HIGH PRESSURE MICROFLUIDICS FOR NANOMATERIALS SYNTHESIS

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Continuous synthesis of nanomaterials 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. The synthesis of inorganic nanostructures generally requires high temperatures to decompose metal organic precursors and to generate nucleation followed by further growth. However, limitations on the number of compatible chemistries and the limited number of available high boiling point solvents have been a major obstacle in the rapid adoption of microreactors as a universal platform for nanomaterials synthesis. One way of improving syntheses in microreactors is to perform experiments at high pressure. Indeed, at sufficiently high pressure, virtually any common solvent, precursor, and ligands will remain either liquid or become supercritical (sc) at the temperatures required for the syntheses.

In this context, we have developed high pressure high temperature continuous-flow Silicon-Pyrex microreactors for the synthesis of nanomaterials. The microreactors consisted in an injection zone maintained at room temperature and in a reaction zone under temperature. The two zones are separated by a thermally isolating halo etch that allowed for a temperature gradient of 250°C/cm. High pressure modular compression fluidic connections were realized by compressing the microreactor between two stainless steel parts using viton O-rings. In this configuration, the set-up allows reaching high pressure (up to 25 MPa) and temperature (up to 500 °C in the heated section) (Figure 1).

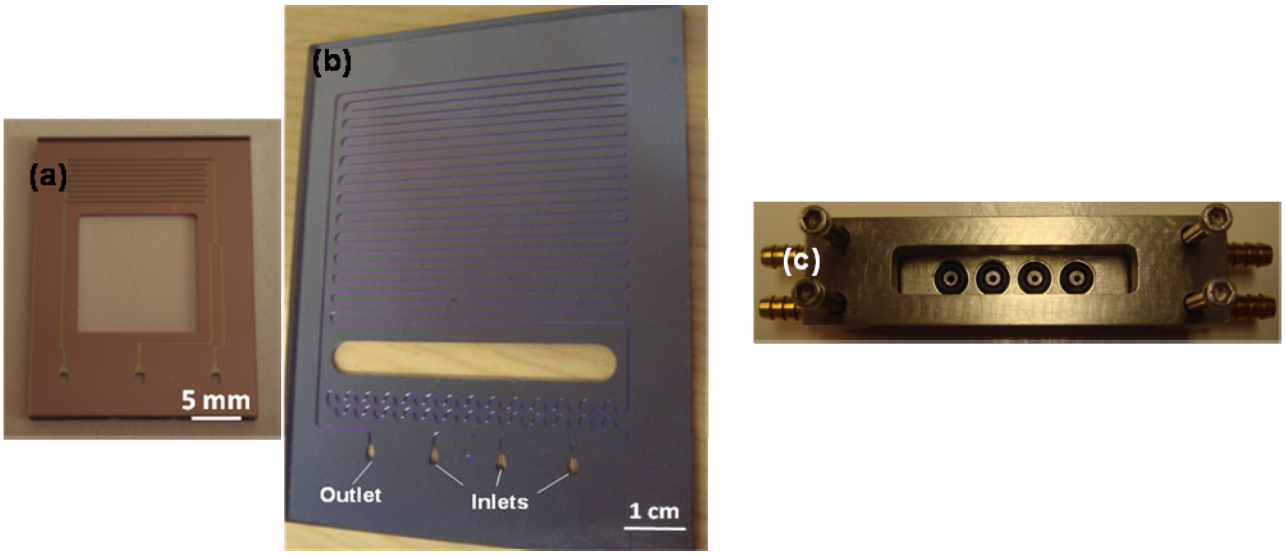

Figure 1. High pressure microreactors for nanomaterials synthesis: (a) 4.5 μL microreactor, (b) 100 μL microreactor and (c) modular fluidic connections.

Model nanomaterials (CdSe QDs, Pd nanoparticles, iron oxide nanocrystals) were synthesized to demonstrate the process under pressure, while tuning several parameters: solvent, temperature, residence time or concentration. In the case of QDs, we demonstrate that the use of supercritical fluids, in particular, shows strong influence on both the concentration of the QDs and on their size distribution, leading to small Full Width at Half Maximum (FWHM) of the emission peak.

CdSe quantum dots were obtained either from either squalane, dodecane, toluene or supercritical hexane, for T ranging from 210°C to 310°C at 50 bars. Iron oxide nanocrystals were synthesized in supercritical toluene at 325°C and 100 bars. Palladium supported nanoparticles on silica were synthesized in supercritical CO_2 – ethanol media at 200°C and 130 bars.

The use of high pressure high temperature microreactors 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.