

Microfluidic synthesis of monodisperse hierarchical silica particles with raspberry-like morphology†

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A novel and facile microfluidic approach is presented to transform silica precursor droplets into uniform hierarchical microparticles with raspberry-like surface morphology. This novel microfluidic method provides a new strategy to make microparticles with unique surface morphology, and could open new opportunities for potential applications in catalysis, energy, biomedical fields.

Colloidal particles with different shapes and structures exhibit distinct properties and open novel avenues for their application in various fields. Microfluidics has attracted enormous interest for engineering a variety of particles with monodisperse size, various shape and diverse structures,¹ such as crescent and multi-pod particles,² foam-like, budding vesicle and dendritic structures.³ Polymeric microparticles with even more complex morphology and chemical anisotropy can be prepared.⁴ However, there remains a significant challenge to generate inorganic particles having various shapes, structure and surface morphology.

Silica particles of uniform size are of particular interest not only due to their wide applications in catalysis, separation and purification, but also because of their potential applications in non-conventional fields such as sensors, biomolecule delivery and electronics. The Stöber method has been widely used to make monodisperse silica particles under alkaline conditions.⁵ By combining surfactants or structure-directing agents, the Stöber method has been extended to produce a variety of mesoporous silica particles.⁶ Microfluidics has also been applied to make silica particles with controlled size and shape, such as mesoporous silica microspheres with a worm-like pore structure,⁷ with mesoporous structure and corrugated surface morphology,⁸ and with doughnut shape.⁹ However, to the best

of our knowledge, there has been no reports on facile microfluidic synthesis of monodisperse hierarchical silica particles with raspberry-like structure. Although a number of methods have been reported to make raspberry-like particles, including two-step approaches¹⁰ utilizing affinity, electrostatic interaction and chemical linking to attach the small spheres to the large spheres, and one-pot methods,¹¹ the particles generated from these methods suffer uncontrolled particle size and size distribution.

Herein we report a novel and simple microfluidic approach for synthesizing monodisperse hierarchical silica particles with raspberry-like morphology. Typically, uniform droplets of a mixture of two solutions, a silica sol and sodium bicarbonate (NaHCO_3) aqueous solution are generated in a microfluidic device (Fig. 1a), and travel along a long channel allowing solvent diffusion to produce silica gel particles near the outlet of a microfluidic device. Upon complete removal of solvent from

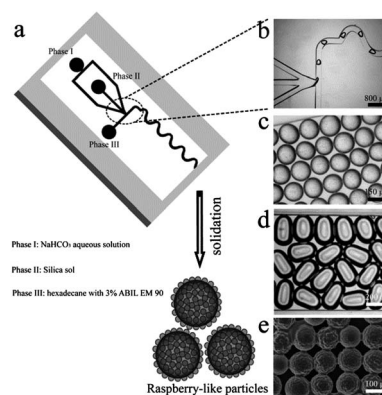


Fig. 1 Microfluidic fabrication of raspberry-like silica particles. (a) Microfluidic device for forming silica particles. (b) Optical micrographs showing the formation of uniform precursor droplets at the T-junction; (c) optical micrographs of uniform spherical gel particles collected at the outlet of the microfluidic device; (d) optical micrographs of uniform ellipsoid gel particles; (e) SEM image of raspberry like silica particles formed after solidification.

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emulsion droplets *ex situ*, hierarchical microparticles with raspberry-like morphology can be produced.

Fig. 1a illustrates the synthesis of monodisperse silica microparticles with raspberry-like morphology in a T-junction microchannel. The droplet phase introduced from a flow-focusing junction consists of two streams, with NaHCO_3 solution (phase I) pumped through the outer inlet and silica sol (phase II) from the inner flow-focusing inlet. Silica sol was prepared by hydrolyzing 1.3 g of tetraethylorthosilicate in 1.5 g of ethanol and 0.675 g of pH 2 hydrochloric acid (0.01 N) for 20 min under mixing. Hexadecane with 3 wt% ABIL EM 90 was used as the continuous phase, allowing the slow diffusion of ethanol from the silica sol precursor droplets. ABIL EM serves as a surfactant to stabilize ethanol-rich droplets. Droplets were regularly generated at the T-junction as shown in optical micrograph Fig. 1b, and then travelled along a channel of length 0.27 m. By the time droplets exited the microfluidic device, a significant amount of ethanol would have been removed through diffusion into the continuous phase, as evidenced by the decrease of droplet size, allowing the formation of silica gel particles. The flow rate could be tuned to vary the shape of the silica gel particles, from spherical (Fig. 1c) to ellipsoid (Fig. 1d). After collecting the gel particles at the outlet of the microfluidic device, they remained spherical or ellipsoid (Fig. 1c and d) and had uniform size. When solvent was fully removed from the gel particles by drying at 60 °C in an oven, the microparticle surface became corrugated, and small particles grew out at the surface of the silica microparticles (Fig. 1e). Finally, spherical gel particles solidified into uniform silica particles with unique raspberry-like surface morphology.

Fig. 2 shows scanning electron microscopy (SEM) images of raspberry-like silica particles produced from the droplets consisting of silica sol and 10 mM NaHCO_3 followed by solidification at 60 °C. A low magnification SEM image (Fig. 2a) demonstrated the formation of uniform particles (94 μm) of size half that of the original droplets (around 200 μm). The

raspberry-like morphology can be clearly observed in Fig. 2b and c, and this kind of hierarchical structure with this unique surface morphology is very distinctive from the smooth or roughened surfaces of silica spheres prepared by other methods in microfluidic devices.^{8,12} The structure of the small spheres on the microparticle surface is shown in a magnified SEM image (Fig. 2d), indicating the small particles were of size around 8 μm and had smooth surface (Fig. 2d). The cross-sectional inner structure of the silica particles can be observed through a broken particle (Fig. 2e and f) showing the internal structure of the microparticles. To the best of our knowledge, this raspberry-like surface morphology of silica microparticles with controlled uniform size has not been reported previously.

A possible mechanism of this raspberry-like microparticle formation is schematically illustrated in Fig. S1.† It is speculated that the unique surface morphology results from two possible kinetic processes: (I) the reaction between HCl and NaHCO_3 and thus the generation of H_2CO_3 (eqn (1)) and CO_2 (eqn (2)), and (II) escape of CO_2 bubbles from the interfacial subphase. Droplets of two different solutions (phase I NaHCO_3 and phase II silica sol) were formed through merging two solution streams at the flow-focusing junction (Fig. 1). Phase I is an aqueous solution of NaHCO_3 , and phase II consists of an acidified silica sol of TEOS in a mixture of ethanol and water in acidic condition (pH 2). The rapid acid-catalyzed hydrolysis of TEOS was achieved by mixing the mixture for 20 min. As sol-gel reactions are time-consuming, the introduction of NaHCO_3 solution plays two important roles in the formation of silica particles. On one hand, the gelation of silicic acid can be accelerated by increasing the pH above the isoelectric point of silica (pH > 3) through the reaction between HCl and NaHCO_3 (eqn (1)). On the other hand, the reaction between HCl and NaHCO_3 can produce carbonic acid (eqn (1)), which readily decomposes to carbon dioxide and water (eqn (2)).

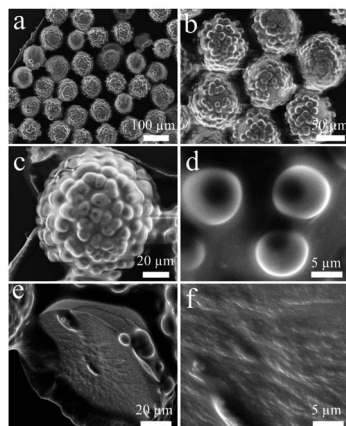
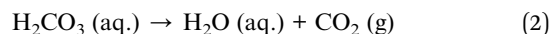
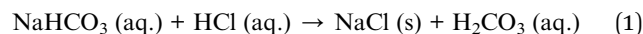


Fig. 2 SEM images of raspberry-like silica particles. (a) and (b): lower magnification; (c) single particles at higher magnification; (d) a magnified image of the surface of raspberry-like silica particles; (e) broken particles and (f) the inner structure of the broken particles. Continuous phase: hexadecane with 3 wt% ABIL EM 90; dispersed phases: phase I was silica sol and phase II was 10 mM NaHCO_3 solution. The gel particles were solidified at 60 °C in an oven.

As the reaction between HCl and NaHCO_3 occurs, the precursor droplets gradually turned into gel particles. Therefore, the viscosity kept increasing, which prevented the CO_2 bubbles that formed inside the gel particles from escaping rapidly. When carbon dioxide slowly moved from the droplet inside to the interfacial subphase, driven by the increasing temperature and removal of ethanol and water from the gel particles, CO_2 finally escaped from the silica gel particles, leading to surface projections that finally grew to small particles. These two kinetic processes lead to the formation of the unique raspberry-like silica microparticles with small spheres on a big sphere. Therefore, incorporating NaHCO_3 into the silica sol droplets is considered essential for the formation of silica particles with this special morphology. Furthermore, the reaction and the formation of gas bubbles and subsequently their rapid escape play very important roles. For instance, with similar silica sol but in the absence of NaHCO_3 , only silica particles with smooth or corrugated surface morphology were

formed based on either the emulsion and solvent evaporation method (ESE),^{12b} or the diffusion-induced self-assembly method.⁸ Chokkalingam *et al.*¹³ accelerated the sol-gel reaction by coalescing an acidic silica sol droplet and a second droplet containing ammonia. Spherical silica particles with small surface corrugation were produced, instead of raspberry-like surface morphology. A comparison of the present study with this prior work suggests that the incorporation of sodium bicarbonate plays a crucial role in the formation of the raspberry-like surface morphology.

Under the two-kinetic-process mechanism proposed above, it would be expected that the surface structures of the hierarchical silica particles could be controlled by changing the reaction between HCl and NaHCO₃, and thus the formation of H₂CO₃, or else by changing the formation and escape of CO₂ bubbles. To simply vary the formation and escape of CO₂ bubbles, the solidification temperature can be varied. As it is a kinetic process, when the solidification temperature is decreased, the formation and escape of CO₂ bubbles should be slowed down, and silica particles with smaller spheres on the surface are expected to be formed. Fig. 4 shows the raspberry-like silica particles formed at a solidification temperature of 50 °C. Monodisperse silica particles were still observed under SEM (Fig. 3a), and their size (around 90 μm) was the same as those prepared at 60 °C (Fig. 2). However, the surface morphology was different (Fig. 3b–d). Although silica microparticles with bigger spheres on the surface were still observed, the surface morphology shifted distinctly to microparticles with smaller spheres on top (Fig. 3c). Moreover, the size of the small spheres was around 3 μm, which was much smaller than those shown in Fig. 2 (8 μm). Additionally, instead of spherical and smooth particles, they became particles with hat-like structure (Fig. 3d). This result provides direct support of the proposed mechanism, as changes in the solidification temperature significantly affected the surface morphology in a predictable manner.

To further investigate the effect of the reaction between HCl and NaHCO₃ and thus the formation of CO₂ on the surface morphology, the concentration of NaHCO₃ was increased from 10 to 20 mM. In this case, it was predicted that the reaction rate would accelerate, leading to more H₂CO₃ and thus CO₂ bubbles. At some critical CO₂ evolution rate a pore structure would be

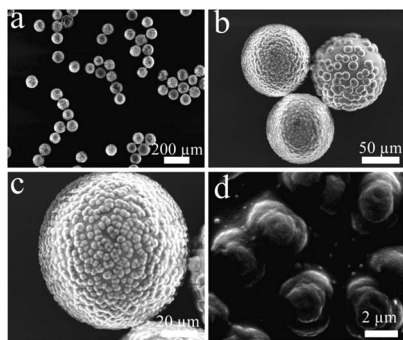


Fig. 3 SEM images of raspberry-like silica particles at different magnifications. Continuous phase: hexadecane with 3 wt% ABIL EM 90; dispersed phases: I was silica sol and II was 10 mM NaHCO₃ solution. Droplets were solidified at 50 °C.

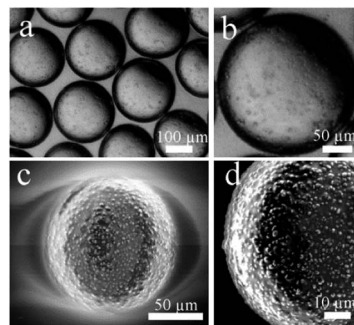


Fig. 4 Optical micrographs of droplets formed in microfluidic devices (a) and (b); and SEM images of raspberry-like silica particles (c) and (d). Continuous phase: hexadecane with 3 wt% ABIL EM 90; dispersed phases: I was silica sol and II was 20 mM NaHCO₃ solution. The droplets were solidified at 60 °C.

predicted to form, even in a microfluidic device. Fig. 4a shows the formation of monodisperse gel particles formed at the outlet of the microfluidic device. From the enlarged optical image in Fig. 4b, a pore structure on the surface can be clearly observed, indicating the formation and burst release of CO₂ because of the accelerated reaction between HCl and NaHCO₃. After solidification at 60 °C, the particle size shrank from around 230 to 120 μm, also about half of the original size, and hierarchical silica particles were also produced, but with even smaller particles on the surface with size of less than 1 μm. This type of surface structure is distinct from those shown in Fig. 2 and 3, demonstrating the significant effects of these two kinetic processes on the hierarchical structure of silica microparticles. Therefore, the two-kinetic-process mechanism proposed above is validated.

In conclusion, we have shown the facile synthesis of monodisperse hierarchical silica microparticles with unique raspberry-like morphology in a simple T-junction microfluidic device. The surface morphology can be controlled by adjusting the reaction between HCl and NaHCO₃, and thus the formation of H₂CO₃ and CO₂, or else the escape of CO₂ bubbles. The simple method reported here shares similarities with the emulsion and solvent evaporation method (ESE), but nevertheless is distinct from the ESE because of the incorporation of NaHCO₃, which plays a crucial role in inducing the formation of the unique raspberry-like surface morphology. A two-kinetic-process mechanism was proposed and validated experimentally. This novel microfluidic method provides a new strategy and a simple way to make microparticles with unique surface morphology, and could open new opportunities to make other microparticles with hierarchical structures, for example using polymers or biopolymers (chitosan, alginate, *etc.*). Furthermore, this facile microfluidic approach can be engineered to make raspberry-like silica particles having porous structure for possible applications in a variety of fields, including for example as chromatography packing materials, or as core-shell structures with different core and shell materials, for example, using titania as a core material for water treatment, catalysis, *etc.* Therefore, there is a great potential to further develop this method to make various materials tailored for a wide range of possible applications.

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References

- (a) C.-X. Zhao and A. P. J. Middelberg, *Chem. Eng. Sci.*, 2011, **66**, 1394; (b) C.-X. Zhao, L. He, S. Z. Qiao and A. P. J. Middelberg, *Chem. Eng. Sci.*, 2011, **66**, 1463.
- Q. Q. Zhang, B. C. Lin and J. H. Qin, *Microfluid. Nanofluid.*, 2012, **12**, 33.
- J. Zhu and R. C. Hayward, *Angew. Chem., Int. Ed.*, 2008, **47**, 2113.
- (a) J.-H. Jang, D. Dendukuri, T. A. Hatton, E. L. Thomas and P. S. Doyle, *Angew. Chem., Int. Ed.*, 2007, **46**, 9027; (b) R. Haghgooeie, M. Toner and P. S. Doyle, *Macromol. Rapid Commun.*, 2010, **31**, 128; (c) P. Panda, K. P. Yuet, T. A. Hatton and P. S. Doyle, *Langmuir*, 2009, **25**, 5986; (d) D. Dendukuri and P. S. Doyle, *Adv. Mater.*, 2009, **21**, 4071; (e) S. K. Suh, K. Yuet, D. K. Hwang, K. W. Bong, P. S. Doyle and T. A. Hatton, *J. Am. Chem. Soc.*, 2012, **134**, 7337; (f) R. F. Shepherd, P. Panda, Z. Bao, K. H. Sandhage, T. A. Hatton, J. A. Lewis and P. S. Doyle, *Adv. Mater.*, 2008, **20**, 4734.
- W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62.
- (a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; (b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834; (c) D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
- S. Q. Xu, Z. H. Nie, M. Seo, P. Lewis, E. Kumacheva, H. A. Stone, P. Garstecki, D. B. Weibel, I. Gitlin and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 2005, **44**, 724.
- I. Lee, Y. Yoo, Z. Cheng and H. K. Jeong, *Adv. Funct. Mater.*, 2008, **18**, 4014.
- A. P. Fang, C. Gaillard and J. P. Douliez, *Chem. Mater.*, 2011, **23**, 4660.
- (a) X. Jiang, G. Wei, X. Zhang, W. Zhang, P. Zheng, F. Wen and L. Shi, *J. Mol. Catal. A: Chem.*, 2007, **277**, 102; (b) B. Bai, N. Quici, Z. Li and G. L. Puma, *Chem. Eng. J.*, 2011, **170**, 451; (c) N. Pureskiy and L. Ionov, *Langmuir*, 2011, **27**, 3006.
- A. Ahmed, H. Ritchie, P. Myers and H. F. Zhang, *Adv. Mater.*, 2012, **24**, 6042.
- (a) V. Chokkalingam, B. Weidenhof, M. Kramer, S. Herminghaus, R. Seemann and W. F. Maier, *ChemPhysChem*, 2010, **11**, 2091; (b) N. J. Carroll, S. B. Rathod, E. Derbins, S. Mendez, D. A. Weitz and D. N. Petsev, *Langmuir*, 2008, **24**, 658.
- V. Chokkalingam, B. Weidenhof, M. Kramer, W. F. Maier, S. Herminghaus and R. Seemann, *Lab Chip*, 2010, **10**, 1700.