Electronic Supplementary Information for

Hydrophobic gold nanostructures via electrochemical deposition for sensitive SERS detection of persistent toxic substances

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1. EDS pattern of the as-prepared gold nanostructures.

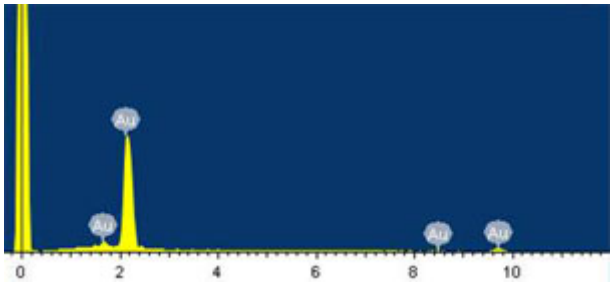

Fig. S1 EDS pattern of the as-prepared gold nanostructures.

2. SERS spectra of 10^{-4} M (A) PATP and (B) fluoranthene from (a) bare gold electrode (b) gold nanostructures substrate.

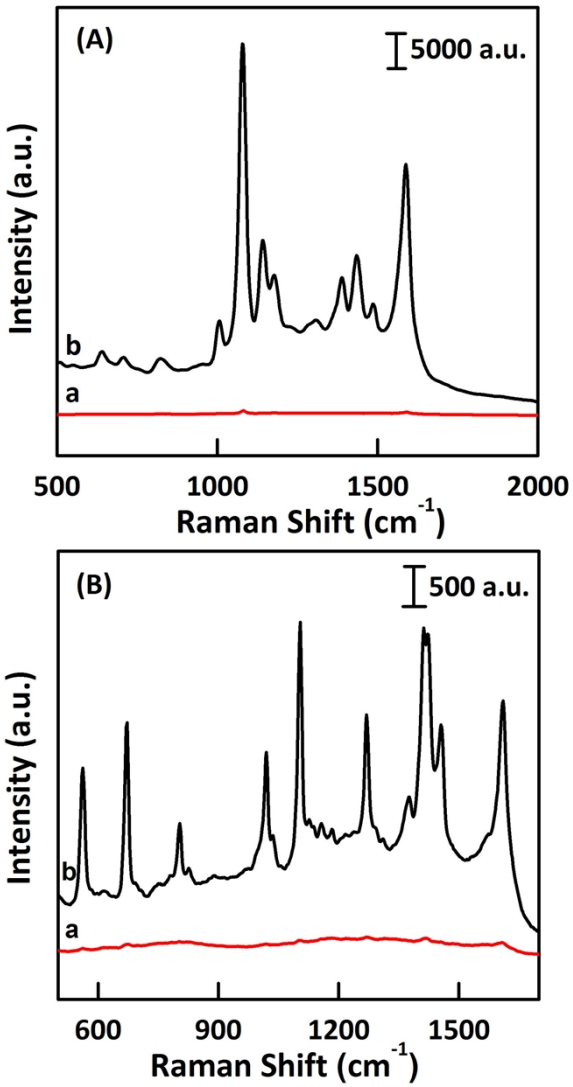

Fig. S2 SERS spectra of 10^{-4} M (A) PATP and (B) fluoranthene from (a) bare gold electrode (b) gold nanostructures substrate.

3. SEM images of gold nanostructures.

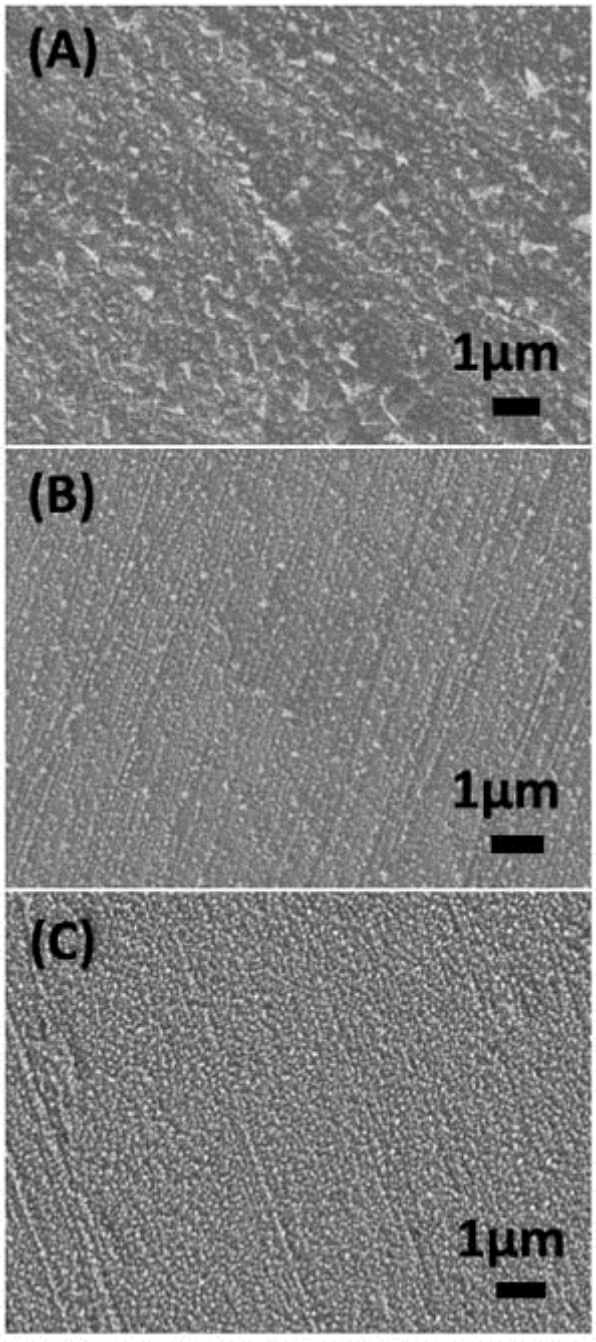

Fig. S3 SEM images of gold nanostructures electrodeposited in the solution of 0.1 M KNO_3 containing 0.4 g L^{-1} $HAuCl_4$ for 600s: (A) E = 0.2 V, (B) E = -1.0 V, (c) E = -0.2 V.

4. SERS spectra of PATP (10^{-4} M) under different potentials.

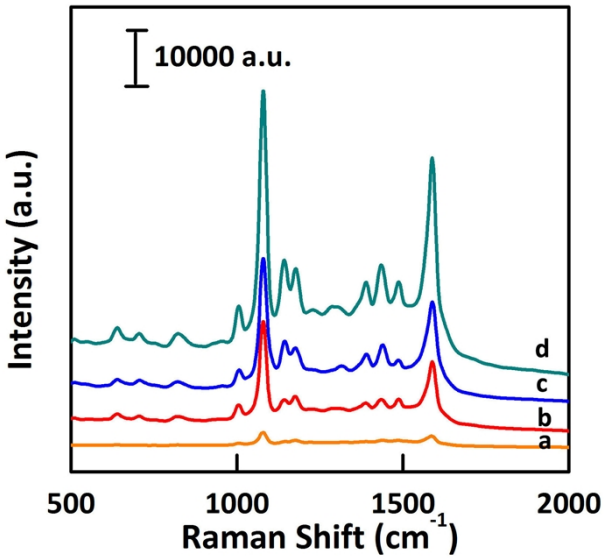

Fig. S4 SERS spectra of PATP (10^{-4} M) under different potentials (a) E= 0.2V; (b) E= -0.2 V; (C) E = -1.0 V; (d) E= -0.6 V.

5. The SERS spectra taken from the SERS substrate with five cycles of adsorption (10^{-4} M fluoranthene solution) and elution (dehydrated ethanol).

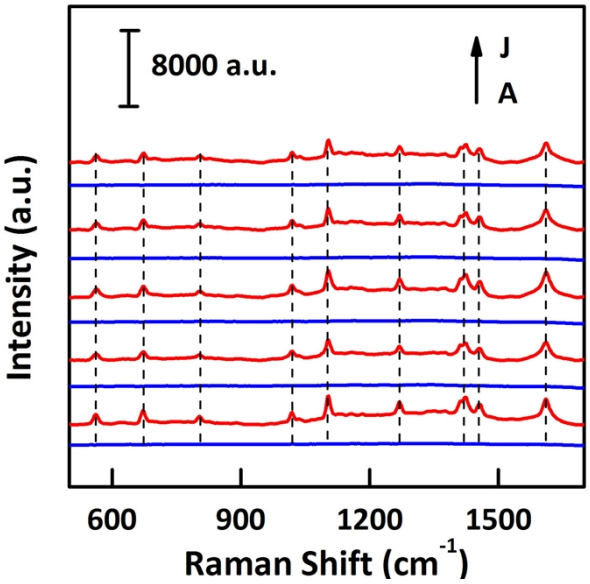

Fig. S5 The SERS spectra taken from the SERS substrate with five cycles of adsorption (10^{-4} M fluoranthene solution) and elution (dehydrated ethanol). The characteristic peaks of fluoranthene are highlighted by vertical lines. The acquisition time of all the spectra was 1 s.

6. (A) (a) Raman and (b) SERS spectrum of fluoranthene (B) (a) Raman and (b) SERS spectrum of BDE-15 (C) (a) Raman and (b) SERS spectrum of PCB-15.

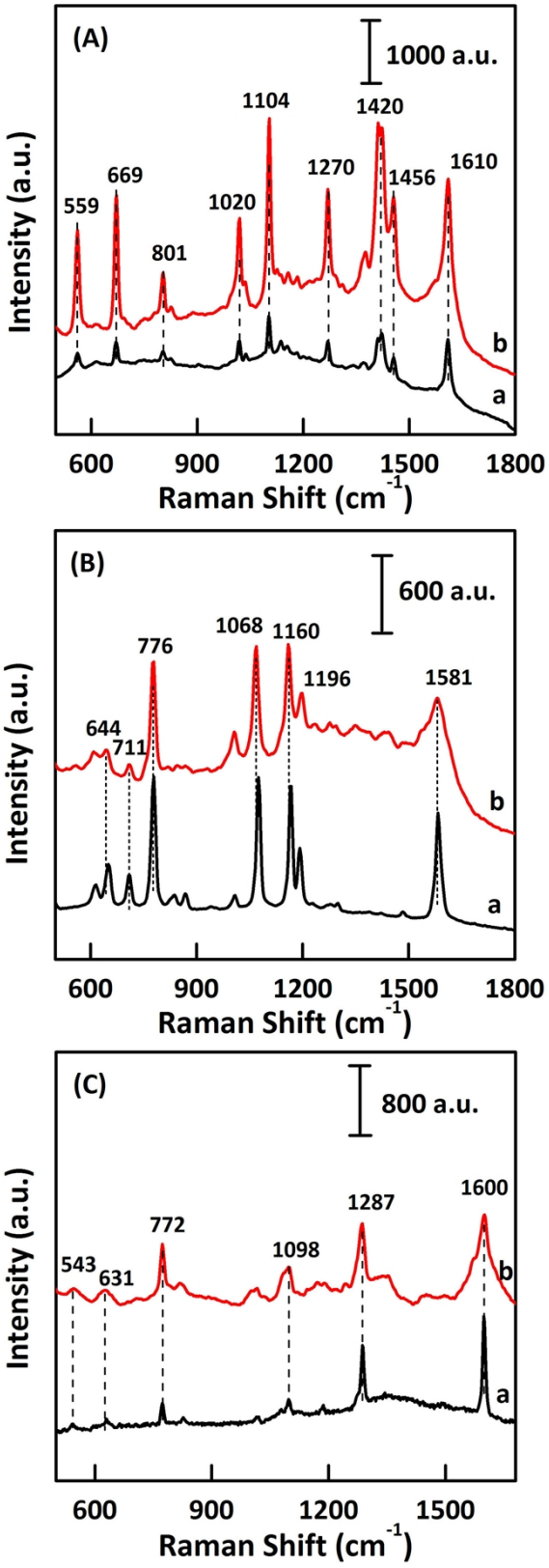

Fig. S6 (A) (a) Raman and (b) SERS spectrum of fluoranthene. (B) (a) Raman and (b) SERS spectrum of BDE-15. (C) (a) Raman and (b) SERS spectrum of PCB-15. The acquisition time of all the spectra was 1 s.

7. Chemical structures of analytes in this work.

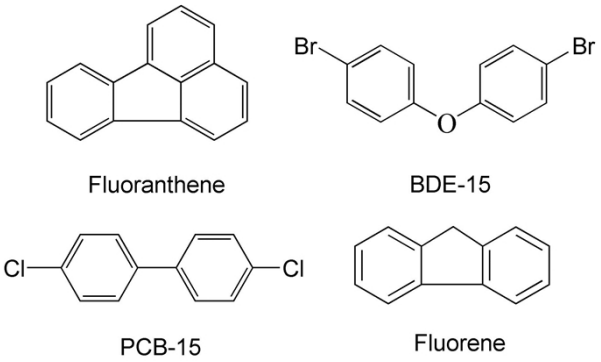

Fig. S7 Chemical structures of analytes in this work.

8. (A) SERS spectra and (B) log–log plot for fluoranthene in simulated water samples at different concentrations.

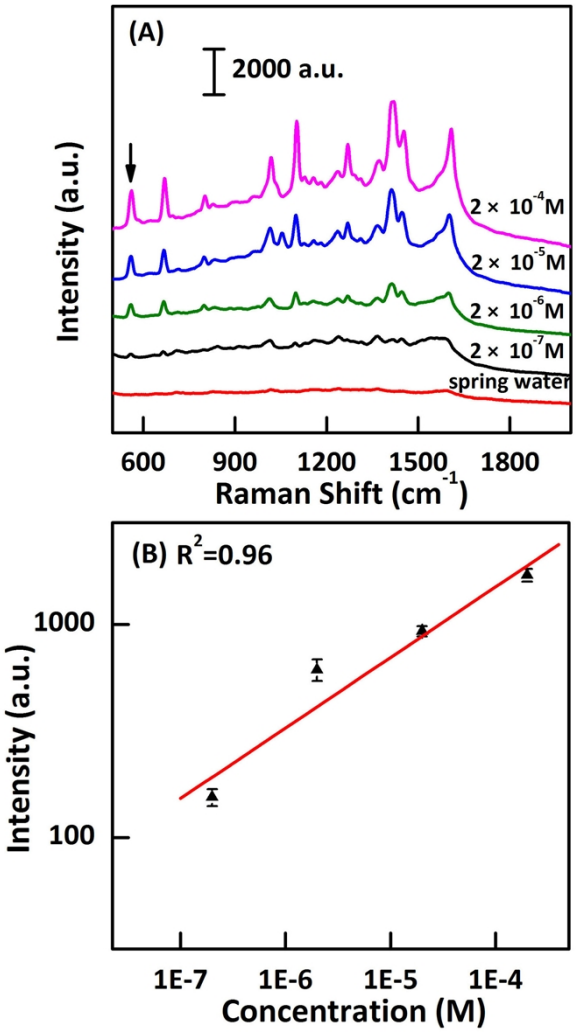

Fig. S8 (A) SERS spectra and (B) log–log plot for fluoranthene in simulated water samples at different concentrations. The acquisition time of all the spectra was 1 s.

9. Surface-enhanced Raman bands of fluoranthene, BDE-15, PCB-15.

Table S1. Surface-enhanced Raman bands of fluoranthene, BDE-15, PCB-15[1-3]

fluoranthene	BDE-15	PCB-15	fluorene
470 skeletal stretching	429 C-H in-plane bending	543 C–Cl stretching	421 skeletal stretching
559 skeletal stretching	493 C-H in-plane bending	631 ring torsion	741 C-H out-plane bending
669 C-H stretching	644 C-Br stretching, ring torsion	772 C–Cl stretching	844 C-H out-plane bending
801 C-H stretching	711 C-H out-plane bending, C-H torsion	1098 trigonal breathing	1020 C-C stretching
1020 C-C stretching	776 C-H in-plane bending	1287 C–C bridge stretching	1149 C-H in-plane bending
1104 C-H in-plane bending	1068 C-Br stretching, ring stretching	1600 ring stretching	1187 C-C stretching
1270 C-H in-plane bending	1160 C-O sym. stretching, C-H in-plane bending		1234 C-H in-plane bending
1410 ring vibration	1196 C-O sym. stretching, C-H in-plane bending		1295 C-H in-plane bending
1420 C-C stretching	1581 C-C stretching		1478 C-C stretching
1456 C-C stretching			1575 C-C stretching
1610 C-C stretching			1610 C-C stretching

10. K_{ow}, Peak position for quantitative analysis, linear range, detection limit of fluoranthene, BDE-15 and PCB-15 and enhancement factor.

Table S2. K_{ow}, Peak Position for Quantitative Analysis, Linear Range, Detection Limit of Fluoranthene, BDE-15 and PCB-15 and Enhancement Factor

Analyte	Log K_{ow}[a]	Peak (cm^{-1})	Linear Range (μM)	LOD (μM)	EF
fluoranthene	5.16	559	0.02 - 200	0.0067	1.5×10^4
BDE-15	5.82	776	0.02 - 200	0.0026	2.6×10^4
PCB-15	5.28	772	0.04 - 440	0.0053	1.2×10^4

[a] K_{ow}: n-octanol-water partition coefficients, indicator for hydrophobicity. [a]Data from Mackay et al.[4]

11. Comparison of the performance of various substrates for SERS detection.

Table S3. Comparison of the performance of various substrates for SERS detection

Substrate	EF	LOD (nM)	Linear Range (μM)
Au nanoparticles[5]	[a] 3.0×10^4	[a] 500	[a] 0.5 - 10
Silver nanoparticle[6]	[b] 2.1×10^5	[b] 24	[b] 0.024 - 49
Ag film[7]	[c] 1.2×10^5	[c] 440	-
dendritic Au film[8]	[d] 3.63×10^4	[e] 7.2	[e] 0.0832 - 0.9975
Our substrate	[b] 1.5×10^4	[b] 6.7	[b] 0.02 - 200
	[f] 2.6×10^5		

[a]Pyrene, [b]fluoranthene, [c]4,4-dichlorobiphenyl, [d]4-mercaptobenzoic acid, [e]formaldehyde, [f]*p*-Aminothiophenol

12. The recovery of fluoranthene in spring water.

Table S4. The recovery of fluoranthene in spring water

Technique	Recovery (%)	RSD (%)
HPLC[9]	97.9[a]	3.6[a]
GC[10]	103[b]	5.0[b]
Our method	108.5[c]	3.8[c]

[a] Tap water, [b] River water, [c] Spring water

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