# Interconnected Macroporous Polymers Synthesized from Silica Particle Stabilized High Internal Phase Emulsions

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Ⓢ *Supporting Information*

**ABSTRACT:** *n*-Octadecyltrimethoxysilane (ODS)-modified silica particles were used as sole Pickering stabilizer to prepare water-in-oil Pickering high internal phase emulsions (HIPEs) with an internal phase volume of 80%. After polymerization of the continuous phase of HIPEs, interconnected macroporous polymers were obtained when modified silica was initially dispersed in water to form a micelle-like structure. However, silica particles in oil phase resulted in closed-cell pores. The pore size, the pore wall morphology, and the interconnectivity of polymer foams could be adjusted finely by the grafted amounts of ODS, modified silica concentrations, and the initial location of Pickering stabilizer. The gas permeation of interconnected porous polymers increased dramatically with the increase of the hydrophobicity of silica particles from 3 to 153 mL/min.
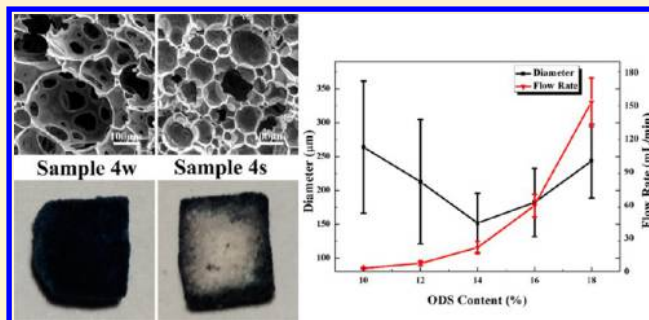
## INTRODUCTION

Porous polymers have gained considerable attention with a wide range of applications such as catalysts,[1−4] gas storage,[5,6] separation,[7] sensors,[8,9] and scaffolds in tissue engineering[10−13] due to their low density and high porosity. The porous polymers can be produced by several methods,[14−16] wherein emulsion templates have attracted great interest due to the well-defined pore structure.[14,17−21] In order to fabricate polymers with high porosity, the high internal phase emulsion (HIPE) is normally utilized as a template, which is often defined as a concentrated emulsion with a minimum internal phase volume ratio of 74%.[22] The prepared porous polymers are also termed poly-HIPEs.

Conventional HIPEs are commonly stabilized by surfactants such as Hypermer 2296,[23] sorbitan monooleate (Span 80),[24−26] poly(vinyl alcohol),[27] and trimethylammonium bromide (CTAB).[28] A large amount of expensive surfactants (5−50 vol % with respect to the continuous phase) is required to prepare stable emulsions.[24,29,30] Because these surfactants have relatively high toxicity,[31] they should be removed by post-treatment, and the high consumption of these surfactants inevitably imposes additional producing cost.[32] In addition, the applications of these porous polymers suffer from their poor mechanical properties.[22,33] Though it has been proven that nanometer- or micrometer-scale solid particles can also be used to stabilize emulsions (Pickering emulsions),[34−39] it is usually difficult to prepare Pickering HIPE because of its high internal phase volume fraction. Most attempts to stabilize HIPEs by particles failed[40,41] until Ikem et al.[42] reported the preparation of HIPEs solely stabilized by functional silica particles and the

corresponding porous polymers with porosity up to 90%. Afterward, various kinds of poly-Pickering HIPEs were synthesized using solid particles as stabilizer. Macroporous graphene oxide−polymer composites have been successfully prepared by us through graphene oxide stabilized Pickering HIPEs.[43] HIPEs can also be stabilized by titania particles,[44] iron oxide nanoparticles,[45] hydroxyapatite (HAp) nanoparticles,[46] polymer particles,[47−50] carbon nanotubes,[51] and bacterial cellulose nanofibrils.[52] Pickering HIPEs as templates to prepare porous polymers have some advantages, including a small amount of stabilizers demanding,[42,43,53] improved mechanical strength,[54] and functionalization of poly-Pickering HIPEs[45,51,55,56] due to the introduction of solid particles.

However, it should be noted that poly-Pickering HIPEs commonly have a closed-cell pore structure,[42−44,53] which leads to very low permeability. Great efforts have been made to enhance the interconnectivity of porous polymers for their applications.[23,57,58] The researchers have taken a cue from conventional HIPEs by adding surfactants into Pickering HIPEs before polymerization of the continuous phase, resulting in the formation of small pore throats. Recently, a particle−monomer coactive Pickering HIPE was presented to prepare interconnected polymer foams.[58] However, these methods are difficult to be applied widely due to the requirement of toxic surfactants or reactive Pickering stabilizer.

In this work, we have successfully fabricated interconnected macroporous polymers with well-defined pore structures from Pickering HIPEs stabilized by modified silica nanoparticles. The pore and pore throat size can be well controlled by the wettability and the amount of particles. The mechanism of pore throat formation in poly-Pickering HIPEs is also demonstrated.

## ■ EXPERIMENTAL SECTION

**Materials.** Silica hydrosol (28 nm, 40.0 wt %) was kindly supplied by Fujian Sanbang Chemical Co. (China). Styrene (99%), toluene (99%), ethanol (99%), hydrofluoric acid (HF, 40%), and hydrochloric acid (37%) were purchased from Sinopharm Chemical Reagent Co. (China). n-Octadecyltrimethoxysilane (ODS, 90%), divinylbenzene (80%), benzoyl peroxide (BPO, 99%), and Sudan black B were provided by Aladdin Chemistry Co., Ltd. Styrene and divinylbenzene were distilled under vacuum, and BPO was recrystallized before use. Deionized water was used throughout the experiments.

**Modification of Silica Particles with ODS.** The silica nanoparticles were modified by ODS in an aqueous ethanol solution. Hydrochloric acid was added to the 5 g of as-received silica hydrosol to adjust the pH to 3.0. 15 g of ethanol was then mixed with the silica hydrosol. Afterward, 0.16, 0.20, 0.24, 0.28, 0.32, 0.36, or 0.40 g of ODS was added to the aqueous ethanol solution, and the mixture was vigorously stirred at 70 °C for 3 h. The modified silica particles were washed with ethanol using a centrifugation−sonication cycle three times to remove excess ODS prior to drying at 60 °C for 24 h. The silica particles modified by various amounts of ODS were labeled as SP-$x$, where $x$ denotes the mass ratio of ODS to silica nanoparticles.

**Preparation of Pickering HIPEs.** The organic phase consists of 99 wt % styrene and 1 wt % divinylbenzene. The modified silica particles were dispersed in the oil phase or aqueous phase via sonication. The other phase was then added to the modified silica particles suspension and sonicated for 3 min. The mixtures were shaken by hand and emulsified with an FJ200-S homogenizer at 400 rpm for 3 min to form Pickering HIPEs. The compositions of emulsions are summarized in Table 1. For sample 1, when the initial

**Table 1. HIPE Recipes**

| sample | particles concn[a] (wt %) | mass ratio of ODS to silica particles | sample | particles concn[a] (wt %) | mass ratio of ODS to silica particles |
|---|---|---|---|---|---|
| 1 | 0.6 | 0.08 | 6 | 0.6 | 0.18 |
| 2 | 0.6 | 0.10 | 7 | 0.6 | 0.20 |
| 3 | 0.6 | 0.12 | 8 | 0.4 | 0.14 |
| 4 | 0.6 | 0.14 | 9 | 0.8 | 0.14 |
| 5 | 0.6 | 0.16 | 10 | 1.0 | 0.14 |

[a]The concentration of silica particles is given with respect to the mass of aqueous phase.

location of particles was water, it was labeled as "sample 1w"; otherwise, it was labeled as "sample 1s". All samples had an aqueous phase volume of 80%.

**Preparation of Poly-Pickering HIPEs.** Before the preparation of Pickering HIPEs, 1 wt % BPO was dissolved in the monomer phase. Pickering HIPEs were then transferred into centrifuge tubes, sealed, and placed in a 73 °C water bath for 24 h followed by drying in a convection oven at 65 °C for 48 h. The obtained poly-Pickering HIPEs were sonicated in ethanol for 10 min and then dried in a convection oven at 60 °C for 24 h.

**Characterization.** The particle size and size distribution of the silica hydrosol and SP-0.14 dispersed in water and toluene were measured via dynamic light scattering (DLS, Malvern ZS90) at 25 °C. The concentration of the suspension was 0.1 wt %.

The original and modified silica particles were characterized using Fourier transform infrared spectroscopy (FTIR, Thermofisher Nicolet 6700). The samples were pressed into KBr pellets for FTIR measurements, and FTIR spectra were taken from 400 to 4000 cm$^{-1}$.

The amount of organic segments on the surface of silica particles was measured by thermal gravimetric analysis (TGA, PerkinElmer Pyris 1 TGA) at a heating rate of 20 °C/min from 100 to 800 °C in air.

Water contact angle measurement (CA, Dataphysics OCA 40) was used to characterize the surface hydrophobicity of the modified nanoparticles. The modified nanoparticles were dispersed in ethanol, and the suspensions were dropped onto glass slides. The silica films were then prepared by placing the glass slides at room temperature for 3 days. A water droplet was added to the surface of sample, and the static contact angle was recorded when the droplet had stopped spreading. Five measurements were performed for each sample.

Atomic force microscope (AFM) images of the particle-coated surfaces were acquired using a Mutimode 8 in the tapping mode. Before the test, the modified nanoparticles were dispersed in ethanol and then dropped onto a freshly cleaved mica plate.

TEM micrographs of SP-0.14 dispersed in water and toluene were recorded using a Tecnai G2 20 TWIN transmission electron microscope. The samples were prepared by dropping the suspensions onto the carbon-coated copper grids.

Photographs of Pickering HIPEs were taken by a Canon Ixus 850IS digital camera, and the size of the emulsion droplets was observed by an EV5680 optical microscope. Emulsion type was inferred by observing the phenomenon when a drop of emulsion was added to a volume of styrene or water.[40] The morphologies of poly-Pickering HIPEs were imaged using scanning electron microscopy (SEM, Tescan 5136MM) and field-emission scanning electron microscope (FE-SEM, Zeiss Ultra 55). The samples were fixed to substrates and sputtered with gold prior to test.

The adsorption behavior of the porous polymers was characterized by using a mixture of ethanol and deionized water (1/1, v/v) containing 0.5 wt % Sudan black B. The porous polymers were cut into specimens with the size of 1.0 × 0.7 × 0.5 cm$^3$, and the specimens were immersed into the solution of Sudan black B at 25 °C for 24 h. The permeability of the porous polymers was determined by measuring the flow rates of nitrogen through the samples under the pressure of 500 Pa. The samples were cylindrical with a length of 1.0 cm and a diameter of 1.4 cm.

## ■ RESULTS AND DISCUSSION

**Surface Modification of Silica Nanoparticles.** Hydroxyl groups on the surface of silica nanoparticles make them hydrophilic and disperse well in water.[34] The size of as-received silica nanoparticles was characterized using DLS measurement, as shown in Figure S1. The silica hydrosol shows a narrow distribution with an average size of 48 nm, slightly larger than 28 nm provided by the manufacturer, which is originated from the interaction between nanoparticles and water.

It has been proven that Pickering emulsions cannot be well stabilized by solid particles with extreme hydrophilicity or hydrophobicity.[31,59] The unmodified silica nanoparticles are so hydrophilic that they cannot stabilize Pickering emulsions. In order to prepare a stable W/O emulsion, the wettability of silica particles was altered by using alkoxysilanes or chlorosilanes which contain hydrophobic organic segments.[40,60−62] Herein, ODS is used to bond covalently with the hydroxyl groups on the surface of silica particles. FTIR spectra are utilized to clarify the chemical structure of surface functionalized silica particles, as presented in Figure 1. The as-received silica nanoparticles exhibit a broad band at 3450 cm$^{-1}$ associated with hydroxyl groups and adsorbed water. The absorption peaks at 1120, 796, and 470 cm$^{-1}$ can be ascribed to the Si−O−Si network. After the surface modification using ODS, two new peaks at 2923 and 2846 cm$^{-1}$ due to CH$_2$ and CH$_3$ are clearly found, indicating successful chemical bonding.
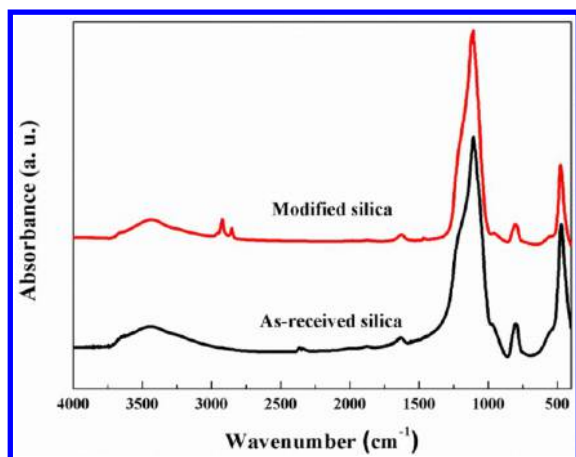
**Figure 1.** FTIR spectra of as-received and modified silica particles.

As mentioned above, the stabilization of W/O Pickering emulsions depends greatly on the hydrophobicity of solid particles. The amphiphilicity of Pickering stabilizer may be controlled by the surface functionalization of silica nanoparticles using different contents of ODS. The TGA curves of these particles are shown in Figure 2. The weight of unmodified
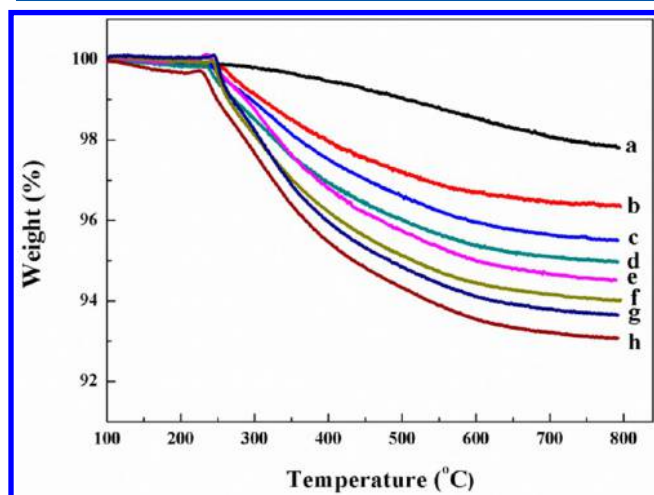


**Figure 2.** TGA curves of (a) as-received silica particles, (b) SP-0.08, (c) SP-0.10, (d) SP-0.12, (e) SP-0.14, (f) SP-0.16, (g) SP-0.18, and (h) SP-0.20.

silica particles slightly decreases from 100 to 800 °C with a mass loss of about 2.2 wt %, which is caused by the condensation of hydroxyl groups on the surface. However, a distinct weight loss is observed for modified silica particles from 250 to 700 °C. This is induced by the thermal degradation of ODS molecules. According to TGA results (listed in Table 2), it is clearly found that the amount of ODS grafted on the surface of inorganic nanoparticles increases with additive ODS content for surface modification. The average surface area of silica particles was estimated by assuming the particle size of 28 nm and the density of 2.2 g/cm$^3$. The surface coverage of particles by ODS was then calculated and summarized in Table 2. It can be found that the surface structure of solid particles is finely tuned. This is necessary for the preparation of stable W/O Pickering HIPEs and the pore structure control of the resulting porous polymers.

**Table 2. Mass Loss and Surface Coverage of As-Received and Modified Silica Particles**

| sample | TGA mass loss (%) | ODS content (%) | surface coverage ($\mu$mol/m$^2$) |
|---|---|---|---|
| SP-0 | 2.2 | | |
| SP-0.08 | 3.7 | 1.8 | 0.5 |
| SP-0.10 | 4.5 | 2.8 | 0.8 |
| SP-0.12 | 5.1 | 3.5 | 1.0 |
| SP-0.14 | 5.5 | 4.0 | 1.2 |
| SP-0.16 | 5.9 | 4.6 | 1.3 |
| SP-0.18 | 6.3 | 5.1 | 1.5 |
| SP-0.20 | 6.9 | 5.8 | 1.7 |

To further illustrate the surface nature of modified particles, the contact angle measurements were conducted by dropping water droplets on modified silica, as presented in Figure S2. The contact angle of as-received silica was also measured, but unfortunately, it was so hydrophilic that the water droplet could not stay on the slide. The contact angles of modified silica particles obviously increase with the amount of ODS grafted on the surface from 93° to 140°. As we know, the roughness of coating has a significant effect on the contact angle. AFM measurement (Figure S3 and Table S1) shows the particle-coated surfaces prepared by different modified silica particles have similar roughness. It means the variation of water contact angles among the samples is determined by the hydrophobicity of modified silica nanoparticles. As mentioned above, the contact angles of modified silica increase with the amount of ODS grafted on the surface, indicating that the particles become more and more hydrophobic. This is consistent with the TGA results. Furthermore, due to the relatively high hydrophobicity, the modified silica particles are potential to be the stabilizer for preparing W/O Pickering HIPEs.

**Pore Structure of Macroporous Polymers.** Pickering HIPEs were produced using modified silica particles with concentration of 0.6 wt % with respect to the internal phase, and the photographs of the obtained emulsions are shown in Figure 3. The initial location of particles is the dispersed phase. It is observed that phase separation takes place when SP-0.08 is employed to stabilize the Pickering HIPE from Figure 3a. The mixture immediately separates into three phases after emulsification ceased. The emulsions were then prepared with higher concentration (up to 1.0 wt %) of SP-0.08 to
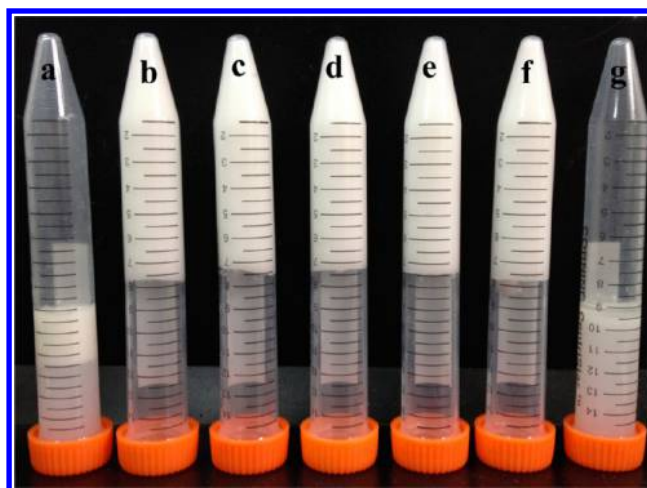


**Figure 3.** Photographs of samples 1w–7w (a–g).

identify whether silica particles were sufficient or not to stabilize the droplets while they were still unstable. The drop test shows an O/W emulsion is formed, indicating that SP-0.08 is too hydrophilic to stabilize a W/O Pickering HIPE. It is found from Figure 3b–f that Pickering HIPEs prepared by SP-0.10, SP-0.12, SP-0.14, SP-0.16, and SP-0.18 have good stability and can be inverted due to their high viscosity. According to contact angle measurements, it can be concluded that the improved hydrophobicity of modified silica helps to form stable W/O Pickering HIPEs. When SP-0.20 is used to stabilize the emulsion, the phase separation also happened (Figure 3g). The drop test shows the external phase of the emulsion layer is styrene, which is different from that of SP-0.08. It has been reported that the emulsion droplets stabilized by very hydrophilic or hydrophobic particles are extremely large and unstable to coalescence due to the low attachment energy.[31,59] Because of the high hydrophobicity of SP-0.20, the W/O emulsion is formed but quickly coalesces. Therefore, the appropriate amphiphilicity is important for solid particles as Pickering stabilizer to prepare W/O Pickering HIPEs.

The droplet sizes of obtained Pickering HIPEs were observed by an optical microscopy, as shown in Figure 4. Samples 1w
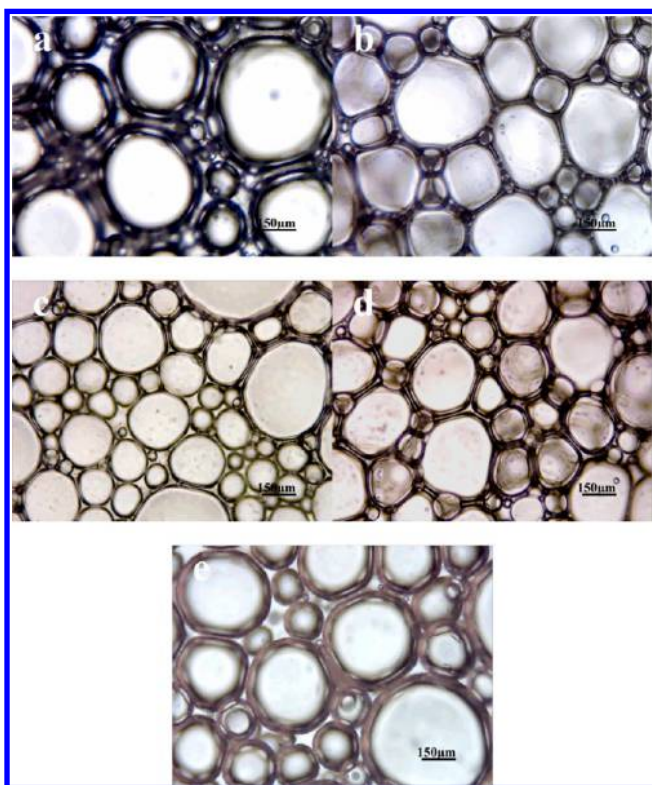


**Figure 4.** Optical microscopy images of Pickering HIPEs for samples 2w–6w (a–e).

and 7w have not been characterized due to their poor stability. SP-0.10 stabilized emulsion has very large droplets, and the size becomes smaller when more ODS molecules are grafted on the surface of silica particles. The emulsion shows minimum droplet size when SP-0.14 is employed as the stabilizer, indicating the appropriate amphiphilicity of particles. However, the emulsion droplet size becomes larger as the hydrophobicity of silica is further enhanced. It has also been reported that the droplets have a minimum size in conventional Pickering emulsions stabilized by solid particles with intermediate

hydrophobicity.[63] Therefore, despite the high viscosity of Pickering HIPEs, the evolution of the droplet size with the amphiphilicity of the stabilizer is in good agreement with conventional Pickering emulsions. It should be noted that the droplet size of Pickering HIPEs is much larger than that of the conventional Pickering emulsions, which is attributed to their high viscosity. Based on the results above, the droplet size of obtained Pickering HIPEs is considerably large and can be tuned by the amphiphilicity of solid particles.

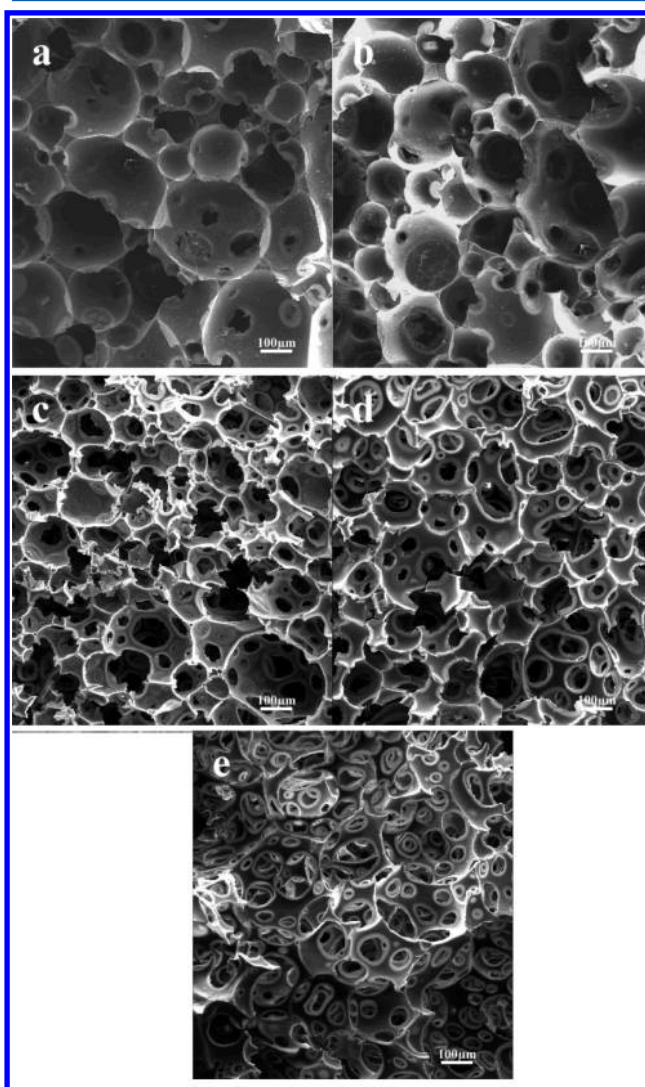After polymeration of Pickering HIPE templates, porous polymers were obtained, as shown in Figure 5. The pore size of



**Figure 5.** SEM images of poly-Pickering HIPEs for samples 2w–6w (a–e).

poly-Pickering HIPEs is similar to the initial droplet size of HIPEs due to the irreversible adsorption of particles on the interface. The porous polymers synthesized using SP-0.10 and SP-0.12 have closed-cell structure with some interconnected pores, which is consistent with other reports.[42−44,53] However, it is of interest to find that SP-0.14, SP-0.16, and SP-0.18 can be used to prepare highly interconnected macroporous polymers. To our knowledge, the HIPEs solely stabilized by particles always produce closed-cell pores.[32] While for HIPEs prepared by surfactants, the HIPEs' films separating neighboring droplets are prone to create pore throats.[23] When solid particles are

adsorbed at the interface between the oil and water phase, they cannot redisperse into the oil or water phase due to the high attachment energy. Thus, Pickering HIPEs are stable, unlikely to coalesce and the films between the droplets cannot break to form pore throats during polymerization of the continuous phase. There are only several reports about Pickering HIPEs concentrating on the formation of open-cell structure until now, and two methods have been proposed to achieve interconnected porous polymers. The introduction of the molecular surfactant into Pickering HIPEs can reduce the interfacial tension and decrease the droplet size, resulting in thinner films between the neighboring droplets.[23] This implies that the open-cell foams are more likely to form. Another effective way to produce open-cell pores is to draw the solid particles from the interface between two phases via monomer–particle reaction.[58] However, neither surfactants nor reactive particles are provided in our systems. Therefore, the formation of open-cell pores can be only related to the wettability of modified silica particles.

It has been proven that the concentration of solid particles may also affect the stability of Pickering emulsions.[43] The photographs of Pickering HIPEs stabilized by various amounts of SP-0.14 are presented in Figure S4. The emulsion with 0.4 wt % particles cannot be inverted, while the others with more Pickering stabilizers have higher viscosity to be inverted. Such result is also reported when utilizing titania particles as stabilizers.[44] When increasing the amount of particles, more interfaces can be stabilized by adsorbed particles, indicating the formation of smaller droplets. Thus, the thinner films between neighboring droplets lead to the high viscosity.[42] As expected, the droplet size of Pickering HIPEs gradually becomes smaller when more modified silica particles are introduced (Figure S5). We also polymerized the continuous phase of these Pickering HIPEs with different amounts of silica particles. All porous polymers display open-cell structures, and the sizes of pores are consistent well with the emulsion droplets (Figure 6). The influence of particle concentration on the formation of pore throats is negligible.

As discussed above, both the wettability and the amount of silica particles have a great influence on the structure of resulting porous polymers. It has been proven that the interconnected polymer foams can be obtained by using relatively hydrophobic particles initially dispersed in water. In fact, in the course of the experiment, we have found that these modified silica particles have better dispersion in oil phase than in water due to their hydrophobicity. From Figure S6, it is clearly seen that silica particles dispersed in toluene have a size below 200 nm, while the size is above 500 nm when they are in aqueous phase. It has been reported that different particle locations can lead to the changes in contact angles the particles adopt at the interface, and the phenomenon is linked to the roughness of particle surface.[59] Therefore, the same silica particles dispersed in the oil phase were also used to prepare Pickering HIPEs, as shown in Figure S7. The appearance of the products is almost the same as the samples in Figure 3, indicating that the initial particle location has no obvious effect on the formation of emulsions. After polymerization, the pore structures of polymer foams are shown in Figure 7, and closed-cell pores of these samples are found. This result is quite different from samples 2w–6w, demonstrating the particle location can obviously influence the interconnectivity of porous polymers. In addition, the pore size of these polymer foams is smaller than samples displayed in Figure 5, even if they are
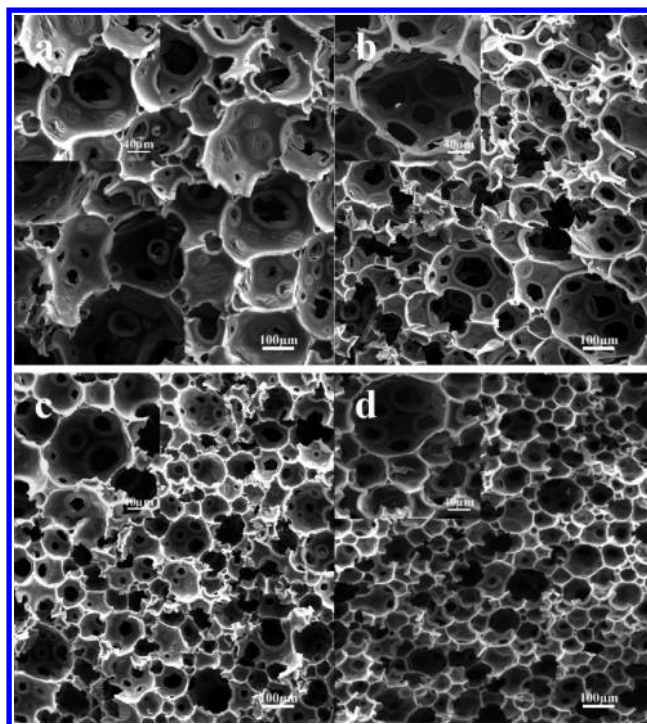


**Figure 6.** SEM images of poly-Pickering HIPEs for (a) sample 8w, (b) 4w, (c) 9w, and (d) 10w.

stabilized by the same modified silica particles. Binks has reported that the average diameter of emulsion droplets increased with the increasing particle size.[64] Based on above, the obvious aggregation of the modified silica particles dispersed in water should be responsible for the formation of larger pores according to DLS results. Our speculation is further verified by TEM observation (Figure 8). It can be seen that silica particles disperse well in organic phase, while aggregates are formed when the modified silica is in aqueous phase.

As mentioned above, the droplet size of Pickering HIPEs is affected by the silica concentration when it is initially dispersed in water. We also prepared Pickering HIPEs using various amounts of SP-0.14 as stabilizer in oil phase. All emulsions can be inverted with high viscosity seen from Figure S8. However, the emulsion stabilized by 0.4 wt % SP-0.14 has low viscosity when the initial location of particles is water. This is also ascribed to the smaller particle size of modified silica dispersed in oil. The morphology of obtained porous polymers is characterized by SEM, as shown in Figure 9. All poly-Pickering HIPEs have closed-cell pore structure, further indicating that the interconnectivity of pores is determined by the initial location of silica particles. The pore sizes of polymer foams with various silica amounts are summarized (Figure 10). As expected, the pore size gradually decreases with increasing particle concentration and the samples stabilized by modified silica dispersed in styrene have smaller pore size. However, the size difference becomes inconspicuous with increasing particle amount, which is induced by the sharp increase of the emulsion viscosity when adding more particles. As the viscosity of emulsion is high enough, emulsification cannot afford sufficient energy to break up individual droplets into smaller ones.

The morphology of pore walls of polymer foams is observed by FE-SEM to explore the effect of the initial location of modified silica particles on the pore structure. From Figure
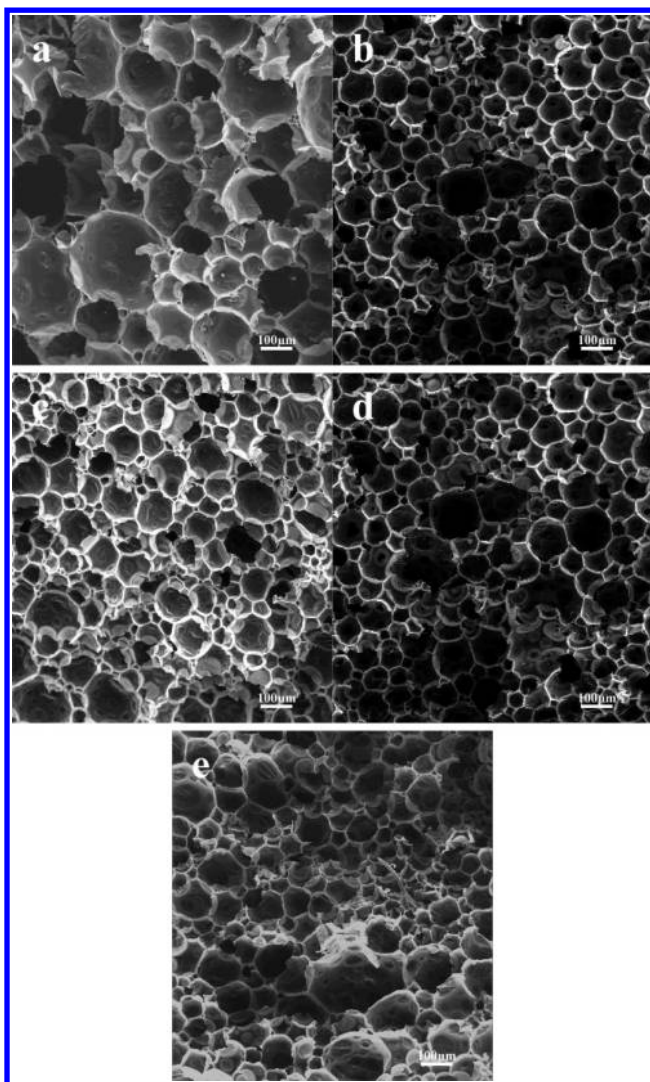
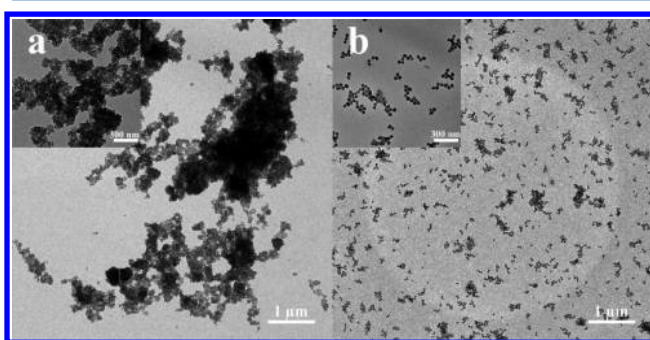**Figure 7.** SEM images of poly-Pickering HIPEs for samples 2s−6s (a−e).



**Figure 8.** TEM images of SP-0.14 dispersed into (a) water and (b) toluene.



**Figure 9.** SEM images of poly-Pickering HIPEs for (a) sample 8s, (b) 4s, (c) 9s, and (d) 10s.
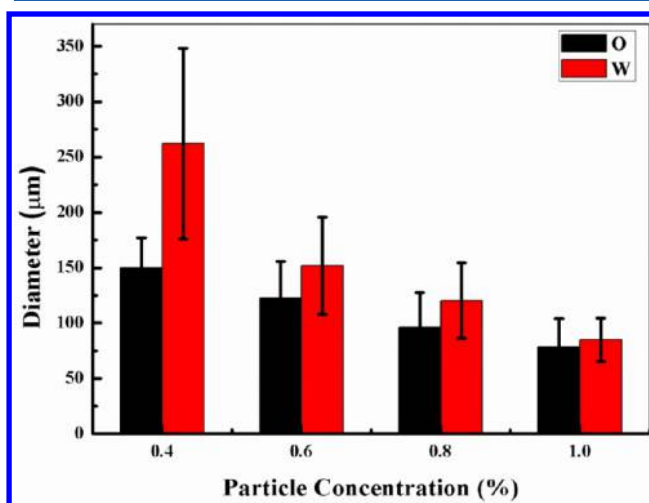


**Figure 10.** Pore size of poly-Pickering HIPEs stabilized by SP-0.14 initially dispersed in oil or in water.

11a,b, it is clearly found that rougher pore surface is formed when silica particles are dispersed in water. After etching by HF to remove silica particles on the pore surface, a significant difference is found. Sample 4w has very rough pore surface with densely packed polymer spheres, while only some holes can be seen on the relatively smooth pore wall of sample 4s. This can only be induced by the initial location of modified silica particles, which affects the surface structure of the aggregates. It
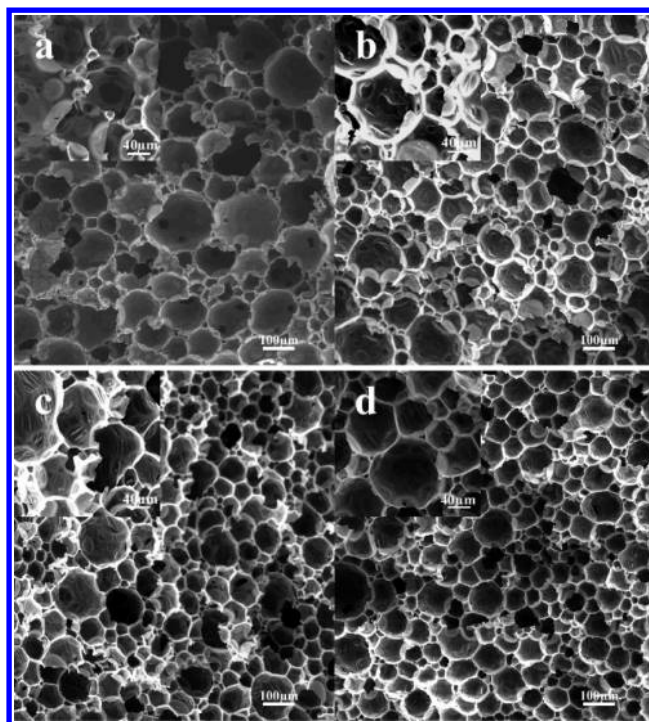
has been proven that ODS grafted silica particles are well dispersed in oil phase because of their hydrophobicity, while the aggregates are formed in water. When two kinds of silica are used to stabilize Pickering HIPEs, it can be speculated that Pickering stabilizer dispersed in styrene is more prone to stay in oil phase, resulting in smooth pore surface of sample 4s. After rinsing by HF, the silica particles and some aggregates on the pore wall are removed to leave several holes. However, it is more complicated for the behavior of the stabilizer dispersed in water during polymerization of Pickering HIPEs. As mentioned above, ODS grafted silica particles will self-assemble in water to form aggregates with hydrophobic cores and relatively hydrophilic surfaces. These silica aggregates have a similar structure as micelle. They are inclined to migrate to the W/O interface during emulsification due to their appropriate
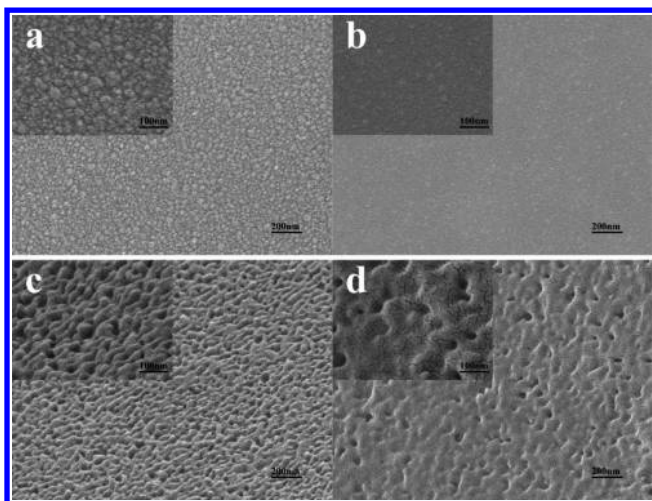
**Figure 11.** FE-SEM images of the pore wall structures of (a, c) sample 4w and (b, d) 4s (a, b) before and (c, d) after etching by HF.



**Figure 12.** Photographs of sample 4s and 4w (a) before and (b) after immersed in Sudan Black B solution for 24 h. The inset shows their cross sections.

6w by recording the flow rates of nitrogen through the samples under constant pressure. By contrast, the flow rate of gas through sample 4s is tested to be near zero. Figure 13 shows



**Figure 13.** Pore size and gas permeability of poly-Pickering HIPEs stabilized by modified silica particles initially dispersed in water.

wettability. Silica aggregates can be easily swollen by monomer in the continuous phase. After polymerization, polymer spheres shown in Figure 11c are formed. Therefore, these silica aggregates not only can stabilize Pickering HIPEs but also can act as micelle to absorb monomer and produce polymer spheres. A similar effect of titania particles has been reported in our previous work, in which polymer hollow microspheres covered by polymer solid particles were produced.[65] However, when silica particles dispersed in oil are used as Pickering stabilizer, only smooth pore surface with some holes is found after polymerization (Figure 11d) as the micelle-like structure is not formed. Based on these results, the formation mechanism of pore throats may also be proposed. It has been proven that the polymerization of Pickering HIPEs usually results in closed-cell macroporous polymers like our samples when silica particles are initially dispersed in oil. As discussed above, silica aggregates in water have a micelle-like structure, which can "extract" monomer from the continuous phase to produce rough pore wall. However, the monomer layer is very thin at the site between two neighboring droplets. When monomer is absorbed, the supply is difficult before the gelation due to the high viscosity of Pickering HIPEs, which results in the formation of pore throats. Furthermore, as it is found from Figure 5, more ODS grafted on the surface of silica particles leads to larger throat size because more hydrophobic cores are formed, which benefits the swelling of monomer. Above all, the special structure of silica aggregates dispersed in water should be responsible for the formation of the rough pore surface composed of polymer spheres and interconnected pores.

We have demonstrated the pore structure of two kinds of poly-Pickering HIPEs by SEM. Closed-cell pores are obtained when silica is dispersed in oil, while Pickering stabilizer in water leads to interconnected porous polymers. Samples 4s and 4w were then immersed in Sudan Black B solution to reveal the difference of their pore structure more macroscopically. Samples 4s and 4w have almost the same appearance seen from Figure 12a. After immersed in the solution for 24 h, both of them become black because of the adsorption of Sudan Black B. They were then carved to observe the inner of samples as shown in Figure 12b. It is found that sample 4s shows white color while sample 4w is black. This conforms well to the SEM observation. To compare the interconnectivity of open-cell polymer foams, we measured the permeability of samples 2w−
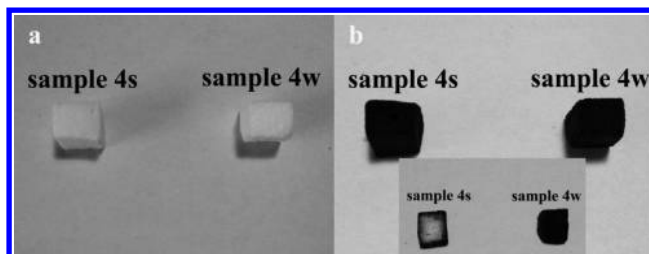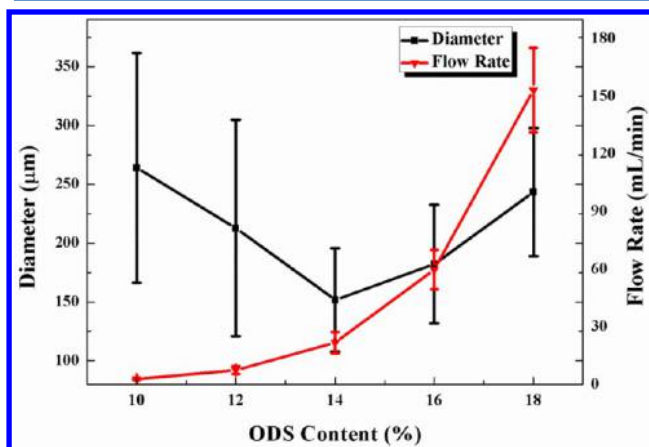
that the porous polymer with the minimum pore size is obtained by using SP-0.14 with intermediate hydrophobicity as Pickering stabilizer, and the flow rate increases dramatically with the increasing hydrophobicity of particles from about 3 mL/min for sample 2w to 153 mL/min for sample 6w. It has been reported that the permeability of polymer foams is affected by the pore size and the pore throat size.[23] Our experiments also prove that the interconnectivity of porous polymers is determined by the size of pore throats. Therefore, the pore size, the pore wall morphology, and the interconnectivity of polymer foams can all be tuned efficiently and finely only via the surface modification of solid particles, which may meet various requirements for their applications.

## ■ CONCLUSIONS

W/O Pickering HIPEs were successfully stabilized by modified silica nanoparticles and the corresponding porous polymers were also prepared by polymerizing Pickeing HIPEs. The hydrophobicity of silica nanoparticles could be adjusted by tailoring the grafted ODS amount on the surface. Solid particles with the intermediate hydrophobicity produced HIPEs with the minimum droplet size, while extreme hydrophilic or hydrophobic silica could not stabilize Pickering HIPEs efficiently. As a result, the pore size of porous polymers was determined by the surface structure and the concentration of silica particles. The initial location of modified silica particles significantly influenced the pore throat formation. Dispersion of particles in

water or in oil resulted in polymer foams with open-cell or closed-cell pores, respectively. Silica aggregates in water had a micelle-like structure and could be easily swollen by the monomer, which should be responsible for the formation of rough pore walls and pore throats. Therefore, the permeability of porous polymers was substantially affected by the hydrophobicity of silica particles. The well-defined pore structure of polymer foams may meet various requirements for the prospective applications.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

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