Supplementary Information

Picoliter Droplets as Microreactors for Ultrafast Synthesis of Multi-color Water-soluble CdTe Quantum Dots

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Experimental details

Reagents and materials

Reduced glutathione (GSH) was purchased from BIOSHARP. Tellurium powder was purchased from Alfa Aesar. $CdCl_2 \cdot 2.5H_2O$ (99.0%) was purchased from China National Medicine Corporation, Ltd. High purity silver paint was purchased from SPi Supplies. Mineral oil and span 80 were obtained from Sigma-Aldrich. Indium tin oxide (ITO) glasses were purchased from LaiBao Hi-Tech Co., Ltd. AZ50XT and AZ1500 (20CP) was purchased from AZ Electronic Materials Corp. PDMS and curing agent were obtained from GE Toshiba Silicones Co., Ltd. The silicon wafers were purchased from Institute of Microelectronics of Chinese Academy of Sciences.

Design and fabrication of microfluidic chip with integrated ITO electrode

A microfluidic chip containing a flow-focusing structure and a heating region was designed (as shown in Fig. S1). The main channels are 60 μm wide, and the throat after the flow-focusing regions is 60 μm long and 25 μm wide. Soft-lithography was used to fabricate the microfluidic chips. Briefly, the designed structure printed on a transparent film was transferred onto a silicon wafer with 30 µm thick AZ50XT photoresist. After casting about 5 mm thick poly-(dimethylsiloxane) with a 10 : 1 polymer/curing agent ratio, onto the silicon master and waiting until the bubbles disappeared, PDMS was cured at 75 °C for 3 h. Then the cured PDMS was peeled off from the master, and inlet and outlet holes were drilled by a metal pipe. After exposed to a plasma treatment for 1 min, the PDMS was bonded to a silicon wafer on which a 50 mm thick PDMS film was coated previously.

The integrated heater was made from indium tin oxide (ITO)-coated glass. Soft-lithography was used to fabricate designed structure on ITO glass with AZ1500 photoresist. Then ITO uncovered with photoresist was etched with 9 mol/L HCl solution. And finally, photoresist was washed off with ethanol solution. The glass with designed ITO pattern was obtained. The PDMS elastomeric stamp was bonded to the glass with designed ITO pattern after exposed to a plasma treatment for 1 min. The PDMS chips were baked at 120 °C for more than 20 h to get the hydrophobic channels.

Temperature control system of microfluidic chip

The temperature of heated region was controlled by temperature-controlling device (XMTD, Yao otlet instrument Co., Ltd, China), showed in Figure S2. The device controlled the voltage applied to the ITO film-based heater depending on the temperature readings from the model PT-100 micro-thermistor (FMC 2101) located under the microfluidic chip. High purity silver paint was prepared to attach copper wires onto an ITO glass substrate and was then dried at 120 °C for 30 min. During this stage, the solvent was then removed and the copper wires adhered onto the substrate.

Droplet Generation and Characterization

Two immiscible fluids, a mineral oil continuous phase and a disperse phase contained a mixture of Te and Cd precursor solution were pumped constantly by syringe pumps (pump 11 Pico Plus, Harvard Apparatus, USA) into the well-fabricated PDMS microfluidic chip. Droplets (W/O) were formed in the flow-focusing structure. The behavior of the flow was observed under an inverted fluorescence microscope (TE2000-U, Nikon Corp, Japan), coupled with a charge coupled device (CCD, Retiga 2000R, Qimaging Corp, Canada) for the recording process. Fig. S5 showed picoliter droplets of precursor solution were generated stably in flow-focusing structure at different flow rates when the reaction channel was heated up to 85 °C.

Synthesis Procedure

The formation of droplet and temperature control of reaction region as previously stated. Reactor set point temperatures ranged from 80 to 92 °C. The droplet residence time, which was calculated by timing several individual droplets traveling through the local reaction region, could be adjusted by changing the flow rates of continuous phase and disperse phase. Furthermore, the microscopic imaging technique and a portable fiber optic spectrometer (QE65000, Ocean Optics, USA) coupled with the microscope were employed to monitor the product solution fluorescence signal of ODs synthesized inside the droplets in situ based on visible light-admitting of ITO film. The peak position of the fluorescence spectra of the GSH-coated nanocrystals at different residence times corresponding with total flow rates are given in the Fig. S6.

Cleaning and Characterization

Reaction products were collected from the outlet of microfluidic chip by glass capillary. The product mixture was centrifuged and the bottom colored aqueous phase was separated, precipitated with ethanol, and centrifuged again to get pure nanocrystals. The cleaned nanocrystals were characterized with transmission electron microscope (JEM-2100F, JEOL, Japan) at 200 kV beam acceleration. UV visible absorption spectra were recorded in quartz cuvettes on a spectrophotometer (UV-2550, Shimadzu, Japan). Fluorescence spectra were recorded on a spectrophotometer (Fluorolog-3, HORIBA JOBIN YVON INC, France).

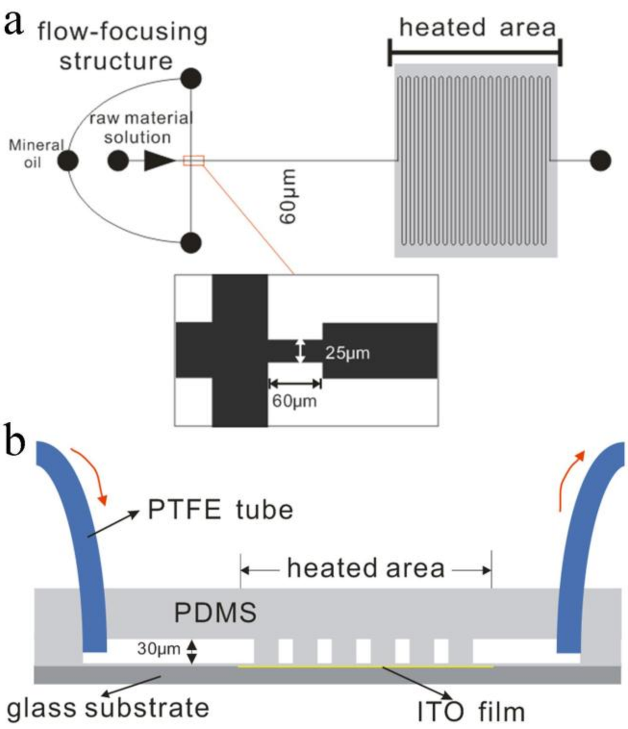

Fig. S1 Schematic representation of the microchip with a flow-focusing structure and a heating region.

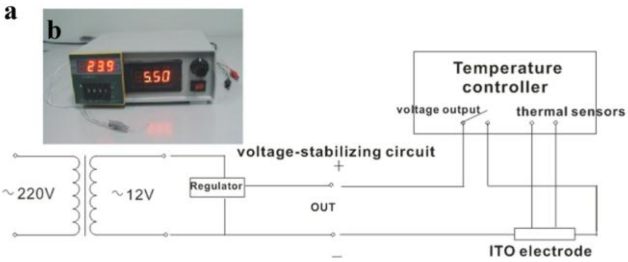

Fig. S2 Schematic illustration (a) and physical map (b) of the temperature controller.

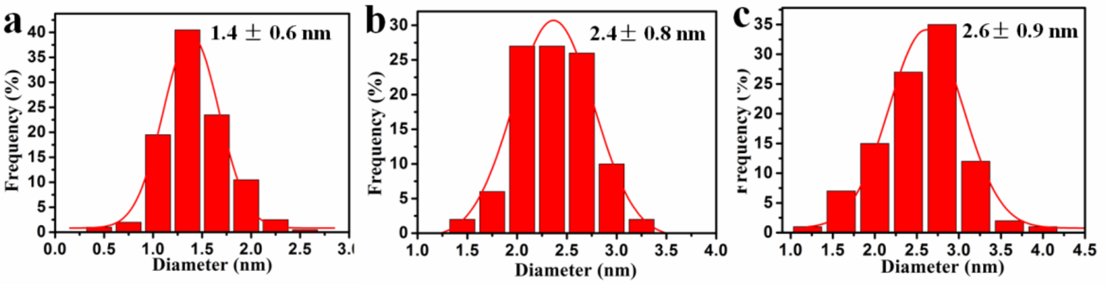

Fig. S3 Size distribution of QDs synthesized at different temperatures of 81.5 °C (a), 87.0 °C (b) and 90.0 °C (c).

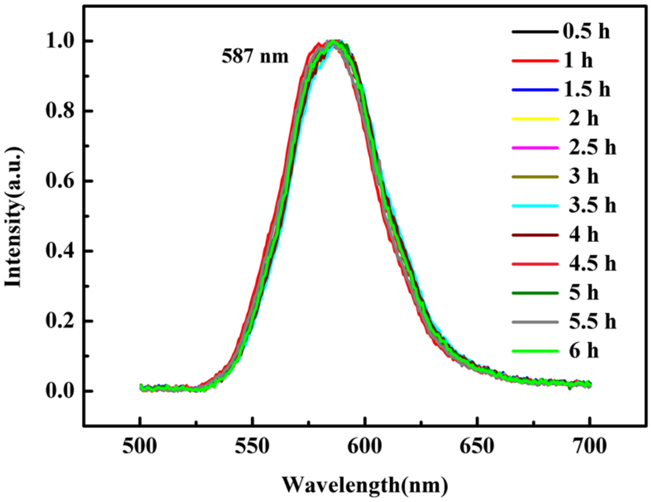

Fig. S4 Time evolution of the emission spectra of droplet-synthesized CdTe QDs. The reaction conditions were fixed at T = 89.0 °C, U_W =10 μL/h and U_O = 30 μL/h.

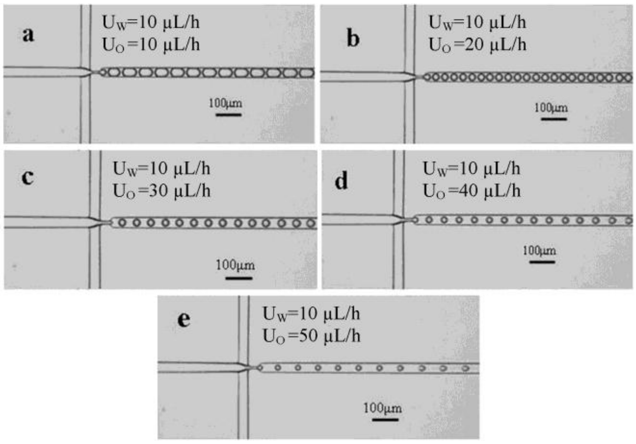

Fig. S5 Optical micrographs of droplet formation at indicated flow rates of the mineral oil continuous phase (U_O) and the disperse phase composed by a mixture of precursor solution (U_W). The volume of a droplet was calculated to be picoliter scale, as the droplet was assumed as an ellipsoid.

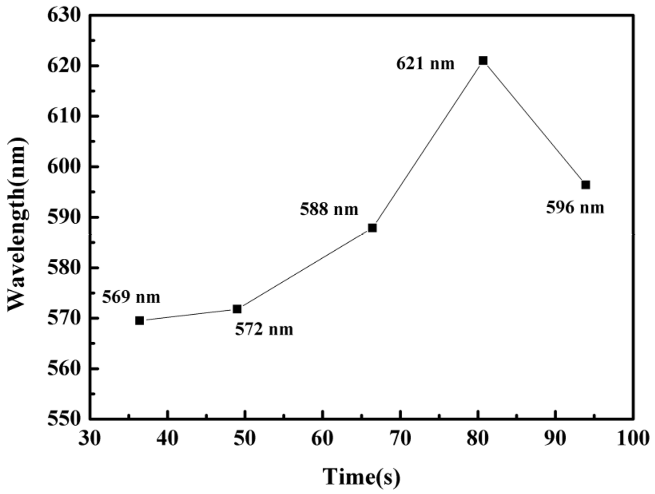

Fig. S6 The peak position of the fluorescence spectra of the GSH-coated CdTe QDs at different flow rates U_W=10 μL/h, U_O=10 μL/h, 20 μL/h, 30 μL/h, 40 μL/h, 50 μL/h. Corresponding residence times are 93.9 s, 80.7 s, 66.4 s, 49.0 s, 36.4 s, respectively. The reaction temperature was fixed at 89.0°C.

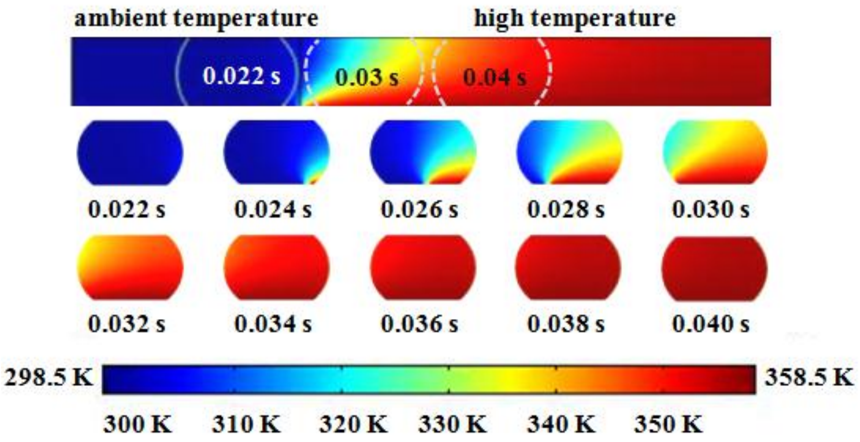

Fig. S7 Schematics of temperature distribution within a droplet in 0.022 s, 0.024 s, 0.026 s, 0.028 s, 0.03 s, 0.032 s, 0.034 s, 0.036 s, 0.038 s, 0.04 s by numerical simulation. The color distribution of colors inside a droplet shows that it is achieved temperature equilibrium.