**Supporting Information**

# Uniform Microparticles with Controllable Highly-Interconnected Hierarchical Porous Structures

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**Supplementary Figures**

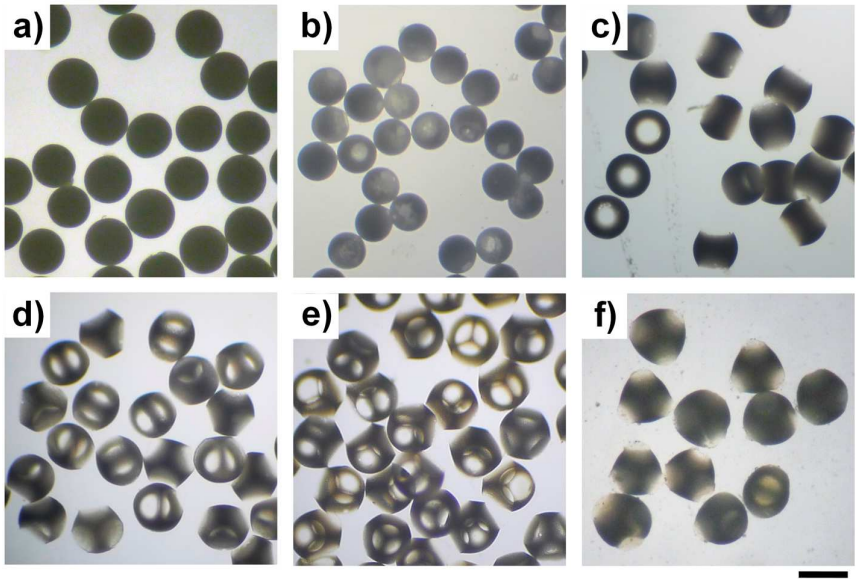


**Figure S1**. Optical micrographs of the hierarchical porous poly(MMA-*co*-EGDMA) microparticles. (a) Nano-porous microparticles. (b-e) Hierarchical porous microparticles containing one (b), two (c), three (d), and four (e) micrometer-sized pores. (f) Hierarchical porous microparticles containing three micrometer-sized pores fabricated with shorter processing time. Scale bar is 200 μm.

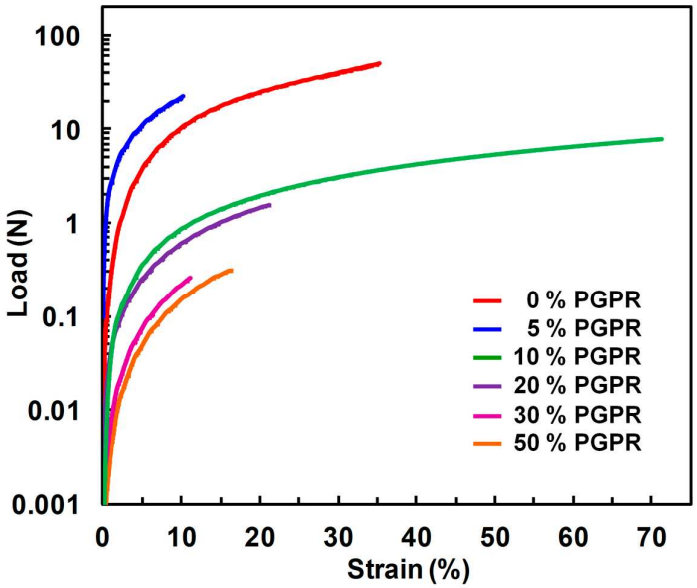


**Figure S2**. Compressive load-strain curves of PEGDMA microparticles prepared with different PGPR contents.

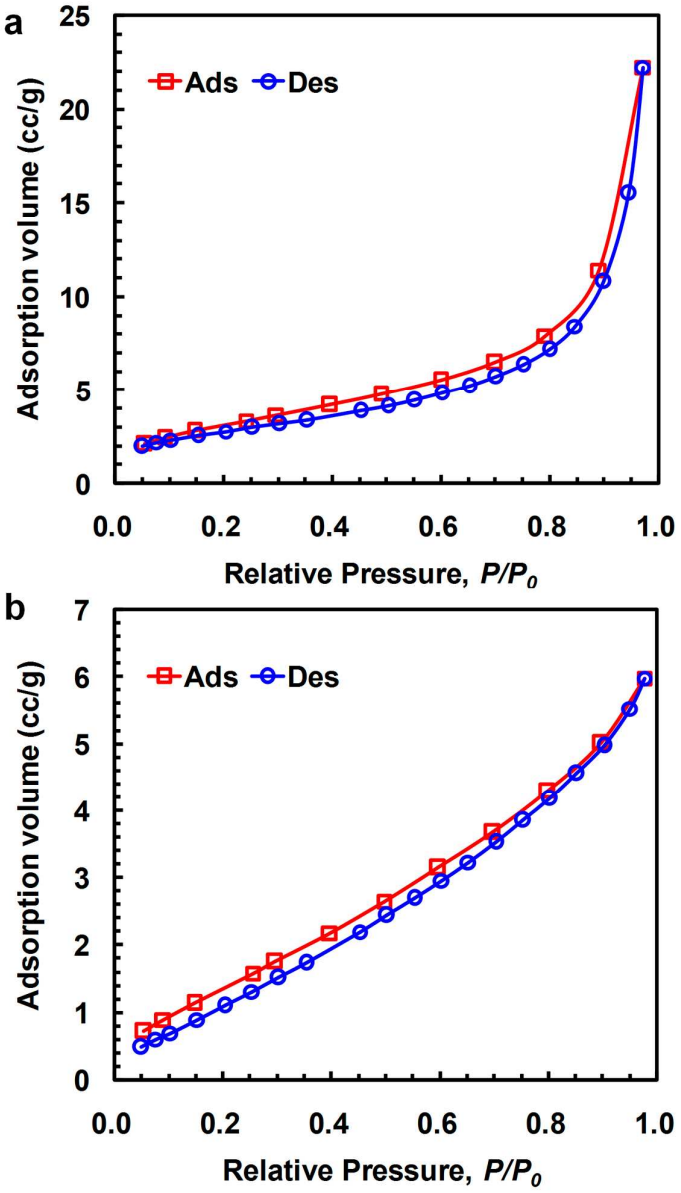


**Figure S3**. $N_2$ adsorption isotherms of nano-porous PEGDMA microparticles (a) and poly(MMA-*co*-EGDMA-*co*-GMA) microparticles (b) with 10 % (w/v) PGPR, measured by using Quantachrome NOVA 1000e analyzer with $N_2$ adsorption at 77 K.

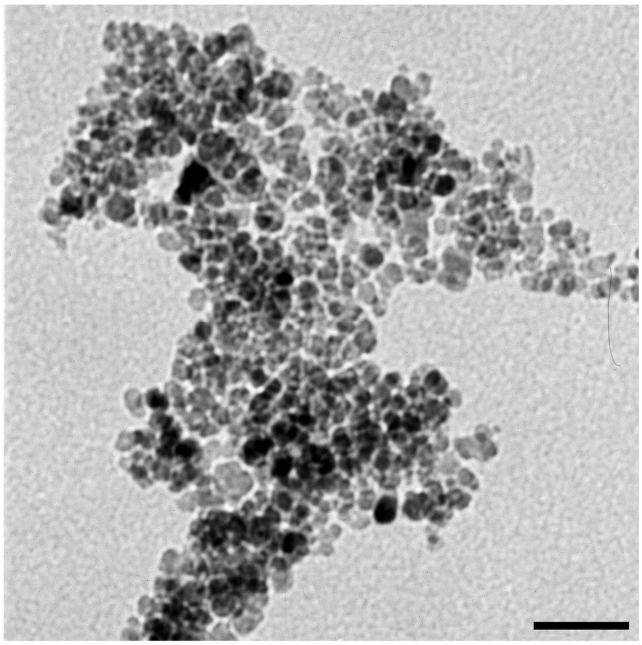

**Figure S4**. TEM image of the oleic acid-modified magnetic nanoparticles. Scale bar is 50 nm.

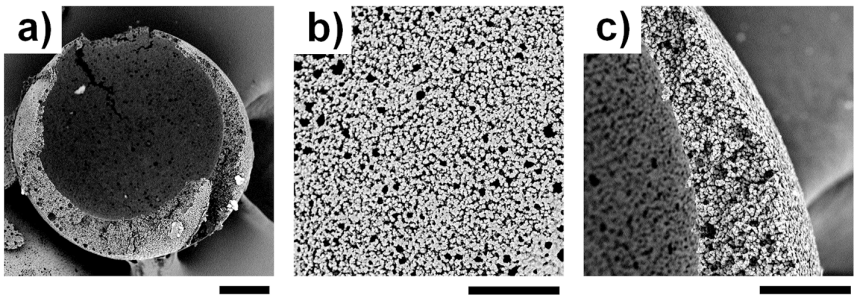


**Figure S5**. SEM images of a ruptured hierarchical porous poly(MMA-*co*-EGDMA) microparticle with one micrometer-sized pore after immersing in ethanol for more than 3 months (a), as well as the magnified outer surface (b) and cross-section (c). The microparticle shows no obvious change in the porous structure as compared with the one after washing and immersing in ethanol for several days (Figure 7a). Scale bars are 50 μm in a, and 20 μm in the rest.

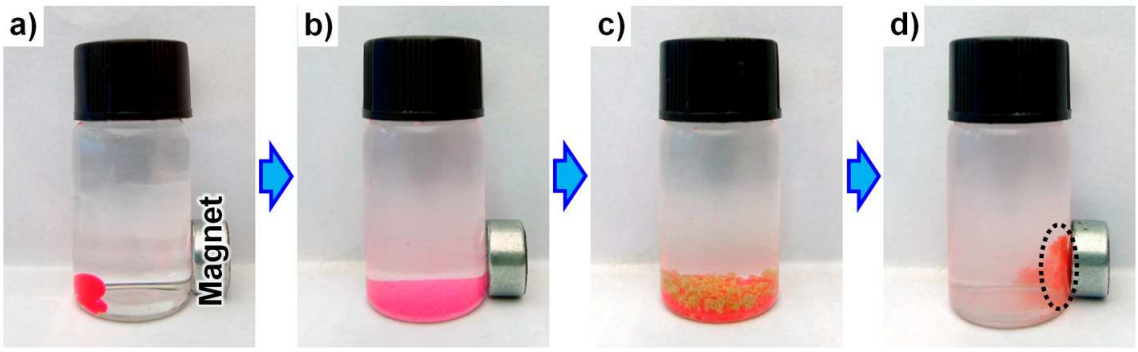


**Figure S6**. Magnetic hierarchical porous poly(MMA-*co*-EGDMA) microparticles for magnetic-guided removal of benzyl benzoate microdrops from water. (a,b) Benzyl benzoate dyed with LR300 (red color) is added into water (a), and then broken into microdrops by shaking (b). (c,d) Hierarchical porous microparticles are added into the water (c), then mixed with the benzyl benzoate microdrops for adsorption, and finally separated by a magnet (d).

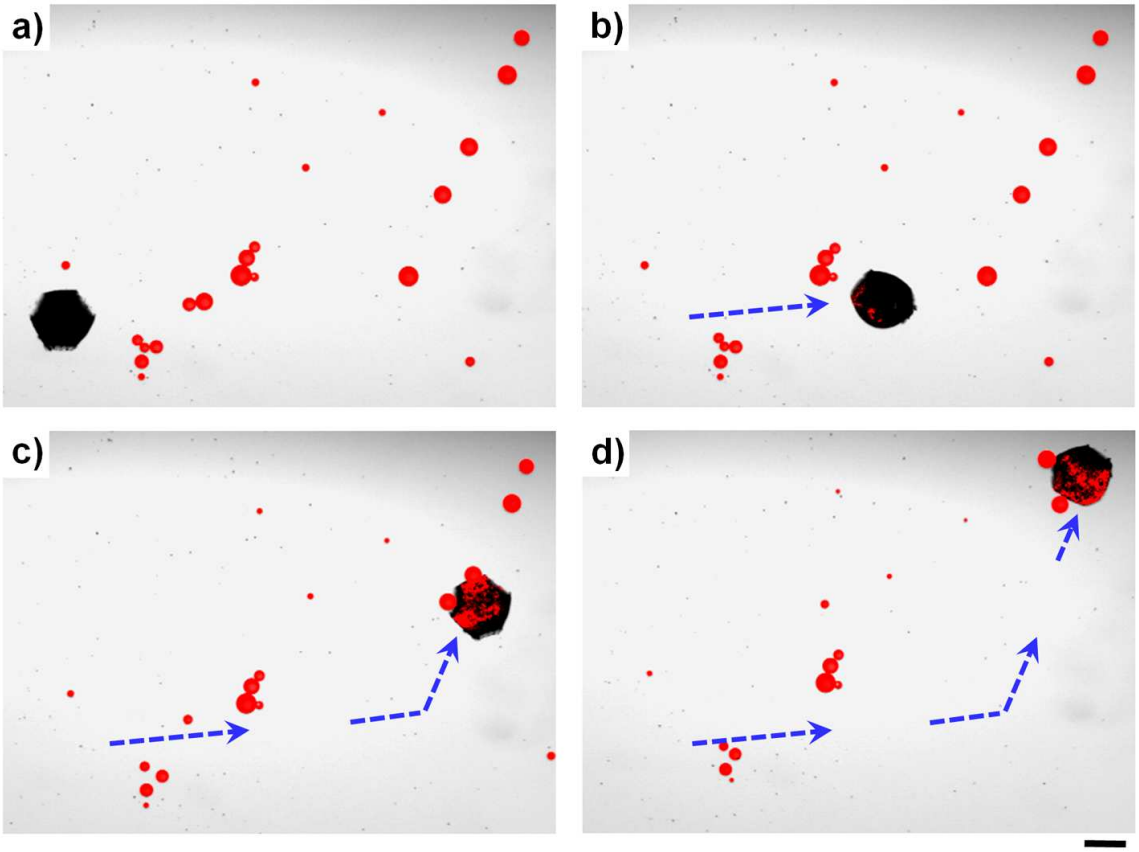


**Figure S7.** Magnetic hierarchical porous poly(MMA-*co*-EGDMA) microparticles for magnetic-guided route-specific adsorption of EGDMA microdrops dyed with LR300 (red color). The blue arrows indicate the moving direction of the microparticle. Scale bar is 200 μm.

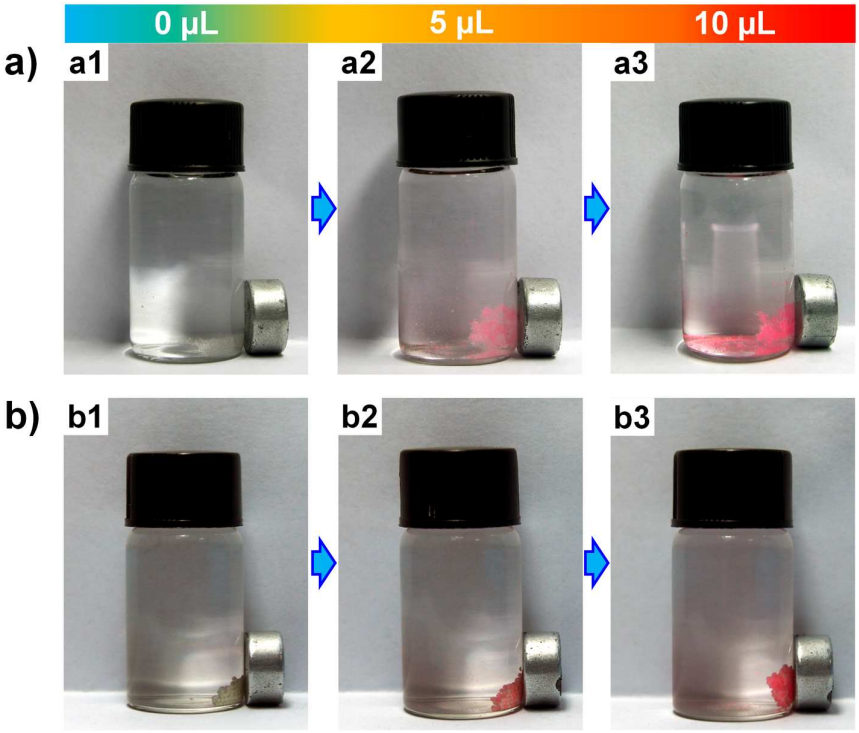


**Figure S8**. Poly(MMA-*co*-EGDMA-*co*-GMA) microparticles with only one micrometer-sized pore (a) prepared from emulsions containing 2.5 % (w/v) PGPR, and with only nanometer-sized pores (b) prepared from emulsions containing 10 % (w/v) PGPR for quantitative oil removal.

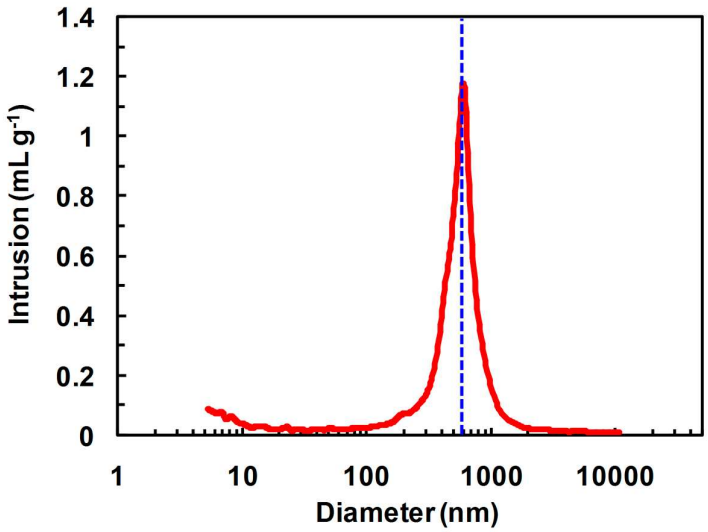


**Figure S9**. Size distribution of the nanometer-sized pores of poly(MMA-*co*-EGDMA-*co*-GMA) microparticles prepared with 10 % (w/v) PGPR, measured by mercury intrusion porosimetry.

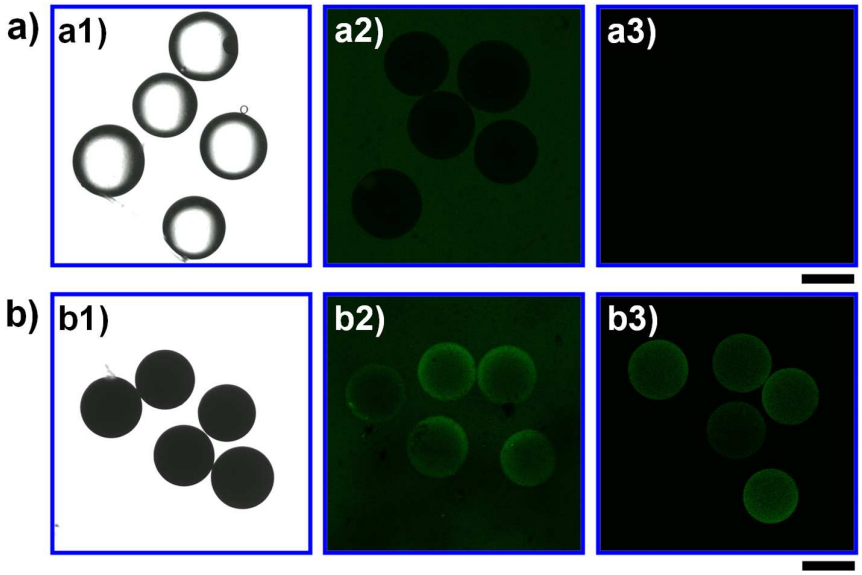


**Figure S10**. CLSM images showing non-porous PEGDMA (**a**) and nano-porous PEGDMA (**b**) microparticles before (a1, b1) and after (a2, b2) FITC-BSA adsorption for 2 h, and after redispersed in water (a3, b3). Compared with the non-porous PEGDMA microparticles (a3), the nano-porous PEGDMA microparticles that are redispersed in water (b3) show obvious FITC-BSA adsorption. Scale bars are 100 μm.

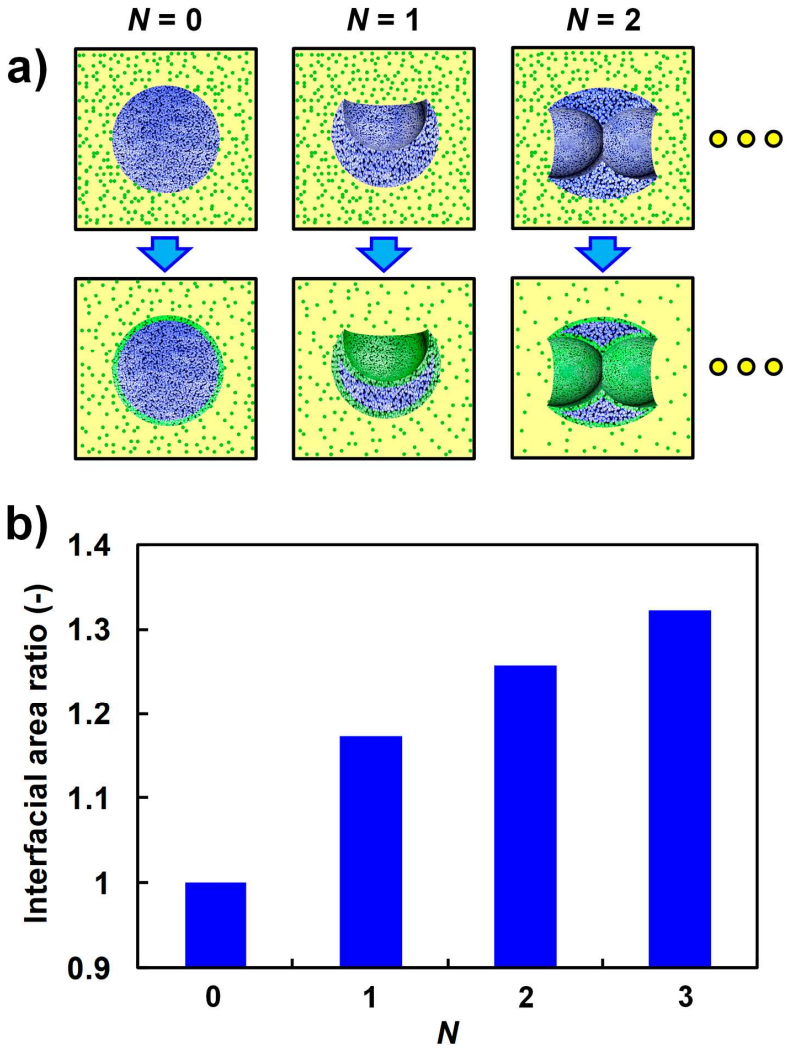


**Figure S11**. Interfacial areas of hierarchical porous microparticles containing different numbers ($N$) of micrometer-sized pores that expose to the BSA bulk solution. (a) Illustrations showing the interfacial areas of microparticles that expose to the BSA bulk solution for BSA diffusing from the bulk solution into the nano-porous matrix. (b) Ratio of the interfacial areas of hierarchical porous microparticles ($N$=1~3) to that of the nano-porous microparticles ($N$=0). Due to the irregular shape of hierarchical porous microparticles, the interfacial areas are calculated from the sizes of the inner drop and outer drop of the deformed double emulsion templates.

**Table S1**. The pore characteristics of hierarchical porous poly(MMA-*co*-EGDMA-*co*- GMA) microparticles

| Micrometer-sized pores* | |
|---|---|
| Pore number | Pore volume (mL $g^{-1}$) |
| 0 | 0 |
| 1 | 0.4083 |
| 2 | 0.5769 |
| 3 | 0.6391 |
| 4 | 0.6797 |

**Note:* For nanometer-sized pores, the pore volume is 0.3762 mL $g^{-1}$, the average pore size is 580 nm, and the surface area is 16.83 $m^2$ $g^{-1}$. Due to the irregular shape of hierarchical porous microparticles, the pore volume of micrometer-sized pores are calculated from the sizes of the inner drop and outer drop of the doubele emulsion templates.