Supporting Information

Lasing Supraparticles Self-Assembled from Nanocrystals

Federico Montanarella†,‡, Darius Urbonas§, Luke Chadwick†, Pepijn G. Moerman‡, Patrick J. Baesjou†, Rainer F. Mahrt§, Alfons van Blaaderen‡,* , Thilo Stöferle§,* and Daniel Vanmaekelbergh†,*

F. Montanarella and D. Urbonas contributed equally to the work

†Condensed Matter and Interfaces and ‡Soft Condensed Matter groups, Debye Institute for Nanomaterials Science, Utrecht University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands

§IBM Research – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland
EXPERIMENTAL SECTION

Chemicals
Sodium dodecyl sulfate (SDS, ≥98.5%), Cadmium oxide (CdO, ≥99.99%), Octadecylphosphonic acid (ODPA, 97%), Trioctylphosphine oxide (TOPO, 99%), Trioctylphosphine (TOP, 90%), 1-octanethiol (≥98.5%), Dextran from Leuconostoc mesenteroides (Mw 670000 g/mol), Hexane (anhydrous, 95%), Cyclohexane (anhydrous, 99.5%), Oleic acid (OA, 90%), Ethanol (EtOH, 99.8%), 1-Butanol anhydrous (BuOH, 99.8%), Methanol (MeOH, anhydrous, 99.8%) and Toluene (anhydrous, 99.8%) were all purchased from Sigma Aldrich and used as received. Selenium (Se, 99.999%) was purchased from Brunswig Chemie CV.

Synthesis of CdSe NCs
The synthesis of CdSe NCs was performed according to literature. For this synthesis we first mixed 60 mg of CdO, 280 mg of ODPA and 3 g of TOPO in a 100 mL three neck flask. The mixture was heated to 150 °C and degassed under vacuum for 1 hour. The reaction was then put under nitrogen flow and the temperature was increased up to 320 °C, where it was kept for 1 hour until a colorless clear solution was obtained. Subsequently, 1 mL of TOP was added to the mixture, and the temperature was increased to 380 °C, at which temperature a solution of Se-TOP (70 mg of Se in 0.5 mL of TOP) was quickly injected. After 30 s, the reaction was quenched by quickly reducing the temperature using compressed air flow over the glass. The resulting particles were diluted with 1 volume equivalent of toluene and centrifuged at 3500 rpm for 10 min at room temperature. The NCs were extracted from the supernatant, while the precipitate, mainly containing TOPO and unreacted ODPA, was partially redispersed in toluene and centrifuged again to extract more NCs. All the collected NCs were then washed through precipitation upon addition of 1 volume equivalent of a mixture of MeOH/BuOh 1:3. This washing procedure was repeated twice, and, in the end, the particles were redispersed in hexane.

Synthesis of CdSe/CdS shell
The synthesis of CdSe/CdS shell was performed according to literature. A 2 mL hexane solution containing 100 mmol of CdSe NCs was loaded in a three neck flask with 3 mL of ODE and 3 mL of oleylamine. The mixture was then degassed at room temperature for 1 hour under vacuum, and then 30 min at 120 °C to remove the hexane, the water and the oxygen. The mixture was then put under nitrogen flow and brought to 310 °C. When the temperature reached 240 °C, two separated solutions of 2.5 mL of 0.10 M Cd(OA)$_2$ in 6 mL ODE and 55 µL of 1-octanethiol in 6 mL of ODE (molar ratio Cd(OA)$_2$:1-octanethiol = 1:1.2) were injected dropwise in the reaction mixture at a rate of 3 mL/h with the aid of a syringe pump. At the end of the injection, 1 mL of OA was injected in the mixture, which was then let react for 60 min at 310 °C. The resulting CdSe/CdS NCs were then washed through precipitation upon addition of 1 volume equivalent of a mixture of MeOH/BuOh 1:3. This washing procedure was repeated twice, and, in the end, the particles were redispersed in cyclohexane.

Characterization of CdSe/CdS NCs
The resulting CdSe/CdS NCs had an overall diameter of 12.4 ± 1.0 nm (from TEM analysis), composed of an inorganic core and an organic ligand shell. The inorganic core had a diameter of 8.6 ± 1.0 nm, composed of a CdSe core of 3.6 nm in diameter and a 2.5 nm thick CdS shell. The ligand shell was made of oleate ligands with an average length of 1.9 nm. The CdSe core NCs in solution had an emission peak centered at 2.134 eV (581 nm), while the core/shell CdSe/CdS NCs had their emission peak centered at 2.015 eV (615 nm).
Synthesis and characterization of CdSe/(Cd,Zn)S NCs with thick (Cd,Zn)S shell

The synthesis of the NCs was performed in accordance to literature (the “red emitting NCs” described in the SI of ref. 2). The so-synthesized NCs consist of a 3.1 nm CdSe core with 5 monolayers (ML) of CdS, 1 ML of CdZnS and 1 ML of ZnS. These core/multi-shell NCs are nearly spherical with a diameter of 11.4 ± 1.5 nm (without considering the oleate capping ligand shell), and the PL emission is centered at 1.977 eV (627 nm).

Description of simulation procedure

The whispering gallery mode (WGM) simulations were performed with the MEEP Finite-Difference Time-Domain (FDTD) solver. We used a 3D FDTD method with a cell size of 18:18:18 µm (x:y:z), 50 nm grid size, and 1-µm-thick perfectly matched layer (PML) boundary conditions. The simulation geometry consists of a SiO₂ bottom layer, a 5 µm radius sphere having a refractive index of the SP and an air cladding. The dipole source is positioned randomly in the SP to excite all the supported modes.

Definition of polydispersity

All the values of sizes in the article are given with the mean (µ) and the standard deviation (σ) in the form: µ ± σ. Polydispersity of size is defined as PD (%) = σ/µ·100.

Electron microscopy

SEM images were acquired using a Phenom ProX electron microscope operated at 10 kV. A dual beam FIB (Fei Helios) operated at 30 kV was used for cross sections of the SPs. TEM images were acquired using a FEI Tecnai electron microscope operated at 200 kV.

Calculation of the refractive index

The refractive index of the SP has been calculated by modeling the SP as composed for the 66% (randomly packed spheres) from NCs and for the 34% by organic material (oleate capping and cyclohexane). The refractive index of the NCs has been calculated considering a core of CdSe with 1.8 nm radius, covered by a 2.5 nm thick shell of CdS and a 1.9 nm thick ligand shell of oleate. We used the refractive index values for each component at 27 °C at a wavelength of 600 nm: 2.48 for CdSe (ref. 4), 2.52 for CdS (ref. 5), 1.46 for oleate (ref. 6) and 1.43 for cyclohexane (ref. 7). The effective refractive index of the SP is calculated by averaging the refractive indexes of the single component according to their volumes which were assumed to be additive, thus obtaining a value of 1.69.

Glass microfluidics for monodisperse droplet production

The ability to produce monodisperse droplets of a controllable size is an essential first step in the production of monodisperse SPs of tunable size. Here we describe a low-cost and simple microfluidic setup that can nonetheless be used to produce emulsions of a tunable size range between 50 µm and 220 µm in diameter with polydispersities under 5 %. We provide a detailed, stepwise description of the device construction and show results that indicate the droplet size range for which this setup is applicable. The style of microfluidics device described here is referred to in the literature as having a coaxial co-flow geometry. The design of the setup is based on earlier studies by Choi and coworkers and Haase and Brujic.
Table S1: Table of four different types of device designs that can be used to make droplets from 50 µm to 220 µm. The displayed capillary sizes are inner diameters for round capillaries and inner edge lengths for square capillaries. *To ensure that the 50 µm capillary is positioned in the middle of the outer capillary and lines up with the outlet capillary, it is encased in a 25 mm long 100 µm wide square capillary and fixed with ultra-violet-curable glue.

Microfluidic device construction

An overview of the device design is provided in Figure S6. A Menzel-Gläser microscope slide of 76 × 25 mm and 1 mm thick is used as support. The microfluidic design can be built using various sizes of capillaries. The choice of capillary size largely determines the size of the droplets that come out. Fine control of droplet size is obtained by flow control.

Step 1: Take a square capillary (VitroCom) of a size as provided in Table S1 and cut it in half to a final length of 25 mm with a Molex 1 × 1 inch cleaving stone. Place it on the middle of the microscope slide across the hole and use 40 Norland Optical Adhesive 68 to fix the capillary to the glass. Place the glue across the capillary, touching the glass slide on both sides, not in between the capillary and the slide to keep the capillary level with the glass. Place the glue close to the hole in the glass slide and use a small amount to avoid covering a large part of the capillary, as it will later be in the way of visualizing droplet formation in the middle of the square capillary or attaching parts on the ends of the capillary.

Step 2: Take two capillaries for dispersed phase inlet and emulsion outlet as chosen from Table S1. Fix the dispersed phase inlet to a stand clamp hanging down. Attach a small weight to the bottom, (such as a hair clip with tissue in the middle to avoid breaking the capillary) to ensure that the capillary hangs vertically. To taper the capillary, quickly heat the middle of the capillary by moving a crème brûlée burner across it sideways. Moving the burner too slowly will cause the capillary to melt, break and fall and moving the burner too slowly will not melt the capillary at all. Ideally the capillary melts slightly and drops but does not break so that the middle has narrowed. Take the tapered capillary and insert it backwards into the square outer capillary to prevent breaking the fragile tapered end. Then carefully insert the non-tapered capillary from the other side and slide it in, so that it encases the tapered capillary. Glue stuck the capillaries with UV glue once they are in place. Use again a small amount across the capillary and place it 1 cm from the end of the square capillary.

Step 3: The opening between the square capillary and the inserted ones are going to be inlet and flush outlet. For tubes to connect to the opening between the capillaries, use a blunt needle tip (Techsil TS21 Green with a polypropylene Luer Lock, and stainless-steel needle with inner diameter 0.51 mm). The hubs have gauge size 23 and length 1.27 cm which results in a large open space which ends up as unwanted dead volume in the device, so cut off 5 mm from plastic bottom. Then make an incision on two sides of the remainder of the plastic part, opposite each other that fit the capillaries. Then place the entire needle on the opening between the two capillaries. Glue the blunt needle tips to the glass slide with 2-component epoxy glue (Scotchwell DP100NS) after the glue has partly polymerized so that the viscosity
has increased, and it does not seep into the capillaries as this would clog the device. Repeat this step for the other opening, so that two needles stick out of the device now.

Step 4: Take two new needle tips and remove the metal part from the plastic. Then bend the metal part in a right angle and slide one part over the glass capillaries stick out of the device. The bend ensures that when pulling on the needles to attach and remove tubing during operation, the needles do not detach from the glass capillaries. Glue the bent capillaries in place with 2-component glue. These will be the dispersed phase inlet and emulsion outlet.

**Droplet size control**

Rough size control is achieved by picking the right size of capillaries, as the largest drop size a device can produce is around the size of the outer capillary. Droplet size fine-tuning is done by varying the dispersed phase flow ratio with the continuous phase flow. Typically, larger continuous flow results in smaller droplets. We used dispersed flow varying between 0.1 and 1 ml/h and continuous flows between 1 and 20 ml/h. Fig. S7 shows that with the four device setups described here, a continuous range of droplet diameters from 220 μm down to 50 μm can be achieved reliably. The polydispersity is between 1 and 5 % and is smaller for smaller droplets.
Additional figures

**Figure S1:** Representative images of droplets and SPs.  
a) Optical image of droplets of cyclohexane containing NCs. The average diameter of the droplets is $109 \pm 4 \, \mu m$;  
b) SEM image of SPs formed from the droplets of panel a. The average diameter of the droplets is $10.2 \pm 0.5 \, \mu m$.  

Figure S2: Focused Ion Beam (FIB) SEM images of SPs. a) SEM image of a single SP; b) FIB-SEM of the SP of panel a, showing that the SP is close-packed with NCs on the inside; c) SEM image of a group of SPs; d) FIB-SEM of one of the SPs of panel c, showing again that the SP is filled on the inside.
Figure S3: Profile and cross section of the excitation beam. a) Excitation spot imaged by monitoring the PL from a spin-coated 35 nm-thick luminescent polymer film on a cover slip; b) Cross section of the excitation beam. In black are the data points, showing a FWHM of 22 µm.

Figure S4: Scheme of Michelson interferometer. Here blue arrows denote optical beam path, and Δt is the variable relative delay of the beam path that is spatially inverted using a retroreflector on a motorized stage. The light from both interferometer arms is recombined as real space interferogram on the camera.
Figure S5: FDTD simulation of WGMs supported by SPs. Dashed lines represent the contours of the SP, the blue colored area shows the SiO\textsubscript{2} substrate, and the normalized electromagnetic field intensity is shown in shades of red where darker color corresponds to higher intensity. a) Cross section in the \( xy \) plane of the SP of a WGM propagating orthogonal to the substrate. When viewed from above, this will appear as linearly polarized light. b) \( zx \) cross section of the same mode presented in a; c) WGM travelling in the \( xy \) plane of the SP. When viewed from above, the rotational symmetry would make it appear as unpolarized light; d) \( zx \) cross section of the same mode presented in c. The seeming asymmetry is an artifact from the cross section where on the left the cut goes through a node and on the right through an antinode of the WGM field. While here the two extreme cases of WGM perfectly normal and perfectly perpendicular to the substrate are shown, WGM with planes at tilt angles in-between are also possible.
Figure S6. Microfluidic chip design and photographs. Transparent shapes represent glass capillaries. Gray tubes represent metal needles from syringe heads. Green shapes represent plastic syringe heads. The numbers indicate the order in which to add parts and correspond to the step number described in the design setup section.
Figure S7: Droplet size control. a) Size range that can be achieved with the four designs given in Table S1, where purple corresponds to design 1, blue to 2, red to 3 and black to 4. Flow rate of the dispersed phase is 0.7 mL/h for all devices except 1. There the dispersed flow rate is 0.1 mL/h. The flow rate of the continuous phase is varied to change droplet size and displayed on the horizontal axis. Error bars represent droplet polydispersity. b) Droplet size can be finely controlled by varying the continuous phase flow rate. The histograms represent droplet size distributions at four different flow rates in a device of type 3 and correspond to red points in panel a. c-f) Micrographs of droplets produced using device of type 3. The images correspond to histograms in panel b with the same color coding.
Figure S8: Lasing from SP of CdSe/(Cd,Zn)S NCs with thick (Cd,Zn)S shell. For sufficiently high excitation fluences, we observe lasing from the thick CdS shell of the NCs in the range 1.975 – 2.15 eV. The curves are vertically offset for clarity. To reduce heating from excess pump photon energy, we used pulsed excitation with a wavelength of 500 nm instead of 400 nm (using a travelling-wave optical parametric amplifier instead of frequency doubling of the regenerative amplifier output) focused to a 10× larger spot.
References

(1) Chen, O.; Zhao, J.; Chauhan, V. P.; Cui, J.; Wong, C.; Harris, D. K.; Wei, H.; Han, H.-S.; Fukumura, D.; Jain, R. K.; et al. Compact High-Quality CdSe–CdS Core–shell Nanocrystals with Narrow Emission Linewidths and Suppressed Blinking. Nat. Mater. 2013, 12, 445–451.

(2) Montanarella, F.; Altantzis, T.; Zanaga, D.; Rabouw, F. T.; Bals, S.; Baesjou, P.; Vanmaekelbergh, D.; van Blaaderen, A. Composite Supraparticles with Tunable Light Emission. ACS Nano 2017, 11, 9136–9142.

(3) Oskooi, A. F.; Roundy, D.; Ibanescu, M.; Bermel, P.; Joannopoulos, J. D.; Johnson, S. G. Meep: A Flexible Free-Software Package for Electromagnetic Simulations by the FDTD Method. Comput. Phys. Commun. 2010, 181, 687–702.

(4) Jensen, B.; Torabi, A. Refractive Index of Hexagonal II–VI Compounds CdSe, CdS, and CdSexS1–X. J. Opt. Soc. Am. B 1986, 3, 857.

(5) Bieniewski, T. M.; Czyzak, S. J. Refractive Indexes of Single Hexagonal ZnS and CdS Crystals. J. Opt. Soc. Am. 1963, 53, 496–497.

(6) O’Neil, M. J. The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals; Merck: Whitehouse Station, N.J., 2001.

(7) Kerl, K.; Varchmin, H. Refractive Index Dispersion (RID) of Some Liquids in the UV/VIS between 20ºC and 60ºC. J. Mol. Struct. 1995, 349, 257–260.

(8) Choi, C.H.; Weitz, D. A.; Lee, C.S. One Step Formation of Controllable Complex Emulsions: From Functional Particles to Simultaneous Encapsulation of Hydrophilic and Hydrophobic Agents into Desired Position. Adv. Mater. 2013, 25, 2536–2541.

(9) Haase, M. F.; Brujic, J. Tailoring of High-Order Multiple Emulsions by the Liquid-Liquid Phase Separation of Ternary Mixtures. Angew. Chemie 2014, 126, 11987–11991.