Supporting Information

Facile Fabrication of Monodisperse Polymer Hollow Spheres

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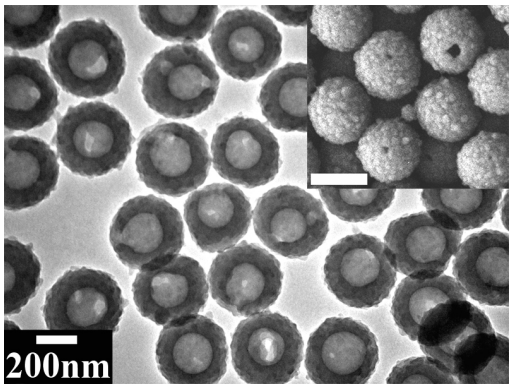

Figure S1. TEM image of hollow spheres prepared by swelling method under the conditions of 5.8:1.0 monomer/seed weight ratio and 11.4:4.3:1.0 MMA:DVB:HEMA molar ratio. The inset shows SEM image and the scale bar is 300 nm.

For comparison, hollow spheres were also prepared by the swelling method. In the experiment, monomers were added to the seed dispersion and allowed to swell into the seeds for 2 h before polymerization. TEM image in Figure S1 shows that the obtained hollow spheres are 369 nm in diameter and their cavity size is 190 nm. It is

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evident that the cavity of the spheres is smaller than that of hollow spheres prepared by the non-swelling method.

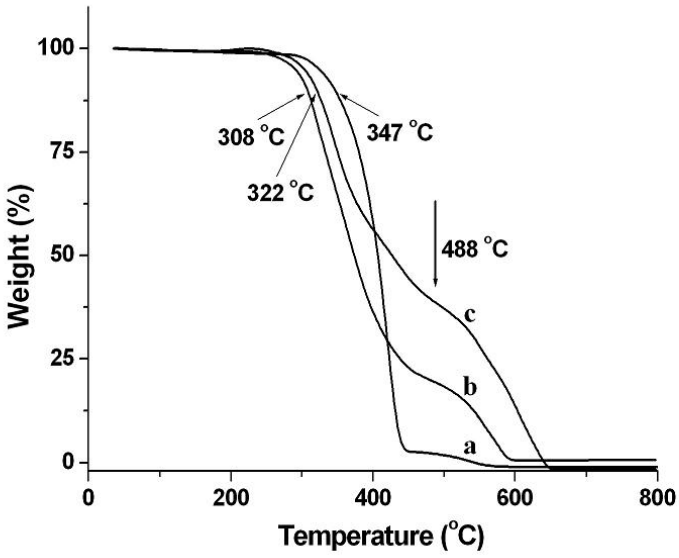

Figure S2. TGA diagrams of seeds (a), hollow spheres (b) and the etched hollow spheres (c).

Figure S2 demonstrates TGA spectra of seeds, the typical hollow spheres and the etched hollow spheres. At a weight loss of 10 wt%, the decomposition temperature of the hollow spheres and the etched hollow spheres is 308 and 322 ^{o}C, respectively, which is obviously lower than that of seeds, 347 ^{o}C. It is because the two types of hollow spheres are mostly composed of PMMA, and its decomposition temperature is lower than PS which is the main composition of seeds. In addition, the secondary decomposition takes place at 488 ^{o}C for the two types of hollow spheres due to the presence of the cross-linked polymer. At the same time, it can be seen that the cross-linked polymer takes smaller percentage in the hollow spheres than in the etched hollow spheres, which means that the linear seed polymer remains within the hollow spheres.

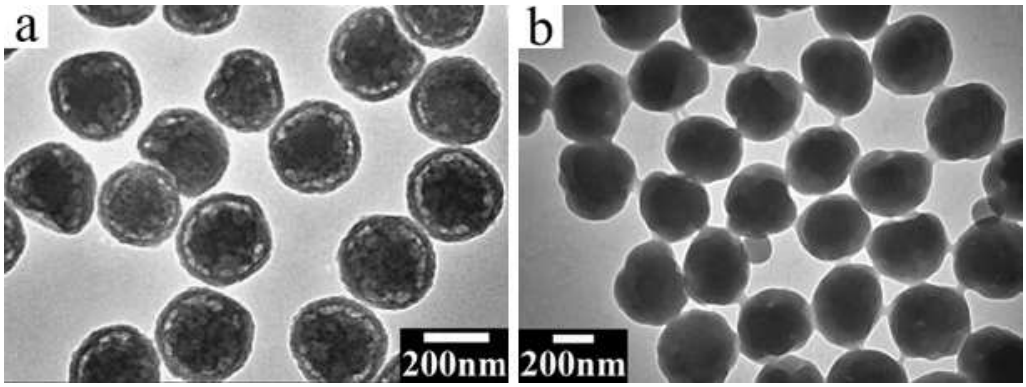

Figure S3. TEM images of polymer spheres prepared under the conditions of (a) 2.7:1.0 MMA:DVB and cross-linked PS particles as seeds; (b) 2.7:1.0 MMA:EGDMA and linear PS particles as seeds. The samples were prepared in the presence of 0.50% (v/v) of HEMA.

We also attempted to carry out seeded emulsion polymerization using cross-linked PS particles as seeds, but no hollow spheres were obtained (Figure S3a). Ineerestingly, gap was formed between the core and the shell of the resulting spheres. That should be aroused by the shrinking of the swollen seeds after monomers ars consumed. If substitute DVB for other crosslinking agent, e.g. EGDMA, it is found that the ultimate spheres are solid particles although seeds are composed of linear polymer, showing EGDMA can not highly swell seeds (Figure S3b). Therefore, the formation of hollow spheres is primarily attributed to the ‘dissolution’ of seeds in monomers.