Microreactors

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Silica-Based Liquid Marbles as Microreactors for the Silver Mirror Reaction**

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***Abstract:** Little attention has been paid to the participation of the shell of silica-particle-based liquid marbles and their influence on chemical reactions. The fabrication of liquid marbles with the encapsulating particle shells not only act as protecting layers to provide a confined environment, but also provide the reactive substrate surfaces to regulate the classical silver mirror reaction. Fabrication of silver mirrors with different morphologies was achieved by modifying particle surface properties, which could further lead to Janus liquid marbles. The different evaporation behavior of microreactors was demonstrated. Micrometer-sized silica particles were used for the preparation of monolayer-stabilized liquid marbles, which show great potential in fabricating Janus particles from superhydrophobic particles that are not attainable from Pickering emulsions.*

Dry waters or liquid marbles, which were first introduced by Dieter et al. in 1968,[1] were once again promoted by Quéré and Aussillous to overcome the difficulty of transporting a small amount of liquid on a solid substrate.[2] Coating the liquid droplets by a thin layer of nano-/microparticles at the air–liquid interface renders the droplets superhydrophobic or superoleophobic, which reduces the adhesion of liquid to the solid substrates significantly so that the motion of the droplets can be easily triggered and thus transported with low friction.[2,3] In the last decade, liquid marbles have been exposed to intensive investigations ranging from basic principles,[3a] static and dynamic properties,[4] surface tension measurements[5] to various potential applications, such as pollution detection,[6] rapid blood typing,[7] and gas sensing.[8] The adsorption of particles at the air–liquid interface also confers the formed liquid marbles excellent mechanical stability, which allows them to maintain their integrated structures when subjected to external forces, such as gravity,[9] electrical fields,[10] or magnetic fields.[11] Given the flexibility in the choice of solid particles and liquids to prepare liquid marbles, it is not surprising that liquid marbles are fast emerging as a versatile platform for a wide range of applications.[1,3b,d,e]

Liquid marbles offer potential applications as miniature reactors owing to many advantages related to the reduced use of chemical reagents and solvents, a well-confined micro-environment, and a versatile platform for chemical reactions.[12] Various applications exploiting their ability for miniaturized chemical processes have been reported. For example, Xue et al. have shown that liquid marbles coated with magnetic powders could be used as smart miniature reactors for chemiluminescence reactions, photochemical polymerization, nanoparticle synthesis, and also acid–base reactions.[13] Tian et al. and Bormashenko et al. have concluded that the permeability of the porous powder shells coating liquid marbles has allowed their application for gas sensing.[8,14] Arbatan et al. presented the use of liquid marbles as micro-bioreactors for biological reactions and diagnostic assays.[7] Also, liquid marbles used for synthesis, self-assembly, and charge transport have been reported.[15] Compared to the traditional examples of microreactors, such as liposomes,[16] polymersomes,[17] colloidosomes, and emulsions,[18] liquid marbles have many advantages in allowing the entry/exit of reactants and products, granting the transport of gas and vapor, and good controllability. However, it is desirable to note that previous studies of using liquid marbles as miniature reactors have been mostly focused on how the encapsulating particle shells can act as inert protecting layers to isolate a small-volume compartment, and less attention has been paid to their participation in the reactions. Dorvee et al. have shown that the surface of liquid marbles stabilized by barcoded porous silicon particles could serve as a substrate-less platform for indication of delivery through spectroscopic analysis,[19] while Lee et al. showed that the plasmonic liquid marbles would be used for quantitative and multiplex ultra-trace molecular detection.[20] Only recently, Miao et al. and Tang et al. demonstrated that particles adsorbed at the air–liquid interface on liquid marbles could act as catalysts to catalyze the chemical reaction in water.[21] Thus, liquid marbles with such catalytic encapsulating particle layers can further enforce their suitability as miniature reactors.

Historically, the silver mirror reaction has been and is still being used as an efficient method for fabricating silver thin

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films on solid substrates for a broad range of applications, such as nanoelectronics, medical diagnostics, and surface-enhanced Raman scattering (SERS) detection. The conventional silver mirror reaction typically involves the reduction of silver salts, such as Tollens' reagent $[Ag(NH_3)_2]^+$ with reducing sugars to render silver nanoparticles depositing on the substrates, such as glass plates. Herein, we demonstrate the fabrication of liquid marbles with the encapsulating particle shells not only acting as inert isolating layers to provide a confined environment, but also providing the reactive substrate surfaces in regulating the classical silver mirror reaction and employing it as an interfacial platform for production of Janus particles. First, we use fumed silica nanoparticles with 50% Si−OH groups (HDK H30) to prepare liquid marbles, of which the encapsulating particle layers at the interface can act as reactive substrates for carrying out the silver mirror reaction. Furthermore, two types of particles with relative Si−OH contents of 50% and 25% (HDK H18) respectively are used as liquid marble stabilizers, in which the hydrophobicity increases with decreasing Si−OH contents. Liquid marbles are formed by rolling liquid (water or reaction solution) droplets over a bed of the hydrophobic silica powders.[3d,9,22] We find that liquid marbles coated with silica nanoparticles of varied hydrophobicities can regulate the rate of silver mirror reaction and thus the formed silver nanoparticle deposition at the interface. Also, Janus marbles can be prepared by collision and coalescence of two liquid marbles coated with different silica nanoparticles,[23] which results in the asymmetric silver mirror coatings on one liquid marble. More importantly, the interfacial reaction has also been found to affect the evaporation behavior of the droplets. Finally, we investigate the partitioning of microsized silica particles at the air–liquid interface and demonstrate the fabrication and tuning of Janus particles at the air–liquid interface.

To demonstrate that the encapsulating particle surface plays an important role in regulating the silver mirror reaction, four liquid marbles were prepared by first placing 15 μL glucose (5 wt%) aqueous solution on a bed of H30 silica particles and then injecting 15 μL diamminesilver(I) $[Ag(NH_3)_2]^+$ (5 wt%) solution. They were barely coated, partially coated (at the top or at the bottom), or fully coated with H30 silica nanoparticles (Figure 1 A–D; Supporting Information, Figure S1). It could be observed that color change in all the marbles was rapidly developed, as the silver mirror reaction took place in the miniature reactors, leading to the formation of silver nanoparticles at the interface.[24] However, after 60 min, reflective silver mirrors were only observed at the liquid marbles where they were coated with the H30 silica particles (Figure 1 B–D, 60 min; Supporting Information, Figure S3). It is worth being noted that the location of the silver mirrors is closely correlated to where the H30 silica nanoparticles adsorbed at the air–liquid interface, indicating that the encapsulating silica particle shells not only prevent any direct contact between the solution and the substrates, but also provide an indispensable reactive liquid–solid interface for the deposition of the formed silver nanoparticles, resulting in silver mirror coatings. The formation of the silver mirror can be explained by the following mechanism:[25]

$$\mathrm{Si{-}OH} \rightleftharpoons \mathrm{Si{-}O^-} \rightleftharpoons \mathrm{Si{-}O^-\cdots Ag_x^+} \rightarrow \mathrm{Si{-}OH\cdots Ag} \qquad (1)$$

Specifically, in the initial stage, the excess ammonia and the free hydroxide can activate the SiO_2 surface to generate reactive silanol groups as a result of the deprotonating hydroxy structure on the surface in basic solution. Driven by the electrostatic interaction between the negatively charged silanol groups and positively charged silver ions, along with the strong chemical bond between the siloxane oxygen and Ag(+), free silver ions in the solution would bind to the surface of colloidal silica spheres to form a silver ion layer, as reported by Johnson and Pepper.[26] When the particles come into contact with the glucose in solution, silver ions bonded to the surface of silica spheres are reduced after accepting electrons from glucose to produce bonded element Ag^0, creating an $Ag^0\cdots HO{-}Si$ bond. Subsequently, the newly formed Ag^0 could serve as a nucleating site for further formation of Ag nuclei by reducing more Ag(+) around it, leading to the formation of silver mirrors after the growth of silver nuclei. In case that there are no sufficient substrate surfaces, the newly reduced silver nanoparticles tend to form aggregates dispersed in the solution.[24,27] As a refractive silver mirror cannot be obtained with a bare uncoated air–liquid interface, the silica nanoparticle shell at the interface has provided an indispensable platform for the silver mirror reaction to take place.

After illustrating the essential roles of silica nanoparticles adsorbed at the interface in the formation of the silver mirror coatings on liquid marbles, we further investigated the influences of the concentrations of $[Ag(NH_3)_2]^+$ and the concentrations of glucose on the silver mirror reaction at the interface of the liquid marbles coated with H30 silica nanoparticles. In both Figure 2 A and B, the results showed that increasing concentration of either reactant could both enhance the reaction rate and improve the smooth and refractivity of the silver coatings at the interface (Supporting Information, Figure S4). However, the results showed that only a small amount of $[Ag(NH_3)_2]^+$ would lead to obvious silver deposition on the shell with very short time, which was different from the influence of glucose. These phenomena

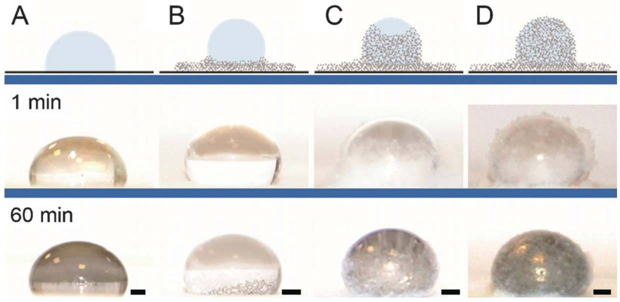

Figure 1. Representations and photographic images of liquid marbles at 1 min and 60 min after preparation: A) an uncoated solution droplet on a glass substrate; B) an only bottom-coated liquid marble; C) a top-uncoated liquid marble; D) a fully-coated liquid marble. Scale bars: 1 mm.

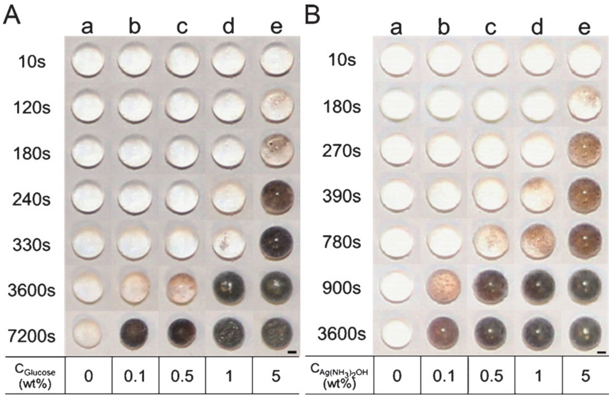

Figure 2. Photogrsaphic images of liquid marbles with various diamminesilver(I) and glucose concentrations captured at different reaction stages: A) liquid marbles with fixed diamminesilver(I) concentration (5 wt%) and increasing glucose concentrations. a) 0, b) 0.1, c) 0.5, d) 1, and e) 5 wt%; B) liquid marbles with fixed glucose concentration (5 wt%) and increasing diamminesilver(I) concentrations. a) 0, b) 0.1, c) 0.5, d) 1, and e) 5 wt%. Scale bars: 1 mm.

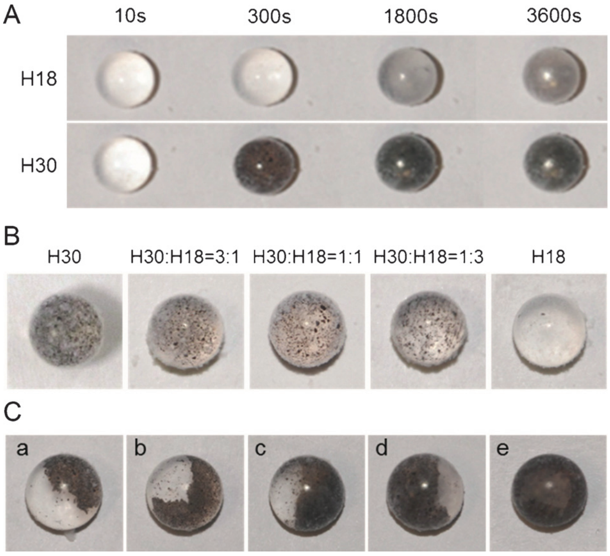

Figure 3. A) Photographic images of liquid marbles coated with H30 particles and H18 particles over time. B) Photographic images of liquid marbles coated with different particle blends at 5 min after preparation. C) The appearance of different Janus marbles at 5 min after preparation: V_{H30}:V_{H18} = a) 1:3, b) 1:2, c) 1:1, d) 2:1, e) 3:1.

might be owing to the microenvironment inside the liquid marbles. According to previous studies, the silver colloids would be redissolved into silver ions in the solution, especially at non-neutral pH, along with the existence of ammonia (ligands) and oxidants.[28] Compared to the liquid marbles in Figure 2Bb,c, the marbles which contained excess ammonia and insufficient reductant in Figure 2Ab,c built a more suitable environment for dissolution of silver colloids. On the other hand, based on the classical nucleation theory, the generation of silver nanoparticles includes two steps: silver monomers Ag^0 form nuclei and subsequently grow upwards. Owing to the dissolution of silver, the missing of silver mirror in Figure 2Ab,c was not surprising.

Apart from the feeding reagent concentrations, the surface features of the supporting substrates have been reported to play important roles in regulating the formation and structure of the resulting silver nanoparticles. For this purpose, we first prepared two liquid marbles coated with two types of silica nanoparticles (H30 and H18; see the Supporting Information for more details) with different hydrophobicities and investigated how the properties of the encapsulating particle layers could affect the silver mirror reaction. Figure 3A shows that using silica H30 particles as the marble stabilizers, the color of the encapsulating shell was visibly changed within a few minutes and eventually turned silvery black; in contrast, no apparent color change of silica H18 nanoparticle-coated liquid marble was observed at the beginning and a more silvery white mirror coating was finally formed. This result indicates that the silver mirror reaction rate on the reactive encapsulating silica H18 nanoparticle layer was much slower than that of on the encapsulating silica H30 particle layer surface. This should be attributed to a higher density of hydroxy groups and a much larger liquid–solid contact area of H30 particles, providing more activated siloxane oxygen for the formation of Si–OH···Ag sites. The higher density of nucleating sites would further accelerate the formation and growth of the silver nanoparticles.

To further confirm the surface features of the support substrates affecting the silver nanoparticle formation, we prepared several liquid marbles coated with silica H30/H18 nanoparticle blends (symmetrical shells) and silica H30//H18 colliding casing (Janus shells; see the Supporting Information for more details).[23a,29] For the particle-blending shells, Figure 3B shows that with increasing content of silica H30 nanoparticles, the density of black dots (that is, formed silver nanoparticles) distributed around the liquid marbles increased, further proving that the silver mirror reaction preferentially took place on the encapsulating silica H30 nanoparticles. However, for the particle-colliding shells, inconsonant appearance would gradually generate instead of star-studded structures. Obviously, the newly formed Janus marbles, which appeared to be almost the same as the normal liquid marbles due to the similarity of these two kinds of particles, progressively exhibited their Janus morphologies. The H30 silica-coated parts turned dark brown while the H18 silica-coated parts remained white (see also the Supporting Information, Figure S7). To better investigate the silver mirror reaction in these Janus microreactors, Janus marbles coated with different ratios of H30 and H18 silica nanoparticles were prepared (Figure 3C, see also the Supporting Information). The percentages of black mirrors had notable differences among different marbles, but increased with the amount of H30 silica nanoparticles in the encapsulating shells. However, the ratios of black to white did not strictly follow the percentages of different particles in the shells, which was very similar to other work.[23a] The differences between the initial particle ratios in the shells and the final coverages of different color on the shells indicated that the marble shells were not monolayer and H30 nanoparticles prefer to stay at the interface.[30]

Not only would the reaction change the marble appearance, but also their evaporation behaviors. This is shown by the fact that liquid marbles underwent obvious deformation during the evaporation process at constant relative humidity and temperature, which has been reported by Dandan et al.,[31] Aberle et al.,[32] and some others.[15b,33] However, the same phenomena that all the shells collapsed should be caused by different reasons. In the others' work, the collapse was owed to the attractive Laplace force overcame the repulsive force stabilizing the particles against aggregation. Thus, the Laplace force, the rearrangement of the particles, and transformation of the shell from a viscous fluid to an elastic solid should all attribute to the buckling of shells. But in this work, the main driving force would not be limited to these factors, and the silver mirror reaction should be taken into consideration. To confirm our hypothesis, three types of liquid marbles were prepared and their evaporation behaviors were recorded (Figure 4). The results showed that buckling of the shells only happened in the microreactors. Excluding the main effect of the solutes, one possibility is that newly formed silver clusters on the shells grew and expanded by continually inducing more silver nanoparticles into precipitation, which finally resulted in interlinks among silica particles. As evaporation continued, the powders on the top lost their mobility, and thus the shell had to collapse in order to reach new equilibrium. For the other two kinds of liquid marbles, the loosely packed particles lacked the interaction to support each other, and so the particles excluded each other and the shells shrank in order to maintain the stable spherical shape, which has the smallest surface area with the same volume. Furthermore, the difference in evaporation behaviors would affect their evaporation rates: the microreactors evaporated much faster owing to their much larger surface, while the liquid marbles containing gluconolactone and diamminesilver(I) had the slowest evaporation rates owing to the addition of nonvolatile solutes, which would stabilize the solvent in the liquid phase and reduce the density of water molecules. In similar work, Bhosale et al. were able to correlate the deviation from sphericity to the increasing of the evaporation rates.[33b,c] However, what we have to point out is that the differences in the evaporation behaviors should be driven by several different factors synergistically, and we are still working on this problem.

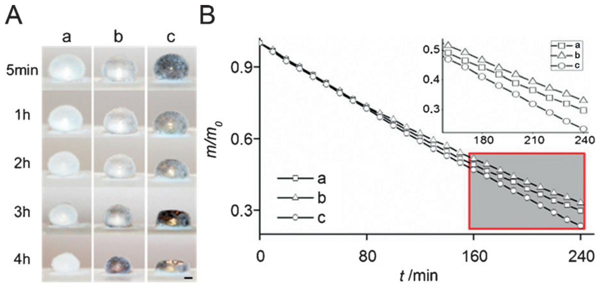

Figure 4. Evaporation behaviors of liquid marbles containing: a) pure water, b) gluconolactone (5 wt%) and diamminesilver(I) (5 wt%), and c) glucose (5 wt%) and diamminesilver(I) (5 wt%). A) Side view of the liquid marbles during evaporation. Scale bar: 1 mm. B) Mass-loss–time plot of liquid marbles during evaporation in the closed chamber (m/m_0 was the ratio of the weight of liquid marble at specific time over the initial weight of liquid marble; RH ≈ 40%, $T \approx 296$ K).

Since Hong et al. first reported preparation of Janus particles in large quantity through particle-stabilized emulsion (Pickering emulsion),[34] this method has attracted increasing attention, as a wide range of particles with different sizes and compositions can be used as emulsifiers.[25d,35] Solid particles adsorbed at an oil–water interface can be modified selectively in the aqueous or oil phase, which in turn can be employed to produce Janus particles.[34,35] Successful stabilization of Pickering emulsions typically requires that the particles have a balanced wettability towards both oil and water and most investigated systems deal with the O/W.[36] Although it is possible to control the position of particles at the interface through addition of surfactants, salts, or organic solvents in the emulsions and subsequently tune the Janus balance of the prepared Janus particles,[35a,37] it still remains a problem for the modification of superhydrophobic particles or large-gauge particles using the emulsion-based methods. Similar to the particles at liquid–liquid interface in Pickering emulsion, the particles at the liquid–air interface of marble shells have provided an ideal platform for modification and fabrication of Janus particles. To further demonstrate this idea, microreactors stabilized by 10 μm hydrophobic silica particles were prepared and the silver mirror reaction was carried out subsequently inside the liquid marbles (Supporting Information). Figure 5 A shows an SEM image of the raw silica particles before the silver mirror reaction, which have an average diameter of 10 μm with a porous surface. In contrast, silver nanoparticles deposited on the silica particle surface could be easily observed in Figure 5 B–D. Since the silica particles at the interface have only one face trapped in the

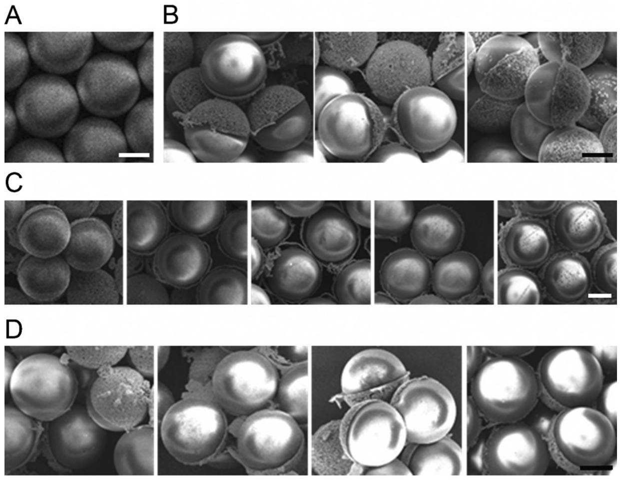

Figure 5. SEM images of raw silica particles and Janus particles synthesized from microreactors: A) Raw silica particles, and B) 0.5 wt% glucose with decreasing diamminesilver(I). From left to right: 0.5, 0.25, and 0.1 wt%; C) 0.5 wt% glucose and 0.5 wt% diamminesilver(I) with increasing ethanol concentration. From left to right: 0, 10, 15, 20, and 25 wt%. D) 0.5 wt% glucose and 0.5 wt% diamminesilver(I) with increasing amounts of Tween 80. From left to right: 0, 0.01, 0.1, and 1 cmc. The critical micelle concentration (cmc) of Tween 80 is 0.013 g L^{-1}. Scale bars: 5 μm.

solution, the deposition of silver would only occur on the moieties of the silica particle surface that protruded into the aqueous phase. Generally, the rotation of the particles at the interface affects the formation of Janus colloids. However, once some parts of a uniform colloid absorbed at the interface have been modified by a different material, colloid rotation will become more difficult and will further facilitate Janus particle formation.[38] In our work, the deposition of silver colloids, along with the porous surface, would completely prohibit the rotation of the silica particles, which is attributed to the asymmetric deposition of silver colloids. Further results showed that the properties of the microenvironment play an important role in determining the Janus morphologies of the particles. For example, increasing the concentration of $[Ag(NH_3)_2]^+$ increased the sizes and density of silver nanoparticles, owing to more silver depositing to unit area (Figure 5B). Furthermore, since the position of the particles at the interface would be affected by the air–liquid interfacial energy, addition of a third component can be used to finely tune the locations of the interfacial particles. For instance, addition of ethanol and Tween 80 can decrease the surface energies of the solutions, which would lead to an expansion of the coverages of silver coatings on the silica particles. The coverages of the silver coatings would gradually increase with the increasing concentration of either ethanol or Tween 80 (Figure 5C,D). Similar to the Pickering emulsion methods, this method does not require any expensive equipment and show high efficiency. Since air acts as the inert protector, particles which are sensitive to the organic solvent could also be modified by this method, while demulsifiers could be introduced in this system. These offer liquid marble excellence for the fabrication of Janus particles that is not attainable from Pickering emulsion methods because particles with extreme wettability for either water or oil cannot produce stable emulsions. However, nanoparticle modification and biphasic modification remain a tough problem for this method.

In summary, silica stabilized liquid marbles could be employed as a substrate to carry out interfacial silver mirror reaction. The influences of shells, feeding composition, and particle properties have been studied systematically, and their different evaporation behaviors have been demonstrated. More importantly, the fabrication of Janus microreactors expands greatly the range of liquid marbles applications. Not only liquid marbles could serve as reaction cells, but also they could be used for simultaneous multireactions, and even selective separation of the reaction products. Fabrication of Janus particles at the interface of these microreactors makes liquid marble a promising method for the mass production of Janus particles in the future, especially for modification the superhydrophobic particles. As silver is utilized extensively in various fields, these microreactors can be used to fabricate in-situ platforms for further applications, such as catalysis, surface-enhanced Raman spectroscopy (SERS), bactericidal action, and so on. The ability to use liquid marbles as microreactors is particularly attractive and competitive, especially when the transportation of the liquids on solid substrate without leakage is a necessity.

Keywords: interfaces · liquid marbles · microreactors · silica particles · silver mirror reaction

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[1] S. Dieter, S. Franz-Theo, B. Helmut (Degussa), US3393155A, **1968**.
[2] P. Aussillous, D. Quéré, *Nature* **2001**, *411*, 924–927.
[3] a) P. Aussillous, D. Quéré, *Proc. R. Soc. London Ser. A* **2006**, *462*, 973–999; b) E. Bormashenko, *Soft Matter* **2012**, *8*, 11018–11021; c) D. Quéré, *Rep. Prog. Phys.* **2005**, *68*, 2495–2532; d) G. McHale, M. I. Newton, *Soft Matter* **2011**, *7*, 5473–5481; e) G. McHale, M. I. Newton, *Soft Matter* **2015**, *11*, 2530.
[4] E. Bormashenko, *Curr. Opin. Colloid Interface Sci.* **2011**, *16*, 266–271.
[5] E. Bormashenko, R. Pogreb, G. Whyman, A. Musin, *Colloids Surf. A* **2009**, *351*, 78–82.
[6] E. Bormashenko, A. Musin, *Appl. Surf. Sci.* **2009**, *255*, 6429–6431.
[7] T. Arbatan, L. Li, J. Tian, W. Shen, *Adv. Healthcare Mater.* **2012**, *1*, 80–83.
[8] a) J. Tian, T. Arbatan, X. Li, W. Shen, *Chem. Commun.* **2010**, *46*, 4734–4736; b) J. Tian, T. Arbatan, X. Li, W. Shen, *Chem. Eng. J.* **2010**, *165*, 347–353.
[9] D. Zang, Z. Chen, Y. Zhang, K. Lin, X. Geng, B. P. Binks, *Soft Matter* **2013**, *9*, 5067–5073.
[10] S. Y. Tang, V. Sivan, K. Khoshmanesh, A. P. O'Mullane, X. Tang, B. Gol, N. Eshtiaghi, F. Lieder, P. Petersen, A. Mitchell, K. Kalantar-zadeh, *Nanoscale* **2013**, *5*, 5949–5957.
[11] a) Y. Zhao, J. Fang, H. Wang, X. Wang, T. Lin, *Adv. Mater.* **2010**, *22*, 707–710; b) Y. Zhao, Z. Xu, M. Parhizkar, J. Fang, X. Wang, T. Lin, *Microfluid. Nanofluid.* **2012**, *13*, 555–564.
[12] a) A. J. deMello, *Nature* **2006**, *442*, 394–402; b) B. P. Mason, K. E. Price, J. L. Steinbacher, A. R. Bogdan, D. T. McQuade, *Chem. Rev.* **2007**, *107*, 2300–2318; c) P. Watts, S. J. Haswell, *Chem. Soc. Rev.* **2005**, *34*, 235–246.
[13] Y. Xue, H. Wang, Y. Zhao, L. Dai, L. Feng, X. Wang, T. Lin, *Adv. Mater.* **2010**, *22*, 4814–4818.
[14] E. Bormashenko, R. Balter, D. Aurbach, *Int. J. Chem. React. Eng.* **2011**, *9*, Note S10.
[15] a) H. G. Braun, A. Z. Cardoso, *Colloids Surf. B* **2012**, *97*, 43–50; b) Y. Chu, Z. Wang, Q. Pan, *ACS Appl. Mater. Interfaces* **2014**, *6*, 8378–8386; c) M. Li, J. Tian, L. Li, A. Liu, W. Shen, *Chem. Eng. Sci.* **2013**, *97*, 337–343.
[16] a) L. Hosta-Rigau, O. Shimoni, B. Städler, F. Caruso, *Small* **2013**, *9*, 3573–3583; b) D. C. Dewey, C. A. Strulson, D. N. Cacace, P. C. Bevilacqua, C. D. Keating, *Nat. Commun.* **2014**, *5*, 4670.
[17] R. J. R. W. Peters, M. Marguet, S. Marais, M. W. Fraaije, J. C. M. van Hest, S. Lecommandoux, *Angew. Chem. Int. Ed.* **2014**, *53*, 146–150; *Angew. Chem.* **2014**, *126*, 150–154.
[18] a) H. C. Shum, A. Bandyopadhyay, S. Bose, D. A. Weitz, *Chem. Mater.* **2009**, *21*, 5548–5555; b) V. Taly, B. T. Kelly, A. D. Griffiths, *ChemBioChem* **2007**, *8*, 263–272; c) C. D. Keating, *Nat. Chem.* **2013**, *5*, 449–451; d) Y. L. Chiu, H. F. Chan, K. K. L. Phua, Y. Zhang, S. Juul, B. R. Knudsen, Y. P. Ho, K. W. Leong, *ACS Nano* **2014**, *8*, 3913–3920.
[19] J. R. Dorvee, A. M. Derfus, S. N. Bhatia, M. J. Sailor, *Nat. Mater.* **2004**, *3*, 896–899.
[20] H. K. Lee, Y. H. Lee, I. Y. Phang, J. Wei, Y. E. Miao, T. Liu, X. Y. Ling, *Angew. Chem. Int. Ed.* **2014**, *53*, 5054–5058; *Angew. Chem.* **2014**, *126*, 5154–5158.
[21] a) Y. E. Miao, H. K. Lee, W. S. Chew, I. Y. Phang, T. X. Liu, X. Y. Ling, *Chem. Commun.* **2014**, *50*, 5923–5926; b) X. Tang, S. Y. Tang, V. Sivan, W. Zhang, A. Mitchell, K. Kalantar-zadeh, K. Khoshmanesh, *Appl. Phys. Lett.* **2013**, *103*, 174104.

[22] S. Ogawa, H. Watanabe, L. Wang, H. Jinnai, T. J. McCarthy, A. Takahara, *Langmuir* **2014**, *30*, 9071 – 9075.

[23] a) E. Bormashenko, Y. Bormashenko, R. Pogreb, O. Gendelman, *Langmuir* **2011**, *27*, 7 – 10; b) B. P. Binks, R. Murakami, *Nat. Mater.* **2006**, *5*, 865 – 869.

[24] Y. Yin, Z. Y. Li, Z. Zhong, B. Gates, Y. Xia, S. Venkateswaran, *J. Mater. Chem.* **2002**, *12*, 522 – 527.

[25] a) V. G. Pol, D. N. Srivastava, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss, A. Gedanken, *Langmuir* **2002**, *18*, 3352 – 3357; b) T. G. Kim, Y. W. Kim, J. S. Kim, B. Park, *J. Mater. Res.* **2004**, *19*, 1400 – 1407; c) S. C. Tang, Y. F. Tang, F. Gao, Z. G. Liu, X. K. Meng, *Nanotechnology* **2007**, *18*, 295607; d) H. Gu, Z. Yang, J. Gao, C. K. Chang, B. Xu, *J. Am. Chem. Soc.* **2005**, *127*, 34 – 35.

[26] K. H. Johnson, S. V. Pepper, *J. Appl. Phys.* **1982**, *53*, 6634 – 6637.

[27] a) N. Koura in *Electroless plating: fundamentals and applications* (Eds.: G. O. Mallory, J. B. Hajdu), American Electroplaters and Surface Finishers Society, Orlando, **1990**, chap. 17, pp. 441 – 462; b) C. Wang, W. Zhang, W. Li, R. Liu, G. Liu, *Micro Nano Lett.* **2014**, *9*, 320 – 324; c) M. Schlesinger in *Modern Electroplating*, 5th ed. (Eds.: M. Schlesinger, M. Paunovic), Wiley, Hoboken, **2010**, chap. 5, pp. 131 – 138.

[28] a) S. Heinonen, E. Huttunen-Saarivirta, J.-P. Nikkanen, M. Raulio, O. Priha, J. Laakso, E. Storgårds, E. Levänen, *Colloids Surf. A* **2014**, *453*, 149 – 161; b) O. N. Starovoytov, N. S. Kim, K. N. Han, *Hydrometallurgy* **2007**, *86*, 114 – 119.

[29] a) J. R. Millman, K. H. Bhatt, B. G. Prevo, O. D. Velev, *Nat. Mater.* **2005**, *4*, 98 – 102; b) Z. Xu, Y. Zhao, L. Dai, T. Lin, *Part. Part. Syst. Charact.* **2014**, *31*, 839 – 842; c) Z. Rozynek, A. Mikkelsen, P. Dommersnes, J. O. Fossum, *Nat. Commun.* **2014**, *5*, 3945; d) H. Chen, Y. Zhao, J. Li, M. Guo, J. Wan, D. A. Weitz, H. A. Stone, *Lab Chip* **2011**, *11*, 2312 – 2315; e) J. Eggers, J. R. Lister, H. A. Stone, *J. Fluid Mech.* **1999**, *401*, 293 – 310.

[30] T. H. Nguyen, K. Hapgood, W. Shen, *Chem. Eng. J.* **2010**, *162*, 396 – 405.

[31] M. Dandan, H. Y. Erbil, *Langmuir* **2009**, *25*, 8362 – 8367.

[32] C. Aberle, M. Lewis, G. Yu, N. Lei, J. Xu, *Soft Matter* **2011**, *7*, 11314 – 11318.

[33] a) N. Tsapis, E. R. Dufresne, S. S. Sinha, C. S. Riera, J. W. Hutchinson, L. Mahadevan, D. A. Weitz, *Phys. Rev. Lett.* **2005**, *94*, 018302; b) P. S. Bhosale, M. V. Panchagnula, H. A. Stretz, *Appl. Phys. Lett.* **2008**, *93*, 034109; c) P. S. Bhosale, M. V. Panchagnula, *Langmuir* **2010**, *26*, 10745 – 10749; d) K. Ueno, S. Hamasaki, E. J. Wanless, Y. Nakamura, S. Fujii, *Langmuir* **2014**, *30*, 3051 – 3059.

[34] L. Hong, S. Jiang, S. Granick, *Langmuir* **2006**, *22*, 9495 – 9499.

[35] a) S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K. S. Schweizer, S. Granick, *Adv. Mater.* **2010**, *22*, 1060 – 1071; b) C. Zhang, W. Wei, F. Liang, Z. Yang in *Janus particle synthesis, self-assembly and applications* (Eds.: S. Jiang, S. Granick), The Royal Society of Chemistry, Cambridge, **2012**, chap. 4, pp. 74 – 89; c) A. Walther, A. H. E. Müller, *Chem. Rev.* **2013**, *113*, 5194 – 5261.

[36] F. Leal-Calderon, V. Schmitt, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 217 – 227.

[37] S. Jiang, S. Granick, *Langmuir* **2008**, *24*, 2438 – 2445.

[38] B. Liu, W. Wei, X. Qu, Z. Yang, *Angew. Chem.* **2008**, *120*, 4037 – 4039.

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