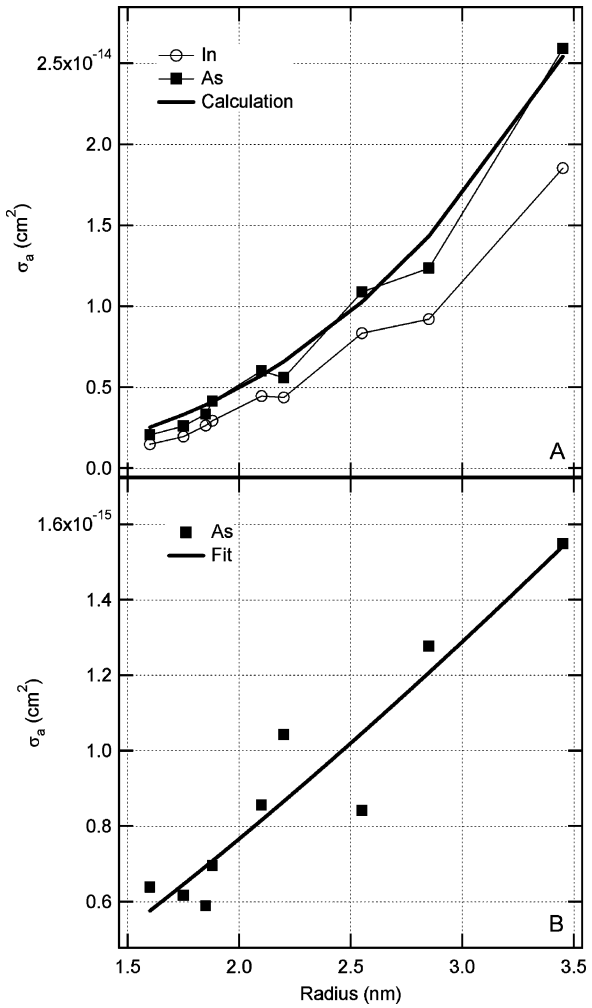

Figure 2. (A) Measured and calculated σ_a values at 2.76 eV (450 nm) of different sizes of InAs QDs. Open circles are for values based on In concentrations, and filled squares are values obtained when using As concentrations. The solid line is the calculated values. (B) Measured σ_a values at the first-exciton peak based upon As concentrations, the line is the fit.

ϵ_0 is the permittivity of free space, c is the speed of light, e is the charge of an electron, and λ is the wavelength of the first-exciton transition peak in centimeters. The integral is performed by first fitting a Gaussian function to the first-exciton band and then integrating over the fitted band shape. The radiative lifetime τ is the inverse of A_i

$$\tau = \frac{1}{A_i} \tag{8}$$

We find that the OS of the first-exciton transition band is constant with QD size (Figure 3). The error bars are estimated from the Gaussian fitting scheme. Thus, our results indicate that InAs joins CdTe[10] and CdS[11] as materials exhibiting a size independence per dot OS, which is consistent with theory.[2,8] However, how large of a size range this size independence would hold remains to be tested. It is to be noted that the OS value, 1.83, is the calculated absolute value. According to the OS sum rule,[20] this indicates that about two electrons are involved in the first-exciton transition.

If the OS is constant, the radiative decay coefficient A_i will change with size, because of the λ factor in eq 7. Thus, the radiative decay lifetime calculated simply from absorption is predicted to increase with size (see Figure 4). In practice, QD

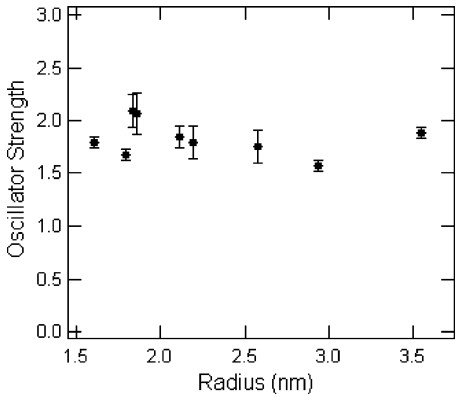

Figure 3. Oscillator strength vs size for InAs QDs. The average OS is 1.83. The error bars are estimated from the Gaussian fitting of the first-exciton bands.

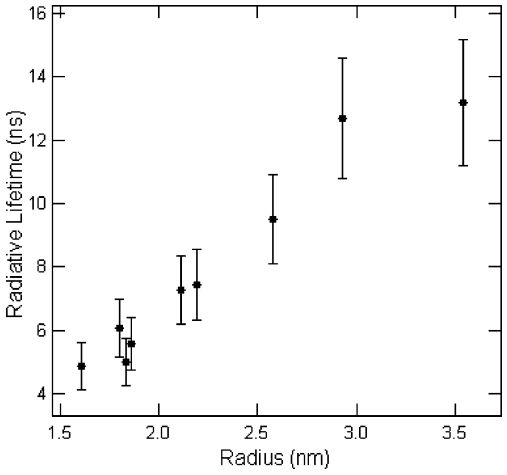

Figure 4. Radiative lifetime of the first-exciton transition vs InAs QD radius.

PL and radiative decay is quite a complex issue, involving such factors as carrier trapping, electron−hole interaction leading to splitting of the ground state into a singlet−triplet pair, local environment fluctuation, and so on.[21] Itoh et al.[22] have found that the radiative decay time increases with decreasing particle size in CuCl microcrystals, which could be successfully explained using the effective mass approximation for weakly confined excitons. It is interesting to note that the radiative decay time in strongly confined InAs QDs might have a totally different dependence on particle size as the weakly confined materials. Of course, further experimental studies are needed to verify these predictions.

Conclusions

In summary, σ_a of InAs QDs measured on the basis of ICP-MS analysis agrees well with calculations based on a simple light-absorption theory. While the per-dot absorption cross-section increases as the cube of the dot radius at high photon energy, σ_a at the first-exciton peak increases approximately linearly with dot radius. We also find that the first-exciton oscillator strength remains constant with dot size for the samples studied, which is consistent with the theory for strongly confined excitons. Consequently, the radiative lifetime of the first-exciton transition calculated from the absorption properties is predicted to increase with increasing dot size.

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