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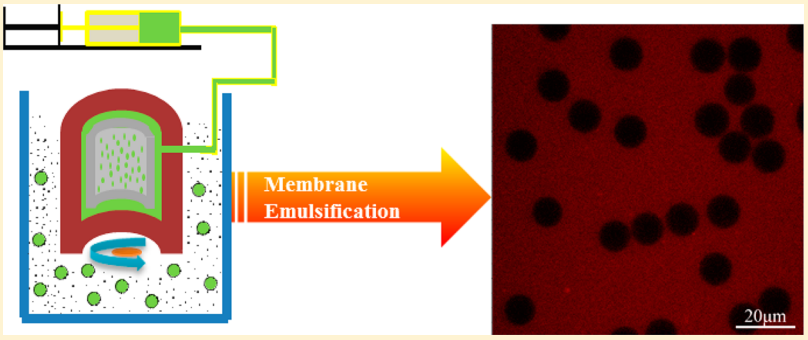
Preparation of Uniform Particle-Stabilized Emulsions Using SPG Membrane Emulsification

Guanqing Sun,[†] Feng Qi,[‡] Jie Wu,[‡] Guanghui Ma,*[,‡] and To Ngai*[,†]

[†]Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

[‡]National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

Supporting Information



ABSTRACT: Various aspects of particle-stabilized emulsions (or so-called Pickering emulsions) have been extensively investigated during the last two decades, but the preparation of uniform Pickering emulsion droplets via a simple and scalable method has been sparingly realized. We report the preparation of uniform Pickering emulsions by Shirasu porous glass (SPG) membrane emulsification. The size of the emulsion droplets ranging from 10−50 μm can be precisely controlled by the size of the membrane pore. The emulsion droplets have a high monodispersity with coefficients of variation (CV) lower than 15% in all of the investigated systems. We further demonstrate the feasibility of locking the assembled particles at the interface, and emulsion droplets have been shown to be excellent templates for the preparation of monodisperse colloidosomes that are necessary in drug-delivery systems.

INTRODUCTION

The phenomenon of the adsorption of colloidal particles at interfaces to stabilize emulsions has been known for more than a century.[1,2] Today, particle-stabilized emulsions, also known as Pickering emulsions, are receiving growing attention in the scientific and industrial communities because of their great potential applications in medicine, home and personal care products, agrochemicals, and cosmetics.[3−6] The advantage of using colloidal particles solely as stabilizers relies on the irreversible adsorption of the particles at an oil−water interface, which densely pack to provide a solid shell for the droplets and confer good protection against coalescence.[3,7] For a colloidal particle of several hundred nanometers at a typical oil−water interface, the energy required to detach the particle from the interface is on the order of a million k_BT, the thermal energy in which k_B is the Boltzmann constant and T is the absolute temperature. This unique property makes the emulsions much more stable than those stabilized by small molecular surfactants. It is now well established that the wettability of the particle, which is quantified as the contact angle θ measured from the aqueous phase, is a key parameter in determining the type of emulsions formed in a manner similar to the Bancroft rule for small molecular surfactants. For hydrophilic particles ($\theta < 90°$), oil-in-water (O/W) emulsions will be preferred and vice versa. Generally, it is quite easy to modify the wettability of the particles so as to control the type and stability of the emulsions.[8,9]

Conventionally Pickering emulsions are mostly prepared by mixing oil and water using a high-pressure valve homogenizer. In this device, a pre-emulsion with large droplets is forced through a high shear region in such a way as to promote turbulence and hence to disrupt large droplets into smaller ones. A drawback of this droplet breakup method is that it is not easy to control the mean drop size of the product emulsion so that the resultant droplets are usually highly polydisperse. As a consequence, this leads to poor reproducibility and a variable quality of the product emulsion per batch. Therefore, many microengineering techniques, such as membrane and microchannel emulsification as well as microfluidic devices, have recently been developed for the production of uniformly sized droplets of tunable size.[10−13] In principle, membrane emulsification can produce droplets at much higher through-

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puts than can be obtained in microfludic and microchannel devices, but at the expense of a lower degree of monodispersity. However, despite the fact that there have been a large number of literature reports on the use of membrane emulsification for the production of uniformly sized emulsion droplets, a majority of these studies have been focused on surfactant-stabilized or protein-stabilized emulsions. The efforts to prepare uniform particle-stabilized emulsion droplets have been hindered greatly by the fact that no feasible methods have been developed to obtain a very narrow distribution. Very little research has succeeded in preparing uniform emulsion droplets stabilized by particles. For example, Giermanska-Kahn et al. have reported the preparation of uniform Pickering emulsions from the size-fractioned surfactant-stabilized emulsions,[14] where the surfactant molecules were gradually removed by dialysis in the presence of silica or polystyrene particles. Recently, Biggs et al. reported using rotating membrane emulsification technique and crossflow membrane emulsification to prepare silica-stabilized emulsions in an attempt to gain better control over the droplet size distribution.[15,16] Stable Pickering emulsions were produced but with coefficients of variation of as large as 70%, and it can be reduced to over 30% under optimized conditions. In addition, droplet diameters below 100 μm could not be achieved. Thompson et al. used stirred cell membrane emulsification to prepare O/W Pickering emulsions stabilized by functionalized polystyrene solid particles. Droplets of 44–269 μm in size and relatively narrow polydispersity can be prepared by controlling the oil flux through the membrane and stirring speed.[17] However, droplet breakup was observed at high stirring speeds, resulting in significantly more polydisperse emulsions.

In this letter, we describe for the first time the preparation of uniformly sized O/W Pickering emulsions stabilized by soft colloidal particles including carboxyl group- or amine group-functionalized microgels and Kollicoat particles using a Shirasu porous glass (SPG) membrane emulsification technique. Narrow polydispersity particle-stabilized emulsions with tunable size and a droplet diameter as small as 10 μm can be obtained by varying the pore sizes of the SPG membrane. More importantly, we show that the as-prepared emulsion droplets are excellent templates for the production of uniform colloidosomes by the sacrifice of the liquid core, which opens the door to the fabrication of functional carrier/delivery systems for active ingredient encapsulation and release.

EXPERIMENTAL SECTION

Materials. *N*-Isopropylamide (NIPAM, J&K Chemicals) was recrystallized from a toluene/*n*-hexane mixture, potassium persulfate (KPS, Riedel de Haën Chemicals) was recrystallized from water, *N*,*N*′-methylene bis(acrylamide) (MBAA, Fluka), methacrylic acid (MAA,-Sigma), Nile red (J&K Chemicals), PolyFluor 570 (Polysciences, Inc.), 2-aminoethyl methacrylate hydrochloride (FARCO Chemicals), Natreon sunflower oil (Dow Argosciences), and Genipin (Linchuan Zhixin Biotechnology, China) were used without further purification. Kollicoat MAE particles were a gift from BASF SE. DI water was used during all experiments. Tubular SPG membranes (2 cm in length and 1 cm in diameter) were purchased from SPG Technology Co. Ltd., Japan.

PNIPAM Microgel Particle Synthesis and Characterization. Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) (PNIPAM-*co*-MAA) microgel particles were synthesized using surfactant-free precipitation polymerization. Typically, 30 g of NIPAM, 0.6 g of MBAA, 1.2 g of MAA, and 0.0014 g of PolyFluor 570 were dissolved into 1200 mL of deionized water in a 2 L three-necked reactor fitted with an nitrogen bubbling inlet and outlet and a reflux condenser and stirred with a magnetic stir bar at about 400 rpm. Then the solution mixture was adjusted to pH 9.5 with sodium hydroxide solution. After the solution was stirred for 40 min at 70 °C under nitrogen bubbling, the polymerization was initiated by adding 0.3 g of KPS dissolved in 10 mL of deionized water. The reaction mixture was kept at 70 °C for 4 h. Poly(*N*-isopropylacrylamide-*co*-2-aminoethyl methacrylate hydrochloride) (PNIPAM-*co*-NH_2) microgel particles were synthesized using a similar procedure as described above and using 2-aminoethyl methacrylate hydrochloride as the comonomer to provide the amino groups. The as-obtained microgel suspension was centrifuged in repeated cycles to remove any free polymer chains.[18] The size of the microgel was measured using Coulter Counter LS 230, which is shown in Figures S1 and S2. For SEM observation, a diluted microgel suspension was dried at room temperature for 24 h and then coated with Au before imaging on a FEI Quanta 400 FEG microscope operating at 10 kV (inset of Figures S1 and S2). Kollicoat particles were used without further purification, and the Kollicoat suspension was diluted to 2 wt % using DI water from an original 30 wt % stock suspension.

Preparation of Pickering Emulsions through SPG Membrane Emulsification. The setup of the SPG membrane emulsification is shown in Figure 1. The infusion rate of the dispersed phase was precisely controlled with a peristaltic pump (PHD 2000 Infusion, Harvard Apparatus) at 2 mL/h. The stirring rate of the magnetic stirrer (coated with PTFE,13 mm in length and 3 mm in diameter, PTFE Labware) was controlled by a magnetic plate (Colorsquid, IKA Instruments) at 400 rpm. The continuous phase containing 2 wt % microgels or 2% Kollicoat was 60 mL in a 100 mL beaker. The operation parameters are the same for all of the experiments. For the continuous phase containing Genipin, the cross-linker was dissolved at a concentration of 2 wt % in the oil phase before emulsification.

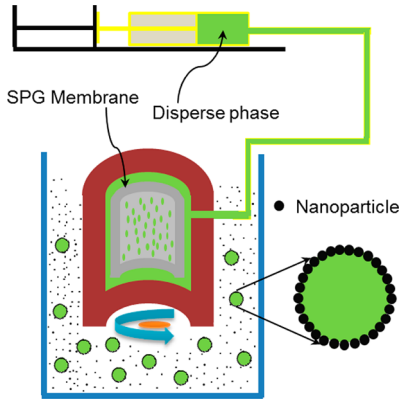

Figure 1. Schematic depiction of the Shirasu porous glass (SPG) membrane emulsification process in the production of uniform Pickering emulsions using soft particles as stabilizers.

Characterization of Emulsion Droplets by CLSM. The confocal microscopy images were taken on a Nikon Eclipse Ti inverted microscope (Nikon, Japan). A 543 nm laser was used to excite the fluorescent microgel particles and Nile molecules. An oil-immersion objective (×60 NA = 1.49) was used to view the samples. The monodisperse emulsions were placed on the cover slides (thickness ≈ 170 μm), and a series of x/y layers were scanned. The size of the emulsion droplets was measured using an EZ-C1 viewer (Nikon, Japan), and an average size and standard deviation were determined by measuring more than 200 droplets from a series of images.

Colloidosome Preparation Templated from PNIPAM-NH_2 Microgel Particles. The as-prepared emulsion droplets stabilized by PNIPAM-*co*-NH_2 microgel particles from the SPG membrane were gently stirred for at least 48 h to allow the full cross-linking of the emulsion droplets at the interface. The oil phase of the emulsion droplets then was removed by repeatedly washing using ethanol. For SEM observation, the colloidosome sample was dried at room

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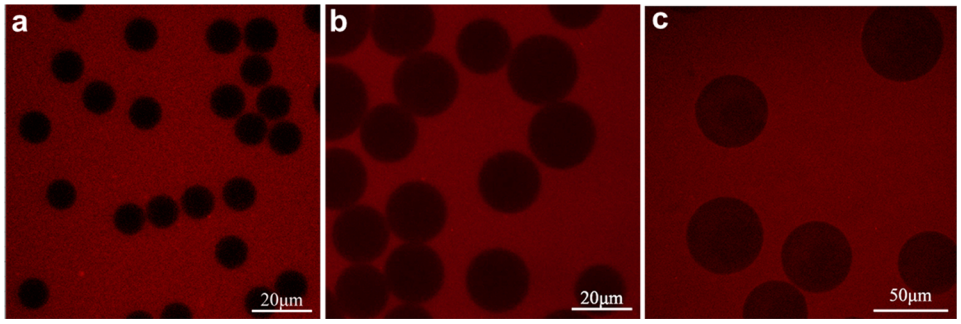

Figure 2. CLSM images of sunflower oil-in-water (O/W) emulsions prepared from the SPG membrane emulsification using different membrane pore sizes. The pore sizes of the membrane are (a) 2.5, (b) 5.2, and (c) 9.2 μm. The pH of the microgel suspension was 5.7, and PNIPAM-*co*-MAA microgels were labeled with rhodamine B molecules (aqueous phase).

temperature for 24 h and then coated with Au before imaging on a FEI Quanta 400 FEG microscope operating at 20 kV.

RESULTS AND DISCUSSION

SPG membrane emulsification was first developed by Nakashima et al. in the late 1980s[19] and has been widely investigated for preparing monodisperse emulsions and microspheres.[20−24] However, earlier work on SPG membrane emulsification has dealt with the production of surfactant-stabilized emulsions or protein-stabilized emulsions.[25,26] In this work we are exploring the use of this technique to produce uniform emulsions stabilized by colloidal particles. Soft particles, PNIPAM-*co*-MAA microgels, were first utilized as stabilizers. Note that a few years ago these microgels started to be studied as emulsion stabilizers and became examples of responsive emulsions.[6,27] The synthesis and characterization of the PNIPAM-based microgels have been described in many previous publications (Figure S1, Supporting Information). As shown in Figure 1, the emulsions were prepared by injecting a pure dispersed phase, in this case, sunflower oil, through the membrane device into the vessel containing the continuous phase using a peristaltic pump at a constant rate. Fine droplets were produced directly at the membrane/continuous phase interface and would be detached by shear force generated by stirring at a controlled rate. The rapid adsorption of microgel particles from the continuous phase and densely packed at the oil−water interface provides an elastic shell to protect against droplet coalescence, resulting in the production of size-controlled low-polydispersity emulsions.

Figures 2 and 2S (Supporting Information) shows a series of uniform O/W Pickering emulsion droplets stabilized by PNIPAM-*co*-MAA microgels by varying the pore sizes of the membrane. The microgel particles were labeled with rhodamine B and would emit red fluorescence under 543 nm laser excitation. The confocal images show that using SPG membrane emulsification allows very narrow droplet size distributions to be obtained. In addition, the Pickering emulsions reported herein are more uniform compared to those prepared by Manga et al. and Thompson et al. using either rotating membrane or stirred cell membrane emulsification techniques. On the other hand, it has been well reported that the size of the emulsion droplets is dependent on the pore size of the SPG membrane, and the emulsion droplet size is normally 3−9 times larger than that of the pore.[28] By keeping other parameters of the membrane emulsification the same and increasing the pore size from 2.5 to 9.2 μm, we show in Figure 2 that the emulsion droplet size has increased from about 10 ± 0.5 μm to about 50 ± 5.3 μm with narrow polydispersity. The CV values of the emulsion droplets are summarized in Table 1,

Table 1. Influence of Membrane Pore Size on the Size and Size Distribution of Emulsion Droplets

pore size/μm	diameter/μm	standard deviation/μm	CV of droplets/%
2.5	10.1	0.5	5
5.2	19.5	1.3	6.7
9.2	50.9	5.3	10.4

and the monodispersity is greatly enhanced compared to that of previously particle-stabilized emulsions prepared from membrane emulsification. Therefore, this technique also enables the systemic variation of the mean droplet diameter since SPG membranes with a wide range of pore sizes are available.

We then evaluate the SPG membrane emulsification for the preparation of uniform O/W Pickering emulsions by using commercially available Kollicoat particles as stabilizers. Kollicoat particles are pH-responsive nanoparticles which contain a copolymer of methacrylic acid/ethyl acrylate. This copolymer is commonly used in the pharmaceutical field to protect active ingredients against the harsh acidic environment in the stomach by delaying their release until they reach the milder environment of the intestines. At pH 5.0, the formulated particles are stable, but they will dissolve readily when the pH is increased to over 6.5. Figure 3 shows that by employing these pH-sensitive Kollicoat particles as stabilizers, uniform Pickering emulsion droplets with a size of around 8.9 ± 1.1 μm can be readily prepared from SPG membrane emulsification. As expected, when the pH was increased to 7.0, the adsorbed Kollicoat particles dissolved at the oil−water interface, the emulsion droplets were destabilized, and coalescence took place (Figure 3b). The unique properties of the emulsions stabilized by Kollicoat particles thus satisfy typical demands by controlled release applications with regard to cargo retention and triggered release. It is desirable to note that by using a particle similar to the stabilizer, Miguel et al. has prepared colloidosomes and investigated their permeability control under pH-triggered release.[29,30] The improvement in the monodispersity of the emulsion droplets will make them much more commercially attractive for the encapsulation of active pharmaceutical and health ingredients since practical and theoretical evaluations, such as the release rate, will become simple and precise if the produced colloidosomes are uniform in size.

Having investigated the versatility of the SPG membrane emulsification in the preparation of uniform particle-stabilized Pickering emulsions, we prepared the uniform emulsions

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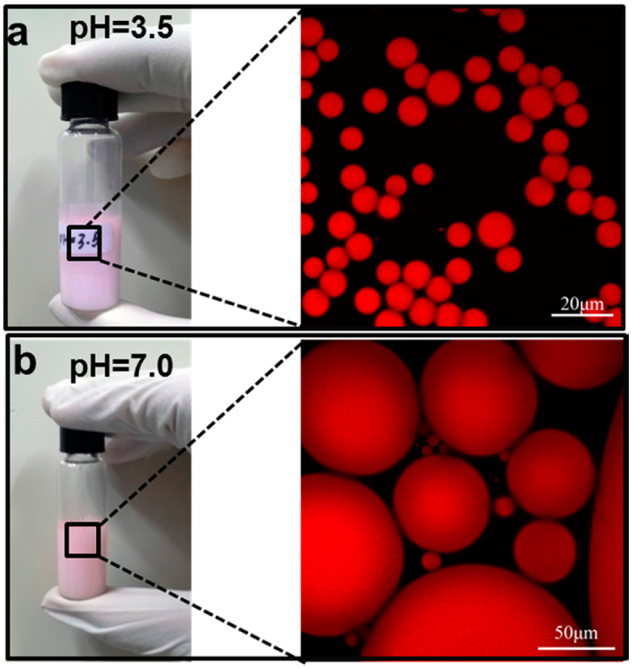

Figure 3. CLSM images of uniform sunflower oil-in-water Pickering emulsions stabilized by pH-sensitive Kollicoat particles. The oil phase was labeled with Nile red.

stabilized by amine-functionalized microgel particles. By dissolving 2 wt % Genipin, a mild cross-linker in the disperse oil phase, the microgel particles adsorbed at the interface can be successfully cross-linked at the interface. Figure 4a,c shows confocal images of emulsion droplets prepared from SPG membrane emulsification. The oil phase was labeled with Nile red, which showed red fluorescence under 543 nm excitation. Figure 4b,d shows the structure of the colloidosomes templated from the emulsion droplets. The internal oil phase was removed by repeated washing of the emulsion using ethanol. The advantage of employing uniform emulsion droplets as templates in the preparation of colloidosomes is that the size distribution can be controlled, which is important for the controlled release of active ingredients from colloidosomes.

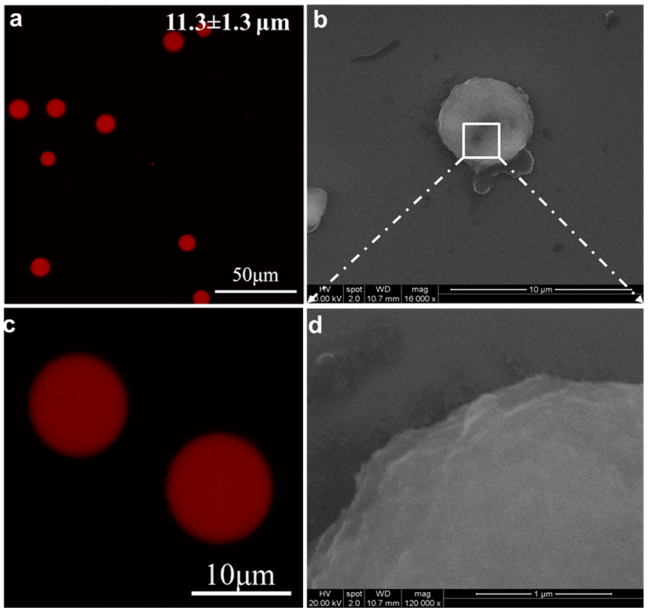

Figure 4. (a, c) CLSM images of the monodisperse sunflower oil-in-water emulsion droplets stabilized by PNIPAM-*co*-NH_2 soft microgel particles. (b, d) SEM images of the colloidosomes after drying at room temperature in air. The oil phase was labeled with Nile red.

CONCLUSIONS

This work has well demonstrated that the SPG membrane emulsification technique can be utilized in the production of uniform Pickering emulsions. The monodispersity of the emulsion droplets has been greatly improved compared to that of conventional homogenization, and the efficiency of SPG membrane emulsification is obviously much higher than that of microfluidic devices. The size of the resultant emulsion droplets can be well controlled from about 10 to 50 μm with a CV of between 5 and 15% by varying the pore size of the membrane. Additionally, we showed that the Kollicoat particle-stabilized emulsions can be easily destabilized by increasing the pH values which satisfy typical demands by controlled-release applications. For the emulsion stabilized by PNIPAM-*co*-NH_2 microgel particles, interfacially assembled particles can be cross-linked into a robust particle shell and can be subsequently dried to colloidosomes. Therefore, the as-prepared emulsion droplets are excellent templates for the production of monodisperse colloidosomes/microcapsules, which opens the door to exploring potential applications in the encapsulation of active pharmaceutical and health ingredients where the delivery of an exact amount is crucial.

ASSOCIATED CONTENT

Supporting Information

Characterization results of the microgel particles and additional CLSM images of the microgel-stabilized emulsions. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: ghma@home.ipe.ac.cn.
*E-mail: tongai@cuhk.edu.hk.

Notes

The authors declare no competing financial interest.

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