Electronic Supplementary Information (ESI) for

Multifunctional polyacrylonitrile-SiO_2/TiO_2 hollow particle nanofibrous membranes with robust ultra-violet-resistance and antibacterial effect

*Xiaxi Pan,[ab] Yuwei Zhu, [*b], Liangdong Liu,[c] Changdao Mu[a] and To Ngai[*b]*

[a] *Department of Pharmaceutics and Bioengineering, School of Chemical Engineering, Sichuan University, Chengdu 610065, P. R. China*

[b] *Department of Chemistry, The Chinese University of Hong Kong, Shatin N. T., Hong Kong, 999077, P. R. China*

c. O-Spheres Limited, Shatin N. T., Hong Kong, 999077, P. R. China.

***Correspondence authors.**

E-mail address: uvyzhu@gmail.com, tongai@cuhk.edu.hk

1. Experimental section

1.1. Materials

Polyacrylonitrile (PAN, average Mw=150,000) was purchased from Shanghai Macklin Biochemical Co., Ltd. N, N-Dimethylformamide (DMF) was purchased from RCI Labscan Limited. Triethoxyoctylsilane (97%) was purchased from Aladdin Scientific Co., Ltd. Toluene (GR grade) was purchased from Duksan Co., Ltd. TiO_2 nanoparticle (CR 828, 95% of TiO_2 content) were bought from Tronox. SiO_2/TiO_2 hollow particles (25% of TiO_2 content) were generously provided by O-spheres Limited. All chemicals were directly used without any treatment.

Escherichia coli (*E. coli*, ATCC 8739) and *Staphylococcus aureus* (*S. aureus*, ATCC 6538) were purchased from the China Center of Industrial Culture Collection.

1.2. Methods

1.2.1. Synthesis and modification of SiO_2/TiO_2 hollow particles

The SiO_2/TiO_2 hollow particles (HPs), templated from Pickering emulsion, were generously provided by O-spheres Limited. Here, triethoxyoctylsilane was employed as surface modifier to enhance the hydrophobicity of SiO_2/TiO_2 HPs. The prepared hollow particles were dispersed in toluene at a concentration of 10 mg/mL, and same concentration of triethoxyoctylsilane was added into the dispersion solution. Subsequently, the mixture was stirred at 50 °C to carry out the reaction for 4 h. Finally, the particles were centrifuged and washed by ethanol for three times and dried at 60 °C to obtain the modified hollow particles (M-HPs).

1.2.2. Characterization of SiO_2/TiO_2 hollow particles and M-HPs

The micromorphology of SiO_2/TiO_2 hollow particles and M-HPs were observed by a scanning electronic microscopy (SEM, Phenom Pro, Thermo Scientific, USA) at the accelerated voltage of 10 kV. And the average diameters of SiO_2/TiO_2 hollow particles and M-HPs were measured using image

J software (version 1.54i) based on the SEM images. Further, TEM (Tecnai G2 Spirit Bio, FEI, USA) analysis followed by energy X-ray dispersive spectroscopy (EDS) was conducted at 120 kV, to examine the internal structure and the elemental composition of SiO_2/TiO_2 hollow particles. The fluorescence areas of Si and Ti in the EDS mapping image were captured using ImageJ software (version 1.54i) and the content of TiO_2 was calculated. The chemical structures of SiO_2/TiO_2 hollow particles and M-HPs were determined by a Fourier transform infrared spectroscopy (FT-IR, Nicolet iS10, Thermo Scientific, USA). Active radicals formed following photo-excitation of M-HPs were identified by a EPR instrument (EMX Plus, Bruker) with spin trapping agent (5,5-dimethylpyrroline-oxide (DMPO)).

1.2.3. Fabrication of PAN/M-HPs nanofibrous membranes (PAN/M-HPs NFMs)

Firstly, PAN powder was dissolved into DMF to gain homogeneous 15 wt% PAN solution with shaking for 24 h at room temperature. Secondly, the M-HPs were blended with PAN solution in different concentration (0, 1, 5 wt% (relative to PAN)) and the mixtures were sonicated until uniform suspensions were obtain. Then, the PAN/M-HPs suspension was loaded in a 10 mL syringe with a 21-guage needle and connected to the electrospinning machine (Tongli Tech Co., Limited, China). And the electrospinning process was carried out at a flow rate of 0.5 mL/h for 4 h, with a high voltage of 19 kV applied to needle, a rotate speed of receiver of 300 rpm and a working distance of 15 cm. Finally, all the prepared nanofibrous membranes were dried overnight at room temperature to allow the solvent to evaporate completely. The fabricated membranes were respectively designated as M-HPs-0, M-HPs-1 and M-HPs-5 according to the doping concentration of M-HPs.

Moreover, a nanofibrous membrane containing 1.25 wt% TiO_2 nanoparticles was set as the control group and named as TiO_2-1.25, which has the same TiO_2 content as M-HPs-5.

1.2.4. Characterization of PAN/M-HPs NFMs

The surface morphology of the nanofibrous membranes and nanoparticles were observed by a scanning electronic microscopy (SEM, Phenom Pro, Thermo Scientific, USA). The distribution of nanoparticles in the nanofibrous membranes were further observes by using a transmission electron microscopy (TEM, Tecnai G2 Spirit Bio, FEI, USA). The average diameters of the nanofiber and nanoparticles were measured using image J software (version 1.54i) based on the SEM images. The porosity of the nanofibrous membranes were calculated by following equation[1]:

$$\text{Porosity (\%)}=\frac{\rho_0-\frac{m_1}{V_1}}{\rho_0}\times 100$$

Where ρ_0 is the density of PAN, which is 1.14 g/cm^3. m_1 and V_1 are the weight and volume of the nanofibrous membranes, respectively.

1.2.5. Measurements of PAN/M-HPs NFMs

Ultraviolet protection factor (UPF) and UV-Vis transmittance spectra were used to evaluate the UV-resistant property of the nanofibrous membranes and nanoparticles. The UPF value were measured using a sunscreen protection factor analyzer (SPF-290AS, Solarlight, USA) according to AATCC 183-2014. And the UV-Vis transmittance spectra of the membranes and nanoparticles were obtained by a UV-Vis spectrophotometer (UV-3600 Plus, Shimadzu, Japan). In addition, rhodamine B was chosen for fluorescence attenuation experiment to evaluate the UV-resistant property of the membranes.

Mechanical properties were measured using a tensile machine (TOHNICHI, Zhuoyue, Dongguan, China) at a stretch rate of 20 mm/min and the tested membranes were cut into 50 mm×20 mm strips (n = 3). Water contact angle (WCA) was measured by using a contour analysis system (OCA 25, Dataphysics, Germany) to evaluate the surface wettability of the nanofibrous membranes. The breathability was assessed using water vapor transmission rate (WVTR) according to standard ASTM

E96 and the test was conducted at 38 °C and 90% relative humidity.

E. coli (Gram-positive) and *S. aureus* (Gram-negative) were chosen as the model strains to investigate the antibacterial activities of the nanofibrous membranes. 20 mg of nanofibrous membranes were immersed into 5000 μL bacteria suspension (1×10^6 CFU) and incubated for 24 h at 37 °C. Subsequently, the bacteria suspensions were diluted and their absorbance at 600 nm were measured by a UV-Vis spectrophotometer. The bacteria inhibition was calculated as following equation:

$$\text{Bacteria inhibition (\%)}=\left(\frac{OD_c\text{-}OD_t}{OD_c}\right)\times100$$

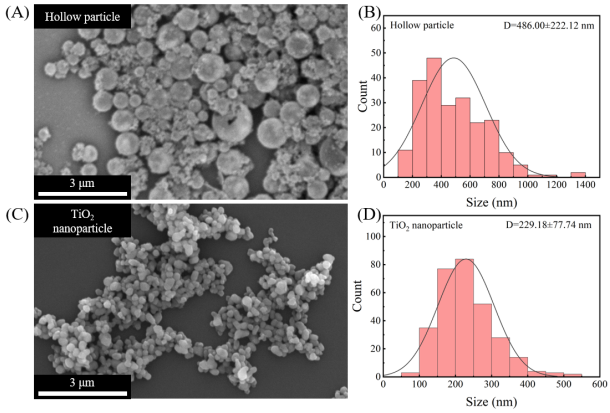
Where, OD_c and OD_t are the absorbance at 600 nm of the control (only bacteria suspension) and test groups, respectively.

In addition, the micromorphology of *E. coli* and *S. aureus* before and after contacting the nanofibrous membranes were observed by SEM (Apreo 2, Thermo Scientific, USA) at the accelerated voltage of 10 kV.

1.2.6. Statistical analysis

All of the quantitative data were analyzed using SPSS 17.0 software for One-way analysis of variance (ANOVA) and presented as the mean ± standard deviation. Duncan's multiple range tests was used to determine the significant differences between groups and the level of significance was p value < 0.05.

2. Results

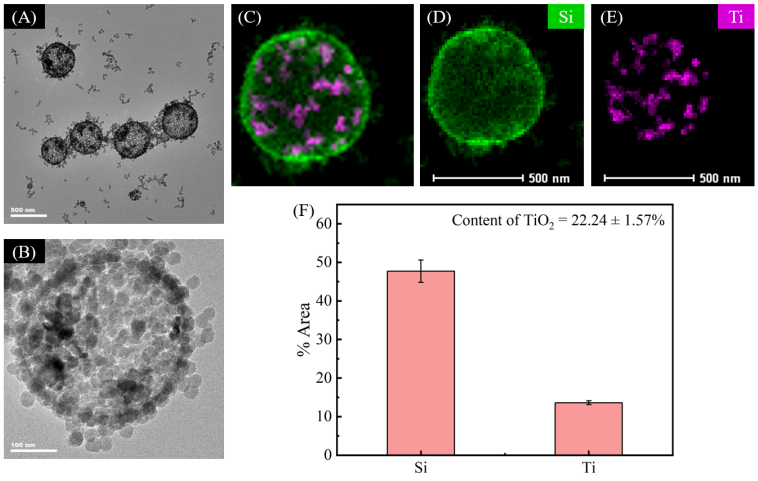


105

106 **Fig. S1.** (A) SEM image and (B) particles size distribution of SiO_2/TiO_2 hollow particles. (C) SEM

107 image and (D) particles size distribution of TiO_2 nanoparticles.

108



109

110 **Fig. S2.** (A-B) TEM images, (C-E) EDS mapping images of SiO_2/TiO_2 hollow particles and (F)

111 quantitative analysis of fluorescence areas of Si and Ti.

112

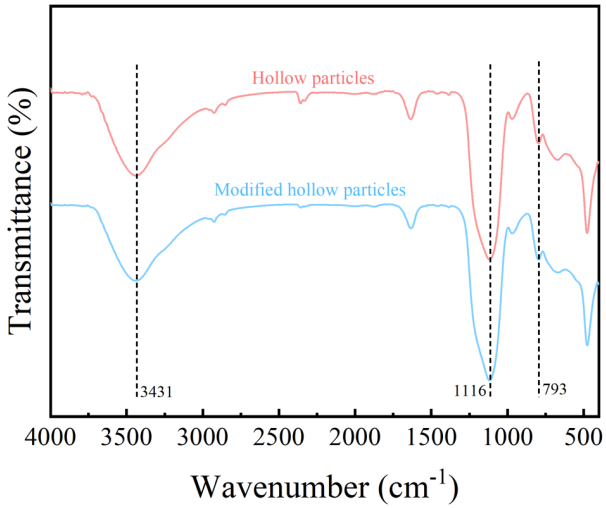


Fig. S3. FT-IR spectra of SiO_2/TiO_2 hollow particles and modified hollow particles.

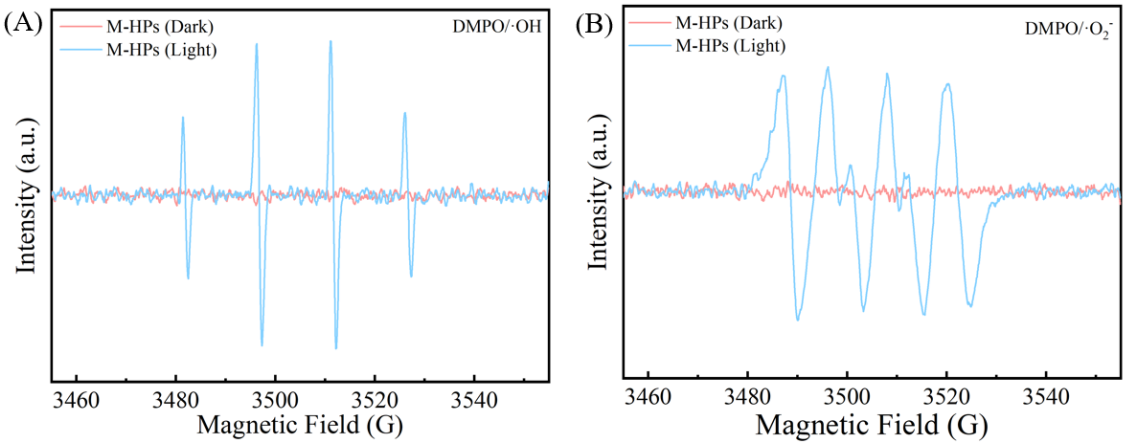


Fig. S4. EPR spectra of modified hollow particles obtained before and after light-excitation in the presence of spin trapping agent DMPO. (A) DMPO/·OH, (B) DMPO/·O_2^-.

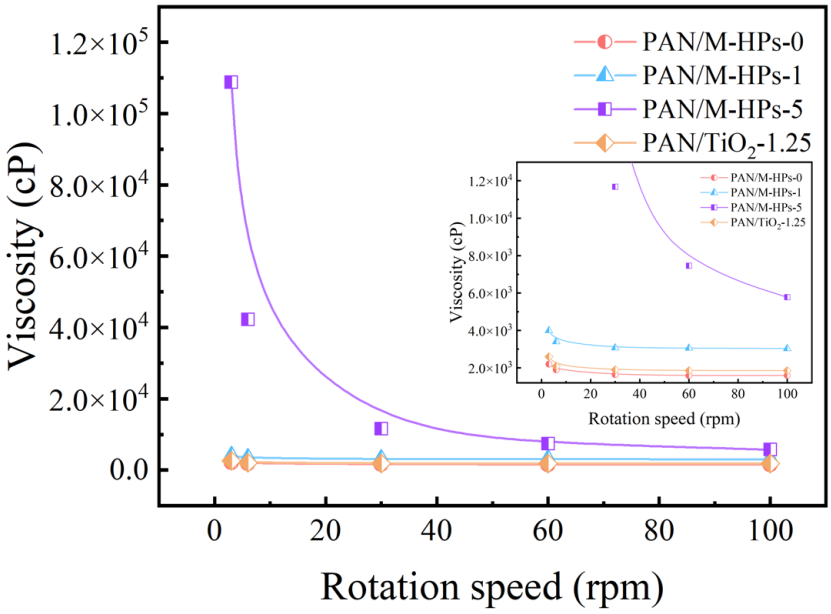


Fig. S5. The viscosity of electrospinning solutions.

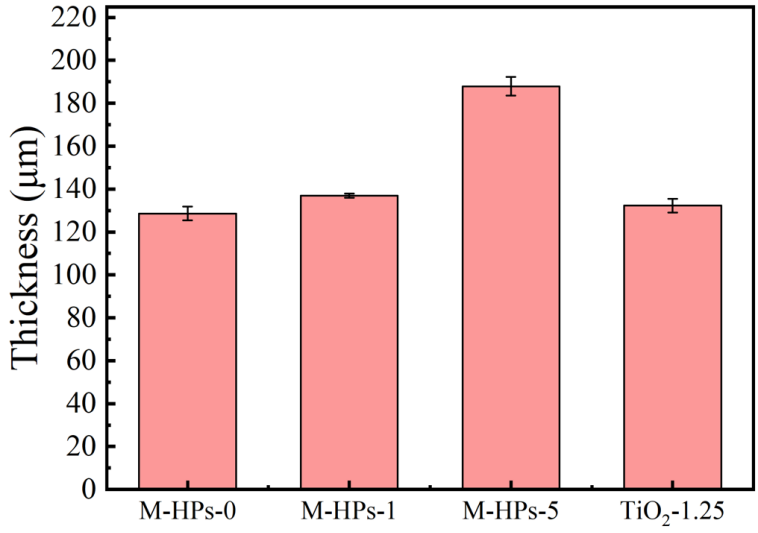


Fig. S6. The thickness of PAN/M-HPs NFMs and PAN/TiO_2 nanoparticle NFM.

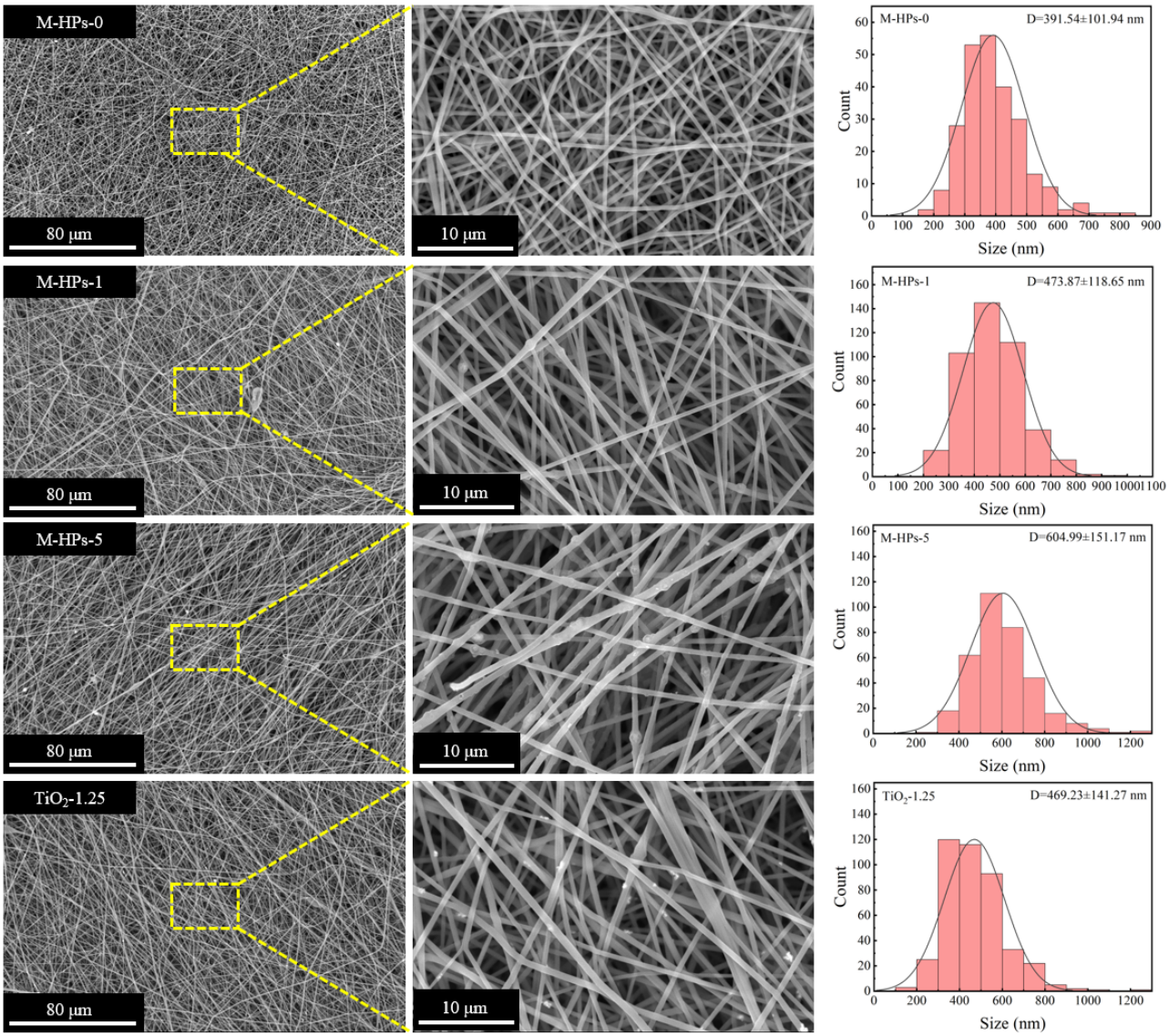


Fig. S7. The SEM images (500× and 3000× magnification) and fiber diameter distributions of PAN/M-HPs NFMs and PAN/TiO_2 nanoparticle NFM.

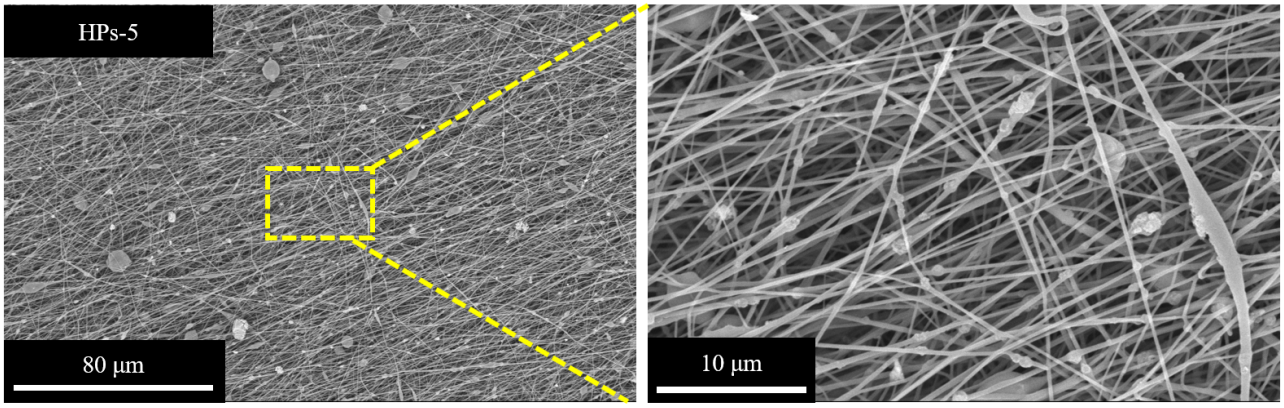


Fig. S8. The SEM images of HPs-5 NFM (500× and 3000× magnification).

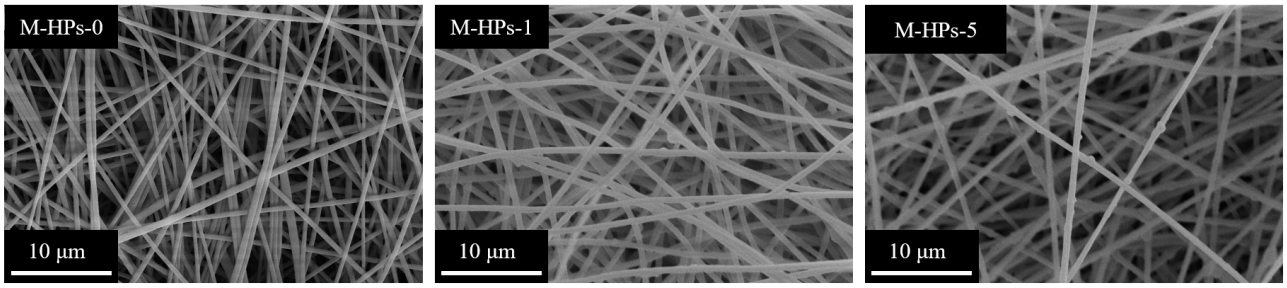


Fig. S9. The SEM images of PAN/M-HPs NFMs after three washing-drying cycles (3000× magnification).

References

1. K. Liu, L. Deng, T. Zhang, K. Shen and X. Wang, *Ind. Eng. Chem. Res*, 2020, **59**, 4447-4458.