

UC Merced

UC Merced Previously Published Works

Title

Resonance Raman excitation profiles of CdS in pure CdS and CdSe/CdS core/shell quantum dots: CdS-localized excitons

Permalink

<https://escholarship.org/uc/item/9ms7827s>

Journal

The Journal of Chemical Physics, 147(22)

ISSN

0021-9606

Authors

Gong, Ke
Kelley, David F
Kelley, Anne Myers

Publication Date

2017-12-14

DOI

10.1063/1.5003099

Peer reviewed

Supporting Information for
Resonance Raman Excitation Profiles of CdS in Pure CdS and CdSe/CdS Core/Shell Quantum Dots: CdS-Localized Excitons

Ke Gong, David F. Kelley, and Anne Myers Kelley*

Test for homogeneous nucleation

A very common source of artifacts in spectroscopic studies of core/shell semiconductor nanocrystals is the presence of small nanocrystals of the pure shell material formed through homogeneous nucleation during shell growth. This is particularly likely to be a problem when thick shells are grown. In order to eliminate this possible source of interference, we have measured the static photoluminescence (PL) spectra of the core/shell sample excited at 350 nm, which is above the band gap of small CdS QDs. Figure S1 shows the resulting emission spectrum. Only core/shell emission near 620 nm is observed; any emission in the wavelength range expected for pure CdS QDs (400-500 nm) is apparently at least three orders of magnitude weaker than the core/shell emission. This provides considerable confidence that the blue-excited Raman spectra of the core/shell QDs do not contain significant contamination from pure CdS QDs.

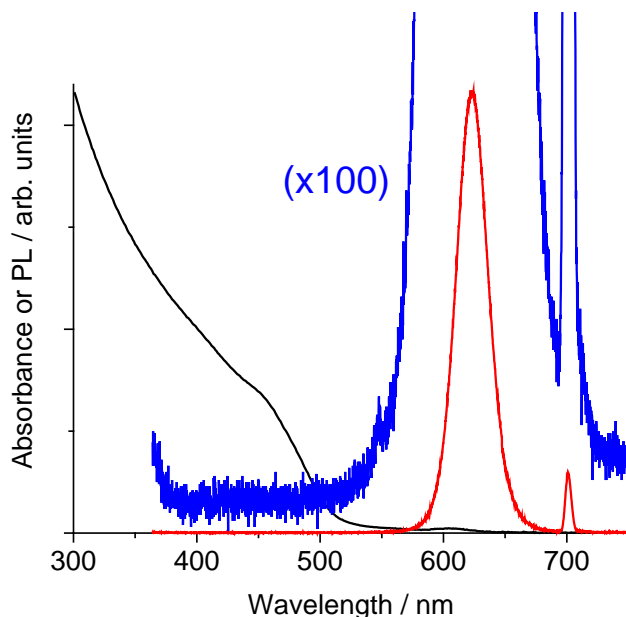


Figure S1. Absorption spectrum of the CdSe/CdS quantum dots (black), emission spectrum excited at 350 nm (red), and the same emission spectrum scaled up by a factor of 100 (blue).

Evaluation of biexciton formation and ionization

A potential complication in many laser experiments on quantum dots is the formation of charged species as a result of Auger ionization subsequent to biexciton formation.¹ This is a particular problem in single dot optical experiments, where the exciting laser is focused very tightly onto a single, stationary QD and

the fraction of time the QD spends in its excited state becomes significant. In our experiments, samples in chloroform solution were held in 1 mm path length cuvettes and translated at a rate of about 5 mm/sec through a laser beam having an average power of 0.2-0.3 mW and an average diameter of about 100 μm , so the average residence time of the sample volume in the beam is about 10 ms. The time between pulses in the pulsed experiments (12 ns) is shorter than the radiative lifetimes of the QDs, so there is essentially no difference between pulsed and cw excitation for the purposes of this calculation. The total illuminated volume is about 2×10^{-5} mL, and at concentrations of about 1 μM , the total number of QDs in the illuminated volume is about 10^{10} . At 450 nm, a power of 0.25 mW corresponds to 5.6×10^{14} photons s^{-1} . A maximum of half of the incident photons are absorbed, so the photon absorption rate is less than 3×10^{14} photons/sec, or 3×10^4 photons s^{-1} per QD. Thus, during a 10 ms transit time each QD absorbs a maximum of $(3 \times 10^4 \text{ photons } \text{s}^{-1})(0.01 \text{ s}) = 300$ photons. Assuming an upper limit on the excited-state lifetime of 50 ns (it is probably much shorter than this for a majority of QDs), the probability that an excited QD absorbs a second photon is the product of the excitation rate and the lifetime, $(3 \times 10^4 \text{ s}^{-1})(50 \times 10^{-9} \text{ s}) = 0.0015$. Thus, the probability that a single QD is excited to a biexciton state during a single pass through the beam is, at worst, $(300)(0.0015) = 0.45$ —that is, about half the QDs form a biexciton at some time during their passage through the beam. The biexciton ionization quantum yield for CdSe in chloroform is a few percent,² and the ionization probability for CdSe/CdS QDs is considerably lower,³ so we calculate that the overall total ionization probability per pass through the beam should be considerably less than a few percent. Thus, we expect that ionized species formed through following biexciton formation should make a very small contribution to our signal.

We also note that very similar resonance Raman spectra and intensities are obtained with pulsed and with cw excitation at similar wavelengths. Figure S2 shows the same data as Figure 5, but plotted with different symbols to distinguish the pulsed and cw points. There is no obvious difference between pulsed and cw excitation.

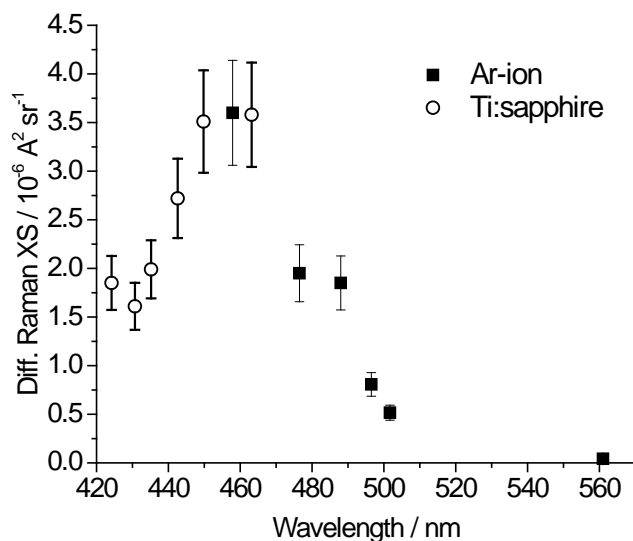


Figure S2. The same data shown in Figure 5, with different symbols used to distinguish data obtained with continuous-wave (argon-ion) and pulsed (Ti:sapphire) excitation.

¹ J. J. Peterson and D. J. Nesbitt, *Nano Lett.* **9**, 338 (2009).

² Y. Zeng and D. F. Kelley, *ACS Nano* **9**, 10471 (2015).

³ Y. Zeng and D. F. Kelley, *J. Phys. Chem. C* **120**, 17853 (2017).