Electronic Supplementary Material (ESI) for RSC Advances.

One-step preparation of flower-like poly(styrene-*co*-zwitterionic ionic liquid) microspheres with hierarchical structures for supported acidic heterogeneous catalysts

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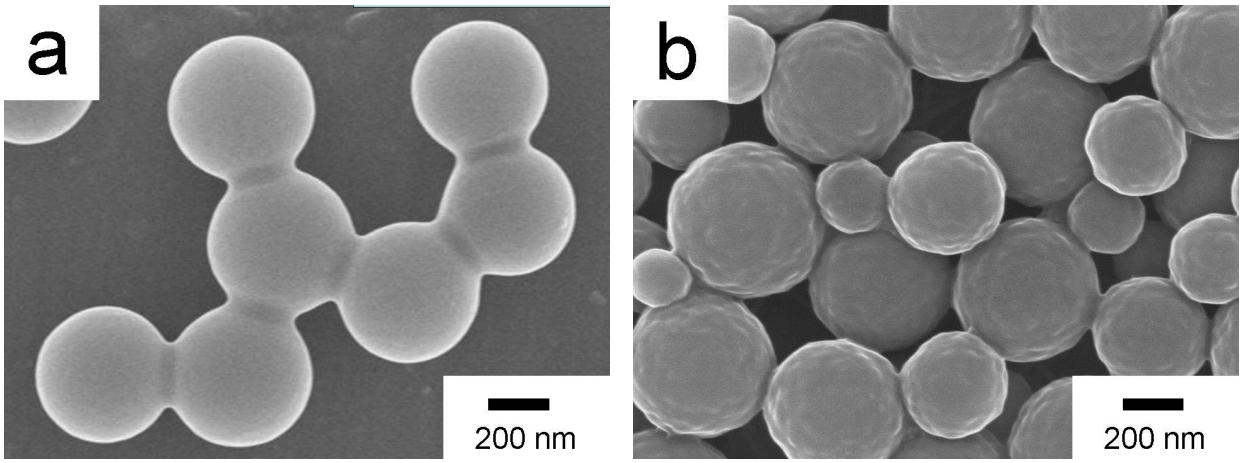

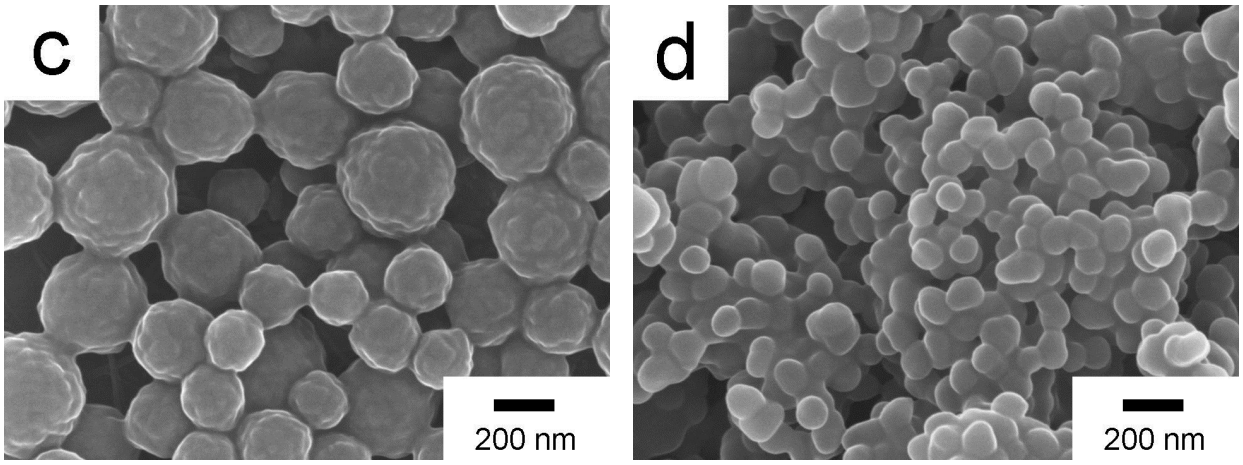

Fig. S1. SEM images of (a) PS microspheres and (b, c, d) poly(St-*co*-VIPS) nanospheres obtained under different [St]/[VIPS]: (a) [St]/[VIPS] = 1:0; (b) [St]/[VIPS] = 1:0.125; (c) [St]/[VIPS] = 1:0.25; (d) [St]/[VIPS] =1:1. Other conditions: [PVP] = 1 g/L (in H_2O), V_{St} = 5 mL, EtOH/H_2O (v/v) = 40/20.

In order to reveal the formation mechanism of flower-like poly(St-*co*-VIPS) microspheres the influence of some reaction conditions, such as the molar ratio of St and VIPS ([St]/[VIPS]), the volume of St (V_{St}), the concentrations of PVP ([PVP]) (in H_2O) and the volume ratio of EtOH and H_2O (EtOH/H_2O (v/v)), on the morphology of obtained poly(St-*co*-VIPS) microspheres was investegated, respectively. Fig. S1 presents SEM images of the products obtained under different [St]/[VIPS]. When the polymerization was carried out without VIPS, the PS microspheres showed a homogeneous size of microspheres having smooth surfaces, with the average diameter of about 450 nm (Fig. S1(a)). However, with the addition of VIPS, the surface of the obtained microspheres, i.e. poly(St-*co*-VIPS) microspheres, became rough, and along with the increase of the content of VIPS, the surface of poly(St-*co*-VIPS) microspheres appeared more and more rough (Fig. S1(b) and S1(c)). It can be clearly found that when [St]/[VIPS] reached to 1:1, only many small poly(St-*co*-VIPS) nanospheres with the diameter in the range of 90-120 nm were observed in Fig. S1(d) instead of the rough microspheres. It is indicated that [St]/[VIPS] used in the copolymerization system was an important factor in the formation of flower-like poly(St-*co*-VIPS) microspheres in the case of other reaction conditions fixed, and the surface roughness was depended on [St]/[VIPS].

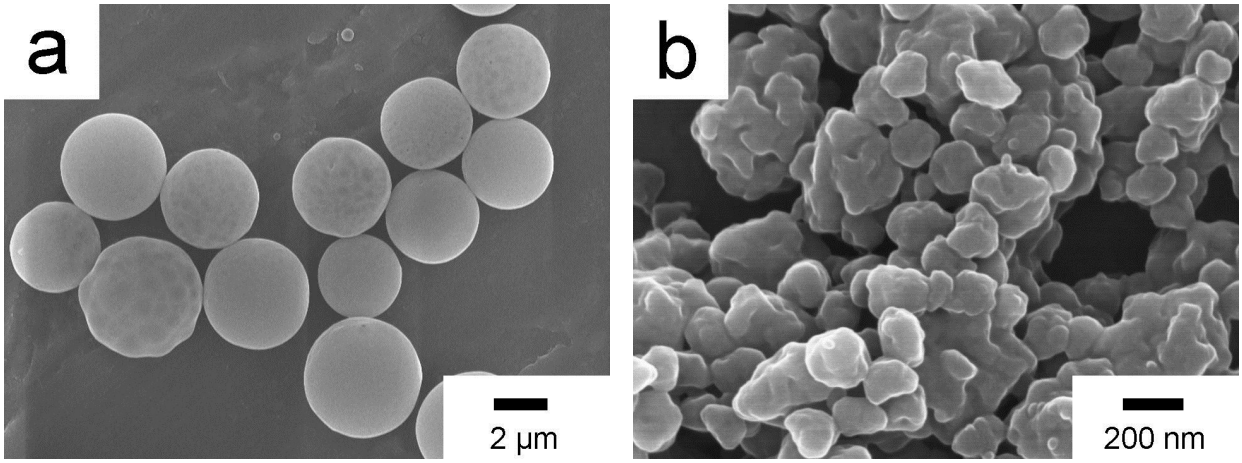

Fig. S2. SEM images of poly(St-*co*-VIPS) microspheres obtained under different V_{St}: (a) V_{St} = 2.5 mL; (b) V_{St} = 10 mL. Other conditions: [St]/[VIPS] =1:0.5, [PVP] = 1 g/L (in H_2O), EtOH/H_2O (v/v) = 40/20.

The influence of the concentrations of monomers (St and VIPS) on the morphology of poly(St-*co*-VIPS) microspheres was investigated by adjusting the volume of St (V_{St}) in the case of [St]/[VIPS] =1:0.5, when the other conditions were kept constant. There is considerable difference among the morphologies of the products obtained under the different V_{St}. As shown in Fig. S2(a), when 2.5 mL of St and corresponding amount of VIPS were used in the copolymerization system, large poly(St-*co*-VIPS) microspheres with the diameter in the range of 3-4.5 μm were obtained, which owned some small holes on their surface. However, smaller poly(St-*co*-VIPS) particles with irregular morphology appeared in Fig. S2(b), when V_{St} was increased to 10 mL. Therefore, besides [St]/[VIPS], the concentrations of the both monomers also influence the formation of flower-like poly(St-*co*-VIPS) microspheres.

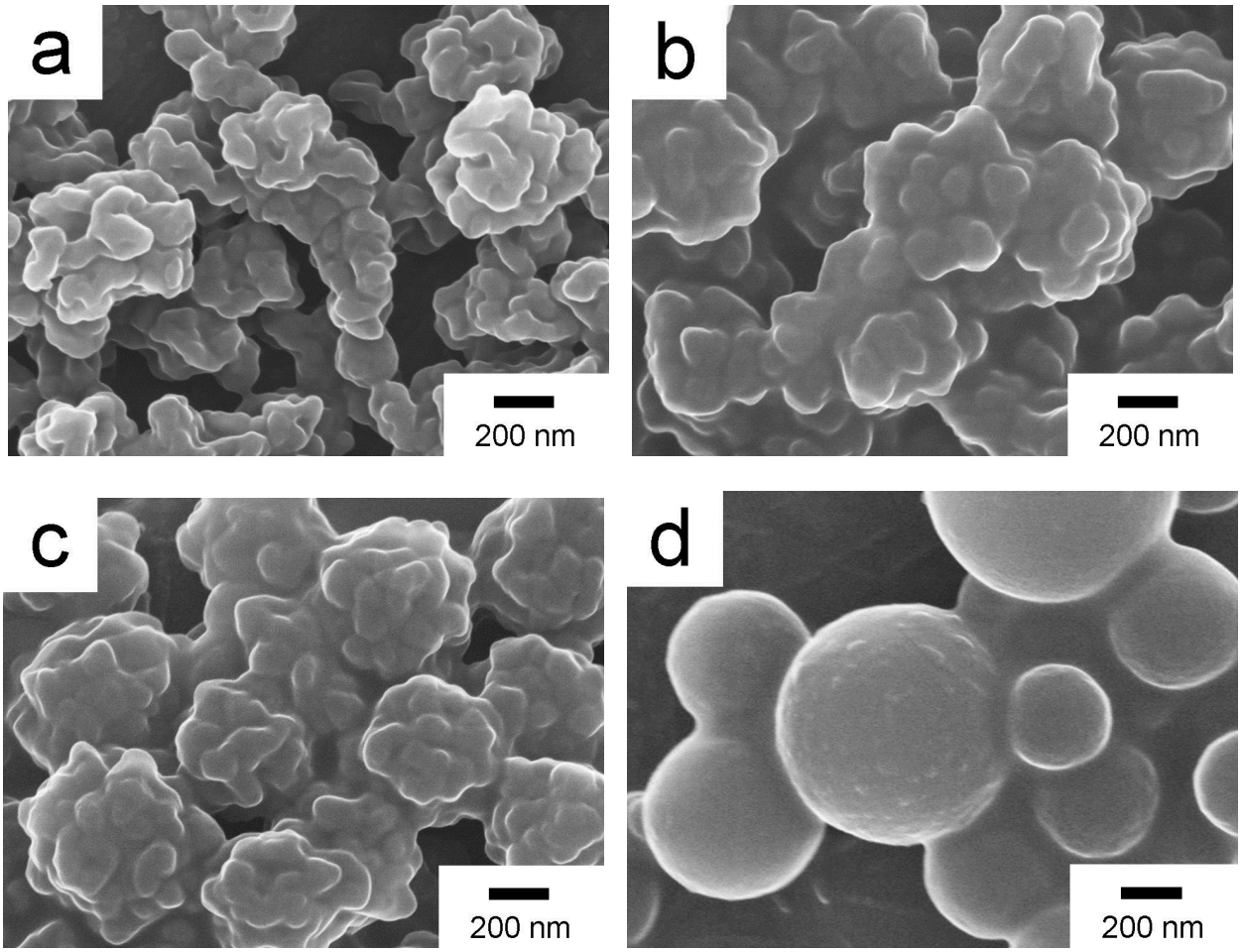

Fig. S3. SEM images of flower-like poly(St-*co*-VIPS) microspheres obtained under different [PVP] (in H_2O): (a) [PVP] = 0 M; (b) [PVP] = 0.75 g/L; (c) [PVP] = 1.5 g/L; (d) [PVP] = 2 g/L. Other conditions: [St]/[VIPS] =1:0.5, V_{St} = 5 mL, EtOH/H_2O (v/v) = 40/20.

It is well known that the kind and amount of surfactants often affect the morphologies and sizes of micro/nano-structures during their growth process,[1] especially so for polymer microspheres. Herein, the influence of [PVP] (in H_2O) on the morphologies of poly(St-*co*-VIPS) microspheres was also investigated. When there was no surfactant added into the reaction system, quite irregular poly(St-*co*-VIPS) blocks with inhomogeneous sizes and much rough surfaces were obtained, (Fig. S3(a)). With the addition of [PVP] (in H_2O) and its content increase, the poly(St-*co*-VIPS) blocks gradually became poly(St-*co*-VIPS) microspheres, its sizes gradually became larger and its surface gradually became

smooth Fig. S3(b)-(d). Therefore, PVP as the surfactant could affect both sizes and roughness of the flower-like poly(St-*co*-VIPS) microspheres.

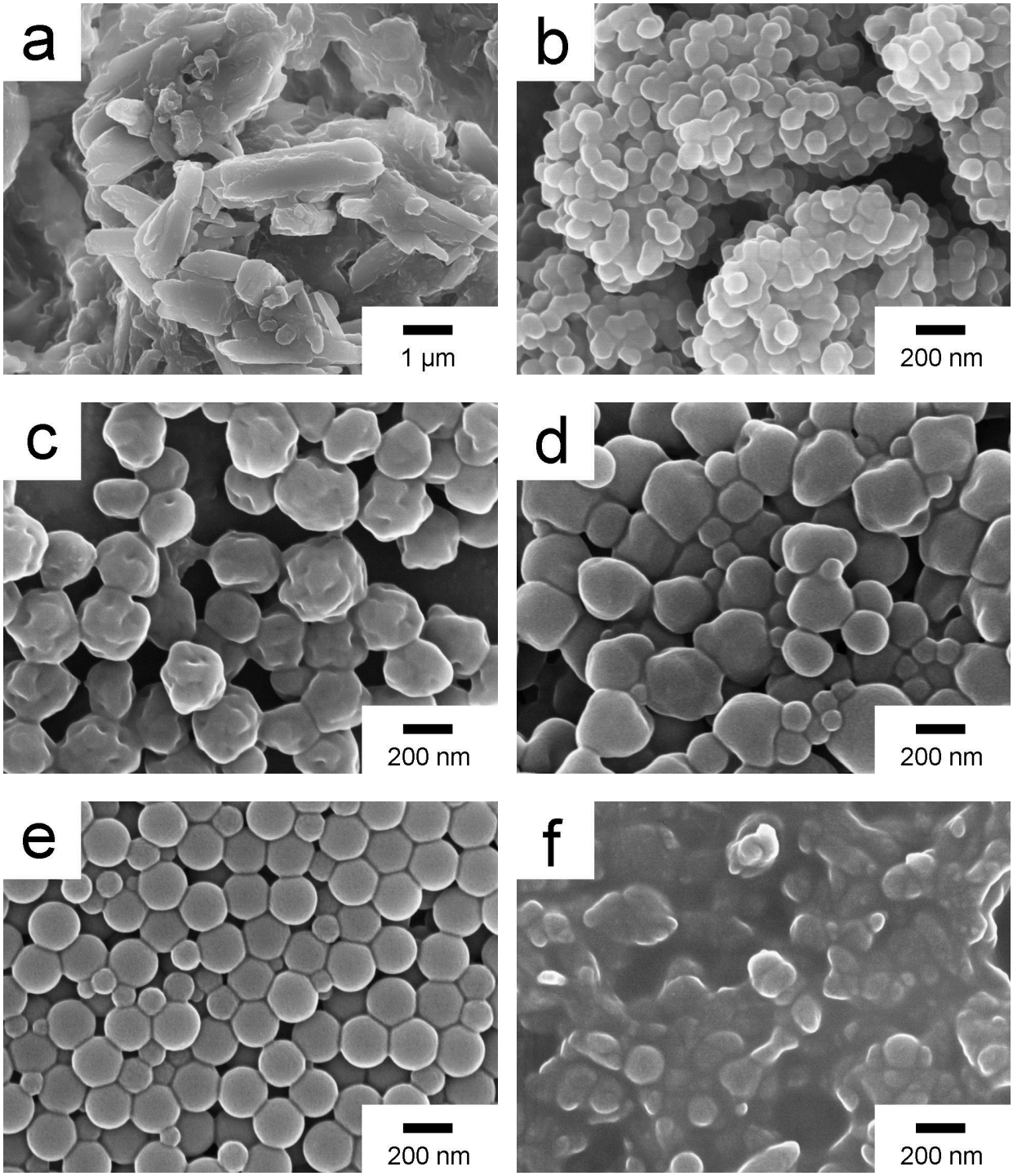

Fig. S4. SEM images of poly(St-co-VIPS) microspheres synthesized under different EtOH/H_2O (v/v): (a) 60/0; (b) 50/10; (c) 30/30; (d) 20/40; (e) 10/50; (f) 0/60. Other conditions: [St]/[VIPS] =1:0.5, [PVP] = 2 g/L (in H_2O), V_{St} = 5 mL.

According to the previous report,[2] addition of EtOH into a polymerization system for preparation of PS microspheres can significantly affect the sizes of micelles, which can further affect the diameter of the obtained PS microspheres. As shown in Fig. S4, for our system, the ratio of EtOH/H_2O (v/v) could also significantly influence the morphologies of obtained poly(St-*co*-VIPS). When the copolymerization of St and VIPS was carried out in 60 mL of EtOH, irregular bulks were obtained (Fig. S4(a)). With the addition of H_2O and the decrease of EtOH/H_2O (v/v), the obtained poly(St-*co*-VIPS) began to have a shape and its surface became more and more smooth (Fig. S4(b)-(e)). When EtOH/H_2O (v/v) was 10/50, most smooth poly(St-*co*-VIPS) microspheres with the diameter of 200 nm were observed in Fig. S4(e), though some small poly(St-*co*-VIPS) microspheres less than 150 nm in diameter also coexisted with them. Moreover, aggregated poly(St-*co*-VIPS) nanoparticles were obtained in Fig. S4(f), when there was no EtOH added into the copolymerization system. These difference in the morphologies of the obtained poly(St-*co*-VIPS) microspheres may be due to the changes of micelles sizes caused by the decrease of EtOH in the copolymerization system.

References

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