

## Ag-nanoplates decorated cavity-nanorod array SERS substrate for trace detection of PCB-77

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Table S1 Orthogonal test of MACE

| Sequence \ Factor | Concentration of AgNO <sub>3</sub><br>(mol · L <sup>-1</sup> ) | Deposition Time<br>(min) | Etching Time<br>(min) |
|-------------------|--|--------------------------|-----------------------|
| 1                 | 5.0×10 <sup>-3</sup>   | 2                        | 3                     |
| 2                 | 5.0×10 <sup>-3</sup>   | 3                        | 4                     |
| 3                 | 5.0×10 <sup>-3</sup>   | 4                        | 5                     |
| 4                 | 7.5×10 <sup>-3</sup>   | 2                        | 4                     |
| 5                 | 7.5×10 <sup>-3</sup>   | 3                        | 5                     |
| 6                 | 7.5×10 <sup>-3</sup>   | 4                        | 3                     |
| 7                 | 10×10 <sup>-3</sup>  | 2                        | 5                     |
| 8                 | 10×10 <sup>-3</sup>  | 3                        | 3                     |
| 9                 | 10×10 <sup>-3</sup>  | 4                        | 4                     |

Table S2 Analyze orthogonal test

| Project          | Level | Concentration of AgNO <sub>3</sub><br>(mol·L <sup>-1</sup> ) | Deposition Time<br>(min) | Etching Time<br>(min) |
|------------------|-------|--|--------------------------|-----------------------|
| K                | 1     | 24951.06   | -                        | -                     |
|                  | 2     | 14175.97   | -                        | 13789.19              |
|                  | 3     | 15619.81   | 19333.31                 | 22576.27              |
|                  | 4     | -  | 18135.31                 | 18381.37              |
|                  | 5     | -  | 17278.22                 | -                     |
| K <sub>avg</sub> | 1     | 8317.02  | -                        | -                     |
|                  | 2     | 4725.32  | -                        | 4596.4                |
|                  | 3     | 5206.6   | 6444.44                  | 7525.42               |
|                  | 4     | -  | 6045.1                   | 6127.12               |
|                  | 5     | -  | 5759.41                  | -                     |
| The best level   |       | 1  | 3                        | 3                     |
| R                |       | 3591.7   | 685.03                   | 2929.03               |
| Quantity         |       | 3  | 3                        | 3                     |
| Repeats          |       | 3  | 3                        | 3                     |

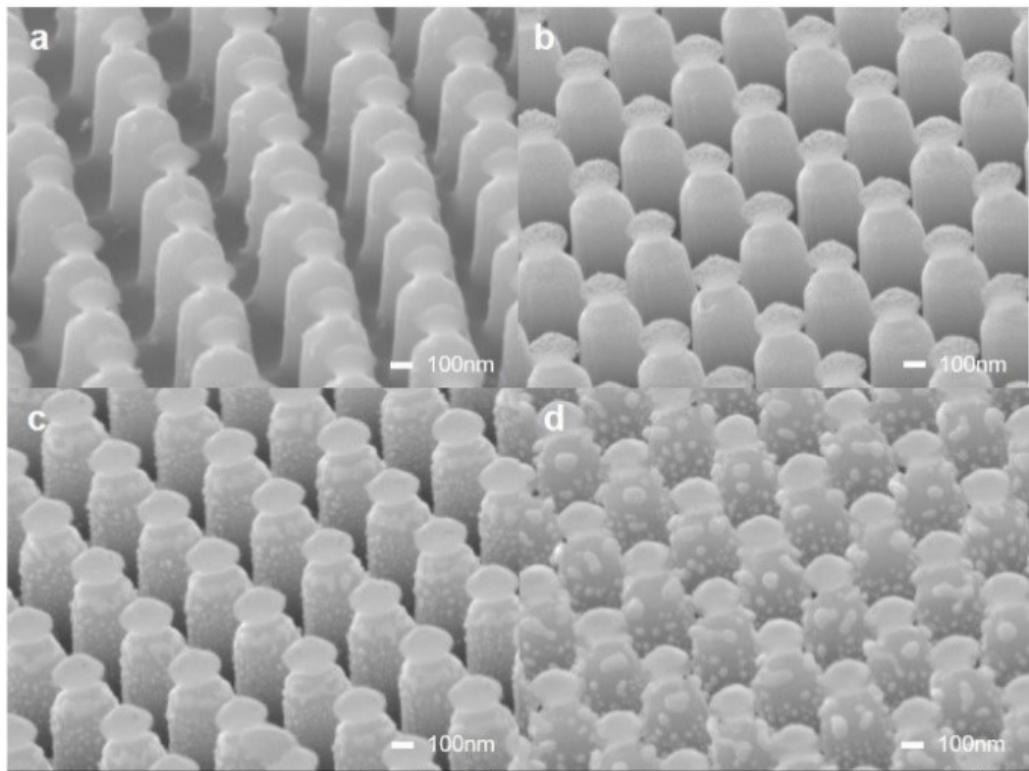


Figure S1 SEM images of sputtering (a) 0 nm, (b) 5 nm, (c) 10 nm, (d) 15nm Au on nanorod substrate.

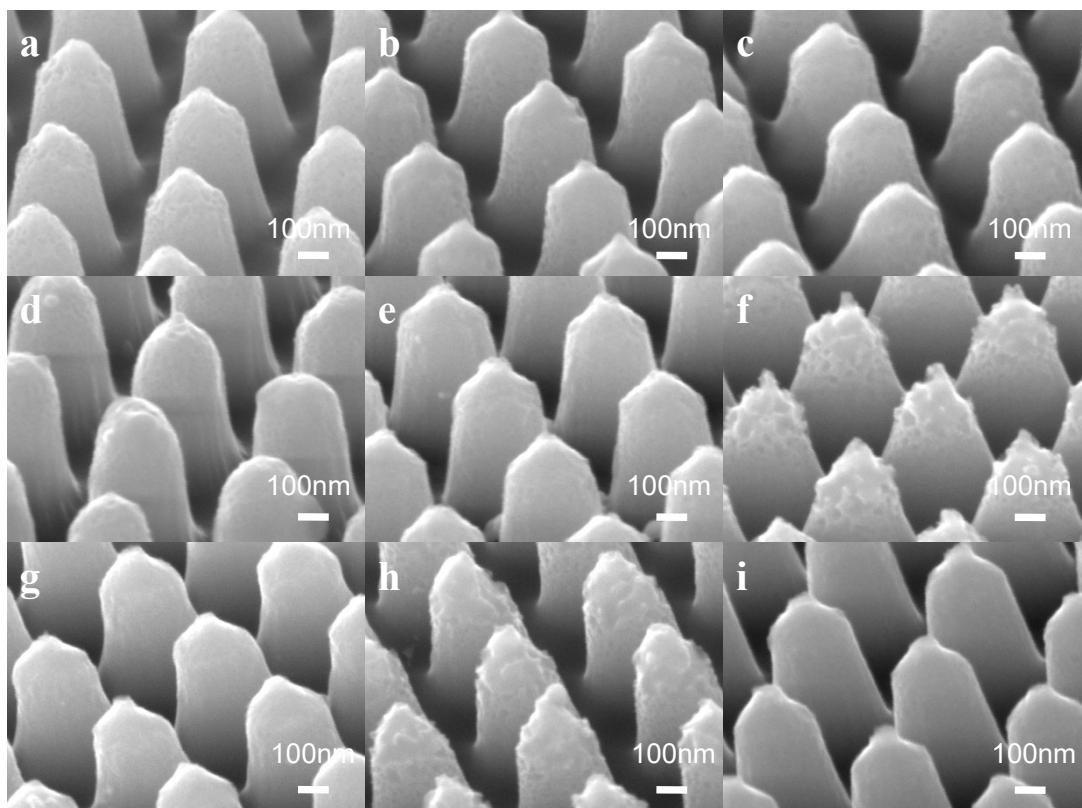


Figure S2 SEM images of substrate (a)~(i) No.1~9 in orthogonal test.

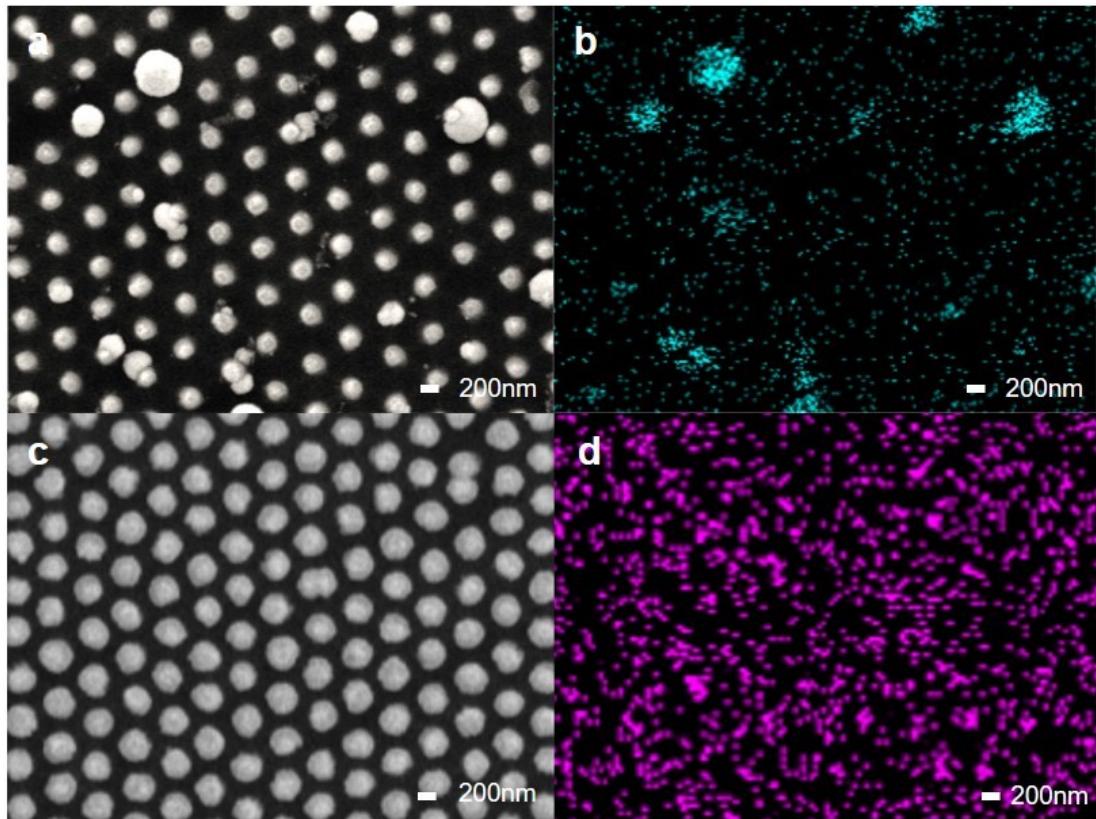


Figure S3 The substrate without gold seeds was deposited in galvanic cell at 10min: (a) SEM image, (b) Ag in EDS mapping; the substrate with gold seeds was deposited in galvanic cell at 10min: (c) SEM image, (d) Ag in EDS mapping.

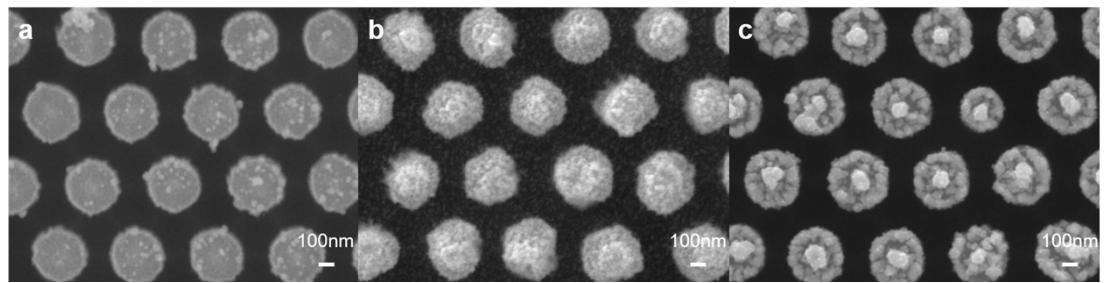


Figure S4 SEM images of No.8 substrates deposit in galvanic cells for (a) 5 min, (b) 10 min, and (c) 15 min.

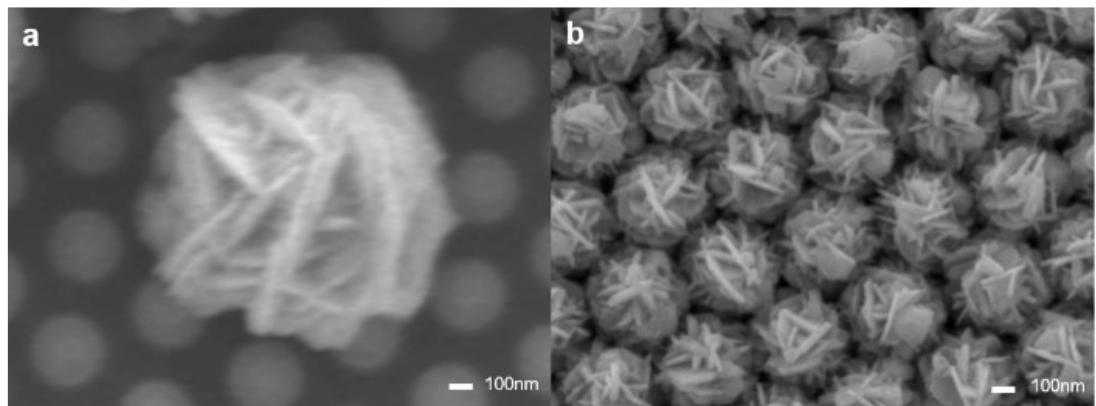


Figure S5 The gold-sputtered substrate and the nongold-sputtered substrate galvanic cells were deposited for 20min.

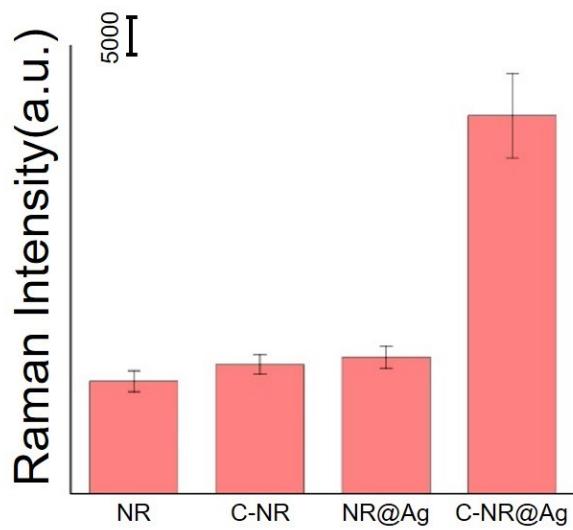


Figure S6 The performance of different substrates using the characteristic peak intensity of  $611\text{ cm}^{-1}$  based on the Raman spectra. The error bar was calculated by three replicated determinations.

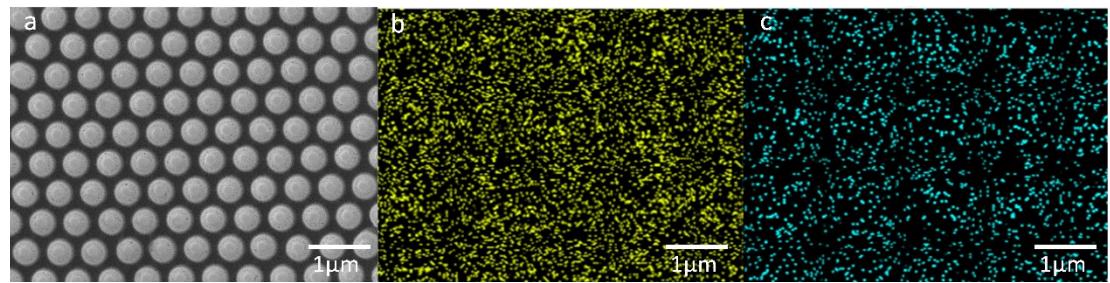


Figure S7 (a) SEM image of C-NR@Ag substrate. (b) EDS mapping results of Au on C-NR@Ag substrate based on a. (c) EDS mapping results of Ag on C-NR@Ag substrate based on a.

Table S3 EDS content analysis of various elements on the surface

| element | Normalized quality (%) | Atom (%) |
|---------|------------------------|----------|
| C       | 6.76                   | 16.90    |
| O       | 1.04                   | 1.94     |
| Si      | 71.94                  | 76.88    |
| Ag      | 9.44                   | 2.63     |
| Au      | 10.82                  | 1.65     |
| Total   | 100.00                 | 100.00   |

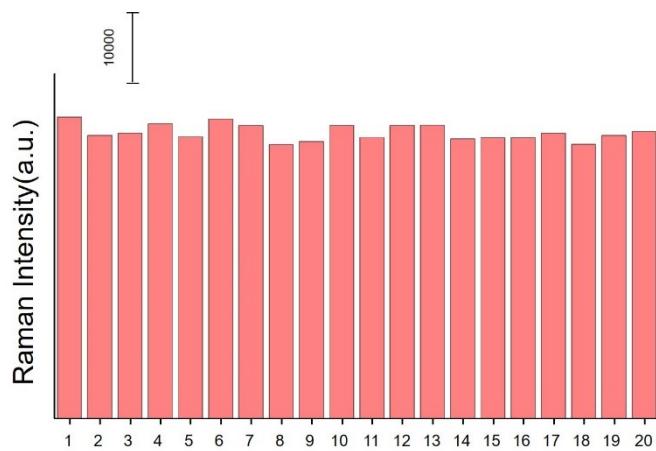


Figure S8 20 points of the peak intensity of  $1078\text{ cm}^{-1}$ .

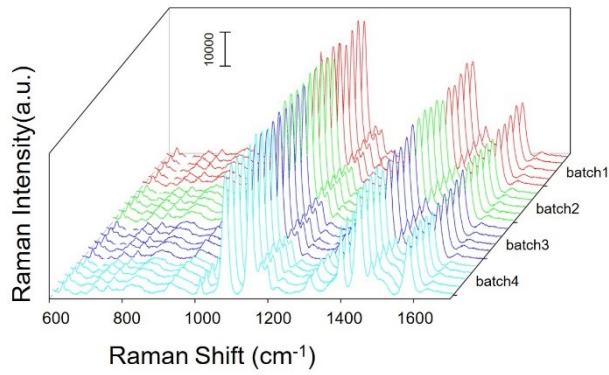


Figure S9 The Raman spectra of the substrate with four batches using  $10^{-5}$  M p-ATP.

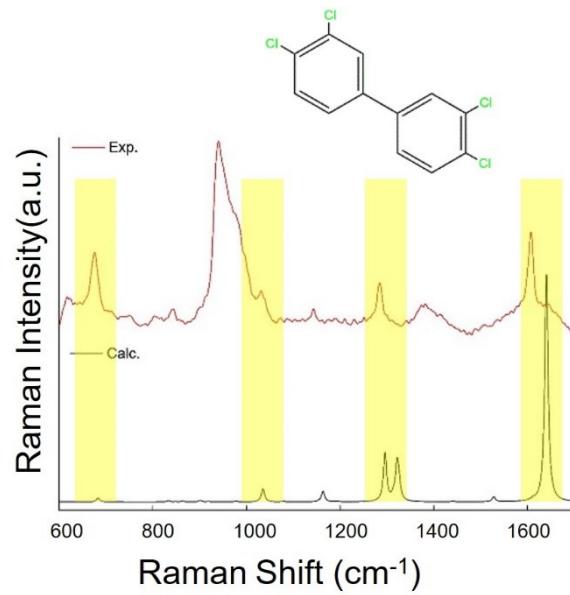


Figure S10 The Raman peak positions of the PCB-77 molecules from theoretical simulation from 650 cm<sup>-1</sup> to 1650 cm<sup>-1</sup>.

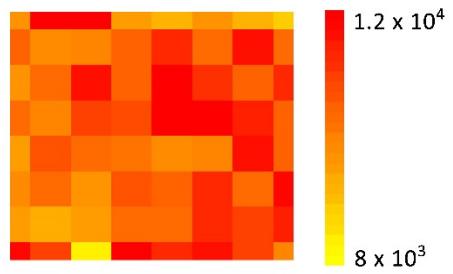


Figure S11 The uniformity of the substrate using the characteristic peak intensity of 1608 cm<sup>-1</sup>.