Scalable Synthesis of Janus Particles with High Naturality

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ABSTRACT. Due to 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 due to 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 (BA) and initiators that can be generated by either bulk or microfluidic emulsification, leading to the formation of amphiphilic soybean oil polymer-ethylcellulose (SBOP/EC) Janus particles. Interfacial anchoring of in situ formed SBOP particle at the interface of the emulsion droplet plays a key role in 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 due to the substantially large detachment energy required to remove them from the interface, and can be designed to enable formation of thermodynamically stable emulsions.[8,9] Moreover, the potential to introduce multi-functional 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] paint[11] and drug delivery.[12–14] To date, a variety of techniques including seeded emulsion polymerisation,[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 rising concerns over the negative health and ecological impact 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 the 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 particles 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 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 by a complex microfluidic device. Moreover, both pectin and alginate are hydrophilic, which limit 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 non-crosslinked 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 polymerisation. Highly uniform SBOP/EC Janus particles are produced at 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 at 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, soybean oil epoxidized acrylate (SBOEA, Figure. 1a), is employed to build the hydrophobic part of Janus particles. The acrylate groups of SBOEA enable the formation of crosslinked soybean oil polymers (SBOP, Figure S1, Video S1). Meanwhile, commercially available ethyl cellulose (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, butyl acetate (BA, Figure 1c), which can be found in many types of fruits and is widely used as fruit flavoring in foods, is employed as the solvent.

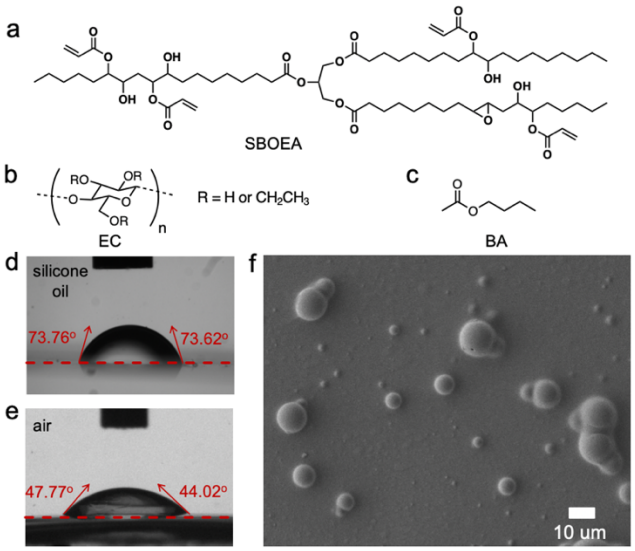

Figure 1, a)-c) Chemical structures of soybean oil epoxidized acrylate (SBOEA), ethyl cellulose (EC) and butyl acetate (BA). Water contact angle of EC film in silicone oil (d) and in air (e). f), Scanning electron microscope (SEM) image of Janus particles synthesized by batch-mode emulsion polymerization.

The SBOP/EC Janus particles are prepared by inducing polymerisation 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*% PVA. Figure 1f shows the scanning electron microscope (SEM) image of SBOP/EC Janus particles at the weight ratio of 1:1 (SBOEA:EC); snowman-like Janus 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 to 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 controllable size, we employ a flow-focusing microfluidic device to generate single emulsion droplets of EC, SBOEA, BA and initiators. Photo-initiator 2-hydroxy-2-methylpropiophenone (HMP) is employed to replace AIBN here to facilitate the *in situ* observation of subsequent polymerization under optical microscopy. The microfluidic device is fabricated from poly(dimethylsiloxane) with two inlets and one outlet as shown in Figure 2a. The oil flow of EC, SBOEA, HMP and 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 um can be easily obtained (Figure S4, S5). Figure 2b shows a typical optical microscope 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.

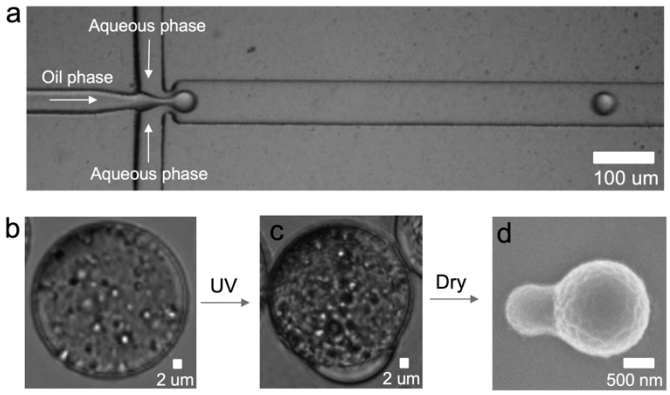

Figure 2, a) Formation of oil microdroplets of EC, SBOEA, HMP and BA in a flow-focusing microfluidic device. Optical microscope images of (b) an oil microdroplet of EC, SBOEA, HMP and BA, (c) Janus particle with cross-linked SBOP and EC/BA components. d), SEM image of the SBOP/EC Janus particle.

Subsequently, the polymerisation of SBOEA in the oil microdroplet is initiated by irradiation of UV light for 1 minute (365 nm). Figure 2c shows the optical microscopy image of an oil microdroplet after polymerization. An anisotropic dumbbell-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 due to 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, 1s). The polymerization of SBOEA is observed after 14 sec of UV irradiation as evidenced by the newly formed dark spot on the upper left region of the oil droplet (Figure 3a, 14s, highlighted by the red arrow). The polymerization of SBOEA starts in the oil droplet close to the liquid-liquid interface (red arrow in 14-sec 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 liquid-liquid interface as shown by the growing dark spot on the surface of the oil droplet (Figure 3a, 16s). 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 18s-60s, Video S3). It is interesting that only one SBOP particle rather than multiple SBOP particles are 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).

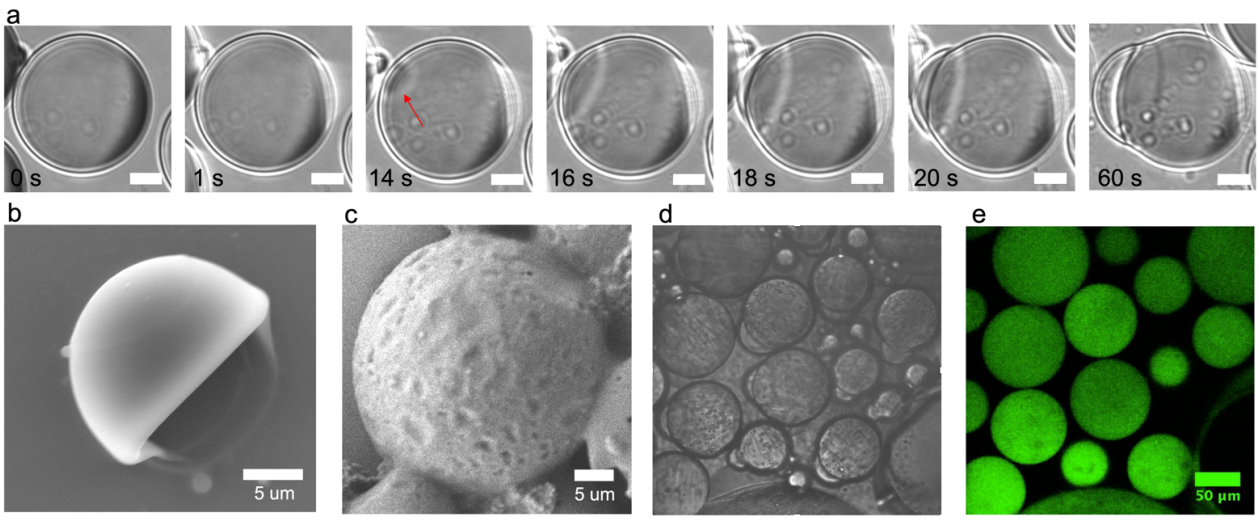

Figure 3, a) Oil microdroplet of SBOEA, HMP and BA upon UV irradiation. Scale bar 10 um. b) SEM image of the oil microdroplet of SBOEA, HMP and BA after polymerization. c) SEM image of oil microdroplet of EC, HMP and BA after UV irradiation. Optical microscope image (d) and the corresponding laser scanning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

When SBOEA is omitted from the preparation of SBOP/EC Janus particles, no specific morphology change of the oil microdroplet 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 Fig 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 crosslinked SBOP at the interface of each droplet due to the anchoring effect.[41] The formed SBOP particle further protrudes from the droplet because of the incompatibility between the crosslinked 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 labelled with FITC dye can be found in the SBOP section after polymerization (Figure 3d and 3e). 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 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 (Video S5, S6) are collected via the two outlets, leading to 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 and 4e show the optical microscope images of the SBOP/EC Janus particles prepared from the high-throughput microfluidic device using initiator AIBN and HMP, respectively.

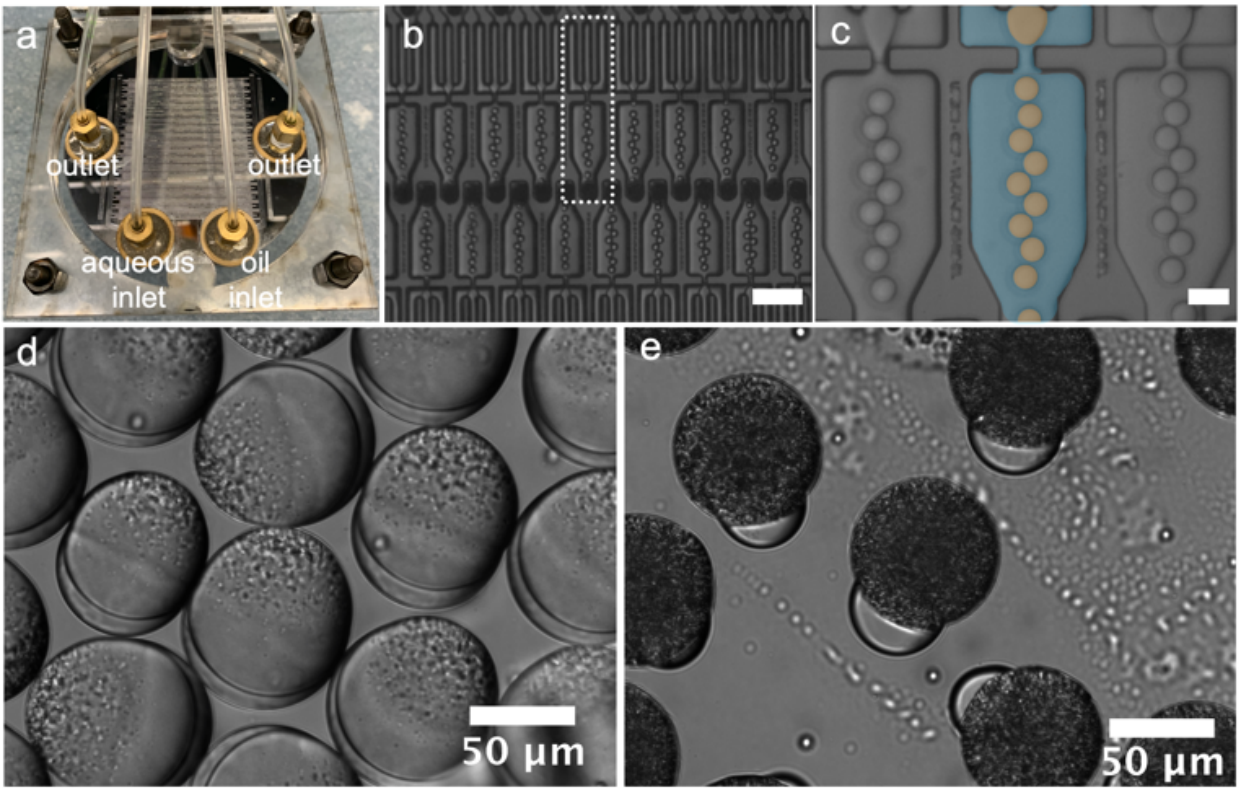

Figure 4, a) Photo of high-throughput silicone-glass microfluidic device. b) Optical microscope image of part of the integrated microdroplet generators in the high-throughput microfluidic device. Scale bar: 200 μm. c) Optical microscope image of droplet formation with in a microdroplet generator. The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

SBOP/EC Janus particles as emulsion stabilizers. Recent studies have demonstrated that amphiphilic Janus particles with an sharp boundary between the two components 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 an emulsion (Figure 5b). Figure 5c shows the photo 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, 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.

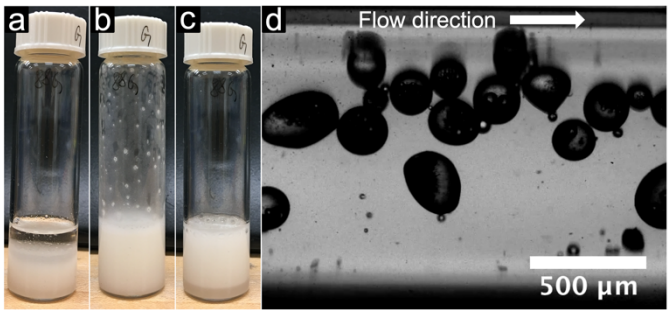

Figure 5, Photo of SBOP/EC Janus particle aqueous dispersion (bottom, 3 mL, 1 *wt %*) and silicone oil (top, 3 mL) before mixing (a), after vortex for 10 s (b) and kept still for further 30 min (c, stable state after creaming). d) Silicone oil droplet stabilized by SBOP/EC Janus particle in water flowing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

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 ethyl celluloses (EC) and hydrophobic cross-linked soybean oil polymers (SBOP), showing a dumbbell-like shape. The synthesis of the SBOP/EC Janus particles is achieved by polymerization of soybean oil epoxidized acrylate (SBOEA) monomers within a single emulsion of SBOEA, EC, butyl acetate (BA) and initiators, and the subsequent removal of solvent BA. It is observed that the formation of the SBOP/EC Janus particles benefits from the anchoring effect of *in situ* formed single SBOP particle 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. Finally, 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 particles size on the emulsion stability are necessary.

EXPERIMENTAL SECTION

Batch-mode synthesis of SBOP/EC Janus particles. A mixture of ethyl cellulose (EC, 0.5 g), soybean oil epoxidized acrylate (SBOEA, 0.5 g), butyl acetate (BA, 9.0 g) and azobisisobutyronitrile (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 ^{o}C for 24 h. After that, the mixture is further stirred at 70 ^{o}C for 24 h open to air in a fume hood. The final product is washed with DI water 5 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 butyl acetate with 8 wt%

SBOEA, 4 wt % EC and 0.1 vol% photo-initiator of 2-hydroxy-2- methylpropiophenone (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 aqueous phase from 500 μL/h 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 continuous phase, which is water with 1 wt% PVA, and the other vessel for the dispersed phase, containing butyl acetate with SBOEA, EC and the photo-initiator of 2-hydroxy-2-methylpropiophenone (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 by two inline flow meters (McMaster Carr: 5084K23). The flow rate of the dispersed phase was kept at a constant rate of 1.1 L/hr while the flow rate of the continuous phase is varied from 1.4 L/h to 3 L/h.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge. Full experimental details, additional characterization (PDF); Video of bulk polymerization of SBOEA, droplet formation within PDMS microfluidic device, UV polymerization of SBOEA in

BA droplets, formation of droplets within high-throughput microfluidic device, and flow of SBOP/EC Janus particles stabilized oil droplets (mp4).

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Conflicts of interest

There are no conflicts to declare

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High naturality Janus particles comprising soybean oil polymer (SBOP) and ethyl cellulose (EC) are synthesized by a scalable single emulsion polymerization method.