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Research Article

Scalable Synthesis of Janus Particles with High Naturality

Yang Lan, Jingyu Wu, Syung Hun Han, Sagar Yadavali, David Issadore, Kathleen J. Stebe,* and Daeyeon Lee*

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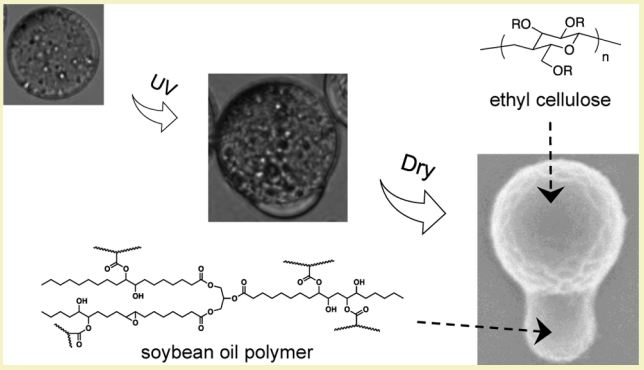
ABSTRACT: Because of the increasing concerns about the ecological damage and negative health effects that may be caused by petrochemical-based microbeads, many countries are banning their use in a wide range of consumer products. One particular class of particles that may never reach their full potential because of such a ban is Janus particles, which are particles with two opposite properties. Despite significant progress in the scalable synthesis of Janus particles, most studies rely on petrochemical-based materials and solvents to enable their synthesis. In this report, we present a single-emulsion polymerization method for scalable synthesis of amphiphilic Janus particles with materials derived from plants. Soybean oil-epoxidized acrylate (SBOEA) monomers are polymerized in single-emulsion droplets of SBOEA, ethyl cellulose (EC), butyl acetate, and initiators that can be generated by either bulk or microfluidic emulsification, leading to the formation of amphiphilic soybean oil polymer/EC (SBOP/EC) Janus particles. Interfacial anchoring of the in situ-formed SBOP particles at the interface of the emulsion droplet plays a key role in the formation of the SBOP/EC Janus particles. Large-scale preparation of uniform SBOP/EC Janus particles is also demonstrated using a glass-silicon microfluidic device. Finally, the SBOP/EC Janus particles show potential to stabilize oil-in-water emulsions that can stay stable under flowing conditions.



KEYWORDS: *Janus particles, green materials, scalable synthesis, interfacial polymerization, microfluidics*

INTRODUCTION

Janus particles are colloidal particles with two distinct domains, each enriched in components of opposite polarities or differing surface chemistry.[1,2] Analogous to molecular surfactants, one of the most intriguing applications of Janus particles is their use as solid surfactants to stabilize multiphasic mixtures such as emulsions.[3−7] Janus particles can stabilize emulsions more effectively than molecular surfactants because of the substantially large detachment energy required to remove them from the interface, and can be designed to enable the formation of thermodynamically stable emulsions.[8−10] Moreover, the potential to introduce multifunctional moieties onto the two components of Janus particles can imbue emulsions with magnetic, catalytic, or electrical properties.[1,2] These features make Janus particles useful in a wide range of applications including cosmetics,[6] paints,[11] and drug delivery.[12−14] To date, a variety of techniques including seeded emulsion polymerization,[7,15] colloidal assembly,[16] controlled modification at interfaces,[17−19] physical deposition,[20] and microfluidic methods[12] have been developed to prepare Janus particles.

Despite these exciting advances, the application of Janus particles in commercial products and industrial processes is threatened by the increasing concerns over the negative health and ecological impacts that can be caused by the so-called microplastics. Many types of microparticles are now commonly used in a wide variety of consumer products (e.g., cosmetics and coatings) and industrial processes (e.g., polishing). Once released into the environment, these particles can persist with deleterious consequences, including entering the food chain, thereby posing a significant threat to human health. For these reasons, a broad ban on plastic microbeads, especially those made primarily from petrochemical-based polymers, has been enforced in several countries.[21,22]

To ensure that recent advances in Janus particle synthesis and applications can lead to their translation, it is essential to develop Janus particles that are made with green materials such as bio-based and eco-friendly materials.[21,22] In particular, materials derived from plant sources are ideal candidates to prepare microparticles for practical applications.[23−27] Although

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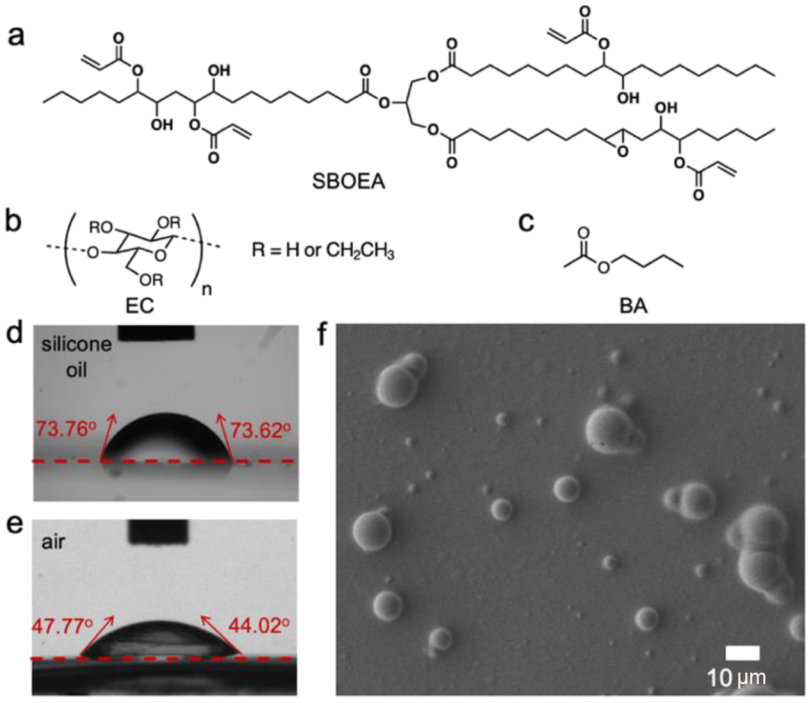

Figure 1. (a–c) Chemical structures of SBOEA, EC, and BA. Water contact angle of the EC film in silicone oil (d) and in air (e). (f) Scanning electron microscopy (SEM) image of Janus particles synthesized by batch-mode emulsion polymerization.

recent reports have demonstrated the synthesis of spherical particles with green materials,[28−32] only a few examples of Janus particles made from green materials have been reported.[33,34] Marquis et al.[33] first demonstrated the fabrication of pectin/alginate Janus microbeads by in situ gelation of well-segmented pectin and alginate solutions. This method requires the formation of Janus emulsion droplets of pectin and alginate in advance using a complex microfluidic device. Moreover, both pectin and alginate are hydrophilic, which limits the application of the Janus microbeads as emulsion stabilizers. Thereafter, Chen et al.[34] reported another type of Janus particle with shellac and alginate. These Janus particles were prepared via interfacial precipitation of shellac and subsequent gelation of alginate in single emulsions. While this approach enables scalable synthesis of Janus particles made with natural materials, because the shellac part is made of noncross-linked small molecules, their stability may be poor, especially in the presence of organic solvents.

In this study, we present the synthesis of Janus particles with high naturality using a single-emulsion polymerization method. Soybean oil-epoxidized acrylate (SBOEA) monomers are polymerized within a single-emulsion droplet of butyl acetate (BA) and ethyl cellulose (EC), resulting in dumbbell-shaped Janus particles with two components made by soybean oil polymers (SBOP) and EC. In addition to these two primary components of Janus particles, the solvent, BA, is found in many types of fruits, making the synthesis protocol more environmentally friendly.[35] We show the mechanism of Janus particle formation via in situ observation of polymerization. Highly uniform SBOP/EC Janus particles are produced on a large scale by use of a glass-silicon microfluidic device. These Janus particles are able to stabilize emulsions that remain stable under flowing conditions.

RESULTS AND DISCUSSION

Synthesis of Janus Particles with High Naturality. Among many types of green materials that can be used for particle synthesis, plant oils[36] and cellulose[37] offer advantages because of their low price and diverse functionalities; both plant oil and cellulose are widely available on large scales and diverse chemical reactions can be performed with these reagents to yield intermediates for different products. In this report, a commercially available soybean oil derivative, SBOEA (Figure 1a), is employed to build the hydrophobic part of Janus particles. The acrylate groups of SBOEA enable the formation of cross-linked SBOP (Figure S1, Video S1). Meanwhile, commercially available EC (Figure 1b), a linear polysaccharide derived from cellulose by replacement of the hydroxyl groups on cellulose with ethyl groups (48% substitution), is chosen to form the hydrophilic part of the Janus particles. Although 48% of the hydrophilic hydroxyl groups are substituted by the hydrophobic ethyl groups, the surface of EC remains hydrophilic as shown by the water contact angle of the EC films in silicone oil (Figure 1d) and in air (Figure 1e). Both SBOP and EC have been reported to undergo degradation to products that are environmentally benign, and thus it is likely that the SBOP/EC Janus particles described in this work will not have major negative impact on the environment.[38,39] To solubilize these two components, BA (Figure 1c), which can be found in many types of fruits and is widely used for fruit flavoring in foods, is employed as the solvent.

The SBOP/EC Janus particles are prepared by inducing polymerization in a single emulsion with a dispersed phase containing EC, SBOEA (EC/SBOEA = 1:1, wt), BA, and initiator azobisisobutyronitrile (AIBN) in a continuous phase of water with 1 wt % poly(vinyl alcohol) (PVA). Figure 1f shows the SEM image of SBOP/EC Janus particles with a weight ratio of 1:1 (SBOEA/EC); snowman-like Janus

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particles can be clearly observed. Because the single emulsion is prepared by shaking the dispersed phase into the continuous phase, Janus particles prepared in this way are polydisperse, ranging in size from about 1−25 μm (Figure 1f). By replacing the neutral AIBN initiator with ionic potassium persulfate (KPS), submicrometer-sized SBOP/EC Janus particles with a more spherical shape can be prepared (Figure S2). Although shaking the mixture provides a simple approach to produce a large quantity of Janus particles, their uniformity is rather low. Moreover, it is worth noting that the formation of Janus particles in this method is quite sensitive to the ratio between EC and SBOEA. When ratios of EC to SBOEA that depart significantly from the 1:1 ratio are used in the synthesis, only patchy spherical particles without clear distinction between hydrophilic and hydrophobic components are obtained (Figure S3).

Monodisperse SBOP/EC Janus Particles. To prepare monodisperse SBOP/EC Janus particles with a controllable size, we employ a flow-focusing microfluidic device to generate single-emulsion droplets of EC, SBOEA, BA, and initiators. Photoinitiator 2-hydroxy-2-methylpropiophenone (HMP) is employed to replace AIBN here to facilitate the in situ observation of subsequent polymerization under an optical microscope. The microfluidic device is fabricated from poly(dimethylsiloxane) with two inlets and one outlet as shown in Figure 2a. The oil phase of EC, SBOEA, HMP, and

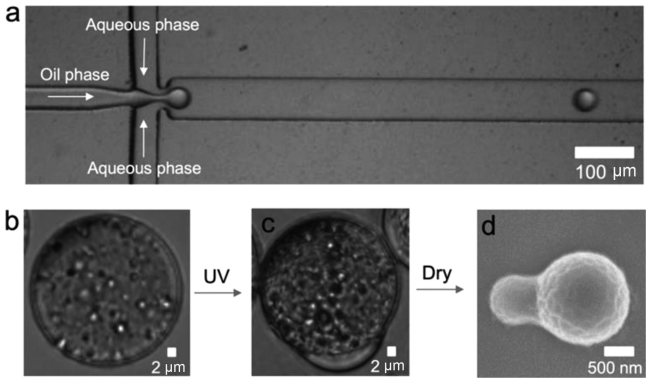

Figure 2. (a) Formation of oil microdroplets of EC, SBOEA, HMP, and BA in a flow-focusing microfluidic device. Optical microscope images of (b) oil microdroplet of EC, SBOEA, HMP, and BA, (c) Janus particles with cross-linked SBOP and EC/BA components. (d) SEM image of the SBOP/EC Janus particles.

BA is emulsified to form monodisperse oil microdroplets at the flow-focusing junction by an aqueous phase with 1 wt % PVA (Video S2). By changing the flow rate of the oil and aqueous flows, monodisperse oil microdroplets of EC, SBOEA, HMP, and BA with size from 25 to 80 μm can be easily obtained (Figures S4 and S5). Figure 2b shows a typical optical microscopy image of an isolated spherical oil droplet (EC/SBOEA/HMP/BA = 100:200:1:2000, wt) within which small EC precipitates can be observed. We believe water diffusion into the droplets upon emulsification induces the precipitation of EC.

Subsequently, the polymerization of SBOEA in the oil microdroplet is initiated by irradiation of UV light for 1 min (365 nm). Figure 2c shows the optical microscopy image of an oil microdroplet after polymerization. An anisotropic dumb-bell-shaped Janus structure can be clearly observed. The smaller component of the Janus particle, formed during the UV irradiation, is inferred to be the cross-linked SBOP. Meanwhile, the majority of EC remains in the microdroplet together with BA after the polymerization as evidenced by the small precipitates in the larger bulb of the Janus structure. Solid SBOP/EC Janus particles with smooth smaller bulbs and rough larger bulbs are obtained after the evaporation of BA at room temperature (Figure 2d). The EC component of the Janus particle is larger than the SBOP part, even though more SBOEA than EC is used in the synthesis. This discrepancy may be because of the fact that SBOP is hydrophobic and highly cross-linked, which could result in the formation of a higher-density solid in water compared to EC. Another potential explanation is that the EC component of the Janus particle may be porous as indicated by the SEM image in Figure 2d.

Formation Mechanism of SBOP/EC Janus Particles. To understand the formation mechanism of SBOP/EC Janus particles upon UV polymerization, two complementary experiments are carried out in the absence of either EC or SBOEA in oil microdroplets. Figure 3a shows the structural evolution of a single oil microdroplet of SBOEA, HMP, and BA (without EC) upon UV irradiation. In this case, the oil microdroplet is originally clear and transparent (Figure 3a, 0 s). No precipitates can be observed because of the absence of EC. UV light is irradiated from the right side of the image as indicated by the bright spot on the right part of the oil microdroplet (Figure 3a, 1 s). The polymerization of SBOEA is observed after 14 s of UV irradiation as evidenced by the newly formed dark spot on the upper left region of the oil droplet (Figure 3a, 14 s, highlighted by the red arrow). The polymerization of SBOEA starts in the oil droplet close to the liquid−liquid interface (red arrow in the 14 s image) and occurs at the opposite site of where UV light irradiation is applied. Further polymerization of SBOEA leads to anchoring of this solid particle at the liquid−liquid interface as shown by the growing dark spot on the surface of the oil droplet (Figure 3a, 16 s). As the dark spot of SBOP continues to grow, a solid particle protruding out of the oil droplet is clearly seen, leading to the formation of anisotropic Janus structure (Figure 3a 18−60 s, Video S3). It is interesting that only one SBOP particle rather than multiple SBOP particles is formed in one emulsion droplet, which avoids the formation of raspberry-like structures.[40,41] A bowl-like particle is observed when this Janus structure is dried and observed under SEM (Figure 3b).

When SBOEA is omitted from the preparation of SBOP/EC Janus particles, no specific morphology change of the oil microdroplets of EC, HMP, and BA can be observed after UV irradiation (Video S4). After the evaporation of BA, spherical particles with rough surfaces are obtained as shown in Figure 3c.

Based on the results obtained above and the previous studies in the literature,[40,41] a possible mechanism for the formation of SBOP/EC Janus particles is discussed. In a droplet of EC, SBOEA, BA, and initiators, the polymerization of SBOEA forms a single particle of cross-linked SBOP at the interface of each droplet because of the anchoring effect.[41] The formed SBOP particles further protrude from the droplet because of the incompatibility between the cross-linked SBOP and the solvent BA. The final morphology of the Janus particle is determined primarily by the balance of three interfacial tensions: water-SBOP, water EC, and SBOP-EC. The protrusion is mainly composed of SBOP; most of the EC polymers remains in the BA droplet as proved by the fact that no dextran polymers labeled with the FITC dye can be found

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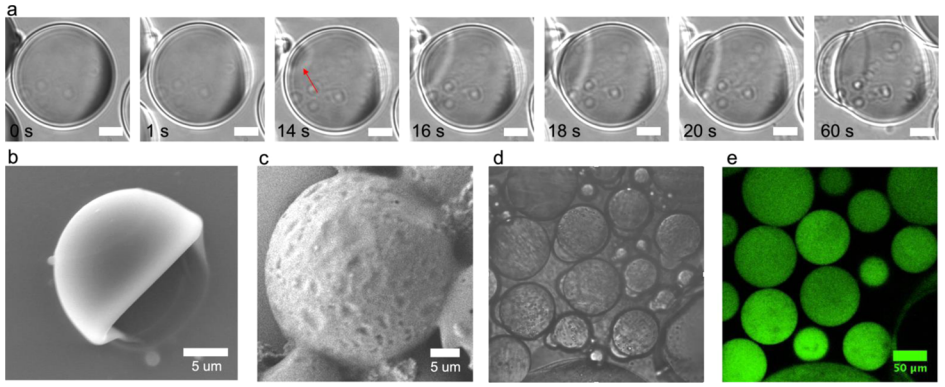

Figure 3. a) Oil microdroplet, of SBOEA, HMP, and BA upon UV irradiation. Scale bar 10 μm. (b) SEM image of the oil microdroplet of SBOEA, HMP, and BA after polymerization. (c) SEM image of oil microdroplet, of EC, HMP, and BA after UV irradiation. Optical microscope image (d) and the corresponding laser scanning confocal microscopy [(e), LSCM, green channel: FTIC] image of oil microdroplets of EC, SBOEA, HMP, and BA after UV irradiation.

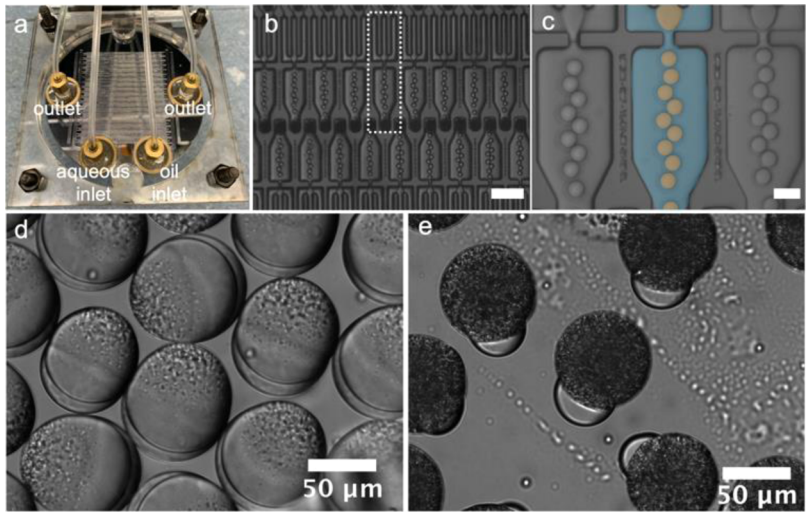

Figure 4. (a) Photograph of the high-throughput silicon-glass microfluidic device. (b) Optical microscopy image of part of the integrated microdroplet generators in the high-throughput microfluidic device. Scale bar: 200 μm. (c) Optical microscopy image of droplet formation within a microdroplet generator. The aqueous continuous phase and the oil-dispersed phase in the middle microdroplet generator are highlighted by false blue and orange, respectively. Scale bar: 50 μm. (d,e) Optical microscopy images of SBOP/EC Janus particles prepared from the high-throughput microfluidic device with AIBN (d) or HMP (e) as the initiator.

in the SBOP section after polymerization (Figure 3d,e). Consequently, the solid SBOP/EC Janus particles are obtained after evaporation of BA. The distinct bulbs of the SBOP/EC Janus particles are bonded together likely via molecular interactions such as hydrogen bonding and polymer entanglement between the SBOP and EC.[34]

Scalable Synthesis of Monodisperse SBOP/EC Janus Particles. To enable commercial-scale production of monodisperse SBOP/EC Janus particles, a recently developed[42] high-throughput microfluidic droplet device (Figure 4a) is employed to generate monodisperse emulsion droplets. The advantage of the microfluidic device lies in the parallelization of 10,260 flow-focusing microdroplet generators (Figure 4b, indicated by the dashed rectangle) in a single silicon-and-glass microfluidic device while having just two inlets for the continuous and dispersed phases, and two outlets for collecting the droplets formed (Figure 4a). Moreover, a silicon substrate and a glass cover are bonded together via anodic bonding. This design renders the device resistant to a wide range of solvents and able to withstand the high pressures required to process viscous fluids for large-scale production of microdroplets.[42]

The oil flow of EC, SBOEA, BA, and HMP as well as the aqueous flow (1 wt % PVA) are driven through the droplet generators under pressure-driven flow. The oil droplets generated by the parallel generators (Videos S5 and S6) are collected via the two outlets, leading to the generation of emulsion templates at the production rate of over 2 L/h (dispersion phase, Video S7, which is equivalent to 0.14 trillion droplets per hour and 265 g/h solid particles). The emulsion templates are highly uniform with the coefficient of variation of ~3% (Figure S6). By changing the pressure of the oil or aqueous feeds, monodisperse oil droplets of EC, SBOEA, BA, and initiators with various sizes can be easily obtained. Droplets are collected and irradiated with UV or heated, depending on the type of initiator used, to initiate polymerization for uniform SBOP/EC Janus particles. Figure 4d,e shows the optical microscopy images of the SBOP/EC Janus particles prepared from the high-throughput microfluidic device using initiators AIBN and HMP, respectively.

SBOP/EC Janus Particles as Emulsion Stabilizers. Recent studies have demonstrated that amphiphilic Janus particles with a sharp boundary between the two components

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can effectively stabilize emulsions as they can pin strongly at oil−water interfaces.[8,9] The emulsification properties of the SBOP/EC Janus particles prepared in this study are also partially investigated. Silicone oil is added to an aqueous dispersion of SBOP/EC Janus particles at an equivolumetric ratio (Figure 5a) and vortexed at 1000 rpm for 10 s to generate

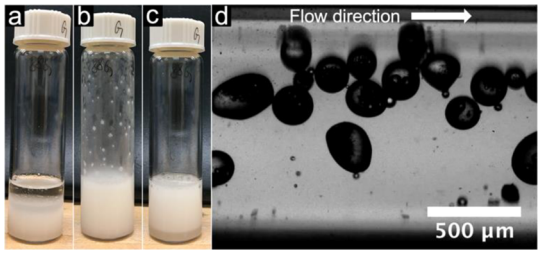

Figure 5. Photograph of SBOP/EC Janus particle aqueous dispersion (bottom, 3 mL, 1 wt %) and silicone oil (top, 3 mL) before mixing (a), after vortex for 10 s (b), and kept still for further 30 min [(c), stable state after creaming]. (d) Silicone oil droplet stabilized by SBOP/EC Janus particles in water flowing through the microchannel (flow rate 10 mL/h).

an emulsion (Figure 5b). Figure 5c shows the photograph of the SBOP/EC Janus particle-stabilized emulsions; droplets cream with an aqueous phase forming at the bottom. The emulsions remain stable after creaming (Figure 5c) for at least one month. Based on the difference in density of silicone oil and water, the observation indicates oil-in-water (o/w) type emulsions are generated using the SBOP/EC Janus particles as stabilizers. The snowman shape of SBOP/EC Janus particles with a large hydrophilic lobe and a small hydrophobic head likely plays an important role in determining the type of emulsion.[7] These o/w emulsions show good stability even when they are subjected to shear in a flow as shown in the optical microscope image (Figure 5d and Video S8). The SBOP/EC Janus particles remain stable without any signs of disassembly under stirring at 700 rpm and under vigorous shaking to make emulsions as will be discussed later.

CONCLUSIONS

In summary, we present the synthesis of amphiphilic Janus particles of high naturality with materials derived from plants. The Janus particles have two distinct bulbs of hydrophilic EC and hydrophobic cross-linked SBOP, showing a dumbbell shape. The synthesis of the SBOP/EC Janus particles is achieved by polymerization of SBOEA monomers within a single emulsion of SBOEA, EC, BA, and initiators, and the subsequent removal of solvent BA. The formation of the SBOP/EC Janus particles benefits from the anchoring effect of the in situ-formed single SBOP particles at the interface of the emulsion droplet as well as phase separation between SBOP and BA. The sizes of the SBOP/EC Janus particles can be easily tuned by changing the sizes of the single-emulsion droplets generated by either shaking or a microfluidic device. Large-scale synthesis of monodisperse SBOP/EC Janus particles is achieved using a glass-silicon microfluidic device with integrated microdroplet generators. These Janus particles are able to stabilize oil-in-water emulsions that are stable under flowing conditions. This straightforward, tuneable, and scalable synthetic method for Janus particles of high naturality provides the potential to meet the demand for replacement of widely used microplastic in industrial applications such as medicine, cosmetics, and sustainable coatings. To enable adoption of these SBOP/EC Janus particles as emulsion stabilizers, future studies to systematically understand the correlation between the emulsion type and the morphology of SBOP/EC Janus particles and the effect of the particle size on the emulsion stability are necessary.

EXPERIMENTAL SECTION

Batch-Mode Synthesis of SBOP/EC Janus Particles. A mixture of EC (0.5 g), SBOEA (0.5 g), BA (9.0 g), and AIBN (10.0 mg) are added dropwise into 90 mL water (1 wt % PVA) while stirring vigorously. The mixture is then sealed and stirred at 70 °C for 24 h. After that, the mixture is further stirred at 70 °C for 24 h open to air in a fume hood. The final product is washed with DI water five times by centrifugation.

Droplet Formation in the PDMS Microfluidic Device. To generate oil droplets, two different liquids were injected into a microfluidic device, via two syringe pumps (PHD, Harvard Apparatus) with controlled flow rates. In a typical experiment, the oil phase of BA with 8 wt % SBOEA, 4 wt % EC, and 0.1 vol % photoinitiator of HMP was used as the dispersed phase. Water with 1 wt % PVA is used as the continuous phase. The flow rate of the oil phase was kept at 100 μL/h while varying the flow rate of the aqueous phase from 500 to 5000 μL/h.

Droplet Formation in the High-Throughput Microfluidic Device. A pressure-driven system is used to operate the high-throughput microfluidic device for droplet generation. Two 1-gallon stainless steel pressure vessels (alloy products) are pumped by two nitrogen tanks to drive the fluids into the microfluidic device. One vessel is for storing the continuous phase, which is water with 1 wt % PVA, and the other vessel for the dispersed phase, containing BA with SBOEA, EC, and the photoinitiator of HMP. The fluidic device is connected to the pressure vessels by PTFE tubings (McMaster Carr 52245K609), and inline filters (McMaster Carr: 9816K72) are used to filter debris in both phases. The flow rates of both phases are controlled by adjusting the pressure valves of the nitrogen tanks and measured using two inline flow meters (McMaster Carr: 5084K23). The flow rate of the dispersed phase was kept at a constant rate of 1.1 L/h while the flow rate of the continuous phase is varied from 1.4 to 3 L/h.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.0c04929.

- Full experimental details and additional characterization (PDF)
- Bulk polymerization of SBOEA (MP4)
- Droplet formation within the PDMS microfluidic device (MP4)
- UV polymerization of SBOEA in BA droplets (MP4)
- UV irradiation on EC in BA droplets (MP4)
- Oil droplets generated by the parallel generators (MP4)
- Oil droplets generated by generators within the high-throughput microfluidic device (MP4)
- Generation of emulsion templates at a production rate of over 2 L/h by the high-throughput microfluidic device (MP4)
- SBOP/EC Janus particles stabilized oil-in-water emulsions flowing in a microchannel (MP4)

AUTHOR INFORMATION

Corresponding Authors

Kathleen J. Stebe − *Department of Chemical and Biomolecular Engineering, University of Pennsylvania,*

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ACS Sustainable Chem. Eng. 2020, 8, 17680−17686

Philadelphia, Pennsylvania 19104, United States; orcid.org/0000-0003-0510-0513; Email: kstebe@seas.upenn.edu

Daeyeon Lee − *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0001-6679-290X; Email: daeyeon@seas.upenn.edu

Authors

Yang Lan − *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; Department of Chemical Engineering, University College London, London WC1E 7JE, U.K.;* orcid.org/0000-0002-6231-9717

Jingyu Wu − *Department of Chemical and Biomolecular Engineering and Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0001-5299-0753

Syung Hun Han − *Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States*

Sagar Yadavali − *Department of Chemical and Biomolecular Engineering and Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States*

David Issadore − *Department of Bioengineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0002-5461-8653

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.0c04929

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Walther, A.; Müller, A. H. E. Janus Particles: Synthesis, Self-Assembly, Physical Properties, and Applications. *Chem. Rev.* **2013**, *113*, 5194−5261.
(2) Du, J.; O'Reilly, R. K. Anisotropic Particles with Patchy, Multicompartment and Janus Architectures: Preparation and Application. *Chem. Soc. Rev.* **2011**, *40*, 2402−2416.
(3) Park, B. J.; Brugarolas, T.; Lee, D. Janus Particles at an Oil-Water Interface. *Soft Matter* **2011**, *7*, 6413−6417.
(4) Poggi, E.; Gohy, J.-F. Janus Particles: From Synthesis to Application. *Colloid Polym. Sci.* **2017**, *295*, 2083−2108.
(5) Bradley, L. C.; Chen, W.-H.; Stebe, K. J.; Lee, D. Janus and Patchy Colloids at Fluid Interfaces. *Curr. Opin. Colloid Interface Sci.* **2017**, *30*, 25−33.
(6) Lan, Y.; Jia, Y.; Lee, D. Chapter 10. Pickering Emulsions Stabilized by Polymer Colloids. *Particle-Stabilized Emulsions and Colloids*; The Royal Society of Chemistry, 2019; 323−348.
(7) Lan, Y.; Choi, J.; Li, H.; Jia, Y.; Huang, R.; Stebe, K. J.; Lee, D. Janus Particles with Varying Configurations for Emulsion Stabilization. *Ind. Eng. Chem. Res.* **2019**, *58*, 20961−20968.
(8) Aveyard, R. Can Janus Particles Give Thermodynamically Stable Pickering Emulsions? *Soft Matter* **2012**, *8*, 5233−5240.
(9) Tu, F.; Park, B. J.; Lee, D. Thermodynamically Stable Emulsions Using Janus Dumbbells as Colloid Surfactants. *Langmuir* **2013**, *29*, 12679−12687.
(10) Hu, J.; Zhou, S.; Sun, Y.; Fang, X.; Wu, L. Fabrication, Properties and Applications of Janus Particles. *Chem. Soc. Rev.* **2012**, *41*, 4356−4378.
(11) Jiang, S.; Van Dyk, A.; Maurice, A.; Bohling, J.; Fasano, D.; Brownell, S. Design Colloidal Particle Morphology and Self-Assembly for Coating Applications. *Chem. Soc. Rev.* **2017**, *46*, 3792−3807.
(12) Yang, S.; Guo, F.; Kiraly, B.; Mao, X.; Lu, M.; Leong, K. W.; Huang, T. J. Microfluidic Synthesis of Multifunctional Janus Particles for Biomedical Applications. *Lab Chip* **2012**, *12*, 2097−2102.
(13) Sanchez, L.; Yi, Y.; Yu, Y. Effect of Partial PEGylation on Particle Uptake by Macrophages. *Nanoscale* **2017**, *9*, 288−297.
(14) Yi, Y.; Sanchez, L.; Gao, Y.; Yu, Y. Janus Particles for Biological Imaging and Sensing. *Analyst* **2016**, *141*, 3526−3539.
(15) Tu, F.; Lee, D. Shape-Changing and Amphiphilicity-Reversing Janus Particles with pH-Responsive Surfactant Properties. *J. Am. Chem. Soc.* **2014**, *136*, 9999−10006.
(16) Zhou, Y.; Wang, D.; Huang, S.; Auernhammer, G.; He, Y.; Butt, H.-J.; Wu, S. Reversible Janus Particle Assembly via Responsive Host-Guest Interactions. *Chem. Commun.* **2015**, *51*, 2725−2727.
(17) Hong, L.; Jiang, S.; Granick, S. Simple Method to Produce Janus Colloidal Particles in Large Quantity. *Langmuir* **2006**, *22*, 9495−9499.
(18) Gu, H.; Yang, Z.; Gao, J.; Chang, C. K.; Xu, B. Heterodimers of Nanoparticles: Formation at a Liquid-Liquid Interface and Particle-Specific Surface Modification by Functional Molecules. *J. Am. Chem. Soc.* **2005**, *127*, 34−35.
(19) Nakahama, K.; Kawaguchi, H.; Fujimoto, K. Novel Preparation of Nonsymmetrical Microspheres Using the Langmuir-Blodgett Technique. *Langmuir* **2000**, *16*, 7882−7886.
(20) Liang, H.; Cacciuto, A.; Luijter, E.; Granick, S. Clusters of Charged Janus Spheres. *Nano Lett.* **2006**, *6*, 2510−2514.
(21) Haider, T. P.; Völker, C.; Kramm, J.; Landfester, K.; Wurm, F. R. Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. *Angew. Chem. Int. Ed.* **2019**, *58*, 50−62.
(22) Rochman, C. M. Microplastics Research—from Sink to Source. *Science* **2018**, *360*, 28−29.
(23) Titirici, M.-M.; White, R. J.; Brun, N.; Budarin, V. L.; Su, D. S.; Del Monte, F.; Clark, J. H.; MacLachlan, M. J. Sustainable Carbon Materials. *Chem. Soc. Rev.* **2015**, *44*, 250−290.
(24) Iwata, T. Biodegradable and Bio-Based Polymers: Future Prospects of Eco-Friendly Plastics. *Angew. Chem. Int. Ed.* **2015**, *54*, 3210−3215.
(25) Mohammadinejad, R.; Karimi, S.; Iravani, S.; Varma, R. S. Plant-Derived Nanostructures: Types and Applications. *Green Chem.* **2016**, *18*, 20−52.
(26) Hillmyer, M. A. The Promise of Plastics from Plants. *Science* **2017**, *358*, 868−870.
(27) Zhu, Y.; Romain, C.; Williams, C. K. Sustainable Polymers from Renewable Resources. *Nature* **2016**, *540*, 354−362.
(28) Pi, C.; Yuan, J.; Liu, H.; Zuo, Y.; Feng, T.; Zhan, C.; Wu, J.; Ye, Y.; Zhao, L.; Wei, Y. In Vitro and in Vivo Evaluation of Curcumin Loaded Hollow Microspheres Prepared with Ethyl Cellulose and Citric Acid. *Int. J. Biol. Macromol.* **2018**, *115*, 1046−1054.
(29) Raza, S.; Yong, X.; Yang, B.; Xu, R.; Deng, J. Biomass Trans-Anethole-Based Hollow Polymer Particles: Preparation and Application as Sustainable Absorbent. *ACS Sustain. Chem. Eng.* **2017**, *5*, 10011−10018.
(30) Yuan, Y.; Yong, X.; Zhang, H.; Deng, J. Biobased Microspheres Consisting of Poly(Trans-Anethole-Co-Maleic Anhydride) Prepared by Precipitation Polymerization and Adsorption Performance. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1446−1453.
(31) Gericke, M.; Trygg, J.; Fardim, P. Functional Cellulose Beads: Preparation, Characterization, and Applications. *Chem. Rev.* **2013**, *113*, 4812−4836.
(32) Mirabedini, S. M.; Dutil, I.; Farnood, R. R. Preparation and Characterization of Ethyl Cellulose-Based Core-Shell Microcapsules Containing Plant Oils. *Colloids Surf., A* **2012**, *394*, 74−84.
(33) Marquis, M.; Renard, D.; Cathala, B. Microfluidic Generation and Selective Degradation of Biopolymer-Based Janus Microbeads. *Biomacromolecules* **2012**, *13*, 1197−1203.

(34) Chen, D.; Amstad, E.; Zhao, C.-X.; Cai, L.; Fan, J.; Chen, Q.; Hai, M.; Koehler, S.; Zhang, H.; Liang, F.; Yang, Z.; Weitz, D. A. Biocompatible Amphiphilic Hydrogel-Solid Dimer Particles as Colloidal Surfactants. *ACS Nano* **2017**, *11*, 11978−11985.
(35) Calvo-Flores, F. G.; Monteagudo-Arrebola, M. J.; Dobado, J. A.; Isac-García, J. Green and Bio-Based Solvents. *Top. Curr. Chem.* **2018**, *376*, 18.
(36) Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Plant Oil Renewable Resources as Green Alternatives in Polymer Science. *Chem. Soc. Rev.* **2007**, *36*, 1788−1802.
(37) Sannino, A.; Demitri, C.; Madaghiele, M. Biodegradable Cellulose-Based Hydrogels: Design and Applications. *Materials* **2009**, *2*, 353−373.
(38) Brydson, J. A. Cellulose Plastics. *Plastics Materials*; Elsevier, 1999; 613−634.
(39) Shogren, R. L.; Petrovic, Z.; Liu, Z.; Erhan, S. Z. Biodegradation Behavior of Some Vegetable Oil-Based Polymers. *J. Polym. Environ.* **2004**, *12*, 173−178.
(40) Fan, J.-B.; Liu, H.; Song, Y.; Luo, Z.; Lu, Z.; Wang, S. Janus Particles Synthesis by Emulsion Interfacial Polymerization: Polystyrene as Seed or Beyond? *Macromolecules* **2018**, *51*, 1591−1597.
(41) Fan, J.-B.; Song, Y.; Liu, H.; Lu, Z.; Zhang, F.; Liu, H.; Meng, J.; Gu, L.; Wang, S.; Jiang, L. A General Strategy to Synthesize Chemically and Topologically Anisotropic Janus Particles. *Sci. Adv.* **2017**, *3*, No. e1603203.
(42) Yadavali, S.; Jeong, H.-H.; Lee, D.; Issadore, D. Silicon and Glass Very Large Scale Microfluidic Droplet Integration for Terascale Generation of Polymer Microparticles. *Nat. Commun.* **2018**, *9*, 1222.

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