Supporting information :

Surface-enhanced Raman Scattering Substrate based on Cysteamine-Modified Gold Nanoparticles Aggregation for Highly Sensitive Pentachlorophenol Detection

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1. The characterization of the AuNPs

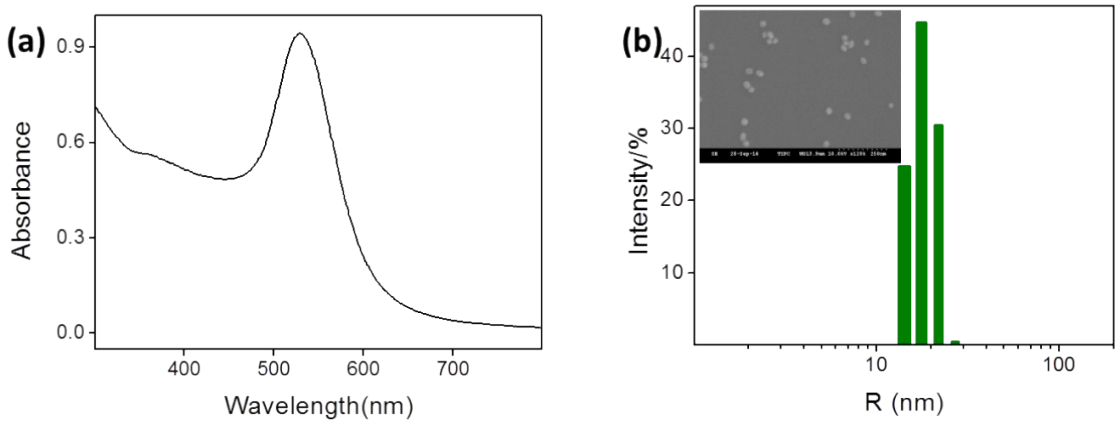

Figure. S1 The AuNPs characterization: (a) UV-vis spectrum of AuNPs; (b) Histogram of size distribution of AuNPs; inset SEM image of AuNPs.

2. SEM image of the substrate after modification of AuNPs

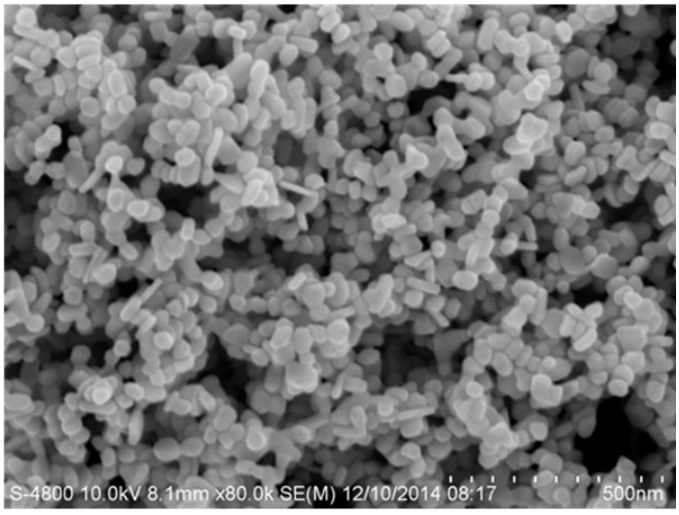

Figure. S2 SEM image of AuNPs immobilized on the substrate.

3. The optimization of the cysteamine concentrations.

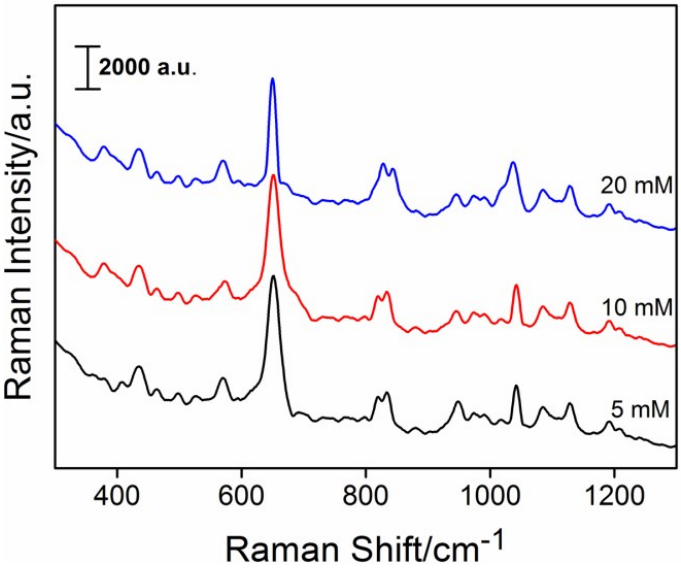

Figure. S3 The SERS spectra of the substrate immersed in 5 mM (black line), 10 mM (red line) and 20 mM (blue line) concentrations of cysteamine hydrochloride solution for 12 h.

4. The optimization of the modification time in cysteamine solution (20 mM).

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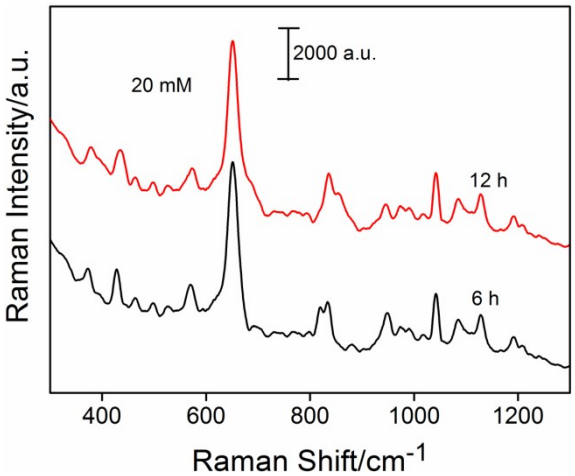

Figure. S4 SERS spectra of the substrate immersed in 20 mM Cys solution for 12 h (red line) and 6 h (black line).

5. SERS spectra of PCP on the cysteamine modified and unmodified substrate and enhancement factor calculation of SERS for Figure 3.

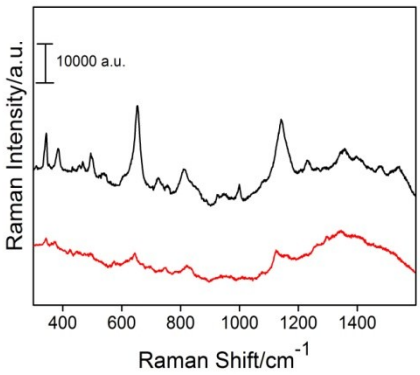

Figure. S5 SERS spectrum of PCP on cysteamine-modified AuNPs substrate (red) and Raman spectrum of PCP on plain glass for comparison (black).

Calculation of Enhancement Factor according to the data as shown in Figure 3

The SERS enhancement factors of PCP molecules on Cys-modified AuNPs substrate and bare AuNPs were estimated according to the following expression:

$$EF = (I_{SERS}/I_{solution}) \times (N_{solution}/N_{SERS}) \quad (1)$$

where $N_{solution}$ and N_{SERS} are the numbers of PCP molecules in a reference of 50 μM PCP in bare AuNPs and on the surface of SERS substrate; $I_{solution}$ and I_{SERS} are the single intensities of PCP molecule Raman spectra probed in bare AuNPs (50 μM) and on the surface of single Cys-modified AuNP.[1]

Firstly, laser sport size has been calculated. The simplified equation to calculate the diameter of the focused laser spot is:

$$d = 0.61\lambda/NA \quad (2)$$

The above equation is extracted from Renishaw notes of the Spectroscopy Products Division; SPD/PN/088 Issue 1.1 June 2003)

Where d is diameter of laser spot size (beam diameter); λ is wavelength of the laser beam which is 785 nm in the present study; NA is numerical aperture. In the present study, 20 × objective was used through the experiment.

Thus, NA = 0.4 (Renishaw standard)

Spot size, d = 0.61x 0.785 /0.4 = 1.197 μm

Radius = 0.6 μm

Illuminated area = 0.6×0.6 ×3.14 = 1.13 μm^2

The depth of field penetration of laser into the sample (h) is determined by the excitation line (λ), the refractive index of surrounding media (n), and NA.[2]

$$h = n\frac{\lambda}{NA^2} = 1.33 \times 0.785 \div (0.4)^2 = 6.525\ \mu m \quad (3)$$

The effective excitation volume of the PCP in bare AuNPs (50 μM concentration) probed with the Raman microscope using 20 × objective was:

$$V = \pi r^2 \mathrm{h} = 3.14 \times 0.6 \times 0.6 \times 6.525 = 7.38\ \mu m^3 \quad (4)$$

Thus, the number of PCP molecules was:

$$N_{solution} = 6.02 \times 10^{23} \times 50 \times 10^{-6} M \times 7.38\ \mu m^3 = 2.22 \times 10^{11} \quad (5)$$

The SERS signal intensity of probed PCP molecules on SERS substrate was estimated from the height of Raman spectra peak at 649 cm^{-1}. Onto the SERS substrate with size of 20 mm×20 mm, 1 mL of 50 μM PCP solution was added. Assuming about 10% of the PCP molecules was retained after rinsing the substrate.[3-4] Thus, the total number of PCP molecules can be estimated as:

$$N_{PCP-all} = 1\ mL \times 10^{-3}\frac{L}{mL} \times 50 \times 10^{-6} M \times 6.02 \times 10^{23} \times 10\% = 3.01 \times 10^{15} \quad (6)$$

The number of active PCP molecules when laser illuminates the sample is:

$$N_{SERS} = \frac{\pi r^2}{a^2} N_{PCP-all} = \frac{3.14 \times 0.6\ \mu m \times 0.6\ \mu m}{20\ mm \times 20\ mm} \times 3.01 \times 10^{15} = 8.43 \times 10^6 \quad (7)$$

According to the equation (1), the SERS enhancement factor is:

$$EF = \left(I_{SERS}/I_{solution}\right) \times \left(N_{solution}/N_{SERS}\right) = (8706.9/402) \times \left(\frac{2.22 \times 10^{11}}{8.43 \times 10^6}\right) = 5.7 \times 10^5$$

6. SERS spectra of PCP on cysteamine and thiol acetic acid modified AuNPs substrate

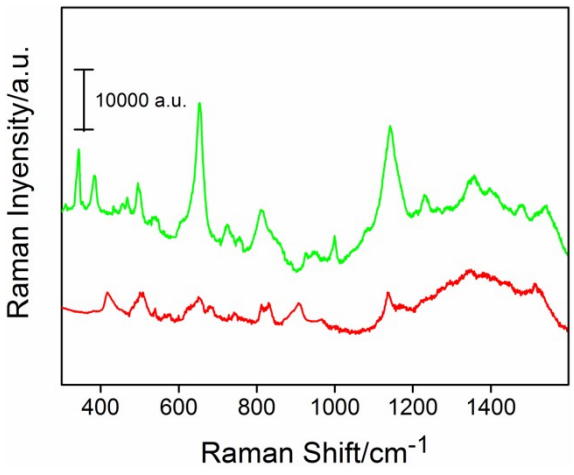

Figure. S6 SERS spectra of PCP on cysteamine (green line) and thiol acetic acid (red line) modified

substrate.

7. Effect of salt concentration on SERS analysis.

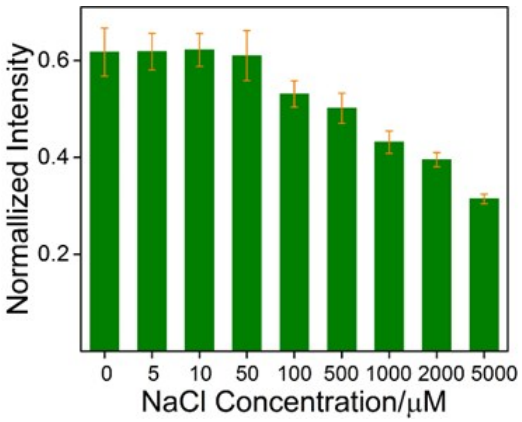

Figure. S7 The normalized intensity change of PCP (10 μM) at 341cm^{-1} with different NaCl concentration and 2h immersion time. The data points correspond to the average ± standard deviation of three measurements.

8. Effect of solution pH on SERS analysis.

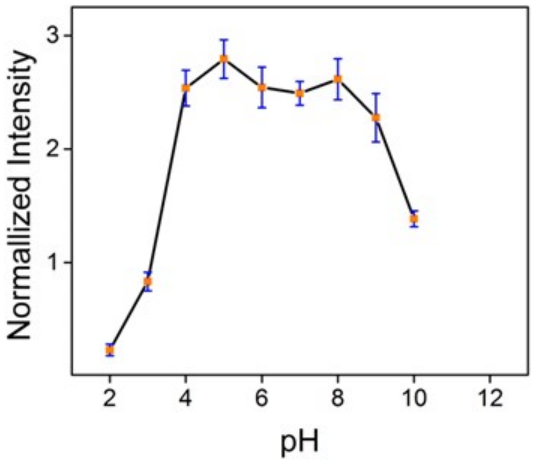

Figure. S8 The normalized intensity change of PCP (10 μM) at 341cm^{-1} with the range of pH range from 2.0 to 10.0 and 2 h immersion time. The data points correspond to the average ± standard deviation of three measurements.

9. Kinetics of PCP adsorption on the cysteamine-modified AuNPs substrate.

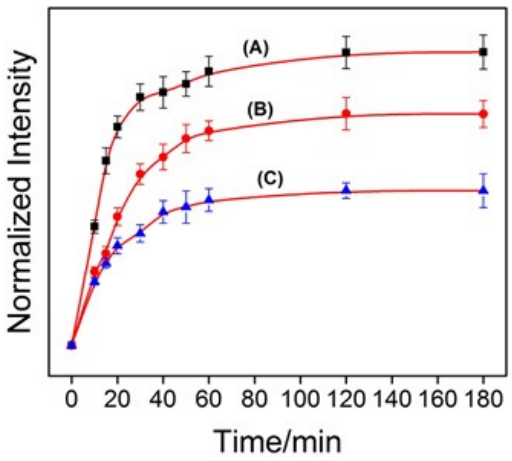

Figure. S9 Kinetic curve of PCP adsorption onto cysteamine-modified AuNPs substrate (A) 20 µM, (B) 10 µM and (C) 5 µM. The data points correspond to the average ± standard deviation of three measurements.

10. SERS detection of PCP in tap water

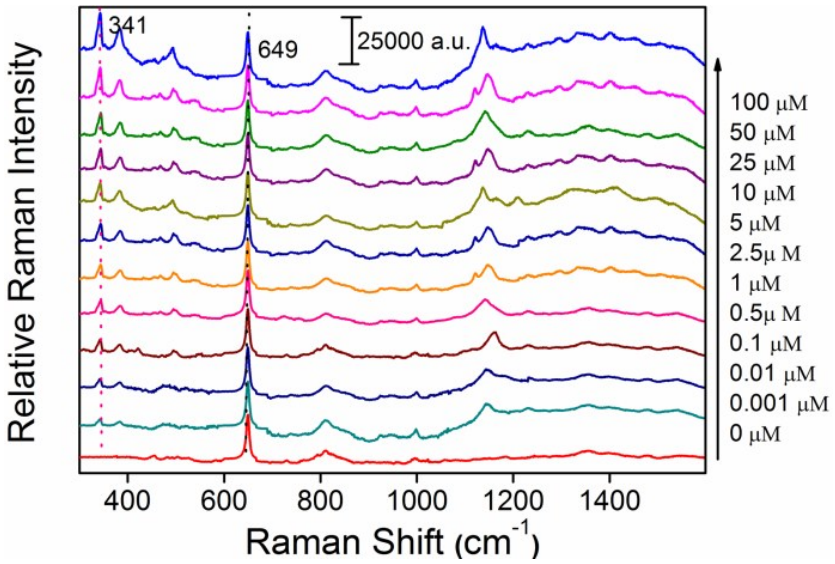

Figure. S10 The SERS spectra of PCP in tap water on cysteamine modified AuNPs substrate with different concentrations (0-100 µM).

11. Log plot for PCP detection in tap water

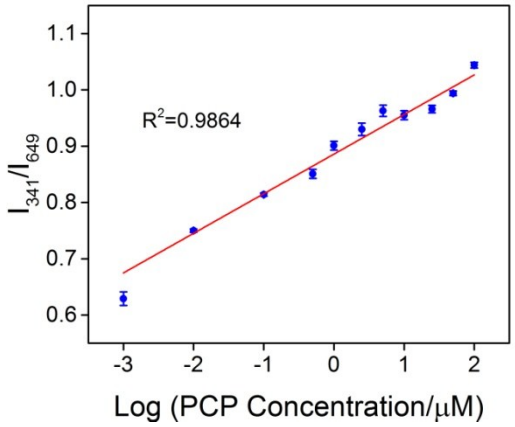

Figure. S11 Log plot for PCP based on cysteamine-modified AuNPs substrate. The data points correspond to the average ± standard deviation of three measurements.

12. Stability test of cysteamine modified-AuNPs substrate.

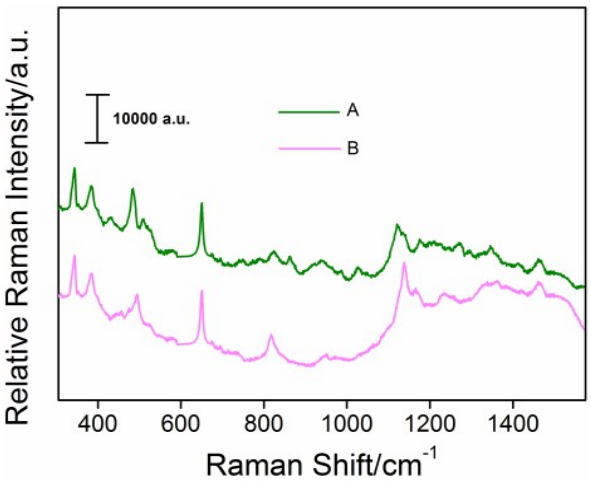

Figure. S12 Long-term stability of cysteamine modified-AuNPs substrate. SERS spectra of 10 μM PCP obtained from (A) the substrate immersed in the analyte solution for a month and (B) the freshly prepared substrate.

13. Structures of PCP and its analogues

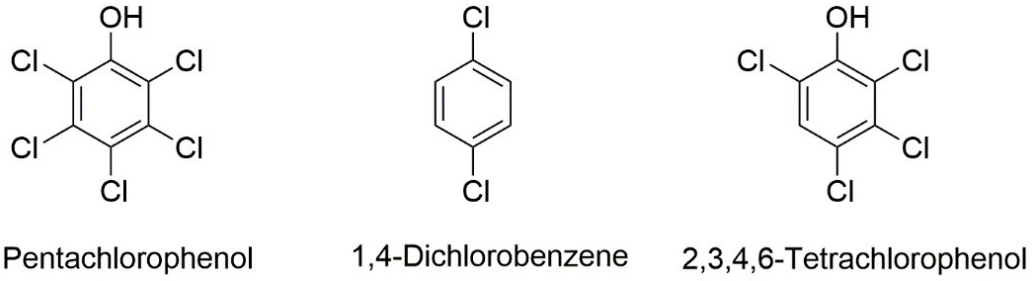

Figure. S13 Structures of PCP and its analogues.

14. Comparison of different methods for PCP determination.

Table S1. Comparison of the analytical performance of various methods for PCP determination.

Technique	Linear range	LOD
HPLC[5]	0.05–500 μg/L	6 ng/L.
Fluorescent spectrometry[6]	0-7.98 mg/L	13.3 μg/L.
SERS[7]	13.3–2660 μg/L	53.2 μg/L
SPME-GC-MS[8]	5–40 μg/L	0.75 μg/L
Our method	2.66-2660 μg/L	0.511 μg/L

Table S2. Comparison the recovery and precision of this method and HPLC for the determination of PCP in real water samples.

Technique	Recovery (%)	RSD (%)
HPLC[1]	91[a]	3.8[a]
HPLC[9]	80[b]	8.8[b]
Our method	95[c]	3.38[c]

a Wastewater b River water c Tap water

References

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