Size Dependence of Radiative Rates in the Indirect Band Gap Material AgBr

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A great deal has been learned about quantum confinement effects in semiconductor clusters, principally from studies of direct band gap (II–VI) materials.[1] By contrast, far less is known about how the photophysical properties of indirect band gap materials are altered by spatial confinement in clusters.[2] In particular, for an indirect gap material, band gap absorbance and emission are formally forbidden, since they involve a change in momentum. It is for this reason that radiative lifetimes of indirect band gap materials are typically microseconds or longer. However, if the wave function is confined in small crystals, where the crystal radius (R_c) is of similar magnitude to the exciton radius (R_{exc}), these selection rules will be modified. The bands are reshaped by mixing in surface atom wave functions. Translational symmetry is lost and a k-space description becomes invalid. Thus, it has been argued that strong band gap luminescence in highly porous Si arises in part from such quantum confinement. Simple analysis[3,4] suggests that these effects should scale as $(R_{exc})^6$. An alternative analysis by Tadakuma[5] predicts a dependence of k_{rad} on R_c^{-2}. We now report a test of these predictions for AgBr clusters in the (weakly confined) size range $R_c \leq 70$ Å.

In earlier work, 50 Å AgBr clusters were synthesized in reverse micelles.[2c] Such clusters indeed showed greatly enhanced band gap emission when compared to the bulk. This enhancement was suggested to involve not only quantum confinement but also impurity exclusion, as well as increased exciton formation due to multiple electron–hole encounters in the small crystals. Preliminary lifetime measurements suggested a short (100 ns) radiative lifetime (τ_{rad}) for these materials. However, such a lifetime seemed inconsistent with the excitation spectra which show no strong exciton absorbance feature. Furthermore, the scaling of τ_{rad} with R_{exc} could not be assessed since only one size could be reproducibly synthesized using the previous method.

Following the approach of Steigerwald in CdSe syntheses,[6] we reasoned that additional kinetic control of cluster synthesis was possible by replacing ionic Br^- with a Br^- precursor, acetyl bromide, which only releases bromide ion upon contact with the inverse micelle "water pool". We indeed find that this approach can reproducibly afford a range of clusters ranging in size from $R_c \approx 30$ Å to $R_c \approx 100$ Å. For example, for an $\omega = 3$ solution ($\omega = [H_2O]/[AOT]$), 0.27 mL of 0.1 M aqueous $AgNO_3$ is added to 25 mL of 0.2 M AOT in heptane. The solution is stirred until clear. While protected from light, 2 mL of the above micelle solution is added to 1 mL of 0.02 M acetyl bromide in heptane. The solution is diluted to 8 mL, vortexed for 30 s, and flash frozen in liquid N_2. Solutions so prepared contain 35 Å (radius) AgBr crysallites which show exciton emission at 434 nm. Details for other preparations including TEM and emission data are contained in the supplementary material.[4] The cluster size as estimated from the exciton emission wavelength with "particle in a box" calculations agrees well with that measured by transmission electron microscopy (Figure 1).

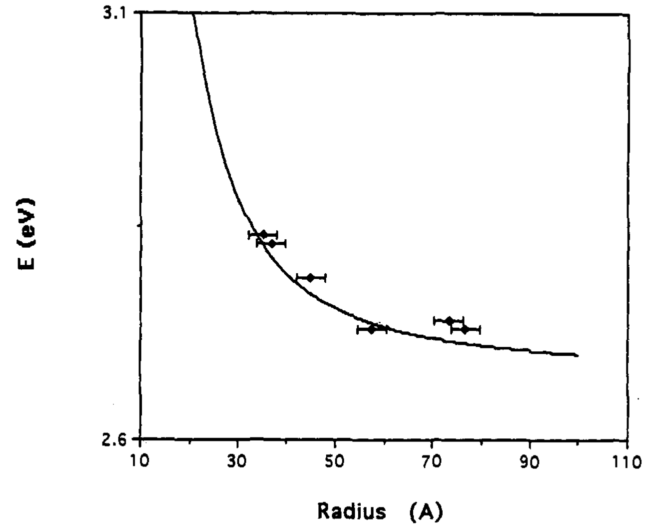

Figure 1. Plot of band gap energy of the observed exciton emission vs crystallite size for several AgBr micelles. The radius values plotted are those obtained from transmission electron micrographs. The solid line is calculated using a particle in a box model, $E = E_g + h^2/8\mu^*R^2$ where E_g is bulk band gap, h is Planck's constant, μ^* is the effective mass (bulk) of electron and hole, and R is the radius of the particle.

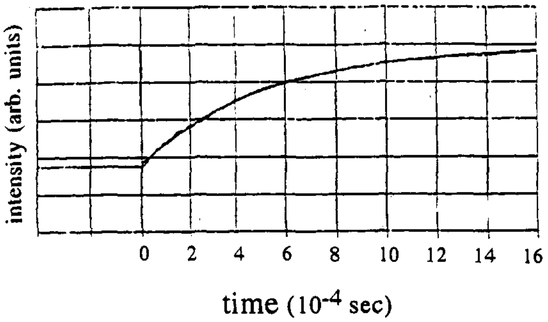

Figure 2. Exciton emission decay from AgBr ($\lambda_{ex} = 337$ nm, $\lambda_{em} \sim 444$ nm, $R \sim 50$ Å) at $T = 6$ K. The fitted line represents a single exponential fit, $\tau = 534$ μs. The intensity is given in arbitrary units while the time scale is 200 μs/division. For this sample, a measured quantum yield (*uncorrected* for scattering) was 15% ± 5%. Both experimental and single exponential fitted data are shown.

With these materials available, we began detailed lifetime studies. The first important result was the realization that the fast (100 ns) component earlier identified in photon-counting studies represented only a small fraction (≤5%) of the total emission, most of which occurs on a much longer time scale. Lifetimes were therefore studied by (laser) flash spectroscopy (Figure 2). As shown by the data in Figure 3, the observed lifetime decreases as cluster size decreases. This is qualitatively expected since the momentum selection rules are rigorously valid only for an infinite lattice and must become invalid at small enough cluster sizes. The lifetime reaches an asymptotic value when $R_c > 70$ Å.

Note that, even for the smallest (30 Å) clusters, the momentum selection constraints remain significant. The radiative lifetimes remain quite long (300 μs), consistent with a rather strongly

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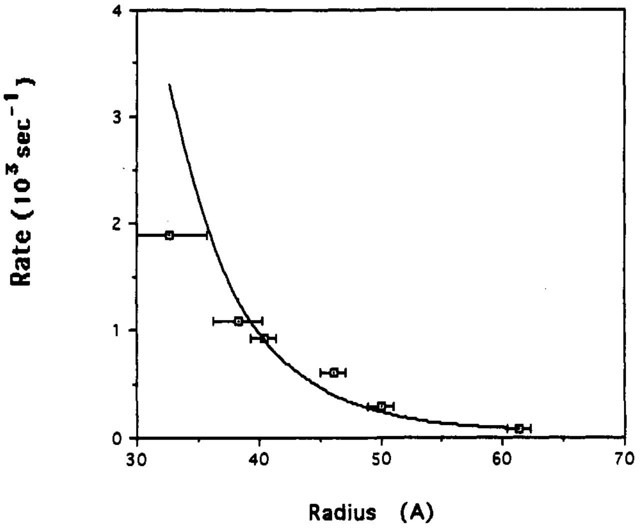

Figure 3. Plot of recombination rate vs crystallite size for several AgBr micelles. Error bars indicate the size distributions (from TEM) associated with the samples in which the size specific wavelengths were monitored. Note that since (some of) the radius values are calculated or interpolated from the emission wavelength, they are not identical to the values in Figure 1, which are directly determined by TEM. The solid line shown is a fit of the data to a (normalized) R^6 dependence: reasonably good (visual) fits can be obtained for any exponential R^n, $2 < n \leq 6$; minimum residuals are obtained for $R = \phi$.

forbidden transition. In order to quantitatively analyze the data, we assume that the observed decay rate contains both a phonon-assisted process with rate constant k°, which is independent of radius ($k^\circ \approx 10^3$ s^{-1}), and a zero phonon rate process, for which the rate constant $k(R)$ depends strongly on R_c.[5] Thus, $1/\tau_{obs} = k_{obs} = k^\circ + k_R[(R_c{}^n)]$. The value for k° was taken as the limited value of k_{obs} for particles of radius >70 Å, where k_{obs} becomes constant. To evaluate the functional dependence of R_c, the k° term is subtracted out, leaving only k_R. The radiative rate constant is normally calculated by dividing k_{obs} by the quantum yield for emission. However, the *apparent* quantum yield ($\phi_{obs} \approx 0.15$) may be complicated by branching of the excess excitation energy *prior* to exciton formation. Furthermore, a precise scattering correction is difficult under these experimental conditions. However, the apparent quantum yield ϕ_{obs} is independent of the value of R_c (within experimental error of ±10%)[8]. For a constant value of the quantum yield, $\phi k_o = k_{rad}$. This equation assumes that (any) branching does not change in a size dependent way that fortuitously cancels the change in ϕ. Thus a plot of log k_0 vs R is equivalent to a plot of log k_r vs R, regardless of the value of ϕ which is reflected in the intercept. A naive extrapolation of this dependence predicts that AgBr would obtain a fully allowed (nanosecond) lifetime only for *extremely* small clusters ($R_c < 6$ Å!) where "translational symmetry" obviously has no meaning.

In summary, by using a modified reverse micelle synthetic approach, we have prepared clusters of the indirect band gap material AgBr in the size range 30–100 Å and measured the relaxation lifetimes. For such clusters the apparent radiative lifetimes scale as a power of cluster radius ($\tau_{rad} \propto R^n$, $2 < n \leq 6$). These results are in agreement with simple theoretical predictions which suggest that the momentum selection rules associated with indirect transitions should begin to break down as quantum confinement begins to modify the band structure. Such a result confirms that normally nonemissive indirect gap materials can become emissive when formulated as small clusters.

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Supplementary Material Available: Details of preparation of size-restricted silver bromide micelles, transmission electron micrographs, and low-temperature luminescence spectra (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[8] The simplest interpretation is that the actual quantum yield after the appropriate corrections is $\phi \approx 1$ so that $k_{obs} \approx k_{rad}$.