# Supporting Information for

## **Electrosprayed Large-Area Membranes of Ag-Nanocubes Embedded**

## **Cellulose Acetate Microspheres as Homogeneous SERS Substrates**

Yan Ke,<sup>1,2</sup> Guowen Meng,<sup>\*,1</sup> Zhuling Huang,<sup>1</sup> Ningning Zhou<sup>1,2</sup>

<sup>1</sup>Key Laboratory of Materials Physics, CAS Center for Excellence in Nanoscience, and Anhui KeyLaboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, China.
<sup>2</sup>University of Science and Technology of China, Hefei, 230026, China.
\*To whom all correspondence should be addressed (gwmeng@issp.ac.cn).

### The Supporting Information includes:

- Part S1. Fig. S1 to S7 and Table S1
- Part S2. Enhancement Factor Calculation
- Part S3. The influence of solvent on the SERS detection





**Fig. S1** SEM images of as-prepared CA fibers or particles from CA in (a)acetone–DMAc (2:1 v/v) solvent, (b) DMAc solvent.



**Fig. S2** (a) Particle size distribution of Ag-NCs analyzed using ImageJ software. (b)Diameter distribution of Ag-NCs@CA microspheres



**Fig. S3** (a) SEM image of as-prepared Ag-NCs@CA-MS membranes with tiny holes on the surfaces of CA microspheres. (b) TEM image of the holes distributed on the surface of CA microspheres.



**Fig. S4** SEM images of slightly (a), moderately (b) and strongly (c) coupled Ag-NCs distributed on the silicon wafer and corresponding SERS activity (d-f). The laser (785 nm) power was set at 0.125 mW and acquisition time was 10 s in all measurements.



**Fig. S5** (a)  $50 \times 50 \ \mu\text{m}^2$  SERS mapping of PATP values of  $1079 \ \text{cm}^{-1}$  peak recorded from moderately Ag-NCs corresponding to Fig. S4b (step size of 2.5  $\mu$ m). (b) Intensity distribution of  $1079 \ \text{cm}^{-1}$  peak of all 441 points corresponding to (a). (c)  $500 \times 500 \ \mu\text{m}^2$  SERS mapping of PATP values of  $1079 \ \text{cm}^{-1}$  peak recorded from moderately Ag-NCs (step size of 25  $\mu$ m). (d) Intensity distribution of  $1079 \ \text{cm}^{-1}$  peak of all 441 points corresponding to (c).



**Fig. S6** (a) The SERS signal evolution of Ag-NCs@CA-MS membranes and abundant holes distributed Ag-NCs@CA-MS membranes (Fig. S3) against adsorption duration. (b) the comparison of SERS activity of Ag-NCs@CA-MS membranes and abundant holes distributed Ag-NCs@CA-MS membranes.



**Fig. S7** SERS mapping of MP (1111 cm<sup>-1</sup>, 500 × 500  $\mu$ m<sup>2</sup>) corresponding to Fig. 6c.



**Fig. S8** The Langmuir fitting plot and equation of the SERS intensity (1111 cm<sup>-1</sup>) versus MP concentration corresponding to Fig. 6b.

SERS substrates	Detected concentration	RSD	Fabrication Methods	Price
commercially	5×10 <sup>-8</sup> M chloramphenicol	45% <sup>2</sup>	Gold-coated Si	About
Klarite substrates	5×10 <sup>-6</sup> M crystal violet <sup>1</sup>		inverted pyramids	100 \$
			arrays	
commercially	5×10 <sup>-5</sup> M chloramphenicol	Below 20%	Gold nanoparticles	about
Q-SERS	10-7 M crystal violet1	claimed	distributed on the	50 \$
substrates			glass slide	
Taro-leaf@Ag <sup>3</sup>	10 <sup>-8</sup> M R6G	9.7%	Silver-coated	
		$120 \times 100 \ \mu m^2$	natural taro leaf	

Table S1 The comparison of our substrates with other SERS substrates

Ag/Si nanowire	10 <sup>-6</sup> M R6G	below 10%	Gold-coated	
array <sup>4</sup>	6×10-6 M crystal violet	$20  imes 20 \ \mu m^2$	Si nanowire array	
-	·		-	
Ag-NCs@CA-MS	10 <sup>-9</sup> M PATP	below 10%	Ag-NCs embedded	
membranes	10 <sup>-7</sup> M methyl parathion	$5 \times 5 \text{ mm}^2$	CA microspheres	

#### Part S2. Calculation of the SERS enhancement factor (EF).

To investigate the enhancement effect of PATP of Ag-NCs@CA-MS substrates, the strongest peak at 1079 cm<sup>-1</sup> was selected as the representation to calculate the SERS enhancement factor (EF) of PATP. The EF can be estimated using the following equation:

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}}$$

where  $I_{SERS}$  and  $I_{RS}$  stands for the intensities of 1079 cm<sup>-1</sup> peak of SERS spectrum and normal Raman spectrum (non-SERS) under the same experimental conditions(laser wavelength, laser power and exposure accumulation time), respectively.  $N_{SERS}$  and  $N_{RS}$ are the number of PATP molecules adsorbed into the Ag-NCs@CA-MS substrates and blank substrate within the focused incident laser spot.

In our experiment, a piece of Ag-NCs@CA-MS substrate with size of  $5 \times 5$ mm<sup>2</sup> (*S*<sub>SERS</sub>) was immersed in 500 µL (*V*<sub>SERS</sub>) of 10<sup>-7</sup> M (*C*<sub>SERS</sub>) PATP solution. For the normal Raman measurement, 50 µL (*V*<sub>RS</sub>) of 0.01 M (*C*<sub>RS</sub>) PATP solution was dispersed on ablank Al foil with size of  $5 \times 5$ mm<sup>2</sup> (*S*<sub>RS</sub>). Then both the substrates were dried in the air and tested under the same experimental conditions. Thus the preceding equation can be rewritten as:

$$\mathbf{E} = \frac{I_{SERS}S_{SERS}/V_{SERS}C_{SERS}}{I_{RS}S_{RS}/V_{RS}C_{RS}} = \frac{I_{SERS}}{I_{RS}} \times 10^5$$

For the peak at 1079 cm<sup>-1</sup>,  $I_{SERS}/I_{RS}$  was about 85.2. Hence the enhancement factor for

the peak at 1079cm<sup>-1</sup> was calculated to be 8.52×10<sup>5</sup>.



**Fig. S9** (a) The SERS spectrum of 10<sup>-7</sup> M PATP solution adsorbed into Ag-NCs@CA-MS substrates. (b) The normal Raman spectrum of 0.01 M PATP solution dispersed on bare Al foil. The measurements were both carried under 785 nM laser wavelength, 0.125 mW laser power and 10 s exposure time.

#### Part S3. The influence of solvent on the SERS detection

It is found that the solvent has significant influence on the SERS signals from the Ag-NCs@CA-MS membranes. The Ag-NCs@CA-MS membranes have been proven effective for not only PATP ethanol solution (Fig. S7a) but also MP aqueous solution (Fig. S7b). Nevertheless, MP ethanol solution are not easy to be SERS detected (Fig. S7b) by using Ag-NCs@CA-MS membranes as SERS substrates. It is widely known that strong Raman signals are only achieved when the target molecules fish on or dwell near the surfaces of plasmonic nanoparticles. In our case, PATP molecules own the thiol groups and thus can directly adsorb onto the surfaces of Ag-NCs (Fig. S7c), thus both the aqueous solution and ethanol solution of PATP can be easily SERS detected (Fig. S7a). However, MP molecules prefer to dwell in organic solvent (ethanol) rather than in the CA polymer networks or directly anchor on the surfaces of Ag-NCs (Fig. S7d). On the contrary, once MP molecules in aqueous solution are driven into CAmicrospheres along with the diffusion of aqueous solution, the strong hydrophobicity makes them difficult to re-disperse in the water and thus naturally retain in the Ag-NCs@CA-MS membranes (Fig. S7e). Therefore, Ag-NCs@CA-MS membranes can efficiently concentrate hydrophobic organic pollutants in aqueous solution.



**Fig. S10** (a,b) SERS spectral comparison of ethanol and aqueous solutions of PATP (a) and MP (b) by using Ag-NCs@CA-MS membranes. (c-e) The schematics of different adsorption results of Ag-NCs@CA-MS membranes immersing in PATP ethanol or aqueous solution (c), MP ethanol solution (d) and MP aqueous solution (e).

#### references

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