Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Responsive Polymeric Janus Cage

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1. Experiment

1.1 Materials

The polystyrene (PS) hollow sphere (HP-1055) emulsion with a solid content of 37.5 wt% was purchased from the former Rohm & Hass. Sodium dodecyl benzenesulfonate (SDS), N,N-dimethylformamide (DMF) and azobisisbutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent. Divinylbenzene (DVB) was purchased from Sigma-Aldrich and purified over Al_2O_3 column. The amine-group capped methoxypolyethylene glycol (PEO-NH_2, Mn=2000), N-isopropylacrylamide (NIPAM), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) and vinylbenzyl chloride (VBC) were purchased from J&K Chemical. NIPAM was recrystallized in toluene and n-hexane. Copper bromide (CuBr), 2-propanol and ethanol were purchased from Sinopharm Chemical Reagent. The other reagents were used as received without further treatment.

1.2 Crosslinked Hollow Sphere of PS@*c*PVBC by Seed Swelling Emulsion Polymerization.

13.335 g of the PS hollow sphere emulsion (solid content of 37.5 wt%) was diluted in 160.0 mL of water achieving the seed emulsion. The mixture of 2.700 g of DVB, 0.300

g of VBC and 0.030 g of AIBN was emulsified in 20.0 mL of water in the presence of 0.048 g of SDS under ultrasonication for 1 min, forming the mixture monomer emulsion. After the monomer emulsion was fed into the seed emulsion, the mixture was stirred at 300 rpm at 30 °C for 8 h to swell the PS shell. The emulsion polymerization was performed at 70 °C for 12 h. An example crosslinked hollow sphere of PS@*c*PVBC was synthesized after centrifugation and freeze drying.

1.3 Janus Cage of *c*PVBC-PEO.

The crosslinked hollow sphere of PS@*c*PVBC was modified to conjugate hydrophilic PEO selectively onto the exterior surface. After 0.100 g of the crosslinked hollow sphere was dispersed in 20.0 mL of ethanol, 0.010 g of PEO-NH_2 was fed under stirring for the modification at 40 °C for 12 h. A layer of PEO was grown at the exterior surface of the shell by the nucleophilic substitution between PVBC and PEO-NH_2. The Janus hollow sphere of PS@*c*PVBC-PEO was obtained after washing with water/ethanol mixture (1:1 vol/vol) and freeze drying. The PS@*c*PVBC-PEO cage powder was dispersed in 50.0 mL of DMF at 30 °C and stirred for 4 h to dissolve PS from the shell. The hollow sphere became a cage along with perforating of the shell. The Janus cage of *c*PVBC-PEO was achieved after washing with ethanol/water mixture and freeze drying.

1.4 Janus Cage of PNIPAM-*c*PVBC-PEO.

PNIPAM was grafted by ATRP at the *c*PVBC-PEO Janus cage. 0.050 g of the *c*PVBC-PEO Janus cage, 0.030 g of PMDETA, 0.600 g of NIPAM were mixed in 6.0 mL of 2-propanol under stirring. After three cycles of freeze pump thaw at 45 °C, 0.015 g of CuBr was fed under nitrogen. After the ATRP at 70 °C for 24 h, the polymerization was terminated by exposure to air. The thermo-responsive Janus cage of PNIPAM-*c*PVBC-PEO was achieved after washing with ethanol and vacuum drying at 35 °C.

1.5 Characterization

TEM (JEOL 1011) operating at 100 kV and SEM (FEI QUANTA FEG 250) operating at 15 kV were used to observe morphology of the samples. The samples for SEM characterization were dried at ambient temperature and sputtered with Pt. Porosity of the *c*PVBC-PEO and PNIPAM-*c*PVBC-PEO Janus cages was characterized by

isothermal nitrogen adsorption-desorption on JW-BK200C at 373K. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) model, while the pore information was derived using the Barrett-Joyner-Halenda (BJH) model. The emulsion type was determined via confocal laser scanning microscopy (CLSM) FV1000 and confocal fluorescence microscopy with IX-81 inverted base and PMT detector. Two channels at 488 nm and 561 nm were used to visualize the cage and dye oil, respectively. Derjaguin-Müller-Toporov (DMT) modulus imaging measurement was recorded on Bruker NanoScope V MultiMode 8 under ambient conditions in the mode of peak force quantitative nanomechanical mapping.

2. Results and Discussion

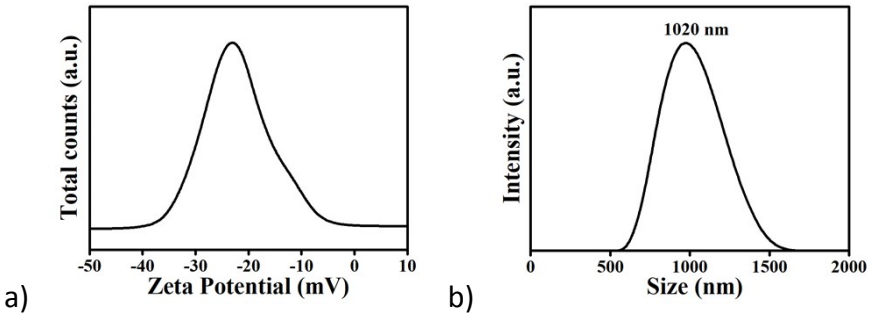
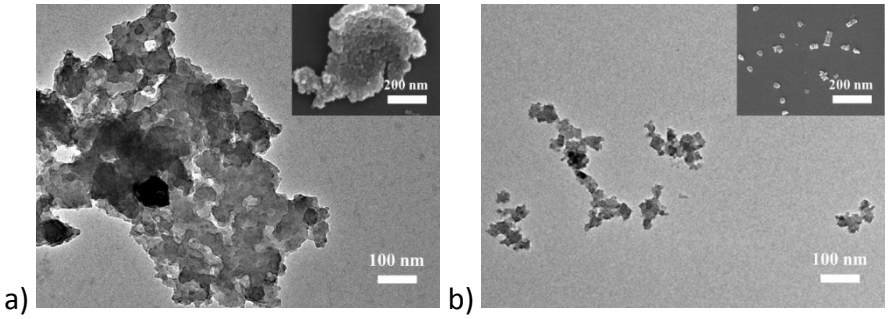
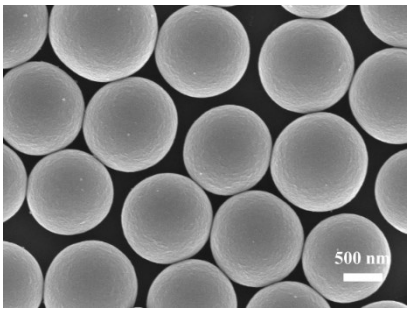


Figure S1. (a) Zeta potential and (b) Size distribution of the polystyrene hollow particle (HP-1055).



c) 

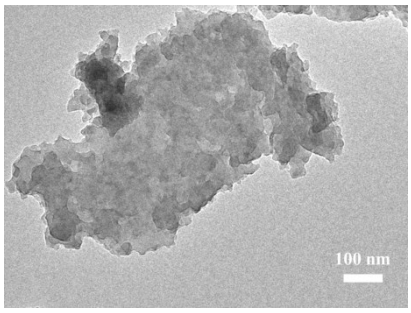
d) 

Figure S2. (a) TEM and SEM images of the *c*PVBC-PEO Janus cage fragment after grinding the PS@*c*PVBC hollow sphere prepared at the monomer/PS weight ratio of 3/5; (b) TEM and SEM images of the *c*PVBC-PEO fragment, derived from the PS@*c*PVBC hollow sphere prepared at the monomer/PS weight ratio of 1/5; (c) SEM image of the *c*PVBC-PEO Janus cage, derived from the PS@*c*PVBC hollow sphere prepared at the monomer/PS weight ratio of 5/5; (d) TEM image of the *c*PVBC-PEO Janus cage fragment after grinding the PS@*c*PVBC hollow sphere prepared at the monomer/PS weight ratio of 5/5.

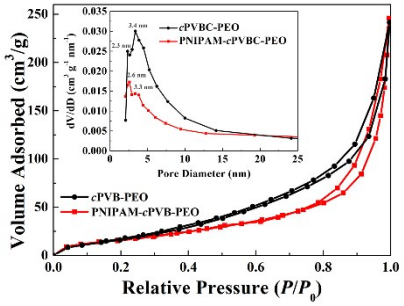


Figure S3. The N_2 adsorption and desorption nitrogen isotherms at 373 K of the two Janus cages of *c*PVBC-PEO and PNIPAM-*c*PVBC-PEO. Inset the corresponding pore size distributions.

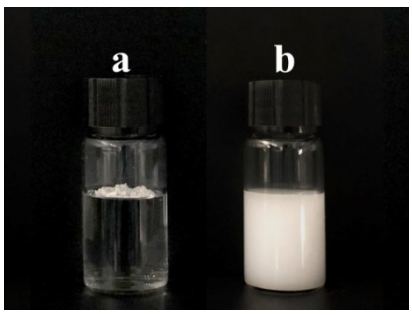
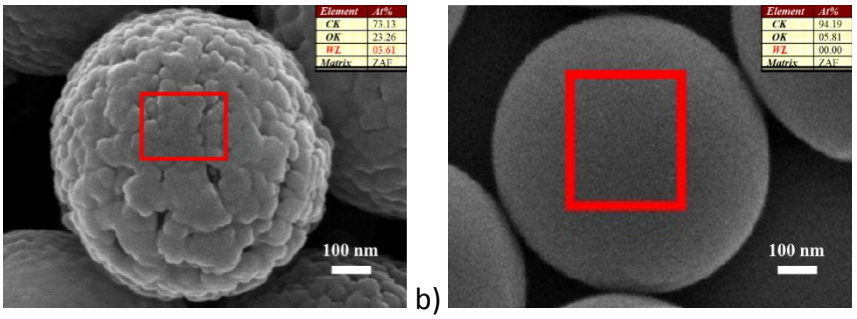
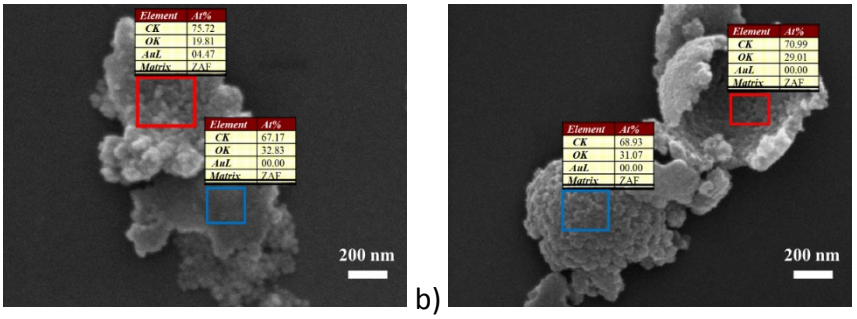


Figure S4. (a) The crosslinked PS@*c*PVBC hollow sphere after washing SDS with ethanol; (b) aqueous dispersion of the *c*PVBC-PEO Janus cage.



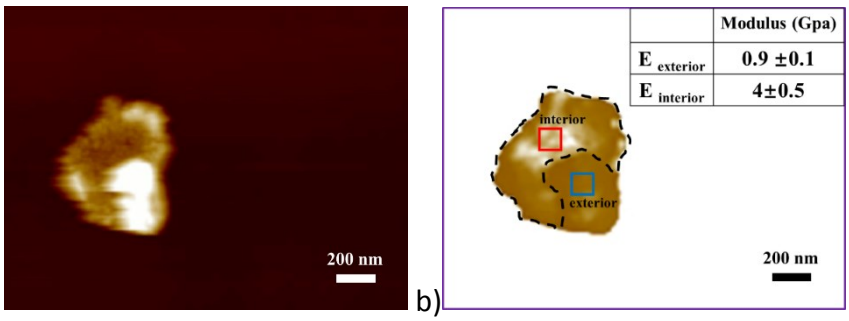
a) b)

Figure S5. (a) SEM image of the *c*PVBC-PEO Janus cage, inset the EDX result; (b) SEM image of the crosslinked PS@*c*PVBC hollow sphere after washing with ethanol. Both samples were treated along with staining with PTA.



a) b)

Figure S6. SEM images and inset EDX results of the fragments of the two different Janus cages: (a) PNIPAM-*c*PVBC-PEO; (b) *c*PVBC-PEO.



a) b)

Figure S7. (a) AFM images and (b) DMT moduli of the two sides of the PNIPAM-*c*PVBC-PEO fragment.

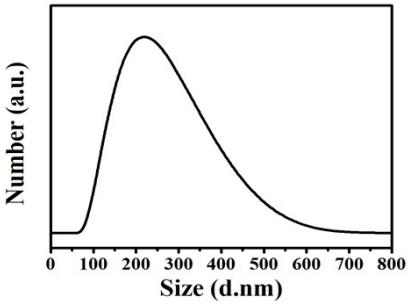


Figure S8. Size distribution of the n-hexane/water emulsion stabilized with CTAB.

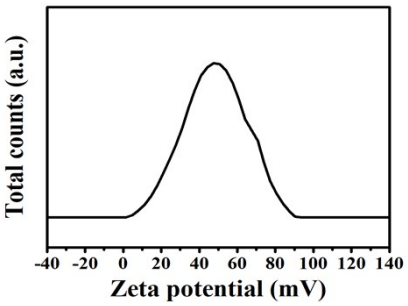


Figure S9. Zeta potential of the n-hexane/water emulsion stabilized with CTAB.

Figure S10. Some representative dispersions of the PNIPAM-*c*PVBC-PEO Janus cage: (1) the dispersion in water; (2) feeding the SDS stabilized n-hexane (Nile red dyed)/water emulsion to the dispersion under stirring at 25 °C, and standing rest; (3) stirring the dispersion (2) for 2 min at 40 °C, and standing rest for 10 min; (4) upon cooling the mixture (3) to 25 °C, n-hexane was released forming the top oil layer, while the cage entered downwardly forming the bottom opaque dispersion.

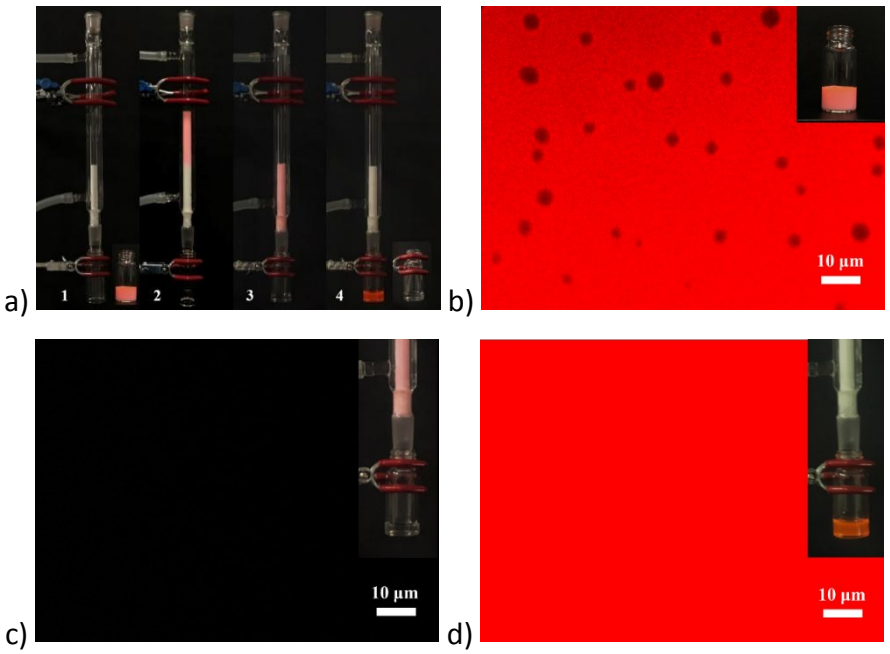


Figure S11. (a) (1) PNIPAM-*c*PVBC-PEO Janus cage column at 40 °C, (2) feeding the SDS

stabilized water/n-hexane emulsion to the column, (3) n-hexane was captured inside the Janus cage while water eluted, (4) n-hexane was released from the cage when cooling down to 25 °C; (b) CLSM image of the SDS stabilized water/n-hexane emulsion; (c) CLSM image of the eluted water phase; (d) CLSM image of n-hexane released from the cage at 25 °C.

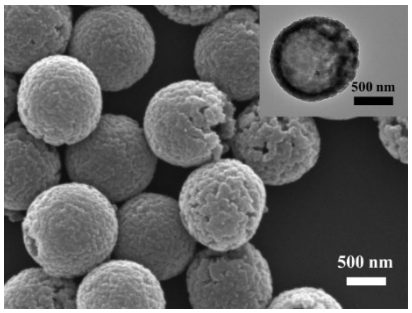


Figure S12. SEM and inset TEM images of the recycled PNIPAM-*c*PVBC-PEO Janus cage.