

SUPERCRITICAL CONTINUOUS MICROREACTOR SYNTHESIS OF NARROW SIZE DISTRIBUTION QUANTUM DOTS

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Colloidal semiconductor quantum dots (QDs) have attracted a lot of attention for use in biological imaging, electroluminescent devices and lasers, due to their size tunable optical properties and chemical stability. Most of these applications require highly crystalline samples with narrow size distributions, which are difficult to obtain in a single step batch process with its often poor control of reaction conditions.

Synthesis of QDs in microfluidic devices offers several advantages over conventional macroscale chemical processes including enhancement of mass and heat transfer, reproducibility, potential for sensor integration for in situ reaction monitoring, rapid screening of parameters, and low reagent consumption during optimization. In addition, applying pressure in microsystems allow using more conventional solvents like hexane, instead of high boiling point solvents (*i.e.* ODE, squalane), generally required for high temperature liquid phase synthesis. At certain pressures, one can even reach the supercritical fluid state of solvent. In contrast to viscous single-phase flow reactors, the low viscosity supercritical fluid flow approach enables narrow residence time distribution as well as higher nucleation rates, factors which have strong influence on the ultimate QD size distribution.

In this context, we have developed a high pressure high temperature continuous-flow Silicon-Pyrex microreactor for the synthesis of CdSe QDs (Figure 1).

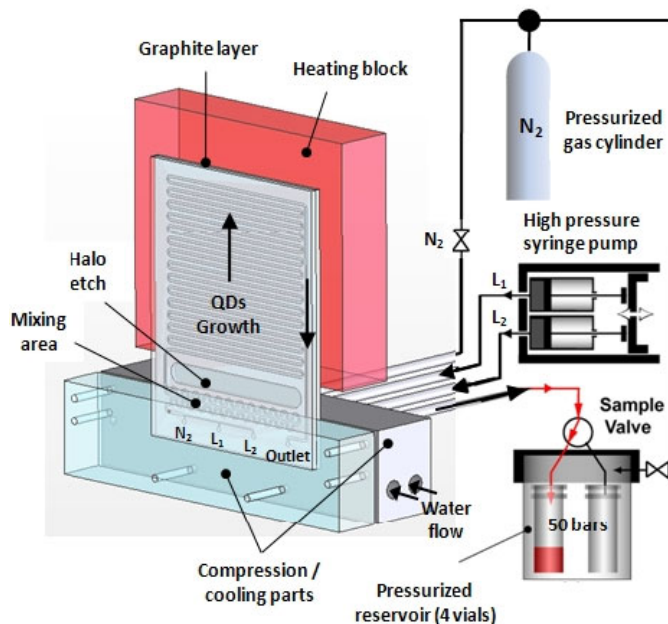


Figure 1. Experimental set-up

The microreactor consisted of a 400 μm wide and 250 μm deep channel with a 0.1 m long mixing zone maintained at room temperature and a 1 m long reaction zone heated up to 350°C. The two zones are separated by a thermally isolating halo etch that allowed for a temperature gradient of over 250°C. High pressure modular compression fluidic connections were realized by compressing the microreactor between two stainless steel parts using viton O-rings.

CdSe QDs were synthesized at constant pressure (5 MPa), while tuning several parameters: Temperature (210 °C to 270 °C), residence time (30 – 150 s) and concentration $3.2 \cdot 10^{-3} \text{ M}$ to $7.4 \cdot 10^{-2} \text{ M}$). We have compared the conventional viscous high boiling point solvent synthesis (using squalane as solvent), with supercritical fluid flow synthesis, using supercritical hexane (sc-hexane, $T_c = 234.7 \text{ °C}$ and $p_c = 3.03 \text{ MPa}$, $20 < \eta < 70 \text{ }\mu\text{Pa}\cdot\text{s}$). In addition to conventional effects of experimental parameters on the characteristics of the obtained nanocrystals, which allow controlling the size (2-8 nm) and the concentration of nuclei ($3 \cdot 10^{-6} \text{ M}$ - 10^{-4} M), the use of sc-hexane has a strong influence on the size distribution of the QDs and consequently the Full Width at Half Maximum (FWHM) of the emission peak. The size distribution for QDs synthesized in sc-hexane, 4 - 6% (FWHM: 25 - 26 nm), is much smaller than for those synthesized in liquid squalane, 9 - 12% (FWHM: 41 - 49 nm) (Figure 2).

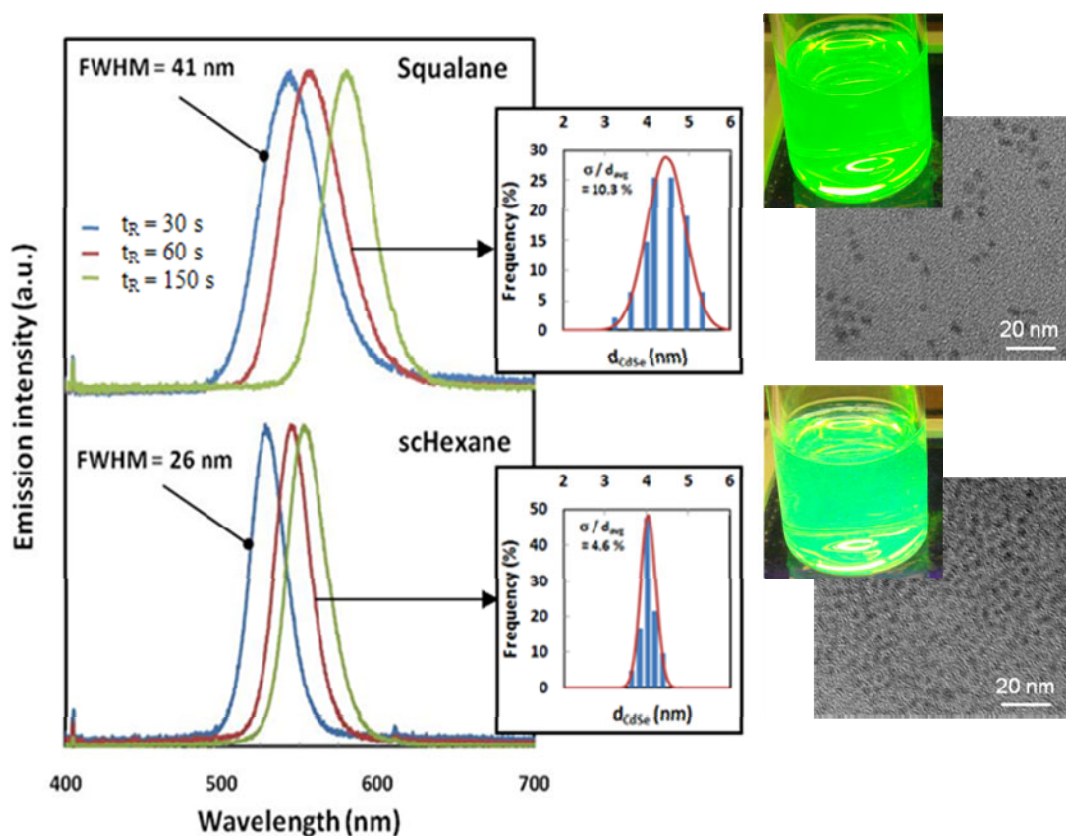


Figure 2. PL spectra at different residence time (t_R) obtained for CdSe QDs synthesized in Squalane and Hexane at 270 °C, 50 bars with $[\text{Cd}] = [\text{Se}] = 3.8 \times 10^{-3} \text{ M}$ and QDs size distributions obtained from TEM measurements for samples run at $R_t = 60 \text{ s}$ with pictures of the QDs and optical characterization.

Supercritical hexane turns out to be a powerful media to overcome some of the limitations of high boiling point solvents synthesis in microreactors. The use of high pressure high temperature microreactor demonstrated in this work opens new routes for nanomaterials synthesis in microfluidic devices by enlarging the set of solvents and phases (liquid, gas, supercritical) available.