Support Information for

Microfluidic generation of droplets with a high loading of nanoparticles

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S1. Materials, characterization, and imaging. Polystyrene (PS) nanoparticles are synthesized by emulsion polymerization with potassium persulfate ($K_2S_2O_8$) as the initiator.[1] The surfaces of the particles are largely hydrophobic, but slightly negatively charged and are stabilized only by electrostatic repulsion. The sizes of the PS particles are characterized by dynamic light scattering (DLS) using a ZetaSizer Nano ZS (Malvern Instruments, Worcestershire, UK) and scanning electron microscopy (FEI, XL30 FEG) (Figure S1). For the SEM analysis, we collected the drops on a glass slide and tilted the slide at a certain angle such as the oil could be drained by gravity. We then transferred the drops to a conducting tape, where the drops were characterized by SEM.

The average particle diameter is 543 nm. The nanoparticle suspension is concentrated to 49 wt% by ultrafiltration (Advantec MFS, Inc., 341300, Model: UHP 76) and then diluted to various concentrations for the PDMS microfluidic experiments. For the microcapillary approach, we prepare the 67 wt% nanoparticle suspension by using dried particles. For the purpose of developing drug delivery systems, we prefer less surfactant so as to avoid immune responses when the particles are injected into the body. Therefore we did not use any surfactant throughout our studies.

The generation of colloidal droplets in microfluidic channels is observed directly using a high-speed video camera (Phantom V9, 1400 frames per second) mounted on a microscope. The viscosity of the nanoparticle colloidal suspension at different concentrations of nanoparticles is measured at different shear rates using a rheometer (Anton Paar, MCR 301). The colloidal droplets are also characterized after formation using a scanning electron microscope (FEI, XL30 FEG).

To measure the differences in nanoparticle concentration between the original suspension and in the colloidal droplets generated in the microfluidic devices, the particle concentration is assessed using under a confocal microscope with fluorescently-labeled PS nanoparticles. Fluorescent nanoparticles were synthesized by doping 2, 2, 10, 10-tetraethyl-6, 14-bis-(triisopropylsilylethynyl)-1, 3, 9, 11-tetraoxa-dicyclopenta[b,m]pentacene (EtTP-5) into the PS nanoparticle.[2] EtTP-5 was synthesized as described previously,[2] and was purified by recrystallization from 1,2-dichloroethane. The PS nanoparticles were loaded with EtTP-5 dye by mixing excess EtTP-5 dissolved in tetrahydrofuran (THF) with a 3 wt% PS nanoparticle solution to obtain a 25 wt% THF aqueous solution. THF is necessary to swell the PS nanoparticles and to sufficiently solubilize EtTP-5 to facilitate mass transfer. The sample was equilibrated for 24

hours after which residual THF was removed by rotary evaporation under a reduced pressure. A small percentage of the fluorescent nanoparticles were added to the original nanoparticle suspension as a tracer. The fluorescence images of the suspension and the colloidal droplets were visualized using a confocal microscope (Leica TCS SP5). To measure the nanoparticle concentrations in the emulsion drops, distributions (number of particles per pixel) of the fluorescent nanoparticles in the suspension and in the droplets were analyzed using a customized image analysis program in Matlab.

S2. Fabrication and setup of PDMS microfluidic devices. Microfluidic chips are fabricated in PDMS using standard soft photolithography techniques. The aqueous and oil phases are loaded in two disposable syringes (Norm-Ject Inc.) and connected to syringe pumps (Harvard Apparatus, PHD 2000). Polyethylene (PE 20) tubes connect the syringe needle to the inlet hole of the channel of the device. Schematics of the microfluidic devices are shown in Figure 1. The height of the channels is 20 μm. The widths of the oil and aqueous channels are 100 μm and the width of the orifice is 20 μm.

Typical experimental setups are shown in Figure 1. PS nanoparticles with an average diameter of 543 nm (SI Figure 1) are dispersed into DI water at different weight percentages to form the initial nanoparticle suspension. The nanoparticle suspension and PDMS 200 oil (viscosity 10 cSt, Aldrich) are injected into the microfluidic device as the aqueous and oil phase, respectively. Aqueous droplets encapsulating nanoparticles are then generated at the orifice of the flow-focusing devices or the junction of the T-junction devices (Figure 1). The generation frequency and sizes of the droplets are recorded by a high-speed camera. The volumetric flow rates of the aqueous and oil phase used in the experiments vary from 1 μL/min to 20 μL/min, and thus the average shear rates in the microfluidic channels are between 400 and 8000 s^{-1} as estimated by

dividing the flow rate by the cross sectional area and the height of the orifice. All the experiments are conducted at room temperature.

S3. Microcapillary devices. Microcapillary devices are made from capillary tubes and consist of an injection tube, a collection tube, and an outer tube.[3,4] The injection tube and collection tubes are tapered using a pipette puller and have inner diameters of 50 μm and 200 μm at the tip, respectively. The two tapered tubes are fitted from the opposite ends of the outer tube, which has an inner diameter of 1.75 mm. An illustration of the microcapillary device is shown in Figure 4A. For a typical experimental setup, the aqueous solution and PDMS 200 oil (viscosity 10 cSt, Aldrich) are input via the injection tube and the outer tube, respectively. The droplets generated in the PDMS oil phase flow through the collection tube and are collected outside the device.

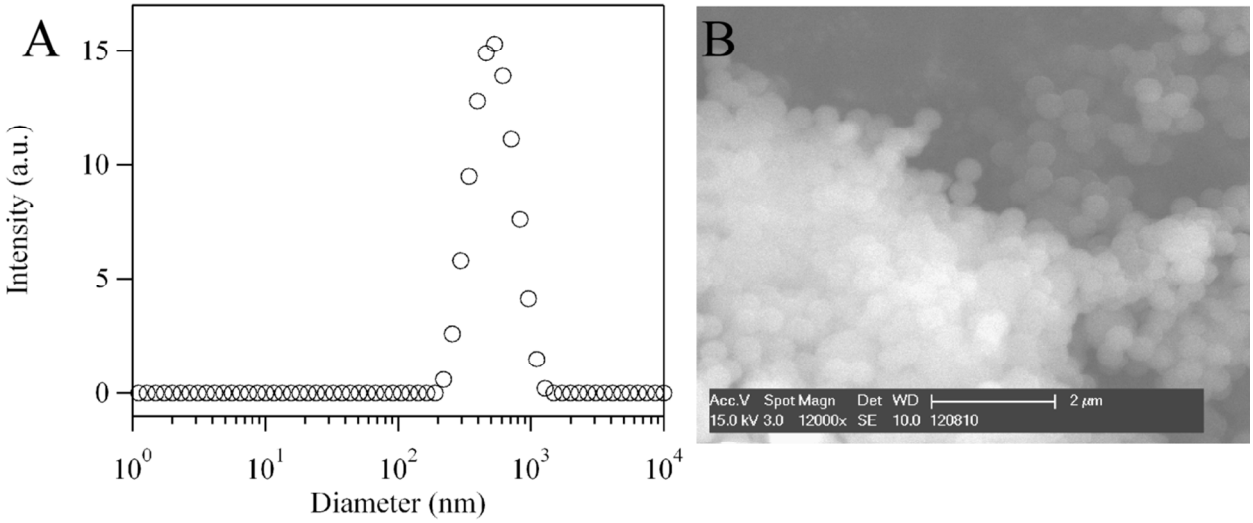

Figure S1. Characterization of polystyrene (PS) nanoparticles. (A) Size distributions of the PS particles from dynamic light scattering measurements. (B) Scanning electron microscope (SEM) image of PS particles.

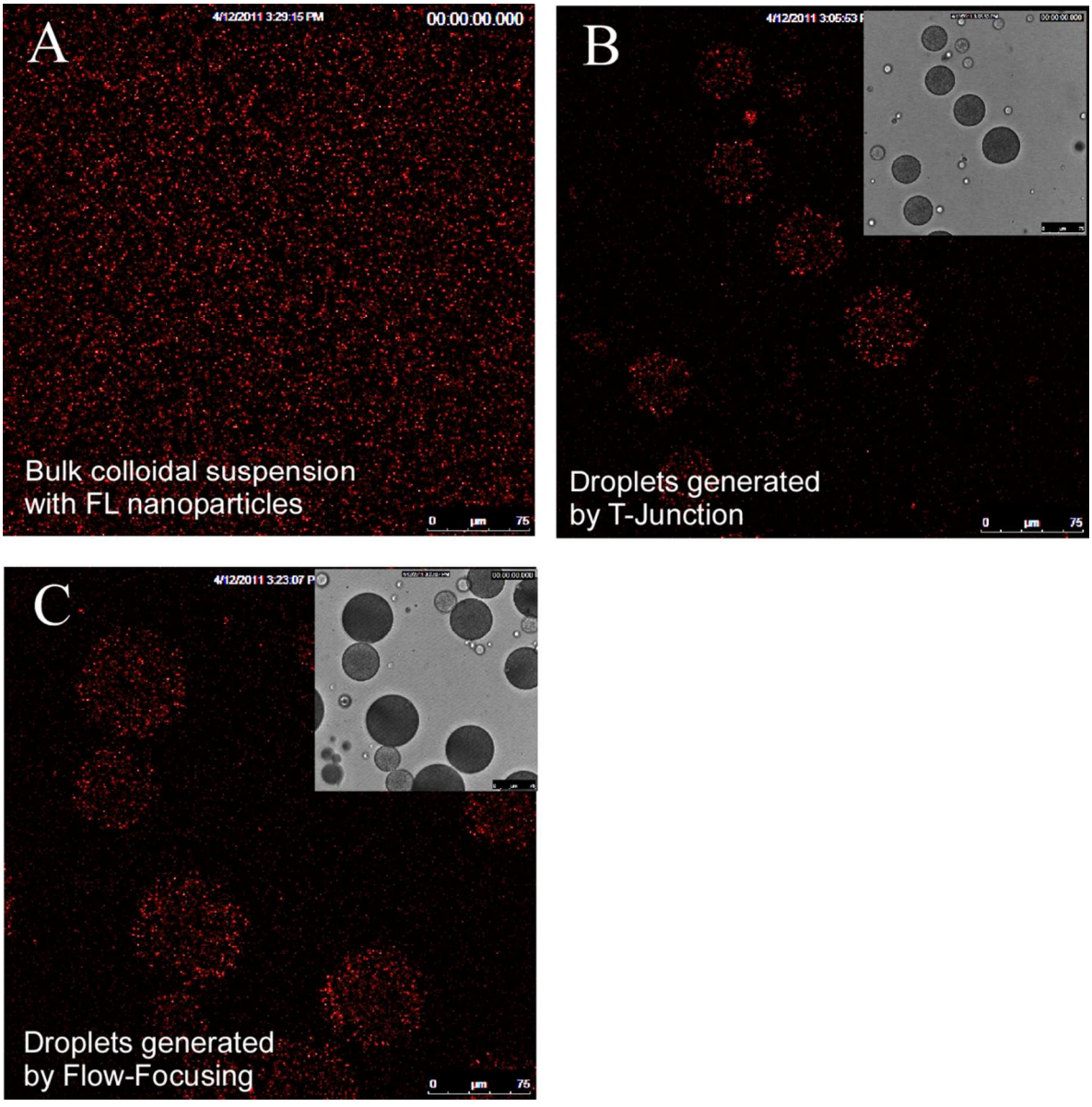

Figure S2. Confocal images of (A) the initial PS particle suspension and droplets generated by (B) a T-junction and (C) a flow-focusing microfluidic device. Insets are the bright-field images of the droplets.

Reference

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