

Supporting Information

Switchable release and recovery of nanoparticles via a pickering-emulsion-templated porous carrier

Ye Hua, Shengmiao Zhang,* Jianding Chen, and Yun Zhu

Closed-cell poly-Pickering-HIPEs

The PNIPAM based poly-Pickering-HIPE with SiO₂ as the sole stabilizer as shown in Fig. S1 has a closed-cell structure. In terms of the volume of porous polymer, when the temperature was raised from 25 °C to 40 °C or 60 °C, the volume respectively turned to be around 60% and 45% of the water-swollen volume at 25 °C. Then the release ability of this poly-Pickering-HIPE was investigated. However, according to the TG result, only 10% of the total SiO₂ particles in the monolith were squeezed into water after five times release process, which should be attributed to the closed-cell structure provided by the poly-Pickering-HIPE (Fig. S1). In specific, although the pore wall of the poly-Pickering-HIPE crumpled up when raising the temperature above LCST (Fig. S2), which could expel the SiO₂ particles from polymer matrix into its large void, these disconnected voids curbed the release of nanoparticles outside the porous sample. Therefore, only the particles exist on the external surface of the total monolith would be released into aqueous phase, and most of the nanoparticles still stayed inside the PNIPAM monolith.

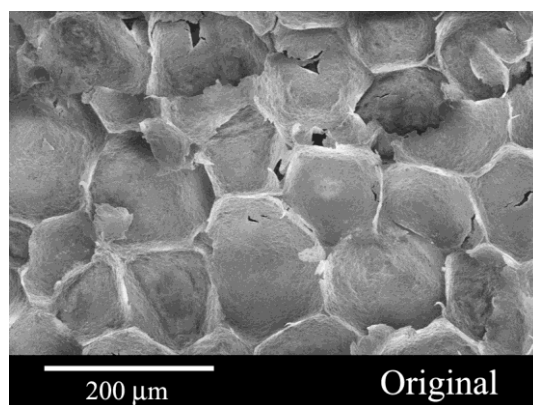


Fig. S1. SEM image for Closed-cell poly-Pickering-HIPE as prepared.

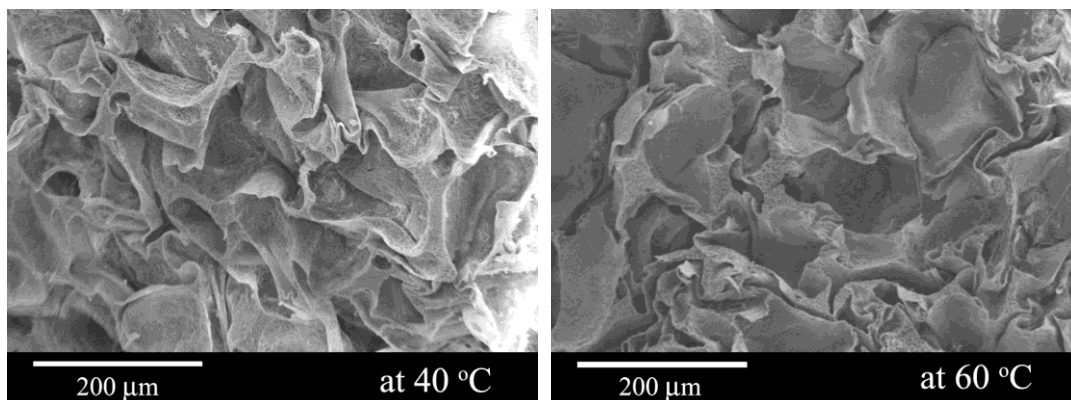
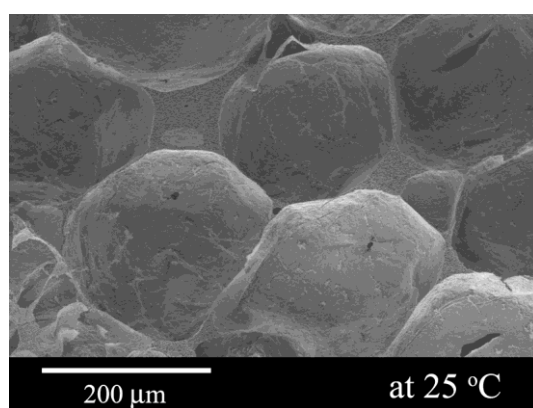


Fig. S2. SEM images for Closed-cell poly-Pickering-HIPE soaked in the water under different temperature.

The particle/surfactant synergy

Non-ionic surfactant Tween 60 was used as the coemulsifier to stabilize Pickering HIPEs, and average void diameter of the corresponding interconnective poly-Pickering-HIPEs (Fig. 1) was much smaller than that of the closed-cell poly-Pickering-HIPE. Except that, the TEM images of the interconnective poly-Pickering-HIPEs (Fig. S3) showed that the nanoparticles tended to be aggregated in the skin layer of the void walls while only small amount of them remained in the polymer matrix. Moreover, there was still part of void wall surface without the embedding of silica nanoparticles. So it was convinced that while emulsification, the surfactant molecules could not only adsorb onto the SiO₂ nanoparticles which enabled the particles to disperse better in the aqueous, thereby making part of the particles likely to stay in the continuous phase rather than adsorb at the oil-water interface, but also adsorb on the oil-water interface competitively with SiO₂ nanoparticles to create new interface and decrease the oil droplet size by lowering the interfacial tension. Hence, this particle/surfactant synergy caused the decrease in void size and brought about some polymer walls with no aggregation of nanoparticles, both of which would promote the formation of interconnecting pores on the void wall. But because of the small quantity of the coemulsifier Tween60 used here (0.1wt% relative to the aqueous phase), the number of the interconnecting pores was not enormous and the size of them was also not large.

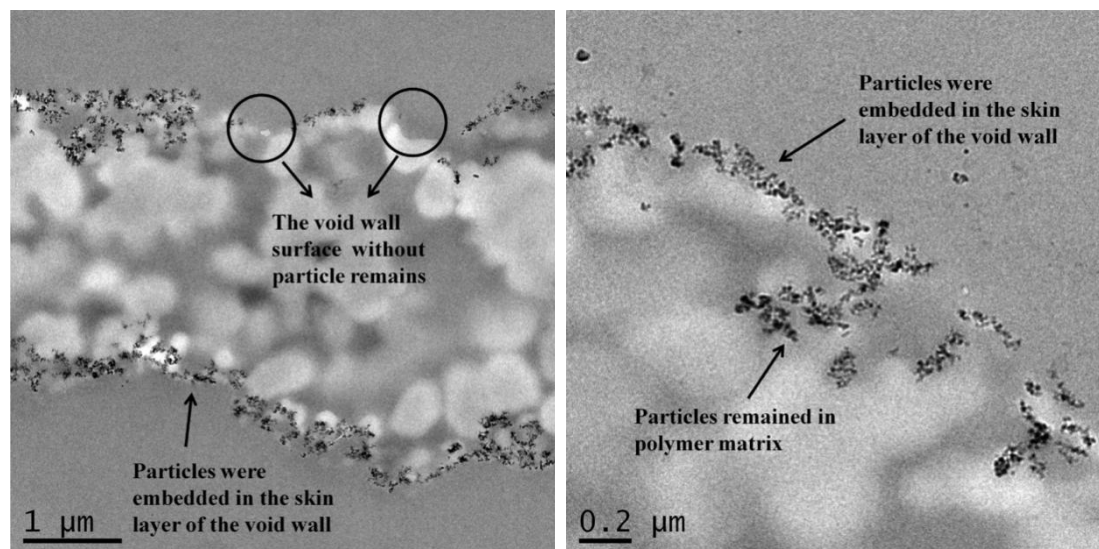


Fig. S3. TEM images of the interconnective poly-Pickering-HIPEs as prepared.

The calculation of the oligomer content in the as-prepared sample

According to the TGA, the nanoparticle content in the as-prepared sample (P) was 6.38 wt% and the nanoparticle content in the water-washed sample (P') was 6.91 wt%. Therefore, if hypothesizing that the nanoparticles were not lost in the washing process, the oligomer content (Co) in the as-prepared sample can be calculated by $1-P/P'$ and be around 7.7 wt%.

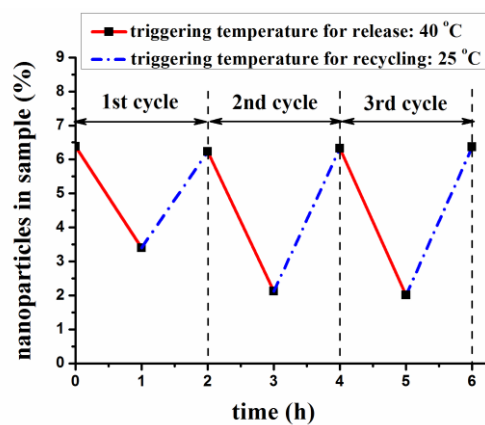


Fig. S4 Changes of the amount of silica nanoparticles remaining in the PNIPAM sample within three cycles of release and recovery. The amount of nanoparticles in the sample was the mass percentage of the nanoparticles based on the mass of the total corresponding sample. The triggering temperature for release was 40 °C.

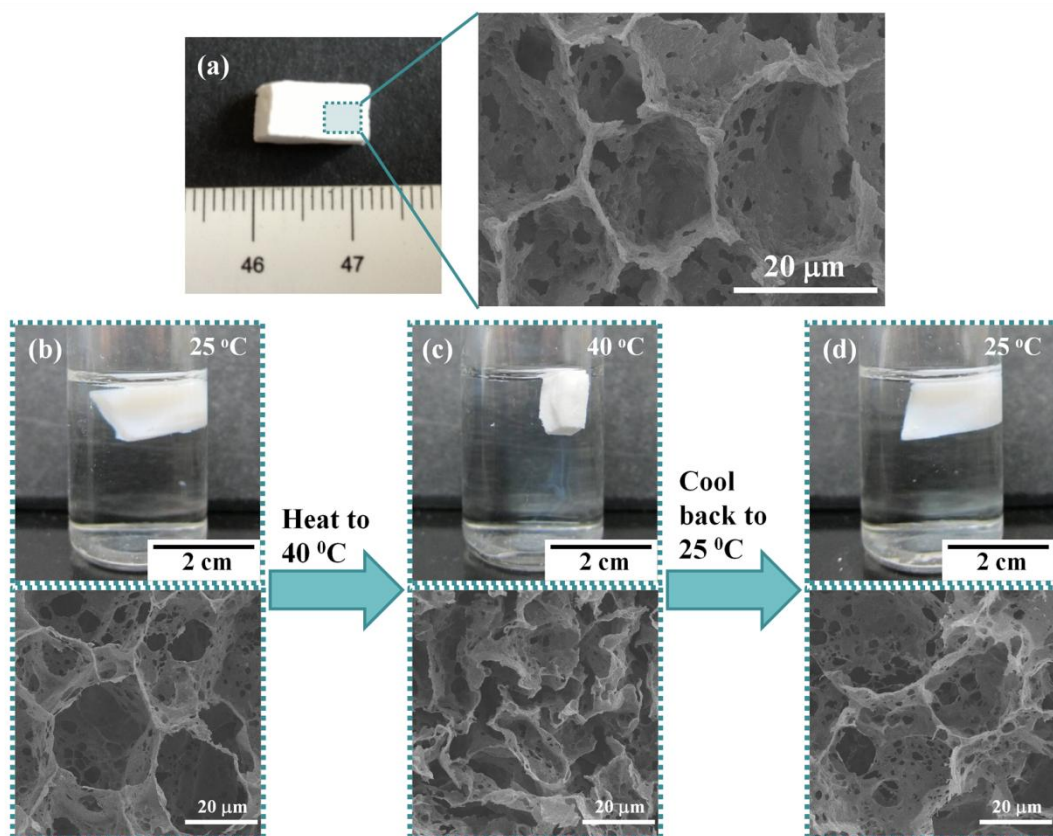


Fig. S5. Photographs and SEM images for open-porous poly-Pickering-HIPE with TiO₂ nanoparticles under different states. (a) As prepared. (b) Treated by soaking in water at 25 °C. Both the sample volume and the average void diameter were increased. (c) Kept in water at 40 °C. The TiO₂ nanoparticles were squeezed out from the PNIPAM foam into water. In terms of the morphology, the polymer matrix shrank and disposed all voids huddle together. (d) Cool the water back to 25 °C. The samples reswelled and the water phase turned to be clear. The polymer wall was spread out again and the void structure recovered back to that at 25 °C.

Porous PNIPAM prepared from Fe₃O₄-nanoparticles-stabilized HIPE

Fe₃O₄ magnetic nanoparticle was also substituted for the model silica nanoparticle to stabilize the paraffin-in-water HIPE here, and the corresponding porous PNIPAM carrier with Fe₃O₄ nanoparticles inlaid in the polymer void walls was prepared. It had the similar thermoresponsive properties and it was able to release and recycle Fe₃O₄ nanoparticles just like it done on SiO₂ nanoparticles (Fig. S6). In this work, this porous PNIPAM was designed to release Fe₃O₄ nanoparticles to accelerate Fenton-like degradation of recalcitrant organic contaminants due to the high catalytic activity of Fe₃O₄ nanoparticles in Fenton-like system^[1]. In specific, the porous PNIPAM sample (30 mg, with 1.66% Fe₃O₄ nanoparticles inside) was first immersed into 15 ml methyl orange aqueous (20 ppm, MO, which was a target organic contaminant) at 25 °C to be fully swollen. Then increase aqueous temperature to 40 °C to make the PNIPAM foam release the catalyst Fe₃O₄ nanoparticles into the MO aqueous and add 0.2ml hydrogen peroxide (H₂O₂, 30%) in to the aqueous to form Fenton-like system. The MO aqueous was slight decoloured after three-hour reaction, which indicated that the MO molecule had been degraded, and the released Fe₃O₄ nanoparticles were recycled into the PNIPAM foam when the temperature was reduced back to 25 °C. Undoubtedly, the recycling capability made the reuse of this release device in Fenton-like system possible. Here, the degradation extent of the MO molecules was also analyzed using UV spectroscopy at 464 nm. Fig. S7 showed that only 3.5% MO could be degraded with H₂O₂ solely added into the MO aqueous while 16.4% MO could be removed with the existence of the Fenton-like system. And there were also 13.7% and 15.4% MO could be degraded in the second and third run respectively (Fig. S7). In a word, this PNIPAM-based poly-Pickering-HIPE could be repeatedly used to form the Fenton-like system and effectively avoid the contamination in the system.

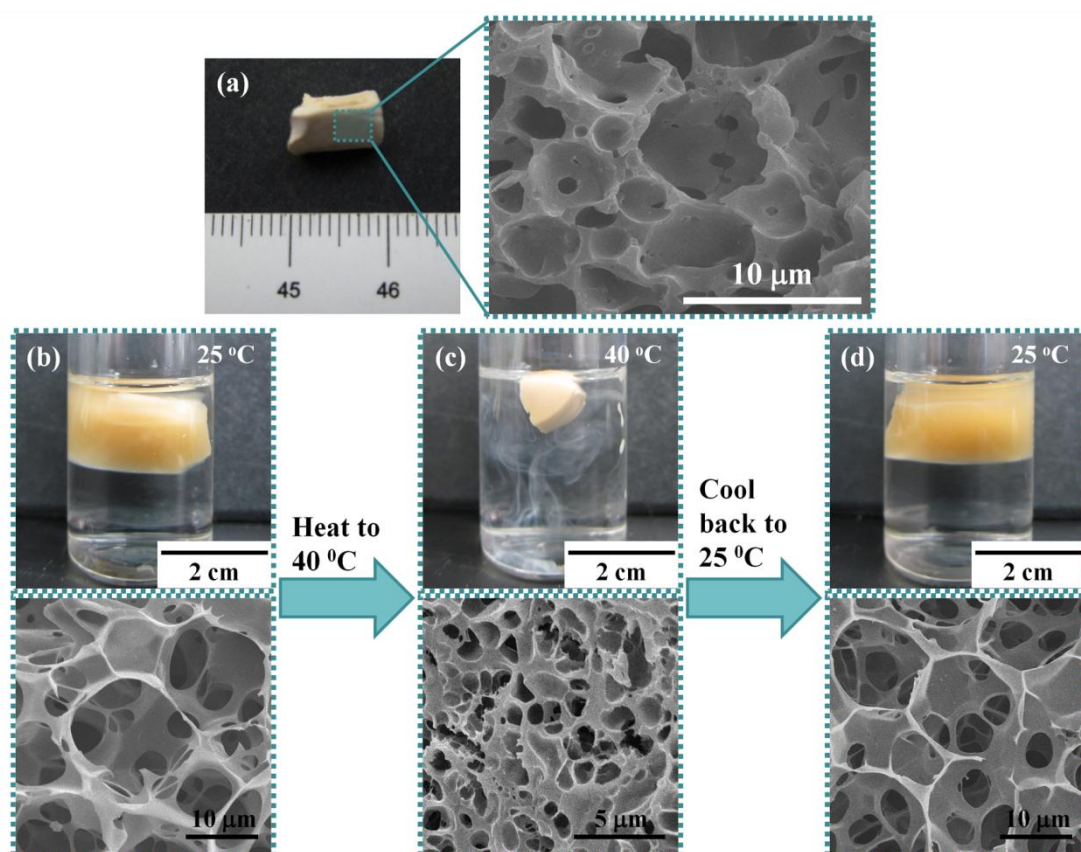


Fig. S6. Photographs and SEM images for open-porous poly-Pickering-HIPE with Fe_3O_4 nanoparticles under different states. (a) Sample as prepared. (b) Sample treated by soaking in water at 25 °C. Both the sample volume and the average void diameter were increased. (c) Sample kept in water at 40 °C. The Fe_3O_4 nanoparticles were squeezed out from the PNIPAM foam into water. In terms of the morphology, the polymer matrix shrank and disposed all voids huddle together. (d) Cool the water back to 25 °C. The samples reswelled and the water phase turned to be clear. The polymer wall was spread out again and the void structure recovered back to that at 25 °C.

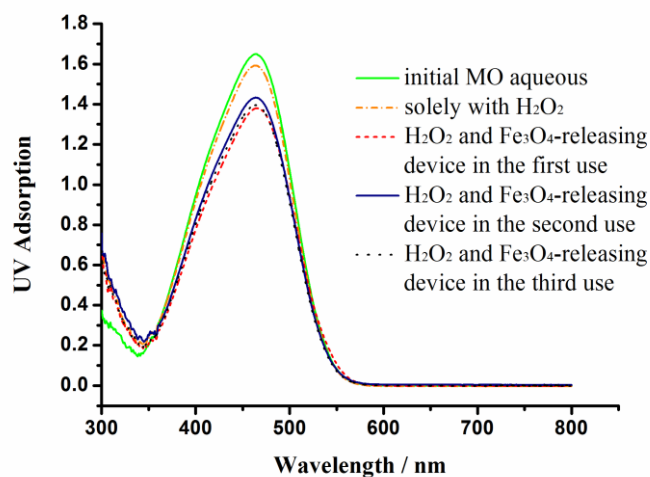


Fig. S7. Plot displaying the repeatedly catalytic effect of the Fe₃O₄-releasing device (poly-Pickering-HIPE with Fe₃O₄ nanoparticles) on Fenton-like degradation of MO as measured using a UV plate read.

Reference

- [1] X. B. Hu, B. Z. Liu, Y. H. Deng, H. Z. Chen, S. Luo, C. Sun, P. Yang, S. G. Yang, *Applied Catalysis B: Environmental* **2011**, *107*, 274.