Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information:

Generation of Polymeric Nano-bowls through 3D Confined Assembly and Disassembly

Jiangping Xu,† Yuqing Wu,† Ke Wang, Lei Shen,* Xiaolin Xie and Jintao Zhu*

State Key Laboratory of Materials Processing and Mold Technology, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

*Corresponding authors, E-mail: lshen@hust.edu.cn (L. S.), jtzhu@mail.hust.edu.cn (J. Z.)

†These authors contributed equally to this work.

Experimental Section:

Materials: Symmetric diblock copolymers $PS_{9.8K}$-*b*-$P4VP_{10K}$ (S4VP-10, the subscripts are the M_n of the blocks, M_w/M_n = 1.08), PS_{20K}-*b*-$P4VP_{17K}$ (S4VP-17, M_w/M_n = 1.08), PS_{22K}-*b*-$P4VP_{22K}$ (S4VP-22, M_w/M_n = 1.15), PS_{110K}-*b*-$P4VP_{107K}$ (S4VP-107, M_w/M_n = 1.15), PS_{57K}-*b*-$P2VP_{57K}$ (S2VP-57, M_w/M_n = 1.05), PS_{133K}-*b*-$P2VP_{132K}$ (S2VP-132, M_w/M_n = 1.15), homopolymer hPS_{876K} (M_w/M_n = 1.19) and $PMMA_{24K}$ (M_w/M_n = 1.25) were purchased from Polymer Source, Inc., Canada. Cetyltrimethylammonium bromide (CTAB, purity ≥ 99%) was purchased from Aldrich. 1, 4-diiodobutane (DIB, purity 99 %) and crystal violet (CV, purity > 90 %) was supplied by Alfa Aesar. All of the materials were used as received without further purification.

Preparation of Nano-bowls: A two-step strategy was applied to synthesize diblock copolymer nano-bowls. First, Janus particle consisted of a dissected onion (S4VP or S2VP) and a solid hPS hemisphere was prepared by the emulsion-solvent evaporation method. In this step, the copolymer (S4VP or S2VP) and homopolymer (hPS_{876K}) were fully dissolved in chloroform at a concentration of 10 mg/mL, respectively. Then, the copolymer solution was mixed with hPS solution with different weight ratios ($r = m_{SIV}:m_{hPS}$). Subsequently, 0.1 mL of the polymer solution was emulsified with 1.0 mL aqueous solution of CTAB (3 mg/mL) via hand-driven membrane-extrusion emulsification. The organic solvent was then allowed to slowly evaporate for 3 days at 30 °C. Janus particles were obtained after thoroughly evaporating the organic solvent.

The second step was attributed to the crosslinking and disassembly of the Janus particles. DIB was used to selectively crosslink P4VP (or P2VP) block. Typically, DIB was dissolved in ethanol at a concentration of 50 mg/mL and then added to the particle suspension (DIB:4VP unit = 10:1). After being stirred at 45 °C for 3 days, the crosslinked particles were separated by centrifugation (14 000

rpm, 6 min) and washed in ethanol for 3 times. Then, the particles were dispersed in THF, which could dissolve PS domains. As a consequence, the dissected onion would be disassembled to nano-bowls with crosslinked P4VP domain as the core. Then, the nano-bowls were separated by centrifugation (18 000 rpm, 15 min) to remove the free hPS_{876K} chains in the solution.

Synthesis of Gold NPs Loaded Hybrid Nano-bowls: The hybrid nano-bowls were prepared via *in-situ* reduction strategy. First, the nano-bowls were redispersed in THF (0.3 mg/mL, 0.5 mL). Then, an aqueous solution of $HAuCl_4$ (0.1 M, 0.02 mL) was added to allow a favorable absorbing of $HAuCl_4$ by P4VP segment for 24 h. Afterward, the nano-bowls were separated by centrifugation at 18,000 rpm for 15 min and washed with ethanol (0.2 mL) to remove the excess $HAuCl_4$. Then, the nano-bowls were redispersed in 0.5 mL THF, and freshly prepared iced solution of $NaBH_4$ (10 mg/mL, 0.02 mL) was dropped under stirring. The mixture was gently stirred for 24 h to complete the reaction. Finally, the composite particles were separated by centrifugation at 18,000 rpm for 15 min, and the precipitates were redispersed in 0.5 mL THF.

Surface Enhanced Raman Scattering (SERS): Silicon wafers were used as substrate in our experiments. The substrates were washed with soap, ethanol and distilled water sequentially. For the control experiment, 2 μL of crystal violet (CV) aqueous solution (10^{-3} mg/mL) was dropped on the silicon surface and dried in vacuum. For the SERS experiment, 3 μL of the gold NPs hybrid nano-bowls THF solution was first dropped on the silicon surface and then 2 μL of CV aqueous solution was added on the nano-bowl layer. Afterward, the sample was dried in vacuum before SERS measurement.

Characterization: Structure of the nano-bowls was investigated using FEI $TecnaiG^2$ 20 transmission electron microscope (TEM) operated at an accelerated voltage of 200 kV. Before TEM

characterization, the samples were selectively stained with iodine vapor for 2 h (for P4VP block). The surface topology of the nano-bowls was characterized by Sirion 200 scanning electron microscope (SEM). The SERS experiment was conducted by using Bruker FRA 106/S.

Supporting Figures:

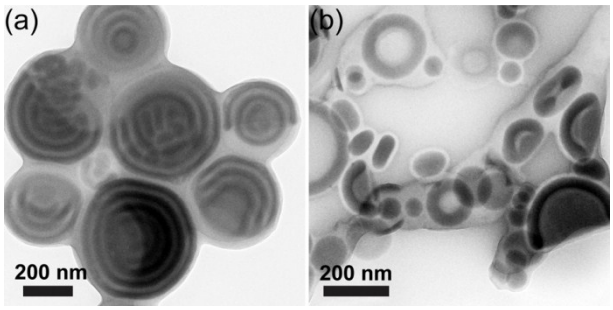

Fig. S1 TEM images of (a) Janus particles obtained at S4VP-22: hPS_{876K} = 3:1; (b) Various nano-objects obtained by crosslinking and disassembling the particles in (a).

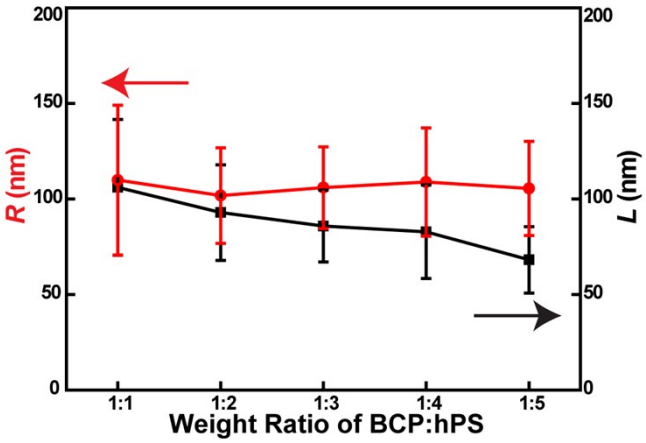

Fig. S2 The opening radius of nano-bowls decreases as the increase in hPS weight fraction, while the curvature radius of the particles remains unchanged. Thus, the opening degree *L*/*R* will decrease as the increase of hPS.

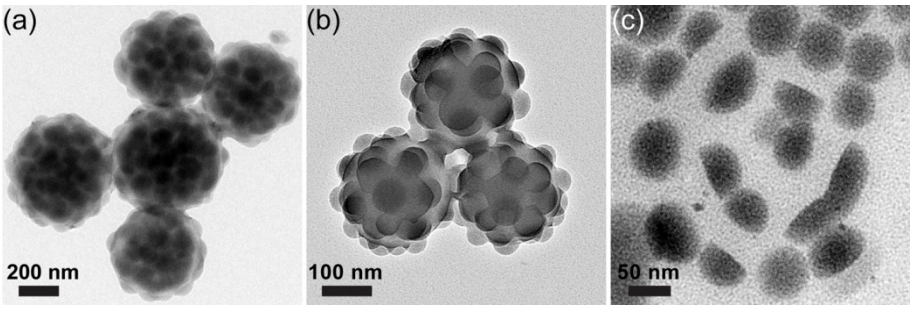

Fig. S3 TEM images of (a) Patchy particles of neat S4VP-107; (b) Patchy particles obtained at S4VP-107: hPS_{876K} = 1:1; (c) Janus NPs obtained by crosslinking and disassembling the particles in (b).

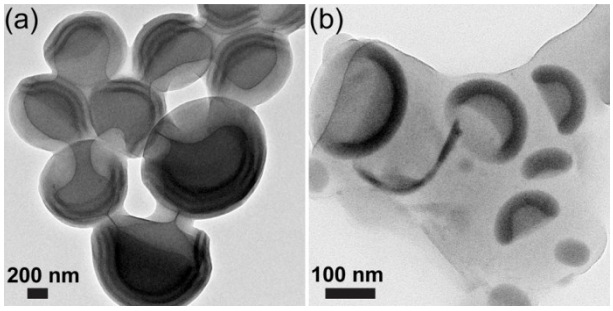

Fig. S4 TEM images of (a) the S4VP-22/$PMMA_{24K}$ Janus particles (weight ratio 1:2). (b) Nano-bowls obtained by crosslinking and disassembling the Janus particles in (a).