Supplementary Information



Figure S1. TEM images of silver nanowires at different magnifications.



Figure S2. UV-Vis absorption spectrum of silver nanowires in water.



Figure S3. EDS mapping of silver nanowire membrane treated by CV with 15 cycles at 20 °C. SEM of the CV treated silver nanowire membrane (**a**). The element distribution of Ag (green) and Cl (red) in this area (**b**, **c**). EDS spectrum of silver nanowire membrane treated by CV with 15 cycles at 20 °C (**d**).



Figure S4. The current–potential curve (**a**), potential–time curve (**b**), current–time curve (**c**), and charge–time curve (**d**) of the silver nanowire membrane during electrochemical treatment.



Figure S5. SEM images of silver nanowire membranes treated electrochemically at different temperatures: 16 °C (a), 18 °C (b), 20 °C (c), 22 °C (d), 24 °C (e), and 26 °C (f).



Figure S6. SERS spectra of raw substrate (red) and substrate washed by sodium borohydride (blue). The black line is background.



Figure S7. SERS intensities of PATP on the treated substrate at 1077 cm⁻¹ form sampling in five locations.



Figure S8. SERS intensity mapping of PATP on the treated substrate at 1077 cm⁻¹ (**right**) and optical microscope image of the sampling area (**left**).



Figure S9. The calibration curve of the detection of crystal violet (**a**), tetramethylthiuram disulfide (**b**), perchlorate (**c**), malachite green (**d**), fluoranthene (**e**) and nitrate (**f**).



Figure S10. The conventional Raman spectra of crystal violet (a) and PATP (b).



Figure S11. The conventional Raman spectra of malachite green (**a**), fluoranthene (**b**) and potassium nitrate (**c**).



Figure S12. SERS spectra oftreated (cycle number: 15; temperature: 20 °C) and untreated substrate when detecting crystal violet (**a**), thiram (**b**), sodium perchlorate (**c**), malachite green (**d**), fluoranthene (**e**) and potassium nitrate (**f**).

Table S1. The AEF of substrates prepared in 15 cycles at different temperatures with the probe molecule of PATP.

| Temperature | untreated | 16 °C | 18 °C | 20 °C | 22 °C | 24 °C | 26 °C |
|---------------|----------------------|--------------------|----------------------|----------------------|----------------------|--------------------|----------------------|
| AEF | 8.60×10^{7} | 4.29×10^8 | 5.66×10^{8} | 1.24×10^{9} | 7.31×10^{8} | 4.00×10^8 | 2.53×10^{8} |
| Magnification | 1.00 | 4.99 | 6.59 | 14.4 | 8.50 | 4.65 | 2.94 |

Table S2. The AEF of substrates prepared in different CV cycles at 20 °C with the probe molecule of PATP.

| Temperature | untreated | 5 cycles | 10 cycles | 15 cycles | 20 cycles | 25 cycles |
|---------------|--------------------|--------------------|----------------------|----------------------|----------------------|----------------------|
| | | | | | | |
| AEF | 8.60×10^7 | 4.92×10^8 | 8.33×10^{8} | 1.21×10^{9} | 9.09×10^{8} | 6.56×10^{8} |
| Magnification | 1.00 | 5.72 | 9.69 | 14.1 | 10.6 | 7.63 |

| Analyte | crystal | thiram | sodium | malachite | fluoranthene | potassium |
|---------|------------------------|----------------------|------------------------|----------------------|----------------------|------------------------|
| | violet | | perchlorate | green | | nitrate |
| AEF | 1.16 × 10 ⁹ | 1.07×10^{9} | 9.42 × 10 ⁸ | 1.02×10^{9} | 8.76×10^{8} | 9.68 × 10 ⁸ |

Table S3. The AEF of substrates prepared in 15 cycles at 20 °C on detecting different analytes.

Table S4. A comparison of performance of the developed SERS substrate with

 other sensors reported in literature for the detection of crystal violet.

| Method | LOD | Linear range | Ref. |
|---|-------------------------------------|--|---------|
| UPLC with EIT-MS | 0.15 µg/kg | 0.5 to 10 μg/kg | [1] |
| CuS film & K2S2O8 | $3.2 \times 10^{-9} \text{ mol/L}$ | $5.0	imes10^{-8}$ to $1.0	imes10^{-5}\mathrm{mol/L}$ | [2] |
| Spectrophotometric | 0.0121 2 /J | 0.75, 10.00 | [2] |
| method | 0.01312 µg/L | 0.75–10.00 µg mL-1 | [3] |
| N-GQDs and K ₂ S ₂ O ₈ | 45 nmol/L | 0.05–5 µmol/L | [4] |
| Cyclic voltammetry | | | Gumman |
| treated silver | $5.1 \times 10^{-11} \text{ mol/L}$ | 10 ⁻¹⁰ to 10 ⁻⁸ mol/L | Current |
| nanowire membrane | | | WORK |

| Spiked levels | Found ± SD | D (0/) | | |
|--------------------------|---|--------|---------|--|
| (10 ⁻⁹ mol/L) | 0^{-9} mol/L (10 ⁻⁹ mol/L) | | KSD (%) | |
| 0.5 | 0.4403 ± 0.0264 | 88.07 | 5.99 | |
| 1 | 0.9804 ± 0.0427 | 98.04 | 4.36 | |
| 5 | 5.0748 ± 0.0854 | 101.5 | 1.68 | |
| 10 | 8.9180 ± 0.1155 | 89.18 | 1.30 | |

Table S5. Determination of crystal violet in various spiked pond water samples using the developed SERS substrate.

*SD, standard deviation; RSD, relative standard deviation

References:

[1] Zhang, Z.G.; Shi, B.; Chen, L.P.; Lin, L.Y.; Zhou, Y. Simultaneous determination and confirmation of malachite green, crystal violet and their leuco metabolites residues in aquatic product by liquid chromatography-visible detection and tandem mass spectrometric detection. *Chin. J. Anal. Chem.* **2006**, *34*, 663–667.

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[3] Sar, S.K.; Verma, C.; Pandey, P.K.; Bhui, A. Reliable Technique for the Determination of Sodium Dodecyl Sulphate by Crystal Violet in Relation to the Effluents of Durg-Bhilai Region. *J. Chin. Chem. Soc. (Weinheim, Ger.)* **2009**, *56*, 1250–1256.

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