Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Material (ESI)

Reliable on-site characterization of aromatic compounds adsorbed on porous particle with SERS in a dynamic adsorption-hydrocyclone separation process

Fei Wang,[a] Yang Qiu,[a] Peng-Bo Fu,[a] Hua-Lin Wang,[*a] and Yi-Tao Long [b]

[a] State Environmental Protection Key Laboratory of Environmental Risk Assessment and Control on Chemical Process, East China University of Science and Technology, Shanghai, 200237, China

[b] State Key Laboratory of Bioreactor Engineering & Department of Chemistry, East China University of Science and Technology, Shanghai, 200237, China

* To whom Corresponding should be addressed. Email: wanghl@ecust.edu.cn

The Supplementary Material includes:

Two text (text S1， S2)

Four figure (Figure S1, S2, S3, S4)

Three tables (table S1, S2, S3)

Text S1

Calculation of Enhancement Factor

A single prepared functionalized porous alumina particle (FPAP) was immerged into the 10 μL of 10 ppm *p*-aminothiophenol (*p*-ATP), after the amount of pollutants adsorbed on the surface of FPAP, FPAP was dried under nitrogen at 30 °C and the SERS spectrum of *p*-ATP was recorded from the surface of FPAP (a of Figure S1). The Normal Raman spectrum of bulk *p*-ATP also was recorded directly (b of Figure S1) and 1081 cm^{-1} was employed to calculate the enhancement factors (EF) through the following equation (1-2):

$EF = (I_{SERS}/I_{Raman}) \times (N_{bulk}/N_{surface})$

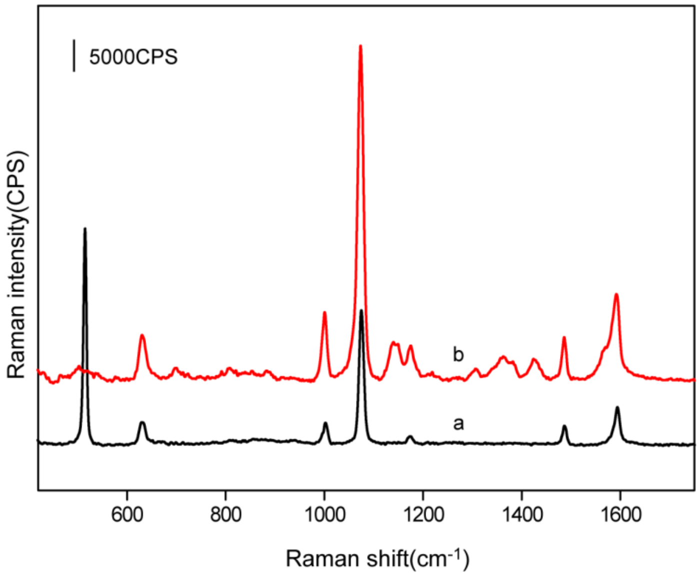
where I_{SERS} and I_{Raman} are the intensities at the same band in the SERS and normal Raman spectrum of *p*-ATP, respectively. N_{bulk} and $N_{surface}$ are the number of molecules for the bulk sample and the number of molecules absorbed on the AgNPs under laser illumination. The $N_{surface}$ and N_{bulk} values can be calculated based on the estimation of the concentration of surface species or bulk sample and the corresponding sampling areas (3). For the bulk *p*-ATP sample, the sampling volume is the product of the area of the laser spot (ca. 10 μm in diameter) and the penetration depth (~2 μm) of the focused laser beam. Because the density of bulk *p*-ATP is 1.17 g cm^{-3}, N_{bulk} can be counted to be 1.47×10^{-14} mol ($N_{bulk} = 1.17$ g $cm^{-3} \times \pi \times (10/2)^2$ $\mu m^2 \times$ 2 μm / (125.19 g mol^{-1}) = 1.47×10^{-14} mol). Since the surface coverage of *p*-ATP monolayer on AgNPs is considered to be $\Gamma_{p\text{-ATP}} = 2.71 \times 10^{15}$ molecules/cm^2 = 4.50×10^{-9} mol/cm^2 (4-5), it can be reckoned that $N_{surface}$ has a value of 3.53×10^{-17} mol ($N_{surface} = \Gamma_{P\text{-ATP}} \times \pi \times (10/2)^2$ $\mu m^2 = 3.53 \times 10^{-17}$ mol) considering the sampling area under laser illumination (about 10 μm in diameter). For the vibrational mode at 1081 cm^{-1}, the ratio of I_{SERS} to I_{Raman} was about 3.2, hence EF was calculated to be 1.2×10^5.

Text S2

Method for SERS detection of aromatic compounds aqueous solution

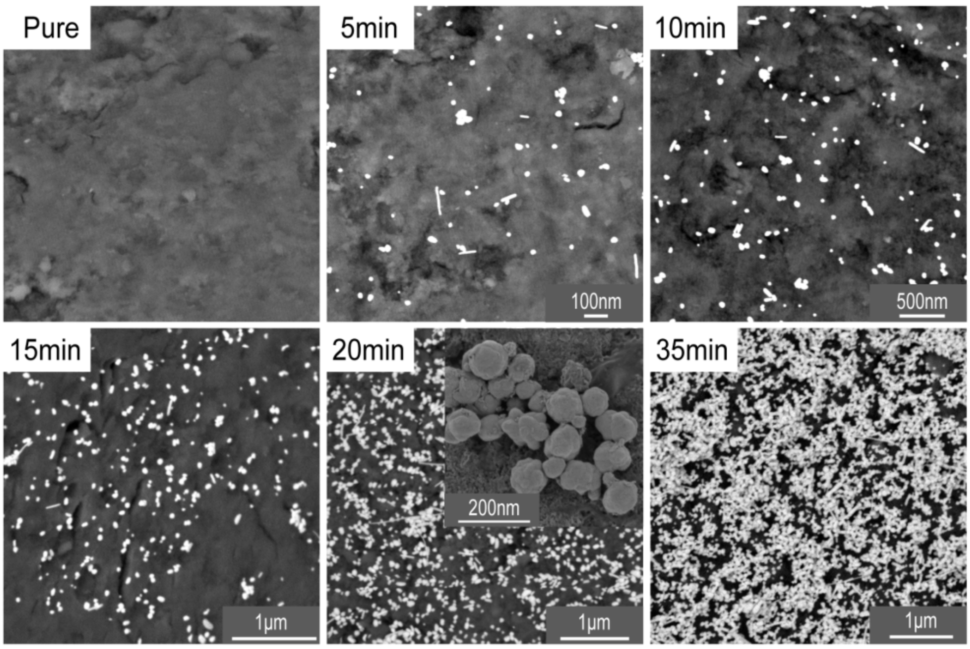
First, silver colloids were prepared according to the pervious reported procedures (6).Then four kinds of aromatic compounds aqueous solution with six different known concentrations were prepared. A mixture solution containing silver colloids, aromatic compounds aqueous solution and 0.1M NaCl (3:1:1 v/v) were then injected into cuvette. Finally, SERS spectra of aromatic compounds were collected under the conditions of 20 mW Laser power and 20s integration time.

Figure S1



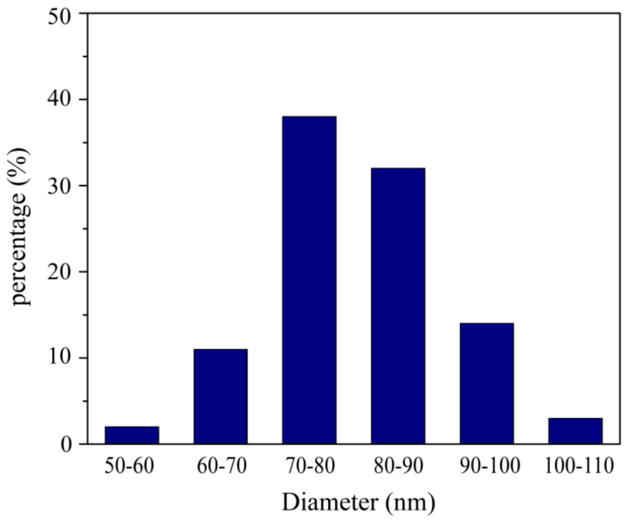
Normal Raman spectrum of bulk *p*-ATP (a) and SERS spectrum of 10 ppm *p*-ATP obtained on the surface of FPAP. Laser power: 30 mW; integration time: 20 s.

Figure S2



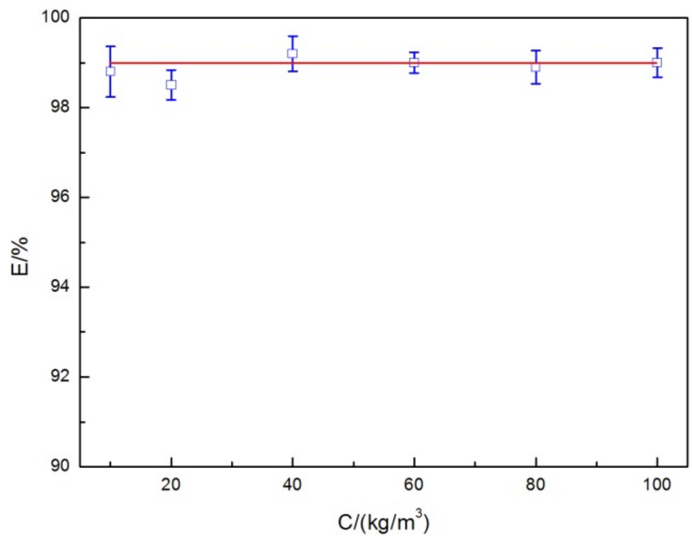
SEM images of silver particles for various soak times

Figure S3



Size distribution of Ag NPs soaked for 20min. Data of histograms was measured by analysis software (Image-Pro. Plus)

Figure S4



Separation efficiency of hydrocyclone under different feed rate of FPAPs

Table S1

Structure dimensions of experimental solid-liquid hydrocyclone

D	θ	W/D	H/D	D_c/D	D_d/D	L/D
25mm	6	0.16	0.32	0.24	0.08	1.48

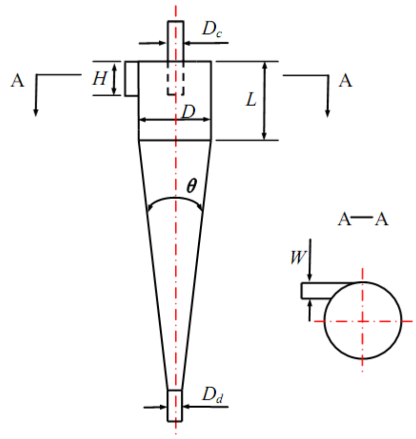


Table S2

Physical parameters of the PAPs used in the experiment

d	ρ	ρ_s	ε_p	S_p
472μm	3.355g/cm^3	0.992 g/cm^3	71%	377m^2/g

Table S3

Detailed data for the log-log curves in Figure 4

	I_{SERSi} (CPS)	I_{SERSo} (CPS)	I_{SERSs} (CPS)	C_i - C_o(ppm)	M(mg/kg)
Benzidine (at 976cm^{-1})	2310	2170	2188	0.30	14.9
	5638	5095	5073	2.36	116.9
	8459	7742	7878	4.35	215.3
	9996	9178	9185	5.69	281.4
	11648	10367	10662	9.95	492.6
	16228	15179	15441	10.86	537.4
Aniline (at 525cm^{-1})	4552	3498	4552	3.63	179.9
	8244	7087	8244	6.71	332.2
	12752	10462	12752	18.57	919.0
	14874	12752	14874	19.80	980.1
	16040	13866	16040	21.63	1070.5
	19706	17158	19706	29.71	1470.5
Parachloroaniline (at 640cm^{-1})	4664	4261	4453	1.51	74.8
	5546	4929	5266	2.63	130.3
	8375	7017	7885	7.90	391.2
	11103	9174	10994	14.00	694.1
	15504	13473	13946	19.70	974.9
	23333	20630	21716	36.71	1816.5
4-aminophenol	3249	2857	3151	1.08	53.5

(at 508cm^{-1})	5686	4951	5123	3.18	157.1
	13081	10525	12989	21.00	1039.7
	17520	15378	16891	23.01	1139.1
	22067	20220	21429	24.30	1202.9
	28817	26610	26723	36.13	1988.2

References

1. W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai, Z. Q. Tian, *Surf. Sci.* 1998, **406**, 9-22.
2. Y. Lu, G. L. Liu, J. Kim, Y. X. Mejia, L. P. Lee, *Nano Lett.* 2005, **5**, 119-124.
3. D. Li, D. W. Li, J. S. Fossey, Y. T. Long, *J. Mater. Chem.* 2010, **20,** 3688-3693.
4. J. Luo, H. Huang, Z. H. Lin, M. Hepel, ACS Symposium Series Chapter 9, ACS: Washington, DC, 2002, 113-127.
5. Y. T. Kim, R. L. Mccarley, A. J. Bard, *J. Phys. Chem.* 1992, **96**, 7416-7421.
6. P. C. Lee, D. Meisel, *J. Phys. Chem.* 1982, **86**, 3391-3395.