Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Electrostatic-driven Solid Phase Microextraction Coupled with Surface Enhanced Raman Spectroscopy for Rapid analysis of pentachlorophenol

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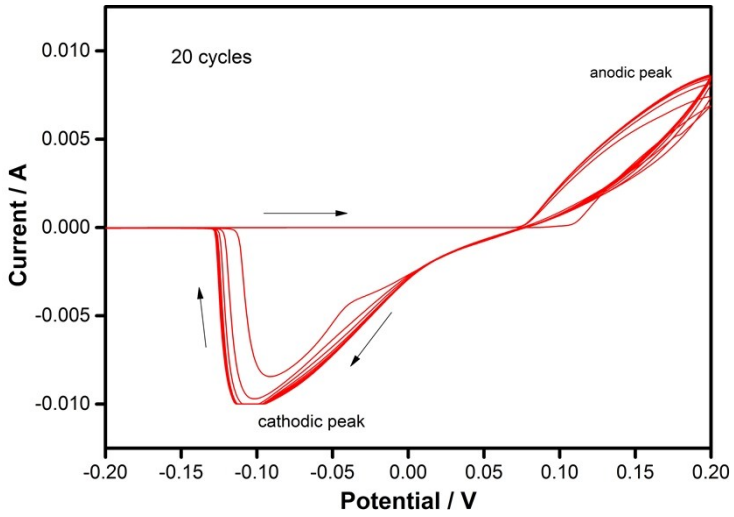

Fig. S1 Cyclic voltammogram of twenty scans in 0.1 M HCl for roughening the silver fiber from -0.2V to +0.2 V vs Ag/AgCl at 2.5 mV/s

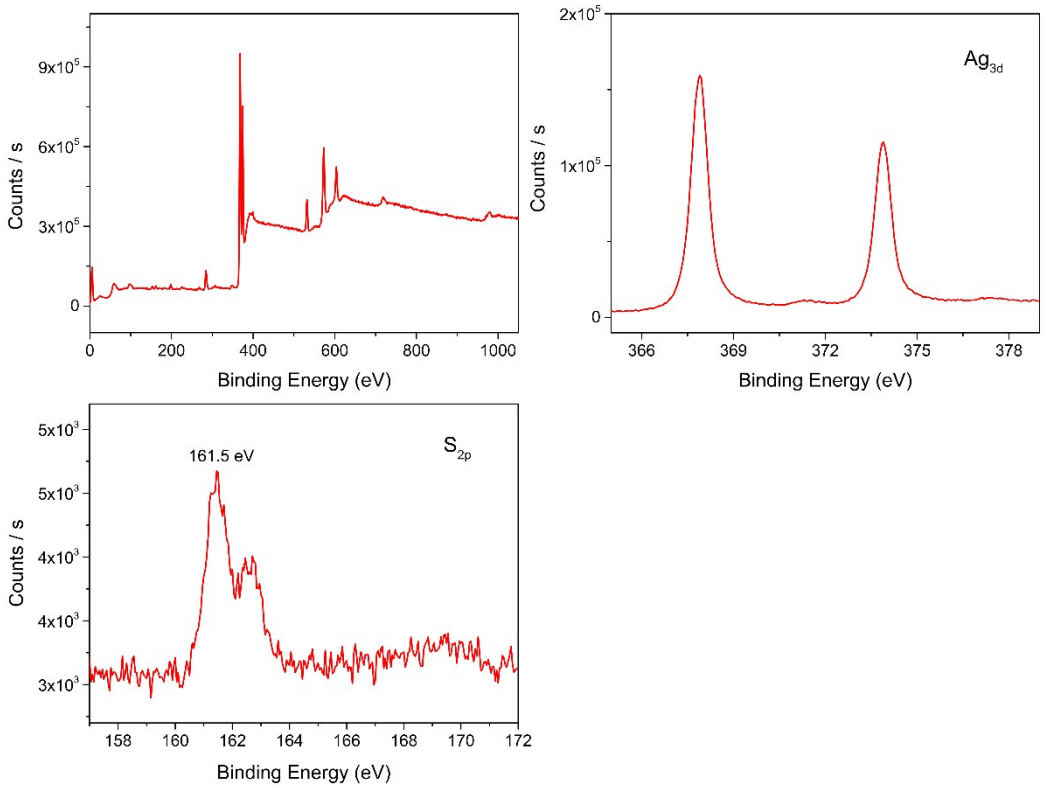

Fig. S2 XPS spectra of the nanoporous Ag fiber after modification with Cys.

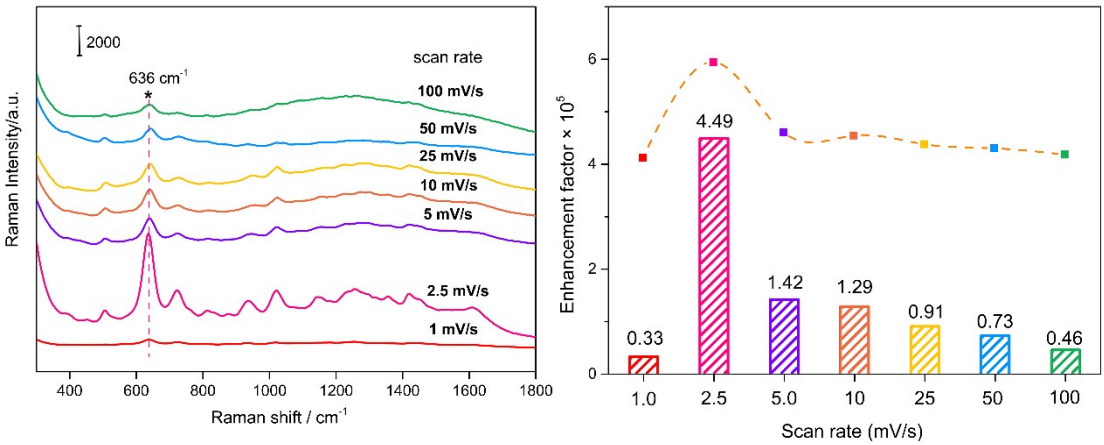

Fig. S3 SERS spectra of Cys on nanoporous Ag fiber synthesized at different scan rate and the influence of scan rate on enhancement factor (peak of Cys at 636 cm^{-1})

The enhancement factor (EF) of porous Ag layer was calculated as following:

$$EF = \frac{I_{SERS}}{I_{Raman}} \times \frac{C_{Raman}}{C_{SERS}}$$

I_{SERS} is the peak intensity of Cys on nanoporous Ag, I_{Raman} is the Raman intensity of Cys powder, C_{Raman} is the concentration of Cys in solution. C_{Raman} is the activity of Cys powder, the value is 1 in this condition. The characteristic peaks were selected at 636 cm^{-1}.

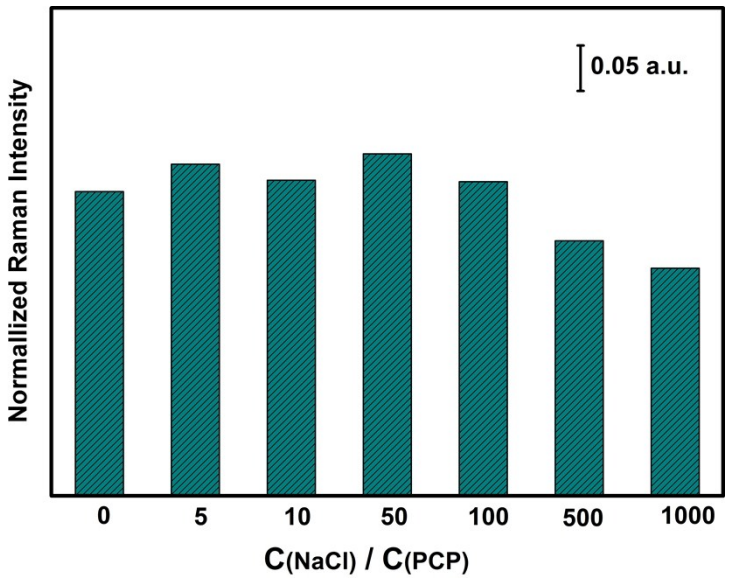

Fig. S4 The effect of salt concentration on pentachlorophenol extraction

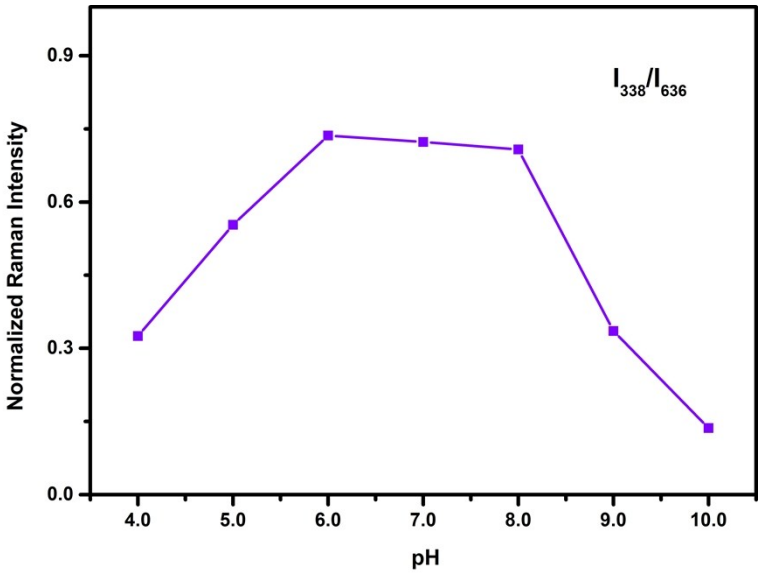

Fig. S5 The influence of pH on extraction

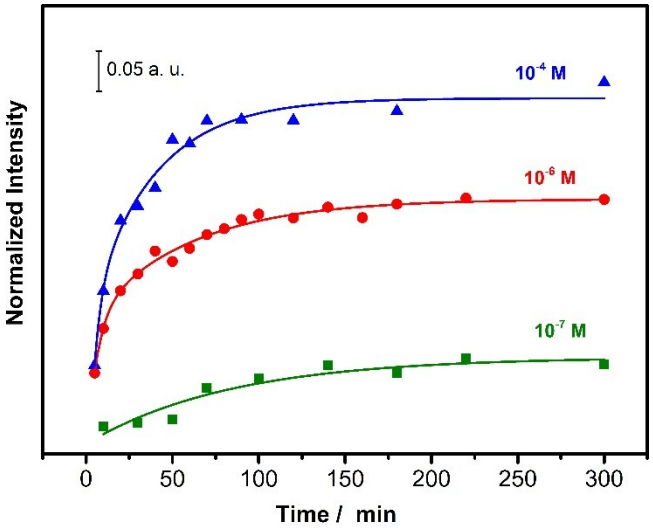

Fig. S6 Extraction equilibrium time in different concentrations of pentachlorophenol

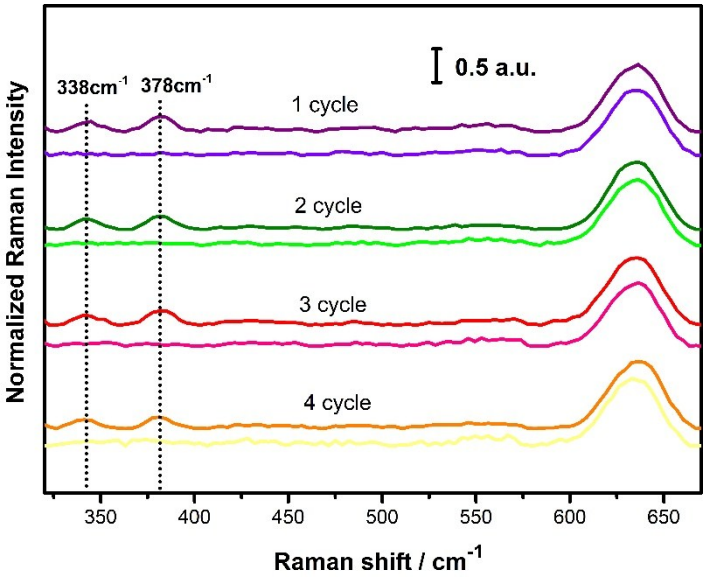

Fig. S7. The reusability of Cys-Ag fiber for 4 cycles. SERS spectra of the repeated process, which were performed by immersing fiber into 100 μM PCP for 5 h (the dark color), then in methyl alcohol for 5 min under ultraphonic cleaning (the light color). All the SERS spectra were normalized using the Raman peak of Cys at 636 cm^{-1} as the reference.

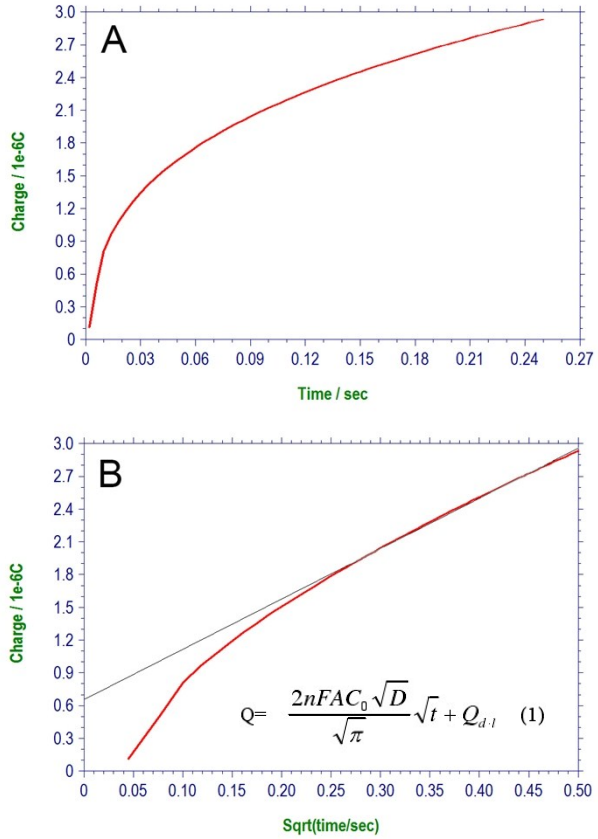

Fig. S8 Chronocoulometry of Cys-Ag fiber in 0.1mol/L KCl solution containing 0.1 mmol/L potassium ferricyanide. (A)Q-t plot and (B)Q-$t^{1/2}$ plot.

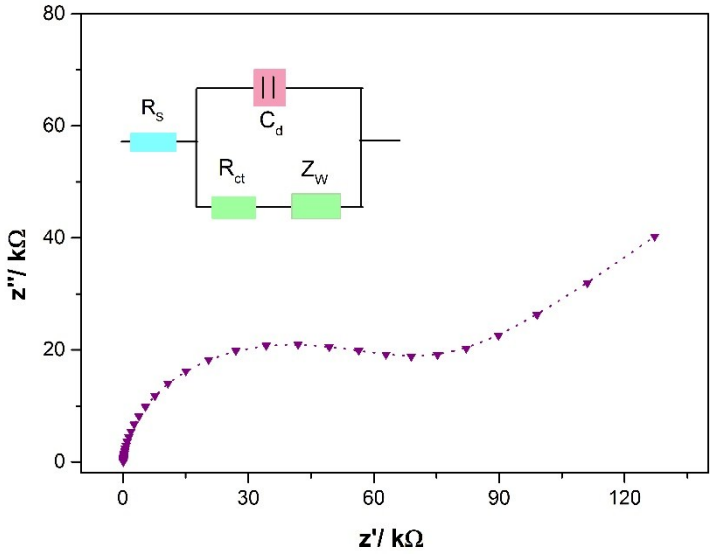

Fig. S9 Electrochemical impedance spectroscopy of Cys-Ag fiber in 0.1mol/L KCl solution containing 10 µmol/L PCP; frequency ranging from 100 kHz to 100 mHz. Rs, Cd, Rct and Zw represent the solution resistance of EDL capacitance, the electron-transfer resistance and the diffusion resistance, respectively.

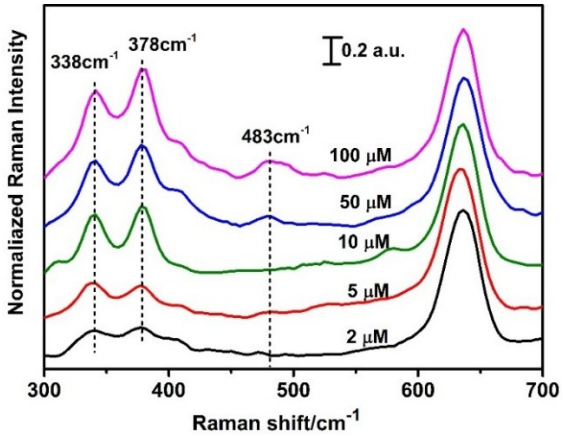

Fig. S10 SERS spectra of different concentrations of pentachlorophenol extracted by Cys-modified roughed Ag fiber in surface water samples.

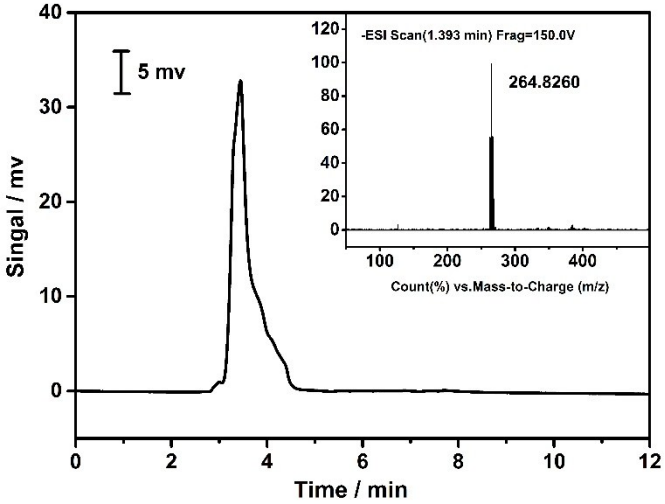

Fig. S11 HPLC of the pentachlorophenol extracted by Cys-modified roughed Ag fiber. The insert was the mass spectrum.

Table S1 Comparison of two analysis methods of pentachlorophenol in surface water

Sample matrix	Technique	Recovery (%)	RSD (%)
Surface water	HPLC[49]	90.0	5.6
	SPME-SERS	92.5	7.4