Electronic Supplementary Information

Preparation of lotus-leaf-like antibacterial film based on mesoporous silica microcapsule-supported Ag nanoparticles

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1. Experimental Details

1.1 Reagents

Fluorinated acrylate monomer (FAM) was purchased from Shandong Fluorine Chemical Technology Co. Ltd with technical grade. Silicone acrylic was purchased from Xingguo Coating of Qingdao Co. Ltd. Polyvinylpyrrolidone (PVP, K30) was purchased from Aladdin Reagent Co. Ltd with analytical grade. Deionized water was purchased from Baiyun Water Station Co. Ltd. Methyl methacrylate (MMA), N,N-dimethyl formamide (DMF), 2,2-Azobisisobutyronitrile (AIBN), vinyltriethoxysilane (VTES), teraethoxysilane (TEOS) and acetic ether, butanone, ethanol, ammonia, silver nitrate were purchased from Sinopharm Chemical Reagent Co. Ltd with analytical grade. All the chemicals were used as received without any further purification.

1.2 Preparation

Preparation of the MSMAs

The mesoporous silica microcapsule-supported Ag nanoparticles (MSMAs) were prepared according to the previous work[1]. Briefly, 50mL of monodisperse sulfonated polystyrene (PS) dispersion with the concentration of 10 mg/mL was mixed with 50mL of silver nitrate aqueous solution (0.1mol/L) and stirred at room temperature for 1h. Then, 20mL of ethanol dissolved with 1.5g of PVP were added into the mixture and stirred at room temperature for 2h, to obtain PS/Ag composite spheres. It were mixed with 3mL of ammonia and stirred for 1h, and then TEOS was added into the mixture drop by drop to obtain silica colloids generated by the hydrolysis and polymerization. After continuously stirring for 2h, the product was collected by vacuum filtration, washed and dried at room temperature. Finally, the samples were calcined at 550°C for 6h with the temperature ramping rate of 1°C/min, obtaining MSMAs.

Preparation of the FSR

The fluoro-silicone resin (FSR) was synthesized as follows: first, FAM, MMA, DMF, VTES and AIBN, of which mass ratio was 1:1:1.5:0.5:0.02, were charged into a four-necked flask with stirrer, thermometer and reflux condenser, and then the mixture was heated to 70°C and stirred for 4h. Subsequently, the mixture was natural cooled to 40°C under stirring, followed by adding mixed solvent (volume ratio of ethanol : butanone=3:1, mass ratio of FAM : mixed solvent=1:40). The solution was continuously stirred for 2h to reach enough conversion. Finally, the synthesized resin was diluted by acetic ether.

Preparation of the MSMAs/FSR film

The typical preparation method of MSMAs/FSR film is as follows: 1.3mL of FSR solution was pipetted onto the center of a clean slide, followed by spin coating at 2000 rpm for 1 min, and then the ethanol suspension of the MSMAs (32mg/mL) was immediately dispensed on top of the FSR wet film by the spin coating process at 800rpm for 10s, and form the MSMAs/FSR wet film. Next, 0.6mL of FSR solution was immediately dispensed on the surface of the MSMAs/FSR wet film. Finally, the assembly was dried in the vacuum at 40°C for 24h.

1.3 Characterization

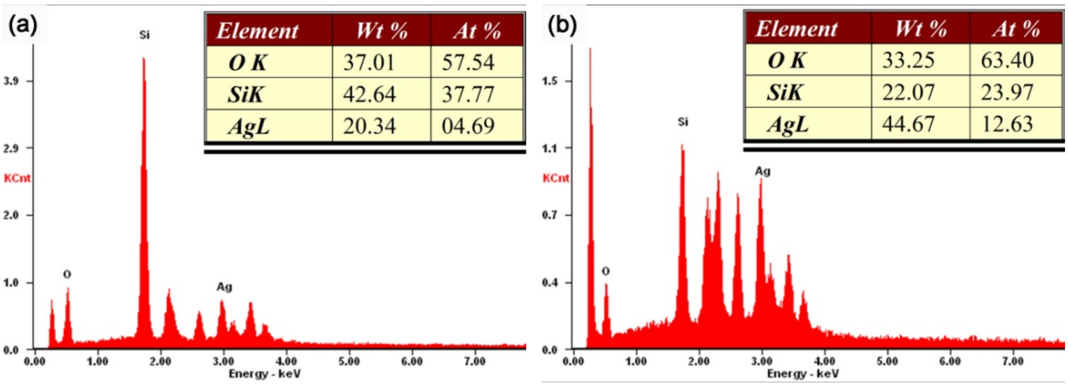
The structures of the obtained MSMAs were characterized by an X-ray powder diffractometer (XRD, APEXII, Bruker Co., Germany) using Ni-filtered Cu K_α radiation (λ=1.542Å). Data were collected at 2θ angles from 10° to 90° with a step of 0.02°. The crystalline phases were identified by referring to data of Joint Committee on Powder Diffraction Standards. FE-SEM was performed using field emission scanning electron microscope (Inspect, FEI Co. Japan). The chemical composition ratio of MSMAs were determined using energy-dispersive X-ray (EDS) attached to FE-SEM. TEM was carried out with TECNAI-10 transmission electron microscopy (Hitachi Co., Japan).

The water contact angles on the films were measured at ambient temperature on a contract angle system (DCA20, Dataphysics, Germany), and all the contact angles were determined by averaging values measured at 6 different points on each sample surface.

To confirm the MSMAs is able to give a prolonged release of Ag and to compare the different release of Ag with different loading AgNPs, the same mass of 0.2g of the MSMAs product were soaked in 20mL of ultrapure water in a beaker at room temperature and shaken in an orbital shaker at a slow-speed vibration of 60 rpm for periods ranging from 6h to 10d, for accelerating the release of Ag. At selected intervals, the supernatant solution was collected after centrifugation, and the concentration of released Ag in the supernatant solution was measured using an inductively coupled plasma mass spectrometer (ICP-MS, XSENIES, Thermo Electron Co., America).

Escherichia coli (E. coli, CMCC44103) were chosen to evaluate the antimicrobial activity of MSMAs/FSR film with contact mode referenced[2, 3]. Briefly, the bacterial suspensions (10^6CFU/mL, 100μL) were put on the surface of the films and the control with the size of 1*1 cm^2 for 10h, respectively. Then, the films were transferred to 10mL PBS buffer solution and vortex. The solution was serially diluted and 100μL of each diluent was placed on the agar plate. Bacterial colonies on the agar plates were counted after incubation at 36.1°C for 24h.

2. Supporting Information Figures



(a)

Element	*Wt %*	*At %*
O K	37.01	57.54
SiK	42.64	37.77
AgL	20.34	04.69

(b)

Element	*Wt %*	*At %*
O K	33.25	63.40
SiK	22.07	23.97
AgL	44.67	12.63

Fig.S1 EDS spectrums of the MSMAs prepared by different initial concentration of $AgNO_3$:(a) 0.075mol/L ; (b) 0.1mol/L.

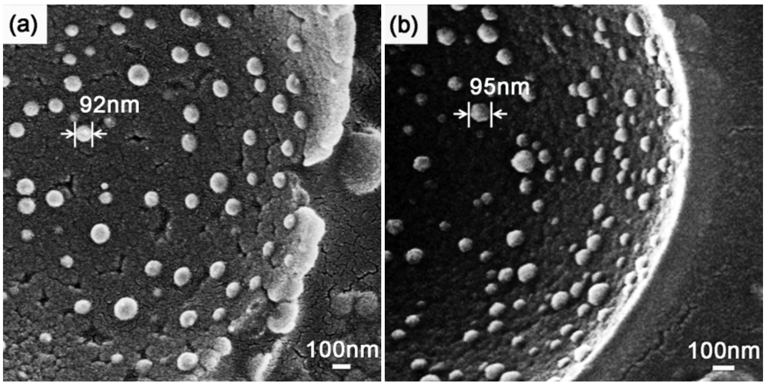


Fig.S2 SEM images of broken MSMAs prepared by different initial concentration of $AgNO_3$: (a) 0.075mol/L ; (b) 0.1mol/L.

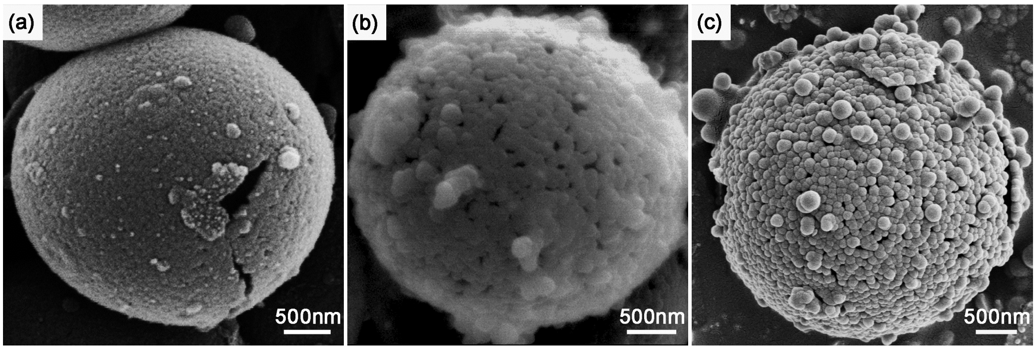


Fig.S3 SEM images of MSMAs prepared by different concentration of TEOS: (a)0.05mol/L; (b) 0.1mol/L; (c) 0.15mol/L.

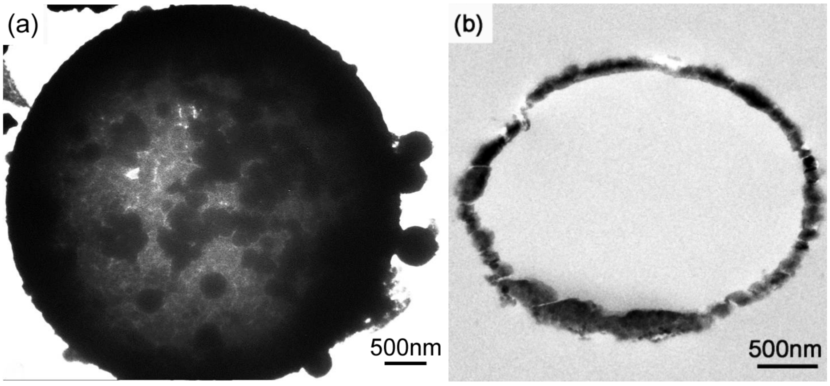


Fig.S4 TEM images of (a) MSMAs; (b) cross section of the MSMAs, which was obtained by cutting the MSMAs embedded in tougher epoxy with a diamond knife.

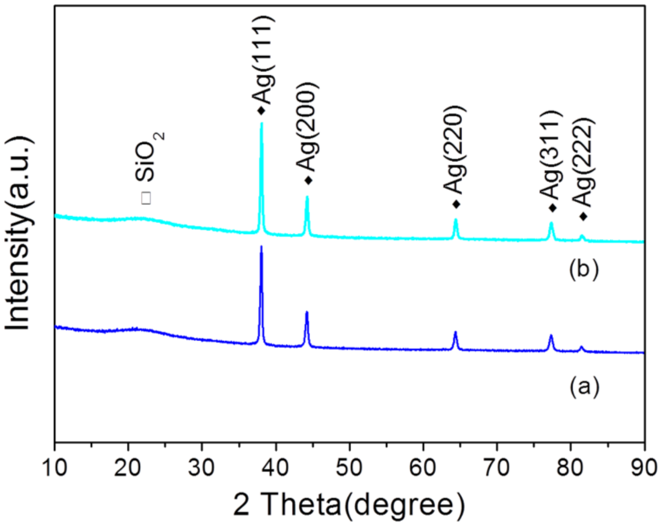


Fig.S5 XRD patterns of the MSMAs prepared by different initial concentration of $AgNO_3$:(a) 0.075mol/L ; (b) 0.1mol/L.

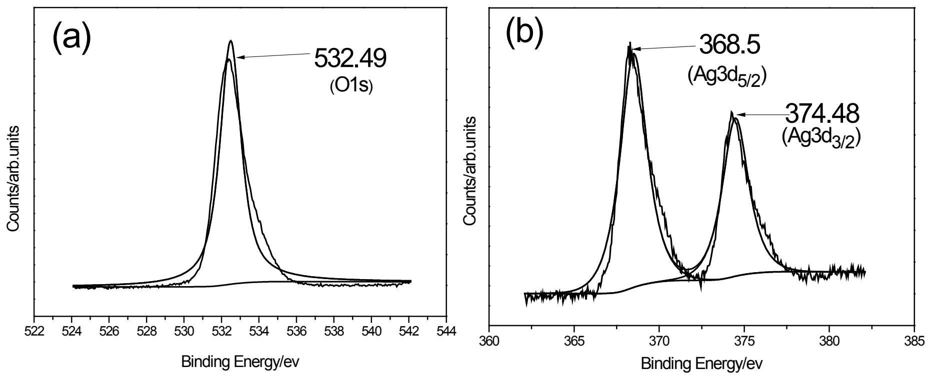


Fig.S6 XP spectra of (a) O1s, (b)Ag3d in MSMAs

The Fig.S6 shows the representative survey of XP spectra of O1s and Ag3d. The O1s spectrum shows a peak of a binding energy of 532.49eV, which is attributed to the O of O-Si bonds present in the silica. In the XP spectra of Ag, Ag $3d_{5/2}$ and Ag $3d_{3/2}$ peaks are located at 368.5 and 374.48eV respectively, whereas the spin-orbit splitting of the 3d doublet is 5.98eV. The binding energy is very typical for Ag in metallic form i.e. in zero oxidation form. No peak of Ag 3d in Ag_2O or other silver oxide was detected.

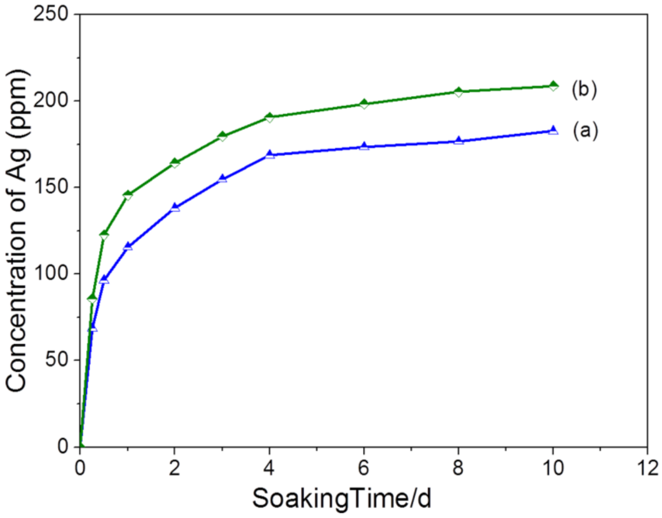


Fig.S7 Concentration of Ag released from the interior of the MSMAs into water with various soaking time. The samples was prepared by different initial concentration of $AgNO_3$:(a) 0.075mol/L ; (b) 0.1mol/L.

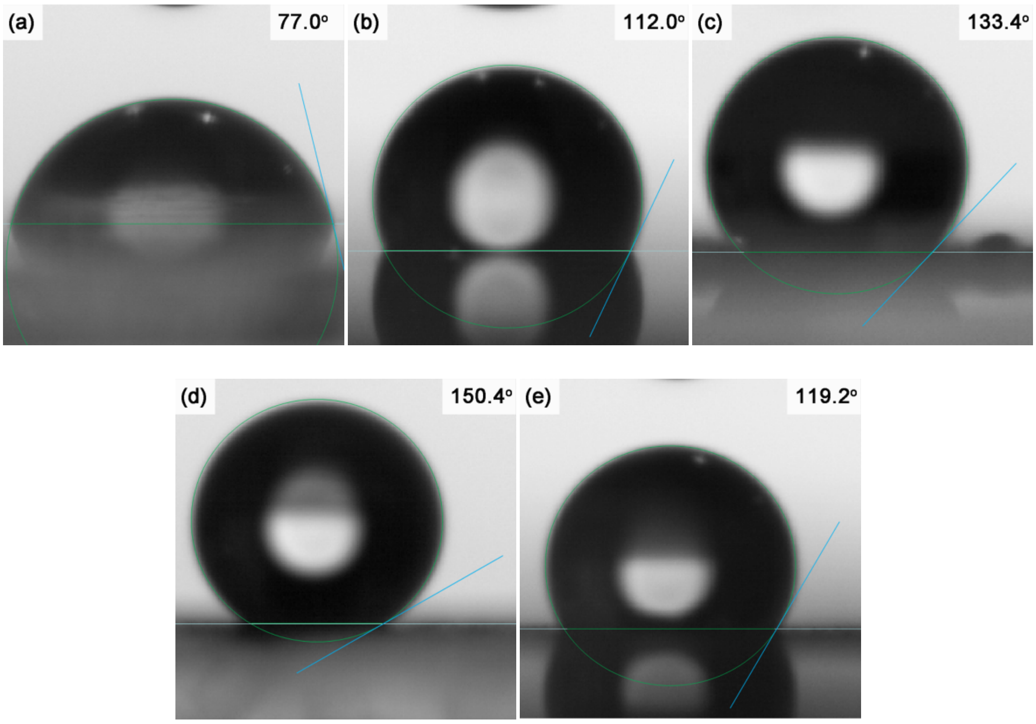


Fig.S8 Images of the water droplet on various films: (a) the pure silicone acrylic emulsion film (b) the pure FSR film; (c) the MSMAs/FSR film without hydrophobic modification; (d) the MSMAs/FSR film hydrophobically modified by 0.6mL of FSR solution; (e) the MSMAs/FSR film hydrophobically modified by 1mL of FSR solution.

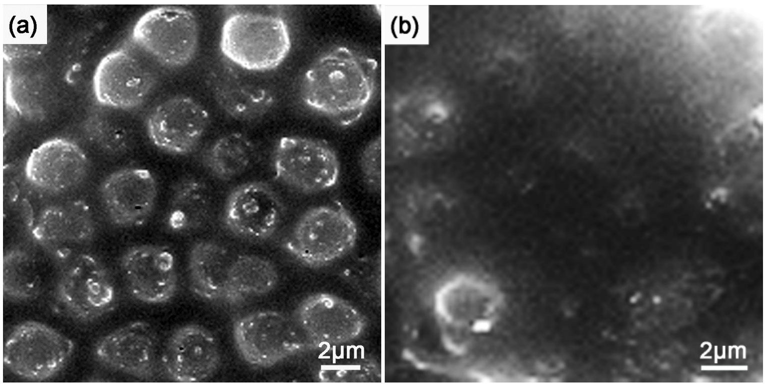


Fig.S9 SEM images of the MSMAs/FSR film hydrophobically modified by different dosages of FSR solution: (a) 0.6mL; (b) 1mL.

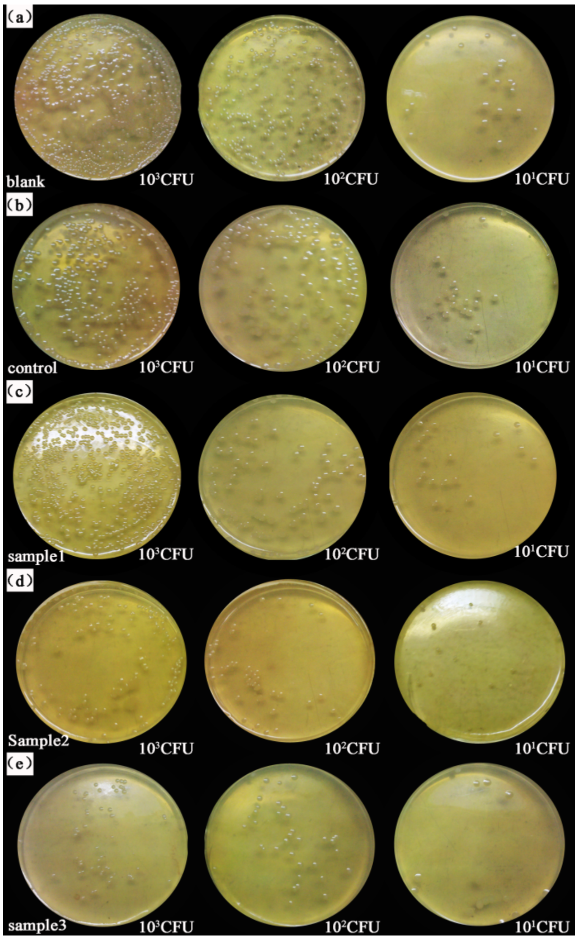


Fig.S10 Antibacterial activities of various samples against E. coli in different initial bacterial concentration: (a) the blank (without film); (b) the control (with the pure silicone acrylic film, 20.5%); (c) the sample1 (with the silicone acrylic film loaded with the pure mesoporous silica microcapsules without AgNPs, 26.5%); (d) the sample2 (with the FSR film loaded with the pure mesoporous silica microcapsules without AgNPs, 71.6%); (e) the sample3 (with the MSMAs/silicone acrylic film, 89.4%).

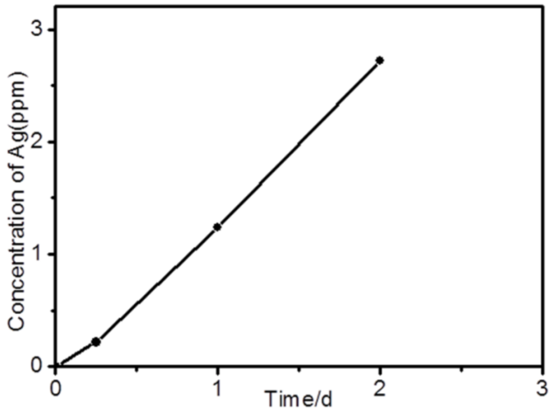


Fig.S11 Concentration of Ag released from the FSR/MSMAs film into water with various soaking time

As shown in Fig.S11, the concentration of released Ag^+ ions is measured about 2.72 ppm after 2 days, which is much lower than that of corresponding MSMAs powders. This may be because that the amount of MSMAs in the MSMAs/FSR film used for testing is less than the MSMAs powders. Moreover, the releasing of Ag^+ ions will also be affected by the hydrophobically modification.

Reference

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2 F.L. Yang, J.R. Yao, X. Chen and Z.Z. Shao, *Acta. Polym. Sin*, 2012, **2**, 125.
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