

Monodisperse Nanocrystal Superparticles through a Source–Sink Emulsion System

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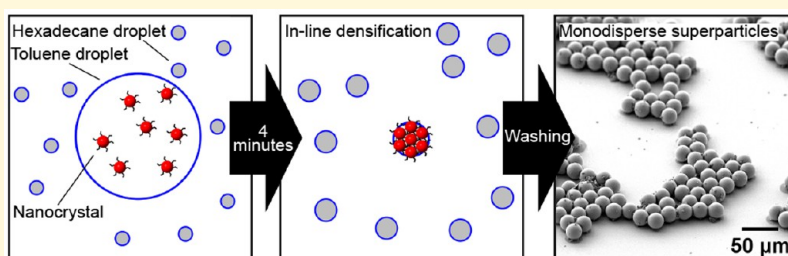
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ABSTRACT: Superparticles made from colloidal nanocrystals have recently shown great promise in bridging the nanoscale and mesoscale, building artificial materials with properties designed from the bottom-up. As these properties depend on the dimension of the superparticle, there is a need for a general method to produce monodisperse nanocrystal superparticles. Here, we demonstrate an approach that readily yields spherical nanocrystal superparticles with a polydispersity as low as 2%. This method relies on the controlled densification of the nanocrystal-containing “source” emulsion by the swelling of a secondary “sink” emulsion. We show that this strategy is general and rapid, yielding monodisperse superparticles with controllable sizes and morphologies, including core/shell structures, within a few minutes. The superparticles show a high optical quality that results in lasing through the whispering-gallery modes of the spherical structure, with an average quality factor of 1600. Assembling superparticles into small clusters selects the wavelength of the lasing modes, demonstrating an example of collective photonic behavior of these artificial solids.

INTRODUCTION

Throughout history, the emergence of complex patterns from the organization of smaller components has captivated humankind. This interest stems from the search for the mechanism driving the assembly process: Through multiple forces,^{1,2} self-assembly leads to the formation of hierarchical superstructures.^{3,4} Frequently, these superstructures perform a higher, collective function than their constituent building blocks.^{5,6} Gaining control over self-assembly, therefore, represents a successful strategy to build materials with new properties.

Over the last three decades, scientists have learned to control the crystallization of atoms into nanoscale structures known as nanocrystals (NCs).⁷ Depending on their morphology, dimension, and chemical composition, NCs can manipulate electromagnetic radiation over a broad spectral range. Upon assembly into 3D mesoscale superstructures,^{2,8–11} the properties of NCs hybridize through excitonic,^{12–14} electronic,^{15–18} magnetic,^{19–22} plasmonic,^{23–25} phononic,^{26,27} and photonic^{6,28,29} coupling mechanisms. While the coupling strength is generally controlled by the distance between NCs,³⁰ the morphology of the superstructure plays an important role in mediating the interaction with external stimuli.

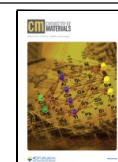
In the case of optical stimuli, Maxwell’s equations predict the confinement of intense electromagnetic fields within a dielectric structure of dimensions comparable to the wavelength,³¹ increasing the probability of absorption and scattering of light.^{6,32} Additionally, when the structure possesses rotational symmetry, light can become trapped at the surface through whispering-gallery modes,^{29,33,34} resulting in a 3D resonator. Since these processes crucially depend on the morphology and refractive index of the structure,³⁵ there is a strong motivation to fabricate optical structures with well-defined size, shape, and composition.

Top-down microfabrication processes have succeeded in producing mesostructures with increasingly complex morphologies and high optical quality³⁶ to optimize and exploit the trapping of light for various applications. For instance, microfabricated ring resonators are regularly used as lasers,²⁸ second-harmonic generators,³⁷ as well as environmental^{38,39}

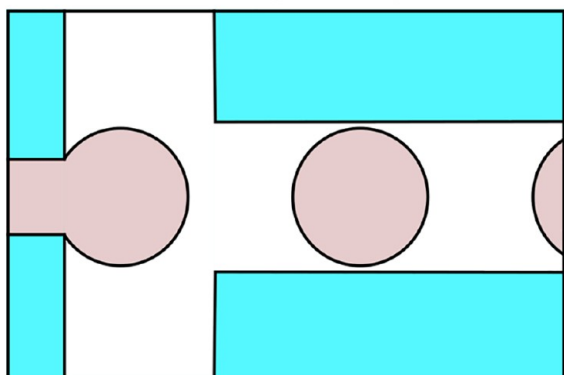
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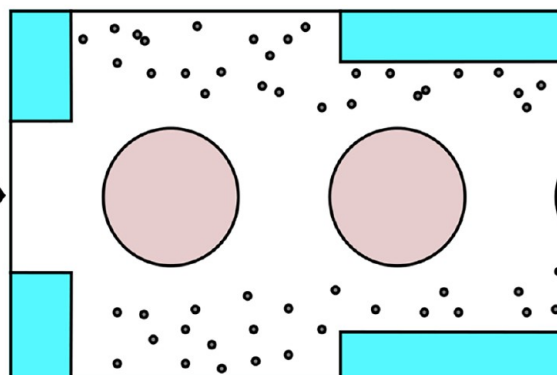
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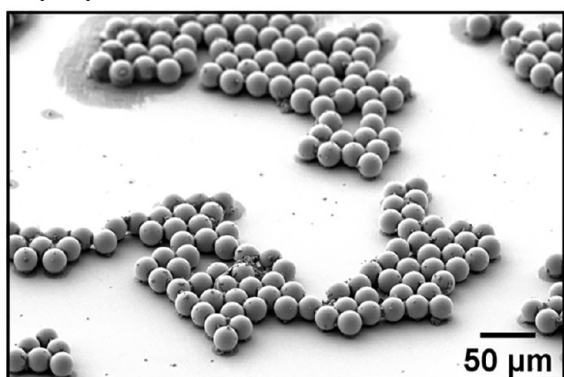
Step 1: Monodisperse "source" toluene emulsion containing nanocrystals



Step 2: Addition of "sink" hexadecane emulsion



Step 4: Monodisperse nanocrystal superparticles



Step 3: In-line source-to-sink mass transport of toluene

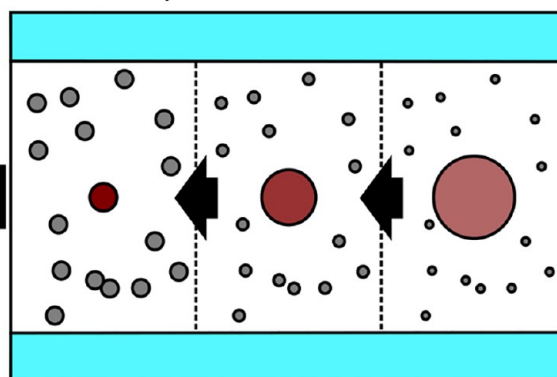


Figure 1. Schematic of the fabrication of monodisperse NC superparticles. Step 1: Generation of a monodisperse toluene-in-water "source" emulsion using droplet microfluidics. Each droplet contains a dispersion of NCs with initial volume fraction ϕ . Step 2: Introduction of a secondary hexadecane-in-water "sink" emulsion. The hexadecane droplets are 3 orders of magnitude smaller than the toluene droplets. Step 3: The sink emulsion swells with toluene from the source emulsion, shrinking the source droplets and ultimately forming NC superparticles. Step 4: After washing away the swollen sink emulsion, the NC superparticles appear monodisperse and spherical.

and mechanical⁴⁰ sensors. However, the fabrication of these optical structures relies on slow, complex, and expensive processes. Moreover, after fabrication these structures are usually bound to a substrate, limiting their deployment for *in situ* sensing. For these reasons, there are significant opportunities to develop more direct and cheaper experimental procedures to fabricate new classes of portable resonators by exploiting a recently developed, versatile,^{41,42} scalable,⁴³ and inexpensive technique known as emulsion-templated assembly.⁴⁴

The simple act of shaking a mixture of oil and water in the presence of a surfactant can generate a polydisperse emulsion. The controlled densification of emulsion droplets that contain a dispersion of NCs leads to the formation of dense NC superstructures.^{41,42,45–48} These superstructures, known in the literature as superparticles,⁴⁹ supraparticles,⁵⁰ or supercrystals,⁴⁵ generally assume a spherical shape imposed by surface tension, although specific processing conditions can yield more complex morphologies, like cubic^{51,52} and toroidal⁴⁴ shapes. These NC superparticles interact strongly with light through Mie⁶ and whispering-gallery modes²⁹ and promise the introduction of more efficient, cheaper, and portable micro-lasers,³⁵ upconversion media,⁵³ and stimuli-responsive dielectric metasurfaces⁵⁴ for structural color applications.^{55–57}

However, since the optical properties of the superparticles strongly depend on their dimensions, all applicative efforts are currently encumbered by the need for a reliable and general method to produce monodisperse NC superparticles.

A monodisperse emulsion is a good starting point to fabricate monodisperse superparticles. Recently, droplet microfluidics has emerged as the technique of choice to generate emulsions with a polydispersity lower than 5%.^{58–60} Yet, the generated emulsions are sensitive to shear forces, and the mixing usually required to densify the droplets into superparticles results in significant size defocusing, as shown in Figure S1, thus jeopardizing the benefits of the microfluidic approach. Polymerizing the surface of the droplets can improve their stability by minimizing mass transport across the liquid/liquid interface.^{59,61,62} However, this strategy inherently impedes densification and is therefore unsuitable to form dense NC superparticles. Fluorosurfactants have shown excellent results in stabilizing water^{63–66} or oil⁴² droplets in fluorinated oil; yet, the use of fluorochemicals is environmentally unsustainable due to their resilience against degradation.⁶⁷

Here, we propose a general method to fabricate monodisperse, dense NC superparticles using a source–sink emulsion system. A schematic of this process is shown in

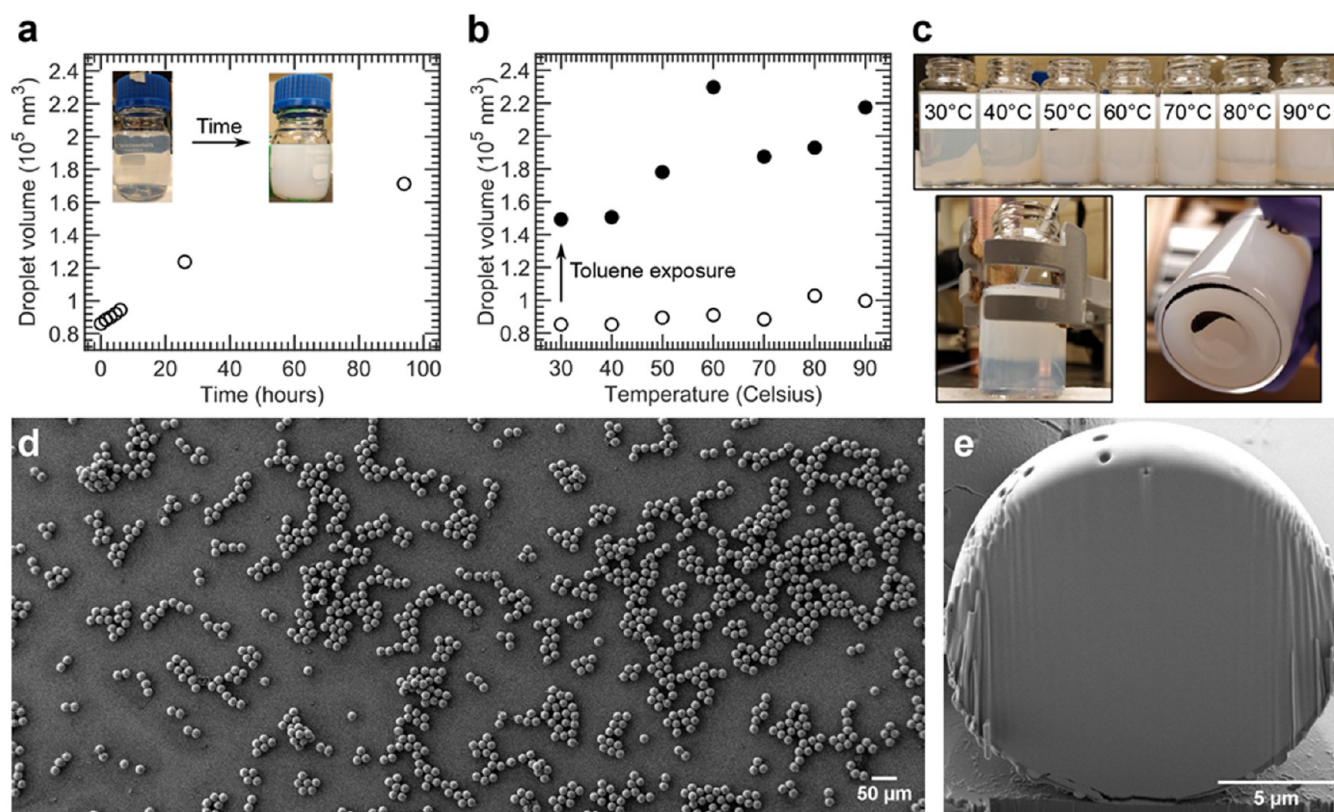


Figure 2. Exposure to a sink emulsion drives the formation of monodisperse NC superparticles. (a) Evolution of the “sink” hexadecane emulsion at room temperature when not exposed to toluene. The droplet volume is calculated from the average hydrodynamic radius extracted through dynamic light scattering. The photographs in the inset highlight the increase in turbidity of the hexadecane emulsion with time. (b) Evolution of the “sink” hexadecane emulsion as a function of temperature immediately prior to (open symbols) and after (closed symbols) exposure to the “source” toluene emulsion. The exposure time is 4 min. (c) (Top) Photographs of the collection vials showing the hexadecane emulsion after exposure to the toluene emulsion at different temperatures. The increase in turbidity with temperature correlates with the results of panel (b). (Bottom-left) Photograph of the 70 °C vial during sample collection. The difference in turbidity between the bottom and the top of the vial is due to the increased buoyancy of the hexadecane emulsion after exposure to toluene. (Bottom-right) The NC superparticles sediment within a few minutes after sample collection, forming a dark sediment. (d) SEM micrograph of the NC superparticles deposited on a silicon substrate. (e) Cross-sectional SEM micrograph of a single NC superparticle prepared by FIB milling.

Figure 1, and photos of the experimental setup are shown in Figure S2. We use droplet microfluidics to generate a monodisperse toluene-in-water “source” emulsion containing a dispersion of NCs, step 1. Then, we introduce a secondary “sink” emulsion consisting of much smaller droplets of an oil insoluble in water, such as hexadecane, step 2. The high internal pressure associated with the smaller emulsion drives the unidirectional mass transport of toluene from the source to the sink emulsion, progressively shrinking the toluene droplets and swelling the hexadecane droplets, step 3. Within minutes, this process yields NC superparticles with a polydispersity as low as 2%, step 4. This approach can be immediately extended to a wide range of hydrophobic NCs to produce monodisperse, dense NC superparticles with core-only or core/shell morphologies and with sizes tunable by varying the initial NC volume fraction within the source droplets. The NC superparticles function as optical resonators, featuring lasing modes modulated by their spontaneous assembly into colloidal clusters.^{68–71} The proposed method represents a timely convergence of self-assembly over several length scales, paving the way to a more widespread use of NC superparticles as functional building blocks.

RESULTS AND DISCUSSION

We use a microfluidic cross junction as a generator for 140 μm monodisperse toluene droplets loaded with 5.7 nm spherical CdSe NCs at an initial volume fraction ϕ_i ; see Figure S3 for NC characterization and the Materials and Methods section for details on droplet generation. These droplets represent the source emulsion and are stabilized by sodium dodecyl sulfate (SDS), a common surfactant for oil-in-water emulsions. Downstream from the droplet generator, we use another cross junction to introduce an emulsion of hexadecane in water, 1% hexadecane by weight, representing the sink emulsion. The sink emulsion, 55 nm $\pm$ 38% in hydrodynamic diameter as measured by dynamic light scattering, is generated separately by extended ultrasonication to reach an overall transparent appearance accompanied by a faint blue hue. A photograph of the sink emulsion is shown in the inset in Figure 2a. When left undisturbed at room temperature, the sink emulsion is remarkably stable with each droplet eventually doubling in volume, from 0.86 to $1.71 \times 10^5 \text{ nm}^3$, in 4 days due to Ostwald ripening;⁷² see Figure 2a. This microscopic change is accompanied by a macroscopic increase in turbidity, as demonstrated by the photograph in the inset. In contrast, exposing the sink emulsion to the NC-loaded source emulsion for only 4 min results in a comparable increase in the volume

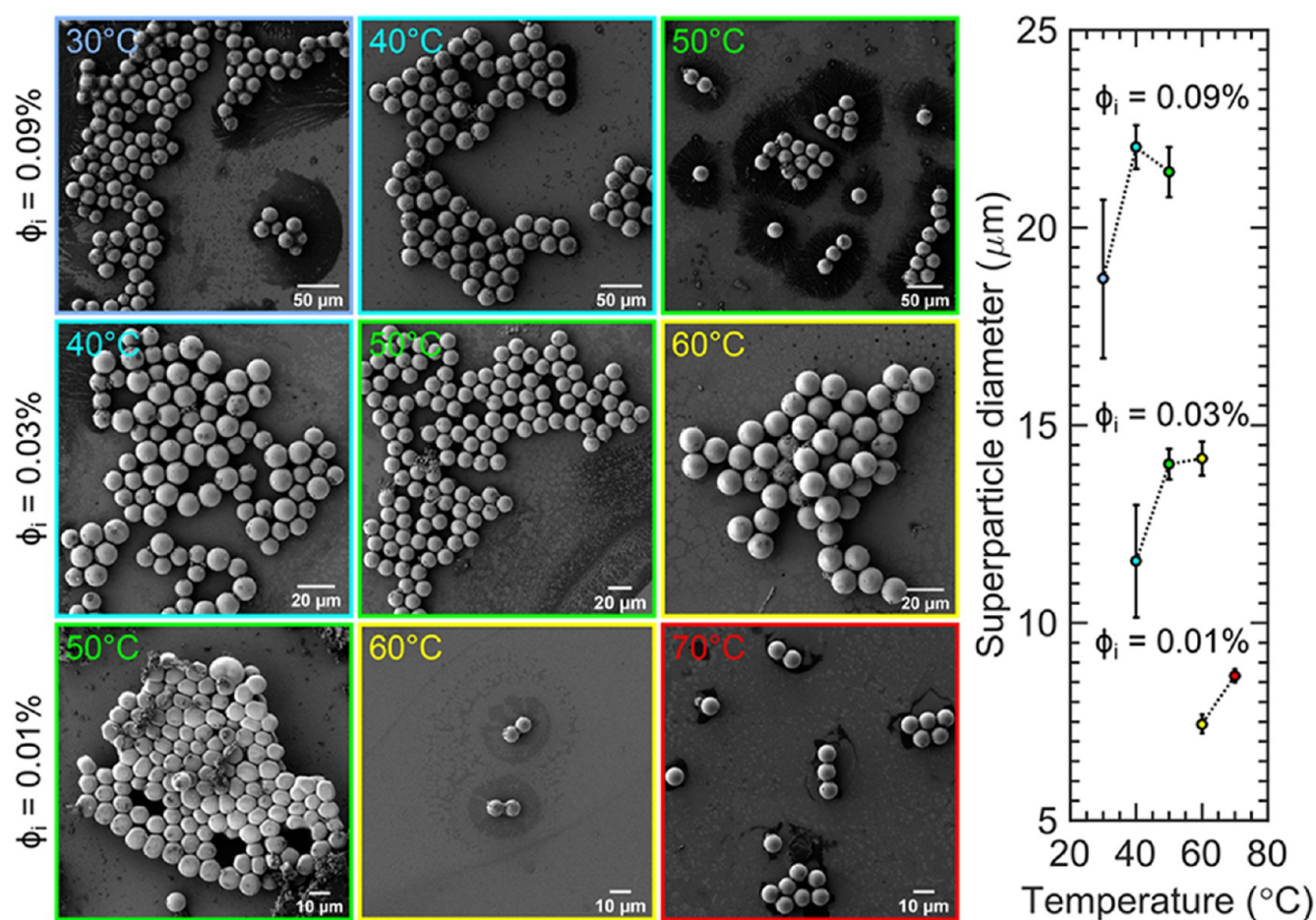


Figure 3. Fabrication of NC superparticles of different sizes and morphologies. (Bottom to top) Increasing the initial NC volume fraction, ϕ_i , results in overall larger superparticles. (Left to right) Increasing the temperature of the aqueous phase results in overall more monodisperse and spherical superparticles. These changes have been quantified in the graph, indicating the average superparticle size (symbol) and standard deviation (error bars) as a function of temperature and ϕ_i .

of the sink emulsion from 0.85 to $1.49 \times 10^5 \text{ nm}^3$, as shown in Figure 2b. This increase in volume of the sink emulsion is temperature-sensitive, with higher temperatures yielding a larger increase up to $2.14 \times 10^5 \text{ nm}^3$ at 90°C . After exposure to the source emulsion, the sink emulsion shows a significant increase in turbidity, shown in Figure 2c. Visually inspecting the bottom of the collection vial reveals a dark sediment. Imaging the sediment with a scanning electron microscope (SEM) reveals an ensemble of monodisperse, spherical NC superparticles that have formed in 4 min; see Figure 2d. Milling a single superparticle using a focused ion beam (FIB) shows that the superparticles are densely packed with CdSe NCs, with no discernible voids, as shown in Figure 2e.

This proceeds by the sink emulsion swelling progressively by depleting toluene from the source emulsion. The relatively high aqueous solubility of toluene, $5.8 \times 10^{-3} \text{ M}$,⁷³ enables this mass transfer, while the much lower solubility of hexadecane, $2.6 \times 10^{-11} \text{ M}$,⁷⁴ prohibits the reverse process. We confirm the generality of the source–sink emulsion approach by replacing hexadecane for another solvent also characterized by a lower aqueous solubility than toluene, such as dodecane, resulting in the formation of NC superparticles. Instead, replacing toluene for a solvent with a lower aqueous solubility, such as hexane, $1.6 \times 10^{-4} \text{ M}$,⁷⁵ inhibits mass transport and does not lead to monodisperse NC superparticles within the investigated

emulsion residence times. Increasing the emulsion residence time, the concentration of the sink emulsion, or the initial NC volume fraction may expand the use of the source–sink emulsion approach to solvents with a lower aqueous solubility than toluene.

The initial NC volume fraction within the toluene droplets, ϕ_i , determines the average size of the resulting superparticles, as shown in Figure 3. Varying ϕ_i from 0.01% to 0.09% increases the average diameter of the spherical superparticles, indicated by the symbols, from 7 to $23 \mu\text{m}$. Using even higher ϕ_i leads to larger superparticles, which sediment in the residency channel before reaching the collection vial. Instead, using lower ϕ_i leads to smaller superparticles that are still buoyant upon reaching the collection vial, creaming to the air/liquid interface. An example of this is shown in the bottom-left panel of Figure 3, where the toluene droplets have reached the air/liquid interface while still buoyant, assembling to form a monolayer. The droplets have then deformed to maximize surface coverage of the interface,^{42,76} creating a tiling pattern of anisotropic superparticles.

Adjusting the temperature of the aqueous phase during the coresidence time of source and sink emulsions affects the formation of the superparticles, as shown in Figure 3. Specifically, increasing the temperature results in an increase in the average diameter of the superparticles while con-

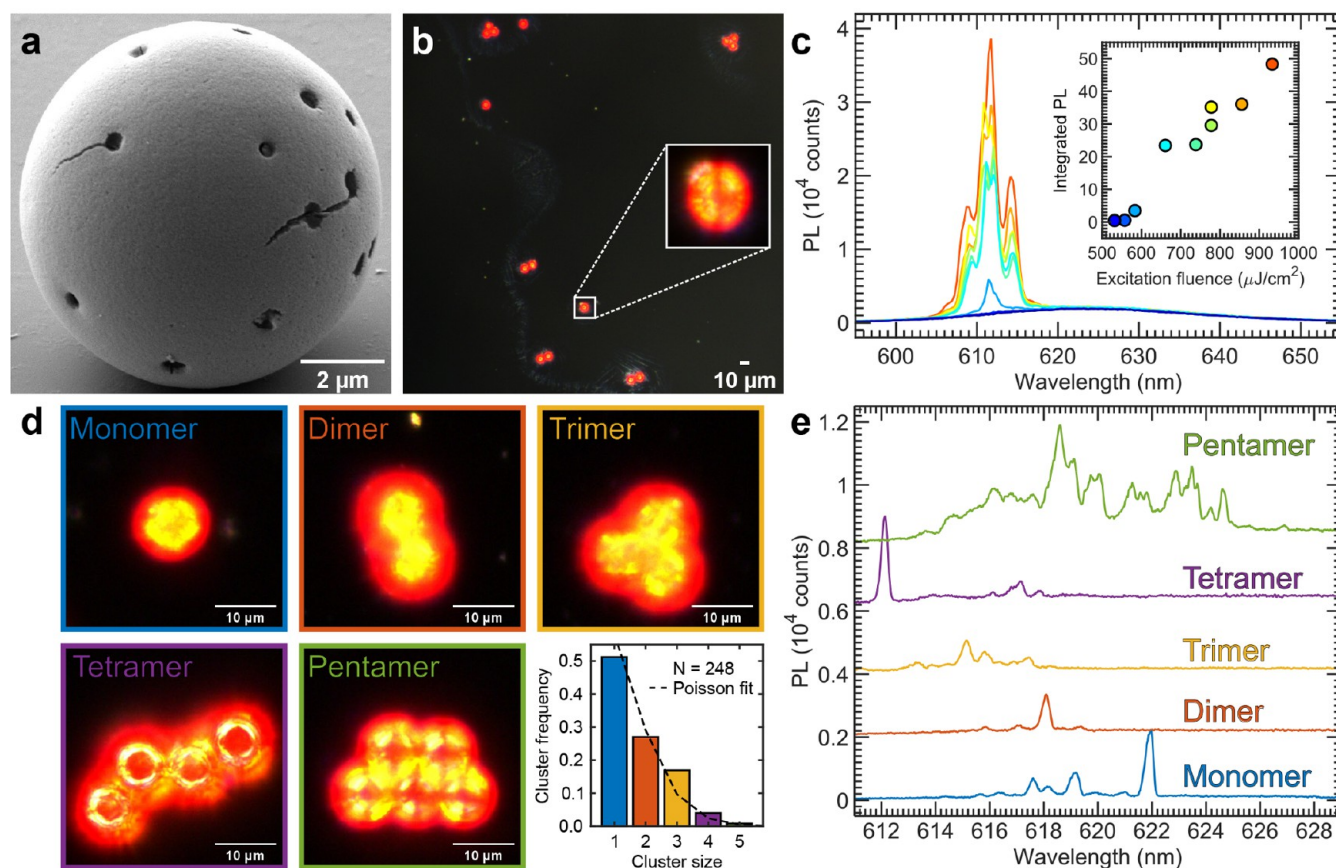


Figure 4. Lasing from NC superparticles produced through the source–sink emulsion approach. (a) SEM micrograph of a spherical superparticle of anisotropic CdSe/CdS NCs with unity PL quantum yield. (b) Dark-field optical micrograph of the monodisperse superparticles. (c) PL spectrum of a superparticle excited at 500 nm as a function of the excitation fluence. The inset shows the integrated intensity of the lasing modes as a function of excitation fluence. (d) Dark-field optical micrographs of various clusters of NC superparticles and a histogram describing their occurrence from a sample of $N = 248$ clusters. A fit to a zero-truncated Poisson distribution is shown by a dashed line. (e) PL spectra of the superparticle clusters shown in (d) when exciting above the lasing threshold. The spectra have been shifted for clarity.

currently decreasing their polydispersity, indicated by the error bars. This is most likely due to the temperature-driven increase in solubility and diffusion rate of toluene in the aqueous phase,⁷³ which decreases the residence time required to form the NC superparticles. In turn, this also decreases the probability of size defocusing,⁷² since the time required by the droplets to form superparticles decreases with increasing temperature, minimizing the possibility of droplet collision and merging; see [Supporting Information Note S1](#) for additional discussion. When using a sufficiently high temperature for a given value of ϕ_i , for instance, 50 °C for $\phi_i = 0.09\%$, this method yields NC superparticles with a polydispersity as low as 2%.

The source–sink emulsion method can be readily generalized to other NC systems. We synthesize 12.2 nm anisotropic core/shell CdSe/CdS NCs with unity photoluminescence (PL) quantum yield by following a recent report;⁷⁷ see [Figure S4](#) for NC characterization. Also in this case, the source–sink emulsion method yields spherical superparticles, as shown in [Figure 4a](#). The 9.0 μm superparticles appear monodisperse, as illustrated by the dark-field micrograph in [Figure 4b](#). Upon excitation with 500 nm light, the superparticles show a photoluminescence (PL) spectrum centered around 625 nm; see [Figure 4c](#). When increasing the excitation fluence above a threshold of 550 μJ/cm², we observe

the emergence of sharp peaks in PL that we attribute to lasing, as demonstrated by the superlinear increase in the integrated PL intensity with excitation fluence shown in the inset. Exciting with wavelengths below 500 nm results in the increase of the lasing threshold, likely because of heating losses due to absorption of light by the thick CdS shell.²⁹

A closer inspection of the micrograph in [Figure 4b](#) reveals that the superparticles spontaneously assemble into small clusters,^{68,69} or colloidal molecules,^{70,71} upon drop-casting. [Figure 4d](#) shows dark-field images of a monomer, a dimer, a trimer, a tetramer, and a pentamer that we are able to locate on the silicon substrate. The frequency with which these clusters occur decreases quickly with cluster size by following a zero-truncated Poisson distribution, as shown by the histogram in [Figure 4d](#). When exciting above the lasing threshold, each of these clusters lases at different wavelengths, as shown in [Figure 4e](#). Lasing of an isolated superparticle occurs via the confinement of light emitted by NCs to the surface of the superparticle through whispering-gallery modes.²⁹ We argue that the assembly of superparticles into clusters likely leads to the hybridization of the whispering-gallery modes of a single superparticle,⁷⁸ determining the wavelength of the lasing modes of a superparticle cluster. The quality factor of the superparticles, measured as $Q = \lambda/\Delta\lambda = 1600 \pm 18\%$, does not depend on the morphology of the cluster and is comparable to

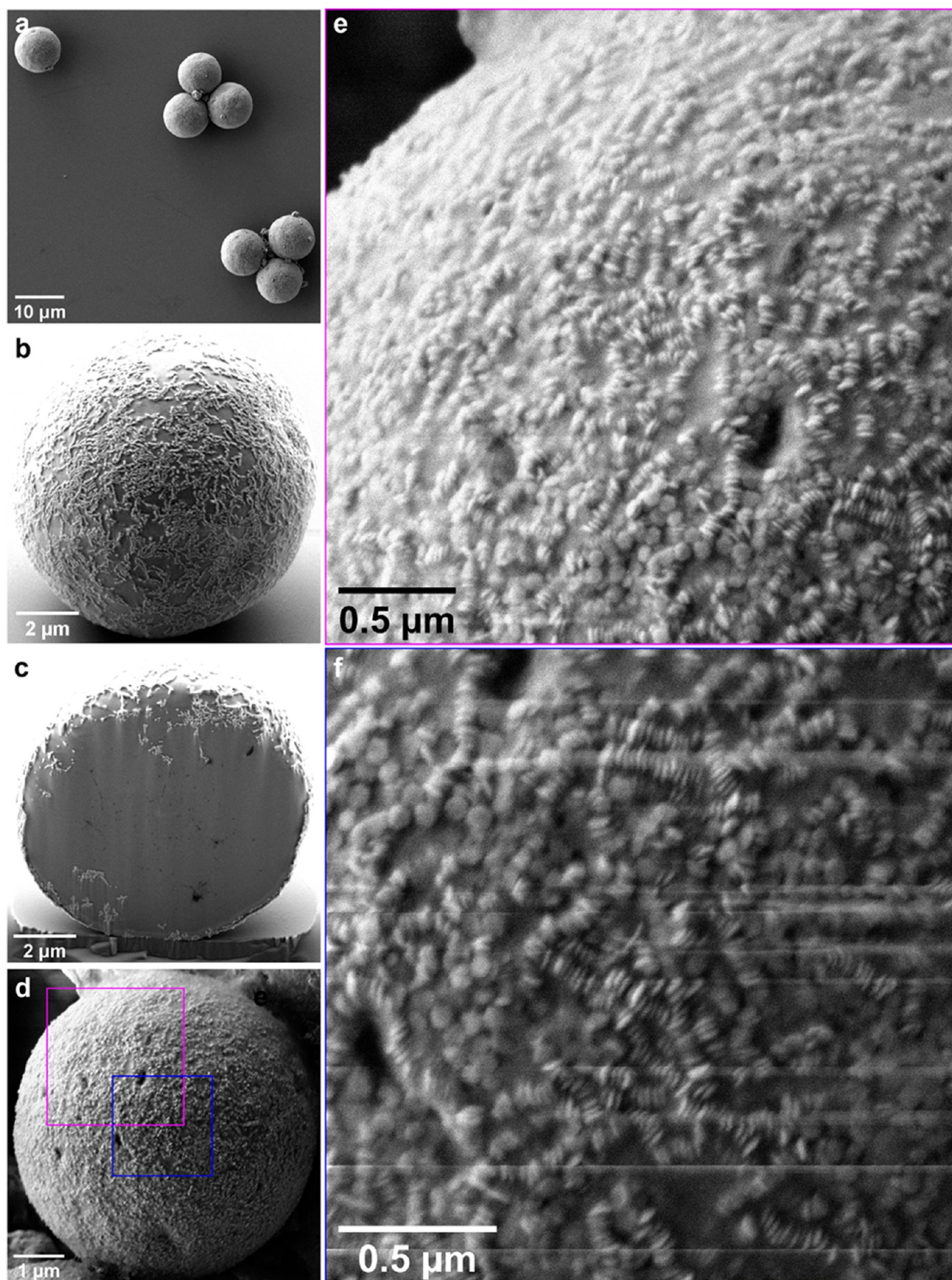


Figure 5. Core/shell NC superparticles. SEM micrographs of (a, b) monodisperse core/shell NC superparticles from PbS/CdS spheres and NaGdF₄ disks and (c) their cross sections prepared by FIB milling, revealing that the spheres mostly reside in the core of the superparticles while

Figure 5. continued

the disks are located in the shell. (d–f) SEM micrographs of the surface of the superparticles show that the disks tend to stack rather than to tile the surface of the superparticles. Streaking features are due to charging.

that of microfabricated ring resonators of equal diameter,²⁸ corresponding to an average lifetime of the energy stored in the resonator of $\tau = Q\lambda/c = 3.3$ ps, where λ is the resonant wavelength, $\Delta\lambda$ the full-width at half-maximum of the resonance, and c the speed of light.

The source–sink emulsion approach can also be used to fabricate more complex superparticle architectures, as shown in Figure 5. Loading the microfluidic source emulsion with a mixture of NCs with different shapes readily results in monodisperse core/shell NC superparticles; see Figure 5a. To achieve this morphology, we purposefully targeted a combination of NC shapes, disks and spheres,^{79,80} that hinder the formation of binary NC phases, therefore triggering the spontaneous phase separation of NCs during the assembly process; see Figures S5 and S6 for NC characterization. Using a total volume fraction of spheres four times larger than that of disks results in superparticles with a dense core occupied by PbS/CdS spheres, 4.3 nm in diameter, and a thin shell formed by NaGdF₄ disks, 57 nm in diameter and 17 nm in thickness, as shown in Figure 5b,c. While the PbS/CdS spheres are too small to be distinguished in SEM, the NaGdF₄ disks are well within the resolution of the microscope and show a tendency to stack rather than to tile the surface of the superparticles, confirming a disk-to-disk affinity stronger than disk-to-sphere;^{79,80} see Figure 5d–f. FIB milling a single superparticle highlights the shape-driven phase separation of NCs, although a few disks are still present below the surface of the superparticle. Due to their higher volume fraction, the smaller spherical NCs likely reach the nucleation threshold first,^{41,45,81} achieving phase separation by segregating the disks to the outer volume of the droplet at the later stages of assembly. Therefore, the observation of a core/shell morphology represents indirect evidence for the homogeneous nucleation of NCs under spherical confinement.

CONCLUSIONS

We demonstrate a general, rapid approach to consistently drive the formation of monodisperse NC superparticles. This approach relies on the interplay of two oil-in-water emulsions: a “source” emulsion of toluene loaded with NCs and a “sink” emulsion of an oil insoluble in water, like hexadecane. Mixing the two emulsions results in the temperature-controlled mass transfer of toluene from the source to the sink emulsion, leading to the formation of spherical NC superparticles within minutes. Using monodisperse toluene droplets generated through droplet microfluidics results in monodisperse NC superparticles, independent of NC size, shape, composition, or polydispersity. However, the use of droplet microfluidics is not necessary for the source–sink emulsion approach to work. Exposing the sink emulsion to a polydisperse source emulsion prepared by vortex-mixing results in the generation of polydisperse NC superparticles, as shown in Figure 6. Importantly, the source–sink emulsion approach provides the crucial benefit of accelerating the removal of the toluene from the source emulsion, achieving in minutes what would otherwise require several hours via evaporation.^{41,45,81}

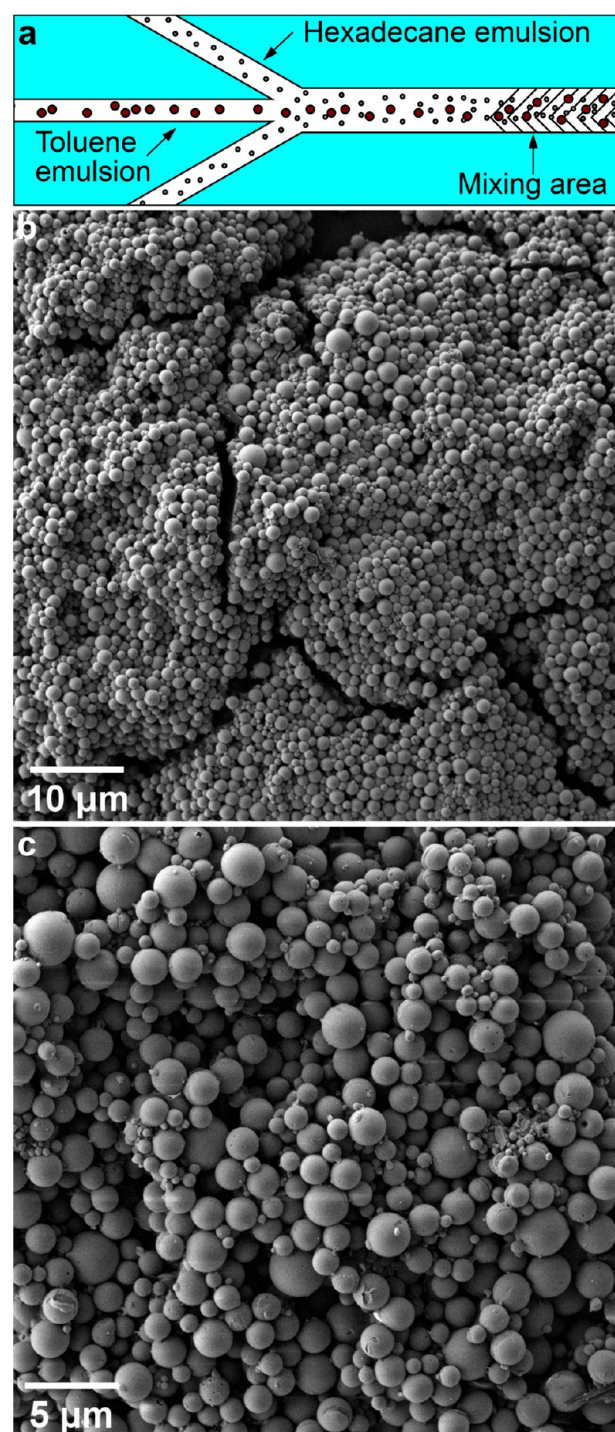


Figure 6. In-line production of NC superparticles without the use of droplet microfluidics. (a) A herringbone mixer can be used to facilitate mass transport between the toluene and hexadecane emulsions. (b, c) By starting with a polydisperse toluene emulsion, large amounts of polydisperse NC superparticles can be readily produced.

We validate the versatility of the source–sink emulsion approach by leveraging recent advances in NC synthesis. Using NCs with unity PL quantum yield leads to clusters of monodisperse superparticles that feature morphology-dependent lasing modes with an average quality factor of $Q = 1600$. Instead, mixing two incompatible NC shapes yields monodisperse superparticles with a complex morphology characterized by the shape-driven phase separation of NCs in the core and the shell of the superparticle. Tailoring the morphology and size of the ligand corona may offer an additional steric knob to influence the final structure of the superparticles.^{82,83} The source–sink emulsion approach leads to the formation of functional NC superparticles of various sizes, shapes, and morphologies in just a few minutes, paving the way to a more extended use of these complex artificial solids toward applications in photonics,^{6,53} magnetotherapy,^{21,22} energy storage,⁸⁴ and catalysis.⁸⁵

MATERIALS AND METHODS

NC Synthesis. Detailed synthetic procedures are provided in the [Supporting Information](#). CdSe,^{45,86} CdSe/CdS,⁷⁷ PbS,⁸⁷ and PbS/CdS⁸⁸ are synthesized according to literature reports and dispersed in toluene after purification. NaGdF₄ NCs are synthesized by following a procedure described in the [Supporting Information](#). The NC concentrations for CdSe⁸⁹ and PbS⁹⁰ NCs are determined from spectrophotometry by following reported sizing curves. The concentration for the other NCs is determined by drying and weighing the pellet.

Preparation of the Sink Emulsion. A total of 90 g of 200 mM SDS in Milli-Q water is added to a 100 mL media bottle (Fisher). A total of 10 g of an oil insoluble in water, such as hexadecane or dodecane, is subsequently added. The media bottle is capped, and the contents are mixed by continuous inversion for a few seconds. The bottle is then sonicated for 90 min by using a bath sonicator (Branson 1510). The bottle is then removed from the sonicator, and the contents are mixed by continuous inversion for a few seconds. At this point, the emulsion appears milky, corresponding to an average hydrodynamic diameter for the droplets of $137 \text{ nm} \pm 35\%$, as determined by dynamic light scattering (Malvern Zetasizer). The bottle is then uncapped and placed in an ice bath. After placing the tip of the ultrasonicator (Misonix Sonicator 3000) in the emulsion, the contents of the media bottle are sonicated for 120 min (peak power 84 W, 50% duty cycle). Afterward, the emulsion has a mostly clear appearance with a faint blue hue, corresponding to an average hydrodynamic diameter of $55 \text{ nm} \pm 38\%$ as measured by DLS. The emulsion is then immediately diluted 10-fold with Milli-Q water to reach an oil concentration of 1% (w/w) in an aqueous solution of 20 mM SDS. The sink emulsion is used immediately or placed in the fridge and used within 24 h.

Microfluidic Droplet Generation. We generate monodisperse toluene droplets by using a commercial droplet generator glass chip (Darwin microfluidics, T-26) connected to a multichannel pressure regulator (Elveflow, OB1MK3+). The dispersed phase of the emulsion consists of a dispersion of NCs with a known volume fraction in toluene, filtered before use with a $0.22 \text{ } \mu\text{m}$ PVDF or PTFE syringe filter. The continuous phase of the emulsion consists of a 20 mM solution of SDS in Milli-Q water filtered before use with a $0.22 \text{ } \mu\text{m}$ PVDF syringe filter. The sink emulsion phase is prepared as described above and consists of 1% (w/w) hexadecane or dodecane in 20 mM SDS in Milli-Q water. The microfluidic chip is operated at pressures of 1 bar/1 bar/2 bar for dispersed phase/continuous phase/sink emulsion channels. Increasing the overall pressure while maintaining the same ratios results in smaller toluene droplets. Instead, the herringbone mixer chip is operated at 1 bar/1 bar pressure for source emulsion/sink emulsion channels. In all cases, the outlet of the chip is connected to PFA tubing (ID 0.5 mm, OD 1.6 mm, Cole Parmer). The tubing has an overall length of 11.5 m and is wrapped around a cylindrical copper rod (OD 38 mm, length 0.33 m,

McMaster Carr) engraved with a spiral of 0.8 mm radius and 3.2 mm pitch to improve thermal contact.⁹¹ The temperature of the rod is controlled by means of a temperature controller (J-KEM) by embedding a heating cartridge (Briskheat) and a thermocouple (J-KEM) within the rod. The samples are collected in 20 mL scintillation vials filled with 5 mL of the sink emulsion. After collection, the vials are left uncapped and undisturbed on a hot plate set at $50 \text{ } ^\circ\text{C}$ for overnight. The samples are then washed three times by centrifuging at 100g and replacing the supernatant with 20 mM SDS in Milli-Q water and eventually concentrated to 1 mL.

Electron Microscopy. The samples are prepared for SEM imaging by drop casting $40 \text{ } \mu\text{L}$ of the superparticle dispersion on a clean piece of silicon wafer, followed by vacuum drying. The wafer is then dipped twice in a cleaning solution of water and isopropanol, 1 to 2 by volume, to remove the excess surfactant without redispersing the superparticles, followed by vacuum drying. The samples are imaged using a Tescan S8252X operated at 2 kV and 100 pA. FIB milling of the superparticles is performed with an ion voltage and current of 30 kV and 100 nA, respectively.

Lasing experiments. The samples are prepared for lasing experiments by drop casting $40 \text{ } \mu\text{L}$ of the superparticle dispersion on a clean microscope glass slide, followed by vacuum drying. The slide is then dipped twice in a cleaning solution of water and isopropanol, 1 to 2 by volume, to remove the excess surfactant without redispersing the superparticles, followed by vacuum drying. The 500 nm light from an optical parametric amplifier (Coherent OperaHP) pumped by an ultrafast laser (Coherent Monaco 1035, 0.272 ps pulse width) is coupled to a multimode optical fiber. The output of the fiber is collimated and directed through a $50\times/\text{NA } 0.8$ objective (Olympus MPlanFL N). The full-width at half-maximum of the spot size in the sample plane is $14.0 \text{ } \mu\text{m}$. Light emitted by the superparticles is collected through the same objective and focused to an optical fiber coupled to a spectrometer (Horiba iHR550 monochromator and Symphony II CCD). The excitation beam is filtered from the signal via appropriate long-pass filters placed before the collection fiber.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00039>.

Detailed description of the microfluidic chips and setups used, NC synthesis, micrographs of the NCs, and optical characterization of the NCs ([PDF](#))

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Author Contributions

E.M. and T.E.K. conceived the project. E.M. and W.L. synthesized the NCs. E.M. and S.v.D. designed the assembly process and performed experiments. E.M. and A.W.K. performed the electron microscopy studies. E.M. and S.J.N. performed the lasing experiments. T.E.K. and C.B.M. supervised the project. E.M. wrote the initial draft. The results were discussed with all authors. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): Aspects of this work have been included in a provisional U.S. patent filing.

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