

*Supplementary Information for:*

**Encapsulation of Inorganic Nanoparticles in Block Copolymer Vesicle Wall  
Driven by the Interfacial Instability of the Emulsion Droplets<sup>†</sup>**

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**S1. Synthesis of PS-Coated AuNPs.**

For Au<sub>1.7</sub>S (1.7 nm is the diameters of the cores of AuNPs), they were synthesized by the Brust two phase method.<sup>1</sup> Specifically, the solution of TOAB (0.8 mL, 50 mM) in toluene was mixed with the prepared HAuCl<sub>4</sub>·3H<sub>2</sub>O (0.3 mL, 30 mM) aqueous solution at first. Then, the HAuCl<sub>4</sub> was gradually transferred into the organic layer under vigorous stirring conditions, and PS2k-SH (18 mg, 9 μmol) dissolved in toluene (0.5 mL) was added to the mixed solution. Next, slowly drop the fresh aqueous solution of ice-cold NaBH<sub>4</sub> (0.25 mL, 0.4M) into the mixed solution under vigorous stirring conditions. The above solution was constantly stirring at high speed at room temperature for 3h and left to stand. After 3h, the organic phase and the water phase were completely separated. Then, the resulting solution was placed in the vacuum

drying chamber overnight to remove the organic phase. Adding the excess methanol to the resulting solution, then the residual TOAB and unbound PS2k-SH were removed by centrifugation (10000rpm, 30min). Subsequently, the aqueous layer was removed from the resulting solution and the nanoparticles were precipitated out of the solution by adding the excessive methanol. The mixture was stayed overnight at -20°C, and then centrifuged (10,000 rpm ,30min) and re-dispersed into chloroform. This process was repeated 3 to 5 times. Finally, the purified dark red Au<sub>1.7</sub>S was obtained and kept at -20°C.

For Au<sub>5.0</sub>S and Au<sub>10.0</sub>S (5.0 and 10.0 nm are the diameters of the Au cores, respectively.), a two-step ligand exchange method was used.<sup>2,3</sup> The first step was to prepare the AuNPs with the diameter of 5.0 and 10.0 nm. Then PS2k-SH was grafted on the surface of gold nanoparticles via ligand exchange reaction. The 5.0 and 10.0 nm AuNPs were synthesized by seeding growth. Firstly, for preparing initial Au seeds, 10 mL aqueous solution consisting of 0.25 mM HAuCl<sub>4</sub>·3H<sub>2</sub>O and 100 mM CTAB was first prepared in a vial. Afterward, 0.6 mL of freshly prepared ice-cold NaBH<sub>4</sub> (10 mM) aqueous solution was quickly injected into the mixture. At this point, it was found that a brown solution was immediately formed, proving that gold nanoparticles were formed in the solution. Then, the solution was left undisturbed at 27°C for 3 h to ensure the complete decomposition of NaBH<sub>4</sub> that remained in the solution. In this process, Au seeds were obtained.

To prepare gold nanoparticles with diameter of 5.0 nm or 10.0 nm, the growth solution was prepared at first. For the preparation of growth solution, the aqueous solutions of HAuCl<sub>4</sub>·3H<sub>2</sub>O (2 mL, 0.5 mM), CTAC (2 mL, 200 mM) were mixed in a glass vial (20 mL). Then, 1.5 mL of freshly prepared ascorbic acid (100 mM) was added to the growth solution. Subsequently, for preparing 5.0 nm AuNPs, 700 μL initial seed solution was added to the growth solution and the reaction was occurred at 27°C for 10 min under gentle stirring. As for preparing 10.0 nm AuNPs, 100 μL seed solution was added to the growth solution following by 10 min stirring at 27°C. For fabricating Au<sub>5.0</sub>S, the synthesized gold nanoparticles solution (100 mL) was mixed with the equal volume THF solution containing PS2k-SH (mole ratio Au: SH=1: 0.3). Then the

mixture was sonicated for 2 h and incubated for 24 h, the ultrasonic frequency was fixed at 100 kHz, which was important to control water temperature of the ultrasonic machine below 30 °C. After 30 min centrifugation at 10000 r/min, Au<sub>5,0</sub>S nanoparticles were obtained and dispersed in chloroform. Moreover, PS2k-SH chloroform solution was added into Au<sub>5,0</sub>S chloroform solution again (mole ratio Au: SH=1:0.15), and followed by the same sonication, incubation and centrifugation process to achieve high grafting density. To further purify Au<sub>5,0</sub>S, quantitative ethanol was added to the above chloroform solution to induce Au<sub>5,0</sub>S to precipitate out of the solution. Put mixed solution at -20°C for the night. Afterwards, the Au<sub>5,0</sub>S were separated by centrifugation (10,000 rpm, 30min). The same purified process was repeated 5-6 times to completely remove the unbonded PS2k-SH. Finally, the purified Au<sub>5,0</sub>S nanoparticles were dispersed in chloroform stored in -20°C. As for the Au<sub>10,0</sub>S, the specific process to fabricate the PS coated nanoparticles was in analogy with that of the Au<sub>5,0</sub>S.

## S2. Characterization of the Au<sub>x</sub>S

The core diameters of the AuNPs were examined by TEM and the graft degree was measured by TGA.

**Table S1.** Characteristic of different AuNPs.

AuNPs	$D_{\text{core}}$ (nm) <sup>a</sup>	$w_{\text{ligands}}$ (%) <sup>b</sup>	$D_N$ (nm) <sup>c</sup>	$D_N/d_{w0}$ <sup>d</sup>
Au <sub>1.7</sub> S	1.7±0.7	70	6.0	0.38
Au <sub>5.0</sub> S	5.0±0.9	31	10.5	0.66
Au <sub>10.0</sub> S	10.0±1.1	16	16.5	1.04

Note: a. The diameter of the Au core, measurable by TEM; b.  $w_{\text{ligands}}$  is the weight fraction of the ligands to the Au<sub>x</sub>S, obtained from TGA; c.  $D_N = D_{\text{core+shell}}$ , the diameter of the sum of the Au core and the ligands shell; d.  $D_N/d_{w0}$ :  $d_{w0}$  ( $d_{w0}=15.92\text{nm}$ ) is the thickness of the PS lamellae in the neat PS<sub>48.4k</sub>-P4VP<sub>21.3k</sub> capsule wall without AuNPs.

## REFERENCES

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