

INTERFACE-TEMPLATED FORMATION OF MONODISPERSE DOUGHNUT-SHAPED SILICA MICROPARTICLES

A. Fang^{1,*}, C. Gosse², C. Gaillard^{3,4}, and J.-P. Douliez⁴

¹NANO, UR 1268, Biopolymères Interactions Assemblages, INRA, Nantes, FRANCE

²Laboratoire de Photonique et de Nanostructures, LPN-CNRS, Marcoussis, FRANCE

³BIBS Microscopie, UR 1268, Biopolymères Interactions Assemblages, INRA, Nantes, FRANCE

⁴ISD, UR 1268, Biopolymères Interactions Assemblages, INRA, Nantes, FRANCE

ABSTRACT

A simple droplet-based microfluidic approach is used to control the formation of monodispersed silica particles in doughnut shape, in which uniform water-in-oil (W/O) emulsion droplets of silica sol were generated and subsequently underwent shrinkage through in situ rapid solvent diffusion within the microfluidic channel. Due to interface buckling, they finally solidify to form doughnut-shaped silica microparticles. The silica microstructures prepared in this way are monodisperse in both size and shape. This approach provides a starting point to control the geometry of a three-dimensional silica microstructure by droplet-based microfluidics. The exciting results could also promote new applications, for example, in shape-specific drug delivery carrier.

KEYWORDS: Emulsion Droplets, Evaporation, Sol-gel transition, Doughnut-shaped silica.

INTRODUCTION

Silica particles have demonstrated potentials in numerous fields such as separation science, drug delivery, or catalysis [1]. However, their polydispersity, either in size or shape, presents a major challenge in understanding and controlling the mass-transport properties, which in turn introduces a striking lack, for example, in understanding the effect of particle size and shape in the fields of drug delivery and material science. On the other hand, microfluidics provides a straightforward and robust approach to obtain highly monodisperse droplets, one at a time and with an incomparable degree of control over size. Therefore, we here applied on chip emulsification and solvent evaporation to synthesize silica particles with controlled size and shape. Differing from the previously reported microspheres [2,3], the object we produce can come in various shape; in this report we focus on monodisperse doughnut-shaped silica.

EXPERIMENTAL

Droplets were achieved on chip using a flow focusing device (Fig. 1). The microfluidic channels were obtained by irreversible bonding a PDMS replica onto a flat PDMS slab; The chip was used directly without any surface modification. The continuous oil phase was supplied to the device through inlet 1 using a digitally controlled syringe pump (Harvard Apparatus PHD 2000, USA). The dispersed aqueous phase was supplied through inlet 2 in the same manner. The respective flow rates were 3.00 and 0.05 mL/hr. After the breakup junction, the emulsion droplets traveled along a 360 mm long channel with a width of 200 μm and a height of 80 μm and finally collected from outlet 3.

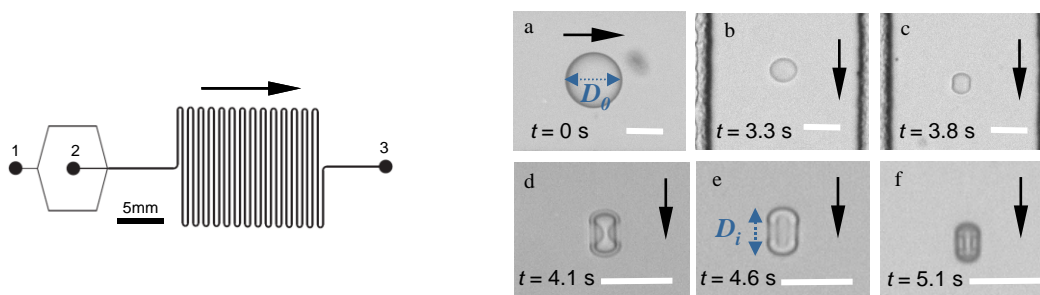


Figure 1: Left: Scheme of the PDMS device used for this work. Right: Evolution of the size and shape of a droplet traveling downstream: (a) generation; (b) shrinkage; (c) deformation; (d) invagination; (e) condensation; and (f) solidification. The arrows depict the flow direction, and the scale bar corresponds to 50 μm . On each panel is indicated the time elapsed since droplet formation at the junction, it was computed from the total flow rate value, 3.05 mL/hr, which was converted in linear velocity of 53mm/s. Droplet diameter evolution from D_0 ($t=0$ s) to D_i ($t=i$ s) was clearly observed.

Dimethyl carbonate (DMC, 99 %, Sigma-Aldrich) was used as a carrying organic phase. Concerning the precursor aqueous phase, it was prepared by mixing 1.0 mL of tetraethyl orthosilicate (TEOS, 99.0 %, Fluka), 0.1 mL of triethyl amine

(TEA, 99.5 %, Fluka) with 5.0 mL of water (MilliQ, 18 M Ω .cm). This mixture was stirred at room temperature until one single homogeneous phase appeared (~ 5 hours).

Droplets and particles were observed in situ using an Olympus IX51 inverse microscope (Olympus) coupled with a digital camera (Sony, SCD-SX90). For size measurement, bright-field images were analyzed using the ImageJ software. SEM and TEM images were equally acquired to better understand the morphology of the monodisperse silica particles.

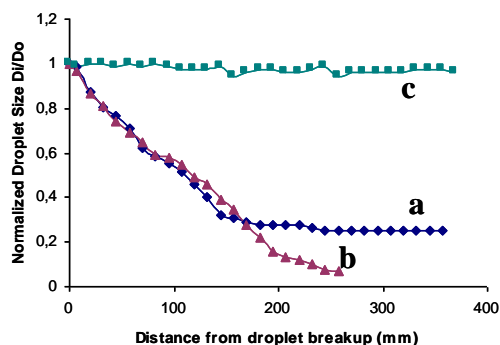


Figure 2: Variation of the droplet size as a function of the distance from the breakup junction for (a) the sol emulsified in DMC; (b) pure water emulsified in DMC; and (c) the sol emulsified in water-saturated DMC. The droplet outer diameter D_i along the flow direction at time i , has here been normalized to that just after generation, D_0 (see Fig. 1 for their measurements).

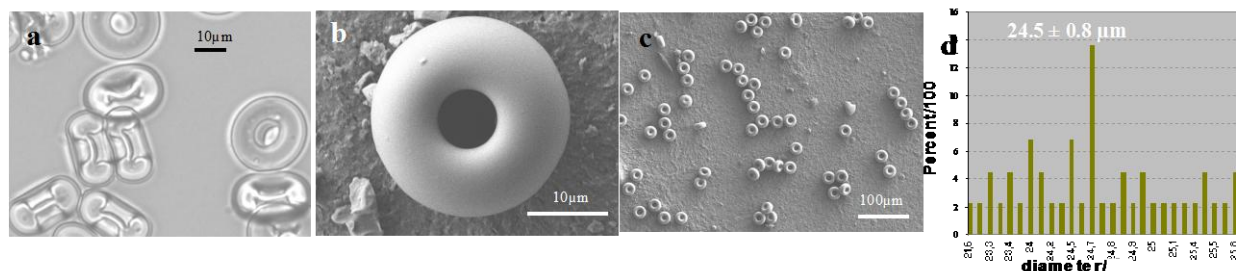
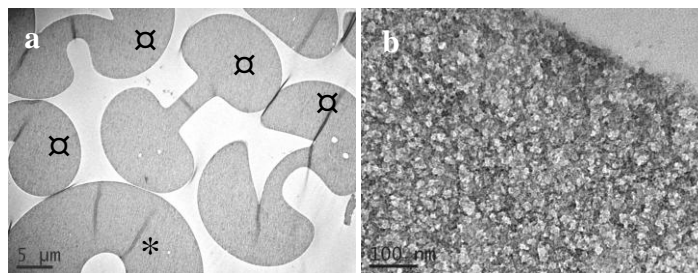


Figure 3: Monodisperse doughnut-shaped silica particles as observed in optical microscopy (a) and scanning electron microscopy (b-c). (d) Size distribution corresponding to the particles in Figure 3c.

Figure 4: TEM images at different magnifications of the silica particles showing its microstructures (a) at top view (*) and side view (⊗) and its amorphous nature (b) consisting of nanoclusters at ~25 nm. Silica beads were cured in epoxy resin, followed by sectioning into ultrathin slices of ~50 nm in thickness.



RESULTS AND DISCUSSION

The dispersed phase and continuous phase were a silica sol and DMC, respectively. Uniform W/O droplets are generated by flow focusing in a PDMS device [5] (Fig. 1a). Although the two phases are immiscible, water is in fact soluble in DMC up to 2.9 % in weight. Hence, subsequently to emulsification the sol droplets start to shrink (Fig. 1a-b, Fig. 2a) due to water loss. To unambiguously attribute this phenomena to H₂O evaporation in the organic carrying fluid, we performed two control experiments. First, we measured the size of a pure water droplet as a function of the distance it travels along the microchannel. Results similar to those obtained with the sol are obtained for this simpler physico-chemical system : we evidence a linear decrease of the diameter D with time t (Fig. 2b). On the contrary, no size variation occurs when the DMC is saturated with water (Fig. 2c). This $D \sim - \alpha t$ behavior has in fact been reported in other cases where the dissolving droplet is in motion [6,7]. With a characteristic particle size of 50 μ m, a flow velocity equal to 53 mm/s and a diffusion coefficient of H₂O in DMC estimated to be 10⁻⁹ m²/s, the Péclet number Pe is around 4000. Thus the effects of hydrodynamic convection on molecular transport cannot be neglected anymore [7] and we necessarily depart from the $D \sim - \alpha t^{1/2}$ scaling law that Epstein and Plesset have computed for still evaporating droplet and that others have observed in microdevices [8].

The sol droplets thus shrink while flowing downstream. However, contrary to the pure water ones, that ineluctably disappear, a plateau is reached at ~ 150 mm away from the junction, for a droplet $D_0 \sim 75 \mu$ m (Fig. 2a-b). A shape transition then take place,

which will finally result in toroidal solid particles (Fig. 1c-f). This kind of evaporation driven transition has already been evidenced in various millimeter and micrometer-size systems: ripening of a polymer solution emulsified in a microfluidic device [4,6], drying of a colloidal suspension deposited on a super hydrophobic surface [9]. We here assume that, similarly to what have been published for a sol drop evaporating in air [10], the silica nanoclusters accumulate at the interface where they crosslink, thus yielding a solid glassy membrane. The latter then buckles as the water volume further diminishes due to molecular diffusion in the continuous phase. The microparticles prepared in this way are all toroidal (Fig. 3a-c), with this shape being an equilibrium one for thin closed membranes. They are also monodisperse in size, with a coefficient of variation of 3.5 % (Fig. 3d).

The morphology of the monodisperse silica particles are further clarified with TEM images showed in Figure 4. The nearly symmetric concaving does not break to form a hole. A thin membrane is always sandwiched between the two cavities inside each doughnut-shaped silica. This unique microstructure is clearly displayed in the TEM image in Figure 4a, revealing a different case from the previous doughnut-shaped toroidal structure penetrated with a hole [6]. The amorphous nature of the silica particles is also clear from Figure 4b. The combined information from optical microscope, SEM, TEM has clearly revealed the morphology of the monodisperse doughnut-shaped silica particles.

CONCLUSION

We introduced a one-step approach for the controlled synthesis of monodisperse silica microdoughnuts: loss of the water contained in the sol triggers both the gel transition and the shape transformation of the initially spherical droplets. This method is completely general and in addition it allows in situ encapsulation of functional molecules such as proteins (not shown). Even if the exact doughnut formation mechanism still has to be unraveled – for instance, why does the buckling instability occur in the cross-flow direction – we believe our technique promising to obtain other complex shapes. Indeed, according to the drying hydrodynamics, it should also be possible to generate dimpled sphere, pancake, etc [11]. One would just need to tune the sol concentration, sol droplet size, the ionic strength, the viscosity, or some other parameters.

ACKNOWLEDGEMENTS

The authors thank Mr. F. Monti and Dr. P. Tabeling for the access to the facilities in ESPCI for the fabrication of replica models. Mr. P. Papineau is acknowledged for kind assistance in image acquisition software.

REFERENCES

- [1] Y. Wan, and D. Zhao, *Chem. Rev.*, **107**, 2821 (2007) and references therein; S. Huh, *et al.*, *Chem. Mater.*, **15**, 4247 (2003).
- [2] N. J. Carroll, *et al.*, *Langmuir*, **24**, 658 (2008); I. Lee, *et al.*, *Adv. Funct. Mater.*, **18**, 4014 (2008).
- [3] V. Chokkalingam, *et al.*, *Lab Chip*, **10**, 1700 (2010).
- [4] H. C. Shum, *et al.*, *Macromol. Rapid Commun.*, **31**, 108 (2010) and references therein.
- [5] A. Fang and B. Cathala, *Colloids Surf. B: Biointerfaces*, **82**, 81 (2011).
- [6] B. Wang, *et al.*, *ChemPhysChem*, **10**, 641 (2009).
- [7] P. Poesio, *et al.*, *Phys. Rev. Lett.*, **103**, 064501 (2009).
- [8] P. S. Epstein and M. S. Plesset, *J. Chem. Phys.*, **18**, 1505 (1950); P.B. Duncan and D. Needham, *Langmuir*, **22**, 4190 (2006); A. Q. Shen, *et al.*, *Langmuir*, **23**, 12821 (2007).
- [9] L. Pauchard and Y. Couder, *Europhys. Lett.*, **66**, 667 (2004); V. Rastogi, *et al.*, *Macromol. Rapid Commun.*, **31**, 190 (2010).
- [10] F. Parisse and C. Allain, *Langmuir*, **13**, 3598 (1997).
- [11] O. D. Velev, *et al.*, *Science* **287**, 2240 (2000).

CONTACT

*A. Fang, Tel: +33- 2 40 67 51 44; aiping.fang@nantes.inra.fr