Electronic Supplementary Information

Simple In-situ Preconcentration for Electrolyte Atmospheric Liquid Discharge Optical Emission Spectrometric Determination of Trace Cadmium on Microplastic

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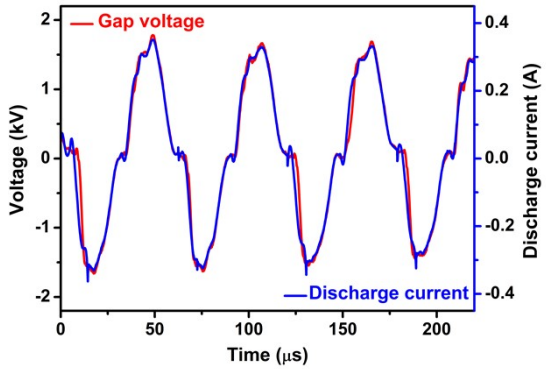

Fig. S1 Waveforms of gap voltage and discharge current

Note: The information of gap voltage and discharge current is of great significance to reveal the ignition and extinction mechanism of a microplasma. Figure S1 shows the waveform of gap voltage and discharge current under the condition of 2.0 mm discharge gap. As shown in the figure, it can be noted that the gap voltage is about 1.5-1.8 kV, and the discharge current changes slowly and lasts for a long time (∽50 μs). The waveforms of gap voltage and discharge current are almost the same, and the discharge is very similar to a typical glow discharge mode.

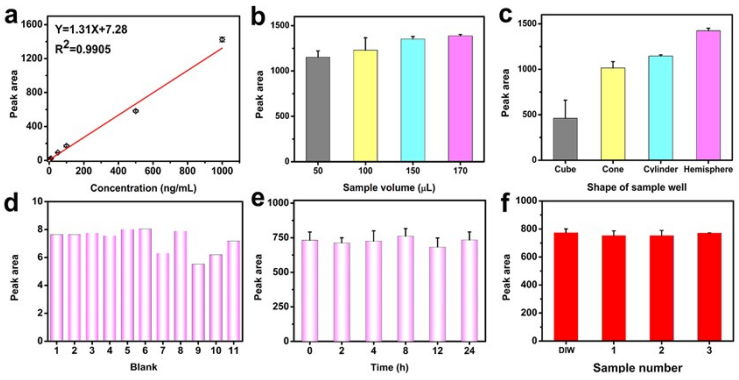

Fig. S2 Analytical performance of ISP-EALD-OES

Note: Cd standard curve (a) of 2.5-1000 ng mL^{-1}; (b) Optimization of sample volume; (c) Optimization of sample well shape; (d) 11 trials of blank peak areas; (e) long-term stability in 24 h (Cd standard solution, 500 ng/mL); and (f) Anti-interference test with deionized water (DIW) and several carwash wastewaters (1-3). The concentrations of Cd added are all 500 ng/mL.

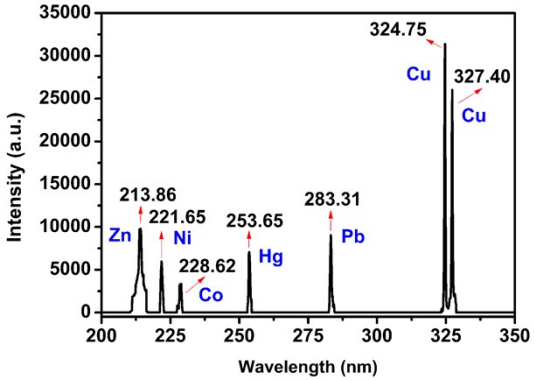

Fig. S3 Signal spectra for a 10 μg mL^{-1} standard containing Co, Cu, Hg, Ni, Pb and Zn.

Table S1 Optimized experimental conditions for other heavy metal elements

Element	Electrode distance (mm)	Discharge voltage (V)	Collection distance (cm)	Peak time (s)
Zn	1	250	2	60
Ni	1	250	2	50
Co	1	250	2	65
Hg	1	250	1.5	5
Pb	2	250	2	55
Cu	2	250	2	62

Table S2 Comparison of LOD by ISP-EALD-OES with those afforded by other microplasma-based OES

Element	LOD (ng mL^{-1})			
	This Work	ELCAD[1]	LS-APGD[2]	SCGD[3]
Zn	5	3	900	-
Ni	8	-	60	6
Co	15	-	200	-
Hg	7	15	-	2
Pb	5	45	-	1
Cu	2	11	80	6

ELCAD: electrolyte cathode discharge; LS-APGD: liquid sampling atmospheric pressure glow discharge; and SCGD : solution cathode glow discharge.

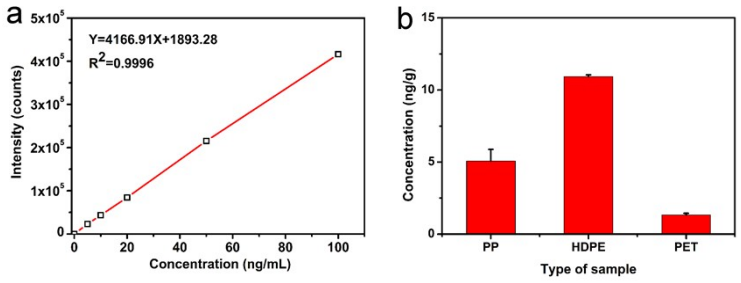

Fig. S4 (a) Cadmium standard curve by ICP-MS and (b) cadmium content of blank microplastic materials

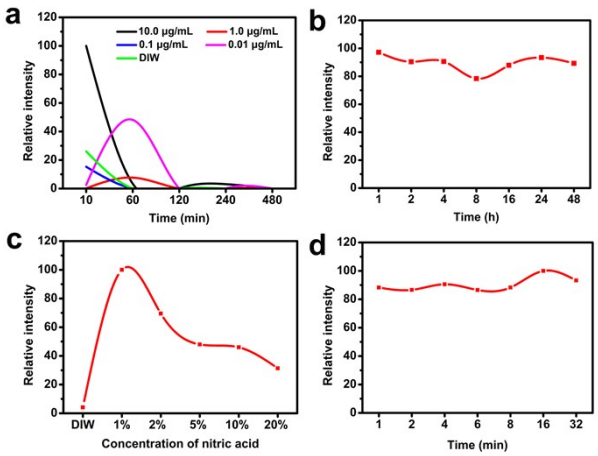

Fig. S5 Simulated adsorption and desorption of Cd on microplastics

Note: (a) The adsorption Cd on PE by treatment with different concentrations of Cd for different times; (b) two-day stability of Cd adsorbed on microplastic samples which were first pretreated in 10 μg mL^{-1} for adsorption of cadmium for 10 min and dried for later test; (c) concentrations of nitric acid on desorption of Cd from microplastic samples; and (d) centrifugation time on desorption of Cd from microplastics with 1% nitric acid.

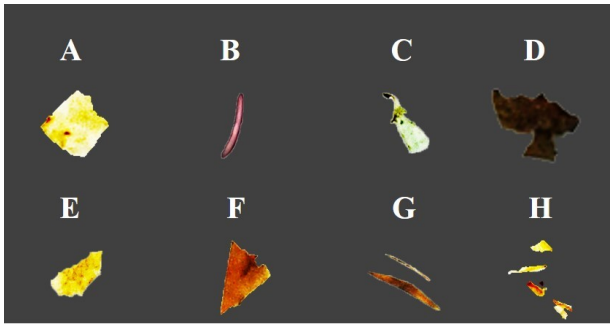

Fig. S6 Photos of real samples of microplastics

Notes: (A) plastic bag fragments; (B) red plastic strip; (C) woven bag fragments; (D) black plastic film fragments; (E) yellow microplastics; (F) unknown samples; (G) shell fragments; and (H) twig fragments.

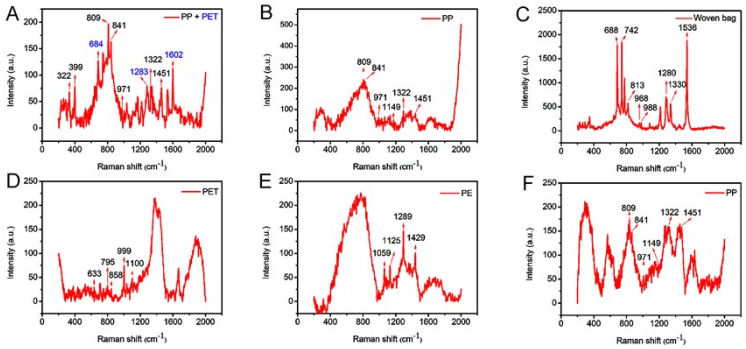

Fig. S7 Raman spectra of real microplastic samples

Note: the components of the microplastic samples are therefore mainly PE, PP, and PET. There are also some hybrid

microplastics.

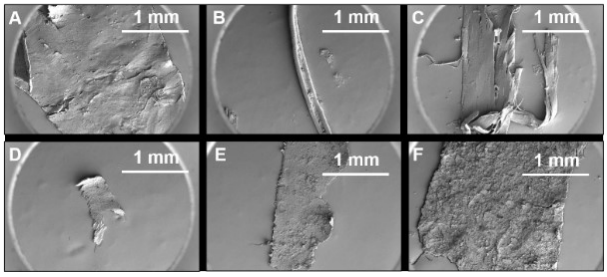

Fig. S8 SEM images of real microplastic samples

Note: The microplastics were basically in the range of 1-5 mm in length, with the largest diameter of ca. 2 mm, and the smallest diameter ca. 0.2 mm. Mainly showing flakes (A, D, E, F), strips (B), bands (C). The surface of the microplastics is relatively smooth, and there are no particularly obvious protrusions. Their edge cracks are relatively straight, and there is no obvious tooth shape, which may indicate that the microplastics should be subjected to greater force or easily decomposed during the decomposition process.

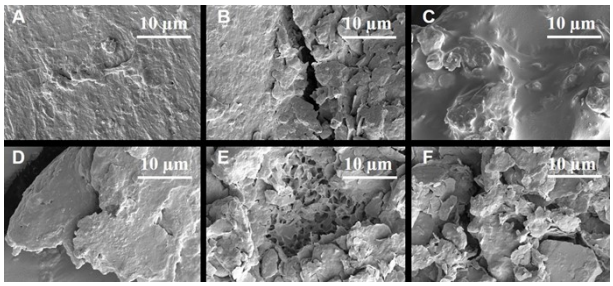

Fig. S9 High resolution SEM images of real microplastic samples

Note: the surfaces of the microplastic samples of A, C, and D were relatively smooth, and the surfaces of B, E, and F have many small holes, gaps, small protrusions.

References

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