

## Microfluidic Preparation of Chitosan-Poly(acrylic acid) Composite Microspheres with Porous Surface Structure†

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### Supplementary:

In a microchannel, the size of formed droplets can be easily controlled in a wider range by varying the flow rate of continuous phase. Then we can obtain microspheres with a wider range of sizes after the droplets are solidified. As is shown in Fig S1, when the flowing rate of dispersed phase was 20  $\mu\text{L}/\text{min}$ , the diameter of formed droplets decreased from 480  $\mu\text{m}$  to 260  $\mu\text{m}$  as the flowing rate of continuous phase increased from 200  $\mu\text{L}/\text{min}$  to 2000  $\mu\text{L}/\text{min}$ . When the flowing rate of continuous phase was 200  $\mu\text{L}/\text{min}$  and 400  $\mu\text{L}/\text{min}$ , diameters of formed droplets were almost the same. This resulted from the restriction of width of microchannel.

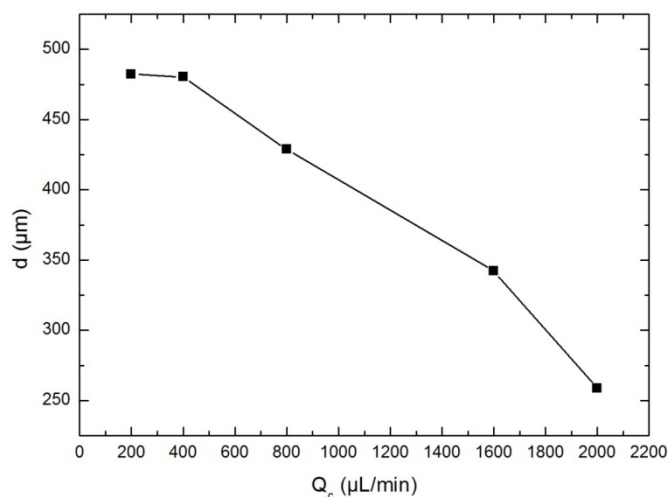


Fig. S1. Effect of flowing rate of continuous phase on size of formed droplets in the microchannel

The size of the microspheres will not affect the porous morphology obviously. In our work, we had prepared chitosan-poly(acrylic acid) composite microspheres with diameters of 120  $\mu\text{m}$ , 150  $\mu\text{m}$  and 170  $\mu\text{m}$ , and their morphology was very similar since they were all with porous surface and a compact core. It is shown in Fig. S2.

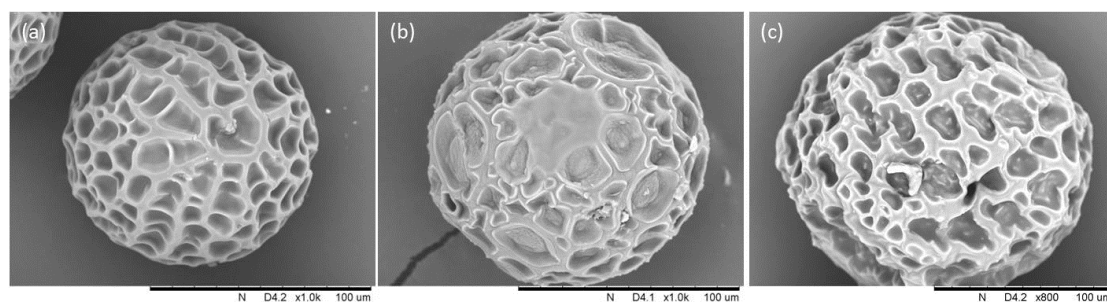
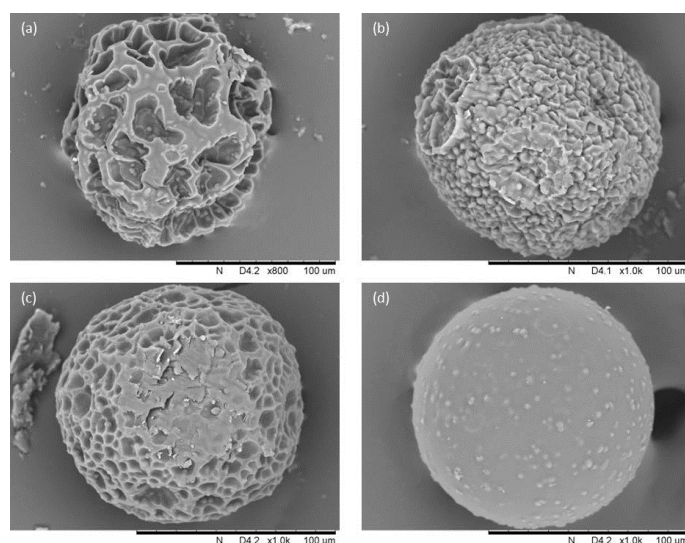


Fig. S2. Structures of chitosan-poly(acrylic acid) microspheres with diameters of (a) 120  $\mu\text{m}$ , (b) 150  $\mu\text{m}$  and (c) 170  $\mu\text{m}$  under the same solidification conditions

When molar ratio of CS and PAA was 2:1 and 1:1, similar structure evolution process was observed. In Fig. S1(a-d), CS-PAA microspheres solidified for 2.5h became compact from distinct porous surface structure as the amount of GLA increased, while molar ratio of CS and PAA was 2:1. When molar ratio of  $-CHO$  and extra  $-NH_2$  was increased to 4:1, the whole CS-PAA microsphere turned compact. But with the same solidification time and the same amount of GLA, the surface structure of CS-PAA microspheres was still porous as molar ratio of CS and PAA was 8:1, as shown in Fig. 4(a). From a series of SEM micrographs, we concluded that the surface structure was easier to become compact as the amount of PAA increased. It was because larger amount of PAA had participated in solidification and composition seemed easier than crosslinking process.



**Fig. S3** Surface structure of CS-PAA microspheres when  $n(-CHO):n(\text{extra } -NH_2)$  was (a)1:1; (b)2:1; (c)3:1; (d)4:1.  $n(\text{CS}):n(\text{PAA})=2:1$  and solidified for 2.5h.