

## Supporting Information

### Facile fabrication of poly(acrylic acid) hollow nanogels *via* in situ Pickering miniemulsion polymerization

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#### Experimental

##### Raw materials

Acrylonitrile (AN) and divinyl benzene (DVB) were purified by passing through a short basic  $\text{Al}_2\text{O}_3$  column before use. 2, 2'-azobis (isobutyronitrile) (AIBN, Fluka) was purified by recrystallization in absolute ethanol and kept refrigerated until use. Hexadecane (HD, Fluka), sodium nitrite ( $\text{NaNO}_2$ ), 2,2,4-trimethylpentane (TMP),  $\gamma$ - (trimethoxysilyl) propyl methacrylate (MPS, Aldrich), tetraethoxysilane (TEOS), and triethylamine (TEA) were used without further purification. Unless otherwise noted all chemicals were purchased from Shanghai Chemical Reagent Co. in their reagent grade. Deionized water was used for all purposes.

##### Preparation of PAA hollow nanogels

In a typical synthesis, 0.8 g of HD and 0.15 g of ABVN were first added in the monomer mixtures of 12.0 g of AN, 10.0 g of TEOS, and 1.2 g of DVB to form an oil phase. A portion of  $\text{NaNO}_2$ /water solution (95.0/0.02, g/g) was employed as a water phase. The mixture of oil phase and water phase was first pre-emulsified by magnetic stirring for 5 min, and the mixture was stirred for about 0.5 h after 1.0 g of TEA (dissolved in 5.0 g of  $\text{H}_2\text{O}$ ) was added. The miniemulsion was prepared by Ultra-Turrax®T18 homogenizer (IKA®, Germany) at 16, 000 rpm for 5 min in an ice bath and the polymerization was carried out at 55 °C in a 250-ml four-neck round flask equipped

with a reflux condenser and an agitator. After the polymerization was carried out for 8 h under N<sub>2</sub> atmosphere, silica/PAN hybrid microspheres were obtained. The hydrolysis reactions of silica/PAN hybrid microspheres were carried out by the addition of 30.0 g NaOH solution (5 mol/L). The reaction continued for 5 h at 80 °C to obtain PAA nanogels. The detailed recipes were listed in Table S1. For the synthesis of PAA (hollow) nanogels, TMP was added into oil phase.

**Table S1** The recipes for the synthesis of PAA hollow nanogels *via* in situ Pickering miniemulsion polymerization

Samples	Oil phase						Water phase	
	AN (g)	DVB (g)	MPS (g)	TEOS (g)	ABVN (g)	HD/TMP (g/g)	Water (g)	NaNO <sub>2</sub>
(g)								
1	12.0	1.20	1.20	0.0	0.15	0.8/0	100	0.15
2	12.0	1.20	1.20	4.0	0.15	0.8/0	100	0.15
3	12.0	1.20	1.20	6.0	0.15	0.8/0	100	0.15
4	12.0	1.20	1.20	8.0	0.15	0.8/0	100	0.15
5	12.0	1.20	1.50	10.0	0.15	0.8/0	100	0.15
6	12.0	1.20	1.80	12.0	0.15	0.8/0	100	0.15
7	8.0	1.20	1.20	8.0	0.15	0.8/4	100	0.15
8	6.0	1.20	1.20	8.0	0.15	0.8/6	100	0.15
9	4.0	1.20	1.20	8.0	0.15	0.8/8	100	0.15

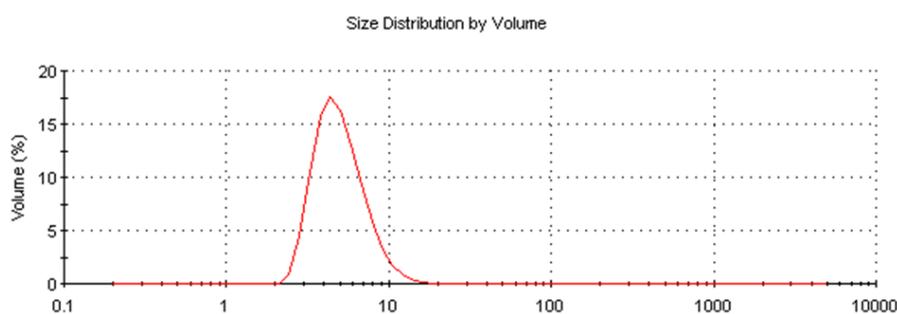
1.0 g of TEA (dissolved in 5.0 g of H<sub>2</sub>O) was added.

## Characterization

Samples of transmission electron microscopy (TEM) were prepared by drying a drop of dilute nanocomposite dispersion onto a carbon-coated copper grid. Analysis was conducted using a JEM-2100 (JEOL, Japan) electron microscope operating at 200 kV. The surface images of microparticles were studied by scanning electron microscopy (SEM, Hitachi S-4800) operating at 20 kV. The samples were previously diluted in water without filtration. Samples of FTIR characterization were dried at 60 °C under vacuum for 24 h and measured in the wavenumber range from 4000 to 400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> using a Nicolet Nexus-870 FTIR spectrophotometer. Thermogravimetric analyse (TGA) was conducted using thermoanalyzer STA449F3 from Netzsch Gerätebau, Selb. Samples were pre-dried in an oven at 70 °C and then heated in air to 800 °C at a heating rate of 20 °C min<sup>-1</sup>.

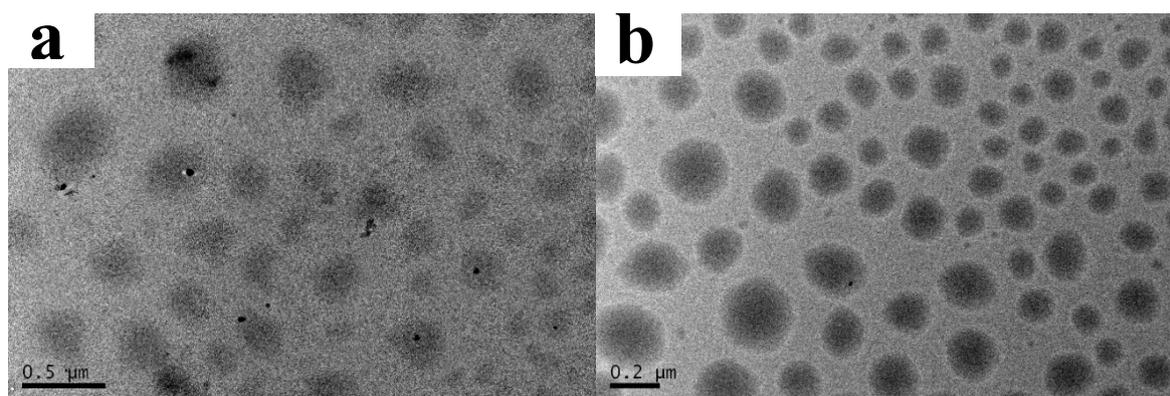
## Size distribution of nanosilica particles

As could be seen from Figure S1, the size of nanosilica was mainly in the range of 4 to 7 nm, which is in accord with the result estimated from TEM characterization.



**Figure S1** Size distribution of nanosilica particles after the full combustion of polymer in air. The residual was dispersed in water and determined by DLS.

### The morphologies of PAN nanoparticles and PAA nanogels



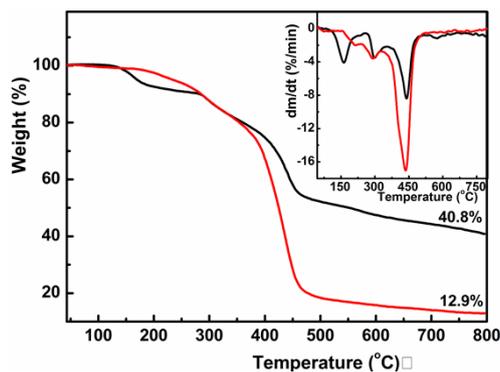
**Figure S2** TEM images of silica/PAA nanogels prepared with 4 g (a) and 8 g (b) of TEOS corresponding to Sample 2 and Sample 4 in Table S1.

TEM images of PAA nanogels prepared from different TEOS content were shown in Figure S2. It could be seen that with the amount of TEOS increased, the average size of PAA nanogels decreased accordingly.

### Thermogravimetric analysis (TGA) of silica/PAN nanoparticles and silica/PAA nanogels

The silica contents of silica/PAN nanoparticles and silica/PAA nanogels were estimated by thermogravimetric analysis (TGA). Figure S3 shows the TGA curves of silica/PAN nanoparticles (curve a) and silica/PAA nanogels (curve b). The total silica content from the TGA results (Figure S3)

was about 40.8 wt%. After the hydrolysis reactions, the silica content from the TGA results was about 12.9 wt%, which were chemically bonded with polymer by the copolymerization of MPS and other monomers. By subtracting the value of curve a from that of curve b, the silica content of silica/PAN nanoparticles, which were located on PAN nanoparticles by physical absorption, was calculated to be about 27.9 wt%. With the addition of MPS in the synthesis, the obtained nanocomposite microspheres were cross-linked by silica particles and thus had improved thermal stabilities.



**Figure S3** TGA and DTG curves of silica/PAN nanoparticles (curve a) and silica/PAA nanogels (curve b) corresponding to Sample 8 in Table S1.

## References

[S1] H. Hu, H. Wang and Q. Du, *Soft Matter*, 2012, 8, 6816.