Electronic Supplementary Information

Flexible membranes of Ag-nanosheet-grafted polyamide-nanofibers as effective 3D SERS substrates

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Part S1: Figure S1 to Figure S8

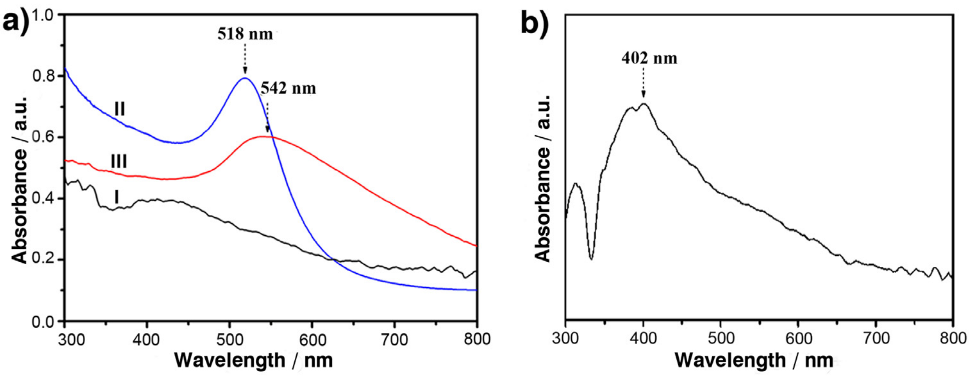

Fig. S1 (a) UV-vis spectra for PA-nanofiber membrane (curve I), solution of Au-nanoparticles (curve II), and Au-nanoparticle-grafted PA-nanofiber membrane (curve III), respectively. (b) UV-vis spectrum for the as-prepared Ag-nanosheet-grafted PA-nanofiber membrane achieved at 12 g L^{-1} of citric acid for 20 min.

Fig. S2 The photographs of bare PA-nanofiber membrane, Au-nanoparticle-grafted PA-nanofiber membrane and Ag-nanosheet-grafted PA-nanofiber membrane from left to right, respectively.

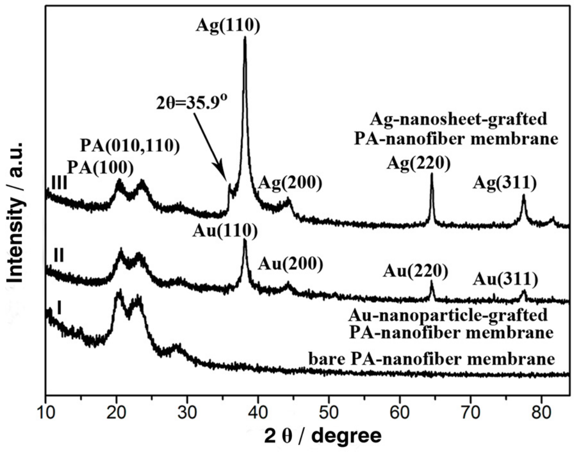

Fig. S3 XRD patterns of bare PA-nanofiber membrane (curve I), Au-nanoparticle-grafted PA-nanofiber membrane (curve II), and Ag-nanosheet-grafted PA-nanofiber membrane (curve III). The crystal phase of PA-nanofibers is alpha phase with two diffraction peaks at 20.3° and 23.7°.[1] Several diffraction peaks at 38.2°, 44.2°, 64.4°, and 77.4° in curve III, can be attributed to the (111), (200), (220), and (311) planes of face-centered-cubic structure of Ag, respectively. It is worth noting that there is one additional peak at 2θ=35.9°, which is probably owing to a defect-induced hexagonal-closed-packed arrangement of Ag atoms in Ag-nanosheets.[2]

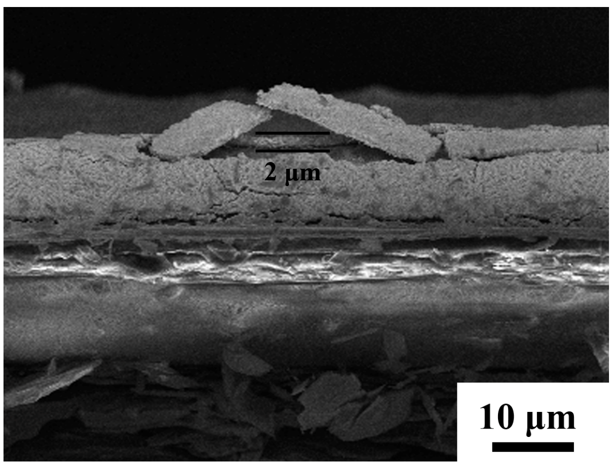

Fig. S4 SEM image of the Ag-nanosheet-grafted PA-nanofiber membrane (side view).

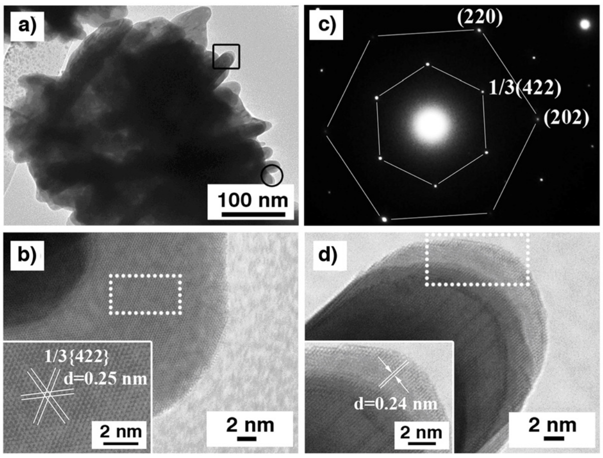

Fig. S5 TEM characterization of the Ag-nanosheets grafted on PA-nanofiber. (a) A typical PA-nanofiber grafted with Ag-nanosheets. (b) and (d) Magnified TEM images taken from the top face (marked by circle) and the side face (marked by rectangle) of the Ag-nanosheets in (a), respectively. The inset images in (b) and (d) are lattice-resolved TEM images taken from the corresponding marked areas. (c) SAED pattern of Ag-nanosheet in (b).

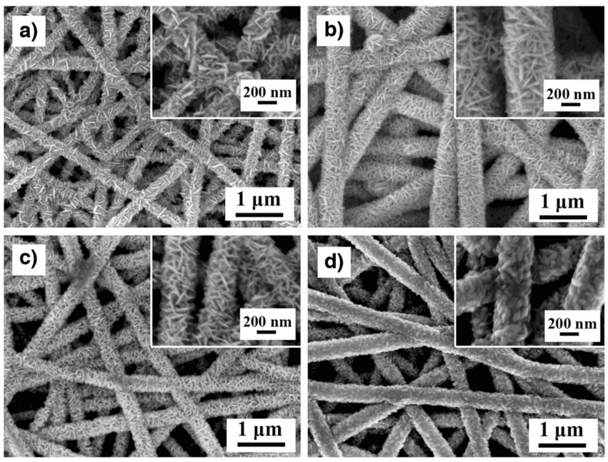

Fig. S6 SEM images of Ag-nanosheet-grafted PA-nanofiber membranes achieved by electrodeposition Ag at different citric acid concentrations: (a) 2 g L^{-1}, (b) 12 g L^{-1}, (c) 16 g L^{-1}, and (d) 36 g L^{-1}. The insets in (a), (b), (c), and (d) are corresponding magnified SEM images, respectively.

Fig. S7 The photograph of the Ag-nanosheet-grafted PA-nanofiber membrane which is tailored into several pieces with any desired shape.

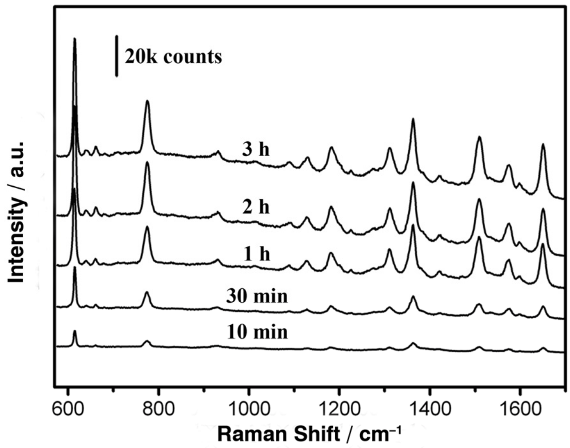

Fig. S8 SERS spectra of 10^{-6} M R6G adsorbed on Ag-nanosheet-grafted PA-nanofiber membranes achieved at the same citric acid concentration (12 g L^{-1}) but different electrospinning time: 10 min, 30 min, 1 h, 2 h, and 3 h. All spectra were acquired with laser power of 0.1 mW and acquisition time of 5 s.

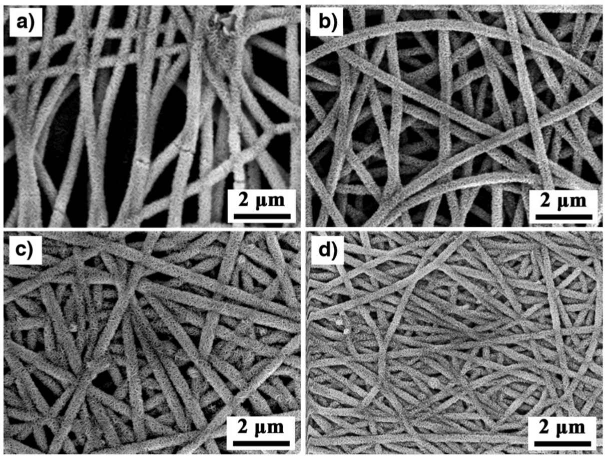

Fig. S9 SEM images of Ag-nanosheet-grafted PA-nanofiber membranes achieved at the same citric acid concentration (12 g L^{-1}) but different electrospinning time: (a) 10 min; (b) 30 min; (c) 2 h; and (d) 3 h.

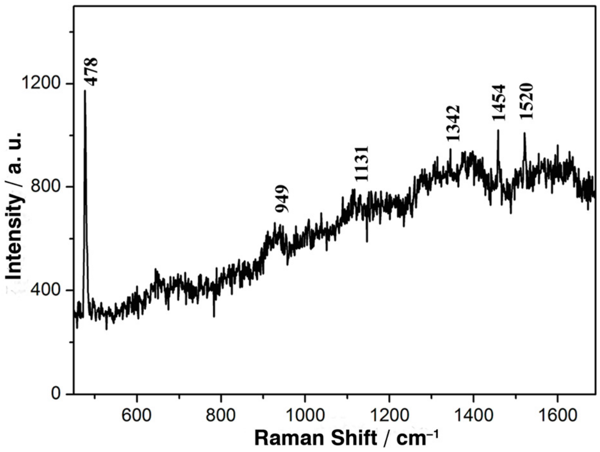

Fig. S10 SERS spectrum of HS-β-CD modified on the Ag-nanosheet-grafted PA-nanofiber membrane. The acquisition time was 30 s.

Part S2: Estimation of the enhancement factor (EF)

The EF of the Ag-nanosheet-grafted PA-nanofiber membrane is calculated by the following equation[3]:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{Nor} / N_{Nor}}$$

Where I_{SERS} and I_{Nor} represent SERS and normal Raman intensities of the same peak, respectively, N_{SERS} and N_{Nor} are the number of probed molecules in the laser illumination volume on the SERS substrate and the bulk sample, respectively.

In the experiments, Raman measurements conducted under identical experimental conditions (laser line 532 nm and laser power 0.5 mW). The laser spot area was estimated to be 0.25π μm^2 and the laser penetration depth was about 100 μm. Thus the N_{Nor} was calculated as 4.7×10^{11} according to the 0.1 M 4-MBA aqueous solution. When determining N_{SERS}, we assume that 4-MBA molecules are absorbed as a monolayer on the surface of Ag-nanosheets and all the molecules contribute to SERS. As shown in SEM images (Fig. 1), nanosheets could be seen as a hemi-disk with an average diameter of 100 nm and with a thickness of 16 nm. The surface area of a nanosheet was about 1.29×10^4 nm^2 [$\pi\times(100/2)^2+\pi\times100\times16 = 1.29\times10^4$ nm^2]. The surface area occupied by one adsorbed 4-MBA molecules was about 0.33 nm^2.[3] The density of nanosheets (the number of Ag-nanosheets per unit area of the nanofiber membrane contained all the nanofibers' layers) on the substrate was estimated as 5.1×10^{10} nanosheets/cm^2. The total number of adsorbed molecules in the laser spot was calculated to be 1.55×10^7 ($N_{SERS} = 0.25\pi\ \mu m^2\times5.1\times10^{10}\ cm^{-2}\times1.29\times10^4\ nm^2 / 0.33\ nm^2 = 1.55\times10^7$). The intensity of the C-C ring breathing mode (~ 1078 cm^{-1}) was used to calculate EF values, and the I_{SERS} = 38367 counts and I_{Nor} = 53 counts as shown in Fig. S11. Thus, EF was estimated to be 2.2×10^7.

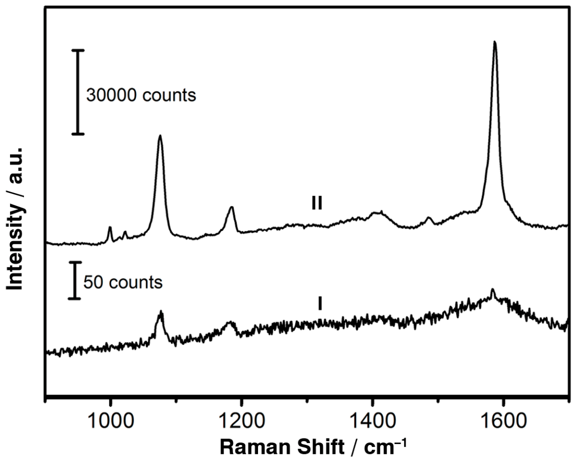

Fig. S11 (I) Raman spectrum of 0.1 M 4-MBA aqueous solution, and (II) SERS spectrum of 1 mM 4-MBA adsorbed on Ag-nanosheet-grafted PA-nanofiber membrane shown in Fig. 1d.

Part S3: References

1 H. Fong, W. D. Liu, C. S. Wang and R. A. Vaia, *Polymer*, 2002, **43**, 775-780.

2 T. C. R. Rocha,; H. Winnischofer, E. Westphal and D. Zanchet, *J. Phys. Chem. C*, 2007, **111**, 2885-2891.

3 S. E. Hunyadi and C. J. Murphy, *J. Mater. Chem.*, 2006, **16**, 3929–3935.