Preparation and Characterization of layer-by-layer assembly of thiols/Ag nanoparticles/polydopamine on PET bottles for the enrichment of organic pollutants from water samples

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Seven Tables and six Figures are included in Supporting Information.

Table S1 Fitting parameters, constraints, and possible assignments for the component peaks used to reproduce the measured C1s envelopes.

SPE bottle	Species	Peak position (eV)	FWHM[a]	Area (%)	Peak shape[b]
Three layers of PDOPA films coated SPE bottle	C-C	284.85	1.19	52.0	%LG (0)
	C-N	285.27	0.95	18.9	%LG (0)
	C-OH	285.85	1.27	19.0	%LG (0)
	C=O	287.87	2.83	10.1	%LG (0)
Thiols/PDOPA coated SPE bottle (LBL three times)	C-C	284.43	1.12	38.2	%LG (0)
	C-N/C-S	284.95	0.79	26.5	%LG (0)
	C-OH	285.49	0.73	17.9	%LG (0)
	C=O	286.13	1.19	17.3	%LG (44)
AgNPs/PDOPA coated SPE bottle (LBL three times)	C-C	284.95	1.43	51.2	%LG (5)
	C-N	285.91	1.01	18.1	%LG (0)
	C-OH	286.82	1.17	14.1	%LG (0)
	C=O	287.95	2.65	16.6	%LG (0)
Thiols/AgNPs/PDOPA coated SPE bottle (LBL three times)	C-C	284.65	1.42	30.1	%LG (0)
	C-N/C-S	284.98	1.02	27.3	%LG (0)
	C-OH	285.50	0.86	20.6	%LG (0)
	C=O	286.13	1.45	21.9	%LG (13)

[a] full width at half maximum [b]% Lorentzian-Gaussian

Table S2 Fitting parameters, constraints, and possible assignments for the component peaks used to reproduce the measured O1s envelopes.

SPE bottle	Species	Peak position (eV)	FWHM[a]	Area (%)	Peak shape[b]
Three layers of PDOPA films coated	C=O	532.18	1.71	37.3	%LG (0)
SPE bottle	C-OH	533.50	1.96	62.7	%LG (0)
Thiols/PDOPA coated	C=O	532.00	1.61	35.2	%LG (32)
SPE bottle	C-OH	532.99	1.44	39.5	%LG (43)
(LBL three times)	C-O-C=O	533.99	1.68	25.2	%LG (22)
AgNPs/PDOPA	Ag-O	530.86	2.01	39.7	%LG (23)
coated SPE bottle	C=O	532.00	1.44	33.1	%LG (34)
(LBL three times)	C-OH	532.98	1.61	27.2	%LG (100)
Thiols/AgNPs/PDOPA	Ag-O	531.42	1.54	41.3	%LG (0)
coated SPE bottle	C=O	532.09	0.98	21.7	%LG (0)
(LBL three times)	C-OH	532.99	1.06	19.5	%LG (0)
	C-O-C=O	533.72	1.48	17.5	%LG (0)

[a] full width at half maximum [b]% Lorentzian-Gaussian

Table S3 Fitting parameters, constraints, and possible assignments for the component peaks used to reproduce the measured N1s envelopes.

SPE bottle	Species	Peak position (eV)	FWHM[a]	Area (%)	Peak shape[b]
Three layers of PDOPA	pyridinic N	397.99	1.64	44.1	%LG (64)
films coated SPE bottle	pyrrolic N	399.32	1.75	25.4	%LG (92)
	$-NH_3^+$	405.47	2.17	30.6	%LG (71)
Thiols/PDOPA coated	pyridinic N	398.24	1.44	33.9	%LG (0)
SPE bottle	pyrrolic N	399.47	2.00	21.7	%LG (0)
(LBL three times)	$-NH_3^+$	405.72	1.54	44.5	%LG (0)
AgNPs/PDOPA coated	pyridinic N	397.98	1.74	65.5	%LG (69)
SPE bottle	pyrrolic N	397.85	1.56	34.5	%LG (73)
(LBL three times)					

[a] full width at half maximum [b]% Lorentzian-Gaussian

Table S4 Analytical parameters of the proposed method

Analytes	Linear range ng L^{-1}	Calibration equation	R^2	Detection limits[a] ng L^{-1}
FluA	2-200	y = 0.3401x + 4.3587	0.9941	0.45
Pyr	2-200	y = 0.377x + 4.9555	0.9939	0.69
BaA	2-200	y = 0.3025x + 3.1653	0.9941	0.43
BaF	2-200	y = 0.3386x + 1.1011	0.9976	0.10
BaP	2-200	y = 0.3275x + 0.3613	0.9973	0.46
BghiP	2-200	y = 0.3344x + 1.7076	0.9943	0.73
4-NP	100-10,000	y = 0.4239x + 0.0735	0.9975	68
4-OP	100-10,000	y = 0.455x + 0.0387	0.9981	53
DCHP	100-10,000	y = 0.3589x - 0.0135	0.9933	52
DOP	100-10,000	y = 0.375x + 0.1078	0.9997	66

[a] The detection limits were calculated by using S/N=3

Table S5 Detected concentration (μg/L) and recoveries of real water samples spiked with 4-NP and 4-OP

Water sample	Blank		Spiked sample			
			0.5 μg/L		2 μg/L	
	4-NP	4-OP	4-NP	4-OP	4-NP	4-OP
Influent water	0.45±11	0.39±12	0.83 75.8±7.6	0.91 105±9.8	2.35 94.9±11	2.57 98.5±8.5
Effluent water	0.38±1.2	0.15±8.3	0.84 92.0±10.5	0.66 101±8.8	2.41 102±9.4	1.95 89.8±9.8
River water	ND	ND	0.44 88.9±9.5	0.43 86.2±6.7	2.16 108±5.4	1.70 85.1±7.8

Table S6 Detected concentration (μg/L) and recoveries of real water samples spiked with DCHP and DOP

Water sample	Blank		Spiked sample			
			0.5 μg/L		5 μg/L	
	DCHP	DOP	DCHP	DOP	DCHP	DOP
Influent water	ND	ND	0.60 120±8.9	0.47 93.4±9.2	4.61 92.2±9.4	3.87 77.4±7.0
Effluent water	ND	ND	0.49 97.2±8.6	0.40 79.3±11	4.12 82.3±6.8	3.66 73.2±6.1
River water	ND	ND	0.36 72.3±1.2	0.34 70±6.7	4.35 87.1±8.8	3.54 70.8±8.7

Table S7 Detected concentration (μg/L) and recoveries of real water samples spiked with PAHs

Analytes	Influent water			Effluent water			River water		
	Detected (ng/L)			Detected (ng/L)			Detected (ng/L)		
	recovery (%)			recovery (%)			recovery (%)		
	Blank	5 ng/L	20 ng/L	Blank	5 ng/L	20 ng/L	Blank	5 ng/L	50 ng/L
FluA	52.5±1.3	57.1	80.3	ND	3.67	18.3	ND	4.59	48.8
		91.8±1.2	112±6.9		73.4±6.2	91.4±8.8		91.8±10	101±15
Pyr	43.7±9.1	49.2	71.9	ND	3.81	17.9	ND	4.94	51.3
		111±4.9	116±10.8		76.2±6.8	89.7±2.4		98.8±5.8	99.5±14.8
BaA	13.2±6.3	16.9	36.3	ND	3.91	18.2	ND	4.51	50.2
		74.0±7.7	115±12		78.1±7.9	91.1±3.0		90.3±9.4	91.6±14.6
BaF	3.96±14.8	9.04	25.9	ND	5.28	19.6	ND	4.93	50.1
		101±8.7	96.1±3.5		105±9.7	97.9±2.4		98.6±4.1	90.7±2.2
BaP	1.82±10.9	6.14	23.1	ND	5.91	18.7	ND	5.76	51.7
		86.4±12.9	104±6.2		118±4.1	93.6±5.0		115±5.0	92.7±1.8
BghiP	0.27±8.2	5.31	17.1	ND	3.58	19.1	ND	5.28	56.9
		100±8.8	82.2±7.5		71.7±4.7	95.4±4.5		106±3.7	92.6±12.6

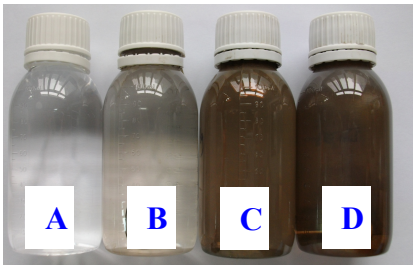

Fig. S1 Images of (A) bare PET bottle, (B) PDOPA film coated PET bottle, (C) AgNPs/PDOPA PET bottle, and (D) thiols/AgNPs/PDOPA bottles.

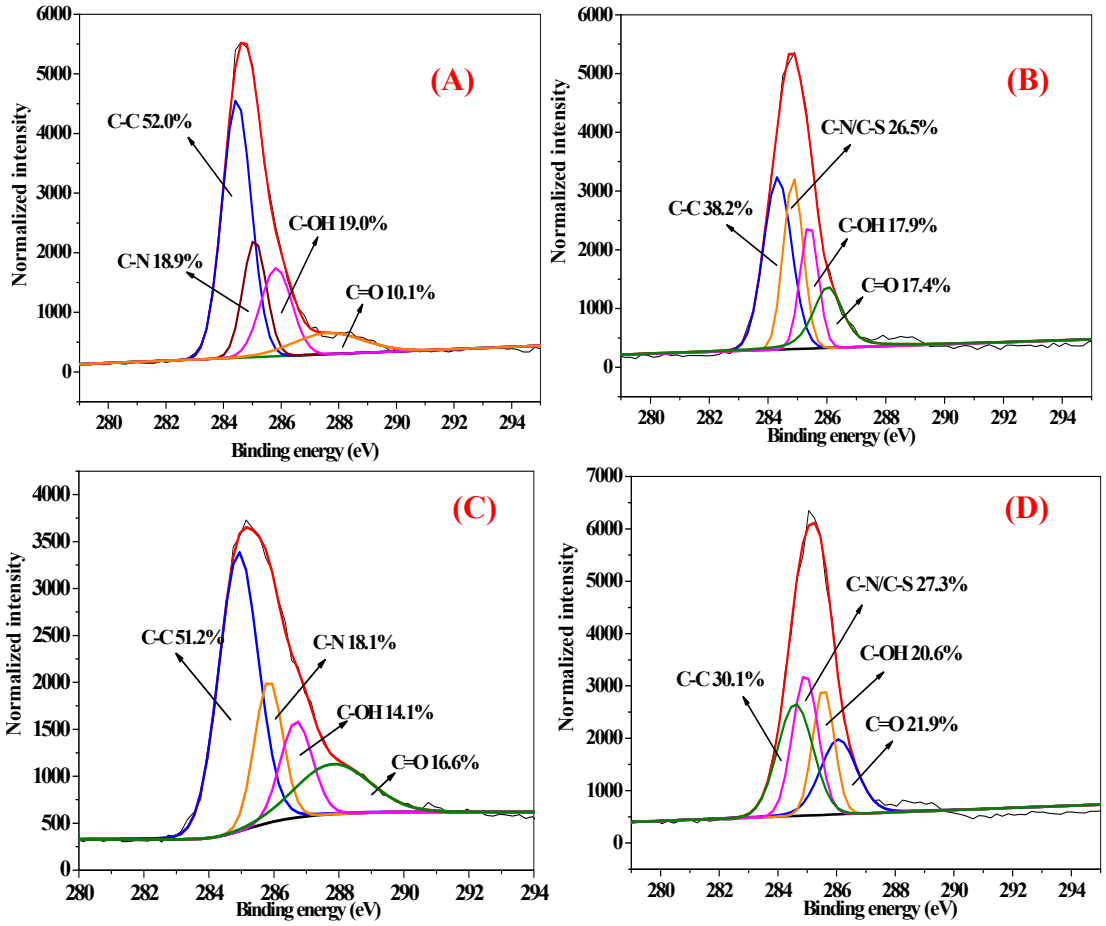

Fig. S2 Peak fitting of C1s spectra of (A) three layers of PDOPA films coated SPE bottle, (B) thiols/PDOPA coated (LBL three times) SPE bottle, (C) AgNPs/PDOPA coated (LBL three times) SPE bottle, and (D) thiols/AgNPs/PDOPA coated SPE bottle (LBL three times).

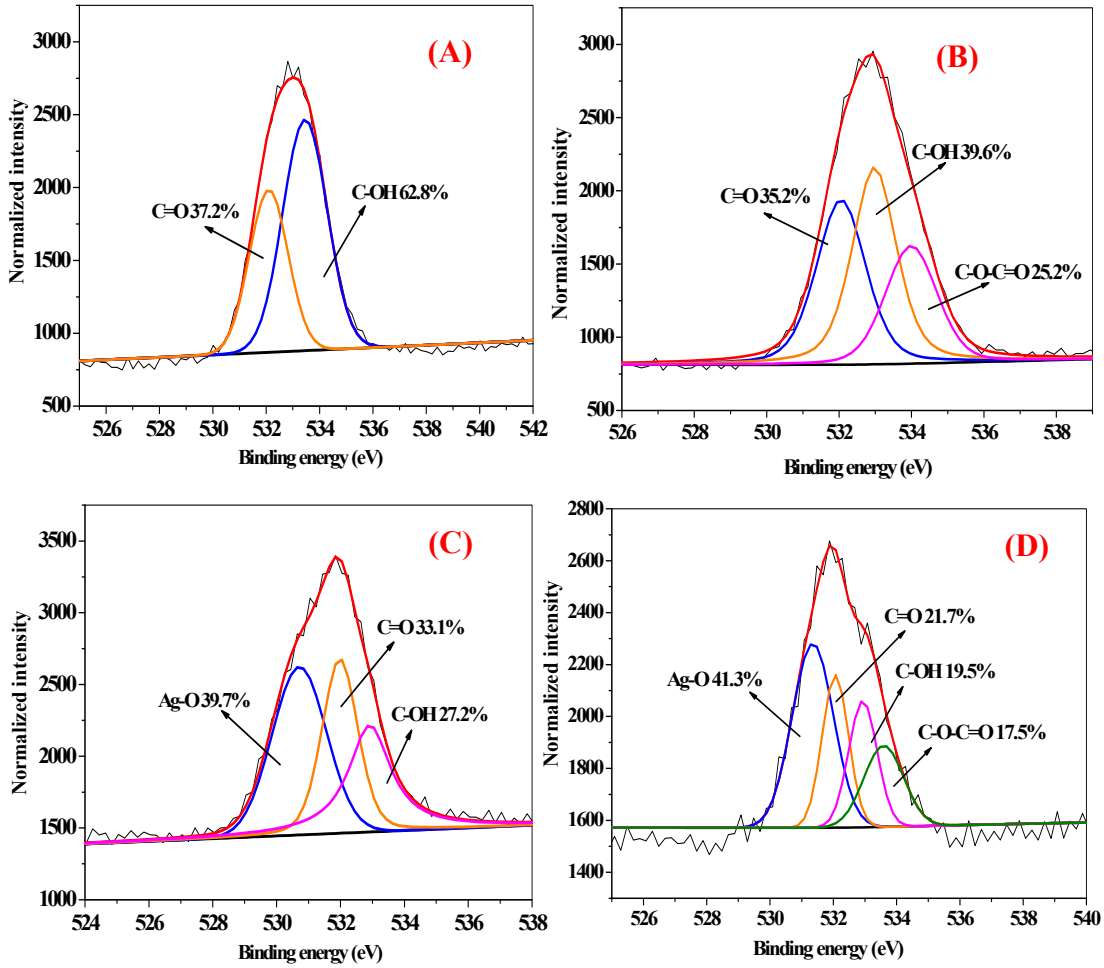

Fig. S3 Peak fitting of O1s spectra of (A) three layers of PDOPA films coated SPE bottle, (B) thiols/PDOPA coated (LBL three times) SPE bottle, (C) AgNPs/PDOPA coated (LBL three times) SPE bottle, and (D) thiols/AgNPs/PDOPA coated SPE bottle (LBL three times).

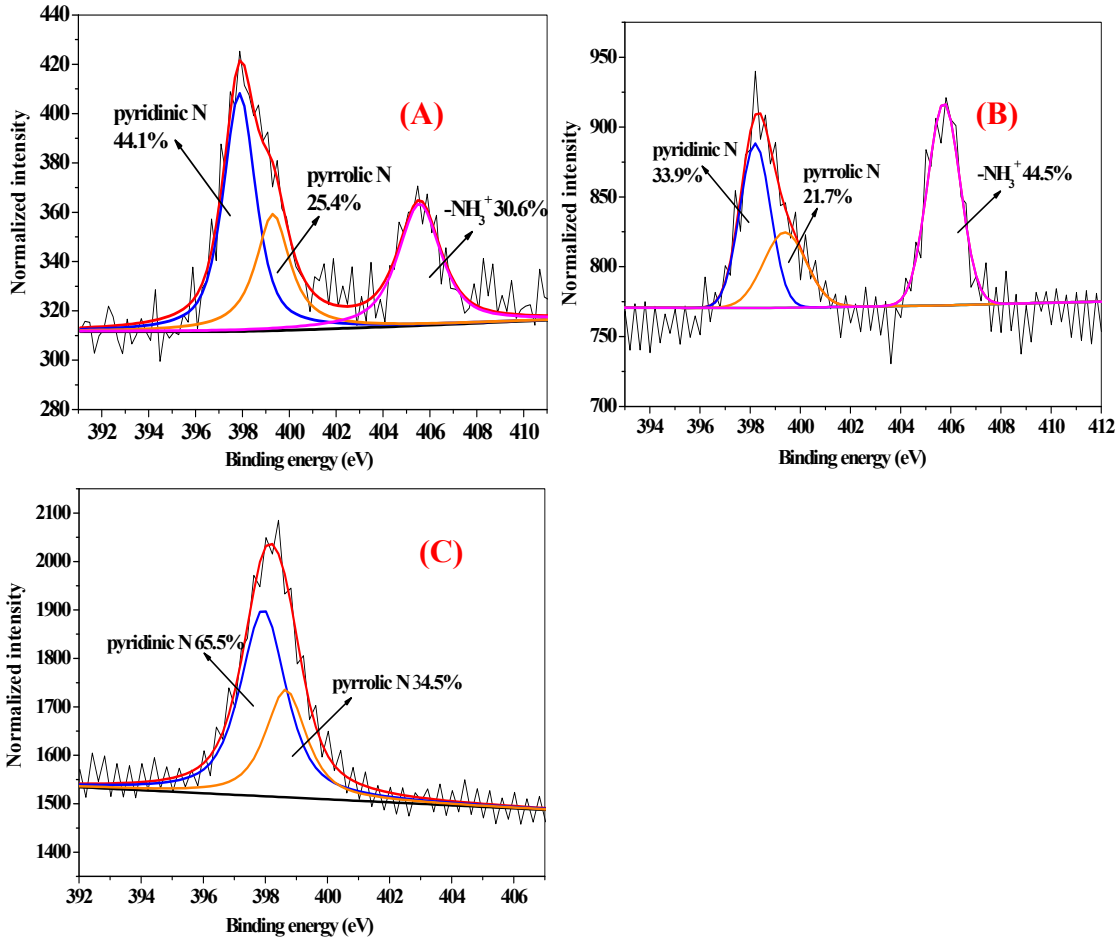

Fig. S4 Peak fitting of N1s spectra of (A) three layers of PDOPA films coated SPE bottle, (B) thiols/PDOPA coated (LBL three times) SPE bottle, and (C) AgNPs/PDOPA coated (LBL three times) SPE bottle.

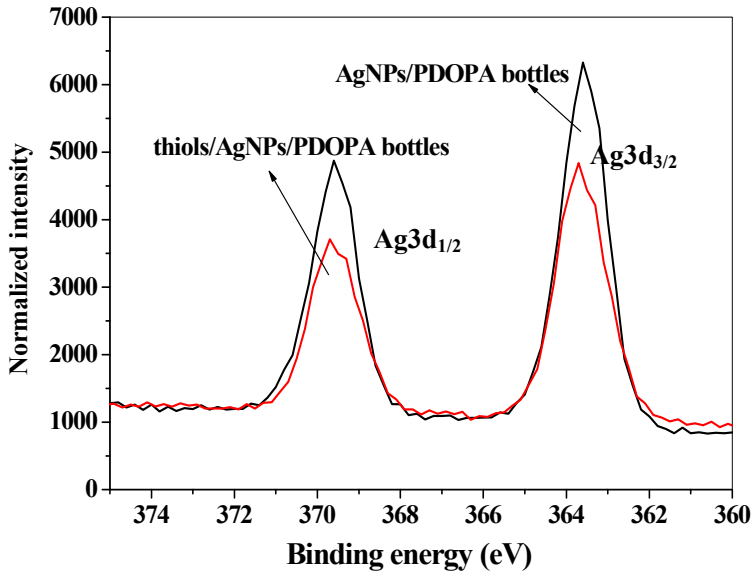

Fig. S5 Ag3d spectra of AgNPs/PDOPA (LBL three times) SPE bottle and thiols/AgNPs/PDOPA SPE bottle.

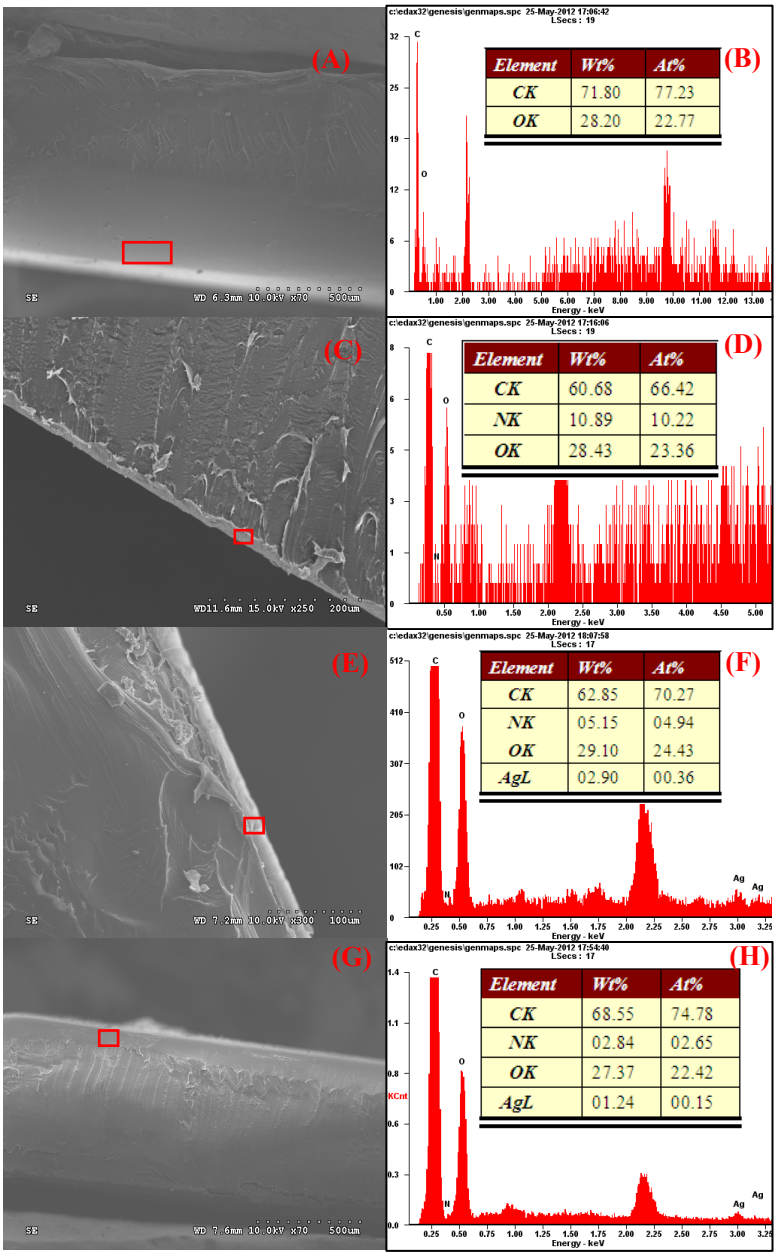

Fig. S6 SEM images of cross-section of (A) PET bottle, (C) one layer of PDOPA film coated bottles, (E) AgNPs/PDOPA coated (LBL one time) bottles, and (G) AgNPs/PDOPA coated (LBL twice) bottles; (B), (D), (F), (H) the corresponding EDX mapping and element composition of the marked section in each bottle sample.