

Supporting Information

ZnFe₂O₄-catalyzed segment imprinted polymer on three-dimensional origami paper microfluidic chip for detection of microcystin

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materials

Microcystin-RR was purchased from Algalchem (Taiwan, China). methacrylic acid (MAA) was obtained from TCI (Shanghai, China). 2,2'-Azobis(2-methylpropionitrile) (AIBN) were purchased from Macklin (Shanghai, China), Ethylene Glycol dimethacrylate (EGDMA), was purchased from Sigma-Aldrich (Shanghai, China). 3,3',5,5'-tetramethylbenzidine (TMB) was supplied from Aladdin (Shanghai, China). Zinc oxide (ZnO), FeCl₃·6H₂O, L-Ascorbic acid, Hydrazine hydrate aqueous solution (85%, v/v%), methanol, acetonitrile, L-Arginine, H₂O₂ (30%, w/v), Glacial acetic acid (HAC), Sodium acetate anhydrous (NaAC), Ethanol and other affiliated materials were ordered from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All solvents, chemicals, and materials were of at least analytical pure grade. Whatman No.1 chromatography paper was acquired from GE Company (Shanghai, China) and used with further adjustment of size. Ultrapure water (18.2 MΩ specific resistance) was produced by a Pall Cascada laboratory water system (Millipore, Bedford, MA, USA).

Instrumentation

The chip was assisted by drawing software (Adobe Illustrator) and a XEROX Phaser 8560DN wax inkjet printer was implemented to pattern wax-based solid ink on the Whatman chromatography paper No. 1 paper, GE with a maximum resolution of 2400 dpi. After printing, the paper was maintained in an oven at 150 °C for 30 s to let the wax penetrate through the paper completely, forming a hydrophobic barrier. Modifications of the paper and materials were recorded by scanning electron microscopy (SEM; JSM 5600 LV). Fourier transform infrared spectroscopy (FT-IR) (thermoficolet, USA) was used to obtain the infrared spectra of the samples. Dynamic light scattering (DLS) size was measured on a Zetasizer NanoZS90 (Malvern Instruments, Malvern, U.K.). Images were collected by smartphone (OPPO R15, Guangdong OPPO Mobile Communication Co. Ltd, China). Use ImageJ software to process the collected images and detect the gray value.

Synthesis of ZnFe₂O₄

The preparation recipe of ZnFe₂O₄ was similar to previous research with small modifications¹. 0.12g ZnO, 0.485g FeCl₃·6H₂O and 0.265g ascorbic acid were dissolved 20 mL ultrapure water and uniformly mixed by ultrasonication for 30 s. Then 5 ml hydrazine hydrate was added into the above mixture to form a uniform dark solution and kept under magnetic stirring for about 20 min. Afterward, the mixed solution was transferred and sealed in a 50 ml Teflon-lined stainless steel autoclave, heated at 180 °C in an electric oven for 12 h, and then cooled to room temperature naturally. The black product isolated by centrifugation and washed with ultrapure water and ethanol, followed by vacuum drying at 60 °C for 6 h. Finally, ZnFe₂O₄ was obtained.

Synthesis of ZnFe₂O₄-Based SMIPs

Synthesis of SMIPs using previously reported methods². SMIPs were prepared via surface imprinting on the surface of ZnFe₂O₄ by using L-arginine as a pseudo-template. MAA, EGDMA, and AIBN were used as functional monomers, crosslinking agents and initiators, respectively. 2 mg ZnFe₂O₄ and 10 mg L-Arginine were dispersed into a mixed solution of 5 mL acetonitrile and 10 mL methanol and stirred for 30 min. Then 50 μL MAA added to the above mixture and kept stirring for 30 min in a 30 °C water bath under nitrogen protection to form pre-complex. Finally, 500 μL EGDMA and 10 mg AIBN dispersed in 500 μL methanol and added to the polymerization solution and maintained at 60 °C 12 hours. The synthesized product was eluted with methanol/acetic acid three times to remove the template completely. NIPs were synthesized in the same way without the addition of L-Arginine.

Fabrication of μPADs

The Paper-based colorimetric chip design was implemented by drawing Freehand software. The reaction area was a circle with a diameter of 6 mm, and the rest part was a wax hydrophobic barrier which was directly printed onto the filter paper by a wax printer. The wax pattern paper was put into the oven at 150 °C for 30 s. This process allowed the wax to penetrate through the whole paper completely and form hydrophobic barriers.

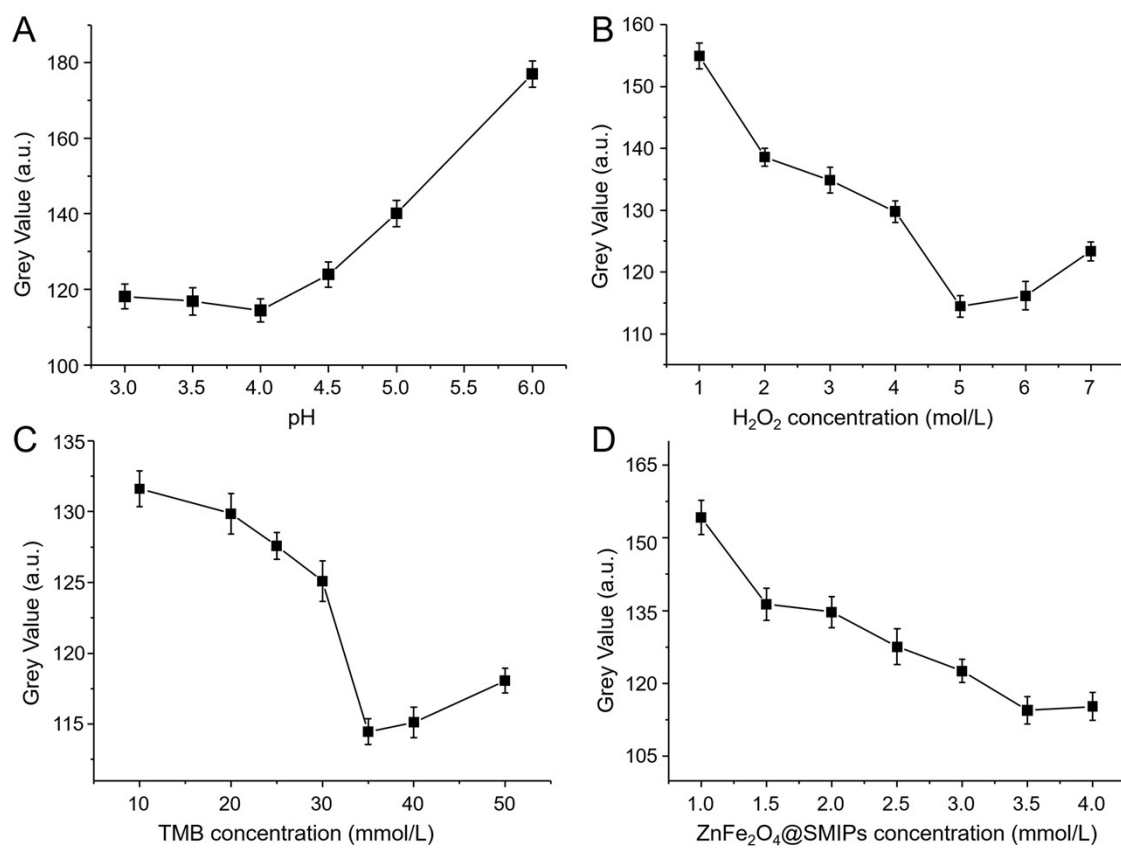


Fig S1. (A) The influence of pH on gray value. (B) The influence of H₂O₂ concentration on gray value. (C) The influence of TMB concentration on gray value. (D) The influence of ZnFe₂O₄@SMIPs concentration on gray value.

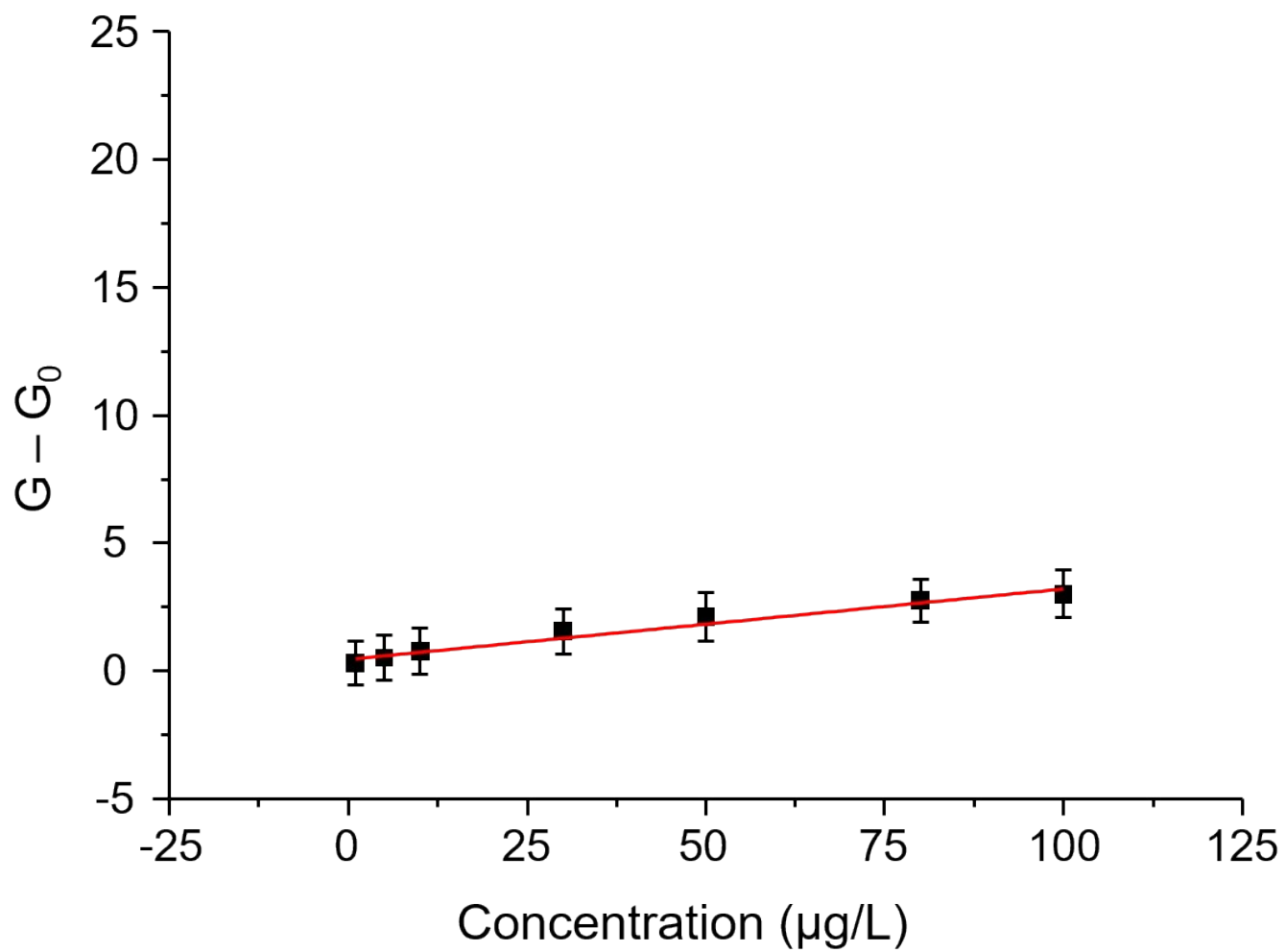


Fig S2. Response curves of NIPs μPADs to different concentrations of MC-RR.

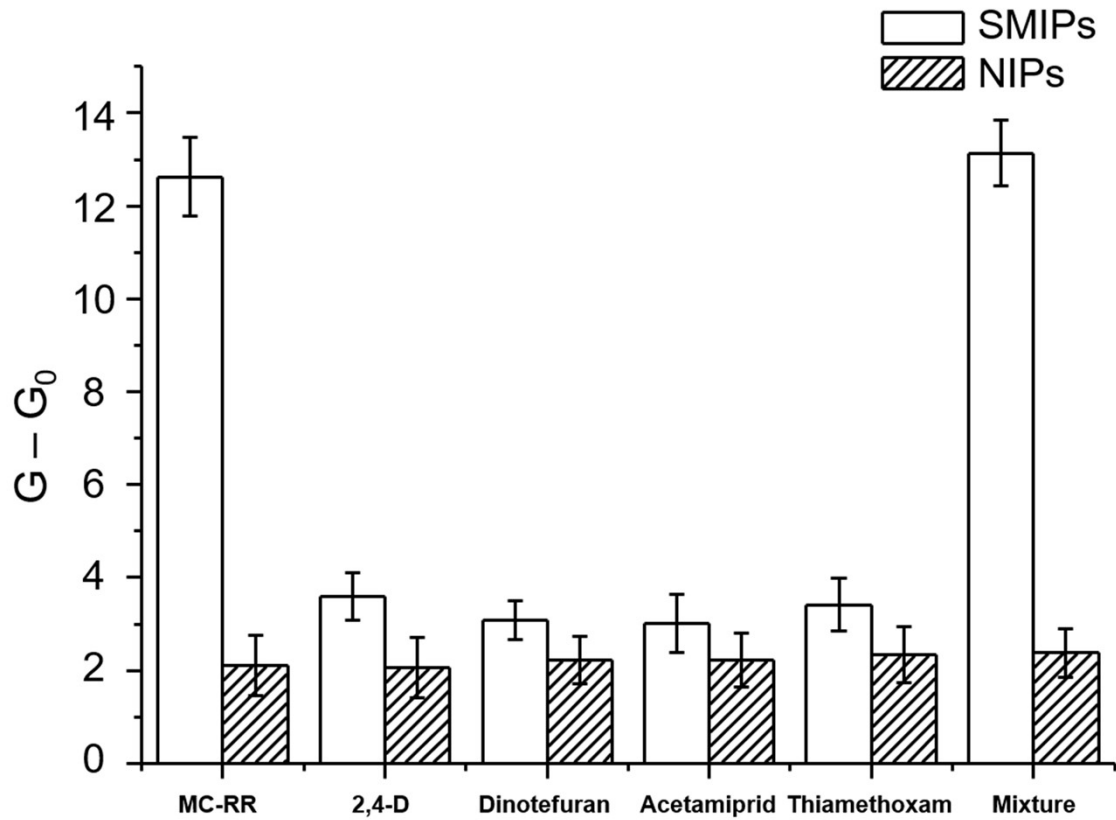


Fig S3. Selectivity of $ZnFe_2O_4@$ SMIPs μ PADs and NIPs μ PADs for solutions of different interfering molecules (2,4-Dichlorophenoxyacetic acid, dinotefuran, acetamiprid, thiamethoxam and mixture of interfering molecules). The concentration of MC-RR and other interference were $50 \mu\text{g/L}$

Table S1. The gray value data of ZnFe₂O₄@SMIPs μ PADs under different time and MC-RR concentration.

	0	1 μ g/L	5 μ g/L	10 μ g/L	30 μ g/L	50 μ g/L	80 μ g/L	100 μ g/L
2 min	117.63	118.55	118.72	119.49	121.83	123.06	124.51	126.05
4 min	112.90	114.80	114.75	116.17	118.76	120.39	121.49	124.20
6 min	109.37	111.18	111.97	114.18	116.26	118.47	121.05	122.29
8 min	105.29	107.23	109.59	110.82	114.31	116.22	118.61	121.06
10 min	103.50	105.19	108.08	109.63	111.35	114.96	117.18	119.68
12 min	101.55	103.02	105.49	107.45	110.19	111.96	115.18	117.24
14 min	101.18	102.13	104.13	105.71	108.64	110.73	113.59	115.89
16 min	99.83	101.30	102.75	104.04	107.93	109.26	111.91	114.03
18 min	100.22	100.83	102.79	103.14	106.67	108.15	110.77	113.83
20 min	98.85	101.90	103.00	102.97	105.78	107.72	109.13	112.99

Table S2 The difference value data between ZnFe₂O₄@SMIPs μ PADs and blank group at different time and MC-RR concentration.

	1 μ g/L	5 μ g/L	10 μ g/L	30 μ g/L	50 μ g/L	80 μ g/L	100 μ g/L
2 min	0.92	1.09	1.86	4.19	5.43	6.88	8.42
4 min	1.90	1.85	3.27	5.86	7.49	8.59	11.30
6 min	1.81	2.60	4.81	6.89	9.10	11.67	12.91
8 min	1.94	4.29	5.53	9.02	10.92	13.32	15.77
10 min	1.69	4.58	6.14	7.85	11.46	13.68	16.18
12 min	1.48	3.95	5.90	8.65	10.41	13.64	15.70
14 min	0.95	2.95	4.53	7.46	9.55	12.41	14.71
16 min	1.47	2.92	4.21	8.10	9.43	12.08	14.21
18 min	0.61	2.57	2.92	6.45	7.93	10.55	13.62
20 min	3.05	4.15	4.12	6.93	8.87	10.29	14.14

Table S3 Recovery of spiked MC-RR in lake, river and sea water detected using ZnFe₂O₄-Based SMIPs μ PADs (n=5)

Sample	Added	Founded	Recovery \pm RSDs
	MC-RR (μ g/L)	MC-RR (μ g/L)	MC-RR (%)
Sanyuan Lake	0	0	-
	10	9.84	98.4 \pm 5.0
	50	52.48	105.0 \pm 4.0
	80	75.88	94.9 \pm 3.9
Fenghuang Lake	0	0	-
	10	10.46	104.6 \pm 4.0
	50	49.27	98.6 \pm 4.0
	80	81.88	102.4 \pm 1.3
Guangdang River	0	0	-
	10	10.53	105.3 \pm 5.8
	50	51.34	102.7 \pm 4.9
	80	80.50	100.6 \pm 6.8
Yellow Sea	0	0	-
	10	10.41	104.2 \pm 5.3
	50	51.54	103.1 \pm 4.5
	80	77.26	96.6 \pm 2.8

Table S4 Performance comparison with other reported methods for MC-RR sensing.

System	Detected method	Analytical ranges ($\mu\text{g/L}$)	LODs ($\mu\text{g/L}$)	References
MC-LR-ovalbumin	Immunoassay	0.1–10.1	0.03	3
MC-LR-SWNHs/GCE	Electrochemical assay	0.05–20	0.03	4
Vesicle–antibody conjugates	Colorimetric assay	1-100	1	5
ZnFe ₂ O ₄ @SMIPs μ PADs	Colorimetric assay	1-100	0.44	This work

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