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Single Emulsion Microfluidic Production of Janus and Core-Shell Particles *via* Off-chip Polymerization*

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Abstract In this work, we describe a straightforward approach to produce monodisperse Janus and core-shell particles by using organic solvent free single emulsion droplet-based microfluidic device combining with off-chip polymerization. To accomplish this, methyl methacrylate (MMA) was used as both the oil phase and solvent to dissolve a polymerizable PEG-based macromolecular surfactant, instead of traditional surfactant, and the photo-initiator. Janus particles can be easily obtained by off-chip UV polymerization due to polymerization induced phase separation between PEG and the formed poly(methyl methacrylate). At the same time, core-shell particles can also be easily attained by inverting the original collecting tube several times and then exposing to UV light. These results may extend the scope of microfluidic technology and the studies on polymerization induced self-assembly/phase-separation into easy fabrication of various new functional materials.

Keywords: Microfluidics; Single emulsion; Core-Shell spheres; Janus particles; Polymerization-induced phase-separation.

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INTRODUCTION

Controllable generation of soft polymeric particles with compartmentalized structures is becoming increasingly important[1–4]. These particles represent a versatile class of materials with manifold applications, including displays[5, 6], encapsulation[7–9], deliveries[10, 11], interfacial stabilizers[12], sensors *etc.*[13, 14]. They can be prepared by various methods, such as emulsion polymerization, dispersion polymerization, suspension polymerization, precipitation polymerization, spray drying and phase-separated polymer precipitation. However, each has limitations, especially their poor control over the particle size and structures. Alternatively, microfluidic technique provides a powerful means of overcoming these limitations due to the easy and precise flow control[15, 16]. The most attractive feature of microfluidic technique is its fabrication of monodispersed droplets with various compartmentalized structures[1, 17, 18]. Different kinds of microchips with various geometrical designs have been developed to generate multifarious microspheres, especially core-shell and Janus particles. Nevertheless, most reported microfluidic methods for preparation of core-shell or Janus particles are limited to the use of complicated microfluidic device with three or more inlets to inject the precursor fluids. To overcome this limitation, Zhao *et al.* used simple T-junction microfluidic device to generate double emulsions having either

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a single internal droplet or many fine droplets through mass-transfer[19]. Choi *et al.* employed dewetting and phase separation to obtain complex structured spheres through single emulsion precursor droplets[20]. Recently, mushroom-like and Janus microgels were also prepared by single emulsion droplets through an off-chip ionic cross-linking method[21].

However, for almost all the previous reports on droplet-based microfluidic, the presence of native or added surfactants are necessary for the long-term stability of emulsions[17, 22]. The presence and migration of these species, which are generally low molecular weight compounds and are mainly associated with the final solidified particles through adsorption, may result in adverse effects and influence the particle's physical, chemical and mechanical properties[23–25]. Desorption of the used surfactants from the surface of the particles during its shelf life or under external stimulus such as high shear, freeze-thaw or washing may cause coagulation and negative effects on the environment[24, 25]. These negative features associated with the surfactants can be avoided by using polymerizable surfactants to covalently bind the surfactant moiety to the particles[26–28]. Another advantage of this kind of surfactants is their polymerization/reaction induced structural changes of templated products resulting in materials with tunable morphologies or structures[27, 29–32]. To the best of our knowledge, there are still no reports on the fabrication of core-shell and Janus particles by the combination of organic solvent free single emulsion microfluidic technique with polymerizable surfactant *via* off-chip polymerization.

In this study, we performed an organic solvents free single emulsion microfluidic approach to fabricate shape-controllable poly(ethylene glycol) (PEG) based polyurethane/poly(methyl methacrylate) (PMMA) microparticles. We used a glass capillary microfluidic device to generate single oil-in-water emulsions. Poly(vinyl alcohol) (PVA) aqueous solution served as the continuous phase without additional surfactants. Polymerizable PEG based polyurethane (PU) acted as macromolecular surfactant. Liquid MMA monomers functioned as both the dispersed oil phase and solvent for photo-initiator and PU. Thus, no other organic solvents are necessary. Janus particles, spheres, or core-shell spheres can be easily obtained by simply tuning experimental parameters, such as the UV irradiation intensities, concentration of reactive PU or shaking of the original droplets. These results display the potential use of organic solvents free single emulsion microfluidic technique and polymerizable macromolecular surfactant to produce shape controllable microparticles, which may extend the scope of their applications into easy fabrication of various new functional materials with tunable size, shape and structures and less negative environmental problems.

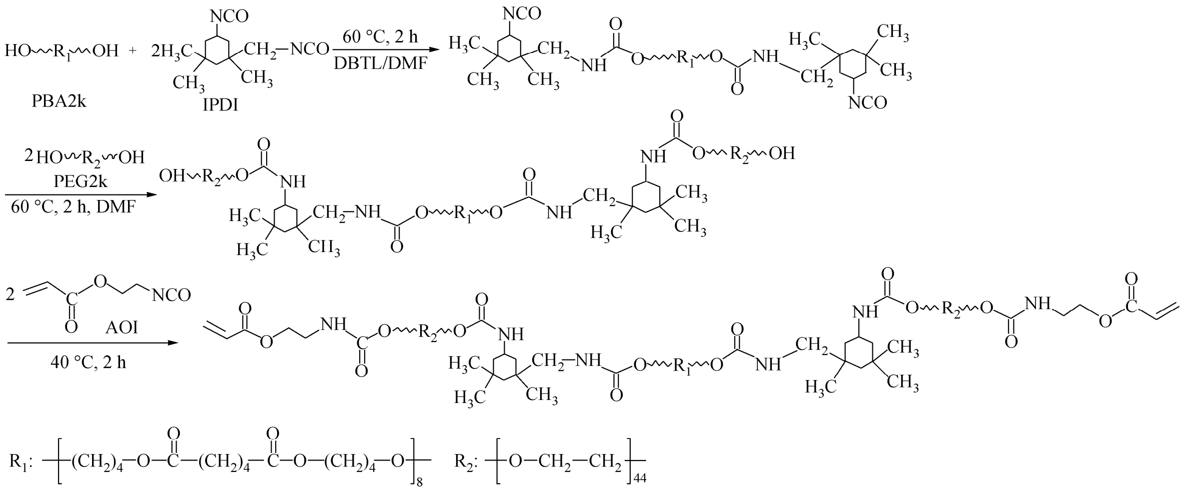
EXPERIMENTAL

Materials

3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI), acrylamide, poly-1,4-butylene adipate glycol (M_w = 2000 g/mol, PBA2k), methyl methacrylate (MMA), *N*,*N*-dimethylformamide, (DMF, dried with 4 Å molecular sieve before use), polyethylene glycol (M_w = 2000 g/mol, PEG2k), 4-methoxyphenol (free-radical inhibitor), 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173, photo-initiator) and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd.. 2-Isocyanatoethyl acrylate (AOI) was kindly donated by Showa Denko Company. The catalyst, dibutyl tin dilaurate (DBTL) was purchased from TCI. PVA (1788) was purchased from Aladdin. All the reagents are of analytical grade and used as received.

Synthesis of the Polymerizable PEG Based Polyurethane (PU)

The polymerizable PU surfactant was prepared according to Scheme 1, details of synthesis and characterization can be found in our previous report[33]. Briefly, PBA2k and PEG2k were dried under vacuum at 80 °C overnight in the presence of P_2O_5. Then 0.01 mol PBA2k (in 10 mL of DMF) and 0.02 mol IPDI (in 5 mL of DMF) were added to a three-necked flask; the catalyst DBTL (0.12 g) was then also added to the flask. The reaction mixture was stirred at 60 °C for 2 h. Then 0.02 mol of PEG2k in 5 mL of DMF was added into the flask and the reaction was continued for another 2 h at 60 °C before cooling to 40 °C. After that, 0.02 mol of AOI monomers in 5 mL of DMF was then added dropwise to the flask and the reaction was allowed to continue at 40 °C for 2 h to obtain the PEG based amphiphilic and polymerizable polyurethane macromolecular surfactant. The products were further purified by precipitation in a large amount of ether and then dried under vacuum at 25 °C. The resultant PU surfactant shows critical aggregation concentration of ~0.001 g/mL in water[33], and can be well dissolved in liquid MMA monomers to form transparent solutions with concentrations ranging from 6 to 16 wt% (Fig. 1). The photo-initiator, 1173, is also soluble in MMA.



Scheme 1 Synthesis procedure of the polymerizable PEG based polyurethane (PU) macromolecular surfactant

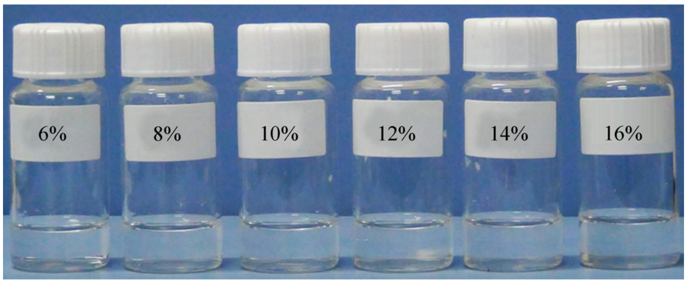


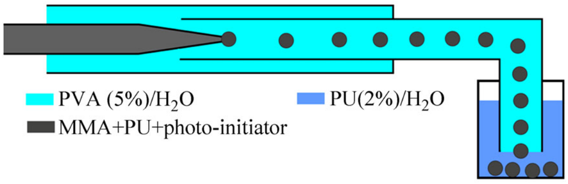
Fig. 1 Photo images of the PU-MMA solutions with various concentrations of PU

Fabrication of the Single Emulsion Microfluidic Device

The capillary microfluidic device was fabricated by assembling glass capillary tubes on a glass slide. The inner dimension of the square glass capillary tube is 1 mm. The outer and inner diameters of all the cylindrical glass capillary tubes are 1 mm and 600 μm, respectively. A micropuller (Narishige, Japan) was used to taper the end of the injection tube, and the orifice dimension of the tapered end was adjusted to about 15 μm by a Microforge (Narishige, Japan). The tapered injection cylindrical capillary and untapered collection cylindrical capillary were coaxially aligned within the square capillary tube.

Formation of MMA-PU Droplets

As shown in Scheme 2, an aqueous solution of 5 wt% PVA was used as the continuous phase (aqueous fluid). Liquid MMA monomers containing PU and photoinitiator (1173) serve as the dispersed phase (oil fluid). The concentration of PU ranged from 6 wt% to 16 wt%. For all the experiments, the concentration of 1173 was fixed at 3 mol % amount of MMA. To prepare the O/W single emulsion droplets, oil fluid and aqueous fluid were separately injected into the channels of microfluidic device by syringe pump (W0109-1B, Baoding Longer Precision Pump Co., Ltd.). The droplets were collected in a transparent plastic tube containing 2 wt% of PU aqueous solution. The collected droplets were then exposed to UV irradiation to be solidified. The resultant solid microspheres were washed with water before microscope imaging.



Scheme 2 Schematic illustration showing the preparation process of uniform MMA-PU droplets

RESULTS AND DISCUSSION

In this paper, we tried to use the simplest single emulsion microfluidic device to produce microparticles with different structures by easily adjusting the off-chip UV polymerization conditions. As shown in Scheme 2, solution of PU (6 wt%–10 wt%) and 1173 in MMA monomers was used as the inner fluid. Aqueous solution of PVA (5 wt%) was used as the out fluid. The two fluids were injected into different channels of the microfluidic device. Due to the shear force and interfacial tension, the oil phase broke up to discrete droplets. The droplets were collected in a transparent plastic tube containing 2 wt% PU (Scheme 2 and Fig. 2a) to avoid diffusion of the PU inside the droplets into the outer aqueous solution. The collection tube vertically stood for a certain time, *T* (Fig. 2b) before UV irradiation (365 nm, 48 W). The distance between the tube and the UV lamp was defined as *H* (Fig. 2c).

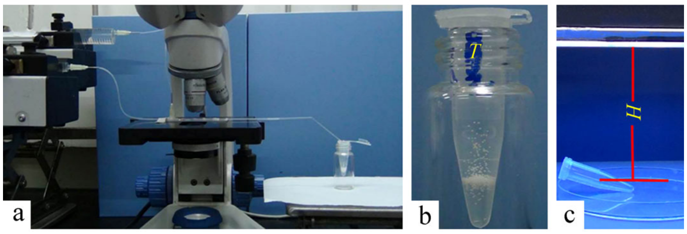


Fig. 2 Photo images of the droplets production device (a), the collected droplets (b) and the UV initiated polymerization process (c)
Note that, *T* in (b) was the time from the end of collection to the beginning of UV irradiation; *H* in (c) was the distance between tube and the UV lamp.

Figures 3(a) and 3(b) show the microscopic images of the monodisperse droplets at different outer fluid flow rates (Q_O) under the same inner fluid flow rate (Q_I). The size of the droplets can be easily controlled by changing the volume flow rates of the outer or inner fluids. The diameter of the droplets increases with increasing Q_I at the same Q_O (Figs. 3a–3c), while decreases with increasing Q_O at constant Q_I (Fig. 3d). This is in well accordance with previous reports[34, 35].

Before solidification of the droplets, we first studied their stability in the collection tube. As shown in Fig. 4, the collected droplets in the aqueous solution of PVA and PU showed almost no shape changing within 180 min. However, the color became lighter and lighter, especially in the first 4 min (Figs. 4a and 4b). This may be due to the diffusion of the surface thin viscous PVA layer (as shown in Fig. 4a) into the outer PU solutions, and thus the diameter obviously decreased from ~260 μm (Fig. 4a) to ~230 μm (Fig. 4b) in the first 4 min. The existences of the surface viscous PVA layer can be observed in Fig. 4(a) and Fig, S1(a), which show core-shell like droplets. The diffusion and disappearance of the PVA thin layer were shown in Figs. S1(b)–S1(d). After that, the diameter of the droplets slowly increased from ~230 μm (Fig. 4b) to ~320 μm (Fig. 4g) with increasing standing time, *T* (Figs. 4b–4g), and remained almost unchanged after 120 min (~320 μm, Figs. 4g and 4h). According to our previous report[33], the critical micellization concentration of PU in water is 0.001 g/mL and can form stable micelle at ~5 wt% in water, but it can be easily dissolved in MMA monomers to form transparent viscous solution at high concentrations (Fig. 1), indicating excellent amphiphilic property of PU. On the other hand, it is well known that MMA monomer shows poor solubility but not totally insoluble in water.

Therefore, with increasing time, more and more water molecules will slowly penetrate into the droplets, and some of the MMA monomers will also slowly diffuse into the outer aqueous solution, resulting in lighter color and bigger size droplets. This may influence the final structures of the obtained microspheres after polymerization.

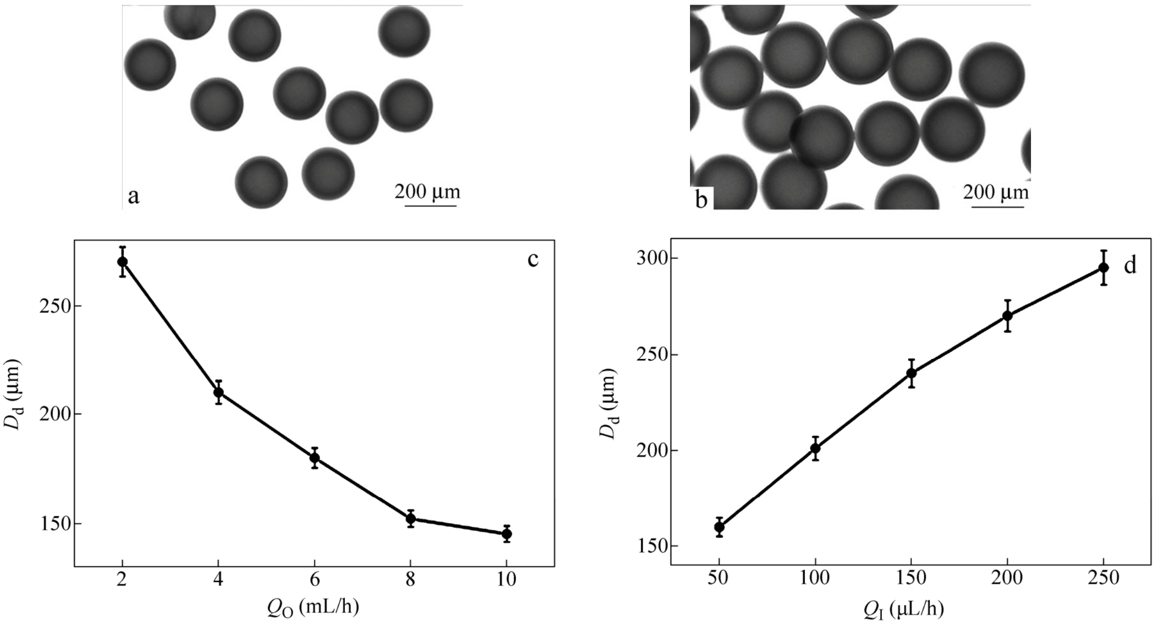


Fig. 3 Microscopic images of droplets: (a) Q_I = 100 μL/h, Q_O = 2000 μL/h; (b) Q_I = 200 μL/h, Q_O = 2000 μL/h; Plots of diameters of the droplets versus flow rates of (c) the outer fluid Q_I = 200 μL/h and (d) inner fluid Q_O = 2000 μL/h
For all the samples, the outer fluid was 5 wt% PVA aqueous solution, the inner fluid was MMA + PU (10 wt%) + 1173 (3 mol% of MMA).

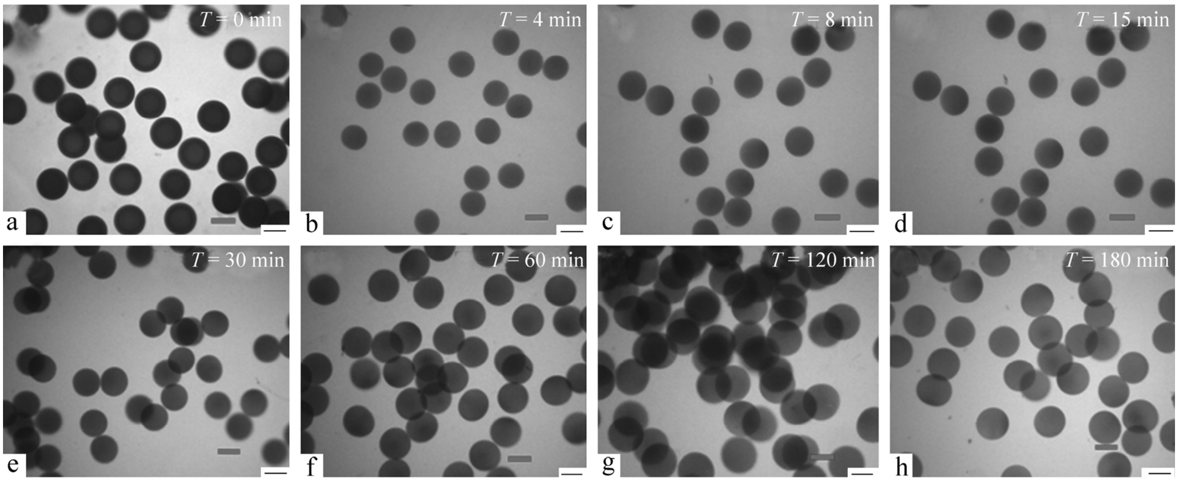


Fig. 4 Optical microscope images of the original droplets (a) and after being collected and standing for various times (b–h) in the collection tube
Q_I = 200 μL/h, Q_O = 2000 μL/h; Outer fluid: 5 wt% PVA; Inner fluid: MMA + PU (10 wt%) + 1173 (3% molar amount of MMA); The scale bars represent 200 μm.

We then investigated the effect of standing time, *T*, at fixed *H* (7 cm) on the structure of the droplets after UV irradiation. As shown in Fig. 5, the particles show normal solid sphere structures when *T* was less than 4 min

(Figs. 5a and 5b). And the color of the spheres also became lighter, which is in accordance with the results as shown in Figs. 4(a) and 4(b). Interestingly, Janus particles appeared when *T* reached 8 min (Fig. 5c). After that, the particles we got were mostly Janus ones (Figs. 5d–5h). We attributed this morphology changing behavior to the factors that the PEG block of PU (Scheme 1) is immiscible with PMMA[36, 37]; the polymerization rate of PU is much faster than that of MMA; the acrylate group terminated PU also acted as crosslinking agent. Upon UV irradiation, the MMA monomer began to polymerize and more and more PMMA chains formed, leading to PEG-rich and PMMA-rich regions inside the droplets due to phase separation and formation of Janus particles. When *T* was less than 4 min, there was still a thin viscous PVA layer on the surface of the droplets and only trace amount of water molecules penetrated into the droplets, thus the just collected droplets still remained highly viscous, which retarded the diffusion of PU and formed PMMA chains and thus the phase-separation. This should be why there were more and more Janus particles formed with increasing *T* (Figs. 5c–5e). On the other hand, in comparing the acrylates to the methacrylates, the increased reactivity of the acrylates was apparent in the greater values (by three orders of magnitude) of both the termination and propagation kinetic constants[38]. Therefore, upon UV irradiation, the acrylate group terminated PU (Scheme 1) first polymerized and crosslinked network formed with MMA monomers and PMMA chains inside (PMMA is soluble in MMA). With further polymerization, more and more PMMA formed and diffused outside the network due to phase separation, resulting in formation of Janus particles. This is a little bit like the previous synthesis of Janus polymer particles by seeded polymerization method[21], where initial phase separation is driven by the elastic stress of the formed network; then, as the polymerization proceeds, the phase separation is enhanced due to the difference of free volumes between the seed polymer network and newly generated polymers. Whereas, the final morphology of the obtained particles should also depend on how fast the formation of the relatively rigid crosslinked network among the original droplets.

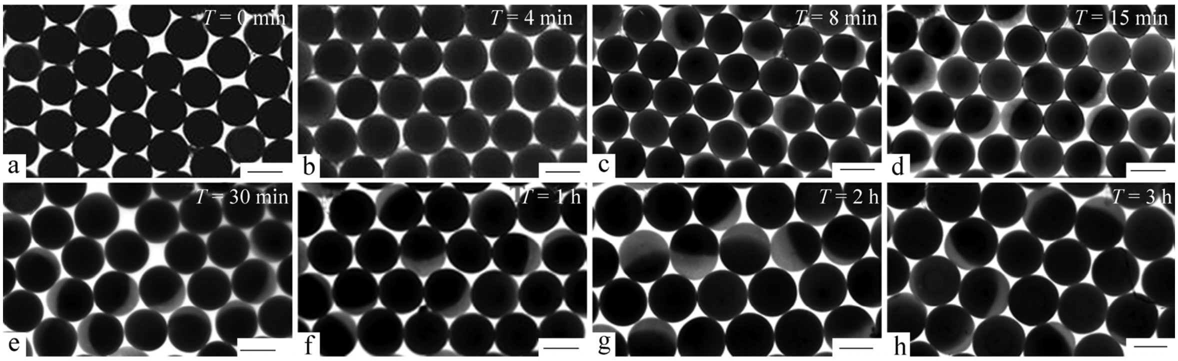


Fig. 5 Optical microscope images of the drops after standing for various time (*T*) and then being UV irradiated for 1 h
For all the samples, the distance between the UV lamp and the collecting tube is H = 7 cm. (The scale bars represent 200 μm.)

We then studied the influence of UV light intensity on the structures of the drops by simply varying the distance between the UV lamp and the collecting tube. As shown in Fig. 6(a), when H = 4.5, no Janus particles can be observed. While, with increasing *H*, more and more Janus spheres formed (Figs. 6b–6d). This is because in the high UV intensity cases (lower *H* values), both the quickly formed rigid network and PMMA would lead to quickly increasing viscosity of the droplets, which retarded the diffusion of PMMA chains to yield Janus particles. These results further confirmed the polymerization rate effect on the formation of Janus spheres we discussed previously. Here, we may conclude that lower UV intensity or polymerization rate benefits diffusion of PMMA chains and thus formation of Janus particles. Note that, the observed black spheres in Fig. 6(d) were in fact also Janus ones, just because the light color PEG rich hemisphere was sticky on the surface of the glass slide, while the upper hydrophobic PMMA-rich hemisphere shielded the light. This was approved by carefully stirring the spheres on the glass slide under optical microscope (see Movie S1 in ESM).

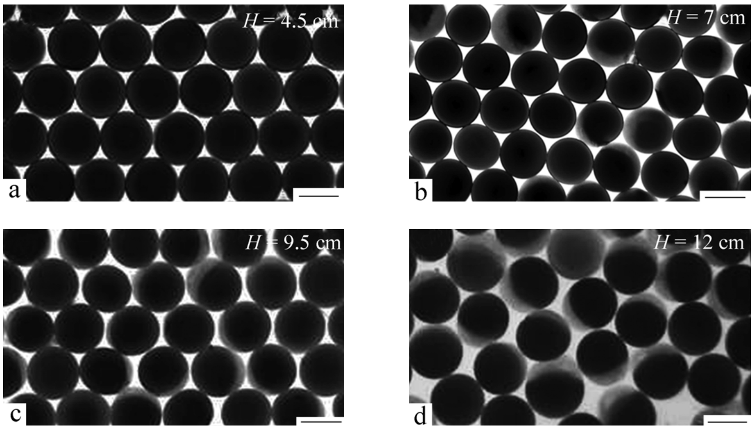


Fig. 6 Optical microscope images of the drops after standing for 8 min and then being UV irradiated for 1 h with different lamp to sample distance (*H*): 4.5 cm, (b) 7 cm, (c) 9.5 cm and (d) 12 cm (The scale bars represent 200 μm.)

We further studied the influence of the concentration of PU on the morphology of the droplets after UV irradiation. As shown in Figs. 7(a)–7(c), Janus particles can be obtained when the concentration of PU was or lower than 10 wt%. Further increases of the contents of PU only resulted in normal spheres. We attributed this change in the morphology to the higher concentration of PU induced higher viscosity of the droplets and faster formation of densely crosslinked PU network, which will retard the diffusion of the subsequently formed PMMA.

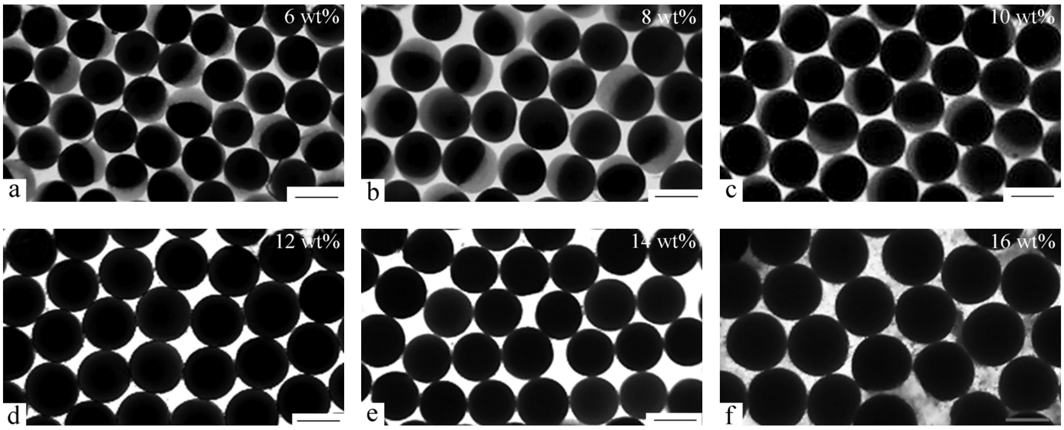


Fig. 7 Optical microscope images of the drops with various concentrations of PU after standing for 8 min and then being UV irradiated for 1 h (For all the samples, *H* = 12 cm. The scale bars represent 200 μm.)

Intriguingly, we accidentally found that these droplets could transform to core-shell droplets by inverting the collecting tube several times. Figure 8(a) (also as shown in Fig. 4c) shows the optical microscope image of the droplets after being collected and then stood for 8 min. While, after the collection tube was inverted several times by hands and vertically stood for another 8 min, core-shell droplets were obtained (Fig. 8b). These obtained core-shell droplets also showed good stability with only increase of diameters and almost no obvious change of their core-shell structures within 12 h (Figs. 8c–8f). The increases of the diameter should also be due to water swelling. As we mentioned above, MMA monomer shows poor solubility in water, and our PU is an amphiphilic macromolecule and can dissolve in liquid MMA monomers to form viscous solution (Fig. 1). Thus, associated with the external shaking energy, the macromolecular PU diffused to the surface of the droplets to stabilize the hydrophobic MMA drops yielding core-shell microspheres (Fig. 8g). Note that, some of the MMA monomers may penetrate into and dissolve in the outer aqueous solution during shaking, and some of them may also exist in the shell layers, thus the core volume of the obtained core-shell droplets is smaller than that of the shell. The excellent stability of the original and core-shell droplets enables us to study their solidification process by photo-initiated polymerization.

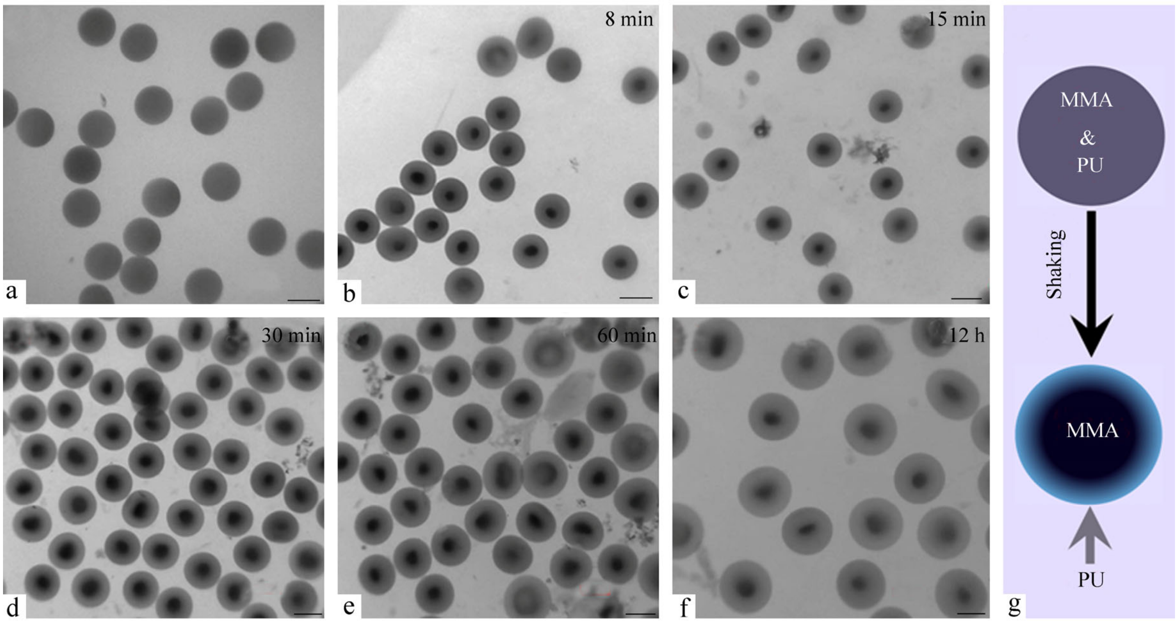


Fig. 8 Optical microscope images of the droplets before (a) and after being inverted several times and then vertically stood for different times (b–f); (g) Schematic illustration of the morphology transition (The concentration of PU is 10 wt%. The scale bars represent 200 μm.)

Figure 9 shows the optical microscope images of the core-shell droplets in Fig. 8(b) after being UV irradiated for 1 h under different UV intensities. As shown in Fig. 9(a), obvious core-shell structure microspheres were observed under high intensity UV irradiation ($H = 4.5$ cm). With increasing distance between the UV lamp and the collecting tube, however, the contrast between the core and shell layers became a little bit unclear (Fig. 8b) and Janus spheres appeared (Figs. 8c and 8d). These results further confirmed the mechanism of lower polymerization rate benefiting better phase separation and formation of Janus particles.

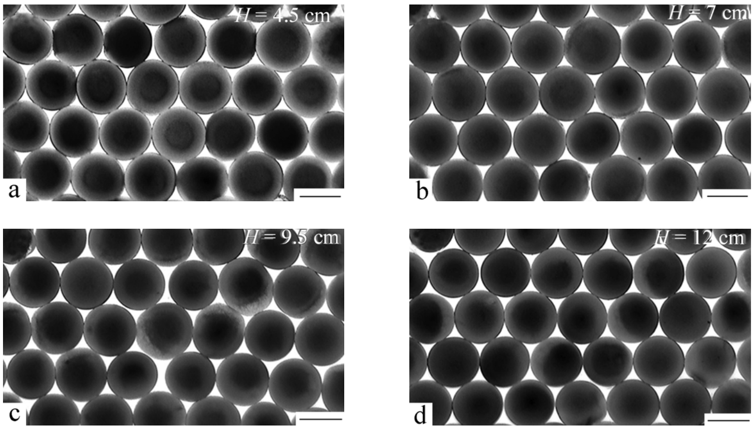


Fig. 9 Optical microscope images of the core-shell droplets in Fig. 8(b) after being UV irradiated for 1 h under different UV intensities (H is the distance between the UV lamp and the collecting tube. The scale bars represent 200 μm.)

The obtained Janus and core-shell particles were also studied by SEM after being freeze-dried. Figure 10(a) clearly shows the different microstructure of the two faces of the Janus particles, with one highly porous PEG rich face and the other low porous PMMA rich phase. The porous rather than smooth surface of the PMMA semi-sphere further confirmed our above said water diffusion process. One can also find that porosity degree of the PEG rich shell of the core-shell particles (Fig. 10b) is lower than that of the PEG rich semi-sphere of the Janus particles. This should be due to their different formation mechanism. As we discussed above, upon UV irradiation, acrylate group terminated PEG based surfactant first polymerized to form a network with low cross-linking density due to high containing of MMA/PMMA solutions, resulting in highly porous PEG rich phase after further polymerization and expelling of the PMMA. While, in the core-shell particle case, PEG rich shell first formed before polymerization, yielding relatively high cross-linking density of the shell layers and thus low porous structure. Moreover, Fig. 10 also shows that both the Janus and core-shell particles clearly collapsed under the high vacuum condition of the SEM measurement. This further proved their porous structures.

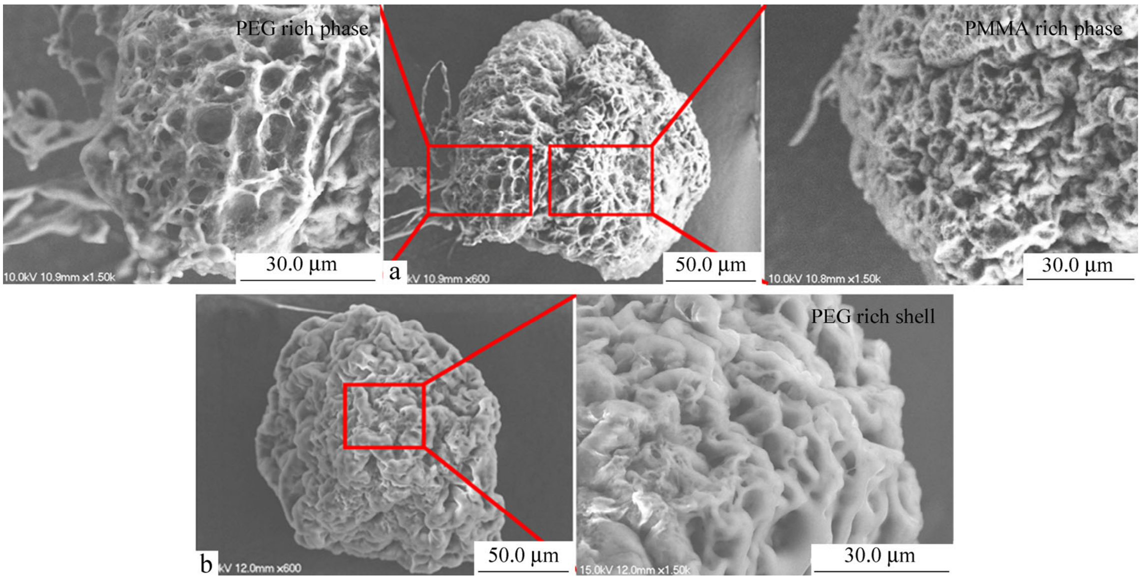
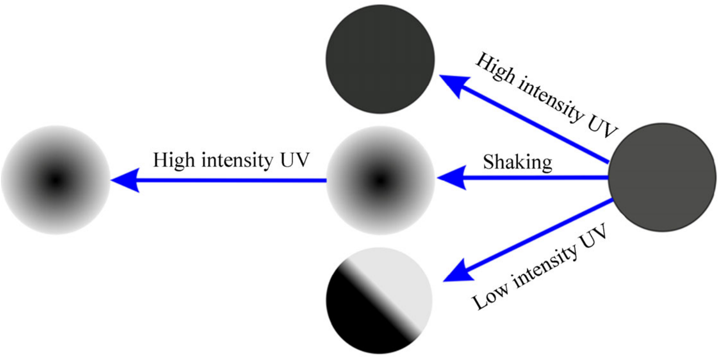


Fig. 10 SEM images of the (a) Janus and (b) core-shell particles

CONCLUSIONS

As schematically summarized in Scheme 3, we report a simple approach for fabrication of spheres, core-shell spheres and Janus particles. Monodispersed and stable droplets composed of photo-initiator, polymerizable



Scheme 3 Schematic representation of the single emulsion microfluidic production of spheres, core-shell spheres and Janus particles *via* off-chip polymerization

macromolecular surfactant and MMA monomers can be easily attained by single emulsion microfluidic technique without using any other organic solvents. Due to phase separation between PEG and PMMA and the different polymerization rates of acrylate group terminated PU and MMA monomers, spheres or Janus particles can be produced by simply adjusting the UV irradiation intensities or the original concentration of PU. Core-shell spheres can also be easily obtained by inverting the collecting tube several times and then exposing to UV light. These results provide a new opportunity to use the simple single emulsion drops to fabricate core-shell and Janus particles *via* off-chip polymerization. The straightforward method of course would promote the applications of the resultant spheres with different structures in various areas, such as new optical materials, superstructure microspheres, target drug delivery system and so on. Considering the widely studied and increasing interests in polymerization induced self-assembly/phase separation, these results may also promote easy fabrication of new functional materials with tunable size, shapes and structures and less negative environmental problems.

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