Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Fabrication of Nanocomposite Film Decorated with Highly Dispersive Nanoparticles by Following Interface-Induced Strategy

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Experimental

1. Materials

Polystyrene (PS) (*M*w=1.92×10^5), Dichlorodimethylsilane (DCDMS), paraffin wax (mp 53-57 °C) were purchased from Sigma-Aldrich. Dopamine hydrochloride, 1-dodecanethiol, tris(hydroxymethyl)aminomethane hydrochloride (Tris HCl), (3-aminopropyl)triethoxysilane (APTES) were obtained from Shanghai Macklin Biochemical Co. Ltd. Chloroform ($CHCl_3$) and toluene were purchased from Hangzhou Gaojing Fine Chemical Industry Co. Ltd. Deionized (DI) water (18.2 MΩ cm^{-1}) was provided by a lab-water system (HK Super PW). Ammonia, tetraethyl orthosilicate (TEOS), ethanol, sodium hydroxide (NaOH), silver nitrate ($AgNO_3$), 4-nitrophenol (4-NP) were purchased from Shanghai Hushi Laboratorial Equipment Co. Ltd. Sodium borohydride ($NaBH_4$) and titanium oxide (TiO_2) particles with an average size of 150 nm (99.5%) were purchased from Aladdin Reagent (Shanghai) Co. Ltd. All the chemicals were used without further purification.

2. Synthesis of SiO_2 Colloidal Particle

The SiO_2 particle with diameter of 450 nm was prepared according to the Stöber method. Firstly, a solution of 9 mL of ammonia, 16 mL of ethanol and 25 mL of deionized water was mixed for reserve. Then another solution containing 4.5 mL of TEOS and 45.5 mL of ethanol was quickly added into the reserved mixture. The resulting solution was incubated at room temperature and stirred at a speed of 800 rpm for 4 h. The product were collected by centrifugation (9000 rpm, 5 min) and washed with ethanol for several times. Afterward, the collected SiO_2 spheres were dried by vacuum at room temperature for 24 h.

3. Synthesis of Janus Particle

3.1 Surface Modification of SiO_2 Particles

The surface of SiO_2 particles was further modified by using silane couple of (3-aminopropyl)triethoxysilane (APTES) and dichlorodimethylsilane (DCDMS). The surface wettability of the particles was regulated by adjusting the concentration ratio of APTES/DCDMS in solution. In short, 0.25 g silica powders were dispersed into 30 mL toluene. Subsequently, APTES and DCDMS were added into toluene solution at a specific concentration ratio and stirred for 2 h. The products were then centrifuged and rinsed for several times with ethanol, and finally dried in vacuum at room temperature for 24 h.

3.2 Preparation of Colloidosomes

The surface-modified SiO_2 particles were used to construct oil-in-water Pickering emulsions. To prepare colloidosomes, 0.25 g SiO_2 powders were added into 8 mL deionized water and heated to 75 °C. 2.5 g paraffin wax (mp 53-57 °C) was then added into the particle suspension. After 10 min of heating and mild stirring, the mixture was submitted to vigorous stirring by homogenizer at 15000 rpm for 120 s and then cooled to room temperature. After cooling the system to room temperature, the solid wax droplets were filtered and rinsed with water with the assistance of a water-circulating-vacuum pump, and then dried at 30 °C vacuum for 24 h.

3.3 Synthesis of SiO_2/Polydopamine Particle

The obtained powder of colloidsomes was re-dispersed into deionized water and added to 100 mL Tris-Buffer (0.1 M, pH = 8.5) under stirring. 0.25 g dopamine monomer was then added into the mixture, and incubated at room temperature for 1 h.

The product of wax-SiO_2/PDA were filtered and rinsed with water, and dried in vacuum at room temperature for 24 h.

While for reserving the SiO_2/PDA Janus particles separately for antibacterial test, chloroform was used to dissolve the paraffin wax way, releasing the SiO_2/PDA Janus particles from the colloidsomes. The products were then centrifuged and rinsed for several times with ethanol, and finally dried in vacuum at room temperature for 24 h.

3.4 Synthesis of SiO_2/PDA-Ag Janus Particle

Ag precursor aqueous solution ($[Ag(NH_3)^2]^+$ ions, 2 mg/mL) was freshly prepared by feeding aqueous ammonia dropwise into the $AgNO_3$ solution. Then, wax-SiO_2/PDA was added into the $[Ag(NH_3)^2]^+$ solution under stirring. This reaction was completed after 1 h. The product of wax-SiO_2/PDA-Ag were filtered and rinsed with water, and dried in vacuum at room temperature for 24 h.

While for reserving the SiO_2/PDA-Ag Janus particles separately, the same procedure as for the SiO_2/PDA Janus particles was taken.

3.5 Synthesis of Amphiphilic SiO_2/PDA-Ag Janus Particle

1-Dodecanethiol was mixed with ethanol to make 10 mM solution. Then the wax-SiO_2/PDA-Ag was immersed in the thiol solution for 24 h, followed by rinsing with ethanol and then deionized water. The amphiphilic SiO_2/PDA-Ag Janus particles were obtained after the removal of paraffin wax with chloroform. The particles were then centrifuged and rinsed for several times with ethanol, and finally dried in vacuum at room temperature for 24 h.

4. Preparation of Nanocomposite Film

4.1 Preparation of Casting Solution

Before the film making, the casting solution was prepared. Firstly, PS was dissolved in chloroform to prepare polymer solutions with a concentration of 15 g L^{-1}. Then, particle/ethanol suspension with concentration of 15 g L^{-1} was prepared for use. Finally, PS solution was mixed with particle suspensions in the volumetric proportion of 25/1 by ultrasonication to prepare the casting solution.

4.2 Film Preparation

Firstly, glass substrates (1 × 1 cm) were cleaned with ethanol and deionized water, then dried with nitrogen before use. The as-prepared casting solution was transferred dropwise onto a clean glass substrate placed in a closed chamber with adjustable temperature and humidity. The casting solution was allowed to evaporate to dryness to yield porous films under the selected condition of temperature and humidity. After solidification, the obtained film was removed from the chamber and further dried in the ambient environment.

5. Characterization

The particles, colloidosomes, upper and cross-sectional surfaces of the obtained polymer nanocomposite film were characterized with a field emission scanning electron microscope (FEI, Nova Nano SEM 650, USA) operating at a 5 kV accelerating voltage. The energy dispersive spectra (EDX) and mapping results were obtained using the same instrument. The cross-sectional samples were obtained by fracturing samples in liquid nitrogen, and all samples were coated with platinum before SEM examination. Transmission electronic microscopy (TEM) image was obtained using transmission electron microscopy (HT7700, Hitachi). The phase structure of the products was identified by powder X-ray diffraction (XRD, Bruker D8 ADVANCE) with Cu-Kα irradiation source ($\lambda = 1.5418$ Å). Furthermore, ultraviolet-visible (UV-vis) spectra and time dependent UV-vis were obtained by using Shimadzu UV-2600 UV-vis Spectrophotometer using quartz cuvette of 10 mm path length.

6. Antibacterial Activity Evaluation

The antibacterial activities of the polymer nanocomposite film were determined against methicillin-resistant *Staphylococcus aureus* (MRSA). MRSA bacteria were frozen at -70 °C before use. The bacteria strains were suspended in trypticase soy broth (TSB) and incubated at 37 °C for 12 h for preparation of bacterial suspensions. In brief, 5 μL bacterial suspensions (in PBS) were added in each well of a 48-well plate, and the nanocomposite films with the decoration of different particles were cut into circular shape with diameter of 5 mm and immersed into the plate. Three parallel samples were used for one type of nanocomposite film. The plate was then put into an incubator at 37 °C for 6 h in a relative humidified atmosphere. Afterwards, 1 mL of sterilized PBS was transferred into each well to re-suspend any bacterial survivors. 100 μL of the bacterial suspension was taken to make 10, 100, 1000, and 10000-fold dilutions in sequence. Then, 10 μL of each diluted suspension was spread on trypticase soy agar (TSA) plates. After incubation for 12 h at 37 °C, the colony-forming units (CFU) on the Petri dish were counted. The results were expressed as antibacterial rate %:

Antibacterial rate (%)

$$=\left(1-\frac{survivor\ bacterial\ count\ of\ experimental\ group}{bacteria\ count\ of\ control}\right)\times 100\%$$

7. Photocatalytic Evaluation of TiO_2 Containing Film

In the quartz cuvette, 1.0 mL $NaBH_4$ (0.2 M), 0.1 mL 4-NP (5 mM) and 2.0 mL deionized water was mixed for reserve. Then the TiO_2 particles containing film was immersed into solution. After 1 h of light-avoiding immersion, the photocatalytic degradation of 4-NP was initiated by irradiating the reaction mixture with a 350 W xenon lamp (420 nm). The light source was placed at a distance of 15 cm from the reaction solution. And the progress of the reaction was monitored by UV-vis spectrophotometry.

Supporting figures

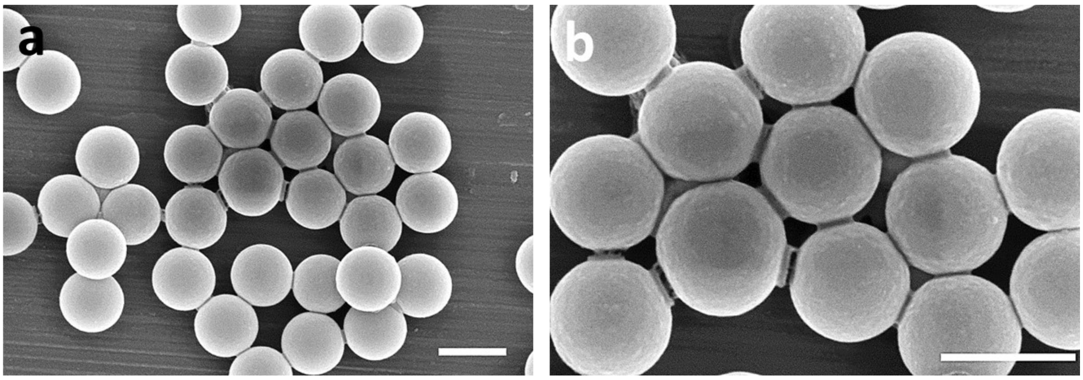

Fig. S1. SEM images of the silica particle. Scale bar: 500 nm.

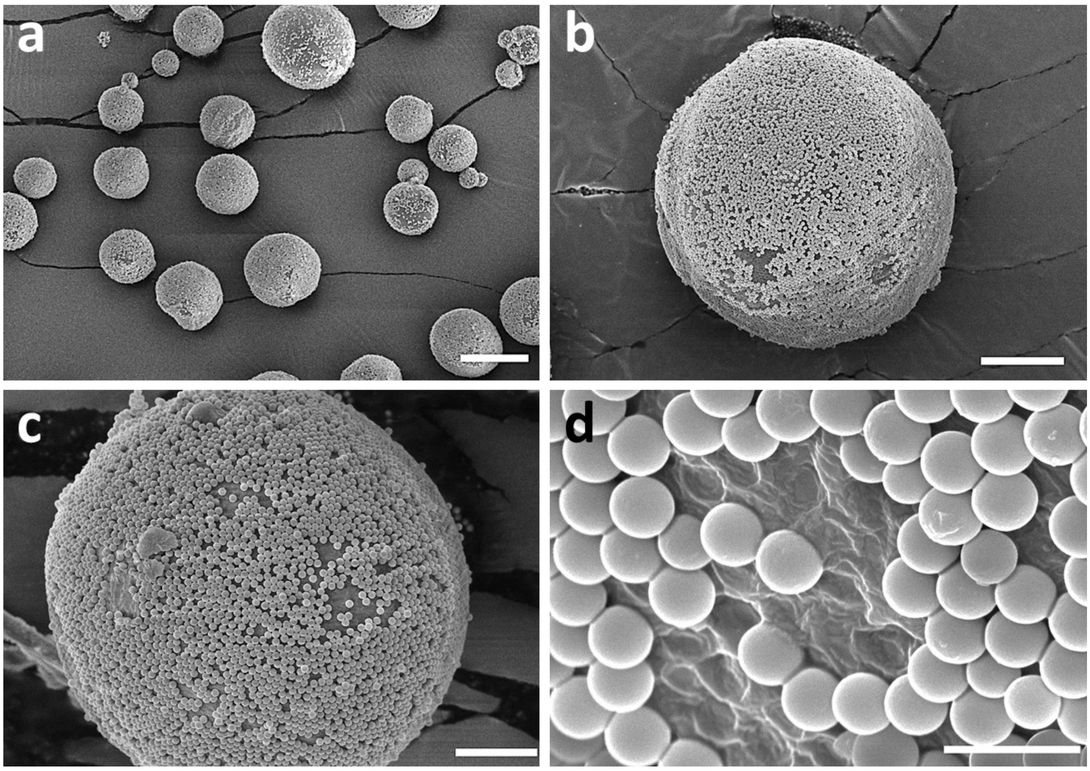

Fig. S2. SEM images of the colloidosome. Scale bar: a) 25 μm; b) 10 μm; c) 5 μm; d) 1 μm.

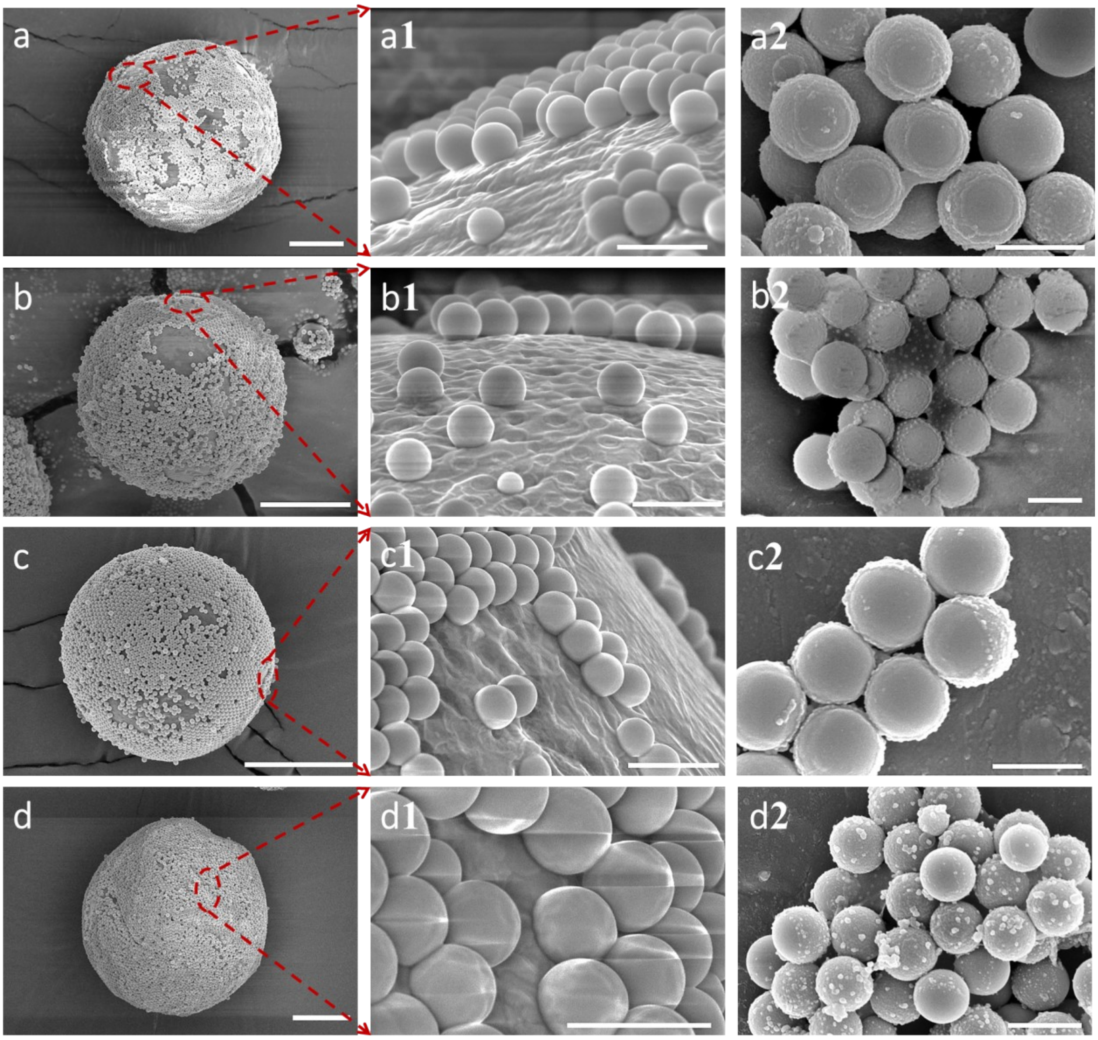

Fig. S3. SEM images of (a-d, a1-d1) the colloidosome and (a2-d2) the Ag NP-coated Janus particle prepared from silane-modified silica particles with different ratios of the silane couple. The $C_{APTES/DCDMS}$ was used to modify the silica particles: a,a1,a2) 1:0; b,b1,b2) 1:0.0636; c,c1,c2) 1:0.106; d,d1,d2) 1:0.116. Scale bar: a-d) 10 µm; a1-d1) 5 µm, a2-d2) 500 nm.

Discussion for Fig. S1-S3: The fabrication of the Janus particles started with the synthesis of silica particles by Stöber method. In the current study, SiO_2 particles with uniform size of 450 nm were prepared (Fig. S1) and further modified with a mixed silane coupling reagent of (3-aminopropyl)triethoxysilane (APTES) and dichlorodimethylsilane (DCDMS) with different concentration ratios. By introducing both hydrophilic and hydrophobic groups onto the particles, the amphiphilic balance could be properly tuned for further preparation of colloidsomes from the silica particles. Pickering emulsion method, firstly reported by Granick, was used to prepare the colloidsomes in which the silica particles were densely embedded into the paraffin spheres (Fig. 1a-b, S2). Fig. S3 revealed the fact that the modulation of the silane couple could effectively tune the embedding depth of the particle into the paraffin matrix due to the varied surface wetting property of the particle. Since the exposed faces of the embedded particles in the colloidsomes were further chemically modified to create the Janus character, the depth variation therefore dictated the Janus balance of the modified particles. The ratio of $C_{APTES/DCDMS}$=1:0.106 was adopted in our study to make the particles half-embedded for further modification of the exposed particle faces by polydopamine (PDA).

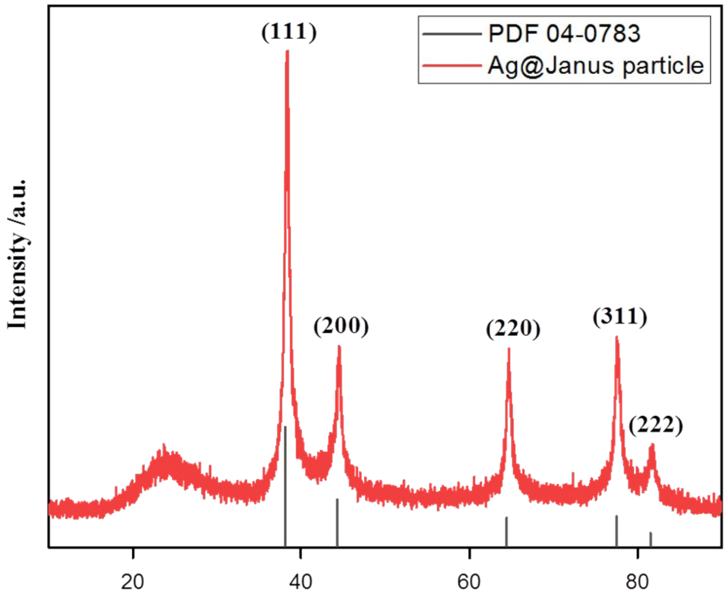

Fig. S4. XRD characterization of SiO_2/PDA-Ag Janus particle prepared through in *situ* metallization. The diffraction peaks at 38.1°, 44.2°, 64.4°, and 77.3° in SiO_2/PDA-Ag are related to the (111), (200), (220), and (311) crystalline planes, confirming that metallic Ag was successfully immobilized on the SiO_2 particles.

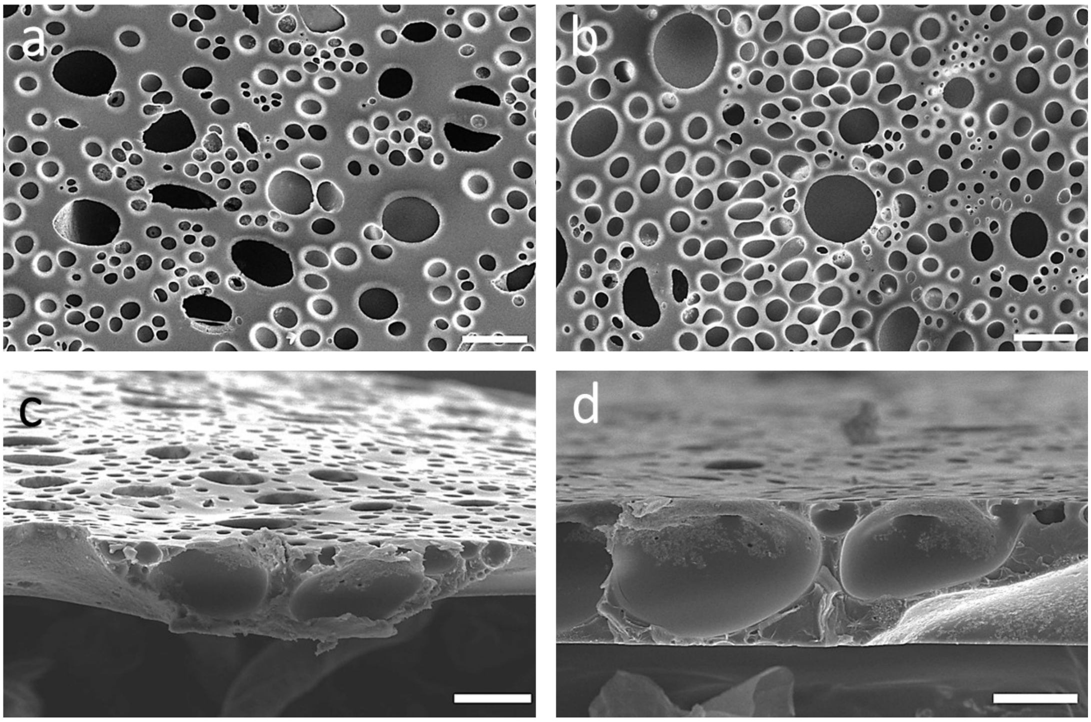

Fig. S5. Top-view (a-b) and cross-sectional (c-d) SEM images of the porous films with the decoration of SiO_2/PDA-Ag Janus particles fabricated under different ambient temperatures. The temperature conditions: a,c) 15 °C; b,d) 20 °C. Scale bar: 25 μm.

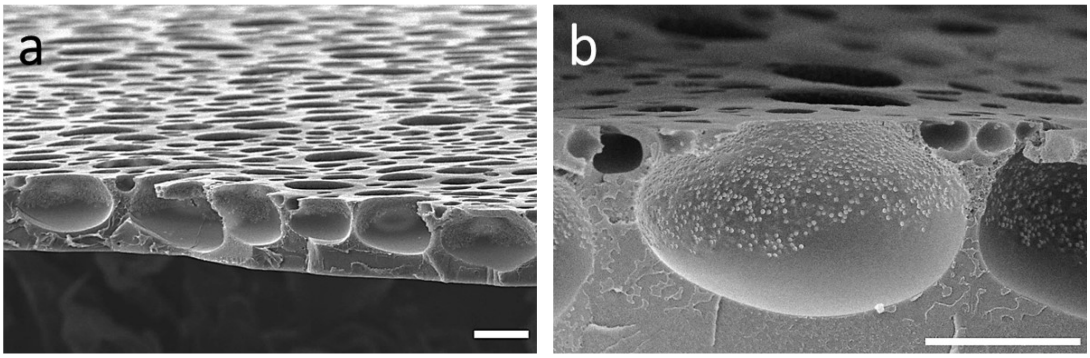

Fig. S6. SEM images of the porous films with the decoration of SiO_2/PDA-Ag Janus particles fabricated under the two different ambient temperatures. The temperature conditions: a) 5 °C; b) 25 °C. Scale bar: 15 µm.

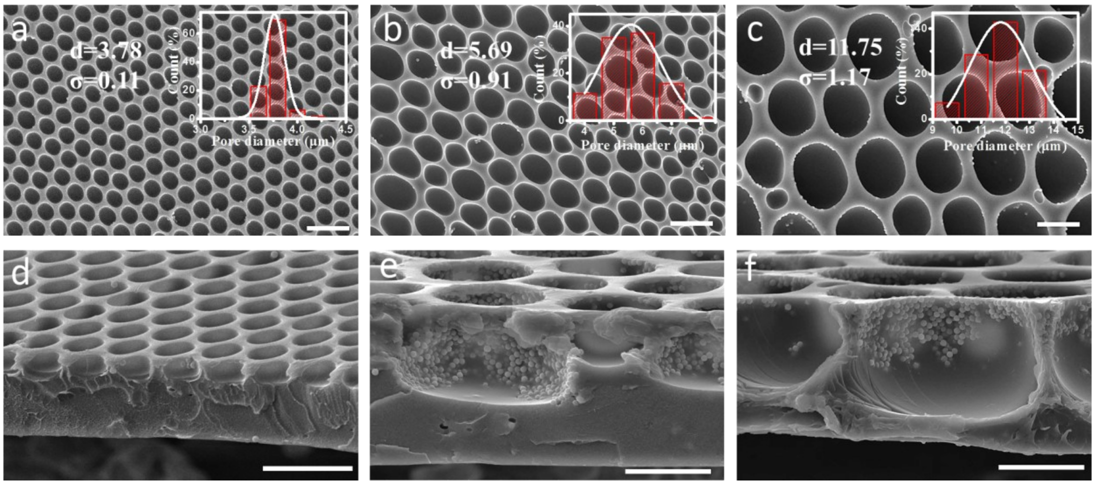

Fig. S7. Top-view (a-c) and cross-sectional (d-f) SEM images of the porous films with the decoration of SiO_2/PDA-Ag Janus particles fabricated under different ambient humidity. The humidity conditions: a,d) 75%; b,e) 85%; c,f) 95%. Scale bar: 10 μm.

Discussion for Fig. S1-S3: Fig. S7 showed the morphologies of the composite films made under different humidity. One could see that both the size of pore openings on the top and the pore depth from the cross-sectional view increased significantly with the increasing humidity. But with the temperature be controlled at 5 °C, the particle decorations of all three samples were not only highly selectivity into the pores but also extensive within the surface pore array.

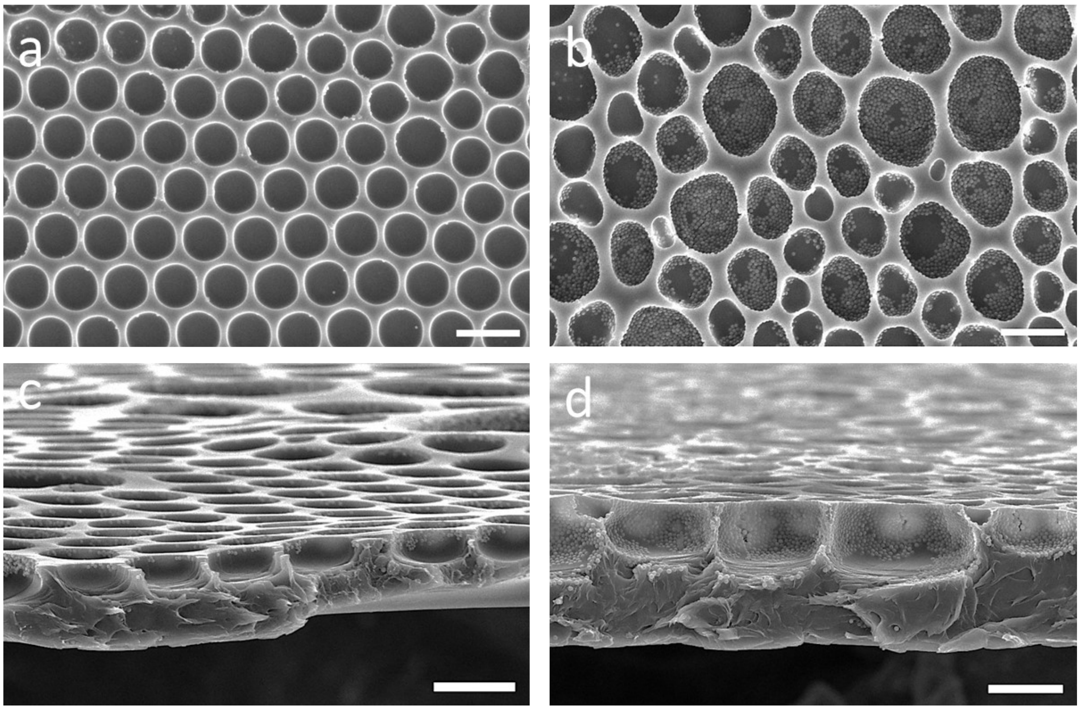

Fig. S8. Top-view (a-b) and cross-sectional (c-d) SEM images of the porous films with the decoration of two different types of particles. The employed particle types: a,c) SiO_2 particle; b,d) SiO_2/PDA Janus particle. Scale bar: 10 µm.

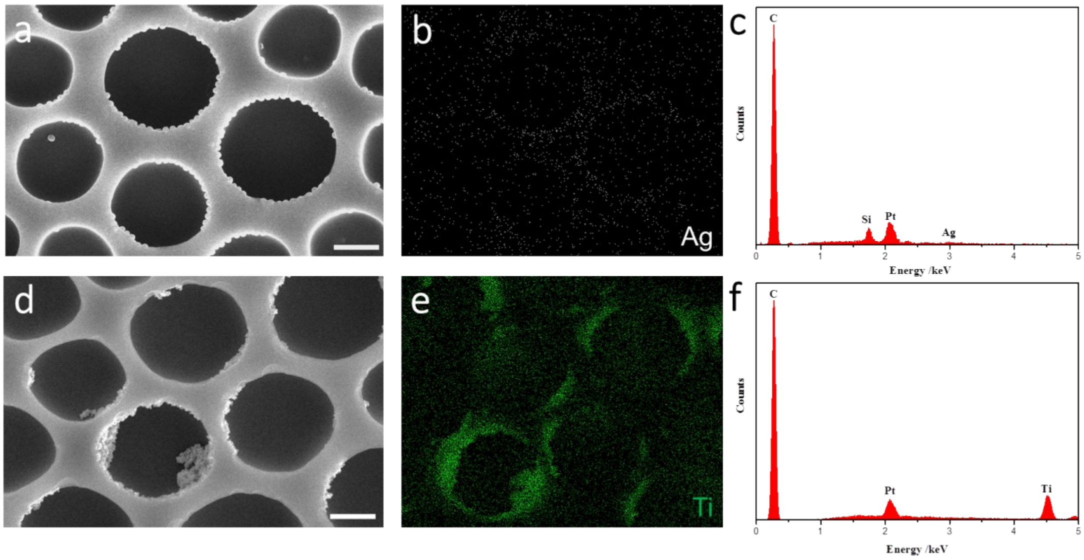

Fig. S9. Characterization of the porous films with the decoration of a-c) Janus silica particles and d-f) TiO_2 particles: a,d) SEM, b,e) elemental mapping images and c,f) EDX spectrums. Scale bar: 5 μm.

Discussion for Fig. S9: For elemental mapping signal of Ag (Fig. S9b), it could be seen that the NP distribution was diffusive. Yet still, the ring-like assembling tendency could be recognized, reflecting the selective accumulation of Janus particles onto the rims of the open pores. While for Ti signal (Fig. S9e), the signal intensity was stronger and the accumulation tendency towards pore rims was greater comparing with the case of Ag.

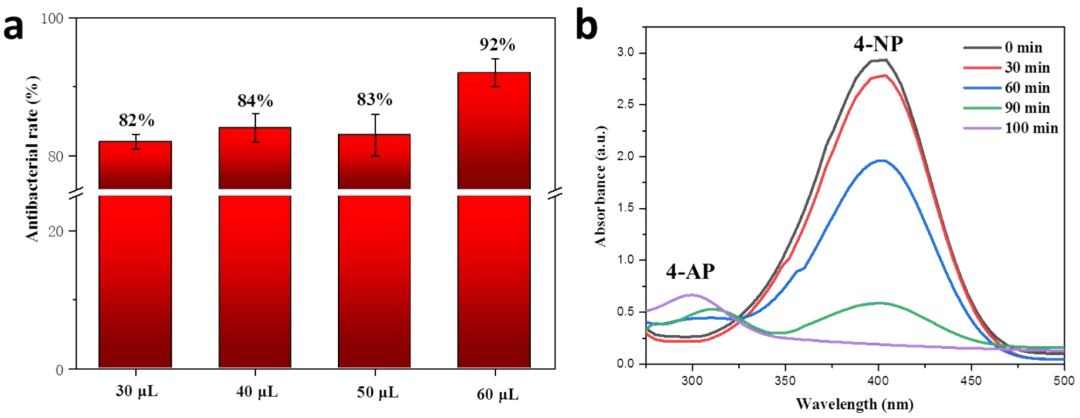

Fig. S10. a) Antibacterial rates of four film samples made from casting solutions with addition of different amount of thiol-treated SiO_2/PDA-Ag Janus particle suspension; b) Time-dependent UV-vis spectrum of the TiO_2-containing film sample during its photocatalytic degradation.

Discussion for Fig. S10b: The 4-NP solution displays strong adsorption peaks at 400 nm because the addition of NaBH4 causes 4-NP ions to form. The UV absorption peak intensity of 4-NP at 400 nm gradually diminished, and a new absorption peak corresponding to 4-AP appeared at 300 nm.