

Responsive Composite Janus Cages^{*}

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Abstract pH responsive composite Janus cages of PS-silica-PEO are prepared using silica nanoparticles to crosslink two PAA contained di-block copolymers at an emulsion interface sequentially. Transverse channels are *in situ* created across the shell, which facilitates mass transfer. Shell is pH responsive owing to the presence of residual PAA chains tethered onto the silica nanoparticles. The Janus cages are capable to preferentially capture oil from their aqueous surroundings. The saturation absorption capacity is determined by pH and oil property. Other composite Janus cages are expected by extension the method using other copolymers and functional nanoparticles.

Keywords: Janus cages; Block copolymer; Composited; pH response; Emulsion.

INTRODUCTION

Janus materials with two compositions and properties distinctly compartmentalized onto one object have attracted great interest in recent years due to their diversify performances and thus potential applications^[1–3]. It has become a crucial concern to tune morphology and composition of Janus materials. The current Janus materials are mainly in the shapes of particulate, disc and rod which are non-centrosymmetric. Two different compositions are compartmentalized onto the same outermost surface. We have recently extended the Janus concept to centrosymmetric hollow spheres with two compositions segmented onto the interior and exterior surfaces of the shell, respectively^[4]. Such Janus hollow spheres can mimic micelles but solid and more robust^[5]. They can serve as specific containers to selectively capture desired compounds from their surroundings arisen from different affinity^[4, 6]. The Janus hollow spheres are potentially useful in controlled loading and release, and confined heterogeneous catalysis^[7–13]. After selective grafting a thermal responsive polymer onto the interior surface, the Janus hollow sphere can load and release desired materials^[14]. The procedure is triggered by changing temperature. After introduction of catalytic for example titania nanoparticles inside the cavity of the Janus hollow spheres, the Janus micro-reactor can integrate responsive Janus performance and confined catalysis^[15]. Creation of transverse channels across the shell can greatly facilitate mass transfer. A kind of Janus cages is derived. Meanwhile, grafting functional brushes onto the channel surface can gate mass transfer.

Herein, we develop a facile method to fabricate Janus cages by crosslinking a self-assembly monolayer (SAM) of an amphiphilic copolymer at a paraffin-in-water emulsion interface (Scheme 1). Poly(styrene)-block-poly(acrylic acid) (PS-*b*-PAA) copolymer is selected as the representative amphiphilic copolymer. The

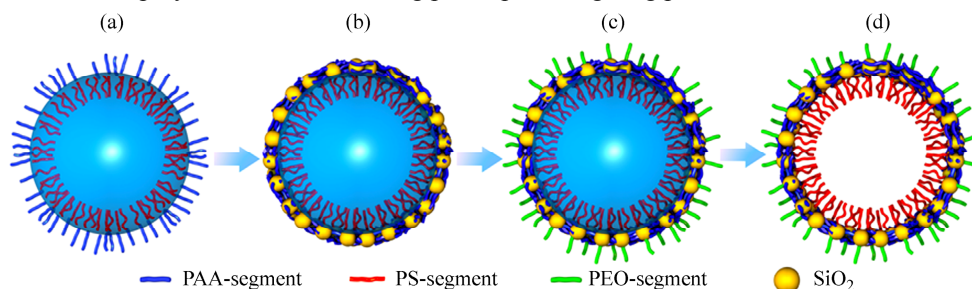
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hydrophobic PS block directs towards the internal paraffin phase whilst the hydrophilic PAA block directs towards the external aqueous phase (a). The paraffin spheres become solidified upon cooling. SAM is thus frozen at the paraffin spheres surface. The PAA blocks can be selectively crosslinked in aqueous phase to form a robust nano-membrane. Amine- group capped silica nanoparticles are used as a crosslinker in order to *in situ* create transverse channels (b). While one side of the silica particles is covalently bound, residual amine-group on the other side can further react with another polymer for example poly(ethylene glycol)-block-poly(acrylic acid) (PEO-*b*-PAA). Sandwiched structure of PS-SiO₂-PEO is created (c). After dissolution of the paraffin core, Janus cages with a sandwiched shell of PS-SiO₂-PEO are achieved (d). It is noted that the channel surface contains PAA from the block copolymers, which can bring pH responsive gating performance.



Scheme 1 Schematic synthesis of the PS-SiO₂-PEO Janus cage

Amphiphilic PS-*b*-PAA copolymer is employed to stabilize a paraffin-in-water emulsion and self-assembly at the oil-water interface (a). The amine- group capped silica nanoparticles are used to crosslink the self-assembly monolayer (b). The PEO-*b*-PAA copolymer is grafted onto the external sides of the silica nanoparticles forming a PS-SiO₂-PEO tri-layered shell (c). After dissolution of the paraffin, PS-SiO₂-PEO Janus cages are obtained (d).

EXPERIMENTAL

Materials

PS_{2.3k}-*b*-PAA_{9.5k} ($M_w/M_n = 1.1$) and PEO_{6k}-*b*-PAA_{5.2k} ($M_w/M_n = 1.15$) were purchased from Polymer Source. Paraffin ($T_m = 50\text{--}52\text{ }^\circ\text{C}$) was purchased from Shanghai Huayong Paraffin. Sodium hydroxide (NaOH), hydrochloric acid (HCl) and the solvents such as *n*-hexane, tetrahydrofuran (THF) and ethanol were obtained from Sinopharm Chemical Reagent. The silica nanoparticle (30R25) was kindly provided by AZ Electronic Materials France SAS. Fluorescein isothiocyanate (FITC), aminopropyltriethoxysilane (APTES), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) were purchased from Aldrich.

Emulsification

After 0.05 g of PS-*b*-PAA was dispersed into 10 mL of water under ultrasonication, 10 μL of NaOH (2 mol/L) aqueous solution was added. After the mixture was heated to 70 $^\circ\text{C}$, 0.1 g of melted paraffin was added at 70 $^\circ\text{C}$. The mixture was emulsified at a speed of 15000 r/min for 5 min to form an O/W emulsion. The emulsion was cooled down to room temperature to solidify the paraffin sphere in the aqueous phase. Residual PS-*b*-PAA copolymer was removed from the continuous phase by centrifugation.

Synthesis of the Amine-Group Capped Silica Nanoparticles

The amine-group capped silica nanoparticles were synthesized^[16]. After 1.0 g of silica nanoparticles was dispersed into 100 mL of ethanol containing 1 vol% APTES, the mixture was heated to 80 $^\circ\text{C}$ and held under stirring for 12 h. The product was washed by ethanol and dispersed in 20 mL water to obtain the amine-group capped silica nanoparticle aqueous dispersion.

Synthesis of the PS-SiO₂-PEO Janus Cages

0.1 g of the paraffin spheres stabilized with PS-*b*-PAA was dispersed in 10 mL of water. 0.01 g of EDC and 0.005 g of NHS were added and held for 12 h to activate the carboxyl-group. 10 μL of the amine- group capped silica dispersion was added at room temperature and held for 12 h. Residual silica nanoparticles were removed

by centrifugation. 100 μL of 1 wt% EDC/NHS activated PEO-*b*-PAA aqueous solution was added into the above mixture and held for 12 h. After dissolution of the paraffin phase with *n*-hexane, the PS-SiO₂-PEO Janus cages were obtained.

Characterization

Very diluted dispersions in ethanol were dropped onto wafer support for SEM sample preparation. The samples were ambient dried and vacuum sputtered with Pt. SEM measurement was performed with a Hitachi S-4800 scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV. Morphology of the Janus cages was characterized by transmission electron microscope (TEM, JEOL1011 operating at 100 kV). Morphology of the Janus cages after capturing oil was characterized with Leica DMLP microscope and confocal laser scanning microscope (CLSM, Olympus FV 1000-IX81). FTIR spectroscopy was performed with the sample/KBr pressed pellets after scanning samples for 32 times using Bruker Equinox 55 spectrometer. Dynamic light scattering (DLS, Mastersizer 2000) was used to measure the size of the cages. Cross-section TEM images were obtained by microtoming the samples embedded in PMMA with a Leica ultramicrotome (UCT-GA-D/E-1/00).

RESULTS AND DISCUSSION

The amphiphilic PS-*b*-PAA copolymer is used as a surfactant to emulsify the immiscible paraffin and water mixture forming an oil-in-water emulsion. At the emulsion interface, the hydrophilic PAA chains face towards water phase and the hydrophobic PS chains face towards oil phase. A self-assembly monolayer (SAM) forms. When the paraffin phase is frozen at room temperature, the SAM is fixated at the paraffin sphere surface. EDC/NHS is used to activate PAA at the spheres surface in aqueous phase. The paraffin spheres are 3–20 μm in diameter (Fig. 1a). The sphere surface is smooth (Fig. 1b). After amidation with the amine-group capped silica nanoparticles, a robust composite Janus nano-membrane is achieved. The sphere surface becomes rather coarsening (Fig. 1c). Onto the other side of the silica nanoparticles, another copolymer of PEO-*b*-PAA is grafted by amidation. The sphere surface remains coarsening (Fig. 1d).

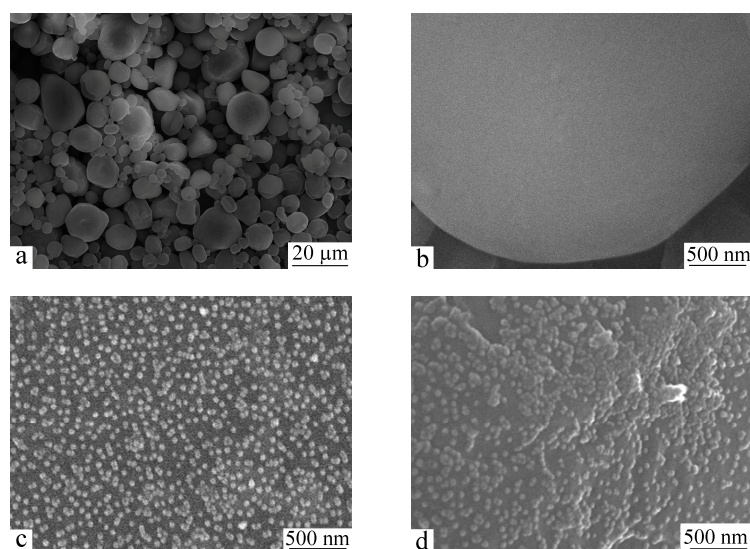


Fig. 1 (a, b) SEM images of paraffin spheres stabilized with PS-*b*-PAA; (c) the paraffin spheres surface after crosslinking between PAA and the amine- group capped silica nanoparticles and (d) the paraffin sphere surface after a further grafting with PEO-*b*-PAA

After dissolution of the paraffin core with *n*-hexane, PS-SiO₂-PEO Janus cages are achieved (Fig. 2a). The cages are collapsed. The silica nanoparticles are homogeneously distributed onto the shell (Fig. 2b). The shell exterior surface is rather coarsening. From the broken Janus cage, the interior surface is smooth without

nanoparticles (Fig. 2c). Cross-section TEM image of the Janus cage indicates that the shell is composed of single layer of the nanoparticles (Fig. 2d). After selectively staining PEO with PTA, PEO becomes clearly discerned onto the exterior surface (Fig. 2e). Another staining with RuO_4 indicates the PS layer onto the other surface (Fig. 2f). Shell of the Janus cages is thus a PS- SiO_2 -PEO triple-layered sandwich structure.

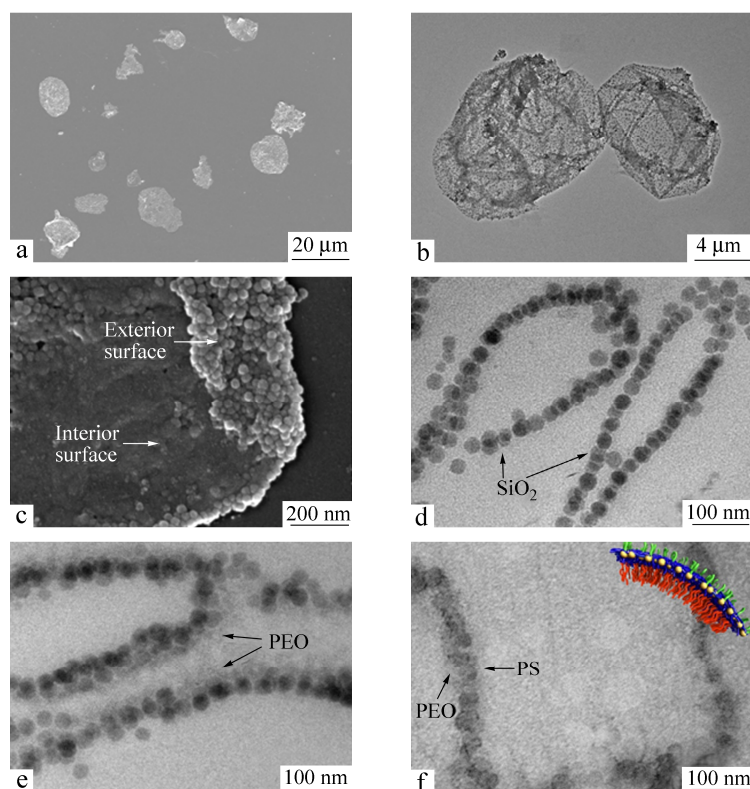


Fig. 2 (a) SEM image and (b) TEM image of the PS- SiO_2 -PEO Janus cages; (c) SEM image of the broken Janus cage; (d) cross-section TEM image of the Janus cage embedded with PMMA; cross-section TEM images of the Janus cage after sequentially staining with PTA (e) and RuO_4 (f)

The peak at 1648 cm^{-1} assigned to amide bond confirms the successful amidation between PAA and the amine- group capped silica nanoparticles (curve b, Fig. 3). Some carboxyl-groups are residual, which is confirmed by the peak at 1729 cm^{-1} . The presence of PEO is verified by the new peaks at 1279 cm^{-1} and 1241 cm^{-1} (curve a, Fig. 3).

Microstructure of the shell is tunable by changing amount of the amine- group capped silica nanoparticles. A saturation absorption amount of the nanoparticles on the paraffin sphere surface is measured 3.0 mg/g (nanoparticle/paraffin). Below the saturation absorption amount for example 0.3 mg/g , the silica nanoparticles are sparsely present on the sphere surface (Fig. 4a). Shell of the cages becomes highly porous after dissolution of the paraffin phase (Fig. 4b).

As above mentioned, the channel surface contains residual PAA chains which will render pH responsive performance. After drying the cage dispersion in water, the cages are larger at $\text{pH} = 7.0$ (Fig. 5a). In comparison, the cages become remarkably shrunk at $\text{pH} = 2.0$ (Fig. 5b). Separation between the silica nanoparticles onto the cage shell surface is much larger at $\text{pH} = 7.0$ (Fig. 5c) than at $\text{pH} = 2.0$ (Fig. 5d). At $\text{pH} = 7.0$, PAA chains are protonated and become highly hydrophilic. The cages are highly expanded. In comparison, the chains are deprotonated at $\text{pH} = 2.0$ and greatly decrease hydrophilicity. The cages become shrunk. This is also confirmed by variation of zeta potential with pH (Fig. 6). At $\text{pH} = 7.0$, the Zeta potential is measured -15 mV , indicating the cages are negatively charged. Zeta potential becomes 9.8 mV at $\text{pH} = 2.0$.

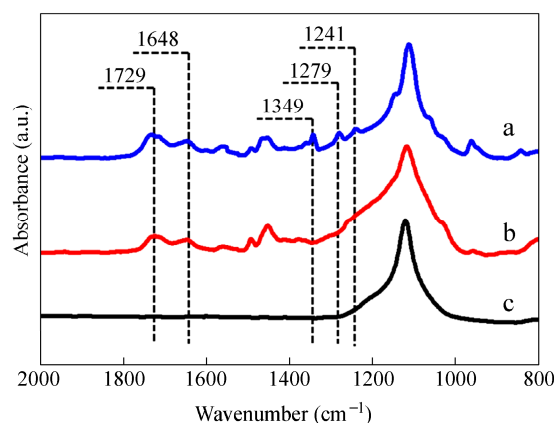


Fig. 3 FTIR spectra of representative samples: (a) PS-PAA/SiO₂-PEO Janus cages, (b) PS-PAA/SiO₂ Janus cage and (c) amino modified SiO₂ nanoparticles

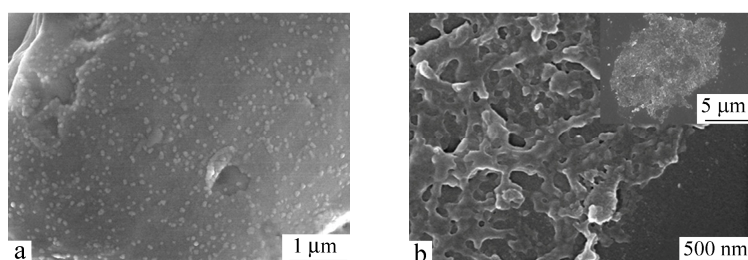


Fig. 4 SEM images of (a) the paraffin sphere absorbed with 0.3 mg/g amine-group capped silica nanoparticles and (b) the corresponding highly porous Janus hollow sphere

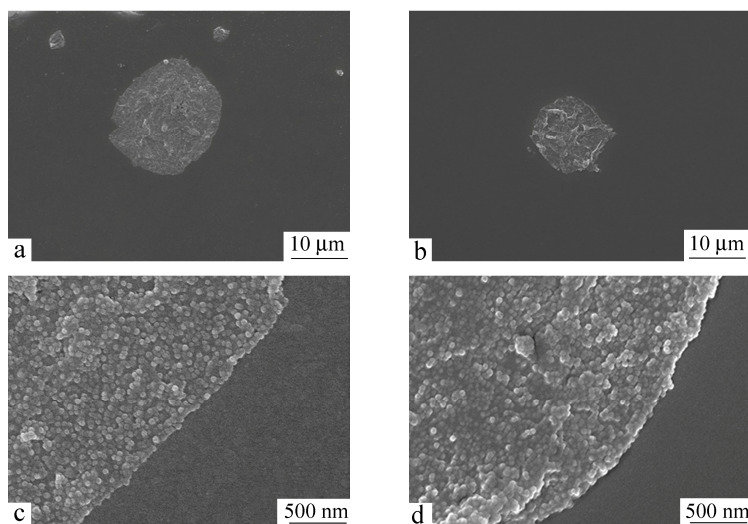


Fig. 5 (a, b) SEM images of the Janus cages after drying the aqueous dispersion at pH = 7.0 (a) and 2.0 (b); SEM images of the cages surface at pH = 7.0 (c) and 2.0 (d)

Janus cages are well dispersible in water. Oil soluble species can be captured into their hydrophobic cavity. The Janus cage as shown in Fig. 2(a) is selected to demonstrate the selective absorption from aqueous surroundings. Paraffin ($T_m = 50\text{--}52\text{ }^\circ\text{C}$) is selected as the model oil. Polarizing microscope image indicates that there exist paraffin crystals inside the Janus cages (Fig. 7a). No paraffin is found on the exterior surface of the cages (Fig. 7b). After capturing paraffin, the average diameter of the cages is $19\text{ }\mu\text{m}$ at pH = 7.0 (curve a, Fig. 8).

At pH = 2.0, the average diameter is decreased to 11 μm (curve b, Fig. 8). This is explained by the pH responsive performance of PAA chains.

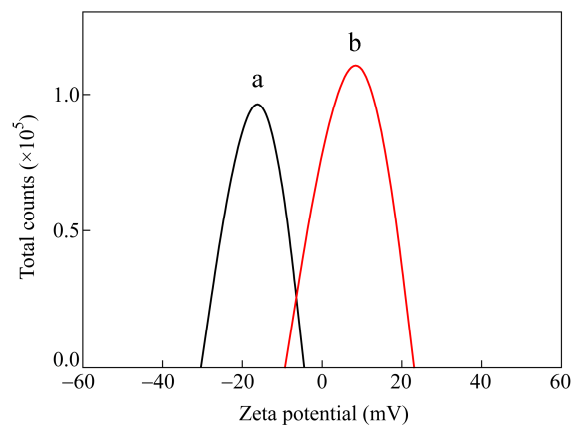


Fig. 6 Zeta potential of the PS-PAA/SiO₂-PEO Janus cages under different environment pH: (a) 7.0 and (b) 2.0

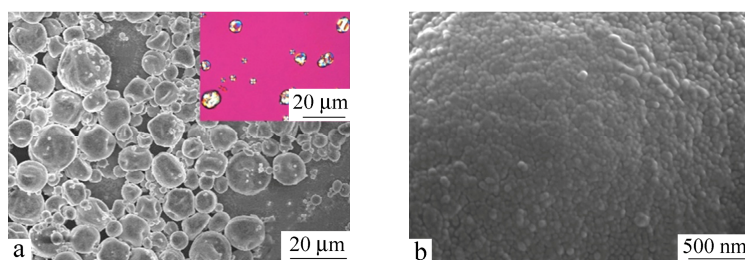


Fig. 7 (a) SEM image and inset polarizing optical microscope image of the Janus cages after capturing paraffin from aqueous phase at pH = 7.0 and (b) magnified SEM image of the Janus cage exterior surface

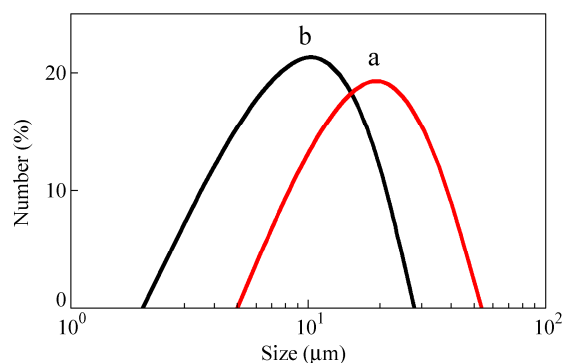


Fig. 8 DLS size analysis of the Janus cages after capturing paraffin at two representative pH values: (a) 7.0 and (b) 2.0

The largest volume of the as-adsorbed oil phase is the saturation absorption capacity of the corresponding Janus cage. When toluene is used, the saturation absorption capacity is 32 mL/g at pH = 7.0. In comparison, the capacity is decreased to 26 mL/g for *n*-hexane. This is understandable that toluene can well swell the composite shell, whilst *n*-hexane is inert for the shell. When pH is decreased from 7.0 to 2.0, the adsorption capacity for toluene is dramatically lowered from 32 to 20 mL/g. CLSM images clearly reveal oil capturing by the Janus cages. The FITC dissolved oil phase can be excited fluorescence signal under laser with wavelength of 488 nm. The oil phase can be absorbed into the cavity of Janus cages, which show green fluorescence in CLSM images (Fig. 9). After capturing toluene at pH = 7.0, the Janus cages become large (Fig. 9a). The Janus cages become

slightly small after capturing *n*-hexane (Fig. 9b). After freeze-drying the oil captured Janus cages in water, the surface morphology is observed under SEM. It is shown that the distance between the silica nanoparticles for cages capturing toluene (Fig. 9c) is longer than for cages that capturing *n*-hexane (Fig. 9d). This is consistent with the cage expansion after capturing toluene. In comparison, the Janus cages are the smallest at pH = 2.0 even after capturing toluene (Fig. 9e). This implies that controlling pH is more important than oil property to determine saturation absorption capacity.

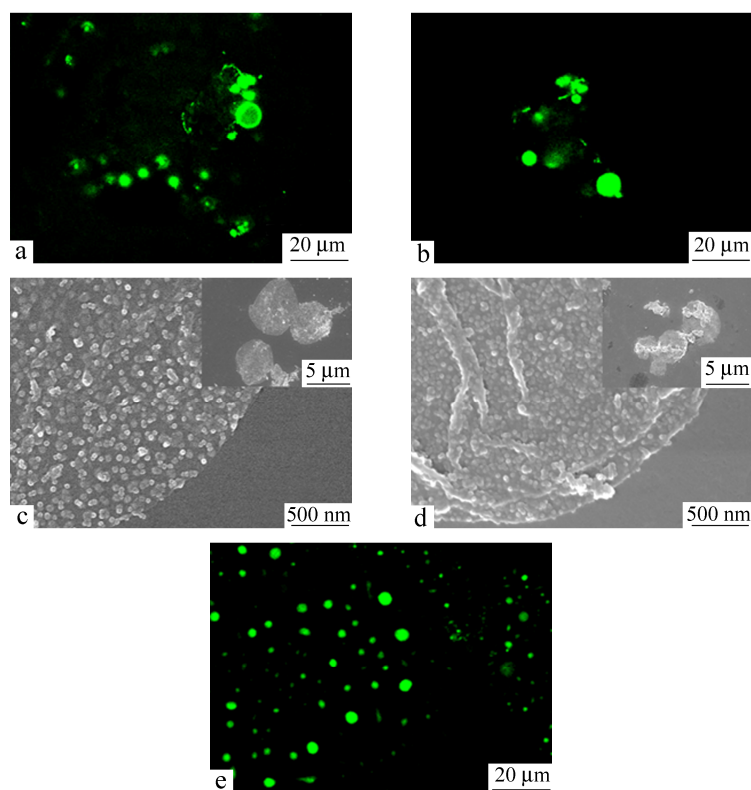


Fig. 9 (a) CLSM image of the Janus cages after capturing toluene at pH = 7.0; (b) CLSM image of the Janus cages after capturing *n*-hexane at pH = 7.0; (c, d) SEM images of the freeze-dried Janus cages after capturing toluene and *n*-hexane respectively at pH = 7.0; (e) CLSM image of the Janus cages after capturing toluene at pH = 2.0

CONCLUSIONS

In summary, we have proposed a facile method to synthesize pH responsive PS-SiO₂-PEO Janus cages. The residual PAA chains tethered onto the silica nanoparticles are responsible for the pH responsive performance. Since the shell is crosslinked with nanoparticles, the transverse channels are *in situ* created. The Janus cages can selectively capture oil-soluble species. The saturation absorption capacity is mainly determined by pH and oil property. The performance is potentially useful in controlled release and treatment of spilled chemicals.

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