

Hybrid Janus Nanotubes with Tunable Internal Pore Size Disassembled from Mesoporous Block Copolymer-based Hybrid Scaffolds

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 Electronic Supplementary Information

Abstract The hybrid Janus nanomaterials have captured considerable attention since the asymmetric structure can combine the properties of each component and display synergistic applications. However, the precise design of the specific hybrid Janus nanostructures still remains a formidable challenge. Here, we for the first time report the fabrication of novel and highly uniform inorganic/organic hybrid Janus nanotubes *via* disassembling the mesoporous inorganic nanoparticles (NPs)/polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) hybrid sheets, which are generated through the *in situ* reduction of functional metal precursors on the prepared PS-*b*-P4VP mesoporous scaffolds. More importantly, the internal pore size of the hybrid Janus nanotubes can be precisely tuned by readily controlling the swelling time of the PS-*b*-P4VP sheet-like assemblies in a selective solvent for P4VP domains, thus generating the particular inorganic/organic hybrid Janus nanotubes with adjustable inner diameter size. We believe that our finding will provide an efficient and universal route to fabricate the particular inorganic/organic hybrid nanotubes for hierarchical functional devices and nanomaterials.

Keywords Hybrid Janus nanotubes; Block copolymer; Inorganic nanoparticles; Disassembly; Mesoporous sheets

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INTRODUCTION

Janus nanoparticles (JNPs), which refer to that the objects possess two asymmetric components and/or shapes on their opposite sides, have gained significant and increasing interest due to the integrated properties and novel applications in emulsifier, compatibilizer, catalyst, and optical sensors.^[1–8] So far, various of synthetic strategies (including seed-mediated polymerization, microfluidics, phase-separation, and nucleation growth) have been proposed to design and fabricate the typical Janus particles.^[9] The achieved JNPs can be mainly divided into three categories (*i.e.*, inorganic, polymeric, and organic/inorganic hybrid Janus materials) according to the intrinsic composition.^[10] Particularly, the organic/inorganic hybrid Janus particles have received considerable attention since the hybrid materials can combine the stability and responsiveness of the polymer with the functionality of the inorganic nanoparticles, which can derive synergistic

multifunctional materials with applications in micromotor direction modulation, photothermal therapy, controlled release, reactive oxygen species, and so forth.^[11,12] For instance, the magneto-plasmonic Janus vesicles (JVs) with asymmetrical distribution of gold nanoparticles (AuNPs) and magnetic NPs in the vesicular membrane were fabricated by co-assembly of amphiphilic polymer, polymer-tethered AuNPs and magnetic NPs.^[13] The obtained JVs exhibit a serial of excellent performance such as near-infrared triggered release, photoacoustic and magnetic resonance imaging. Although great efforts have been made to design the Janus particles, there remains a great challenge to construct the organic/inorganic hybrid Janus particles and materials with desired and specific nanostructures.

On the other hand, block copolymers (BCPs) can be utilized as remarkable and prominent polymer scaffolds for the preparation of the inorganic/organic hybrid nanostructures since the BCPs can spontaneously self-assemble into abundant phase-separated structures driven by the incompatibility of the covalently linked polymers.^[14–20] Therefore, a variety of BCP scaffolds are developed to construct the multifunctional inorganic/organic nanostructures and materials ranging from the thin film, sphere or rod micelles, hollow vesicles, to the specific particles with controlled shape.^[21–25] For example, Kim *et al.* first reported the convex lens-shaped hybrid

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particles with highly ordered channels prepared from the confined co-assembly of the polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) and size-controlled AuNPs within emulsion droplets by tuning the neutralized interfacial interface.^[26] More interestingly, exquisite Janus-like polymer scaffolds are achieved by disassembling the prepared specific BCP assemblies in a selective solvent, providing a powerful platform for the preparation of the inorganic/organic hybrid Janus materials.^[27,28] For example, Zhu *et al.* proposed a facile approach towards synthesis of the Janus nanodiscs through stepwise disassembling phase-separated and disc-stacked particles assemblies.^[27] The disassembled nanodiscs were then used as polymer templates to guide the selective growth of the functional inorganic nanoparticles (including AuNPs and magnetic NPs), eventually obtaining the inorganic/organic hybrid Janus nanodiscs. Until now, however, only a few inorganic/organic hybrid Janus particles are fabricated by complexation of inorganic precursor with the disassembled polymer templates because there remain critical difficulties to fabricate the freestanding and high-quality Janus polymer templates with uniform shape and narrow size distribution.

Herein, we report the preparation of the uniform inorganic/organic hybrid Janus nanotubes with adjustable inner diameter size by disassembling the BCP-based mesoporous hybrid sheets. The mesoporous polystyrene-block-poly(4-vinylpyridine) (PS_{27k}-*b*-P4VP_{17k}, the subscripts are the number average molecular weight of the corresponding polymers) sheets with uniform thickness and hexagonally-packed porous P4VP channels are first generated *via* selectively swelling the P4VP domains of the PS_{27k}-*b*-P4VP_{17k} sheet-like assemblies in ethanol, which are prepared according to our previously reported “flat-emulsion-droplet confined assembly” strategy. Then, the functional inorganic species, such as AuNPs, palladium NPs (PdNPs), can be selectively loaded with the P4VP channels of the mesoporous PS_{27k}-*b*-P4VP_{17k} sheets, forming the mesoporous NPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets. After selectively disassembling the continuous PS domain, the specific inorganic NPs@P4VP/PS hybrid Janus nanotubes are eventually generated. Moreover, the internal pore size of the mesoporous PS_{27k}-*b*-P4VP_{17k} sheets can be precisely adjusted by simply tuning the swelling time of P4VP domains in ethanol, resulting in the hybrid Janus nanotubes with tunable inner diameter size. The preparation of the novel and high-quality hybrid Janus nanotubes may open a new avenue for the precise design and construction of the hierarchical hybrid nanomaterials with desired shape and internal nanostructures.

EXPERIMENTAL

Materials

Diblock copolymer polystyrene-block-poly(4-vinylpyridine) (PS_{27k}-*b*-P4VP_{17k}; the subscripts refer to M_n of each block, $M_w/M_n=1.15$) was purchased from Polymer Source, Canada. Cetyltrimethylammonium bromide (CTAB; purity: 99%) and sodium borohydride (NaBH₄; purity: 98%) were supplied by Aladdin. Hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O; purity: 99.99%) was purchased from Alfa Aesar. Palladium chloride (PdCl₂; purity: 99.9%) and tetraethyl orthosilicate (TEOS; purity: 99%) were obtained from Sigma-Aldrich. Ultrapure

deionized water was used in all experiments. Other chemical reagents were supplied by Beijing Chemical Factory. All the materials were used directly without further purification.

Preparation of Mesoporous PS_{27k}-*b*-P4VP_{17k} Sheet-like Scaffolds

The PS_{27k}-*b*-P4VP_{17k} block copolymer sheets were firstly prepared by the flat-emulsion-droplet confined assembly strategy that was proposed in our previous study.^[20] Typically, 0.1 mL of PS_{27k}-*b*-P4VP_{17k} chloroform solution (0.5 wt%) was emulsified with CTAB aqueous solution (1.2 wt%) by gentle stirring for 4 min at 450 r/min. The organic emulsion droplets were evaporated for 3 days without disturbing at room temperature. After repeated centrifugation (10000 r/min, 30 min), the PS_{27k}-*b*-P4VP_{17k} block copolymer sheets with periodic hexagonal-packed P4VP cylindrical domains in the PS matrix were prepared. In order to obtain the mesoporous PS_{27k}-*b*-P4VP_{17k} scaffolds, the PS_{27k}-*b*-P4VP_{17k} block copolymer sheets were re-dispersed in ethanol and stored at 30 °C for 48 h. Since ethanol could selectively swell the P4VP domains, the hexagonally-packed porous PS_{27k}-*b*-P4VP_{17k} block copolymer scaffolds were obtained after the swelling and shrinking of the P4VP blocks. Finally, the mesoporous assemblies were washed using DI water by repeated centrifugations (10000 r/min, 15 min), followed by redispersion in DI water for further using.

Preparation of Mesoporous AuNPs/PS_{27k}-*b*-P4VP_{17k} Hybrid Sheets

The precursor aqueous solution of HAuCl₄·3H₂O (0.5 mL, 0.5 mg/mL) was mixed with the mesoporous PS_{27k}-*b*-P4VP_{17k} sheet aqueous solution (0.5 mL, 10 mg/mL), followed by gentle stirring for 4 h at room temperature to accomplish the adsorption of precursor to the protonated P4VP blocks. The solution was centrifugated for at least 3 times to remove the redundant HAuCl₄·3H₂O precursors. Then, the mesoporous structures were redispersed in DI water and the ice-cold NaBH₄ aqueous solution (20 μL, 1 mg/mL) was dropwise added into the above mixture solution with stirring. The mixture solution was gently stirred for 6 h to fully reduce the adsorbed HAuCl₄·3H₂O precursor into AuNPs. After the reduction process, the hexagonally-packed porous AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets were obtained and washed with DI water (2–3 times) to remove the excess NaBH₄ reducing agent. The neat AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets were eventually re-dispersed in DI water for further characterization.

Preparation of AuNPs@P4VP/PS Hybrid Nanotubes *via* Disassembly

The highly uniform AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid nanotubes were obtained by the disassembly process from the hexagonally-packed porous AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets. The dried mesoporous AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets were annealed in toluene vapor for 5 days. Since toluene was the selective solvent for the continuous PS domain, the AuNPs@P4VP/PS hybrid nanotubes were obtained after the spontaneous collapse of the internal hexagonally-arranged AuNPs@P4VP cylinders. The detailed disassembly dynamic process was studied at different annealing times.

Preparation of the AuNPs@P4VP/PS Hybrid Nanotubes with Tunable Inner Diameter Size

The mesoporous PS_{27k}-*b*-P4VP_{17k} sheets with tunable pore size

were firstly obtained by dispersion of the $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets in ethanol at 50 °C for different time (*i.e.*, 30 s, 1 min, 2 min, 5 min, 20 min, and 40 min). After the adsorption of $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ precursor solution to the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets and the disassembly of the mesoporous AuNPs/ $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ hybrid sheets, the AuNPs@P4VP/PS hybrid nanotubes with tunable pore size were generated.

Preparation of the PdNPs@P4VP/PS Hybrid Nanotubes with Tunable Inner Pore Size

The mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets that have been swollen in ethanol at 50 °C for 40 min were used for the *in situ* adsorption of the PdNPs. For adsorption of the PdNPs, the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets were dispersed in PdCl_2 aqueous solution (0.05 mg/mL) with different pH values (*i.e.*, pH=2.0, 2.5, and 3.0). After the reduction by NaBH_4 (20 μL , 1 mg/mL) and the disassembly by toluene vapor, the PdNPs@P4VP/PS hybrid nanotubes with tunable inner diameter size were obtained.

Characterization

Transmission electron microscopy (TEM) measurements were performed on JEOL JEM-1400 with the operation voltage of 120 kV. Energy-dispersive X-ray (EDX) elemental mapping images and scanning transmission electron microscopy (STEM) were carried out using FEI Tecnai G2 S-Twin instrument at an accelerated voltage of 200 kV. The samples for TEM, EDX and STEM were prepared by dropping the sample aqueous dispersion onto the carbon-coated copper grids, followed by spontaneously evaporation of water at room temperature under atmosphere condition. The P4VP domains were stained with iodine vapor for 2 h to distinguish the PS and P4VP domains. Scanning electron microscope (SEM) images were captured by Hitachi S-4800. The samples were prepared by dropping the aqueous solution onto the silicon wafer. The samples were then dried under atmosphere condition. Small-

angle X-ray scattering (SAXS) was performed on a modified Xeuss system of Xenocs (France) with an X-ray wavelength of 0.154 nm. The samples for SAXS were prepared by freeze-drying the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets and pressing the mesoporous sheet powder into solid film.

RESULTS AND DISCUSSION

Typically, the $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ block copolymer in chloroform (0.1 mL, 0.5 wt%) is emulsified with surfactant aqueous solution containing cetyltrimethylammonium bromide (CTAB, 1.0 mL, 1.2 wt%) as surfactant. After the complete evaporation of the emulsion droplets, the specific two-dimensional (2D) $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ nanosheets with highly uniform thickness and periodically hexagonally-packed P4VP cylinders in PS matrix are generated according to our previous study.^[20] Subsequently, the $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets are redispersed in ethanol for 48 h at 30 °C and the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ nanostructures can be obtained since ethanol is a selective solvent for P4VP blocks. As shown in Fig. 1 and Fig. S1(a) (in the electronic supplementary information, ESI), hexagonally-packed mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ block copolymer sheets with long-range ordered and periodically penetrative P4VP channels are massively generated. Figs. 1(a) and 1(b) show the representative TEM and SEM images of an individual mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets, respectively. Magnified TEM images (Figs. 1c and Fig. S1b in ESI) clearly show that the nanopores within the polymer sheets are perpendicular to the surface of the 2D sheets and display the perfectly hexagonal arrangement across the whole polymer sheets with an inter pore distance of 64.5 ± 1.1 nm. Associated fast Fourier transform (FFT) image of the porous nanostructures (inset in Fig. 1c) further demonstrates a highly ordered internal nanostructure of the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheets. Moreover, the PS and P4VP domains can be distinguished by staining the P4VP domains

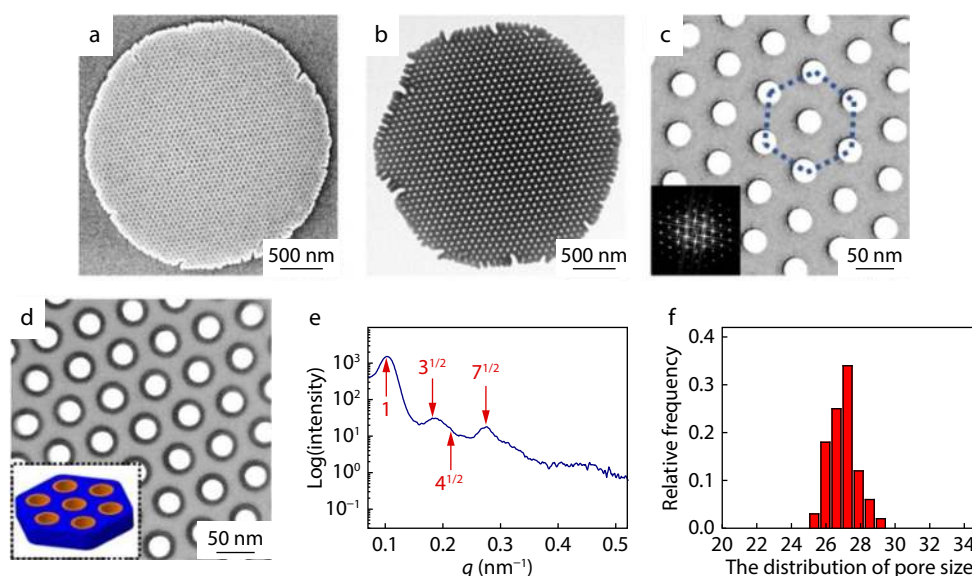


Fig. 1 Hexagonally-packed mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ block copolymer sheet scaffold. Representative SEM (a) and TEM (b) images of the mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ sheet scaffold; (c) Magnified hexagonally-ordered porous structure. The inset is the associated FFT of porous nanostructures of $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$; (d) The P4VP domains appear darker than PS domains after staining with I₂ vapor; (e) SAXS profile of hexagonally-packed mesoporous $\text{PS}_{27k}\text{-}b\text{-P4VP}_{17k}$ nanostructures; (f) Size distribution histogram of the cylindrical pore diameter.

with iodine (I_2) vapor. As shown in Fig. 1(d), it is clearly observed that the inner wall of the nanopores is formed by the reconstructed P4VP blocks, forming the typical mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ block copolymer sheets with hexagonally-arranged P4VP channels. SAXS profile (Fig. 1e) presents the obvious diffraction peaks at positions of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ with the primary peak at $q^*=0.1027\text{ nm}^{-1}$, which can also be assigned to the hexagonal arrangement of the nanopores. According to the equation $d = 4\pi/\sqrt{3}q^*$, the interpore distance is calculated to be $\sim 70.6\text{ nm}$ that is comparable to the interpore distance observed with TEM image. The pore diameter of the mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ nanostructure is $27.0 \pm 0.8\text{ nm}$ measured from the TEM images, demonstrating the extremely narrow size distribution of the obtained nanopores, as shown in Fig. 1(f).

Furthermore, various of functional species, such as metal NPs and inorganic materials, can be preferentially grown on the exposed P4VP domains to construct hierarchical hybrid materials by electrostatic interaction.^[29–31] Therefore, the prepared mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ block copolymer sheets are subsequently applied as polymeric scaffolds to guide the selectively complexation of functional NP precursors on the inner P4VP wall of the nanopores. Specifically, the mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ sheets are re-dispersed in the gold precursor solution ($HAuCl_4 \cdot 3H_2O$) and stirred for 4 h. The 4VP groups are protonated in the acid aqueous solution and adsorb the anion $[AuCl_4]^-$ by electrostatic interaction. After the removal of the excess $HAuCl_4 \cdot 3H_2O$ precursor by repeated centrifugation, freshly-prepared sodium borohydride ($NaBH_4$) aqueous solution is added to *in situ* reduce the $[AuCl_4]^-$ into AuNPs. As shown in Fig. 2(a) and Fig. S2 (in ESI), the hybrid AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ block copolymer sheets can be obtained after the adsorption and reduction process. Compared with the neat mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ sheets, the whole shape and the internal hexagonally arrangement of the nanopores remain unchanged. Magnified TEM image of the hybrid sheets (Fig. 2b) clearly shows that AuNPs are located at the inner wall of the nanopores and complexed with the P4VP do-

main, forming the specific AuNPs@P4VP hybrid nanopores within the continuous PS matrix. The successful complexation of AuNPs with P4VP domains is further confirmed by the STEM and EDX elemental mapping images, as shown in the hexagonally-packed bright and the corresponding red rings in Figs. 2(c) and 2(d), respectively. Therefore, the mesoporous hybrid AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ block copolymer sheets with highly ordered and hexagonally-arranged AuNPs@P4VP nanopores are generated using the neat mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ block copolymer sheets as polymeric scaffolds. Moreover, the nanopore diameter of the mesoporous AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ sheet is $19.4 \pm 0.6\text{ nm}$, which is slightly smaller than that of the neat mesoporous $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ scaffolds due to the adsorption and reduction of AuNPs on the inner walls of the nanopores.

It is worth noting that the prepared mesoporous AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ hybrid sheets have uniform thickness and regularly hexagonal arranged AuNPs@P4VP nanopores within the PS matrix, which can be further utilized as perfect structure for preparation of the highly uniform nanotubes by simply disassembling the continuous PS domain. The disassembly approach refers to selective disassembly of the majority phase and matrix, providing facile yet efficient strategy to construct novel nanostructures and inorganic/organic hybrid nanoparticles from the self-assembled scaffolds. For the AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ hybrid sheets in our current study, toluene is chosen as the selective solvent to disassemble the PS phase since the solubility parameter of toluene ($\delta=18.2\text{ MPa}^{1/2}$) is closer to that of the PS blocks ($\delta=18.6\text{ MPa}^{1/2}$) rather than P4VP blocks ($\delta=22.5\text{ MPa}^{1/2}$).^[32] Therefore, the internal hexagonal nanopores are released after selectively disassembling the continuous PS support, as shown in Fig. 3. Fig. 3(a) shows the representative TEM image of the obtained 1D hybrid nanostructure with uniform shape and narrow size distribution, in which the densely black dots represent the reduced AuNPs on the inner wall of the nanopores within the AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ hybrid sheets. It is clearly observed

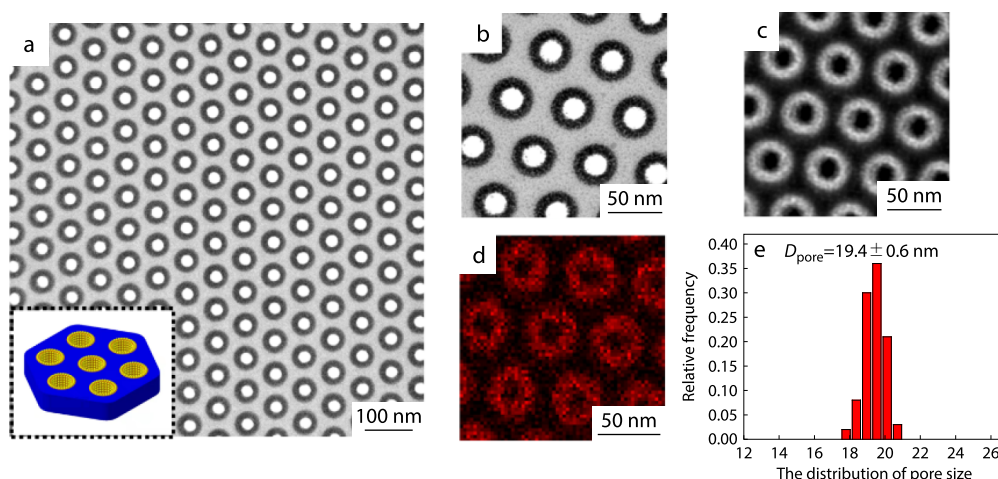


Fig. 2 The mesoporous AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ hybrid nanostructure with AuNPs adsorbed on the inner wall of the nanopores, (a) and (b) are TEM images of the mesoporous AuNPs/ $PS_{27k}\text{-}b\text{-}P4VP_{17k}$ hybrid nanostructure at different magnification; (c) The magnified STEM image of the hexagonally-packed hybrid nanopores; (d) The corresponding EDX mapping image of Au, where the red nanorings demonstrate the incorporation of AuNPs on the inner wall of the nanopores; (e) Size distribution histogram of the pore diameter after adsorption and reduction of the metallic precursor solution.

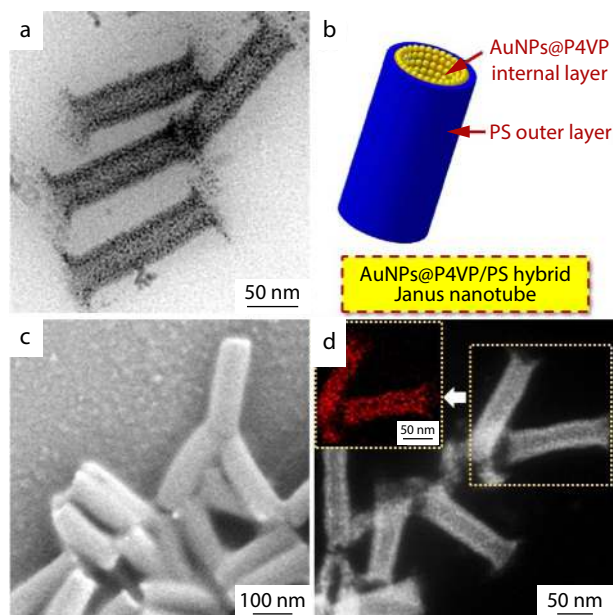


Fig. 3 The novel AuNP@P4VP/PS hybrid Janus nanotubes disassembled from the mesoporous AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets using toluene as annealing solvent. (a) Representative TEM image of the AuNPs@P4VP/PS hybrid Janus nanotubes. (b) The schematic illustration of the prepared novel nanotube. SEM (c) and STEM (d) images of the Janus nanotubes. The inset in (d) is EDX mapping image of Au element.

that the edge area is much darker than the internal area due to the difference of electron beam penetration, indicating the internal hollow nanostructures and the generation of the hybrid nanotubes. In addition, the AuNPs originated from the AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets are complexed with the P4VP blocks and only located at the inner wall of the nanotubes, whereas the covalently grafted PS blocks are distributed outside the nanotubes after disassembling the PS matrix. Consequently, the exquisite and high-quality AuNPs@P4VP/PS Janus hybrid nanotubes are obtained after disassembling the prepared AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets, as illustrated in Fig. 3(b). SEM image in Fig. 3(c) shows the cylindrical external shape of the AuNPs@P4VP/PS Janus nanotubes. The successful preparation of the inorganic/organic hybrid nanotubes is also verified by the STEM image and the corresponding EDX mapping of Au, as shown in Fig. 3(d). Up to now, a variety of fancy nanostructures that are precisely designed at nanoscale have been generated through the bottom-up assembly and followed disassembly method, such as cylindrical micelles,^[33] nanodiscs,^[27] nanocups and nanotoroids.^[28] However, the nanotubes, especially for the well-defined Janus-like inorganic NP/block copolymer hybrid nanotubes, are seldomly reported.

In order to reveal the formation process of the unique AuNP@P4VP/PS Janus nanotubes, the disassembly dynamics and the intermediate nanostructures of the AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets annealed in toluene vapor is systematically investigated at different annealing time, as shown in Fig. 4. The initial nanostructure is the prepared AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets that have been discussed above, in

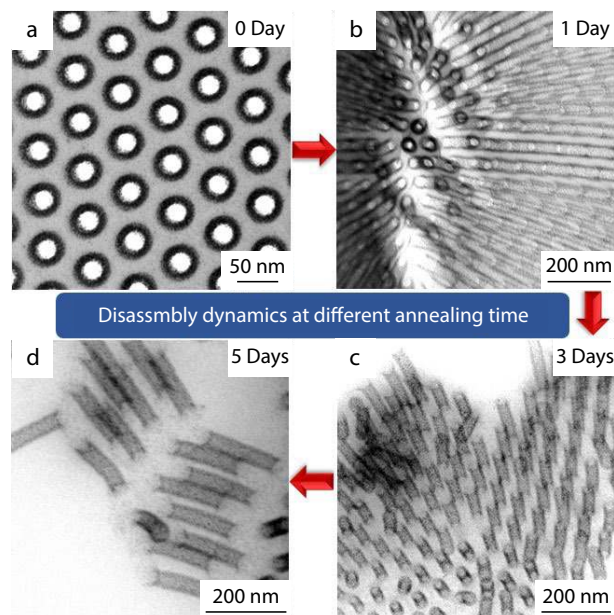


Fig. 4 TEM images showing the formation of the AuNP@P4VP/PS Janus nanotubes and the intermediate nanostructures of the AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets annealed in toluene vapor at different annealing time: (a) 0 day (*i.e.*, the initial nanostructure of the hybrid sheet), (b) 1 day, (c) 3 days, (d) 5 days.

which the AuNPs are adsorbed on the inner wall of the hexagonally arranged nanopores, as shown in Fig. 4(a). When the hybrid sheets are annealed in toluene vapor for 1 day, the PS continuous domains begin to swell and crack, leading to the slight separation of the vertically stacked nanopores decorated with AuNPs from the scaffolds (Fig. 4b). With the further swelling and disassembly of the PS blocks by toluene vapor (Fig. 4c), most of the nanotubes originated from the AuNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets are obviously collapsed due to the disassembled and movable PS molecules. However, the collapsed nanotubes have a distinct orientation since the linked PS blocks are not completely separated. When the annealing time is extended to 5 days, the PS blocks located at the outside of the nanotubes drive the further migration and separation of the nanotubes, forming the free-standing AuNP@P4VP/PS Janus nanotubes, as shown in Fig. 4(d). As described above, the internal diameter of the obtained hybrid Janus nanotubes mainly depends on the original pore size of the mesoporous PS_{27k}-*b*-P4VP_{17k} block copolymer sheets. Since the hexagonally-arranged porous structure of the PS_{27k}-*b*-P4VP_{17k} sheets is obtained by swelling in the selective solvent (*i.e.*, ethanol) for the P4VP cylindrical domains, the pore size can be precisely controlled and tuned by readily regulating the swelling parameters, such as swelling temperature and time. TEM images of the mesoporous PS_{27k}-*b*-P4VP_{17k} block copolymer sheets after swelling in ethanol at 50 °C for different time are shown in Figs. 5(a)–5(f). Increasing the swelling temperature can improve the mobility of the PS ligands and interaction strength between the P4VP blocks and selective solvent, enabling fabricate the mesoporous structures with controllable pore size by changing the swelling time. As shown in Fig. 5(g), the pore diameter is 10.9±0.9

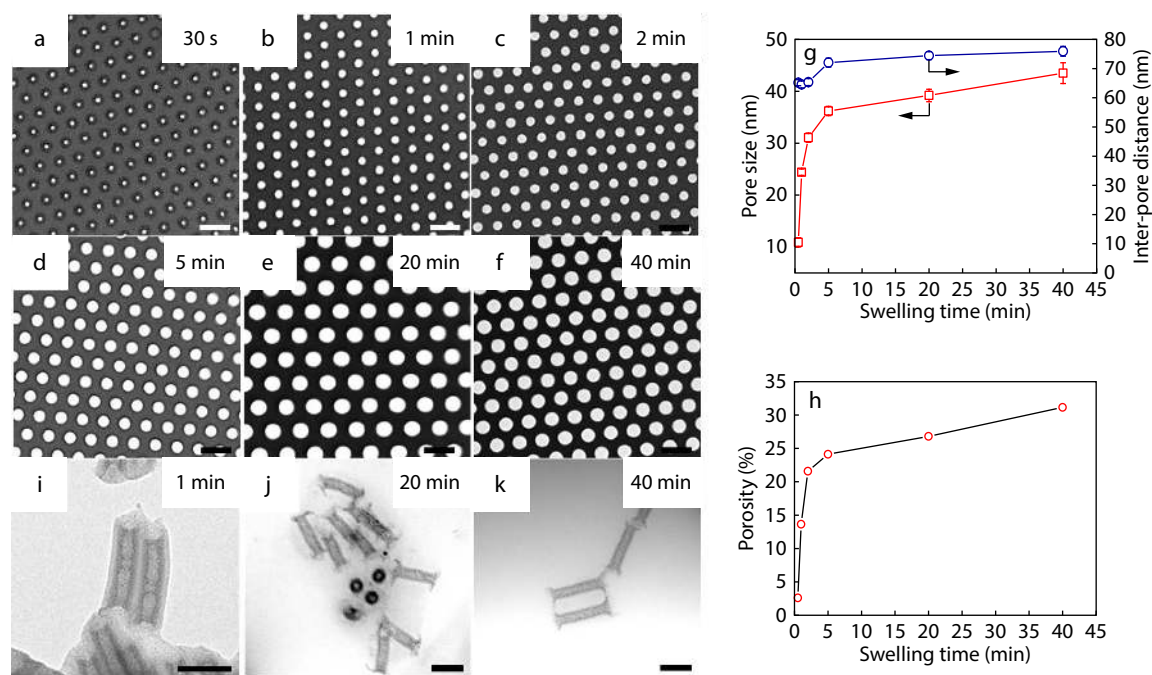


Fig. 5 (a–f) The TEM images of the porous PS_{27k}-*b*-P4VP_{17k} scaffolds obtained by swelling in ethanol at 50 °C for different time: (a) 30 s, (b) 1 min, (c) 2 min, (d) 5 min, (e) 20 min, (f) 40 min. The scale bars in the TEM images are all 100 nm. (g) Plots of the average pore size and the inter-pore distance as a function of the swelling time in ethanol. (h) Plots of the porosity of the mesoporous PS_{27k}-*b*-P4VP_{17k} scaffolds as a function of the swelling time. (i–k) are the disassembled hybrid Janus nanotubes with controllable internal pore size.

nm after swelling in ethanol for only 30 s. Subsequently, it is observed that the pore diameters display dramatic increase to 36.2±0.9 nm in only 5 min, which has reached the original P4VP domain size in the neat PS_{27k}-*b*-P4VP_{17k} block copolymer sheets. With the further extension of the swelling time, the size growth rate of the pores decreases (*i.e.*, 39.2±1.1 nm for 20 min and 43.5±2.1 nm for 40 min) due to overcoming the motion hindrance of the surrounding PS domain. During the continuous swelling of the P4VP domains, the inter-pore distance increased slightly from 65.2±1.0 nm to 75.9±1.7 nm, as shown in Fig. 5(g). Moreover, the porosity (ϵ) of the mesoporous PS_{27k}-*b*-P4VP_{17k} sheets at different swelling time at 50 °C can be estimated using the following equation for cylindrical pores:

$$\epsilon = \frac{n\pi r^2}{S} \quad (1)$$

where n is the number of pores, r is the diameter and S is the area of the mesoporous sheets. As shown in Fig. 5(h), the porosity increases from 2.6% to 31.2% with the increase of the swelling time in the selective solvent, displaying the well-control on the pore size and porosity of the mesoporous PS_{27k}-*b*-P4VP_{17k} block copolymer scaffolds. Using the mesoporous sheets as the scaffolds, the hybrid Janus nanotubes with controllable internal pore size can be fabricated, as shown in Figs. 5(i)–5(k).

Furthermore, the prepared mesoporous PS_{27k}-*b*-P4VP_{17k} sheets can provide a robust yet universal scaffold to design the specific inorganic/organic hybrid Janus nanotubes. Consequently, other functional precursor solution (palladium chloride, PdCl₂) can also be used to prepare the hybrid nanotubes based on the mesoporous PS_{27k}-*b*-P4VP_{17k} sheets. Typ-

ically, the prepared mesoporous PS_{27k}-*b*-P4VP_{17k} sheets (swelling in ethanol for 40 min) are re-dispersed in Pd precursor solution (0.05 mg/mL) with different pH values (*i.e.*, pH=3.0, 2.5 and 2.0) in order to accomplish the complexation between the Pd precursor with the P4VP channels in the mesoporous structure. After reduction by the NaBH₄ aqueous solution, the mesoporous PdNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets are obtained (Figs. 6a–6c). The pore diameter of the hybrid sheets is directly related to the complexation ability and interaction strength between the P4VP blocks and Pd precursor. As the pH values decrease from 3.0 to 2.0, the interaction strength increases significantly attributed to the protonated P4VP blocks, resulting in more precursor adsorbed to the inner wall of the pores. Thus, the mesoporous PdNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets with regulated pore size are obtained. Similar to the preparation of the hybrid AuNPs@P4VP/PS Janus nanotubes, the PdNPs@P4VP/PS hybrid Janus nanotubes can also be obtained from the prepared mesoporous PdNPs/PS_{27k}-*b*-P4VP_{17k} hybrid sheets. Therefore, the PdNPs@P4VP/PS hybrid Janus nanotubes with tunable inner pore size are obtained after selectively disassembling the PS domain in toluene vapor, as shown in Figs. 6(d)–6(f).

CONCLUSIONS

In summary, we proposed a universal strategy to design the novel inorganic/organic hybrid Janus nanotubes with tunable inner pore size. First, the hexagonally-packed porous PS_{27k}-*b*-P4VP_{17k} template is obtained by swelling the P4VP cylinder domains of the neat PS_{27k}-*b*-P4VP_{17k} sheet-like assemblies in

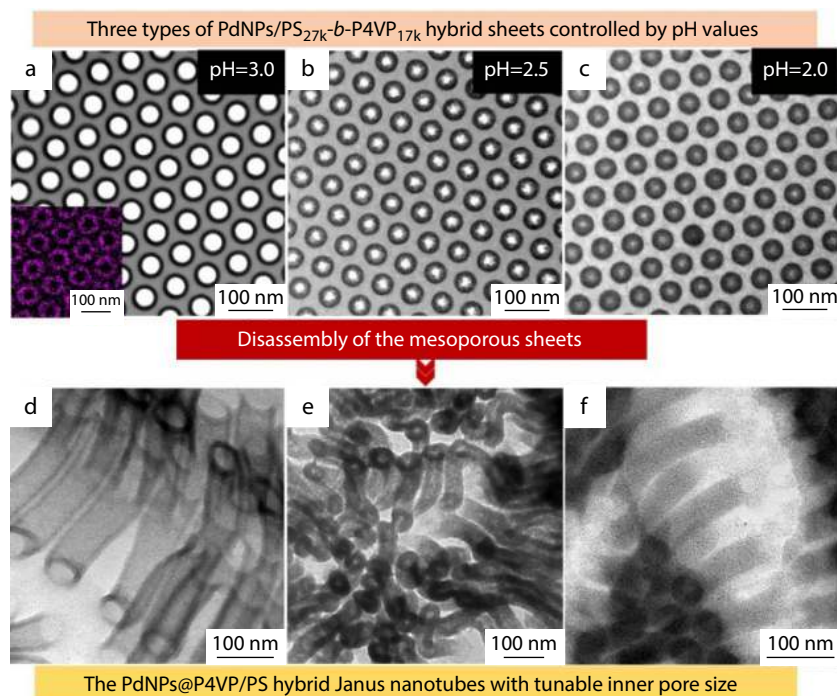


Fig. 6 (a–c) TEM images of the mesoporous PdNPs/PS_{27k}-b-P4VP_{17k} hybrid sheets with tunable internal pore size by precisely tuning the pH values of the Pd precursor solutions. (d–f) The PdNPs@P4VP/PS hybrid Janus nanotubes obtained by disassembling the corresponding prepared mesoporous PdNPs/PS_{27k}-b-P4VP_{17k} hybrid sheets.

ethanol. The functional inorganic NPs/PS_{27k}-b-P4VP_{17k} hybrid sheets are then prepared by complexation and adsorption of inorganic precursor solution on the inner wall of the porous template, followed by reduction process. After selectively disassembling the continuous PS domain, the specific inorganic@P4VP/PS hybrid nanotubes are finally obtained. In addition, the inner pore size of the nanotubes can be precisely and readily tuned by the swelling time of the neat PS_{27k}-b-P4VP_{17k} sheet-like assemblies or the complexation strength between the precursor and P4VP domains. Our findings not only enrich the library of the inorganic/organic nanostructure and materials, but also pave a new way to design and fabricate novel hybrid Janus materials.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2704-6>.

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