

Acknowledgments

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Summary

Cadmium selenide quantum dots offer photoluminescence that can be tuned across the visible spectrum by adjusting particle size on the scale of a few nanometers. With decreasing nanocrystal radius, R (in nm), the photon energy of the first absorbance peak becomes greater than the bulk semiconductor bandgap energy (1.7 eV) by an increasing energy shift of $0.82 \text{ eV}\cdot\text{nm} / R$. The peak photoluminescence (PL) photon energy is slightly lower than the absorbance peak energy.

Quantum dot versatility leads to numerous photonic and biomedical applications. Combining the optical properties of quantum dots with the economical processing of polymers may yield emitters for polymer-based color displays, light emitting diodes, fiber amplifiers and low-threshold lasers, as well as optical, thermal, and chemical sensors. Present photonic devices with quantum dots suffer from low efficiencies compared to bulk semiconductor devices. However, biomedical imaging has become a commercially viable use of cadmium selenide (CdSe) quantum dots, due to their superior performance compared to organic dyes. CdSe quantum dots conjugated with appropriate antibodies can optically label multiple proteins simultaneously, providing a valuable tool for cancer research. All of these applications prefer narrow emission with a high photoluminescence quantum yield (PLQY), which is the ratio of photons emitted per photons absorbed.

Numerous methods have been developed to produce CdSe nanocrystals, but organometallic synthesis yields quantum dots with superior performance, due to high temperature annealing during growth and effective surface passivation. Over the past

decade, organometallic synthesis has been adapted and improved in a quest for economical performance enhancement. Theoretical studies have shown how particle size distributions could be focused during diffusion-limited growth, but not reaction-limited growth, as long as competitive ripening was avoided. However activation energies have not been measured for the organometallic synthesis of quantum dots.

A diffusion-limited model was developed to facilitate optical monitoring of growth rates. Assuming Arrhenius diffusion down linear concentration gradients around spherical nanocrystals, the model predicted the evolution of quantum dot radius and the consumption of Cd precursors during the growth phase after nucleation and before the onset of Ostwald ripening at a completion time t_c , when precursors are exhausted.

Organometallic synthesis kinetics were compared in three different solvents, stearic acid, dodecylamine, and trioctylphosphine oxide (TOPO), keeping all other precursor components and initial concentrations the same. The evolution of quantum dot size was monitored, using PL and absorbance spectroscopy, as a function of synthesis time and temperature (from 205 °C to 335 °C), in order to monitor the nanocrystal molecular growth rate, ν , from changes in the emission wavelength with reaction time, *i.e.* from the “redshift rate.” Activation energies were estimated from Arrhenius plots redshift rates or reaction completion rates versus reciprocal absolute temperature. Brightness was quantified by comparing emission from quantum dot solutions to reference solutions of rhodamine 6G. After redesigning the reactor to improve temperature control, growth in TOPO was rapidly sampled to see the effects of excess Se on nucleation and growth.

When CdSe quantum dots were formed via organometallic synthesis, the gradual transition from rapid to slow redshift rates during the early stage of growth was adequately described by the diffusion model, based on increasing nanocrystal surface area and decreasing precursor concentration with time. At t_c , the wavelength λ_c , at which the redshift rate reached its minimum, always corresponded with the wavelength of narrowest PL emission, and λ_c had a characteristic value that depended on the reaction solution composition, but not on the synthesis temperature. Increasing the synthesis temperature decreased the time needed to achieve a given wavelength, including λ_c .

Generally, synthesis with a lower activation energy, Q , produced faster initial nanocrystal growth, and yielded narrow emission at progressively longer wavelengths by choosing solvents in the following order: TOPO ($\lambda_c = 560 \pm 5$ nm, $Q = 0.92 \pm 0.26$ eV), dodecylamine ($\lambda_c = 565 \pm 5$ nm, $Q = 1.05 \pm 0.1$ eV), and stearic acid ($\lambda_c = 590 \pm 5$ nm, $Q = 0.6 \pm 0.1$ eV). All three solvents tested produced CdSe quantum dots with a minimum relative emission width of about 2.0 ± 0.1 %, based on the ratio of the standard deviation to the mean of the PL photon energy distribution. The agreement of the synthesis activation energy in stearic acid with the activation energy for self-diffusion in liquid sodium stearate at similar temperatures suggested that diffusion played a prominent role for synthesis in stearic acid. Since increasing molecular weight correlated with increasing synthesis activation energy from stearic acid to TOPO, diffusion probably also played a significant role in regulating TOPO synthesis. However, decreasing the molecular weight, going from TOPO to dodecylamine, resulted in similar activation energies. This suggested that some contribution from the unknown Cd-chelate interaction energy may have compensated for the decrease in molecular weight.

Separate experiments would be needed to sort out the interaction between the reaction rate and the diffusion rate in each solvent. Since all solvents produced emission with progressively narrower emission with longer synthesis times during early growth, and since theoretical treatments of reaction-limited growth consistently predict no narrowing of the PL emission full width at half max, it is doubtful that observed synthesis in any of these three solvents could be entirely reaction-limited. However, mixed control is possible, especially in TOPO or dodecylamine.

Regardless of the synthesis solvent, quantum dots generally exhibited their highest PLQY near 26 ± 3 % at emission wavelengths shorter than λ_c and at reaction times before t_c , while cadmium precursors were still available. To explain this result, it is hypothesized that nanocrystals with a moderate growth rate (which does not exceed the mobility of surface atoms) may undergo surface reconstruction at elevated temperatures that can minimize surface defects to enhance PLQY. Generally, for growth in a given solvent, the evolution of PLQY and emission peak width correlated more consistently with the emission wavelength than with the synthesis temperature. Some singularities of exceptional properties occurred at ideal temperatures that depended on the solvent.

Higher selenium levels led to the formation of more initial nuclei, which in turn increased the rate at which Cd precursors were depleted. Even so, the evolution of quantum dot radius, determined by the first absorbance peak position, was virtually unaffected by the initial Cd:Se precursor ratio.

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Links to Publications

Information from this dissertation has been adapted and published in several publications, and other submissions are in progress. Therefore, internet access to the full dissertation was postponed until April 2006, to comply with copyright policies. To be directed to the publishers of these articles, [CLICK HERE](#).