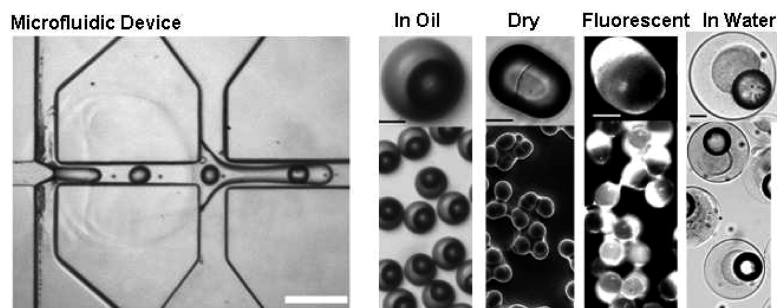


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Janus Particles Templated from Double Emulsion Droplets Generated Using Microfluidics

Chia-Hung Chen,^{*,†} Rhutesh K. Shah,^{‡,§} Adam R. Abate,^{‡,§} and David A. Weitz^{‡,§}

[†]*Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom,* [‡]*School of Engineering and Applied Science, Harvard University, 40 Oxford Street, Cambridge, Massachusetts 02138* and [§]*Department of Physics, Harvard University, 17 Oxford Street, Cambridge, Massachusetts 02138*

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We present a simple microfluidics-based technique to fabricate Janus particles using double-emulsion droplets as templates. Since each half of the particles is templated from a different immiscible fluid, this method enables the formation of particles from two materials with vastly different properties. The use of microfluidics affords excellent control over the size, morphology, and monodispersity of the particles.

Microfluidic techniques are valuable means of fabricating highly monodisperse particles suitable for many applications.^{1–9} For example, flowing a UV-curable monomer mixture through a microfluidic device and photopolymerizing the monomers using continuous flow lithography with a mask-based template^{2,3} enables the fabrication of particles of different shapes and sizes. Alternatively, droplets produced^{1,4–7,9} with a microfluidic device using either a coflow or a flow-focusing geometry can be polymerized using UV-radiation, heat, or chemical means to form spherical and discoidal shaped particles.^{1,4,6,7,9,10} The microfluidic techniques yield monodisperse particles whose dimensions can be precisely controlled. These techniques can also be used to make anisotropic particles, or Janus particles.^{10–15} Such particles possess two sides with distinct compositions^{16–18}

and, depending upon their functional anisotropy, can be useful for various applications, such as emulsion stabilization^{19–21} and optical probing of chemical, biological, and rheological phenomena.^{22–25} The microfluidic principles for fabricating Janus particles are similar to those for fabricating homogeneous particles; however, instead of flowing one stream of monomer, two separate streams are coflowed through the same channel of the microfluidic device. To successfully fabricate Janus particles, the coflowing streams must remain parallel at all times; any perturbations can lead to cross-mixing of the fluids and to the formation of particles with a mixed internal morphology instead of particles with two distinct sides.¹³ In addition, the interface between the two fluids must be stable and independent of both location and time; this requires the two fluids to be miscible, limiting the type of chemicals that can be used. Almost all reported examples of microfluidically fabricated Janus particles are composed of two hydrogel phases and are made from two dissimilar but completely miscible hydrophilic monomer streams.^{10–14} Although these techniques can be extended to fabricate Janus particles from immiscible fluids, the values of the interfacial tension between the fluids need to be within a certain range. Outside of that range, the two “halves” of the Janus particles do not adhere to each other and produce individual droplets. Thus, fabrication of Janus particles from a broad range of immiscible fluids requires new microfluidic techniques. This would expand the portfolio of chemicals that can be used for forming the two sides of Janus particles and would result in the fabrication of particles with more diverse properties, which could eventually lead to several new applications.

*Corresponding Author. E-mail: chc43@cam.ac.uk.

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In this Letter, we introduce a general microfluidics-based method to form Janus particles from two immiscible fluids with vastly different properties. We template the particles from photopolymerizable double emulsions formed in spatially patterned poly(dimethylsiloxane) (PDMS) microfluidic devices. The particles exhibit a precisely tunable morphology and are highly monodisperse. The relative size of each lobe can be adjusted by varying the fluid flow rates. Moreover, since the double emulsions are composed of immiscible fluids, problems associated with the cross-mixing of fluids in microfluidic channels are eliminated. The use of immiscible fluids also allows fabrication of Janus particles with two halves that exhibit stark contrasts in properties, including optical index of refraction and swellability in different solvents and oils. We demonstrate this technique by fabricating Janus gel particles with a hydrophilic side and an organophilic part. Such particles can be useful for the simultaneous transportation and release of both hydrophilic and organophilic macromolecules.

Our microfluidic device is made from a silicon elastomer of PDMS using soft-lithography methods. We coat the channels with a sol-gel layer that is functionalized with photoreactive silanes. This chemical treatment allows the wettability of the channels to be spatially patterned and, thus, allows the formation of double-emulsion droplets.²⁶ The sol-gel mixture is prepared by combining 0.2 mL of tetraethylorthosilicate (TEOS), 0.2 mL of methyltriethoxysilane (MTES), 0.1 mL of (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane, 0.2 mL of photoinitiator-silane, 0.2 mL of pH 2 water adjusted with HCl, and 2.6 mL of methanol.²⁶ The PDMS channels are first treated with plasma to form silanol groups and are then immediately bonded to a glass slide. These channels are filled with the photoreactive sol-gel mixture. The device is then placed on a hotplate set to 225 °C, which results in evaporation of the solvent and curing of the sol-gel on the channel walls. The sol-gel is fluorinated by fluorosilanes and is, therefore, very hydrophobic by nature. To spatially pattern the wettability, we graft hydrophilic patches of poly(acrylic acid) onto the channels. To accomplish this, we fill the sol-gel coated channels with an aqueous monomer solution comprising 0.2 mL of acrylic acid with 0.8 mL of 5 mM NaIO₄·H₂O, 0.1 g of benzophenone, 0.9 g of acetone, and 1 mL of ethanol. We expose the channels to UV light to control the location where poly(acrylic acid) is grafted to the channel walls, making them hydrophilic.

To form Janus particles with a hydrophilic-organophilic structure, we form oil-water-oil double-emulsion droplets from immiscible monomer mixtures. We graft poly(acrylic acid) to the region of the microfluidic device between the first and second drop maker, making it hydrophilic; the default properties of the sol-gel make the rest of the device hydrophobic, as shown in the diagram in Figure 1a. Thus, in the first stage, the oil monomer is encapsulated by the aqueous monomer solution, which wets the hydrophilic walls of channel A (Figure 1a), forming an oil-in-water single emulsion. The droplets then flow into the second drop maker, where the wettability of the long channel B is inverted. This causes the water to lift off the hydrophobic interface and become encapsulated by the fluorocarbon oil, forming the oil-water-oil double emulsions shown in Figure 1b.

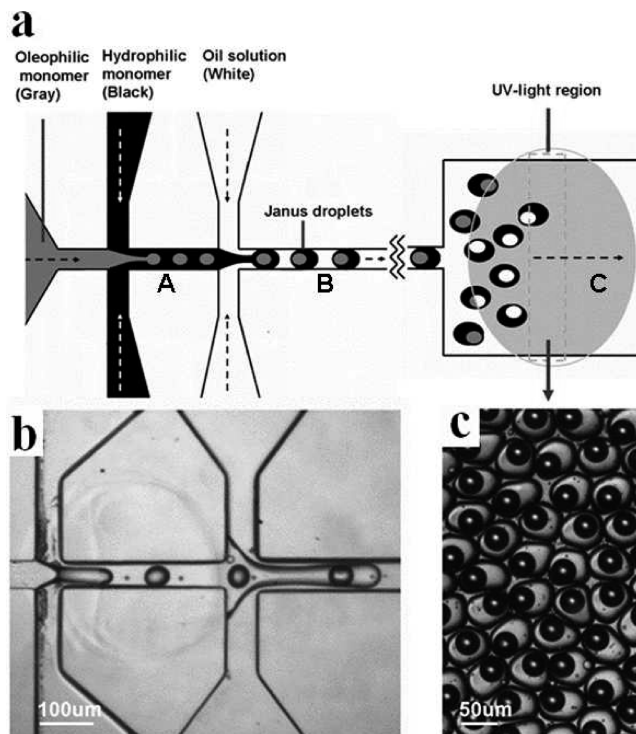


Figure 1. (a) Schematic representation and (b) photomicrograph of the PDMS device for fabricating double-emulsion droplets. The double-emulsion droplets consist of an organophilic monomer core (gray) that is encapsulated by a water monomer droplet (black) in a fluorocarbon oil (white). The thickness of the channel is 50 μm . (c) A collection of these double emulsions in a large channel on the same device, where they are exposed to a UV beam, which initiates polymerization of the monomers and locks in the anisotropic Janus structure.

The inner oil core drop composed of 99% 1,6-hexanediol dimethacrylate (Polysciences Inc.) with 1% Darocur 1173 (Ciba) forms the hydrophobic part of the Janus particles. The outer shell of the double-emulsion drop made with 10% acrylamide (Sigma), 2% *N,N'*-methylenebisacrylamide (Fluka), 1% Darocur 1173 (Ciba), and 87% water with fluorescein (3M) and surfactant, 0.25% SDS, and 0.25% Tween forms the hydrophilic side of the particles. For the continuous phase, we use fluorocarbon oil, HFE-7500 (3M), with surfactant Krytox 157FSL (Dupont). Later on in the discussion of our results, one may question how important was the buoyancy effects of our double-emulsion droplets. The oleic monomer inner drop has a density of 0.995 g/cm³, which is similar to that of the aqueous drop, so that buoyancy effects are small.

The double-emulsion diameter is larger than the height of the channel, so that the double emulsion is flattened into a pancake shape as it flows through the channel. Due to viscous friction, this induces a flow in the double emulsion that causes the inner drop to move toward the back of the outer drop. The droplets are then flowed into a large basin channel C, shown to the right in Figure 1c, where they are flooded with UV radiation. Here, we permanently lock the asymmetric droplet structure by photopolymerization. This solidifies the drops, producing anisotropic particles having a permanent Janus structure, as shown in Figure 1c. To complete the polymerization, the still squishy particles are collected into a vial and are further exposed to UV light for 10 min.

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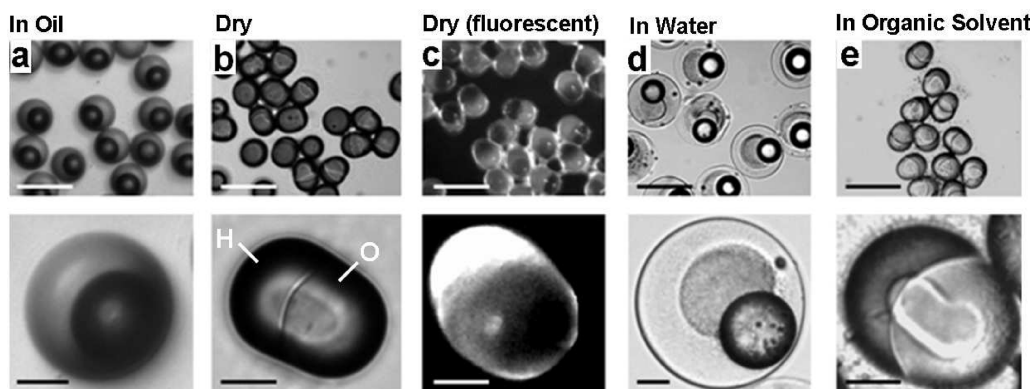


Figure 2. Photomicrograph of the organophilic–hydrophilic Janus particles (a) dispersed in fluorocarbon oil, (b,c) dried, (d) dispersed in water, and (e) dispersed in acetone. The images below show magnified views of individual Janus particles (left, identified as H, hydrophilic lobe; right, identified as O, organophilic lobe). The scaling bar in the top row is 100 μm , and the scaling bar in the bottom row is 20 μm .

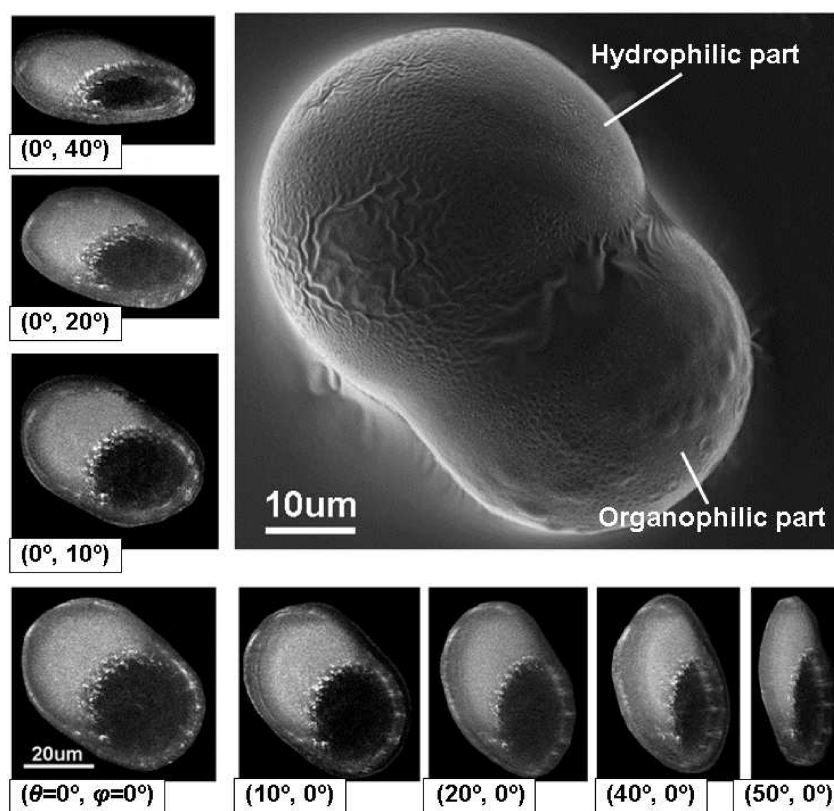


Figure 3. SEM image (right) of an organophilic–hydrophilic Janus particle. The two halves of the Janus particle are spherical due to the spherical shape of the double-emulsion drops from which it is templated. The size of the two halves can be adjusted by controlling the flow rates of the fluids forming the double emulsions. Confocal microscope images of a particle are presented in the vertical and horizontal columns. A stack of images for a 5 μm thick section from the center of a particle are rotated in the zenith (vertical column) and azimuth (horizontal row) angles.

Once polymerized, the Janus particles are robust and can be washed, dried, and redispersed into a variety of solvents. Depending upon their affinity, solvents are absorbed selectively into different halves of the Janus particles. We show a sample of collected double emulsions suspended in the fluorocarbon oil in which they are formed in Figure 2a. The hydrophilic shell of the particles is immiscible with the fluorocarbon oil; hence, the Janus particles adopt a spherical shape to minimize their surface energy, as shown in the magnified view of Figure 2a. Upon evaporating the volatile fluorocarbon oil and water, the particles become more compact and adopt an ovular shape because they shrink, as shown in the bright field image in Figure 2b and the

fluorescent image (fluorescent dye, Sigma, 10 μM in water) in Figure 2c; in the magnified view, the interface between the immiscible organophilic and hydrophilic halves of the Janus particles can be seen. When the dried Janus particles are redispersed into water, the water is absorbed into the hydrophilic shell, causing it to swell. The particle diameters increase from 50 μm in fluorocarbon oil to more than 80 μm in water. The double ring pattern in Figure 2d is probably due to the concentration of polyacrylamide varying as a function of particle radius, which causes the index of refraction to vary as a function of radius, which then causes the optical effect we see in the images. The swelling of the particles can be controlled by varying the cross-linker concentration of the

polyacrylamide gel.²⁷ Similarly, when the dried particles are dispersed in acetone, the solvent is absorbed in the organophilic gel, changing the particles' morphology, as shown in Figure 2e. The organophilic core becomes more spherical and increases in size when the particles are dispersed in acetone; by controlling the cross-linker concentration, the intake of organic solvents can be controlled. Similar swelling features of the inner cores are also observed in other organic solvents, such as toluene.

To gain a better understanding of the morphology of our Janus particles, we probed their microstructure using scanning electron microscopy (SEM) and confocal microscopy. A high magnification SEM image of a dried Janus particle reveals the peanutlike shape of the particle, as if it is composed of two spherical caps that are joined at the base (Figure 3). The spherical shape of the caps is a consequence of the high surface tension between the acrylamide shell and the fluorocarbon oil. However, what cannot be seen in the SEM image is that the two halves are made of up two completely different materials polymerized from immiscible monomer solutions. This fact is revealed by the confocal microscope images. The polyacrylamide gel phase contains a fluorescent dye (Sigma, 10 μ M in water) which was added to enhance the visual contrast between the two phases. To obtain a clear presentation under the index mismatch conditions, we capture a stack of images for a 5 μ m thick section of the particle and reconstruct its

three-dimensional structure; the particle shown is rotated about the zenith angle in the vertical column of images and about the azimuth angle in the horizontal row of images in Figure 3. From the rotated images, the particle can be seen to have a biphasic internal structure, with one-half of the particle composed of the fluorescent hydrophilic polyacrylamide gel and the other half of the organophilic gel. The confocal reconstruction also enables the internal interface between the two halves to be visualized, as shown, for example, by the image at angles $\theta = 0^\circ$ and $\varphi = 0^\circ$ in Figure 3. The interface has a circular shape, suggesting the structure of the double emulsions, from which the particles are templated, is preserved during solidification.

This method combines the control of droplet microfluidics with the ability to control particle chemistry, morphology, and structure. Such particles should be useful for applications including the absorption, transport, and delivery of diverse chemicals and the stabilization of interfaces between immiscible fluids.

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