

Fabrication of Ceramic Microspheres by Diffusion-Induced Sol–Gel Reaction in Double Emulsions

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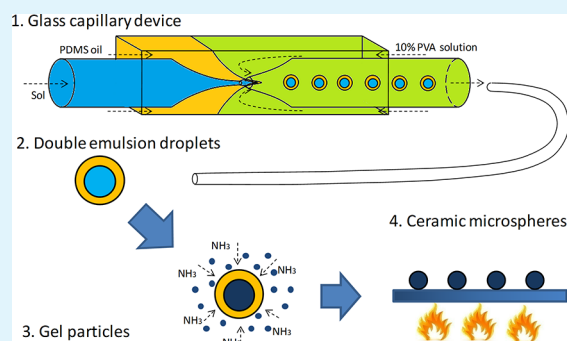
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S Supporting Information

ABSTRACT: We demonstrate an approach to prepare zirconium dioxide (ZrO_2) microspheres by carrying out a diffusion-induced sol–gel reaction inside double emulsion droplets. A glass capillary microfluidic device is introduced to generate monodisperse water-in-oil-in-water (W/O/W) double emulsions with a zirconium precursor as the inner phase. By adding ammonia to the continuous aqueous phase, the zirconium precursor solution is triggered to gel inside the emulsions. The double emulsion structure enhances the uniformity in the rate of the sol–gel reaction, resulting in sol–gel microspheres with improved size uniformity and sphericity. ZrO_2 ceramic microspheres are formed following subsequent drying and sintering steps. Our approach, which combines double-emulsion-templating and sol–gel synthesis, has great potential for fabricating versatile ceramic microspheres for applications under high temperature and pressure.

KEYWORDS: diffusion, microfluidic emulsification, double emulsions, sol–gel, ceramic microsphere, zirconium dioxide



INTRODUCTION

Ceramic materials are widely used as a strength enhancer^{1–4} in cutting tools and structure materials because of their stability at high temperature, as well as high resistance against wear and corrosion.⁵ Recently, ZrO_2 ceramic microspheres are demonstrated to be particularly useful in applications such as electrochemistry,⁶ biotemplated materials fabrication,⁷ high-performance liquid chromatography (HPLC)⁸ and oxygen sensing.⁹ Moreover, ZrO_2 microspheres are also proposed as a template for generating uranium dioxide (UO_2) coated fuel particles in nuclear power plants.¹⁰ The performance of ZrO_2 microspheres in these applications depends on their size distribution,¹¹ sphericity,¹⁰ and structures.⁶ For example, when used as the templates of nuclear fuel particles, ZrO_2 microspheres need to have both a narrow size distribution and a high sphericity to eliminate weak spots in the coated layers, which contain gaseous fission products.^{10,12} Traditional methods for fabricating these microspheres include vibration dispersion,¹³ stirring emulsification,¹⁴ and polymerization-induced colloidal aggregation (PICA).¹⁵ Microspheres prepared using the vibration dispersion and stirring emulsification techniques often have a wide size distribution and a low sphericity, while PICA often results in microspheres with a porous structure, thus lowering the strength of the microspheres.¹⁵ Therefore, monodisperse ceramic microspheres with

high density and high sphericity are still difficult to prepare despite their growing demands in the mechanical engineering and energy applications.¹⁶

By flowing the precursor fluids in microchannels with strictly laminar conditions, microfluidic emulsification offers a means to generate a large number of droplets with a high degree of size and shape uniformity.^{17,18} The laminar flow conditions in microchannels ensure that the droplets are not overly deformed due to gravity or turbulence during mixing; consequently, the high sphericity of the droplets is maintained. This microfluidic approach has been introduced to generate spherical preceramic polymer or hydrogel, which can act as precursors for ceramic microspheres, such as ZrO_2 and SiO_2 .^{19,20} However, this approach cannot be easily adapted for external gelation, in which reactants diffuse into the aqueous sol droplets to trigger the onset of gelation.¹³ Reactants, such as ammonium solution in this application,¹³ are hard to add to the oil-based continuous phase to trigger the gelation process because of the immiscibility of ammonium solution and oils. After addition of ammonium solution to the single emulsion precursor droplets, the large amount of the oil continuous phase prevents

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the hydroxide ions from diffusing evenly into the sol droplets. This compromises the sphericity of the resultant gel particles.

In this work, we combine sol–gel chemical synthesis with microfluidic emulsification techniques to prepare ZrO₂ ceramic microspheres. We use a glass capillary microfluidic device to generate monodisperse water-in-oil-in-water (W–O–W) double emulsions, where the inner phase is a sol of zirconium precursor, the middle phase is silicone oil and the continuous phase is water with polyvinyl alcohol (PVA) as the surfactant. To trigger the gelation, ammonia is added to the continuous phase after the double emulsion droplets are prepared. The uniform gel spheres obtained by this method are sintered at 1500 °C after washing and drying. The double emulsions enable diffusion of additional aqueous components across the oil shells into the aqueous cores in a more controlled manner. The technique results in highly monodisperse ZrO₂ ceramic microspheres with excellent sphericity.

EXPERIMENTAL SECTION

In the experiment, we chose the approach of external gelation to carry out the sol–gel reaction. The external gelation process did not start until ammonia was added to the chemical system. Comparing with the internal gelation process, where ammonia was typically released from hexamethylenetetramine pre-encapsulated internally within the droplets, the external gelation process in which ammonia was added to the continuous phase was more versatile and allowed subsequent replenishment of the ammonia for continuous gelation.

The W/O/W double emulsions were prepared in glass capillary microfluidic devices. The inner phase was a sol that contained the zirconium precursor. The middle phase was silicone oil (20cst, Sigma-Aldrich, USA) with 2% v/v surfactant (Dow Corning 749 fluid, USA). The continuous phase was water with 10 wt % polyvinyl alcohol (PVA, *M_w* 13 000–23 000 g/mol 87–89% hydrolyzed, Sigma-Aldrich, USA).

Preparation of Sol. We dissolved 4% v/v tetrahydrofurfuryl alcohol (THFA, Sinopharm Chemical Reagent Beijing Co. China) into water with 8 wt % PVA (KURARAY CO. LTD, Japan). The solution was stirred at about 50 °C. Zirconium oxychloride (ZrOCl₂, Sinopharm Chemical Reagent Beijing Co. China), urea (CON₂H₄, Sinopharm Chemical Reagent Beijing Co. China), citric acid (C₆H₈O, Sinopharm Chemical Reagent Beijing Co. China) and yttrium nitrate (Y(NO₃)₃, Sinopharm Chemical Reagent Beijing Co. China) were added to the solution subsequently, forming a solution mixture with 1 M ZrOCl₂, 2.5 M CON₂H₄, 0.1 M C₆H₈O and 0.05 M Y(NO₃)₃. To avoid the collapse of the particles during the gelation process, we also added 2.5 wt % acrylamide (Sinopharm Chemical Reagent Beijing Co. China), 0.2 wt % N,N-methylene diacrylamide (Sinopharm Chemical Reagent Beijing Co. China) and 0.15 wt % ammonium persulfate (APS, Sinopharm Chemical Reagent Shanghai Co. China) into the sol solution.

Fabrication of Double Emulsion Droplets. To make the capillary microfluidic device where double emulsions were generated, we used a pipet puller (P-97, Sutter Instrument Inc., USA) to taper two cylindrical capillary tubes each with an outer diameter of 1 mm. The two tapered capillaries with the inner diameter of about 50 and 100 μm respectively were inserted into each end of a square capillary with an inner dimension of 1.05 mm. The inner phase was injected through the tapered capillary with a small tip diameter. The middle phase flowed through the interstices between the square capillary and the cylindrical capillary with the small tip. The continuous phase

entered the device through the interstices from the other end. At the junction, the coaxial compound jet of middle and inner phases was flow-focused by the continuous phase and formed double emulsion droplets, as shown schematically in Figure 1. The diameters of the cores and the droplets were controlled by adjusting the flow rates of the different phases (see the Supporting Information, Video S1)

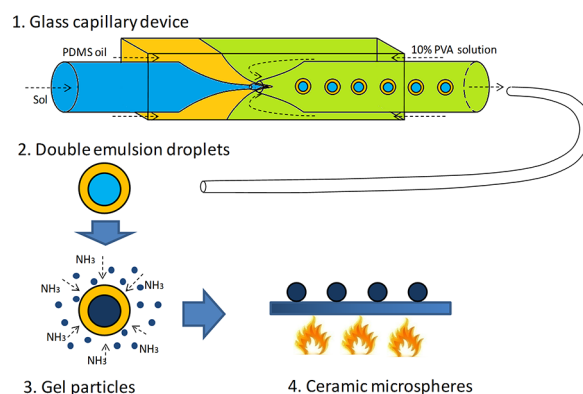
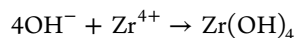
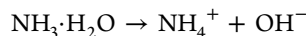


Figure 1. Schematics illustrating the generation of ZrO₂ ceramic microspheres using a microfluidic double-emulsion-templated approach. In step 1, double emulsion droplets with inner cores of sol are generated. In step 2, the double emulsion droplets are heated at 70 °C. In step 3, gelation of the sol droplets is triggered upon addition of the ammonium solution. In step 4, the gel particles are sintered at 1500 °C.

Preparation of Gel Particles. The fabricated emulsions were put in a water bath at 70 °C for 30 min to polymerize the acrylamide monomers. In the absence of poly(acrylamide) (PAM), the water would leak out, resulting in an additional water droplet and thus disruption of the droplet structure. The hydrophilic groups of PAM help retaining water within the polymer matrix during gelation. After the heating step, ammonium hydroxide solution was added to the continuous phase of the emulsions. Zr(OH)₄ precipitates were formed, and gelation of the sol core was triggered in the double emulsions, according to the following chemical equations



Making Ceramic Microspheres. After gelation, the gel particles were washed with the deionized water several times to remove the oil shell. Propanol (Sinopharm Chemical Reagent Beijing Co. China) was subsequently added to replace the remaining water in the particles. The propanol was eventually removed by evaporation at room temperature. After that, the gel particles were heated to 1500 °C for 17 h, and ZrO₂ ceramic microspheres formed as a result.

RESULTS AND DISCUSSION

To obtain the spherical gel particles, the sol droplets are suspended in ammonium solution. The droplets in the suspension maintain high sphericity because of the surface tension effects, which lead to a reduction of the total interfacial area. To ensure that the droplets are well-suspended in the ammonia solution, we fabricate particles with a very thin shell. The variation in shell thickness is therefore not significant, when compared to particles with thick shells. The spherical

shape of the droplets ensures an even diffusion of the OH^- ions into the sol droplets. With the microfluidic emulsification technique, the shell thickness of the double emulsion droplets is precisely controlled by changing the flow rate ratios of the middle phase to the other two liquid phases, as shown in Figure 2. The shells of the double emulsion droplets separate the sol

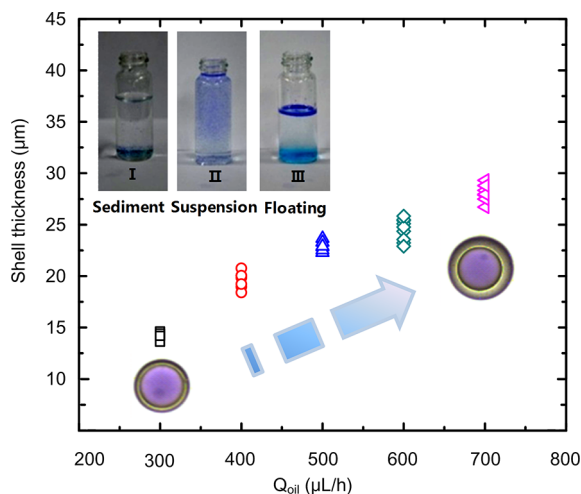


Figure 2. By adjusting the flow rate ratios of the middle phase to the other two liquid phases, the shell thickness of the double emulsions is manipulated. In this figure, the flow rates of the continuous phase and the inner phase dyed with Berlin blue are kept at 3000 and 200 $\mu\text{L}/\text{h}$, respectively, whereas the flow rate of the middle oil phase is systematically varied.

cores from each other, thus avoiding aggregation of the resultant gel particles. Moreover, the oil shells help to prevent contamination of the sol cores by impurities in the continuous phase.

When the double emulsions are mixed with ammonium solution, the concentration of the OH^- ions around the droplets is uniform, leading to their uniform diffusion into the sol cores. Thus, the rate of gelation triggered by the OH^- ions around the core is also spatially uniform, facilitating the fabrication of gel particles with spatial homogeneity,²¹ as shown in panels a and b in Figure 3. The resultant gel particles maintain the high sphericity and size uniformity, as shown in Figure 3c. For comparison, we also use single emulsion templates to generate monodisperse sol droplets, as shown in Figure 3d. Since the ammonium solution cannot be added uniformly to the continuous phase, the sol droplets stay at the interface between the oil and the ammonium solution. The concentration of the OH^- ions around the sol droplets is different, which is higher near the interface, preventing uniform diffusion of the OH^- ions into the sol, as shown in Figure 3e. The uneven diffusion results in deformation and collapse of the resultant gel particles, as shown in Figure 3f.

The gel particles are converted to ZrO_2 ceramic microspheres after sintering at 1500 $^\circ\text{C}$ for 17 h in an alumina (Al_2O_3) crucible. All organics are burnt away and the diameter of ceramic microsphere decreases to about 1/3 of the original diameter of the gel particle. The ceramic microspheres have high sphericity and fine grains, as shown by the Scanning Electron Microscope (SEM, Quanta 200 FEG, FEI Co.) images in Figure 4a. The ceramic microspheres are then placed in a self-curing denture base made of an acrylic resin. The resin, which contained the ceramic microspheres, are grinded after

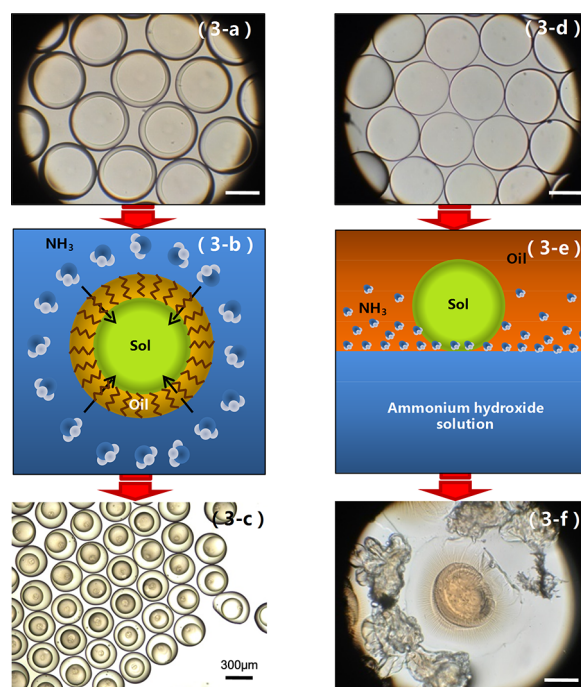


Figure 3. (a) Monodisperse double emulsion droplets generated in a capillary microfluidic device. The outer phase is 10 wt % PVA water solution; the middle phase is silicone oil with 2%v/v surfactant (Dow Corning 749 Fluid); the inner phase is a zirconium precursor. (b) The double emulsions are mixed with ammonium solution and the hydroxide ions diffuse across the oil shell, thus triggering the gelation process. (c) After gelation, the gel particles maintain the high sphericity and size uniformity of the original emulsion precursors. (d) Single emulsion droplets are generated in a capillary microfluidic device. The continuous phase is silicone oil with 2%v/v surfactant (Dow Corning 749 Fluid) and the inner phase is the zirconium precursor. (e) The single emulsions are mixed with ammonium solution and the sol droplet stays at the interface between the oil and the ammonium solution. As a result, the diffusion of hydroxide ions is uneven. (f) Gelation triggered by uneven diffusion of OH^- ions results in the deformation and collapse of the final gel particles. The scale bar is 200 μm .

curing for observation of the inner structure of the microspheres, as shown by the confocal laser microscopy image in Figure 4b. The particles are composed mainly of zirconium and oxygen, as confirmed by energy-dispersive spectroscopy (EDS) results shown in Figure 4c. The ceramic microspheres are also examined by the X-ray diffraction (XRD), which confirms the presence of ZrO_2 monoclinic crystal in the ceramic microspheres, as shown in Figure 4d.

The ZrO_2 ceramic microspheres fabricated using the double emulsion templates (DET microspheres) are compared with those made by traditional vibration dispersion method (VD microspheres, offered by the Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing), as shown in panels a and b in Figure 5. The gels and the sintered DET microspheres are highly monodisperse, with a size range well within the range²² (30–1200 μm) expected for the fuel application, as shown in Figure 5c. The eccentricity ϵ , which is defined as the ratio of the diameter of the smallest circle that contains the microsphere to that of the largest circle inscribed inside the microsphere, of the DET microspheres is lower than that of the VD microspheres, as shown in Figure 5d. Moreover, when similar particles are used as the kernels of the fuel

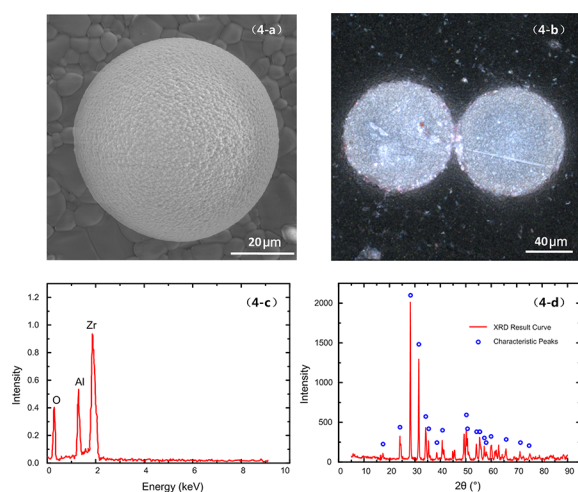


Figure 4. (a) SEM image of a typical ceramic microsphere with high sphericity obtained after sintering. (b) Solid inner structure of the ceramic microspheres. (c) Elements of zirconium and oxygen found in the obtained ceramic microspheres, as shown in the EDS analysis. Aluminum observed in the data comes from the crucible that contains the gel particles during the sintering. (d) ZrO_2 monoclinic crystals are found in the obtained ceramic microspheres, as shown by the XRD analysis; the open circles represent the characteristic peaks.

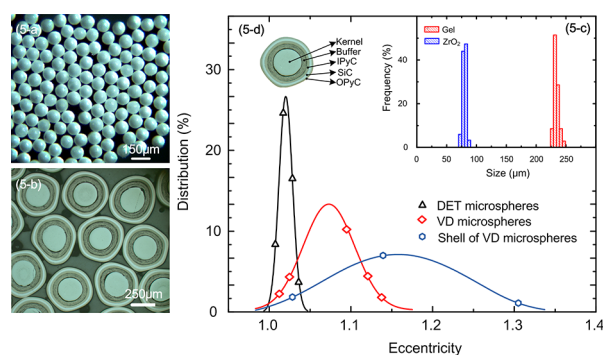


Figure 5. (a) Image of the DET ZrO_2 microspheres with high sphericity and a narrow size distribution. (b) Coated VD ZrO_2 microspheres. (c) Size distributions of gel particles and DET microspheres. (d) Eccentricity of the DET microspheres, the VD microspheres and the shell of the VD microspheres. Coated VD ZrO_2 microsphere consists of a kernel surrounded by the buffer, the inner pyrolytic carbon layer (IPyC), the silicon carbide layer (SiC) and the outer pyrolytic carbon layer (OPyC). SiC layer is chosen as the shell for measurement and calculation because it is the main barrier for gases released due to nuclear fission.

particles in a nuclear reaction, they will be coated by shells of carbon and silicon carbide to contain the fission gas released from the kernels. These additional shells tend to enlarge the eccentricity, as shown in Figure 5d. Poor eccentricity of the kernel particles will reduce the strength of the shell. The maximum stress on the shell of the microsphere can be calculated from eq 1²³

$$\sigma_{\max} = pR_{\min}\epsilon/2s \quad (1)$$

where R_{\min} is the radius of the smallest circle that circumscribes the microsphere, s is the average thickness of the shell, p is the pressure of the fission gas. A typical value of the fission gas pressure is around 17 MPa.²³ ϵ has a linear relationship with the maximum stress σ_{\max} as indicated by eq 1, and an increase in the maximum stress on the shell at large ϵ will greatly increase

the failure probability of the fuel particles and reduce their working life. The failure probability has a power-law relationship to the ϵ calculated according to the model provided by Nabelek and Verfondern.^{12,23} The failure probability of these DET microspheres is calculated to be 1.6×10^{-6} , whereas that of the VD microspheres is 1.36×10^{-5} . It proves that the DET microspheres are much stronger and can bear higher pressures because of the gas released from the kernels in nuclear applications, thus improving the safety during operation.

CONCLUSIONS

In this work, we demonstrate microfluidic double emulsions as promising templates for fabricating monodisperse ceramic microspheres with high sphericity. The double emulsion structure ensures an even diffusion of the external reactants into the sol cores to retain the sphericity of the resultant gel particles, while microfluidic fabrication method affords a narrow size distribution of the particles. After sintering, the resultant ceramic microspheres still keep the high sphericity, which is advantageous in nuclear applications. Due to the improved sphericity, microspheres fabricated using the double emulsion templates experience a lower maximum stress on the coated shell than microspheres generated using conventional methods. The production rate can be increased by parallelizing the production in multiple microchannels.²⁴ With the ability to achieve high sphericity and narrow size distribution, this double-emulsion-templated approach will not only improve the performance of the ZrO_2 ceramic microspheres in the nuclear applications, but also offer great potentials in electrochemistry, biotemplated materials fabrication, HPLC, and oxygen sensing.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- Wang, L. N.; Adams, A.; Luo, J. L. *J. Biomed. Mater. Res.* **2011**, *99B*, 291–301.
- Osiko, V. V. *Mendeleev Commun.* **2009**, *19*, 117–122.
- Galimov, E. M.; Sevastyanov, V. S.; Babulevich, N. E.; Tyurina, E. N. *Rapid Commun. Mass Spectrom.* **2009**, *23*, 2461–2466.
- Tsai, M. C.; Lin, G. T.; Chu, H. T.; Lee, C. Y. *J. Nanopart. Res.* **2008**, *10*, 863–869.
- Bocanegra-Bernal, M. H.; De La Torre, S. D. *J. Mater. Sci.* **2002**, *37*, 4947–4971.
- Xu, J.; Liu, C. H.; Teng, Y. L. *Microchim. Acta* **2010**, *169*, 181–186.
- Dubok, V. A. *Powder Metall. Met. Ceram.* **2000**, *39*, 381–394.
- Henry, R. A.; McNeff, C. V.; Yan, B. W.; Hoye, T. R. *Am. Lab.* **2005**, *37*, 22–24.

- (9) Chen, C. Y.; Liu, C. L. *Ceram. Int.* **2011**, *37*, 2353–2358.
- (10) Couland, M.; Fourcaudot, S.; Abril, R. J.; Fernandez-Carretero, A.; Somers, J. J. *Am. Ceram. Soc.* **2012**, *95*, 133–137.
- (11) Keshmiri, M.; Kesler, O. *Acta Mater.* **2006**, *54*, 4149–4157.
- (12) Miller, G. K.; Wadsworth, D. C. *J. Nucl. Mater.* **1994**, *211*, 57–69.
- (13) Zhou, X. W.; Ma, J. T.; Hao, S. C.; Zhao, X. Y.; Wang, Y.; Deng, C. S.; Liang, T. X.; Guo, W. L.; Tang, Y. P.; Tang, C. H. *Nucl. Eng. Des.* **2012**, *250*, 192–196.
- (14) Chang, Y.; Dong, S. J.; Wang, H. H.; Du, K. H.; Zhu, Q. B.; Luo, P. *Mater. Res. Bull.* **2012**, *47*, 527–531.
- (15) Annen, M. J.; Kizhappali, R.; Carr, P. W.; McCormick, A. J. *Mater. Sci.* **1994**, *29*, 6123–6130.
- (16) Chandradass, J.; Balasubramanian, M. *Ceram. Int.* **2005**, *31*, 743–748.
- (17) Shah, R. K.; Shum, H. C.; Rowat, A. C.; Lee, D.; Agresti, J. J.; Utada, A. S.; Chu, L. Y.; Kim, J. W.; Fernandez-Nieves, A.; Martinez, C. J.; Weitz, D. A. *Mater. Today* **2008**, *11*, 18–27.
- (18) Utada, A. S.; Lorenceau, E.; Link, D. R.; Kaplan, P. D.; Stone, H. A.; Weitz, D. A. *Science* **2005**, *308*, 537–541.
- (19) Ye, C. W.; Chen, A.; Colombo, P.; Martinez, C. J. *R. Soc. Interface* **2010**, *7* (Suppl. 4), S461–S473.
- (20) Chokkalingam, V.; Weidenhof, B.; Krämer, M.; Maier, W. F.; Herminghaus, S.; Seemann, R. *Lab Chip* **2010**, *10*, 1700–1705.
- (21) Shum, H. C.; Bandyopadhyay, A.; Bose, S.; Weitz, D. A. *Chem. Mater.* **2009**, *21*, 5548–5555.
- (22) Haas, P. A.; Begovich, J. M.; Ryon, A. D.; Vavruska, J. S. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 459–467.
- (23) Verfondern, K.; Nabielek, H. *Forschungs-zentrum Jülich Report Jül-Spez-298*; Research Center Jülich: Jülich, Germany, 1985.
- (24) Romanowsky, M. B.; Abate, A. R.; Rotem, A.; Holtze, C.; Weitz, D. A. *Lab Chip* **2012**, *12*, 802–807.