Facile in situ synthesis of core-shell MOF@Ag nanoparticles composites on screen-printed electrodes for ultrasensitive SERS detection of polycyclic aromatic hydrocarbons

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SERS enhancement factor

The enhancement factor (EF) can be calculated using the following formula: ¹

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

where I_{SERS} and I_{bulk} are the vibration intensities in the SERS of 4-aminothiophenol (Atp) and normal Raman spectra of Atp, respectively. N_{bulk} and N_{SERS} are the number of molecules under laser illumination for the bulk sample, and the number of molecules in the self-assembled monolayers (SAMs), respectively. The N_{SERS} and N_{bulk} values can be calculated on the basis of the estimate of the concentration of surface species or bulk sample and the corresponding sampling areas. It is reported that the average surface density of Atp molecules in densely packed monolayers is approximately one Atp molecule per 0.2 nm^{2,1} Then the surface coverage of Atp monolayer on HKUST-1@Ag is 8.31×10^{-10} mol cm⁻² ($\Gamma = 1 / [(0.2 \times 10^{-14}) \times (6.02 \times 10^{23})]$ mol cm⁻²= 8.31×10^{-10} mol cm⁻²). Taking the sampling area (*ca.* 10 μ m in diameter) into account, N_{SERS} has a value of 6.52×10⁻ ¹⁶ mol (N_{surf} =I' × π × (10/2) μ m²=6.52×10⁻¹⁶ mol). For the solid sample, the sampling volume is the product of the area of the laser spot (ca. 10 μ m diameter) and the penetration depth (~ 2 μ m) of the focused beam. Assuming the density of bulk Atp is 1.14 g cm⁻³ laser (https://www.chemicalbook.com/ProductChemicalPropertiesCB3289884 EN.htm), N_{bulk} can be

calculated to be 1.43×10^{-12} mol (N_{bulk} =1.14 g cm⁻³ × π × 25 µm² × 2 µm / (125.19 g mol⁻¹)=1.48×10⁻¹² mol). For the vibrational mode at 1070 cm⁻¹, the ratio of I_{SERS} to I_{bulk} was about 25.7 (Fig. S6), so *EF* was calculated to be 5.6×10⁴ (25.7 × [1.43×10⁻¹²/ (6.52×10⁻¹⁶) = 5.6×10⁴).



Fig. S1 SEM images of the surface of the SPCE with low (A) and high (B) magnifications.



Fig. S2 TG curve of the as-synthesized HKUST-1@Ag with the increase of AgNO₃ concentration (0.00 M, 0.01 M, 0.05 M, 0.10 M and 0.20 M).



Fig. S3 (A) N₂ adsorption-desorption isotherm and (B) Pore size distribution of the HKUST-1 and HKUST-1@Ag.



Fig. S4 E-field amplitude patterns obtained from 2D FDTD calculations of (A) three dimensional disordered Ag NPs arrangement and (B) three dimensional HKUST-1 decorated with ordered Ag arrangement.



Fig. S5 SERS spectra of Atp with various concentrations on the poly-HKUST-1@Ag and the SH-modified Ag NPs aggregates. The unit is M (mol/L).



Fig. S6 Normal Raman spectra of solid Atp (A) and SERS spectra of Atp (10 μ M) recorded on randomly selected five spots on the surface of poly-HKUST-1@Ag (B). Exposure time was 20 s, laser wavelength was 785 nm, and laser power was 10 mW.



Fig. S7 UV-vis absorption spectra of the aqueous dispersion of Ag NPs colloids at different pH value.



Fig. S8 XRD pattern for the HKUST-1@Ag measured for chemical stability tests: (a) assynthesized sample and that soaked in water 2 days, (b) as-synthesized sample and that soaked in an aqueous HCl solution (pH = 2) for 24 hours, and (c) as-synthesized sample and that soaked in an aqueous NaOH solution (pH = 12) for 24 hours.



Fig. S9 XRD patterns of the HKUST-1@Ag before spiking into aqueous solution (a), and dispersed in an aqueous HCl solution (pH = 2) for 1 day (b); 2 days (c); 3 days (d); 5 days (e); and 7 days (f).



Fig. S10 The concentrations of Cu²⁺ and Ag⁺ releasing from HKUST-1@Ag under different pH for 1 h. Each data point represents the average value from three measurements on the same samples. Error bars show the standard deviations.



Fig. S11 Effect of sample temperature on sensitivity to PAHs. The correlation between the I_{1070} intensity and the concentration of anthracene (ANT) (a1, 746 cm⁻¹), pyrene (PYR) (a2, 1404 cm⁻¹), perylene (PER) (a3, 1569 cm⁻¹), and 4-chlorobiphenyl (4-CBP) (a4, 1590 cm⁻¹) under different temperature. The LOD of ANT (b1), PYR (b2), PER (b3), and 4-CBP (b4) under different sample temperature.



Fig. S12 SERS spectra investigation of the recyclability of poly-HKUST-1@Ag after $1\sim10$ stripping and electrodeposition of Ag cycles. SERS spectra of poly-HKUST-1@Ag after exposed to 10 µL droplet containing 1 µM Atp. A fresh prepared poly-HKUST-1@Ag (a), after 1 stripping and electrodeposition of Ag cycle (b), after 2 stripping and electrodeposition of Ag cycles (c), after 5 stripping and electrodeposition of Ag cycles. The inset shows the intensity at 1070 cm-1 variation with cycles of Ag stripping and electrodeposition. Each data point represents the average value from three SERS spectra on each sample. The error bars represent typical intensity variations obtained from the same sample measured at three different spots.



Fig. S13 Optimization of the reaction conditions ((A) AgNO₃ concentration, (B) deposition potential, (C) deposition time and (D) ionic strength) for 1 μ M Atp detection.



Fig. S14 The morphology change of the HKUST-1@Ag nanostructures before (A) and after (B) the detection of the PAHs in seawater.

BET surface area Samples (m ² g ⁻¹)		Langmuir surface area (m²g⁻¹)	Total pore volume (cm ³ g ⁻¹)	Pore size (nm)
HKUST-1	735	1036	0.53	1.3,13.8
HKUST-1@Ag	516	702	0.36	1.1

Table S1 The porosity analysis of the HKUST-1 and HKUST-1@Ag

 Table S2 Comparison of detection performance of various SERS sensors for PAHs.

Materials	Analytes	Linear range (nM)	Detection limit (nM)	References	
	pyrene	1 x 10 3 to 1 x 10 5	1000	2	
rgo-agnp	perylene	1×10^{2} to 1×10^{4}	100	-	
	anthracene	2.5×10^2 to 1×10^4	250		
AuNPs/SNW-1	pyrene	1 x 10 2 to 1 x 10 4	100	3	
Ag aggregates	1-OHPyr	50 to 1 x 10 ⁵	50	4	
Au NPs/nickel	pyrene	10 to 1 x 10 ⁶	10	5	
	pyrene	63 to 1 x 10 ⁶	63	c	
Aunes	fluoranthene	20 to 1 x 10 ⁶	20	0	
BCP-tethered AuNPs	Benzo(a)pyrene	0.039 to 390	0.039	7	
	anthracene	1×10^{3} to 1×10^{5}	1000	8	
Au Coffee Ring	pyrene	5 x 10 2 to 1 x 10 5	500	Ū	
AgNP	pyrene	1×10^{2} to 1×10^{5}	100	9	
	anthracene	5.8×10^{2} to 3.5×10^{5}	520	10	
has-ay nes	pyrene	7.5 x 10 2 to 3.5 x 10 5	550	10	
	anthracene	50 to 1 x 10 ⁸	20		
	pyrene	0.5 to 5 x 10 ⁸	0.15	This second	
HKUSI-I@Ag	perylene	10 to 1 x 10 ⁸	3	This work	
	4-chlorobiphenyl	20 to 2 x 10 ⁸	5		

	Spiked		This method			GC-MS method		
Compound	(μM)	Found (µM)	R ^b (%)	RSD (%)	Found (µM)	R (%)	RSD (%)	
	0	ND ^a	-	_	ND	_	-	
ANT	10	11.23	112.3	6.3	9.65	96.52	4.3	
	50	55.62	111.2	5.6	48.93	97.86	3.8	
DVD	0	ND	-	-	ND	_	-	
PIK	10	11.55	115.5	6.9	9.25	92.51	3.2	
	50	56.51	113.0	4.2	49.16	98.32	4.1	
PER	0	ND	-	-	ND	-	_	
	10	8.56	85.61	6.6	10.55	105.5	3.6	
	50	46.55	93.10	3.9	51.05	98.50	4.2	
4-CBP	0	ND	-	-	ND	_	-	
	10	8.75	87.53	6.8	11.31	113.1	4.2	
	50	47.55	95.12	4.3	49.35	98.73	3.5	

Table S3 Recoveries and precisions (RSD%, n=5) of the four PAHs in river water samples by the SERS and GC-MS method.

^a ND: lower than LOD ^b R: recovery of the method

	Spiked		This method			GC-MS method		
Compound	(μM)	Found (µM)	R ^b (%)	RSD (%)	Found (µM)	R (%)	RSD (%)	
	0	ND ^a	-	-	ND	_	-	
ANT	10	8.06	80.62	7.5	10.12	101.2	4.8	
	50	51.31	102.6	4.8	51.25	102.5	3.1	
DVD	0	ND	-	-	ND	_	-	
PTK	10	11.68	116.8	5.3	10.31	103.1	4.6	
	50	53.26	106.5	3.6	48.36	96.72	3.5	
PER	0	ND	-	-	ND	-	-	
	10	11.35	113.5	7.2	9.26	92.63	3.6	
	50	52.35	93.10	4.8	51.36	102.7	4.1	
4-CBP	0	ND	-	-	ND	_	-	
	10	8.65	86.51	8.1	11.32	113.2	3.8	
	50	48.16	96.32	4.6	48.95	97.92	2.3	

Table S4 Recoveries and precisions (RSD%, n=5) of the four PAHs in sewage water samples by the SERS and GC-MS method.

^a ND: lower than LOD

^b R: recovery of the method

	Spiked		This method			GC-MS method		
Compound	(μM)	Found (µM)	R ^b (%)	RSD (%)	Found (µM)	R (%)	RSD (%)	
	0	ND ^a	_	-	ND	_	-	
ANT	10	11.82	118.2	6.3	9.31	93.14	3.8	
	50	48.63	97.26	5.1	51.35	102.7	2.6	
DVD	0	ND	-	-	ND	_	-	
PYR	10	8.35	83.51	6.8	9.85	98.51	4.1	
	50	51.58	103.2	4.2	50.92	101.8	2.8	
PER	0	ND	-	-	ND	-	-	
	10	9.03	90.32	5.3	11.06	110.6	4.3	
	50	48.71	97.42	3.6	49.28	98.56	2.5	
4-CBP	0	ND	-	-	ND	-	_	
	10	11.05	110.5	6.5	8.96	89.63	4.2	
	50	51.32	102.6	5.6	49.31	98.62	3.6	

Table S5 Recoveries and precisions (RSD%, n=5) of the four PAHs in seawater samples by the SERS and GC-MS method.

a ND: lower than LOD

^b R: recovery of the method

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