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Bioinspired Multifunctional Janus Particles for Droplet Manipulation

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Supporting Information

ABSTRACT: Inspired by the nipple arrays covering mosquitoes' eyes and the heterogeneous textured bumps on beetles' backs, we have developed a new kind of Janus particle with multiplexed features, such as different boss arrays and wettability compartmentalized on the same surface, and an anisotropic color and magnetic properties. The prepared Janus particles can be anchored at the air—water interface and act as a highly flexible barrier for preventing coalescence of water droplets. The incorporation of magnetic nanoparticles can give the Janus particles magnetic responsiveness for controlled transportation and coalescence of liquid marbles, while the structural colors in the Janus particles can be employed for barcoding of the encapsulated liquid marbles. We believe that these small Janus particles have great potential as components for constructing intelligent interfacial objects.

Controlled manipulation of small volumes of liquids is extremely important in miniaturized systems for chemical and biological applications.[1] Techniques to achieve this goal are usually based on two-dimensional manipulation of discrete droplets by an external electric field, magnetic field, or acoustic action.[2] In these approaches to droplet manipulation, stable droplets in air are needed; one exciting way to achieve this is to coat the droplets with micro- or nanoscale particles (termed "liquid marbles").[3] Since the droplets are surrounded by air, the fluidic resistance is low, facilitating their transport on solid substrates. Coating the droplet surface with a layer of particles could also avoid wetting of the substrate by the droplet, thus effectively reducing any resistance against motion arising from dynamic contact-angle hysteresis of the droplets moving on a solid substrate.[3a,4] These characteristics make liquid marbles a particularly attractive platform for manipulating discrete droplets. However, most studies of liquid marbles have focused on methods for preparing superhydrophobic particles with homogeneous structures and surfaces.[5] New approaches to generate particles with nonhomogeneous surface properties for coating droplet surfaces remain inadequate.

In nature, the ability to manipulate droplets can significantly affect an organism's survival. As part of the evolutionary drive to survive, some organisms have developed fascinating mechanisms to manipulate the droplets around them.[6] For example, with the covering of an approximately hexagonal close-packed arrangement of nipples on compound eyes, mosquitoes can effectively prevent fog droplets from accumulating on their eyes, thus maintaining clear vision in a humid habitat.[6a] With heterogeneously textured bumps (having hydrophilic peaks and hydrophobic bases) on their backs, some beetles can harvest fog droplets and survive in extreme desert environments.[6b] Inspired by these organisms, scientists have developed many functional surfaces with special wettability properties for the manipulation of droplets.[7] However, most of these studies have focused on the engineering of flat solid surfaces to achieve the desired wettability and mimic only a single property of the organisms.

Here we present bioinspired Janus particles with special wettability for controlled droplet manipulation. Taking inspiration from multiple organisms in nature, such as the nipple arrays and heterogeneous decoration mentioned above, we designed and fabricated Janus particles with spatially varying wettability. These amphiphilic Janus particles offer unique interfacial properties that cannot be achieved on conventional solid films and homogeneous particles. Moreover, by manipulating the arrangements of the particles on droplet interfaces, barcoding can be achieved through the structural colors of the particles. Furthermore, by incorporation of magnetic nanoparticles (NPs) in one of the compartments of the Janus particles, the resultant liquid marbles can be actuated in a magnetic field. Thus, our approach creates new opportunities to achieve multifunctional liquid marbles.

To create particles with the desired surface morphology, we generated Janus Pickering emulsions in microfluidic devices and used the emulsions as templates for the final particles. Although many microfluidic devices have been developed to fabricate Janus emulsions, most of the capillary-based microfluidic devices employ a dual-channel geometry to deliver only two dispersed phases at a time; as a result, only one type of Janus emulsion can be fabricated in a single operation.[8] In this work, we achieved on-demand generation of Janus emulsions by incorporating four channels for injecting four different dispersed phases in a single device, as illustrated schematically in Figure 1a. Different oil phases are injected through the

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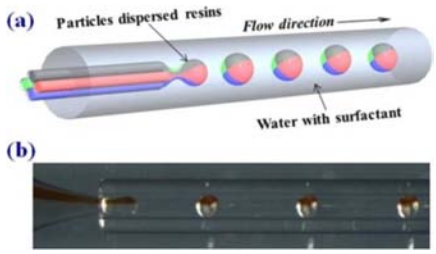

Figure 1. Generation of multicomponent emulsions in a capillary microfluidic device: (a) schematic illustration of the emulsion generation; (b) optical microscope image showing the generation of multicomponent emulsions in dripping mode.

channels while an aqueous continuous phase is injected into the device through the region between the four-barrel capillary and the outer square capillary in the same direction. The aqueous phase focuses the oil phases into a jet, which can be triggered to break up into monodisperse oil-in-water emulsion droplets at the tip of the four-barrel capillary. Although the capillary microfluidic device enables separate injection of multiple oil phases, these oil phases tend to coalesce at the tip of the capillary and form a single multicomponent emulsion droplet, as shown in Figure 1b and movie S1 in the Supporting Information (SI). This ensures that the final particles are not separated into multiple homogeneous particles.

We used colloidal crystal solutions as the dispersed oil phases for the emulsions. These solutions were prepared by dispersing monodisperse silica or α-Fe_2O_3 NPs in ethoxylated trimethylolpropane triacrylate (ETPTA) resin. At relatively high silica NP concentrations, significant interparticle repulsion occurs. Therefore, the NPs are separated from each other with a certain average interparticle spacing, and they self-assemble into a non-close-packed colloidal crystal array (CCA) structure in the ETPTA resin. Because of the periodic arrangement of these NPs, the prepared ETPTA resins display iridescent colors due to diffraction of light. The reflection wavelength depends on the diameter and volume fraction of the silica NPs and can be estimated by Bragg's law. Therefore, by dispersion of silica NPs with different sizes at different concentrations with respect to the ETPTA resin, the characteristic reflection peaks of the fluidic colloidal crystal solutions can be tuned. In the present experiment, we chose three kinds of oil solutions with red, green, and blue structural colors. In addition, we also used a fourth solution with α-Fe_2O_3 and silica NPs codispersed in the ETPTA resin as a dispersed phase. With these four dispersed phases, droplets with four compartments were generated. By photopolymerization of these emulsion templates through UV illumination, monodisperse four-compartment particles, each with a distinct structural color, were generated (Figure 2a). By variation of the flow rates of the dispersed oil phases, the number and relative sizes of the compartments could be tuned (Figure 2b−f). With a single microfluidic device, particles with the desired structures can be generated on-demand.

The silica NPs have three roles in the generation of the multicomponent particles: First, addition of the NPs in the ETPTA resin leads to an increase in the viscosity of the oil phases from 50 to ~300 cSt, thereby achieving stable multicomponent emulsion templates. Second, as mentioned above, the silica NPs form CCAs in the emulsion templates and impart the solidified particles with the iridescent structural colors. Third, the hydrophilic silica NPs can spontaneously adsorb to the interface to minimize the total interfacial energy of the emulsions. When the NPs are anchored at the water-ETPTA interface, the reduction in the energy per silica NP is much larger than their thermal energy, and therefore, once trapped, the NPs cannot escape from the interface. Thus, the arrangement of these silica NPs can be maintained after solidification of the emulsions, as confirmed in Figure 3, which shows a dense hexagonal arrangement of NPs on the surface and inside the solidified particles.

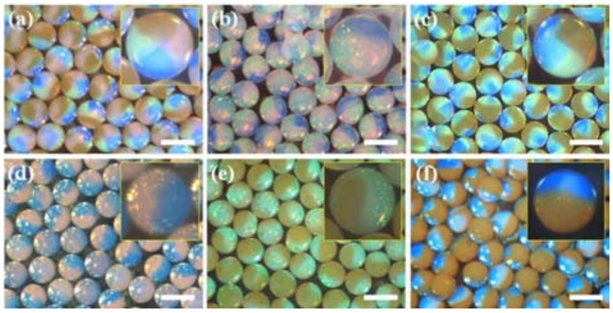

Figure 2. Photographs of multicompartment particles: (a) four-compartment particles with red, blue, and green structural colors and a gray magnetic component; (b, c) three-compartment particles; (d−f) Janus particles. Scale bars are 100 μm.

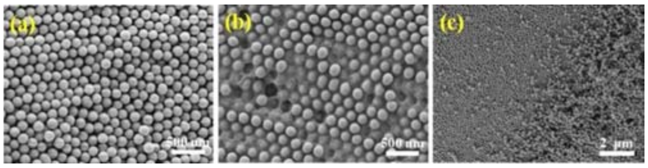

Figure 3. Scanning electron microscopy images of the ETPTA resin with silica NPs embedded in the matrix: (a) surface of the Janus particles; (b) cross-section of the Janus particles; (c) NPs with a domain boundary on the surface of the Janus particle.

As the multicompartment particles were covered by hydrophilic silica NPs alone, their surface was hydrophilic. To impart the particles with additional functionality, we surface-treated the Janus particles to give them amphiphilic surface properties for droplets. To engineer the surface properties of the Janus particles, we first treated them with fluoroalkylsilane (FAS) to make them hydrophobic (Figure S1 in the SI). The treated particles were then arranged into a monolayer on a flat substrate in a magnetic field. This step was achieved by making the Janus particles magnetically responsive by encapsulating magnetic NPs in one of the hemispheres while applying the desired structural color in the other hemisphere. The orientation of the resultant particles could be manipulated to achieve different visual appearances (movie S2). Here we fixed the particles in such a way that the hemisphere with the structural color was facing upward while the magnetic hemisphere was embedded in a layer of wax on the substrate surface. Afterward, the exposed colorful hemispheres of the Janus particles were treated with oxygen plasma to render them hydrophilic (Figure S2), giving the resulting Janus particles opposite wettability on the two sides. The procedures are summarized in Figure 4a.

To verify the dual wettability, the Janus particles were dispersed on a water surface. As expected, the particles formed a monolayer at the air−water interface. The plasma-treated color surfaces of the Janus particles tended to face the bottom water layer, while the FAS-decorated magnetic hemispheres

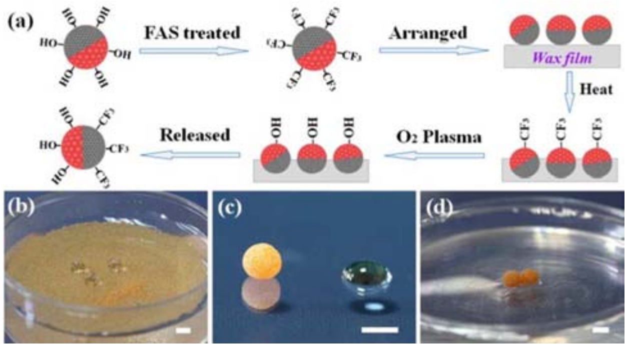

Figure 4. (a) Schematic illustrating the procedure for fabricating Janus particles with spatially varying surface wettability. (b) Photographs of water droplets sitting on a monolayer of Janus particles. (c, d) Photographs showing Janus-particle-coated liquid marbles placed on (c) a glass slide and (d) a water surface. Scale bars are 2 mm.

faced the air. The exposed magnetic hemisphere arrays were water-resistant because of their hydrophobic coating as well as the bioinspired nanostructured surface (Figure 4b). To take further advantage of their specially varying wettability, we also used the Janus particles with dual wettability to coat the surface of dripping 5 μL water droplets, forming liquid marbles. The as-prepared liquid marbles were stable and could be readily handled by tweezers without breaking up. Moreover, they remained intact even after they were transferred onto a hydrophilic glass substrate and even a water surface (Figure 4c,d).

Apart from their stability, the liquid marbles could also be easily actuated. Because of the presence of magnetic NPs in the hydrophobic hemispheres, liquid marbles decorated with Janus particles could be manipulated using a magnetic field on both flat and curved surfaces. In close proximity of a magnet, the Janus particles could rearrange on the surface of the liquid marbles, leading to a change in the wettability of the liquid marble surface. Therefore, under a strong magnetic field, several originally stable liquid marbles could be triggered to coalesce with each other. Interestingly, two liquid marbles tended to coalesce to form a dumbbell shape instead of the original spherical shape (Figure 5a and movie S3). So far as we know, nonspherical droplets have been achieved in liquid media with the assistance of colloidal particles as a stabilizer,[9] but there has been less research about their formation at air–liquid interfaces. Here, because of the irreversible anchoring of our Janus particles at the water–air interface, the reduction in the droplet surface-to-volume ratio accompanying the coalescence process led to an increase in the droplet surface coverage by the particles. Thus, the particles could form a rigid layer during coalescence of the liquid marbles, providing support for the dumbbell shape. Arbitrarily squeezing the liquid marbles resulted in the formation of a variety of morphologies, including disk-shaped, ellipsoidal, and even brainlike morphologies (Figure S3).

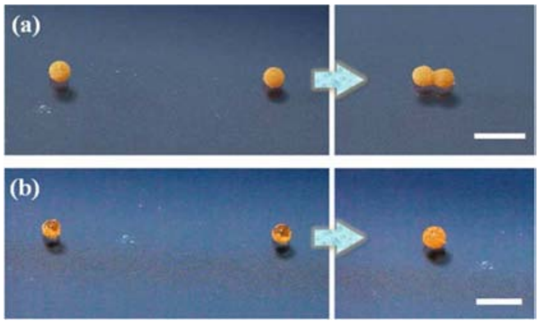

Figure 5. Forced coalescence of liquid marbles under magnetic force: (a) two liquid marbles coated completely by Janus particles attained a dumbbell shape; (b) forced coalescence of two half-coated liquid marbles resulted in a single spherical liquid marble. Scale bars are 5 mm.

In addition to the nonspherical shape, the coalesced droplets could also adopt a spherical shape when we applied a magnetic field in such a way that all of the particles were collected on one side (Figure 5b left) and the droplets were forced to coalesce with each other on their respective sides without particles (Figure 5b right and movie S4). By encapsulating different chemical reactants in different liquid marbles, this coalescence process can be applied to realize on-demand chemical reactions in droplets.

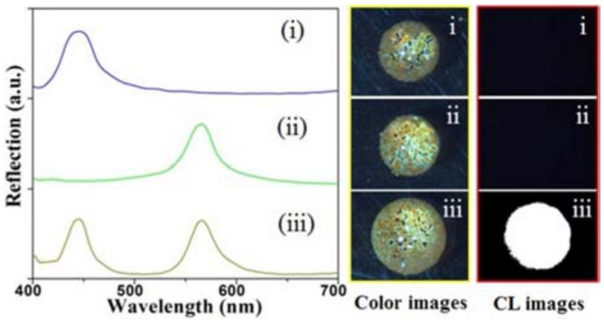

Figure 6. (left) Reflection spectra, (middle) digital photographs, and (right) CL images of (i, ii) liquid marbles half-coated with (i) blue and (ii) green Janus particles and (iii) the coalesced liquid marble.

While the incorporation of magnetic NPs enables magnetic actuation, encapsulation of CCAs in the Janus particles results in different structural colors that can be used for barcoding the particle-decorated liquid marbles. To demonstrate this concept, we prepared two liquid marbles whose surfaces were decorated with blue or green Janus particles [Figure 6 middle, (i) and (ii)]. The resultant marbles showed detectable optical reflectivity spectra [Figure 6 left, (i) and (ii)]. Both the colors and the spectra can be used for encrypting information regarding the content in the liquid marbles. After the two marbles were mixed, the coalesced marble showed a dual-peak spectrum that is a mixture of the two original reflectivity spectra [Figure 6 left, (iii)]. Thus, this approach could identify not only the as-prepared droplets but also the original compositions of the droplets before merging. As a demonstration, we used the system for qualitative analysis of glucose. Glucose oxidase-pretreated analyte solutions were first coated with the different Janus particles with their distinctive reflectivity peaks. The potential chromogenic solutions, such as the solution of horseradish peroxidase and luminol, were also decorated with the particles and encrypted using a different set of codes. When the two solutions were mixed, the coalesced droplets showed bright chemiluminescence (CL) if the analyte solution contained glucose (Figure 6 right). The dual-peak spectrum of the merged droplets could not only reflect the composition of the analyte, which could potentially correspond to different patients, but also could identify the target compound for detection. The barcoding of the liquid marbles remained detectable even in the presence of dyes (Figure S4). This suggests that colorimetric reactions can also be performed for sample analysis using our system.

In conclusion, inspired by the nipple arrays covering mosquitoes' eyes and the heterogeneous textured bumps on beetles' backs, we created a new type of Janus particle with multiple features, such as spatially varying wettability on the same surface and a tailored arrangement of structural colors and magnetism in different compartments. The desired Janus particles were generated using microfluidic emulsification followed by emulsion polymerization and surface treatment. The prepared Janus particles can stick strongly to the air−water interface and act as a flexible barrier preventing coalescence of water droplets. More attractively, the incorporation of magnetic NPs can impart the Janus particles with magnetic responsiveness for the manipulation and triggered coalescence of the droplets, while the structural colors in the Janus particles can be employed as barcoding elements in liquid marbles. We believe that these small Janus objects have great potential as important components for constructing intelligent interfacial structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section and characterization details of Janus particles and liquid marbles. 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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