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Janus composite nanorings by combinational template synthesis and skiving micro-process

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ABSTRACT

Janus composite nanorings are fabricated by skiving the corresponding arrayed nanotubes. Polymer nanotubes and their arrays are polymerized from the pore surface via ATRP inside porous anodic aluminium oxide membrane (AAO) templates. By a selective partial modification of the interior surface of the polymer nanotubes followed by a favorable growth of other materials, double-shelled composite nanotubes and their arrays are derived. After skiving, the corresponding Janus composite nanorings are obtained with two different compositions compartmentalized onto both interior and exterior surfaces, respectively. Characteristic dimension, microstructure and composition of the Janus composite nanorings can be tuned. As examples, Janus composite nanorings of sulfonated PS/PS, titania/PS, silica/PS and PANi/PS are prepared.

1. Introduction

Nanometer sized rings (nanorings) have gained increasing interests since they may demonstrate promising performances such as persistent current in metallic [1,2] and superconducting rings [3], tunable optical resonance in metallic rings [4] and magnetic optical behavior in semiconductor rings [5]. Besides, an ordered arrays of those nanorings can display some new physical behavior arisen from the coupling effect between the adjacent rings [6]. In order to achieve desired performances, it is key to tune their size, microstructure, composition and uniformity. Recently, some methods have been proposed including electron bean lithography (EBL) [7,8], self-assembly of nanocrystals [9–11], nanosphere lithography [12,13] and template synthesis [14–16]. However these methods have their own restrictions. For instance, EBL involves expensive facilities. Self-assembly of nanocrystals brings polydispersity in size. The synthetic efficiency by nanosphere lithography is rather low. Opal template method is only valid for specific components. Recently, Whitesides et al. have developed an effective method to fabricate rings by skiving an array of nanotubes [17,18]. In principle, the procedure can be scaled up to produce uniform rings with controlled wall thickness within nanometers. Height of the rings can be controlled by alteration of skiving step length starting from tens nanometers. However, it is difficult to further decrease the cross-section size to nanometers since characteristic size of the stamp printing molds achieved from lithography is usually above micrometers. Another key concern for nanorings is to control spatial distribution of components. Janus nanorings with two different compositions compartmentalized onto both interior and exterior surfaces respectively, may display some new performances. Although Janus objects have been extensively reported, they are mainly focused on those morphologies such as spheres, rods and discs [19–21]. To our best knowledge, no large scale synthesis of uniform Janus composite nanorings has been reported.

Herein we report a facile and effective method to synthesize composite nanorings especially Janus nanorings, as illustrated in Fig. 1. An array of crosslinked polystyrene (PS) nanotubes is synthesized from the pore surface by atomic transfer free radical polymerization (ATRP) inside a representative porous anodic aluminium oxide membrane (AAO) template. The exterior surface of the nanotubes closely adhered to the pore surface is thus protected. This allows a selective modification for example sulfonation with sulfuric acid starting from the interior surface, giving sulfonated PS/PS double-shelled nanotubes and their arrays. Sequential favorable growth of other materials within the sulfonated polystyrene derives the corresponding double-shelled composite nanotubes and their arrays. After poly(methyl methacrylate) (PMMA) is polymerized thus filled inside the internal cavity of the nanotubes forming the corresponding core-shell nanorod/AAO composite membrane, the AAO membrane is etched from the edge in acid. Again the interstitial voids between the nanorods are

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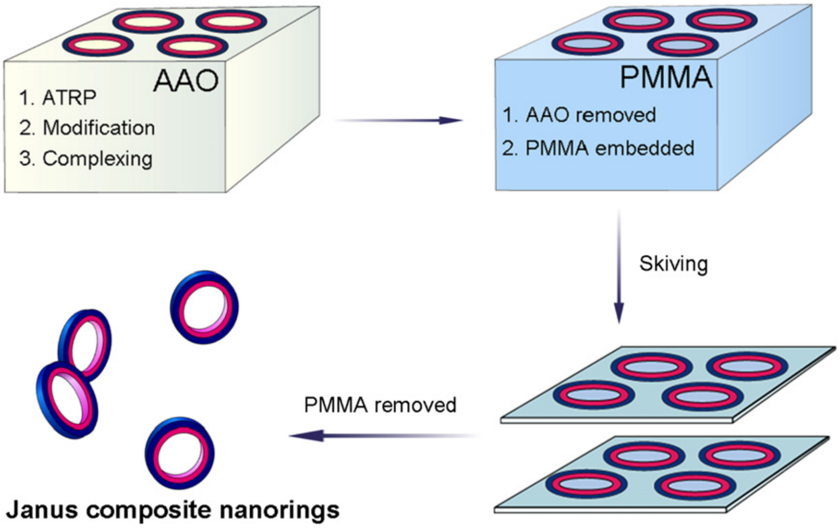

Fig. 1. Illustrative synthesis of the Janus composite nanorings by skiving nanotube arrays synthesized in AAO template.

filled with PMMA. The core-shell nanorod arrays embedded within PMMA matrix are vertically skived at a given step length for example 100 nm, composite slices with a desired thickness are obtained. Upon removal of PMMA by dissolution from the slices, nanorings are fabricated. In the case of double-shelled composite nanotubes, the corresponding composite nanorings are derived with two different compositions compartmentalized onto both exterior and interior surfaces respectively. Such composite nanorings are Janus. The AAO membrane templates are promising with aligned straight channels whose pore size and shape are tunable, which have already been extensively used to synthesize nanotubes and their arrays with varied compositions [22,23]. In principle, characteristic dimension and composition of the nanorings can be guaranteed.

2. Results and discussion

As the example, crosslinked PS nanotubes were synthesized by ATRP from the pore surface [24]. The interior surface of the nanotubes is smooth. Shell thickness of the nanotubes is controlled by polymerization time. Eventually, the internal cavity becomes rather small even disappears after polymerization for 24 h. At a given skiving step length of 100 nm, the corresponding slices were obtained (Fig. 2a). The relatively uniform PMMA/PS core-shell composite discs are orderly arrayed within the slice, similar to the pore arrangement in the AAO membrane. Both the internal cavity of the PS nanotubes and the interstitial voids between them are completely filled with PMMA, which can support the nanotubes to avoid deformation during skiving. After dissolution PMMA from the slice, the resultant nanorings can preserve their ring contour. Both interior and exterior surfaces of the nanorings are smooth. The PS nanotubes polymerized for 1 h are very thin with a shell thickness about 20 nm (inset Fig. 2b). The corresponding nanorings (Fig. 2b) are easily deformed. Onto a substrate, they are stacked into an ordered mesh. From the PS nanotubes with a shell thickness about 40 nm after polymerization for 3 h (inset Fig. 2c), the corresponding nanorings can preserve their ring shape better. Accordingly, the internal cavity is decreased. For the nanorings from those PS nanotubes after polymerization for 24 h, the internal cavity becomes rather small even disappears (Fig. 2d). Therefore, the internal cavity size and shell thickness of the nanorings can be synchronously and continuously tunable within the whole cross-section size. In order to show consistency of the height with the given skiving step length, the example sample as shown in Fig. 2c was measured by atomic force microscopy (AFM) (Fig. 2e). The measured height is about 100 nm, the same as the given skiving step length. Height of the nanorings is thus controlled by adjusting the skiving step length. For instance, when the step length was increased from 100 nm to 500 nm, the nanorings with a larger height were obtained (Fig. 2f).

Starting from the crosslinked PS nanotubes inside the AAO membrane template, sulfonated PS/PS double-shelled composite nanotubes were derived by partial sulfonation for example 0.5 h [25]. Since their tubular contour is well preserved, the exterior sulfonated polystyrene surface keeps smooth (Fig. 3a), while the interior surface becomes slightly wrinkled (Fig. 3b). Successful sulfonation is confirmed by the presence of S element by energy dispersive X-ray (EDX) analysis (Fig. 3d). Accordingly, the interior surface of the corresponding nanorings becomes coarsened (Fig. 3c), while the exterior surface remains smooth. Janus sulfonated PS/PS composite nanorings are thus created. Thickness of the sulfonated polystyrene is controlled by sulfonation time and temperature [26]. If the sulfonation time was prolonged to 24 h, the nanotubes become too weak to maintain their shape. The sulfonic acid group can induce a favorable growth of other materials forming composite double-shelled nanotubes. Accordingly, the composite nanorings were prepared from the corresponding nanotubes. Considering different compositions are distinct compartmentalized onto both the interior and exterior surfaces respectively, such composite nanorings are Janus. As the first example, a sol-gel process of tetrabutyl titanate (TBT) occurred favorably within the sulfonated PS forming titania/PS composite double-shelled nanotubes [26]. After skiving, the corresponding Janus titania/PS composite nanorings were prepared (Fig. 4b). The presence of Ti element is confirmed by EDX analysis (Fig. 4c). The interior surface becomes rough with some small titania nanoparticles observed, while the exterior surface remains smooth. This implies that titania is present predominantly within the interior surface. Similarly, after monomer aniline was preferentially absorbed within the interior sulfonated PS by specific interaction [27], polyaniline/PS double-shelled nanotubes were formed after oxidative polymerization at room temperature. The corresponding Janus composite polyaniline/PS nanorings with a rough interior surface were derived (Fig. 4e). The presence of N element is

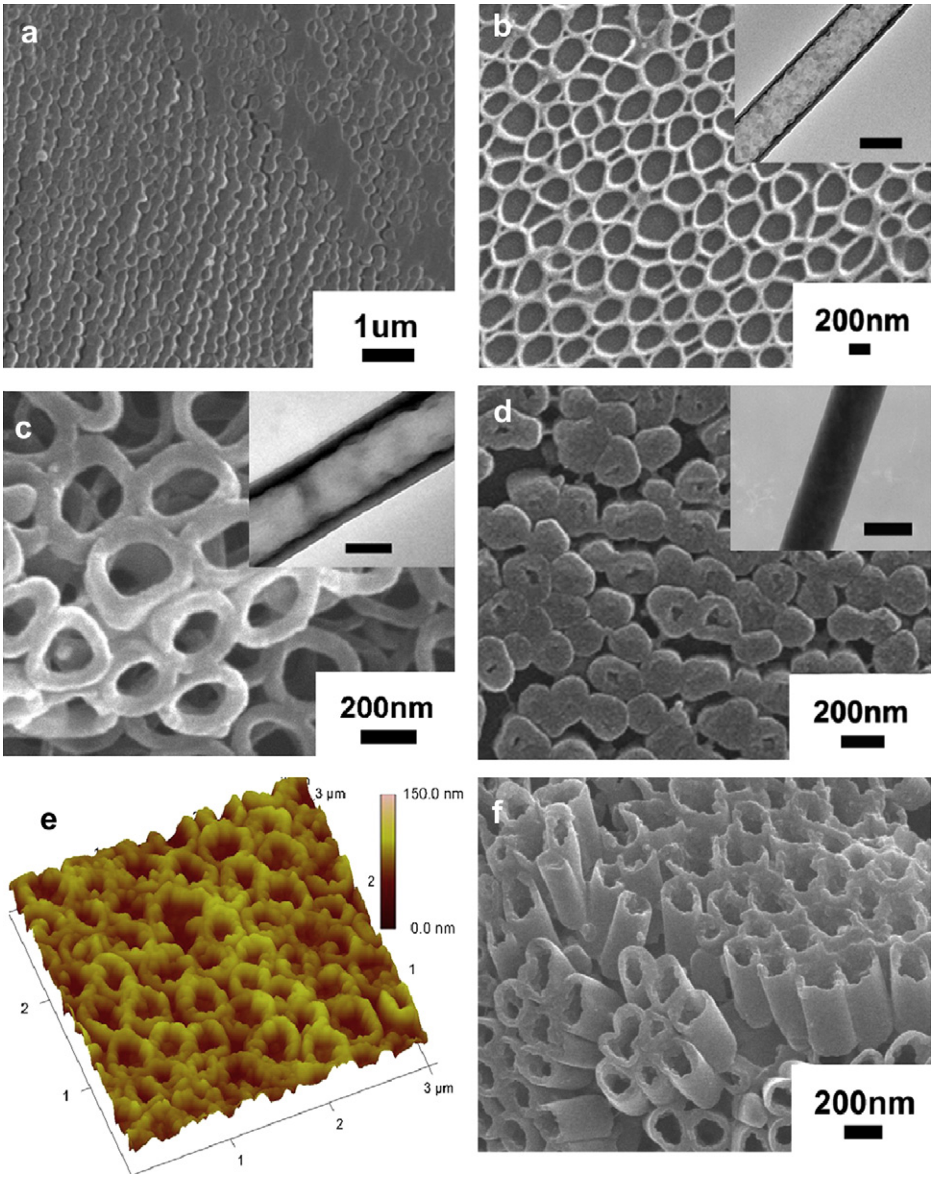

Fig. 2. Morphologies of some representative PS nanotubes and the corresponding nanorings. (a) top view of SEM image of the composite slice; (b–d) SEM images of the nanorings by skiving three representative PS nanotubes (inset) with varied shell thickness, which are polymerized at 120 °C for 1 h, 3 h and 24 h respectively. For the nanorings, the height is fixed at 100 nm; (e) AFM image of the PS nanorings as shown in Fig. 2c; (f) SEM image of the PS nanorings with a height about 500 nm skived from the PS nanotube as shown in inset Fig. 2c. The inset scale bars are the same as in the corresponding images.

confirmed by EDX analysis (Fig. 4f). As another example for composite, silica/PS double-shelled composite nanotubes were prepared through the sol-gel process of TEOS within the sulfonated PS since the sulfonated PS nanotubes are acidic and can catalyze the sol-gel process [27]. Thus, the corresponding silica/PS composite nanorings could be obtained.

3. Conclusion

In conclusion, we have developed a general method to fabricate composite nanorings by skiving the arrayed nanotubes synthesized in AAO membrane templates. Both composition and dimension of the nanotubes thus nanorings are tunable. Especially, Janus composite double-shelled nanorings are firstly synthesized. This method can be easily extended to other systems with varied compositions, deriving a huge family of Janus composite nanorings.

4. Experimental

4.1. Preparation of crosslinked PS nanotubes

A representative anodic aluminium oxide (AAO) membrane (Anodisc 47, 60 μm thick and average pore diameter 220 nm as specified, Whatman International Ltd., UK) was modified with an atom transfer radical polymerization (ATRP) initiator by a two-step method [24]. After being treated with H_2O_2 at 80 °C for 24 h, the AAO membrane was modified with 3-aminopropyltrimethoxysilane (APTMS) in toluene at 120 °C for 12 h and then washed with ethanol. The modified AAO was further reacted with 2-bromoisobutyryl bromide in dry dichloromethane containing dry triethylamine at 25 °C for 10 h. The product was washed with acetone and ethanol, and dried under vacuum at room temperature.

Crosslinked PS nanotubes were synthesized by ATRP inside the modified AAO membrane. After the modified AAO membrane,

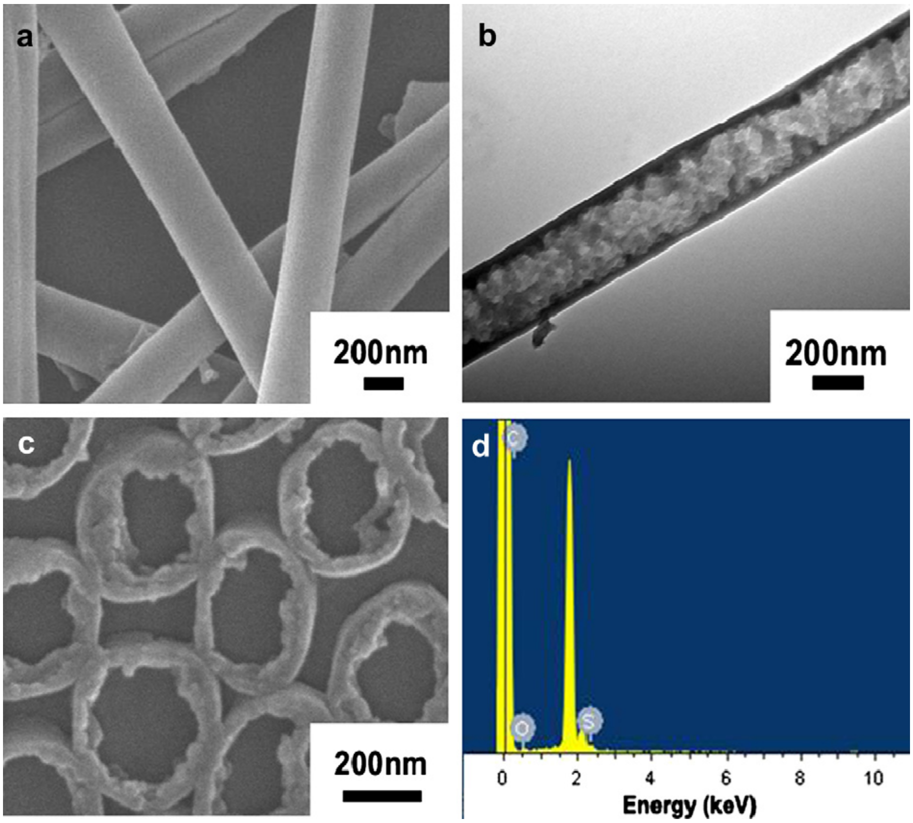

Fig. 3. (a) SEM image of the sulfonated PS nanotubes shown in Fig. 1c; (b) TEM image of the corresponding sulfonated PS nanotubes shown in Fig. 1c; (c) SEM image of sulfonated PS nanorings from the sample as shown in Fig. 3a; (d) The corresponding EDX spectrum of the sample shown in Fig. 3c.

styrene/divinylbenzene (2 mL, 1:1 vol/vol) mixture, *N, N*-dimethylformamide (DMF) (3 mL) and CuBr (0.0124 g) was mixed in a 10 mL flask under stirring and degassed by N_2 for 30 min, *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (0.064 g) was added. After being heated to 120 °C, the ATRP onto the pore surface was initiated and polymerized for varied time in order to control the shell thickness. The composite membrane was washed with excess toluene and ethanol, and then dried at 60 °C under vacuum.

4.2. Preparation of PS nanorings

Poly(methyl methacrylate) (PMMA) oligomer was synthesized by free radical polymerization of methyl methacrylate (2 g, MMA) using benzoyl peroxide (0.02 g, BPO) as the initiator, and polymerized at 95 °C for 10 min. Then the PS nanotube/AAO composite membrane was immersed in the oligomer at 60 °C for 4 h to polymerize inside the internal cavity of the PS nanotube. After PMMA was scratched from the membrane edge, the AAO membrane was dissolved with aqueous hydrochloric acid (5 mol/L) at 60 °C for 48 h. The PMMA/PS core-shell nanorod array was embedded in PMMA oligomer again to allow another polymerization of PMMA within the interstitial voids between the nanorods forming a PS/PMMA composite membrane. By skiving the membrane vertically to the array at a given step length, PMMA/PS composite slices were prepared. After dissolving the PMMA with acetone, PS nanorings were obtained.

4.3. Preparation of sulfonated PS/PS double-shelled nanotubes

The PS nanotube/AAO composite membrane after polymerizing for 3 h was selected as the example. Similar to sulfonation of PS [26,28], PS nanotube/AAO composite membranes were immersed in concentrated sulfuric acid at 40 °C for varied time for example 0.5 h. Afterwards, the sulfonated PS/PS double-shelled nanotubes were rinsed with ethanol and water. The example sulfonated PS/PS double-shelled nanotubes after being sulfonated for 0.5 h were prepared (S1).

4.4. Preparation of titania (TiO_2)/PS double-shelled composite nanorings

The example sulfonated PS/PS double-shelled nanotube S1 was immersed in tetrabutyl titanate (TBT)/ethanol (1:1 vol/vol) solution for 24 h to allow a complete absorption of TBT within the sulfonated PS, and then rinsed with ethanol to remove excess TBT. Afterwards, the membrane was transferred into a closed vessel containing ethanol (5 mL) at ambient temperature. Water (5 mL) was then added under stirring, and the sol-gel process occurred for 4 h. Titania/PS double-shelled composite nanotubes were obtained after rinsing with ethanol. Similarly, the Janus titania/PS composite nanorings were derived.

4.5. Preparation of polyaniline (PANi)/PS double-shelled composite nanotubes and nanorings

S1 was immersed in 10 ml of water containing varied amount of aniline (0.01–0.2 g) under stirring at room temperature for 3 h to allow a complete absorption of aniline into the sulfonated PS. After rinsing with water to remove excess aniline, 1 ml of ammonium persulfate aqueous solution (1 M) was added to initiate the oxidative polymerization for 24 h forming the polyaniline/PS

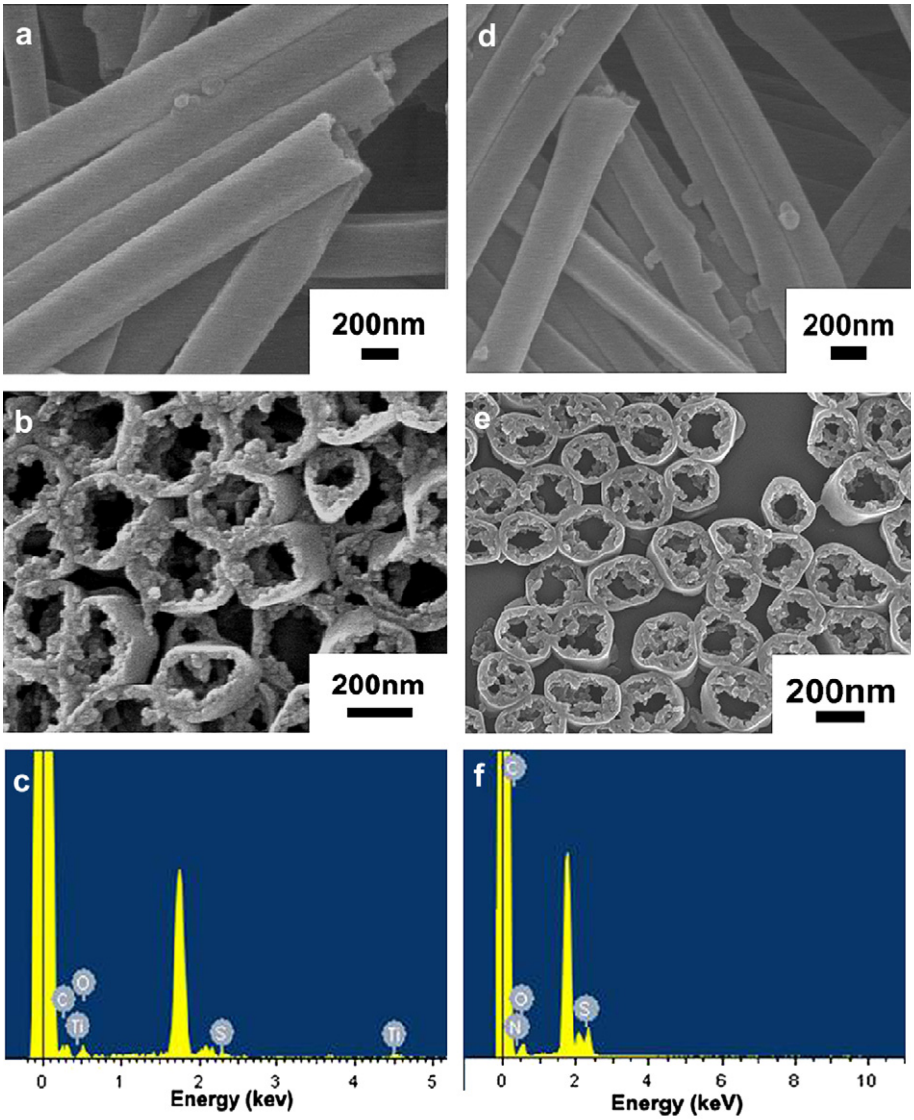

Fig. 4. (a) SEM image of titania/PS composite nanotubes; (b) SEM image of titania/PS composite nanorings with height about 100 nm from the sample shown in Fig. 4a; (c) The corresponding EDX spectrum of the sample shown in Fig. 4b; (d) SEM image of polyaniline/PS composite nanotubes; (e) SEM image of polyaniline/PS composite nanorings with height about 100 nm from Fig. 4d; (f) The corresponding EDX spectrum of the sample shown in Fig. 4e.

double-shelled composite nanotubes. Similarly, the Janus PANi/PS composite nanorings were derived.

4.6. *Preparation of silica (SiO_2)/PS double-shelled composite nanotubes and nanorings*

After S1 was immersed in a mixture of water (5 g) and ethanol (5 g), a mixture of tetraethoxysilane (5 g TEOS) and ethanol (5 g) was added. The sol-gel process was carried out for 24 h at ambient temperature. Silica/PS double-shelled composite nanotubes were obtained after rinsing with ethanol. Similarly, the Janus silica/PS composite nanorings were derived.

4.7. *Characterization*

Morphology observation of the samples was performed with a Hitachi S-4800 scanning electron microscope (SEM, Japan) equipped with an energy dispersive X-ray (EDX) analyzer operating at an accelerating voltage of 15 kV and transmission electron microscopy (JEOL 1011 and JEOL 100CXII at 100 kV, Japan). Atomic force microscopy (MultiMode 3D Scanning Probe Microscope, Veeco, USA) was operated in the tapping mode. The samples for SEM characterization were prepared by vacuum sputtering with Pt on the ambient dried samples. TEM samples were prepared by spreading very dilute dispersions in ethanol onto carbon-coated copper grids.

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