

## Electronic Supporting Information

### A microfluidic process for on-chip formation of assemblies of oxide nanoparticles

V. K. Parashar, J. B. Wacker, D. Necula, and M. A. M. Gijs

#### EXPERIMENTAL SECTION

***Preparation and activation of silica nanoparticles.*** In total, 4.5 mL of tetra-ethylorthosilicate (TEOS) and 10 mL of hydrolyzing mixture containing 40 vol. % water, 12 vol % ethanol and 48 vol % aqueous ammonia (29.5 wt.%  $\text{NH}_3$ ) are used to prepare the nanoparticles. First, 500  $\mu\text{L}$  TEOS and 1 mL hydrolyzing mixture are mixed in a 20 mL closed flask at 25 °C by magnetic stirring at 300 rpm. The same quantities of TEOS and hydrolyzing mixture are added after an interval of 5, 4, 3, 2, 2 minutes, respectively, and the rest of the TEOS and hydrolyzing solution is added after 5 minutes of the last addition. Then the flask is transferred to a water bath maintained at 40-42 °C. The stirring speed at this point is increased to 600 rpm for 30 minutes. The resultant silica nanoparticles, 250 nm in diameter, are dried under vacuum at 180 °C and further calcined at 600 °C. Silica nanoparticles of 100 nm to 500 nm in size are prepared via multiple silica coating steps generated by applying additional doses of TEOS + hydrolyzing solution to the initially formed silica nanoparticles. Activation of the silica nanoparticles is done at 120 °C for 10 minutes in de-ionized water under nitrogen atmosphere at a pressure of 6-8 bar in a high pressure reaction vessel (type 4768, Parr Instrument Company, Moline, IL, USA).

***Preparation and activation of titania nanoparticles.*** Spherical titania nanoparticles were prepared by hydrolysis and condensation of titanium isopropoxide with dodecylamine as a catalyst in a co-solvent of methanol/acetonitrile. 360  $\mu\text{L}$  water was added to 50 mL methanol and 25 mL acetonitrile, after which 1.24 g dodecylamine was dissolved in this mixture. After complete dissolution, 2 mL titanium isopropoxide was added and stirred for 18-24 hours. The resulting titania nanoparticles of around 160/200 nm in size were washed with the same solvent mixture and centrifuged twice. The nanoparticles were subsequently dried and calcined at 250 °C for a day.

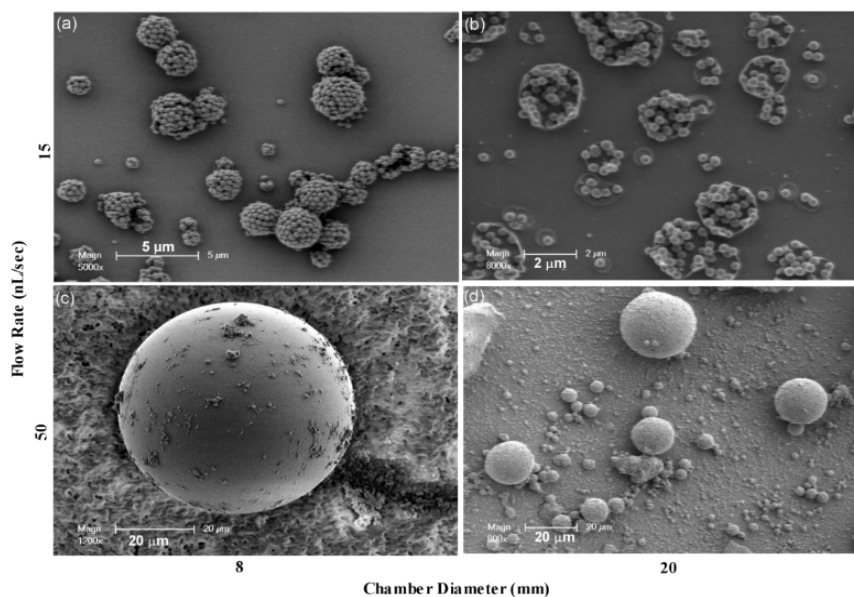
$\text{H}_2\text{O}_2$  activation of the titania nanoparticles was done at room temperature (22 °C) by preparing a 8 wt% titania dispersion either in a 1% or 10%  $\text{H}_2\text{O}_2$  (30% w/w) solution, and stirring it for 10 minutes followed by centrifugation and re-dispersing of the nanoparticles in water.

***Preparation of the emulsions.*** Emulsions to use in the spherical assembly process were prepared using a 15 vol % oxide aqueous colloid (oxide content 10 and 25 wt%) in DOP medium containing 1 % TX-100 using a homogenizer or vortex at 40 Hz.

***Fabrication of the microfluidic chip.*** Microfluidic PDMS chips were made using the soft lithography technique. A microstructure mold was fabricated using a negative photoresist SU8 on a silicon wafer. A 40  $\mu\text{m}$  thick layer of SU8 (GM1070, Gersteltec, Switzerland) was spread on a silicon wafer by spinning it at 2000 rpm for 40 sec. Soft baking of the resist was done by heating it to 130°C during 50 min, keeping the temperature at 130°C for 5 min and cooling it down to room temperature during 50 min. The resist layer was microstructured by putting it under a mask and exposing with UV light with a total dose of 360 mJ/cm<sup>2</sup>. This was followed by a post-exposure bake to 100°C ramping in 40 min and kept at 100°C for 40 min before cooling down to room temperature in 1 h 30 min. The resist was then developed in propylene glycol monomethyl ether acetate and cleaned with isopropanol to get the SU8 microstructure mold. PDMS chips containing microchannels were then obtained by pouring a degassed mixture of PDMS and polymerization catalyst (Sylgard 184, Dow Corning) into the mold and curing it at 60°C overnight. After punching holes for the inlets and the outlet into the chip, the microchannels were formed by bonding a piece of PDMS-coated glass to the PDMS molded part using an air-plasma. To recover the native hydrophobicity of PDMS, the chips were reheated to 120°C for 2 h.

***Scanning electron microscopy.*** A Philips XL30 FEG microscope is used at low electron acceleration voltage (3-5 keV) to prevent charging effects after depositing spherical assemblies on a substrate. A SEM-coupled EDX spectrometer (Thermo Noran System Six, Thermo Electron Corporation) was used to estimate the elemental composition of nanoparticle assemblies.

## Effect of microfluidic chamber diameter on assembly formation



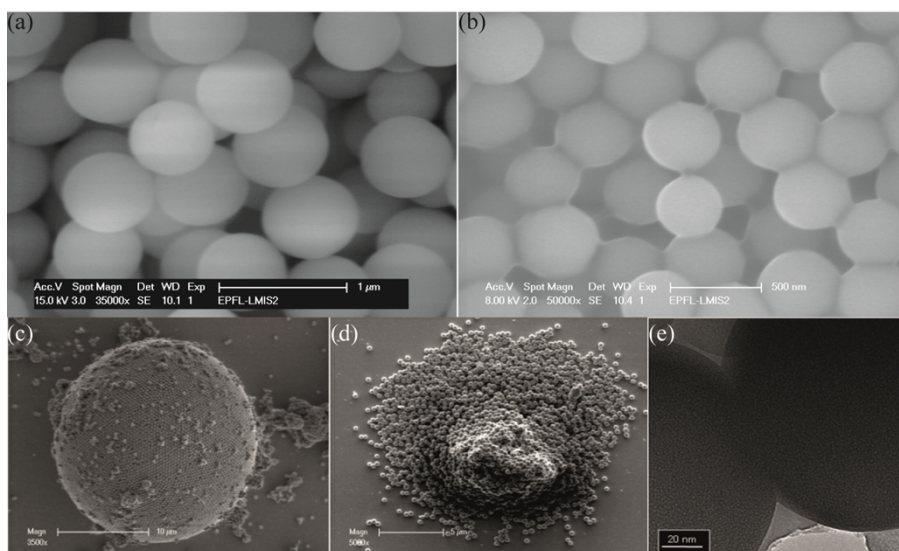
***Fig. S1 Effect of microfluidic chamber diameter on assembly formation.***

Fig. S1 (a and c) show SEM photographs of assemblies prepared in a 8 mm diameter chamber on a microfluidic chip at a flow rate of 15 nL/sec and 50 nL/sec, respectively. Figure S1 (b and d) show assemblies formation in a 20 mm diameter chamber. The latter induces a wider spatial distribution of microdroplets within the chamber, resulting in multiple sites for convective current generation and thus leading to formation of multiple assemblies. The 8 mm chamber allowed accommodation of all microdroplets to a single site of convective current. The 8 mm diameter chamber combined with the higher flow rate of 50 nL/sec (providing more thermally induced agitation due to the higher water supply) of the emulsion having 25 wt% oxide content provided single and homogeneous assemblies.

### **Pre-activation of nanoparticles and its effect on robust assembly formation.**

An additional leading edge of our assembly formation process is pre-activation of nanoparticles, resulting in permanent inter-particle bonds after sintering of the assembly. Hydrothermal treatment of silica nanoparticles at 120 °C for 10 minutes in de-ionized water under nitrogen atmosphere at a pressure of 6-8 bar in a high pressure reaction vessel generates a layer of silica gel, mainly comprising of silanol groups on the outer surface of nanoparticles. These pre-

activated silica nanoparticles when come in contact amongst each other form a continuous gel layer and strong oxide network.

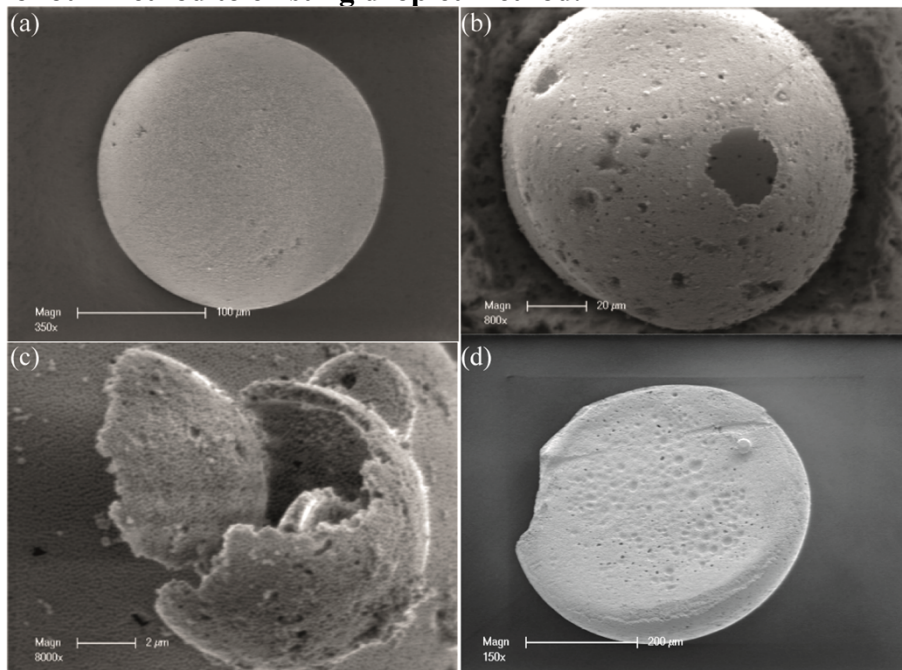


**Figure S2 : Pre-activation of nanoparticles and its effect on assembly formation.**

Figure S2(a) is a SEM photograph of native silica nanoparticles. Figure S2 (b) is a SEM photographs of pre-activated silica nanoparticles. Pre-activation generates a gel layer comprising hydroxyl groups on the silica surface. These reactive groups, when coming in contact amongst each other, form strong metal-oxide-metal linkages (like Si-O-Si, Ti-O-Ti), which are further consolidated during final heating of superstructures at a temperature of  $\sim 600^{\circ}\text{C}$ . Figure S2(c) is a SEM photograph showing a superstructure made of *pre-activated* silica nanoparticles. Figure S2(d) shows a SEM photograph of a loose assembly of the *native* (not pre-activated) nanoparticles. Non-activated nanoparticles, even though they formed a spherical assembly in our process, result in no direct linkages amongst the nanoparticles due to the absence of reactive hydroxyl or peroxy groups on the oxide surface. Taking these assemblies out of the process container inevitably leads to decomposition and collapse of the spherical assembly after drying. On the other hand, when using pre-activated nanoparticles, a coherent superstructure is obtained due to formation of permanent siloxane bonds and interparticle joints, as shown in the HRTEM

photograph of Figure S2(e). Therefore an additional leading edge of our superstructure formation process is the pre-activation, resulting in permanent inter-particle bonds after sintering of the superstructure.

#### **Comparison of our method to existing droplet method.**

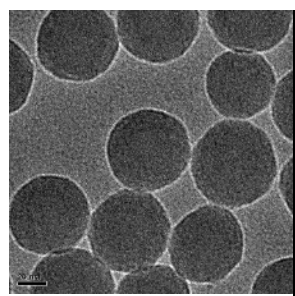


***Figure S3: Comparison of the classical droplet method and our new process to form spherical assemblies***

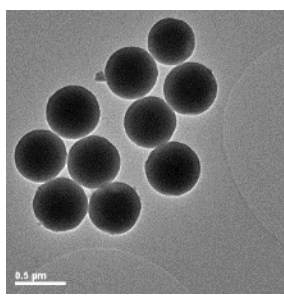
Compared to the up to now used classical droplet method [1-4], which favors formation of hollow spheres or smaller spherical assemblies in the range of 2-10  $\mu\text{m}$ , our process enables realizing larger superstructures and at the same time offers size control by adjusting the number of nanoparticles in the emulsion and flow duration to the microfluidic chamber. Figure S3(a) is a SEM photograph showing a spherical superstructure made of silica nanoparticles prepared by our process, while Figure S3(b) shows a silica nanoparticle assembly made by the classical droplet method [2, 3, 5], which is based on dripping of colloidal aqueous droplets into an oil medium. Subsequent heating causes the evaporation of the water and assembles the nanoparticles into a spherical shell along the oil/water interface. This leads to the formation of either a hollow sphere

or smaller spherical assemblies, which are brittle and easily decompose (Figure S3(c)). Attempts to form bigger spheres by the droplet method, using more concentrated colloidal solutions, failed due to fast sedimentation (Figure S3(d)). Apart from the possibility to realize large superstructures, our new process has the advantage of controlling the size of the final superstructure by choice of the total number of nanoparticles used in the colloid-in-oil emulsion enter the microfluidic chamber.

### TEM Photographs of silica and titania individual nanoparticles used in the present study



*Silica Nanoparticles*



*Titania Nanoparticles*

### References

1. G. R. Yi, V. N. Manoharan, E. Michel, M. T. Elsesser, S. M. Yang and D. J. Pine, Colloidal clusters of silica or polymer microspheres, *Adv Mater*, 2004, **16**, 1204-+.
2. V. N. Manoharan, Colloidal spheres confined by liquid droplets: Geometry, physics, and physical chemistry, *Solid State Commun*, 2006, **139**, 557-561.
3. A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz, Colloidosomes: Selectively permeable capsules composed of colloidal particles, *Science*, 2002, **298**, 1006-1009.
4. V. N. Manoharan, A. Imhof, J. D. Thorne and D. J. Pine, Photonic crystals from emulsion templates, *Adv Mater*, 2001, **13**, 447-450.
5. C. S. Handscomb, M. Kraft and A. E. Bayly, A new model for the drying of droplets containing suspended solids, *Chem Eng Sci*, 2009, **64**, 628-637.