Electronic Supplementary Information

Fast, Sensitive and Selective Simultaneous Determination of Paraquat and Glyphosate Herbicides in Water Samples Using a Compact Electrochemical Sensor

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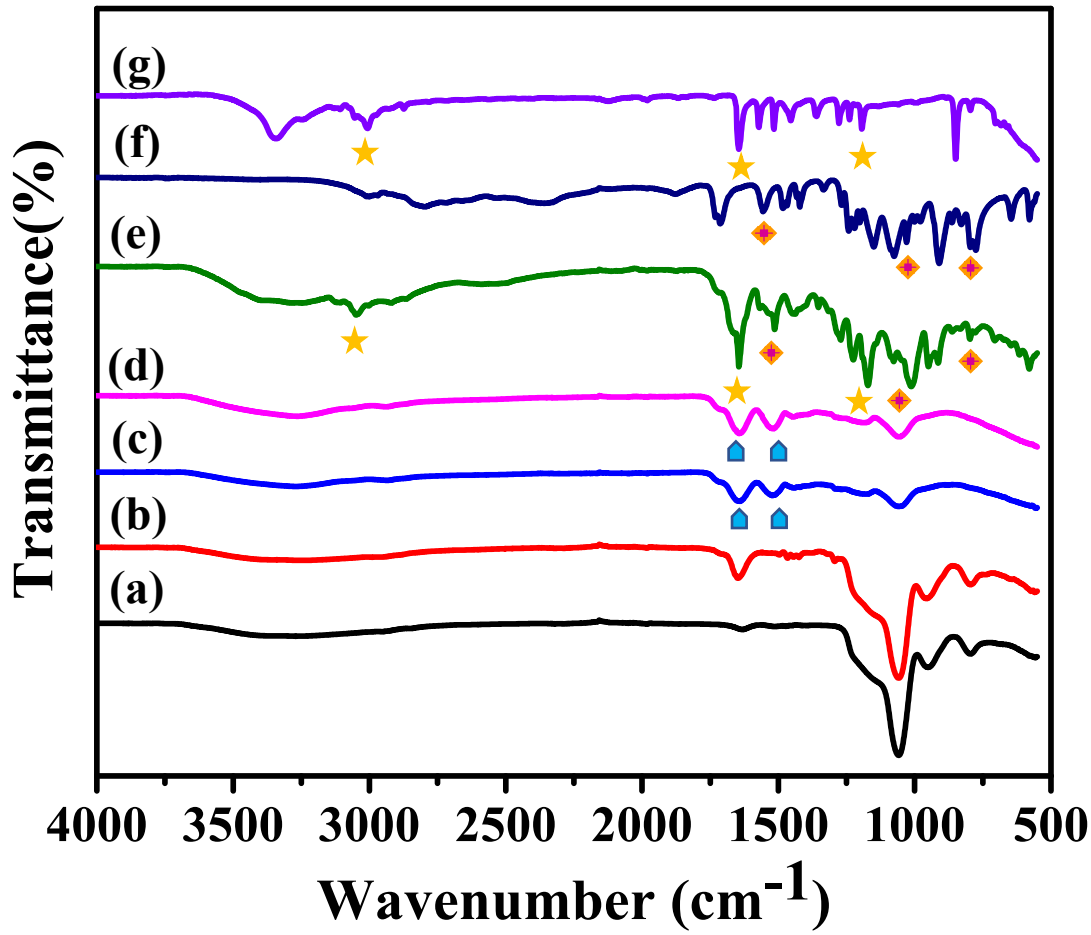

Fig. S1 FT-IR spectra (a) MSN, (b) MSN-PtNPs, (c) MSN-PtNPs@NIP, (d) MSN-PtNPs@d-MIP after template removal, (e) MSN-PtNPs@d-MIP before template removal, (f) GLY, and (g) PQ.

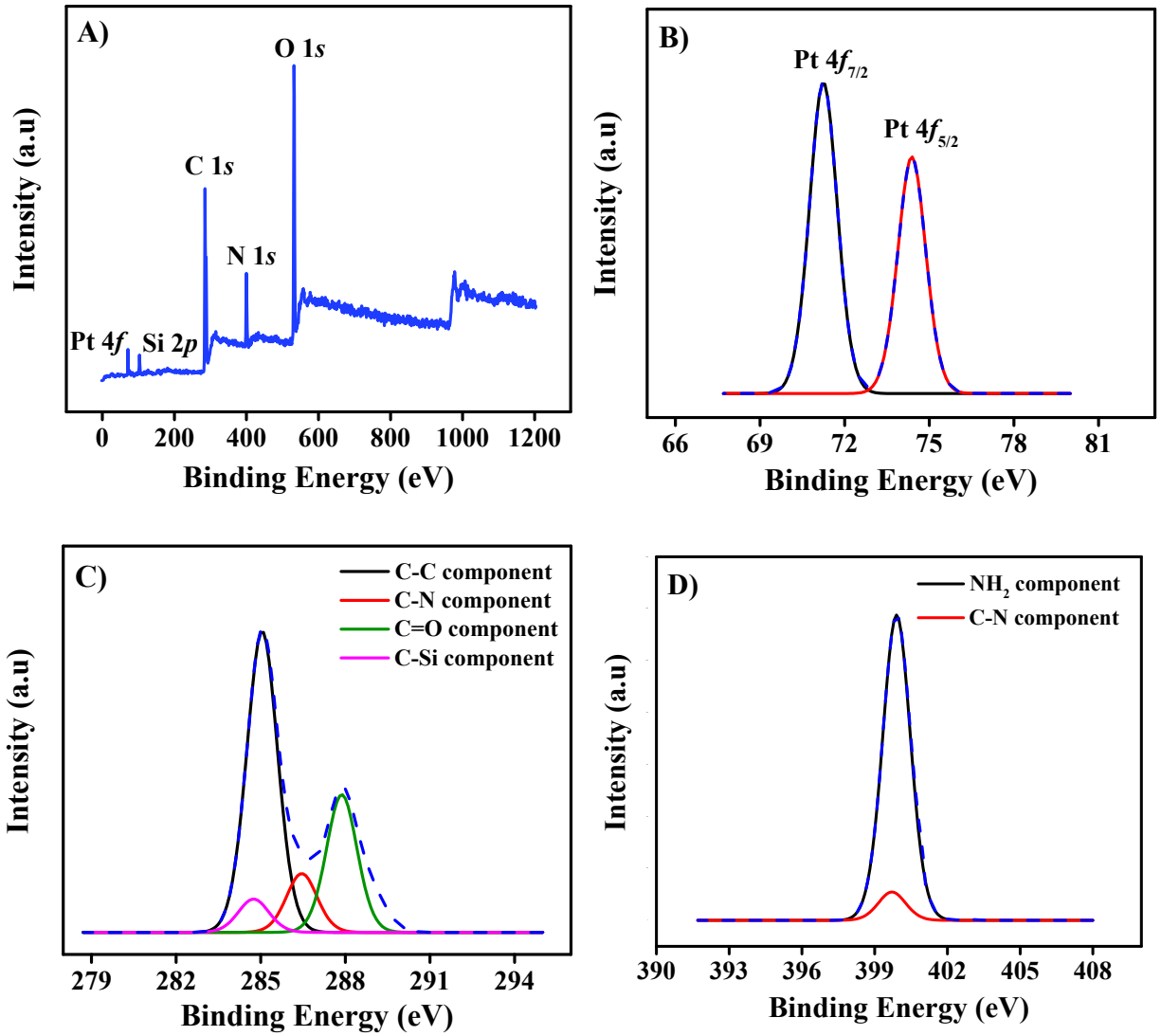

Fig. S2 XPS survey spectrum of (A) MSN-PtNPs@d-MIP, and core level spectra; (B) Pt 4f, (C) C 1s, and (D) N 1s.

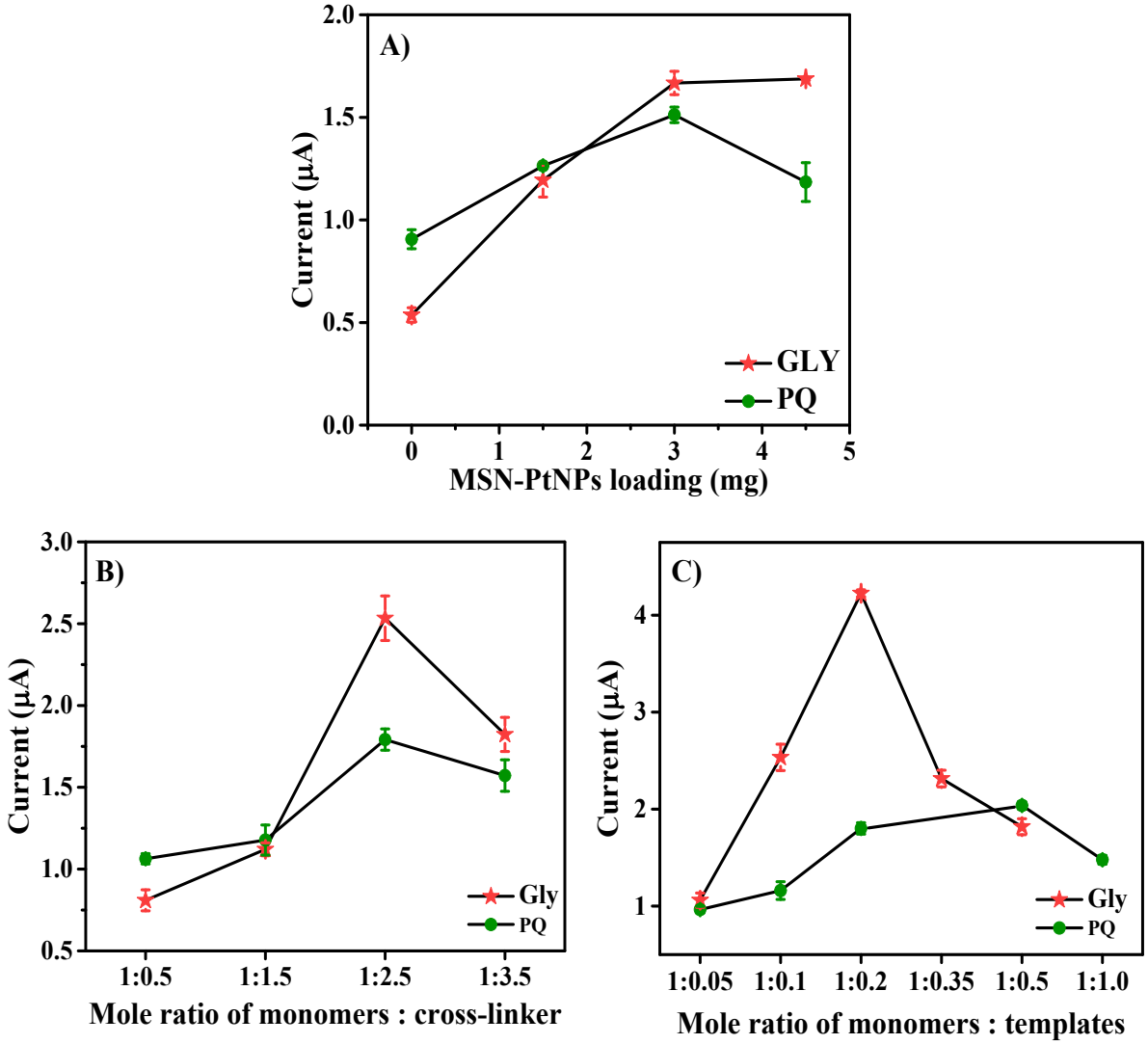

Fig. S3 Optimization conditions affecting the determination of PQ and GLY. Variation of electrode response of (A) MSN-PtNPs loading, (B) monomer : cross-linker mole ratio, and (C) monomer : template mole ratio and on the peak current of 100 µM PQ and GLY at the resulting MSN-PtNPs@d-MIP/GSPE in 0.1 M acetate buffer (pH 6); scan rate: 0.05 Vs^{-1}.

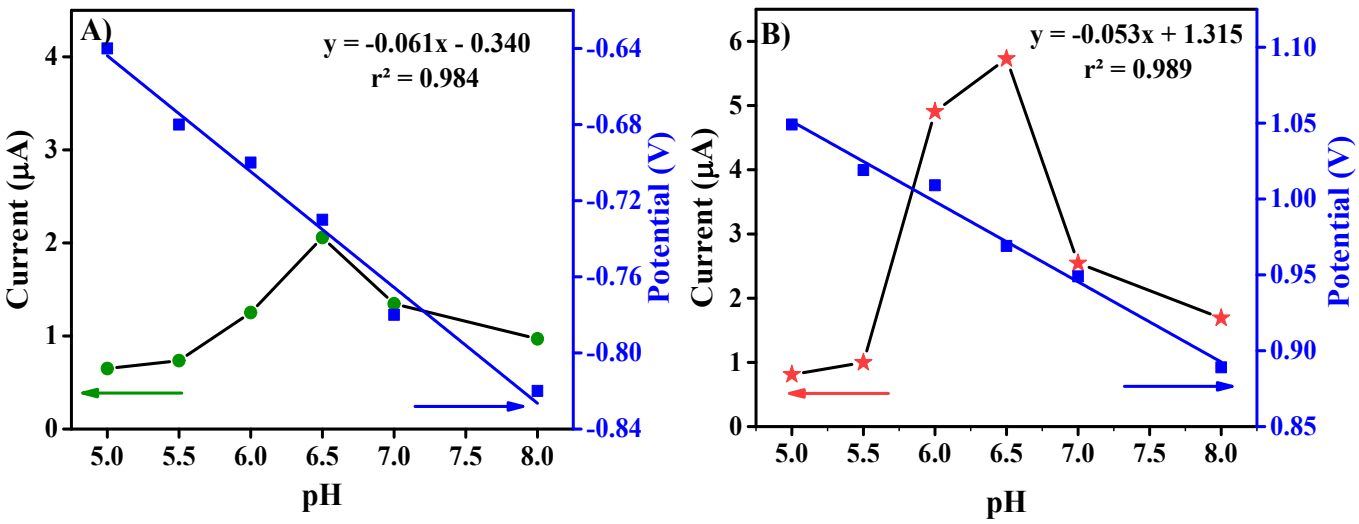

Fig. S4 Effect of solution pH obtained from the MSN-PtNPs@d-MIP/GSPE for determination of 100 µM (A) PQ and (B) GLY on peak currents ($I_{p,a}$) and peak potential ($E_{p,a}$); scan rate: 0.05 Vs^{-1}.

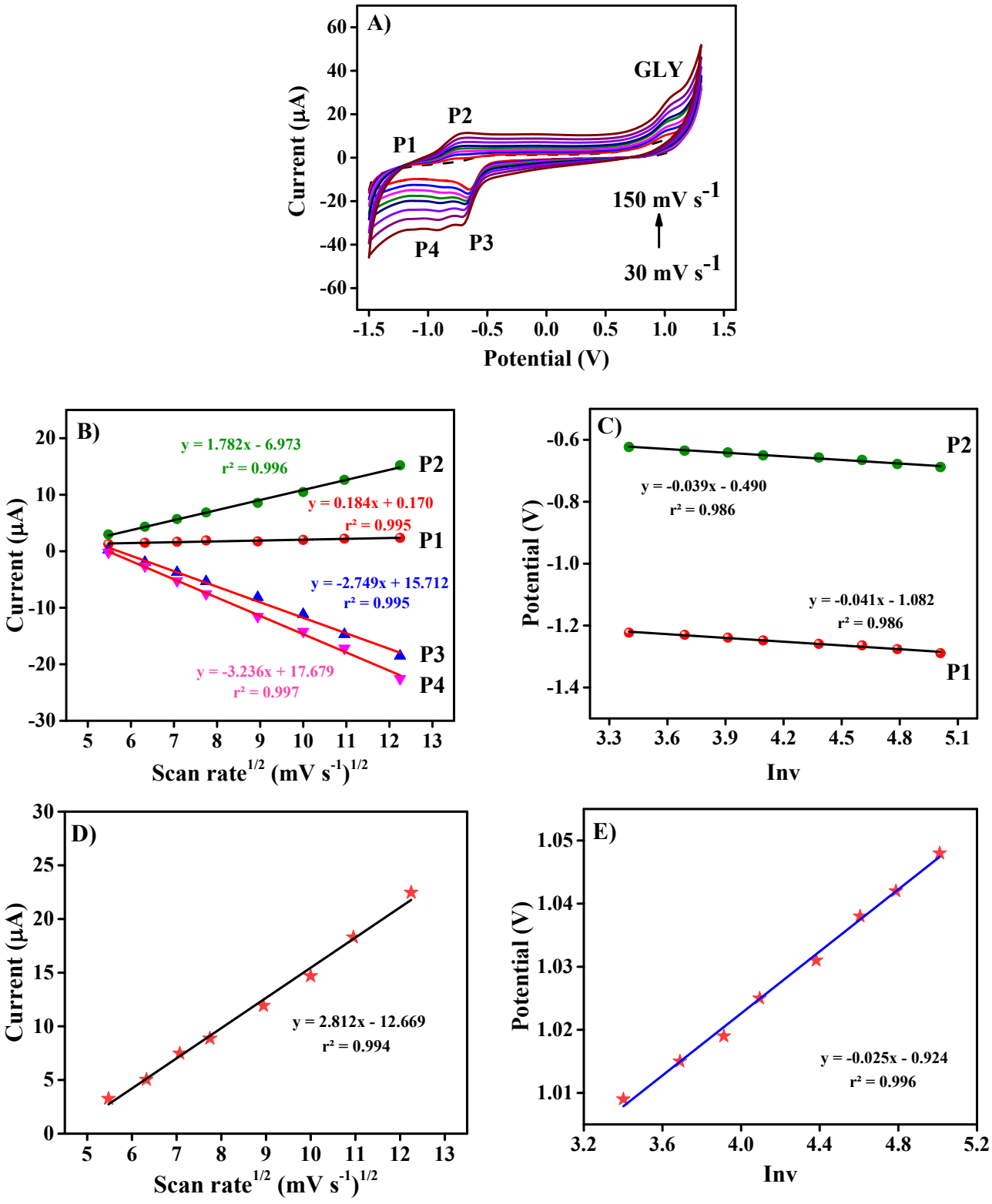

Fig. S5 (A) Influence of solution pH on peak current. In 0.1 M acetate containing 100 µM PQ and GLY; scan rate: 50 mV s^{-1}; the plot for peak currents ($I_{p,a}$) and peak potential ($E_{p,a}$) for PQ (B) and GLY (D), the plot for peak potential (Ep,a) and lnv for PQ (C) and GLY (E).

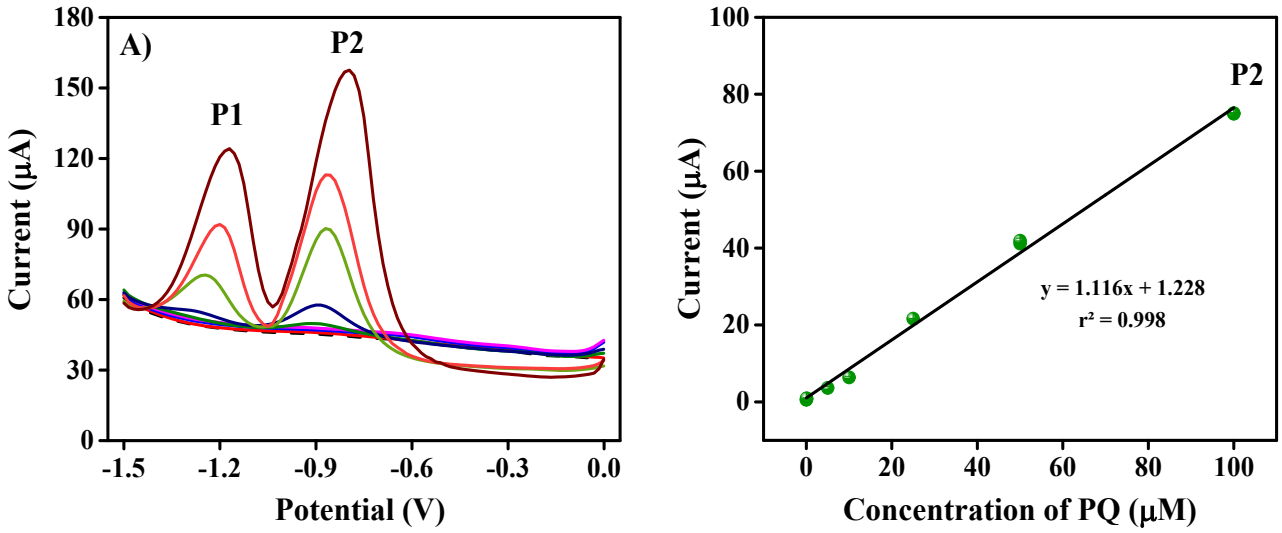

Fig. S6 (A) ASV of PQ and at MSN-PtNPs@d-MIP/GSPE, (B) The calibration curve for PQ concentration range 0.001 and 100 µM in 0.1 M sodium acetate buffer (pH 6.5); scan rate: 50 mV s^{-1} (under open circuit).

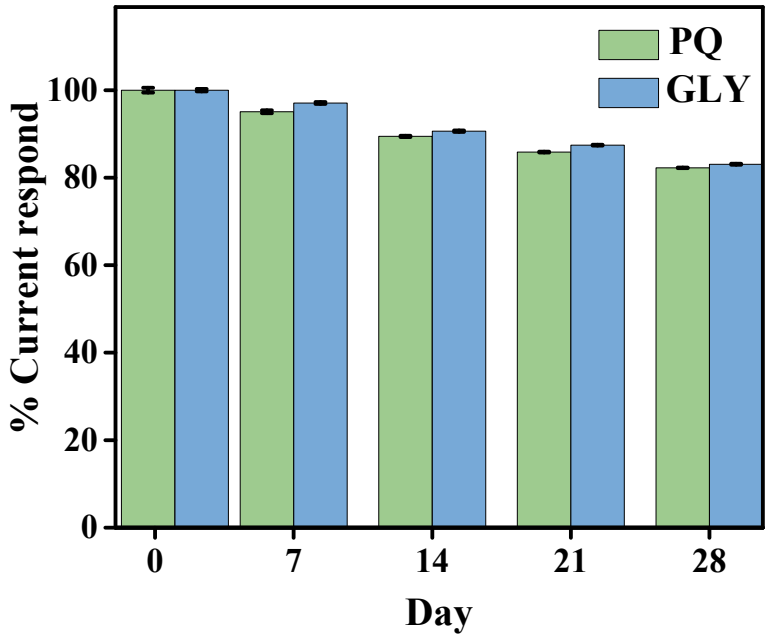

Fig. S7 The storage stability of the MSN-PtNPs@d-MIP/GSPE obtained from measuring the signal from 50 μM PQ and GLY at various intervals.

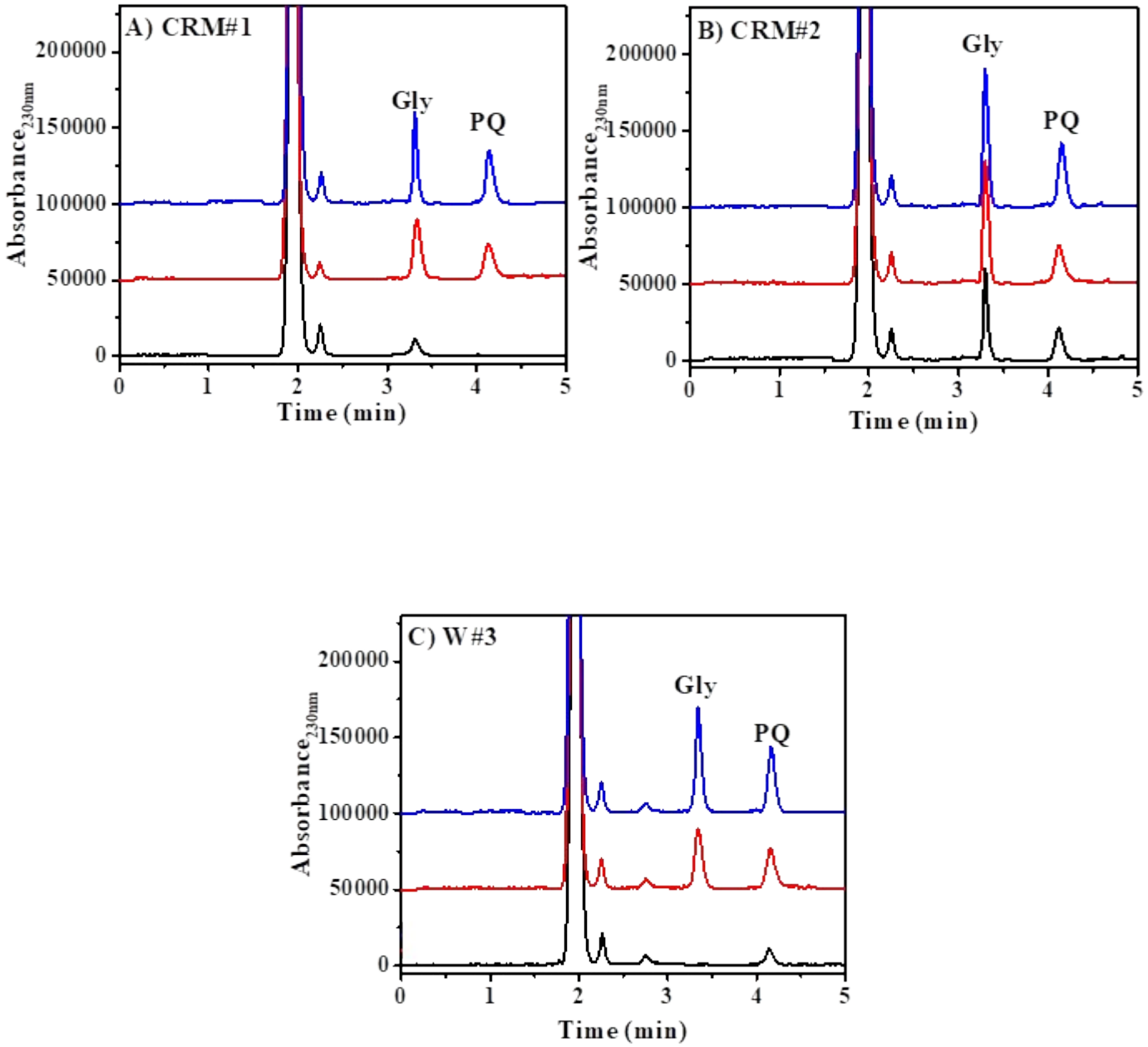

Fig. S8 Examples of the HPLC chromatograms of A) the CRM#1 sample (black line) and spiked CMR#1 sample (red and blue lines, 0.5 and 1.0 µM), B) CRM#2 sample (black line) and spiked CRM#2 samples (red and blue lines, 0.5 and 1.0 µM), and C) W#3 sample (black line) and spiked W#3 samples (red and blue lines, 0.5 and 1.0 µM). The separation was carried out under the following conditions: Inertsil ODS-3 (150 × 3.9 mm, 5 µm) separation column, isocratic elution with a mixture of 0.0125 M NaOH in water and 0.0125 M NaOH in methanol mobile phase, 1.0 mL min^{-1} flow rate, 20 µL injection volume, 230 nm absorbance detection, and column temperature of 25 °C.

Table S1 Comparison of PQ determination in certified reference materials (CRM #1 and CRM #2) and water samples (W#1-W#4) by using the proposed d-MIP sensor and the reference values obtained from HPLC.

Sample	Added (µM)	PQ				Relative error
		Our method			HPLC	
		Found (µM)	Recovery (%)	RSD (%)	Found (µM)	
CRM#1	0	-	-	-	-	-
	0.5	0.50	100.00	1.28	0.51	-1.96
	1.0	1.00	100.00	0.49	1.04	-3.85
CRM#2	0	0.25	-	3.79	0.26	-3.84
	0.5	0.75	100.00	0.42	0.76	-1.32
	1.0	1.25	100.00	0.59	1.27	-1.57
W#1	0	< LOD	-	-	< LOD	-
	0.5	0.50	100.00	1.11	0.48	+4.16
	1.0	1.01	101.00	0.29	1.03	-1.94
W#2	0	< LOD	-	-	< LOD	-
	0.5	0.51	102.00	0.53	0.50	+2.00
	1.0	1.07	107.00	2.57	1.10	-2.73
W#3	0	0.21	-	1.10	0.21	0.00
	0.5	0.71	100.00	1.01	0.72	-1.39
	1.0	1.23	102.00	1.82	1.22	+0.82
W#4	0	1.32	-	0.66	1.30	+1.54
	0.5	1.83	102.00	2.44	1.82	+0.55
	1.0	2.33	101.00	0.97	2.31	+0.87

CRM#1 = 44690-U, with the certified value of GLY 5914.600 ± 171.524 µM.
CRM#2 = QC1435-2ML, with the certified value of PQ 0.259 ± 0.003 µM, GLY 2.969 ± 0.030 µM.
W#1 and W#2 are water samples from reservoir and pond around the university,
W#3 is waste water sample from sewage pond, W#4 is synthetic waste water.
%Relative error = $([PQ]_{\text{Our method}} - [PQ]_{\text{HPLC}})/([PQ]_{\text{HPLC}})$ X 100