Tuning silica particle shape at fluid interfaces†

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By exploring the phenomenon of water diffusion induced self-assembly of silica particle in microfluidic channels, we show that both the geometric confinement experienced by the droplet and the local Peclet number are responsible for the final particle shape. This study will facilitate the understanding and ultimately control of self assembly at fluid interfaces.

Silica particles with well-defined mesoporosity and morphology are of great interest for separation, adsorption, catalysis and drug delivery.1–3 Since the early 1990s, soft matter, such as amphiphilic surfactants, block polymers and biomacromolecules, have been successfully harnessed as templates for the control of their pore size.4,5 Meanwhile, hard templates have also been applied to achieve hollow silica spheres.6 Recently, there has been a great attention to the synthesis of anisotropic silica particles.7–15 These silica particles will inspire new research in the fields where their mesoporosity and shape may have a strong impact on their performance, such as in nanomedicine16 or controlled release.17 In spite of the great success in various synthesis routes, their monodispersity, however, in either size or shape, is often poorly controlled, which presents a major challenge in understanding and controlling the mass-transport properties in their applications.

The microfluidic technique provides a straightforward and robust approach to the formation of highly monodisperse emulsion droplets. Due to its incomparable control over size, microfluidic emulsion droplets have been demonstrated as morphological templates for the synthesis of monodisperse silica or titania/silica core/shell microspheres.18 However, it remains a challenge to control the shape of particles at the microlscale as the effect of surface tension favours spherical particles. For the first time, we report a new approach to achieve doughnut-like silica by droplet-based microfluidics.19 In this approach, 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. Sol–gel transition was assisted by a microfluidic diffusion-induced self-assembly (µDISA) process and the as-achieved silica particles were monodisperse in both size and shape. Here we further explore the phenomenon of µDISA and study silica particle shape by tuning the parameters of geometric confinement and the local Peclet number, PE. The drying mechanism and resulting shapes are compared with those in spray drying.20 Their high similarity suggests a common buckling problem. However, µDISA additionally offers precise control of shape.

The experimental setup and method were the same as previously described.19 The flow focusing PDMS devices were fabricated in the same manner, except that the serpentine microchannel height, h, varied in the range of 60–240 μm while its width, w, was kept constant at 200 μm (indicating a channel aspect ratio, R = h/w, of 0.3 to 1.2). Its total drying length, l, was either 36, 84, 109 or 137 cm, depending on the drying time required. In order to achieve W/O emulsions, precursor solution and dimethyl carbonate (DMC, 99%, Sigma-Aldrich) were applied as water disperse and oil continuous phase, respectively. The continuous and dispersed phases flow rates were set constant at 3.00 and 0.05 mL h−1, respectively. Precursor solution was prepared in the same way as before.19 To vary PE, DMC with a water content in the range of 0–saturation was used as the continuous phase. Water-saturated DMC was prepared by magnetic stirring DMC in the presence of a large quantity of water for at least 2 h. The bottom phase was used as water-saturated DMC. DMC with a water content between 0 and saturation level was prepared by stoichiometrically mixing DMC with its water-saturated counterpart. An Olympus IX51 inverted microscope equipped with a digital camera (Sony, SCD-SX90) was used for high-speed imaging.

As previously stated, uniform W/O droplets were generated with the flow focusing PDMS devices and subsequently underwent in situ rapid solvent diffusion in microfluidic channel. After their generation, the sol droplets were subject to consecutive stages of shrinkage, deformation, buckling, condensation and solidification.19 The resulting silica particle shape, however, strongly depended on the geometric confinement experienced by the droplet. Besides a doughnut-like shape, we also reproducibly achieved a bowl-like shape. Here, geometric confinement experienced by a droplet has been previously21 expressed as DH/h (where DH is the droplet initial diameter at breakup, see Fig. 1Aa), which is closely related to R as well as other factors, such as interfacial tension, flow rate, etc. By varying R while keeping other factors constant, we can reliably manipulate the geometric confinement.

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buckling and eventually to bowl-like silica particles (Fig. 1B d–f). It particles by TEM in Fig. 1h clearly demonstrates their different kept its long axis parallel to the flow direction while continuing to observed in the case of doughnut-like shape, where the droplets was also observed that, after deformation, the droplets start tumbling while continuing to travel downstream in the case of asymmetric in the cross flow direction after shrinkage, resulting from the lateral walls of serpentine channel (l = 36 cm). Scale bar is 50 µm unless otherwise stated.

Fig. 1 compares the real-time droplet transformations in the microfluidic channels at two different R_vap and their resulting morphology characterized by scanning electron microscope (SEM) and tunneling electron microscope (TEM).19 From Fig. 1Ac, it is evident that when D_vap/h = 0.92, deformation tends to deform symmetrically in the cross flow direction after shrinkage, resulting in lateral buckling toward a final doughnut shape (Fig. 1A d–f); on the contrary, when D_vap/h = 0.57, deformation can occur at any point of the droplet free surface (Fig. 1Bc), leading to asymmetric buckling and eventually to bowl-like silica particles (Fig. 1B d–f). It was also observed that, after deformation, the droplets start tumbling while continuing to travel downstream in the case of bowl-like shape. This tumbling movement, however, was not observed in the case of doughnut-like shape, where the droplets kept its long axis parallel to the flow direction while continuing to travel downstream (see ESI†). The cross sectional view of the particles by TEM in Fig. 1h clearly demonstrates their different morphologies simply through varying the D_vap/h.

It has to be mentioned that the above two shapes are constantly achieved when P_e is much greater than unity. Here, P_e is defined as the ratio of two characteristic times in the drying process,22 time required for a sol nanocluster (SN) to diffuse from the edge of the droplet to its centre, R^2/ D_{diff}. R and D_{diff} are the radius of the droplet (R = 1/2 D_0, see Fig. 1) and the SN diffusion coefficient, respectively, while the other is the time required for a droplet to dry, τ_{diff}. D_{diff} is calculated by Stokes–Einstein equation22 with the size of SN at 25 nm.19 Thus, P_e = R^2/τ_{diff} D_{diff}. In order to explore this phenomenon further, we varied h for R_vap in the range of 0.3 to 1.2 while keeping P_e much greater than unity. The as-formed silica particle shapes are summarized in Fig. 2 where two zones corresponding to two different particle shapes are demonstrated, that is, either doughnut-like or bowl-like shape. At P_e >> 1, it is clear that their shape depends solely on the parameter of D_vap/h. With D_vap/h > 0.8, doughnut shape is constantly achieved; with D_vap/h < 0.8, bowl-like shape is reproducibly attained.

While we are able to demonstrate that D_vap/h plays a dominant role in silica particle shapes when P_e >> 1 in µDISA, one may question the outcome when P_e is reduced close to unity. Reducing P_e means increasing droplet drying time in microfluidic channel or/ and decreasing diffusion time of SNs. In our case, a high water content in surrounding continuous phase indicates slow diffusion. Thus, we used DMC with high water content as the continuous phase. Accordingly, the drying serpentine channels were prolonged up to 137 cm to allow sufficient drying.

In Fig. 3, silica particles with various shapes are displayed from tuning both D_vap/h and P_e. When P_e is small enough (P_e < 10), the silica particle shape is independent of D_vap/h and found spherical (Fig. 3a & 3d). When P_e is increased to a medium value around 10, dimpled spheres are observed. However, in the case of D_vap/h < 0.8, single-dimpled spheres are achieved (Fig. 3b) instead of double-dimpled spheres in the case of D_vap/h > 0.8 (Fig. 3e). The symmetrically dimpled spheres in Fig. 3e are actually very close to the doughnut-like shape in Fig. 3f where P_e is further increased to a value much greater than unity. Those asymmetrically dimpled spheres in Fig. 3b correlate with bowl-like shape in Fig. 3c. The
results imply that, in $\mu$DISA, a small $P_e$ generally favours a spherical shape independent of the $D_i/h$. When $P_e > 10$, the parameter $D_i/h$ starts to play a dominant role, yielding two dominant shapes with a threshold at 0.8: bowl-like and doughnut-like shape for $D_i/h < 0.8$ and $D_i/h > 0.8$, respectively.

In order to understand the formation of silica particles with tunable shapes, it is interesting to investigate the $\mu$DISA process at fluid interfaces. First of all, colloidal droplets show a combination of fluidic and elastic behaviour during drying.\(^{23}\) Shape transformation from evaporation-induced self-assembly (EISA) has already been observed in spray-drying of colloidal droplets.\(^{20}\) In spray drying of a glycopolypeptide solution,\(^{20}\) for example, particle morphologies were observed to change from sphere, dimpled sphere to bowl-like structure when increasing evaporation rate, nevertheless with significant polydispersity. Previous studies\(^{22}\) have elucidated the EISA process in spray drying as following: at the very initial stage of drying, the droplets shrink isotropically. If the drying is sufficiently slow ($P_e < 1$), colloids within the droplet have adequate time to redistribute by diffusion throughout the evaporating droplet, yielding spherical dense particles. By contrast, if the drying of the droplet is very quick ($P_e > 1$), colloids within the droplet have insufficient time to diffuse from the surface to the centre of the droplet, and instead accumulate near the drying front of the droplet. As drying proceeds, new colloids join to form a viscoelastic shell enclosing the remaining solution. At a critical point, the rheological nature of the shell undergoes a transition from viscoelastic to elastic so that the droplets do not shrink but buckle. This enclosing solution escapes by further evaporation from the shell leading to hollow structures.

This mechanism in EISA explains well the consecutive drying stages observed in $\mu$DISA process. However, EISA cannot explain the effect of $D_i/h$ on buckling behaviours. To elucidate $\mu$DISA mechanism, it makes sense to also consider the fluid velocity profile of laminar flow in microfluidic channels. The velocity distribution at a cross section will be parabolic in shape with the maximum velocity at the centre, essentially zero in contact with the wall. As a result, water within an emulsion droplet is removed at a different rate across the circumferential region of droplets. Due to the stagnation zones at the front and back of the droplet,\(^{24}\) water diffusion from these positions can be neglected compared to other positions on droplet free surface. A droplet’s circumferential region on the $xz$ plane (channel cross section view as showed in Fig. 4) is subject to a different rate when it translates downstream with an entourage of the continuous phase. This difference becomes significant as soon as either the $R_{up}$ or the confinement becomes large. In the fast drying regime ($P_e \gg 1$) when $D_i/h > 0.8$, the significant confinement renders solvent diffusion minimum at the top and bottom of the droplet surface, maximum at the lateral direction (right in Fig. 4A), yielding the first formation of the viscoelastic shell at the lateral direction. This is confirmed by the lateral deformation of a droplet in forming the doughnut-like shape in Fig. 1Ac. On the contrary, confinement is not significant when $D_i/h < 0.8$. Water diffusion is uniform in all radial positions (left in Fig. 4A). The droplets tend to shrink isotropically and viscoelastic shell forms in any energy well at the free surface of droplet (Fig. 1Bc). Further drying and buckling results in a bowl-like shape, as observed in Fig. 1Bd–f.

In the slow drying regime when $P_e < 10$, the global internal mass transfer is much faster compared to the hindered water transfer at the fluid interface, resulting in homogenous SN distribution across the droplet. As seen from Fig. 4B, the droplets do not buckle but shrink isotropically, and undergo a sol–gel transition to form spherical dense particles. The characteristic parabolic velocity profile in microfluidic channels renders $\mu$DISA a unique method to prepare silica particles with morphology control.

In summary, we developed a new approach to fabricate shape-specific silica particles from a $\mu$DISA process. Particles with a characteristic size down to 5 μm could be obtained with the demonstrated microfluidic device at a typical throughput of 2.6 × 10² particles/h. A unique drying mechanism different from that of spray drying is proposed based on the unique capillary effect and characteristic parabolic velocity profile in microfluidic channels. The microfluidic drying and buckling can be tuned by varying the parameters of $D_i/h$ and $P_e$, providing a starting point to control the geometry of a 3D microstructure by droplet-based microfluidics. To the best of our knowledge, this is the first trial for accurate engineering of anisotropy in silica particles by a microfluidic approach. This work should be extended in several ways: (1) to profoundly understand the buckling in $\mu$DISA. We propose to change other parameters, for example, channel cross sectional shape, and to correlate the observed results with numerical studies; (2) to use other complex fluids (e.g. nanoparticles, quantum dots, biopolymers) to fabricate hierarchical structures; or (3) to explore potential applications of the as-achieved mesoporous silica particles (their average pore size is around 3.5 nm, characterised from nitrogen adsorption–desorption isotherm).

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**References**

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