

## Supporting Information for:

Massage ball-like, hollow porous Au/SiO<sub>2</sub> microspheres templated by Pickering emulsion derived from polymer-metal hybrid micelles emulsifier

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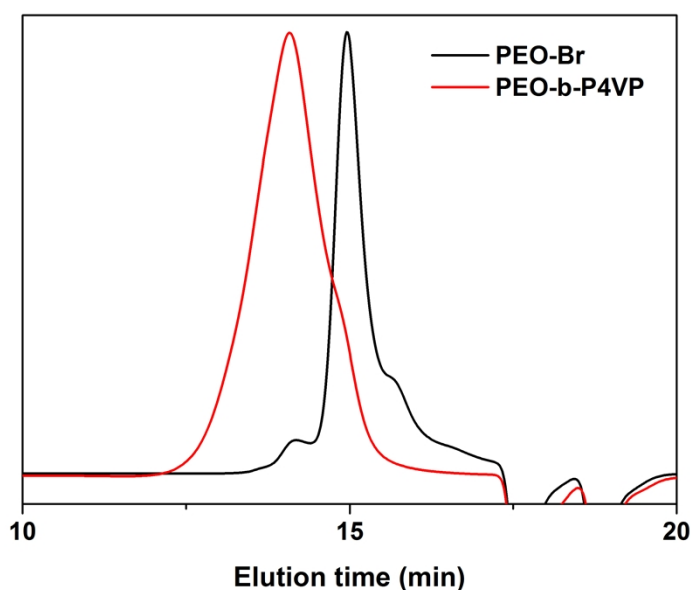
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### **S1. Synthesis and characterization of PEO-Br macromolecular ATRP initiator and PEO-b-P4VP block polymer**

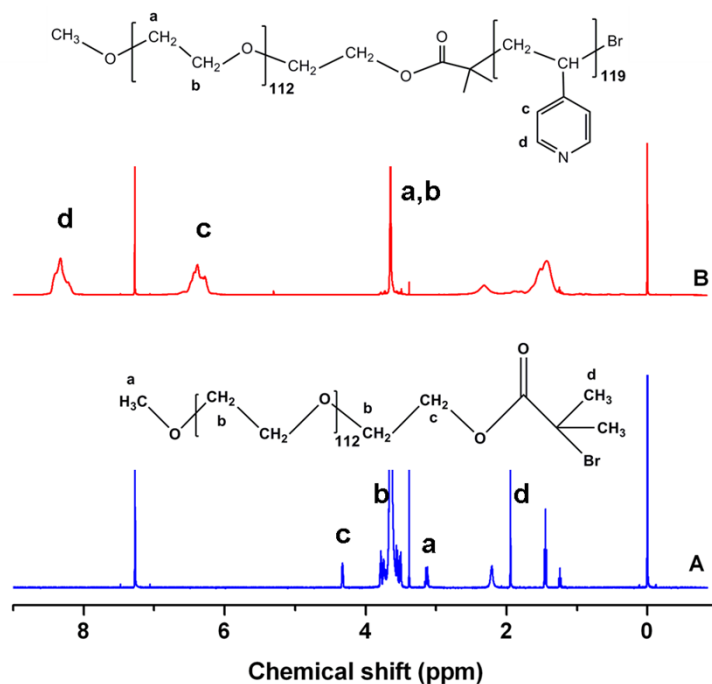
The PEO-Br macromolecular ATRP initiator and PEO-b-P4VP block polymer were synthesized as reported elsewhere[1-3]. 3.0 g of Poly(ethylene oxide) (PEO, Mn=5000 g/mol, PDI=1.03) was dissolved in 50 mL of dried toluene in a 100 mL three-neck flask at elevated temperature. Secondly, 1.0 mL of triethylamine was added into the flask. Finally, 1.0 mL of 2-bromoisobutryl bromide was dissolved in about 40 mL of dried toluene and the solution was added into the reaction flask using a bump at a rate of 0.03 mL/min. The reaction mixture was magnetically stirred for 24 h. After the reaction, filtered, most of the toluene was removed from the filtrate by rotary evaporation prior to precipitation into a 10-fold excess of cold ether. The crude polymer was dried under vacuum before being dissolved in water at pH 8-9. The aqueous solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic layer was collected. The dichloromethane solution was dried by anhydrous MgSO<sub>4</sub> overnight, filtered, precipitated three times in cold diethylether and dried at 40 °C under vacuum.

PEO<sub>113</sub>-*b*-P4VP<sub>119</sub> was synthesized by ATRP of 4-vinylpyridine with PEO<sub>113</sub>-Br as the macroinitiator and CuCl complexed by Me<sub>6</sub>TREN as the catalyst. The typical polymerization procedure to synthesize PEO<sub>113</sub>-*b*-P4VP<sub>119</sub> can be introduced as follow. 500 mg of PEG<sub>113</sub>-Br, 10 mg of CuCl and 28  $\mu$ L of Me<sub>6</sub>TREN were added to a reaction flask followed by addition of 1.0 mL of solvent mixture consists of 0.7 mL butanone and 0.3 mL isopropyl alcohol. The solution mixture was first stirred with ultrasonic and then degassed under nitrogen purge. Subsequently, 1.0 g 4-vinyl pyridine was added into the flask. The reaction mixture was degassed by three freeze-thaw cycles and flame-sealed under vacuum. Polymerization was performed at 60 °C for 6 h. After the end of the polymerization, the reaction mixture was dissolved in dichloromethane followed by passing through an Al<sub>2</sub>O<sub>3</sub> column to remove the copper catalyst. The dichloromethane solution was condensed by rotary evaporation and poured into 10-fold excess of cold ether. The precipitate of PEO<sub>113</sub>-*b*-P4VP<sub>119</sub> was filtered under vacuum and dried in vacuum at room temperature.



**Fig.S1.** GPC traces of PEO<sub>113</sub>-Br and PEO<sub>113</sub>-*b*-P4VP<sub>119</sub> diblock copolymer.

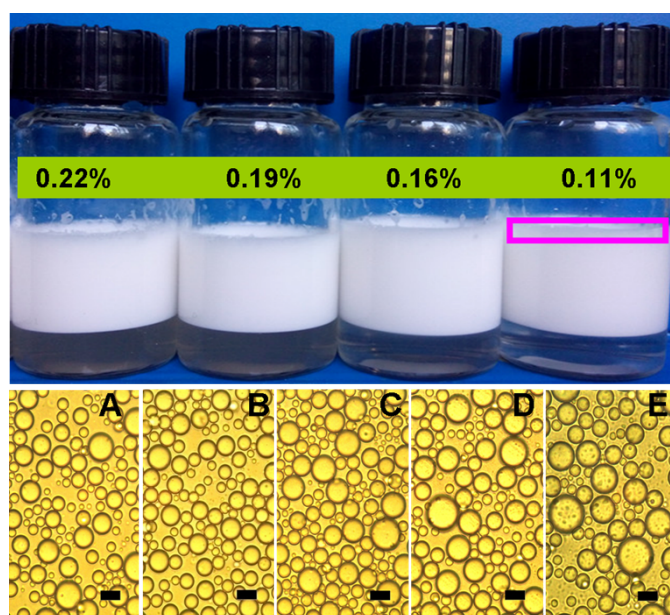
Fig.S1 was GPC traces of PEO<sub>113</sub>-Br and PEO<sub>113</sub>-b-P4VP<sub>119</sub> diblock copolymer. A distinctive shift towards high molecular weight was observed after chain extension, indicating successful ATRP polymerization reaction. According to GPC analysis, the average molecular weight of block polymer was 17600 g/mol. Therefore, the block length of P4VP was 119.



**Fig.S2.** <sup>1</sup>H NMR spectra of PEO-Br (A) and PEO<sub>113</sub>-b-P4VP<sub>119</sub> (B) in *d*-CHCl<sub>3</sub>.

In spectrum A, typical resonance peaks at chemical shifts 3.64 (b), 3.11 (a), and 1.94 (d) ppm were observed, corresponding to the proton signals of  $-CH_2CH_2O-$ ,  $-OCH_3$ , and  $-CH_3$ . Based on <sup>1</sup>H NMR analysis, the integral area ratio at 1.94 ppm to that at 3.11 ppm was about 2, indicating that the end hydroxyl groups in PEO were fully esterified. Fig.S2B was the <sup>1</sup>H NMR spectrum of PEO<sub>113</sub>-b-P4VP<sub>119</sub>, the typical resonance peaks at chemical shifts 8.33 (d) and 6.5 (c) ppm appeared, which were assigned to the proton signals of pyridine ring of 4VP repeat units.

**S2. The digital photographs of n-decanol in water Pickering emulsion and the optical microscopy photographs of the emulsions droplets stabilized by different content of Au@PEO-b-P4VP hybrid micelles.**

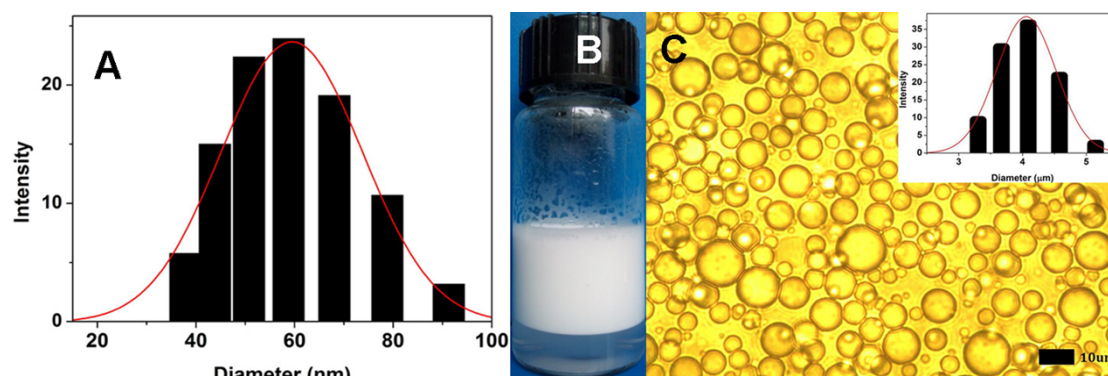


**Fig. S3.** Digital photographs of the n-decanol in water (volume ratio=1/1) emulsion droplets stabilized by varied content of Au@PEO-b-P4VP hybrid micelles. Optical microscope images of the emulsion droplets stabilized by Au@PEO-b-P4VP hybrid micelles at different content (A: 0.22 wt%; B: 0.19 wt%; C: 0.16 wt%; D: 0.11 wt%) after 24 h of displacement. (E) Optical microscope image of the emulsion droplets stabilized by 0.27 wt% of Au@PEO-b-P4VP hybrid micelles after 6 months of displacement. The photographs were taken after 24 h standing at room temperature. Scale bar: 10  $\mu\text{m}$ .

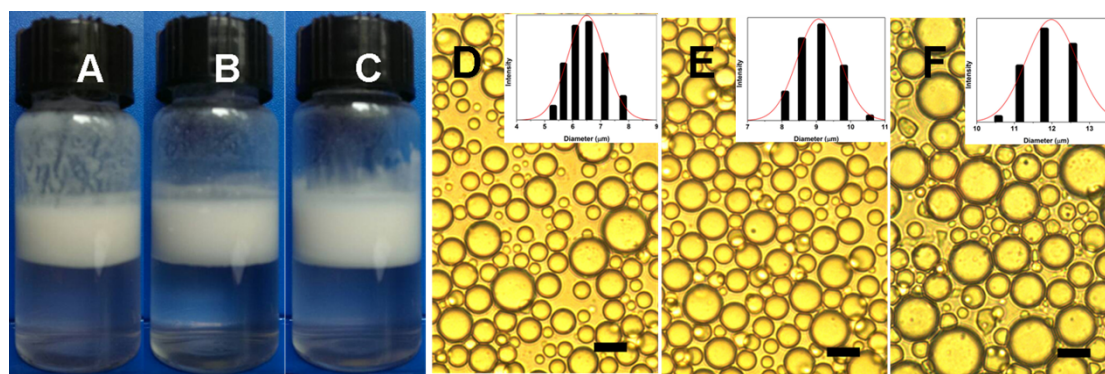
**S3. (A) DLS curve of PEO-b-P4VP micelles prepared by self assembly process of PEO-b-P4VP diblock polymer in selective solvent of water; (B) The digital photographs of (TEOS+n-decanol) in water Pickering emulsion with fixed oil/water volume ratio of 1/1, stabilized by 0.27 wt% of PEO-b-P4VP micelles and the corresponding optical microscopy photographs of the emulsions droplets. The photographs were taken after 24 h standing at room temperature. Inset: the droplets size distribution histogram.**

Based on DLS measurements, the  $\langle D_h \rangle$  of PEO-b-P4VP micelles was 56.3 nm (A). The  $\langle D_h \rangle$  of pure PEO-b-P4VP micelles was larger than that of Au@ PEO-b-P4VP hybrid micelles. The pure PEO-b-P4VP micelles also presented an excellent emulsifying performance, and stabilized o/w Pickering emulsion could be generated at 0.27 wt% of micelle concentration

(B). The thickness of emulsion layer reached 62.5%. The droplets size had a broad distribution, whose average diameter was 4.9  $\mu\text{m}$ .

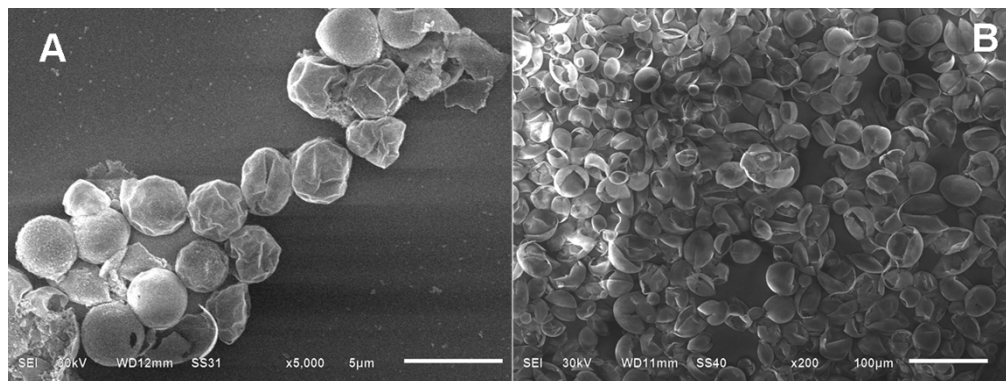


**S4. The digital photographs of (TEOS+n-decanol) in water Pickering emulsion with fixed oil/water volume ratio of 1/3 and different TEOS/n-decanol volume ratio (A: 2/1; B: 1/1; C: 1/2) stabilized by 0.27 wt% of Au@PEO-b-P4VP hybrid micelles and the optical microscopy photographs of the emulsions droplets generated by different TEOS/n-decanol volume ratio (D: 2/1; E: 1/1; F: 1/2). Insets: droplets size distribution histograms.**



According to the digital photographs, stable emulsion was generated and the thickness of emulsion layer was almost the same for different TEOS/n-decanol volume ratio, i.e., about 36 % of the total liquid volume. Optical microscopy observation indicated that the mean size of the corresponding emulsion droplets was 6.5, 9.6, and 12.9  $\mu\text{m}$ , corresponding to the 2/1, 1/1, and 1/2 of TEOS/n-decanol volume ratio, respectively. Scale bar: 10  $\mu\text{m}$ .

**S5. SEM images of SiO<sub>2</sub> microspheres obtained from Pickering emulsion templates with different TEOS/n-decanol volume ratio (A: 2:1; B:1:2).**



Deflated SiO<sub>2</sub> microspheres with many wrinkles on the surface were obtained (A) when the volume ratio of TEOS/n-decanol was 2:1. On the other hand, many broken SiO<sub>2</sub> microspheres were obtained (B) when the volume ratio of TEOS/n-decanol was 1:2.

**References**

- [1] Ma, R. J.; Wang, B. L.; Liu, X. J.; An, Y. L.; Li, Y.; He, Z. P.; Shi, L. Q. *Langmuir* **2007**, *23*, 7498-7504.
- [2] Zhang, W. Q.; Shi, L. Q.; Gao, L. C.; An, Y. L.; Wu, K. *Rapid Commun.* **2005**, *26*, 1341-1345.
- [3] Zhang, W. Q.; Shi, L. Q.; Ma, R. J.; An, Y. L.; Xu, Y. L.; Wu, K. *Macromolecules* **2005**, *38*, 8850-8852.