

Making Non-aqueous High Internal Phase Pickering Emulsions: Influence of Added Polymer and Selective Drying

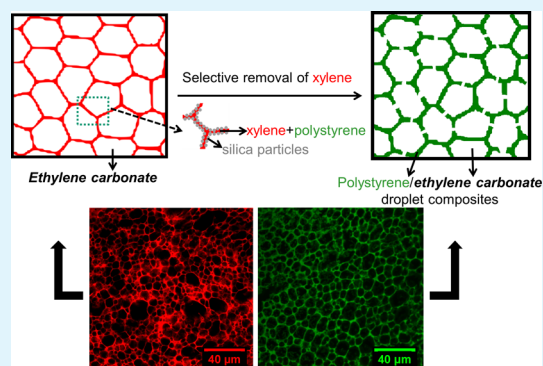
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S Supporting Information

ABSTRACT: We report the first example of a non-aqueous (oil-in-oil) Pickering high internal phase emulsion (HIPE) stabilized by chemically modified fumed silica. In this case, a 75 vol % ethylene carbonate (EC)-rich internal phase is emulsified in 25 vol % *p*-xylene (xylene)-rich continuous phase using interfacial nanoparticles. It is revealed that no phase inversion takes place during the HIPE formation process when using the appropriate wettability of solid particles. Incorporating polystyrene (PS) into xylene enables one-step formation of PS-filled HIPEs in place of a multi-step polymerization of the continuous phase. We observe that the size of droplets changes with the addition of PS, and we associate this with the change in the viscosity of the continuous xylene-rich phase. Drying the pure HIPE results in the selective removal of xylene and coalescence of EC-rich droplets. With the PS in the xylene-rich continuous phase, we show that EC-rich droplets can be retained even though the xylene is evaporated off, and a new semi-solid composite containing both liquid phase and solid phase is formed via this non-aqueous Pickering-HIPE template.

KEYWORDS: Pickering emulsions, polymer composites, confocal microscopy



1. INTRODUCTION

Pickering emulsions are a class of three-component soft matter: solid particles stabilize the interface between two liquid phases.¹ They make a versatile platform for assembling multi-phase composite materials for advanced applications. One of the success stories is making highly porous materials from high internal phase (Pickering) emulsions (Pickering-HIPEs), which are defined to have a minimum internal phase volume fraction of 0.74.^{2,3} Fundamental studies indicate that the formation of Pickering-HIPEs relies on the surface chemistry of solid particles and the emulsification approach.^{4–8} Solid particles need to be trapped at liquid–liquid interface and must be preferentially wet by the minority phase, leading to droplets of the majority phase. Alternatively, squeezing w/o Pickering emulsions into biliquid foams by centrifugal compression is also a successfully route to Pickering-HIPEs.⁹ To the best of our knowledge, immiscible water/oil pairs have exclusively been used to prepare Pickering-HIPEs. As an important type of microreactor, non-aqueous HIPEs are increasingly required to carry out water-sensitive or high temperature reactions, but available choices are limited so far.¹⁰ For the non-Pickering case, Cameron and Sherrington reported a triblock polymer-stabilized oil-in-oil (o/o) HIPE with a non-polar organic solvent (petroleum) as the internal phase dispersed in various polar organic solvents (formamide, *N,N'*-dimethylformamide and dimethyl sulfoxide).¹¹ Shirshova et al. reported another example of surfactant-stabilized non-aqueous HIPE containing the droplet phase of an ionic liquid stabilized in a mixture of

apolar monomers and crosslinkers.¹² Further to this work, researchers from the same group recently produced a similar surfactant-stabilized non-aqueous HIPE containing cyclic carbonate electrolytes as the internal phase.¹³ In this paper, we report for the first time an o/o Pickering-HIPE based on a pair of partially miscible organic solvents, ethylene carbonate (EC) and *p*-xylene (xylene).¹⁴ We find that chemically modified fumed silica can be utilized to stabilize this o/o Pickering-HIPE with EC-rich internal phase in xylene-rich continuous phase.

Post-processing is an essential step in converting soft Pickering emulsions to hard materials, this generally includes solidifying the continuous phases using crosslinked polymers and removing both the dispersed and continuous phases to form pores in a polymer matrix. The formation of crosslinked polymer is achievable by polymerization of monomer (with crosslinkers) used as the continuous phase¹⁵ or dissolved in the continuous phase.¹⁶ However, these strategies are non-ideal for oil-in-oil systems. For instance, we observe non-selective partitioning of acrylates (polar) and styrene (apolar) monomers in the mixture of 75 vol % EC-rich and 25 vol % xylene-rich phase in our preliminary experiments. Here, we are strongly motivated to introduce thermoplastic polystyrene (PS) directly into our HIPEs because PS is only soluble in xylene. This is conceptually simple but practically challenging:

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polymers are much more viscous than monomers, and the dispersal of polymers in the continuous phase becomes difficult without any mechanical agitation. Furthermore, concern arises over the stabilization of the emulsion when mechanical agitation is applied. Once PS filled HIPEs are formed, the only requirement for solidification is the removal of xylene because PS is a thermoplastic polymer. Removing a single liquid from a HIPE is another result of our work (i.e., how to stabilize EC-rich droplets without a liquid continuous phase). This paper will describe our technical strategy and will also present the understanding developed along the way. A semi-solid foam-like structure is created to contain EC droplet phase stabilized in a PS matrix once the xylene has been removed by drying. Designing this composite structure was, in part, driven by our interests in developing semi-solid electrolytes for rechargeable batteries as it is well-known that EC is a very common constituent used in the liquid electrolyte. Our findings here provide a novel route to creating an electrolyte within a solid matrix.

2. EXPERIMENTAL SECTIONS

Materials. EC and xylene were purchased from Sigma-Aldrich (U.K.) and used as received. The chemicals for modifying silica particles were also from Sigma-Aldrich (U.K.) including hexamethyldisilazane (HMDS) and ammonia solution (35 wt %). Hydrophobic fumed silica particles (HDK H30) were supplied by Wacker-Chemie, which has 50 wt % hydroxyl groups converted to methyl groups. The particle diameter of this fumed silica ranges between 5 and 30 nm (Supporting Information Figure S1). Related fumed silica particles with different percentages (32%, 42%, 50%, 62%, 70%, 88%, and 100%) of hydroxyl group were a gift from Prof. Binks. Polystyrene (PS, ICORENE@N6404) powders were kindly provided by ICO Ltd (U.K.). It is a general purpose PS grade with a melt mass flow rate (200°C/5.0 g) of 21 g/10 min (manufacturer's data sheet). Tensile stress (break), tensile strain (break), and Charpy notched impact strength is 40 MPa, 2.0% and 10 kJ/m² respectively.

Preparation of EC/Xylene Pickering-HIPEs. H30 silica particles were chemically modified using HMDS following the procedure described below: 0.5 g H30, 0.4 g HMDS, and 2 g ammonia solution were mixed together in 15 g ethanol; the silanization process lasted for 20 h at room temperature. The HMDS-modified particles were washed several times using ethanol, and the wet particles were dried at 50 °C for 24 h before use. To make an EC/xylene Pickering-HIPE, the EC and HMDS-modified particles were mixed at 60 °C and sonicated using an ultrasound probe (VCX 500, Sonics and Materials Inc., Newtown U.S.A.) for 30 s at 20% maximum tip oscillation amplitude. After adding xylene, the mixture was warmed up to 35 °C, and then mixed for 5 s on a Vortex mixer (Fisons). The operation temperature was kept above 35 °C in order to avoid the solidification of EC with a melting point of 35–38 °C. Finally, a HIPE resulted with 75 vol % EC-rich droplets in 25 vol % xylene-rich continuous phase. The liquid–liquid phase diagram of EC-xylene system from ref 14 was used to calculate the volume fraction of EC-rich phase. For example, mixing 58 vol % (72 mol %) EC and 42 vol % (28 mol %) xylene (A1 in Figure 1) at 35 °C generates 75 vol % EC-rich phase and 25 vol % xylene-rich phase (A2 in Figure 1).

Preparation of PS-EC Droplet Composites. Wet PS-HIPE composites were formed by filling PS into the HIPEs, which followed the procedure as described for the pure HIPEs without PS. The only difference is PS/xylene solution was used to replace xylene in the procedure. PS(5 wt %)-HIPE and PS(10 wt %)-HIPE denoted the sample with 5 and 10 wt % pre-dissolved in xylene, respectively. The concentration of PS (e.g. 5 and 10 wt %) is relative to the total mass of xylene. The PS-EC droplet composites were made by evaporating xylene from the wet PS-HIPE composites at 65 °C on a hot stage.

Characterization. The imaging was performed by confocal microscopy using a Zeiss Observer.Z1 inverted microscope in

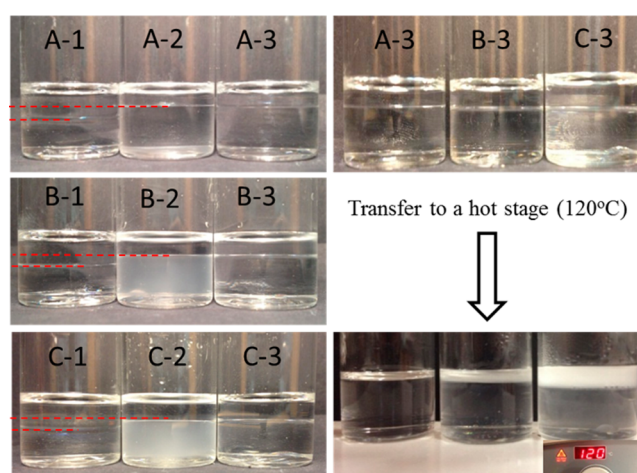


Figure 1. Showing the effect of PS on liquid exchange after mixing 58 vol % EC and 42 vol % xylene without silica particles. A-1, B-1, C-1 denotes to the sample with 58 vol % EC and 42 vol % xylene in which 0, 5, and 20 wt % PS is pre-dissolved in xylene, respectively. After mixing, A-2 and A-3 is labelled for the sample left for 1 h and 24 h, respectively. This labelling rule is also shared by sample B and C.

conjunction with a Zeiss LSM 700 scan head and a 20 × 0.4 NA air objective or a 40 × 1.3 oil objective. The fluorescent dye, Nile Red, was added to the xylene-rich phase and excited with a 488 nm laser line. Though we observed partitioning of Nile Red into both EC and xylene-rich phases, careful selection of emission filters allowed separate imaging of the xylene-rich phase (red region in Figure 2a). Alternatively, anthracene-labelled PS was used as fluorescent dye to

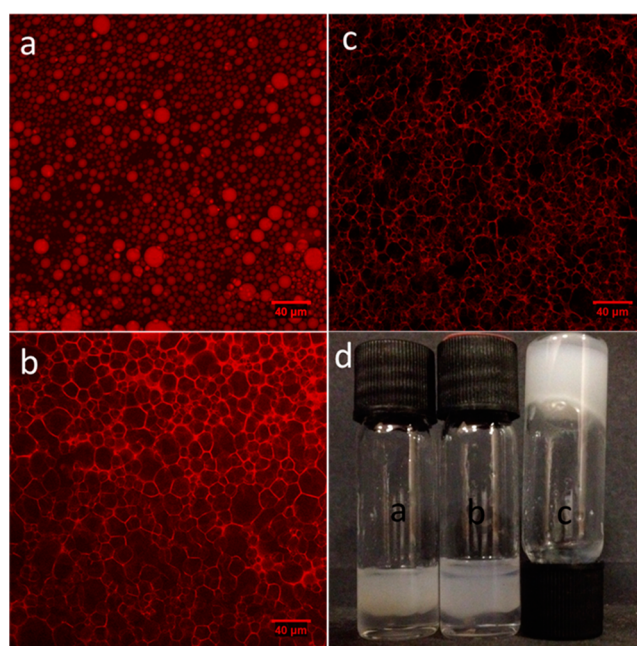


Figure 2. (a) Confocal image of the sample made by emulsifying 58 vol % EC and 42 vol % xylene with 0.9 vol % H30 silica particles, indicating that xylene-rich droplets (red region) are produced; (b) EC-rich droplets are formed in xylene-rich continuous phase (red region) when 0.9 vol % HMDS-modified H30 silica particles is used for the same liquid formulation of the sample (a); (c) confocal image of a foam-like structure containing EC-rich droplets stabilized by 1.8 vol % HMDS-modified H30 silica particles; (d) sample of parts a, b, and c, in macroscopic scale without adding dye. Note that Nile red is used as the dye to label the xylene-rich phase.

label PS phase, which was excited using a 406 nm laser line in dried PS-EC droplet composites. Wet and dried samples were placed between a glass substrate and cover slide for imaging. Drying wet PS-HIPE composites manually spread on a glass substrate was carried out on a hot stage (65°C) and weight loss was recorded every 10 min.

3. RESULTS AND DISCUSSION

W/o or o/w Pickering-HIPEs have been widely investigated; more broadly, these can be stabilized by mixtures of organic surfactants and solid particles. Whereas catastrophic inversion rarely takes place in surfactant-stabilized HIPEs, it is commonly observed in Pickering-HIPEs when the volume fraction of internal phase reaches a threshold which is determined in part by the wettability of the particles.^{17,8} This is because w/o and o/w Pickering-HIPEs can be stabilized by the same type of particles. Very recently, the relationship between w/o Pickering-HIPEs and catastrophic inversion has been understood from kinetic point of view, which indicates that catastrophic inversion is sometimes avoidable with appropriate emulsification approaches.⁸ o/o Pickering-HIPEs preparation presents even more stringent demands, in particular, because we require a robust template for post-processing. The first priority here is to find the right particles for the EC/xylene liquid pair. Fumed silica is a readily available commercial particle. Preliminary experiments were carried out to test a range of these particles with different fractions of methyl groups, which suggested that silica coated with hydroxyl or methyl groups is preferentially wet by EC and xylene, respectively. We found that the particles (H30) with 50 wt % hydroxyl groups converted to methyl groups are suitable for stabilizing xylene-in-EC Pickering emulsions. However, we failed to produce an EC/xylene Pickering-HIPE with the majority EC phase inverted into droplets using H30 directly although we tried different H30 concentrations and shearing protocols. We conclude that the interfacial silica particles need to be more hydrophobic so as to have higher affinity for the xylene-rich phase. An appropriate amount of HMDS (as indicated in the Experimental Section) was used to tune the surface chemistry of H30 silica by introducing more methyl groups to the silica surface. Supporting Information Figure S2 shows the contact angle of a water droplet on a glass slide with different silica coatings, indicating that HMDS-modified H30 is substantially more hydrophobic than pristine H30 and slightly more hydrophobic than the 32% hydroxyl group particles. The confocal image in Figure 2a shows that xylene-rich droplets (red region) are formed when 0.9 vol % H30 silica particles are added. The volume fraction of the particles is calculated with respect to the total volume of EC and xylene. The creaming of these droplets is observed from the vial (a) in Figure 2d because xylene is less dense than EC. The vial (b) in Figure 2d shows a similar “creaming” phenomenon with an identical amount of HMDS-modified H30 silica particles. However, the confocal image in Figure 2b demonstrates that a high concentration of EC-rich droplets is formed in the xylene-rich continuous phase (red region). Without sufficient silica particles, there is a surplus EC-rich phase at the bottom of the vial (b) as EC-rich phase ($\rho_{\text{EC}} = 1.32 \text{ g/cm}^3$) is denser than xylene-rich phase ($\rho_{\text{xylene}} = 0.89 \text{ g/cm}^3$). When the concentration of HMDS-modified particles is doubled, the sample in vial (c) shows that an emulsion gel is formed in a single step and the confocal image in Figure 2c confirms that EC-rich droplets (75 vol %) are closely packed together and a foam-like structure is generated. Therefore, the formation mechanism of

our o/o Pickering-HIPEs could be that a low concentration of silica particles produces a small quantity of EC-rich droplets in the xylene-rich phase with surplus EC-rich phase, and all of the EC-rich phase is homogeneously converted to droplets in the minority xylene-rich phase with sufficient silica particles. We believe that catastrophic inversion is avoided because the HMDS-modified particles are more easily wet by the xylene-rich phase. HIPE formation is only relevant at high particle concentration. The key step involved in post-processing HIPE templates is introducing polymer into the continuous phase. Following the protocol established in w/o systems,³ we attempted to introduce styrene into the xylene-rich phase followed by polymerization of styrene into polystyrene. However, this approach was not successful here as we find that styrene is able to partition into both phases. Therefore, our focus moved to dissolving PS directly into the xylene-rich phase. Here we take advantage of the fact that PS is not soluble in EC-rich phase. It can be seen from Figure 1 that the liquid exchange of xylene and EC is independent of dissolved PS in xylene although PS is not compatible with EC. The pictures of B-2 and C-2 are taken 1 h after mixing and show that EC-rich phase becomes non-transparent in comparison with A-2, which is ascribed to the formation of some xylene-rich droplets. After 24 h, we observe that, as shown in B-3 and C-3, these droplets are not stable and the EC-rich phase becomes transparent. This indicates that PS does not act as an organic surfactant for these droplet interfaces. At 120 °C, the xylene and EC are fully miscible in the absence of PS. In the presence of PS in xylene, we can see that xylene is still miscible with EC, but PS separates from xylene and emerges on the top indicating PS is not compatible with EC-rich phase. The confocal images in Figure 3 demonstrate that the addition of 5 or 10 wt % PS does not result in catastrophic inversion of the HIPE, and the wet PS-HIPE composites are dominated by a high volume fraction of EC-rich droplets. PS should be located in the xylene-rich phase

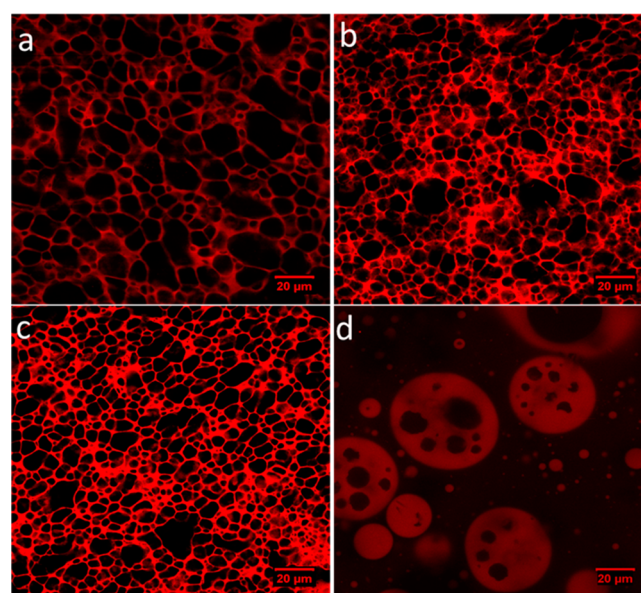


Figure 3. Showing the confocal images of emulsified samples with the incorporation of (a) 0 wt % PS, (b) 5 wt % PS, (c) 10 wt % PS, and (d) 20 wt % PS into xylene prior emulsification, respectively, all of which contain 75 vol % EC-rich and 25 vol % xylene-rich liquid phase with 1.8 vol % HMDS-modified H30 silica particles. Red region (Nile Red) indicates the xylene-rich phase or xylene-rich phase with PS.

as it is not compatible with EC-rich phase. It also can be observed from Figure 3 that the size of EC-rich droplets is slightly smaller when xylene is filled with PS in the first place. Droplets with size of 10-20 μm dominate the original HIPE whereas the PS-filled HIPEs has droplets ranging between 5 and 10 μm . The viscosity of the xylene phase increases after the PS has been dissolved (Supporting Information Figure S3). A slight increase in the viscosity of the continuous phase increases the shearing force in the mixture, which is responsible for reducing the size of the droplets.¹⁸ When the concentration of PS in xylene reaches 20 wt %, we observe in Figure 3d that multiple xylene-rich droplets are formed with EC-rich cores instead of a foam-like structure with pure EC-rich droplets. The formation of EC-rich cores is due to the wettability of silica particles with respect to the xylene phase. However, the high viscosity of the xylene phase appears to push the system towards an inversion albeit with some remaining EC-rich droplets.

Drying generally causes the removal of both liquid phases from Pickering emulsions to form porous structures.¹⁹ It is difficult to retain the droplets after selectively removing the continuous phase unless solid particles at liquid interfaces strongly interact with each other and form a network to withstand the destabilization of the droplets.^{20,21} Here, we demonstrate a new route to remove the continuous liquid phase from a non-aqueous Pickering emulsion. The evaporation model of o/w Pickering emulsions has been proposed including two key points:²² (1) the evaporation of the continuous water phase is identical to that of pure water, and a thin layer of water is formed on the surface of emulsions; (2) oil needs to cross this thin layer to be evaporated, and the evaporation rate is mainly dependent on the oil solubility in the water layer and the thickness of the water layer. In EC/xylene Pickering-HIPEs, both liquids co-exist in the droplet and continuous phase, and this is also true when PS is incorporated. Several studies on the evaporation of a binary liquid mixture reveal that the evaporation of individual liquids is not affected by the co-existing liquid, and the fast evaporating component leaves the mixture first. The evaporation rate of the more volatile component is dependent on its concentration in the mixture.^{23,24} The boiling points of EC and xylene are 260 $^{\circ}\text{C}$ and 138 $^{\circ}\text{C}$, respectively, and the evaporation rate of xylene is much faster than that of EC due to their relative vapor pressures. That is, the vapor pressure of xylene is around 850 and 58 times of that of EC at 37 $^{\circ}\text{C}$ and 98 $^{\circ}\text{C}$, respectively.^{25,26} According to the evaporation model and vapor pressures of these two liquids, xylene in the continuous phase evaporates first accompanied by very slow evaporation of EC, and xylene in the droplet phase evaporates faster than EC as well because its higher vapor pressure and solubility in xylene-rich thin film formed in the first stage. This significant difference in evaporating rate allows us to selectively remove xylene from the Pickering-HIPEs consisting of EC-rich droplets. We observe that EC-rich droplets coalesce into a continuous phase when the pure HIPE (no PS) is dried. However, the incorporation of PS into the xylene-rich continuous phase can ensure the integrity of EC-rich droplets after xylene is taken off. The weight loss profile (Figure 4) is measured for drying ~ 0.4 g wet PS(10 wt %)-HIPE composite spread on a glass slide at 65 $^{\circ}\text{C}$. It exhibits a sharp loss of ~ 30 wt % in first 20 min followed by much slower loss in the next 4 h, and weight loss in both stages varies almost linearly with drying time. As the evaporation of xylene is faster than EC, the initial weight loss in

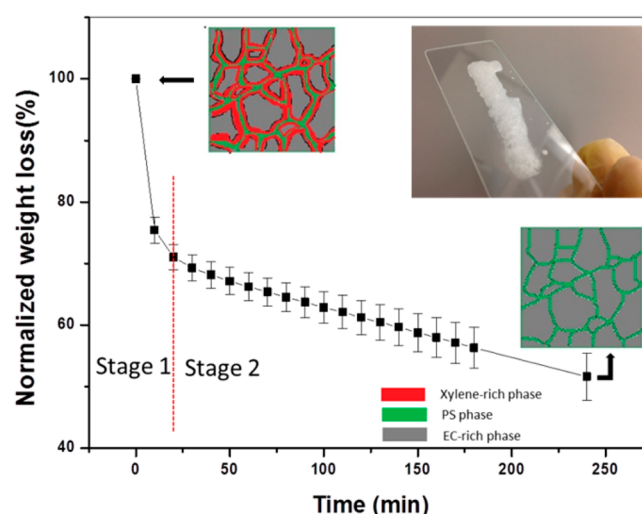


Figure 4. Showing a profile of normalized weight loss against drying time at 65 $^{\circ}\text{C}$ for wet PS(10 wt %)-HIPE composite. The cartoons illustrate the wet PS-HIPE composite before and after drying. A piece of dried sample on a glass slide is demonstrated inside the graph.

the first stage is dominated by the loss of xylene, which nearly matches with original xylene percentage of ~ 29 wt % in the wet PS-HIPE composite. The second stage is mainly attributed to the loss of EC with lower evaporation rate. It confirms that xylene can be selectively removed from the wet PS-HIPE composite. The photo inset to the graph shows that the dried material cannot flow on a glass slide and exhibits semi-solid characteristics. In Figure 5, parts a and c show the confocal image of the PS-EC droplet composite after removing xylene from the PS(5 wt %)-HIPE and PS(10 wt %)-HIPE composite, respectively. Optical microscopy images (b and d) are recorded

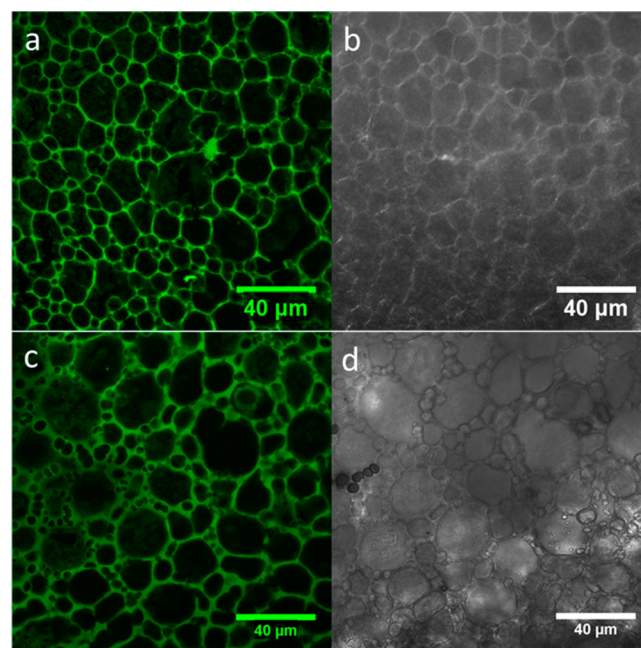


Figure 5. (a and c) Confocal image of the PS-EC droplet composite after removing xylene from the PS(5 wt %)-HIPE and PS(10 wt %)-HIPE composite, respectively. (b and d) Bright-field microscopic counterpart of parts a and c, respectively. PS continuous phase (green region) is illuminated by adding anthracene labelled PS.

simultaneously. It can be seen that closely packed EC-droplets survive in the PS continuous phase (green region) that is doped with anthracene-labelled PS. It has been demonstrated that PS does not behave as a surfactant for the stabilization of the interfaces. When xylene is evaporated, PS is solidified to lock the droplets in place, and a new liquid-solid interface is created to replace the liquid-liquid interface.

4. CONCLUSIONS

This study demonstrates the first example of an o/o Pickering-HIPE, which has 75 vol % EC-rich droplets stabilized in 25 vol % xylene-rich continuous phase. The solid stabilizer is partially hydrophobic fumed silica, which may be adaptable to other polar and apolar liquid pairs. It is interesting to see that catastrophic inversion can be avoided due to the wettability of the silica particles. Post-processing of HIPEs follows a new route in which PS is pre-dissolved in xylene and joins in the formation of the HIPE in one-step. The addition of PS increases the viscosity of the xylene phase and consequently influences the droplet size of the HIPE. However, catastrophic inversion results from overloading PS into xylene. A high volume fraction of EC-rich droplets is arrested in the PS matrix after the removal of xylene. This is a new composite structure, which is different from the highly porous structure (polymer-air composites) commonly created via HIPE templates. This work provides a novel route for solidifying non-aqueous Pickering-HIPEs, which could open a new avenue for making advanced composite materials.

■ ASSOCIATED CONTENT

Supporting Information

TEM image of H30 silica particles, the effect of silica coatings on the contact angle of a water droplet (5 μ L) on a glass slide, and the effect of loaded PS on the viscosity of xylene at room temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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