Electronic Supplementary Information

Visible light-driven self-powered aptasensor for ultrasensitive Microcystin-LR detection based on the carrier density effect of N-doped graphene hydrogel/hematite Schottky junction

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Contents.

Materials and reagents

Concentrated sulfuric acid (H_2SO_4), potassium nitrate (KNO_3), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), dimethylformamide (DMF), hydrochloric acid (HCl), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), glycine and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Natural flake graphite was obtained from Tsingtao Longyuan Carbon Materials Co., Ltd. The MC-LR was achieved from Enzo Life Sciences, Inc. and its aptamer was gained from Sangon Biotech Co., Ltd., with the following sequence: 5'−GGC GCC AAA CAG GAC CAC CAT GAC AAT TAC CCA TAC CAC CTC ATT ATG CCC CAT CTC CGC −3'.

Synthesis of Graphite Oxide (GO)

A modified Hummers method was used to prepare GO in this experiment.[1] Briefly, flake graphite (5 g) and $NaNO_3$ (3 g) were put into a flask, and concentrated H_2SO_4 (120 mL, 98%) was added under stirring in an ice bath. $KMnO_4$ (22.5 g) was slowly added to the above mixture over 1 h and followed by continuously stirring at 23℃ for 2 h. Then H_2SO_4 aqueous solution (700 mL, 5 wt %) was slowly added under stirring, and the temperature was kept at 98℃. When the temperature was decreased to 60℃, H_2O_2 aqueous solution (15 mL, 30 wt %) was added. The product was washed with HCl solution (5 wt %) and distilled water several times and freeze-dried.

Synthesis of different nitrogen content NGH/Fe_2O_3

To further studied the effect of nitrogen content on porosity and photoelectricity, the as-synthesized NGH/Fe_2O_3 samples with different glycine mass of 0 mg, 100 mg, 200 mg, and 300 mg were prepared in the meanwhile with the same method. (Among these, the sample with 0 mg glycine was marked as G-Fe_2O_3.)

Results and discussion

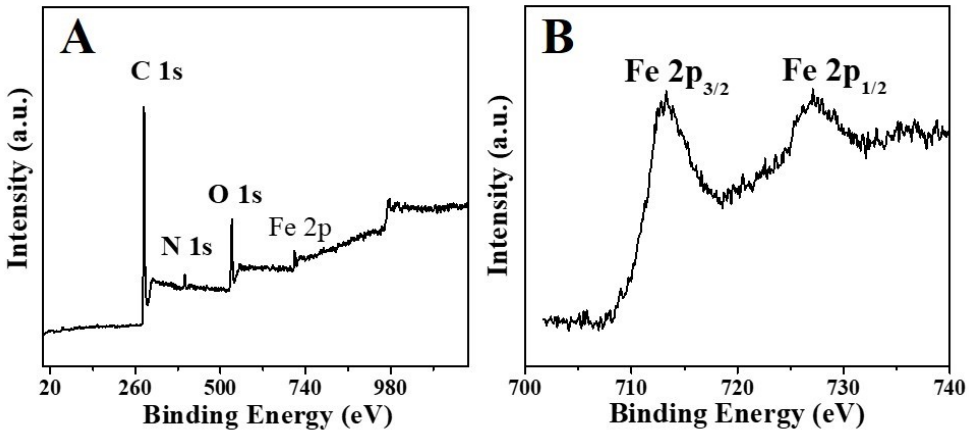

Fig. S1. XPS survey patterns of NGH/Fe_2O_3 (A) and high-resolution spectra of the Fe 2p in NGH/Fe_2O_3 (B).

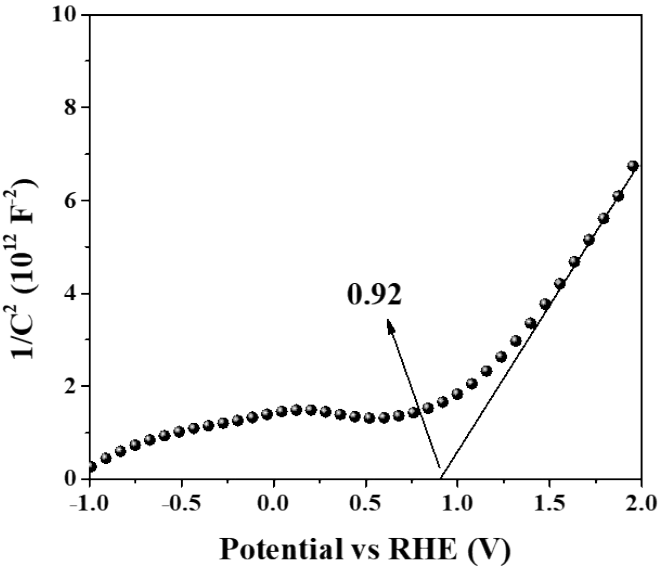

Fig. S2. Mott-Schottky plot of pure Fe_2O_3.

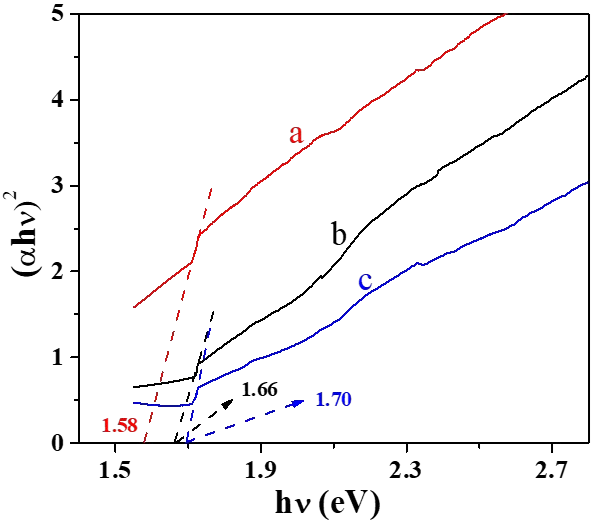

Fig. S3. Tauc plots showing $(\alpha h\nu)^2$ versus $h\nu$ curves of (a) NGH/Fe_2O_3, (b) G/Fe_2O_3 and (c) Fe_2O_3.

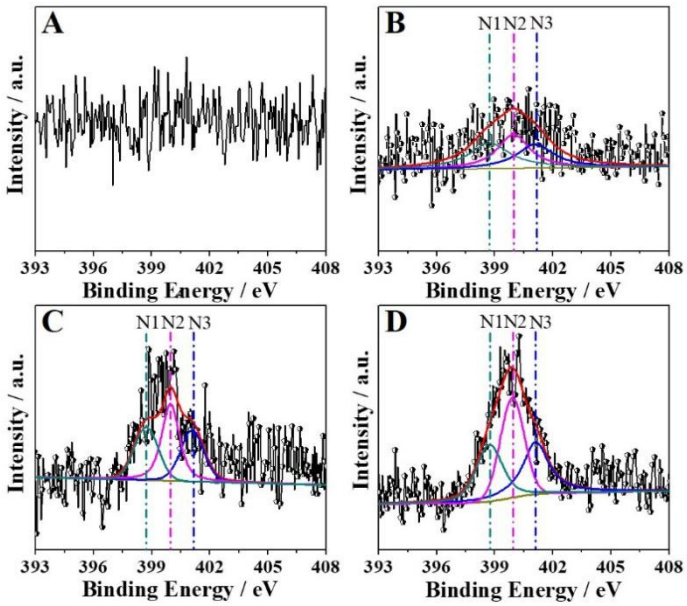

Fig. S4. XPS patterns of NGH/Fe_2O_3 with different glycine: (A) 0 mg, (B) 100 mg, (C) 200 mg, and (D) 300 mg.

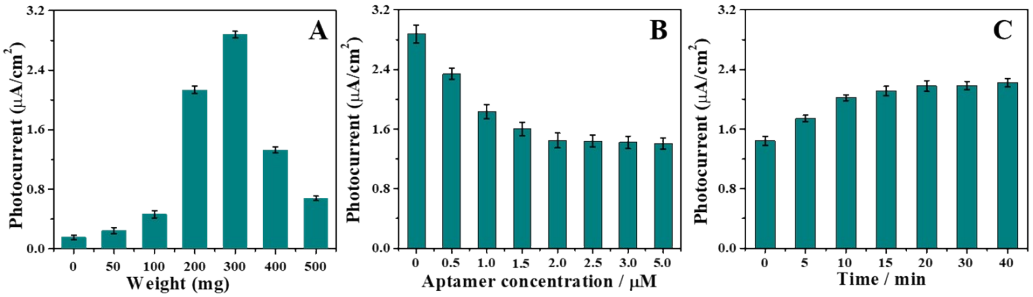

Fig. S5. Photocurrents of NGH/Fe_2O_3 with different (A) glycine additions (B) aptamer concentrations and (C) incubation time.

Table S1. Comparison of different methods for the determination of MC-LR

Method	Linear range (nM)	Detection limit(nM)	Ref.
Protein phosphatase inhibition	0.93 ~ 40.51	0.93	2
Fluorescent aptasensor	0.4 ~ 1200	0.138	3
Colorimetric sensor	0.5 ~ 7500	0.37	4
PEC immunoassay	0.005 ~ 503	0.001	5
PEC immunoassay	0.01 ~ 10	0.055	6
PEC aptasensor	0.001 ~ 5	0.23×10^{-3}	This work

References

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