Photoluminescence Spectroscopy of Quantum Dots

Introduction

Quantum dots (QDs) have potential applications in optoelectronics, biosensing, biolabeling, memory devices, and sources of laser light. We show that alloyed CdSeTe QDs possess a nonlinear change in their photoluminescence spectra, correlated to size and composition, as monitored by the versatile benchtop FluoroMax® spectrofluorometer. QDs' emission can be as long as 850 nm, which may aid imaging deeper into living tissue than visible light can penetrate.
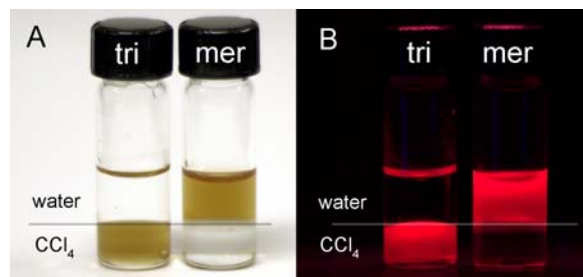

Fig. 1. *QDs coated with tri-*n*-octyl phosphine oxide (tri) and mercaptoacetic acid (mer) under ambient (A) and ultraviolet (B) illumination. The upper layer is water; the lower layer is CCl₄.*

Experimental procedure and results

The procedure for synthesizing alloyed CdSeTe QDs (2.7–8.6 nm dia.) is given elsewhere.[1] QDs were purified by precipitation and centrifugation, then stored at room temperature. Absorption spectra were recorded on a Shimadzu spectrophotometer (slit = 1.0 nm). Fendler, *et al.*'s method[2] for absorption data determined absorption onset and bandgap energies. Photoluminescence

[1] R.E. Bailey and S. Nie, *J. Am. Chem. Soc.,* **125**, 7100–7106 (2003).
[2] Y. Tian, *et al., J. Phys. Chem.*, **100**, 8927–8939 (1996).

spectra were recorded on a FluoroMax® (λ_{exc} = 475 nm, slits = 2.0 nm bandpass). All spectra were corrected for detector response.

QDs coated with tri-*n*-octyl phosphine oxide remain in CCl₄ (lower layer) while those coated with mercaptoacetic acid are in the aqueous (upper) layer (Fig. 1).
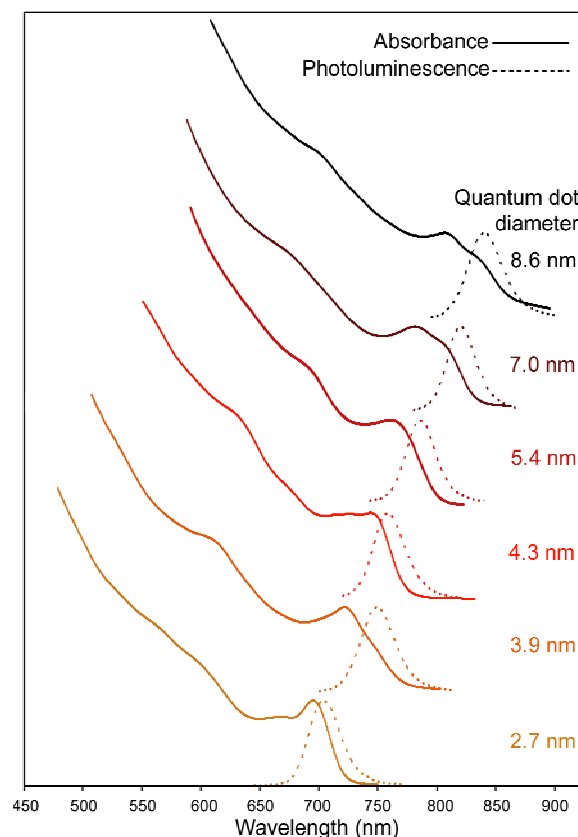

Fig. 2. *Diameter vs absorption and photoluminescence of various sizes of CdSe$_{0.34}$Te$_{0.66}$ QDs.*

Various alloyed QDs was examined via absorption and photoluminescence spectroscopy. Absorption and photoluminescence wavelengths smoothly rise with QD diameter (Fig. 2). Bandgap energy is plotted against

variation in Te content in Fig. 3. Fig. 4 shows emission peak wavelength as a function of Te content. Comparative literature values for bulk alloys are shown in Figs. 3 and 4.[3]
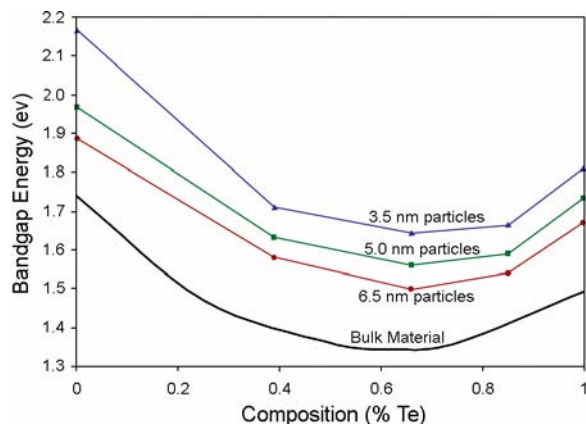

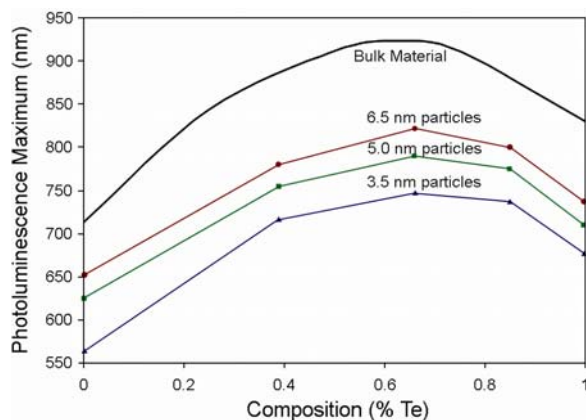**Fig. 3.** *Absorption-energy onset vs QDs' Te content.*

Fig. 4. λ_{em} *vs Te content of QDs.*

Graphs resolve electronic transitions, plus fluorescence emission at the band-edge, including an unexpected depression in band-gap for all QD sizes at ~

60% Te. Vegard's Law[4] for predicting band-gaps of thin-film and bulk alloys is linear but only a first approximation; others[5] have found this "optical bowing" in bulk CdSeTe, so this effect is not solely caused by quantum confinement.

Zunger, *et al.*,[6] suggest the observed effects arise because of various ionic sizes in the alloy, various electro-negativities of these ions, and that the binary structures of these ions have various lattice constants. Relaxation of ionic bonds to equilibrium positions may lead to local order and a larger-than-expected reduction in the band-gap.

Conclusions

Particle size and composition can control quantum confinement. QDs may assist deep-tissue molecular imaging in living systems, because of their near-IR and far-red fluorescence away from aqueous absorption. QDs also provide absorption coefficients much larger than typical organic dyes. The ultrasensitive FluoroMax® spectrofluorometer is useful for research related to nanostructures and materials science.

Acknowledgements

[3] R.K. Richardson and H.L. Goering, Eds. (*Compound Semiconductors*, Reinhold, New York, 1962).

[4] L.Z. Vegard, *Z. Physik*, **5**, 17–26 (1921).
[5] H.C. Poon, *et al.*, *J. Phys.: Cond. Matter*, **7**, 2783–2799 (1995).
[6] J.E. Bernard and A. Zunger, *Phys. Rev. B*, **36**, 3199–3226 (1987); S.H. Wei, *et al.*, *J. Appl. Phys.*, **87**, 1304–1311 (2000).

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