

A Stable Droplet Reactor for High Temperature Nanocrystal Synthesis

Electronic Supplementary Information

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METHODS

Chemicals

Unless otherwise stated, chemicals were obtained from Sigma Aldrich. All water used was ultrapure (~14 MΩ, Purite).

Precursors for CdSe synthesis

The Cd precursor solution was made as follows: 520 mg of CdO (99.99+ %), 24 mL of oleic acid (90 %) and 400 mL of ODE (90 %) were added to a 500 ml round bottom flask. The mixture was degassed under vacuum, left under a nitrogen atmosphere and then heated by immersion in an oil bath to ~200 °C, at which point the mixture clarified to become a colourless solution. The solution was then allowed to cool before being loaded into a 10 ml gas-tight syringe.

The Se precursor solution was made by adding 600 mg of Se (99.5+ %), 32 mL of trioctylphosphine (95 %) and 400 mL ODE to a 500 mL round bottom flask, degassing under vacuum, and then stirring at room temperature under a nitrogen atmosphere until all the Se had dissolved. The solution was then loaded into a 10 ml gas-tight syringe.

Precursors for TiO₂ synthesis

TiCl₃ solution (~10 wt% in 20 – 30 wt% HCl) was loaded, as received, into a 1 ml gas-tight syringe.

A 0.25 M NaOH (99 %, VWR) solution was prepared and loaded into a 10 ml gas-tight syringe.

Precursors for Ag synthesis

1.470 g PVP (MW ~29000 Da) was dissolved in ~20 ml water in a 25 ml volumetric flask. Once dissolved, 0.102 ml AgNO₃ (0.1N soln, Alfa Aesar) solution was added, and the volume was then made up to 25 ml with water. The solution was loaded into a 10 ml gas-tight syringe.

A 20 mM solution of NaBH₄ was made by dissolving 0.0189 g in 50 ml water in a volumetric flask. 0.0665 ml of the NaBH₄ solution was added to 0.0125 ml of 1 M NaOH solution in a 50 ml volumetric flask and made up to 50 ml with water. This solution was loaded into a 10 ml gas-tight syringe.

Construction of Droplet Reactor for CdSe synthesis

Two 45° incisions were made on opposite sides of a ~15 cm length of silicone tubing (VWR, ID 1 mm, OD 3 mm), approximately 1 cm from the end. Into the incisions were inserted two ~7 cm glass capillaries (Polymicro, ID 150 µm, OD 375 µm), taking care to ensure that the mouths of the capillaries met in the centre of the silicone tubing. A 1.5 m length of PTFE tubing (VWR, ID 1 mm, OD 2 mm) was inserted into the end of the silicone tubing and forced inwards until the PTFE tubing was within 1.5 mm of the capillary tips. 1 m of the central section of the PTFE tubing was coiled and then placed into a variable temperature oil bath. The precursor solutions were loaded into 10 ml syringes to which fluorinated ethylene propylene (FEP) tubing (Upchurch Scientific, ID 356 µm, OD 1.57 mm) was attached using polyether ether ketone (PEEK) luer-lock interconnects (Upchurch scientific). The FEP tubing was slipped over the glass capillaries. Perfluoropolyether (PFPE, Fomblin Y 06/6) carrier fluid was loaded into a 50 ml syringe fitted with a luer-lock dispensing tip (Intertronics, OD 1.5mm) which was inserted into the vacant end of the silicone tubing.

In-line fluorescence spectroscopy was carried out as follows. The opaque PTFE tubing was connected to a 10 cm length of optically transparent FEP (VWR, ID 1 mm, OD 2 mm) using a short length (~ 1.5 cm) of silicone tubing (VWR, ID 1 mm, OD 3 mm) – see Fig 1. As PTFE and FEP have similar surface chemistry, the droplet flow is unaffected by the change in channel material. The droplets were excited using a 355 nm diode-pumped laser, and the emission spectra were recorded using a fibre-optic coupled CCD spectrometer (Ocean Optics S2000) controlled via Labview (National Instruments). A 395 nm long-pass filter (CVI Melles-Griot) was positioned in front of the fibre-optic to prevent scattered excitation light from reaching the spectrometer.

Droplet Reactor for TiO₂ synthesis

The droplet reactor was constructed in the same way as for CdSe synthesis, except for the following differences. ODE was used as the carrier fluid. The PTFE tubing used had an ID of 0.82 mm, and was 4.5 m long, 4 m of which was immersed in an oil bath at 90 °C. No in-line spectroscopy was used.

Droplet synthesis was carried out using ODE / TiCl₃ soln / NaOH solution flow rates of 55 / 0.5 / 16.5 µL/min.

Droplet Reactor for Ag synthesis

The droplet reactor was constructed in the same way as for CdSe synthesis, except for the following differences. ODE was used as the carrier fluid. The PTFE tubing used had an ID of 0.82 mm and was

30 cm long. No heating was used. In line spectroscopy was carried out using an absorption flow cell (FIALab instruments SMA-Z-10). The PTFE tubing was connected to the flow cell using PEEK interconnects (Upchurch Scientific), a deuterium lamp (Analytical Instruments Systems Inc. Model D 1000CE) was used as light source and the spectrum was recorded using a CCD spectrometer (Ocean Optics USB 2000) and Spectra Suite software (Ocean Optics).

Droplet synthesis was carried out using ODE / Ag soln / NaBH₄ soln flow rates of 75 / 8.3 / 16.7 µL/min.

Continuous-Flow Ag Synthesis

The droplet reactor was adapted for continuous flow usage by forcing the auxiliary capillaries into the PTFE tubing as shown below in Supplementary Fig. S4. The same reagent flow-rates were used as for the droplet synthesis, but with the carrier fluid kept stationary.

Off-line Analysis

Samples for TEM were prepared by dropping a dilute suspension of the nanoparticles onto a grid and allowing the solution to evaporate. The grids were composed of a Formvar/carbon thin film on a Cu mesh (Agar Scientific S162-3). TEM was performed using a JEOL 2010 microscope fitted with a 200 kV electron gun.

A Nonius PDS 120 powder diffraction system consisting of an INEL curved, position-sensitive detector (PSD) within a static beam-sample geometry, fitted with a GeniX system with Xenocs FOX2DCU10_30P mirror to generate ultra-high brightness copper K radiation was used for XRD analysis. The ultra-high brightness x-ray beam was restricted to 25 µm using a pinhole system. The position of the x-ray beam was determined by recording its image on a fluorescent screen. Silver behenate (C₂₂H₄₄O₂ · Ag) and silicon powder were used for the calibration of this instrument.

The samples were dispersed in acetone and dried on a quartz substrate. Different areas of the sample were then analysed to ensure sample homogeneity.

SUPPLEMENTARY DATA

Supplementary Videos

Supplementary Video 1 shows ODE droplet formation in PFPE carrier fluid at flow-rates of 95.2 µL/min for PFPE and 2.4 µL/min for each ODE inlet stream. To enable visualisation of the mixing dynamics, low concentrations of the dyes Solvent Blue 45 and Sudan III were added to the upper and lower ODE streams respectively. The turbulent nature of the mixing process is clearly visible, with homogenous droplets obtained after approximately three seconds. Supplementary Video 2 shows droplet formation in the same reactor at much faster flow-rates of 677 and 133 µL/min for PFPE and ODE, respectively.

Calculation of Theoretical Dripping / Jetting Transition Boundary

The transition from dripping to jetting is formally characterised by a change from absolute- to convective-instability as has been studied analytically by Guillot and co-workers^{1,2} for the closely related situation of co-axially injected immiscible flow-streams. They showed that droplet formation is favoured by high channel radius (r), low fluid viscosities (η) and high interfacial tension (Γ).

Applying their analysis to the current situation of ODE in PFPE with $r = 500 \mu\text{m}$, $\eta_{\text{ODE}} = 4 \text{ mPa.s}$,³ $\eta_{\text{PFPE}} = 113 \text{ mPa.s}$,³ and $\Gamma = 8.3 \text{ mN/m}$,³ we obtain the theoretical phase diagram shown in Fig. S1(a), where the white and grey shaded regions define the domains of dripping (absolute instability) and jetting (convective instability), respectively. The dripping zone encompasses the entire domain of Fig. 2a (shown in Fig. S1(a) by the solid black boundary lines) as expected. The dripping zone is even larger for the case of water droplets in ODE (where $\eta_{\text{H}_2\text{O}} = 1 \text{ mPa.s}$ and $\Gamma = 19 \text{ mN/m}$,⁴) due to the lower viscosities of both phases and the higher interfacial tension (see Fig. S1(b)). The dotted line in each figure shows the phase boundary recalculated for a smaller channel diameter of $100 \mu\text{m}$, which leads in both cases to a substantial reduction in the extent of the dripping domain – indicating the importance of using a wide capillary for effective droplet formation.

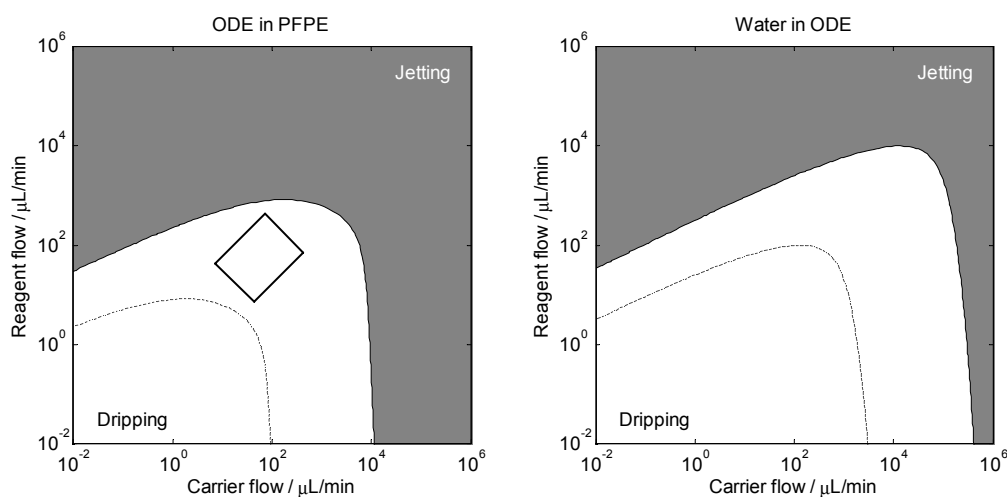


Fig. S1 (a) Theoretical phase diagrams, illustrating the operational boundary between dripping (white) and jetting (grey) for co-axially injected immiscible fluids in a cylindrical channel of diameter 1 mm for (a) ODE droplets in PFPE carrier fluid and (b) water droplets in ODE carrier fluid. The dotted lines indicate for the two situations the phase boundary for a reduced channel diameter of $100 \mu\text{m}$. The rectangular area in (a) defines the boundary of the flow conditions investigated experimentally in Fig 2(a).

TEM and size analysis of typical CdSe quantum dots prepared in droplet reactor

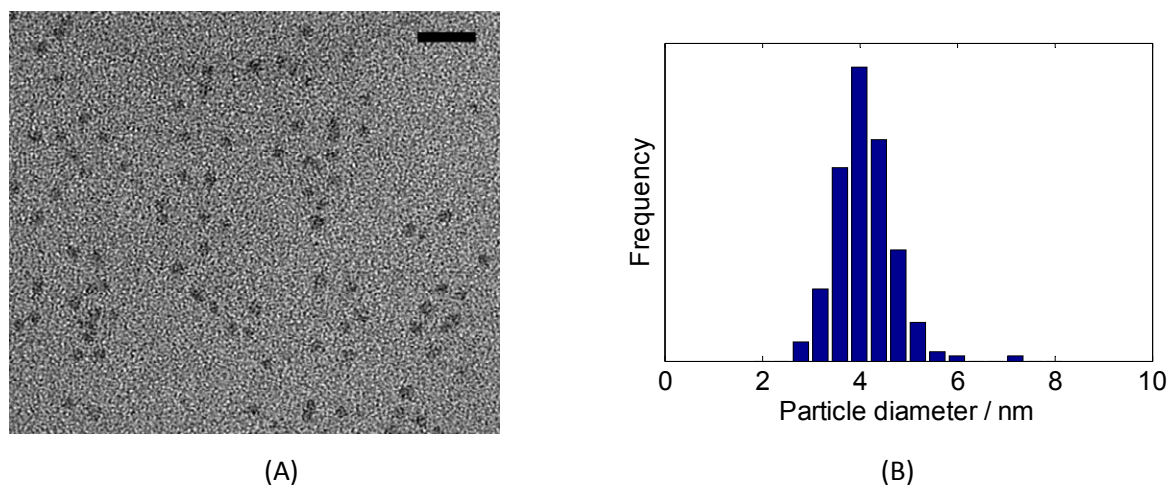


Fig. S2 Typical TEM image of CdSe quantum dots produced by the droplet reactor, using a reaction temperature of 210 °C, a residence time of 6.0 min and a Cd : Se flow ratio of 1 : 1. The scale bar indicates 20 nm.

TEM and size analysis of typical Ag nanoparticles prepared in droplet reactor

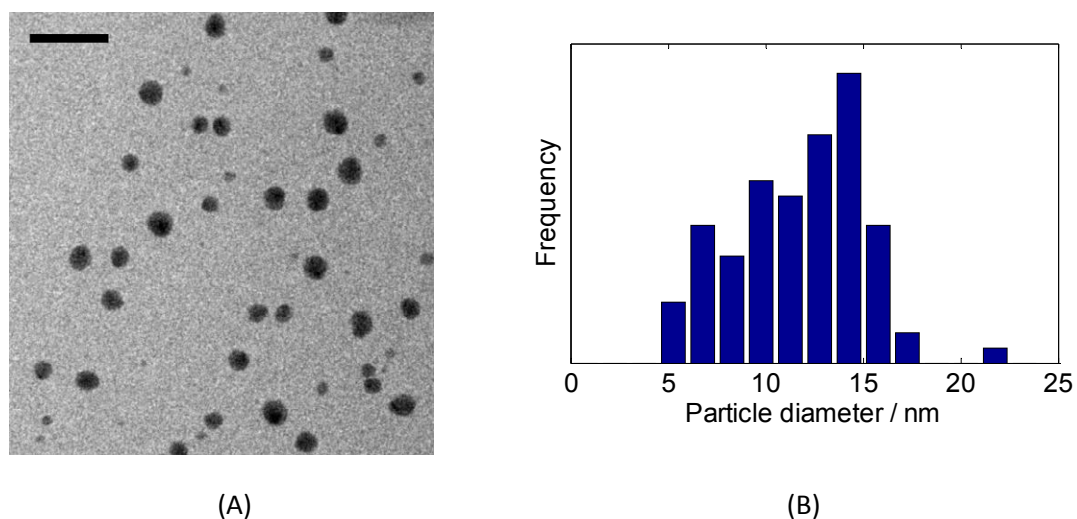


Fig. S3 Typical TEM image of Ag nanoparticles produced by the capillary reactor operating in droplet flow under the conditions specified in the main text. The scale bar indicates 50 nm.

Schematic of continuous flow reactor

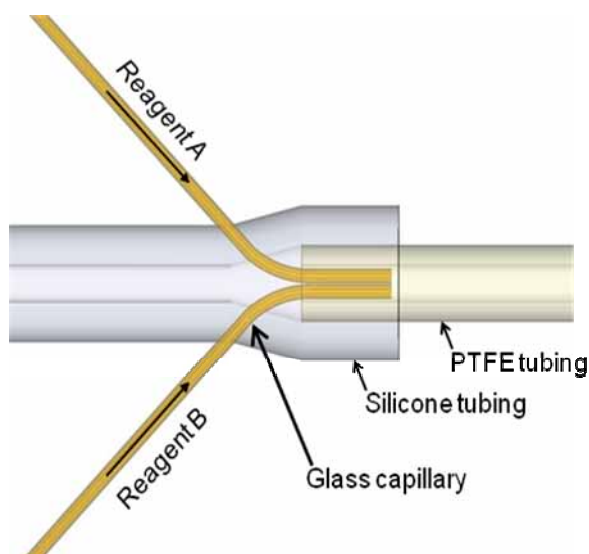


Fig. S4 Schematic of capillary reactor configured for continuous flow operation.

References:

1. Guillot, P., Colin, A. & Ajdari, A. Stability of a jet in confined pressure-driven biphasic flows at low Reynolds number in various geometries. *Physical Review E* 78 (2008).
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4. Ivosevic, N., Zutic, V. & Tomaic, J. Wetting equilibria of hydrocarbon droplets at an electrified interface. *Langmuir* 15, 7063-7068 (1999).