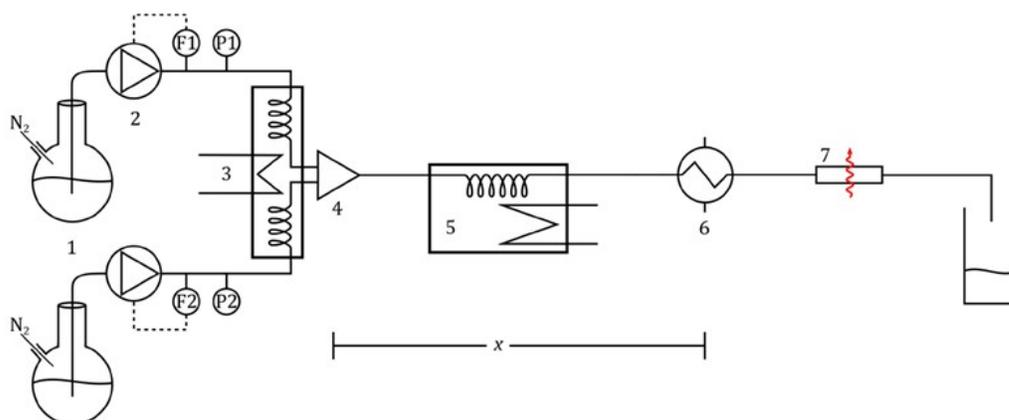


In-situ and real time study of the formation of CdSe NCs

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Supporting Information

Schematic of the reactor



Scheme S1. Schematic of the continuous-flow reactor. The different components are numbered from the precursors solution to the sample collection.

The continuous-flow reactor set up can be divided into three stages: the precursor stage, the reaction stage and the characterization stage (7). The precursor stage includes the storage flasks (1), the pumps (2) and the flow controllers (3). The reaction stage comprises all the heated zones of the reactor, and comprises the pre-heating ovens (3), the micro-mixing device (4), where nucleation takes place, the delay growth ovens (5), in which growth occurs, and the heat exchanger (6), used to quench the reaction. The characterization stage is comprised by the optical and X-Ray flow cells.

Within the precursor stage, the Cd- and Se- precursors (1) are stored under constant nitrogen supply, connected to a Schlenk line. They are pumped into the reactor through continuous pumps (2), which are fitted with upstream inline filters. The pumps are controlled via digital flow controllers (F1, F2), which allow to set the flow rates. The flow controllers are connected to pressure sensors (P1, P2), which measure the pressure separately in both fluid streams. Up to the pressure sensors all flow connections are made of 1/8 inches PEEK tubing. The pressure sensors are connected to the reaction stage, in which all the tubing (1/16 inches), connections, ferrules, nuts, etc are made of titanium. At the starting of the reaction stage, two pre-heating ovens (3) allow the precursors to heat up individually, below the nucleation temperature. The pre-heating ovens connect to the micro-mixing chamber (4), in which both precursors are mixed and heated up to the nucleation temperatures. Nucleation occurs at this micro-mixing device. The exit of the micro-mixing device is connected to a growth oven (5). Each the pre-heating ovens, micro-mixing device and growth ovens are connected with heating cartridges and thermocouples, enabling an individual and fine control of the temperature on each of the devices. All temperatures are controlled using a 16-zone PID controller, which is connected to a computer. The micro-mixing device has a very low volume of 3.8 μL , while the volume of growth oven is variable. The reaction times can be finely tuned by varying the flow rates and/or the growth oven volumes. Since each of the heating elements can be set to a different temperature, nucleation and growth events can be detached by simply applying different temperatures. In this way, our continuous-flow reactor transports the classical hot injection approach for the synthesis of nanocrystals. Analogously, a drastic temperature drop induces the reaction quenching in the reactor, by passing the reaction mixture through a heat exchanger (6). For *in-situ* characterization, the reaction mixture can be connected to an optical flow cell in which the UV/VIS absorbance is measured using an online absorption spectrometer. Additionally, a kapton-based X-Ray flow cell can be also connected, which allows measuring X-ray

scattering patterns at synchrotron radiation facilities. After *in-situ* characterization, the reaction mixture can be collected for further *ex-situ* characterization. Each and every component of the reactor can be remotely controlled by computer. The reactor set up has been described as used for the current experiments, although it can be modified significantly, based on the aim of the experiments.

Figures

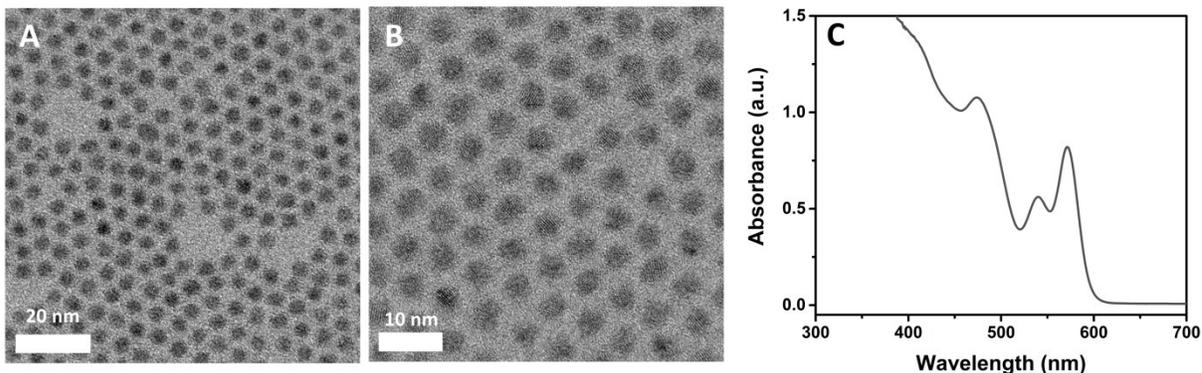


Figure S1: TEM images of CdSe NCs obtained from precursors in the continuous-flow reactor at 350 °C and 7.6 s (A, B). (C) Corresponding *in-situ* absorption spectrum.

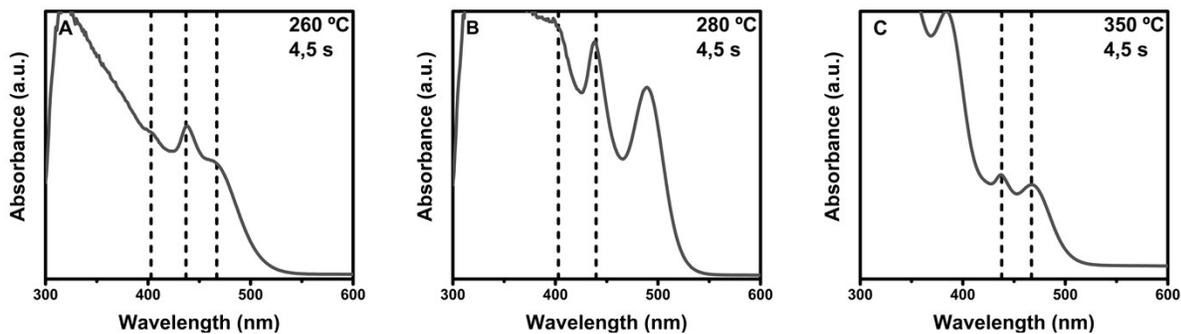


Figure S2: *In-situ* absorption spectra taken at 4.5 s at 260 °C (A), 280 °C (B) and 350 °C (C). The dashed lines indicate the MSCs positions.

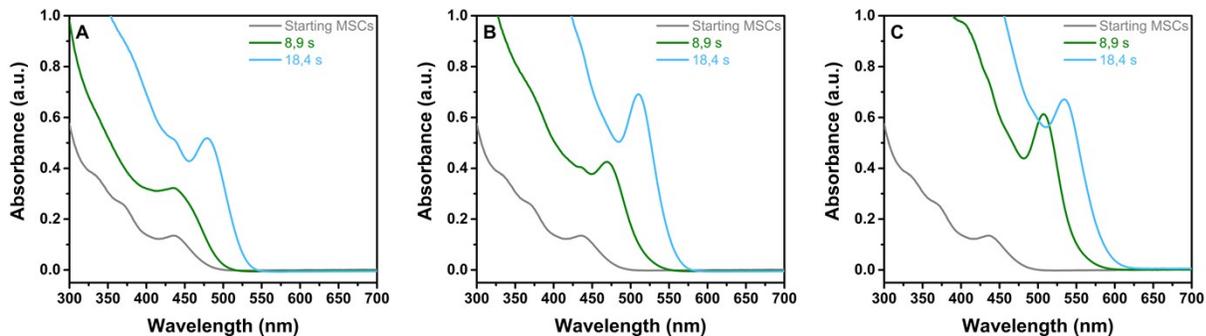


Figure S3: Temporal evolution of the *in-situ* absorption spectra at (A) 260 °C, (B) 280 °C and (C) 350 °C.

Experimental Details

Chemicals. Cadmium acetate (CdOAc, > 99.99 %) was purchased from ChemPur. 1-Octadecene (ODE, 90 %) was purchased from Sigma Aldrich. Octadecylphosphonic Acid (ODPA, 99 %) was purchased from PCI synthesis. Selenium shots /Se, > 99.999 %) were purchased from Alfa Aesar. Trioctylphosphine (TOP, 97 %) was purchased from abcr. The solvent used is a commercial mixture of alkylphosphines and alkylphosphine oxides manufactured by Cytec. All the chemicals have been used without further purification.

Precursor preparation. The selenium precursor was prepared under inert conditions in a nitrogen-filled glovebox. In a 2 L Sure/Stor flask, 64.5 g of selenium shots were mixed with 600 mL of ODE (previously degassed) and 600 mL of TOP. The mixture was degassed for several hours and stored under nitrogen. The cadmium precursor solution was prepared as follows: In a 2 l three neck flask connected to a Schlenk line 46 g of ODPA were solved in 666 mL of the solvent at 80 °C. The mixture was degassed for several hours at 100 °C, until a clear solution was obtained. On a similar separate flask, also connected to a Schlenk line, 17.633 g of CdOAc were mixed with 450 mL of TOP. The mixture was degassed at 40 °C for three hours. The solution containing ODPA was then heated to 110 °C and the CdOAc solution was transferred to the ODPA solution also keeping the inert atmosphere. The resulting mixture was turbid. It was kept at 90 °C under vacuum for several hours. The Cd complexation was achieved by heating up the mixture at 210 °C, until the turbidity disappeared. Subsequently, the mixture was kept under vacuum at 140 °C for several hours, in order to remove the acetic acid formed as side product of the Cd complexation. Finally, the Cd precursor solution was stored under nitrogen.

Synthesis of CdSe MSCs and NCs in the continuous-flow reactor. The Cd- and Se- precursor solutions (previously prepared) were stored in Sigma-Aldrich Sure/Stor flasks under constant nitrogen supply. Each of them was pumped via HNP micro annular gear pumps fitted with upstream filters. Two Bronkhorst Mini Cori-Flow flow controllers were used to control the flow rates. The pressure in both fluid streams is monitored with Cetoni Qmix P modules. The tubing after the pressure sensors directs both liquids individually to pre-heating ovens. Both liquids are mixed in a heatable nucleation device, purchased from micro4industries. This micromixing device has an interdigitated inside chamber in which both liquids get in contact. The inner volume is 8.4 μ l. The nucleation chamber has only one outlet, which connects directly with one (or more) growth ovens. The nucleation device, pre-heating ovens and growth ovens can be heated individually. The nucleation takes place in the nucleation device and the growth is limited to the growth ovens. The overall reaction time can be controlled either by variations in the flow rates and/or on the lengths of the growth ovens. The reaction is quenched afterwards by sudden temperature drop induced by circulating cold water around the tubing. The reaction time is considered to be the one at which the reaction mixture is kept at high temperature. The temperatures of the reaction zone (pre-heating ovens, nucleation chamber and growth ovens) are controlled via thermocouples and heating cartridges coupled in each of these elements. An Elotech R2500 PID controller serves as temperature controller. In all the cases, the total flow rates used produced turbulent flows, ensuring a proper mixing. Before and after each experiment the continuous-flow reactor was flushed with solvent to rinse it and to remove all possible reactants. After all the set temperatures were reached, the system was left for stabilization the time correspondent with three times the reactor volume.

In-situ optical spectroscopy. To conduct the *in-situ* absorption measurements optical flow cells purchased from Knauer were connected to the continuous-flow reactor via 1/16" HPLC connections. The flow cells contain quartz windows, and are connected to the MultiSpec Desktop spectrometer (Tec 5) through optic fibers. The optical flow cells used in the work had path lengths of 0.5 mm or 3 mm. Before each measurement a reference spectrum was taken and subtracted from the acquired spectrum as a background. The reference spectra were taken while the starting solutions (either Cd- and Se-precursors or precursor-free MSCs) were pumped through the reactor. The *in-situ* UV/VIS absorption data showed in this work was obtained averaging spectra taken in the continuous-mode.

Ex-situ optical spectroscopy. A Varian Cary 50 UV/VIS spectrometer was used to record the optical spectra to characterize each of the fractions obtained via size-selective precipitation of CdSe solutions. Samples were contained in quartz cuvettes with an optical path length of 10 mm.

Synchrotron SAXS. SAXS patterns were measured at beamline ID02 at ESRF. For all the measurements, the photon energy was 12.456 keV, the sample to detector distance was 2.02 m and the exposure time was 0.1 s per single SAXS pattern. To conduct *in-situ* SAXS patterns the continuous-flow reactor was coupled with a custom-made Kapton-based flow cell, along which the reaction mixture flowed at a constant flow. *In-situ* SAXS patterns of the starting precursors were conducted in quartz capillaries (Hilgenberg, wall thickness 0.01 mm, diameter 0.7 mm). The two-dimensional SAXS patterns were azimuthally integrated to obtain $I(q)$. Afterwards, the data was corrected for transmission as well as solvent and background scattering. The so-obtained SAXS curves were analysed using the software McSAS [I. Bressler, B. R. Pauw and A. F. Thünemann. *J. Appl. Cryst.* 2015, 48, 962.] assuming distributions of spherical with radii in the nm range.