Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

One-step electrodeposition of MWCNTs-Cu MOFs film for the ratiometric electrochemical analysis of glyphosate

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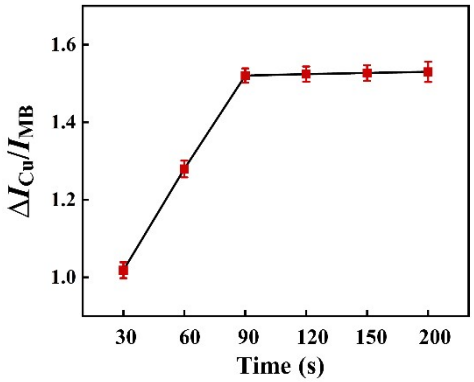

Fig. S1. The relationship between value of $\Delta I_{Cu}/I_{MB}$ and reaction time obtained at GC/MWCNTs-Cu MOFs/MB electrode in 0.1 M PBS solution (pH=7.0) containing 40 mM Cl^- in the presence of 10 nM GLYP.

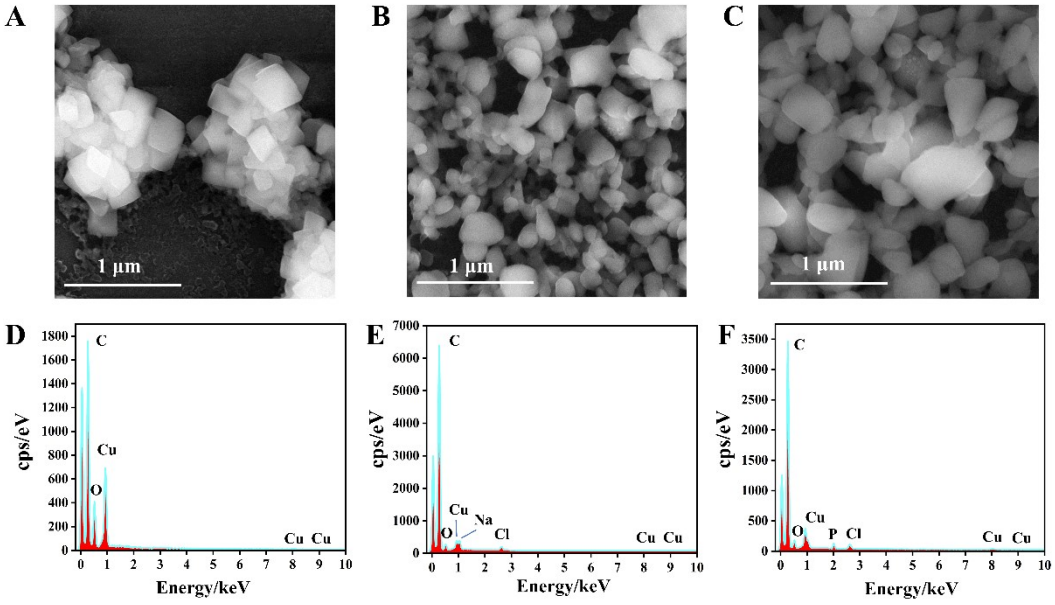

Fig. S2. SEM images and the corresponding EDX of (A, D) GCE/MWCNTs-Cu MOFs with the addition of (B, E) Cl^- and then adding of (C, F) GLYP.

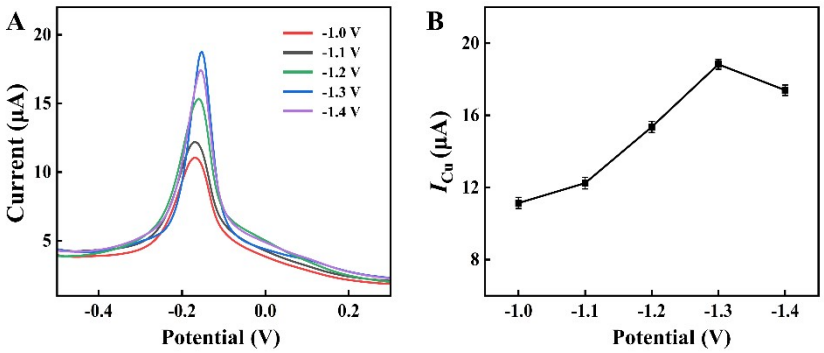

Fig. S3. (A) DPVs of GC/MWCNTs-Cu MOFs modified electrode in 0.1 M PBS (pH=7.0) containing 40 mM Cl^- under different electrodeposition potentials. (B) The impact of deposition potential on the oxidation peak current of I_{Cu}.

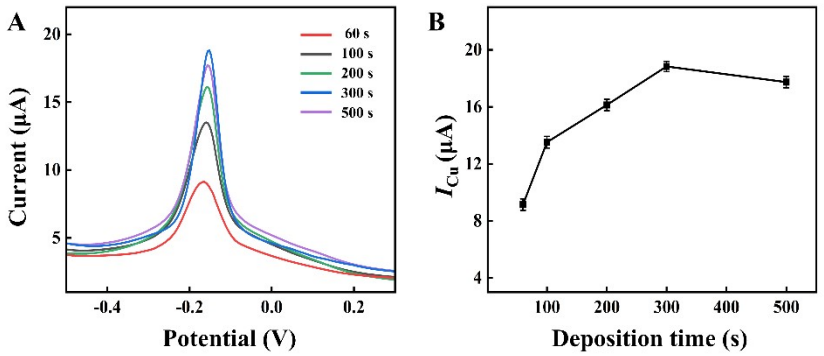

Fig. S4. (A) DPVs obtained at GC/MWCNTs-Cu MOFs modified electrode in 0.1 M PBS (pH=7.0) containing 40 mM Cl^- under different deposition times. (B) The impact of deposition time on the oxidation peak current of I_{Cu}.

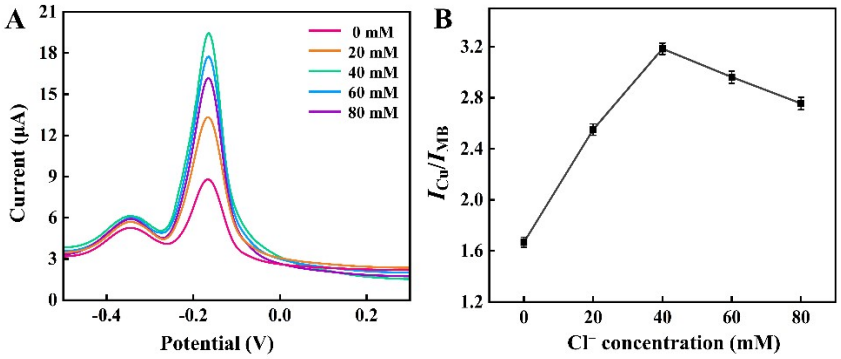

Fig. S5. (A) DPVs of GC/MWCNTs-Cu MOFs/MB electrode in 0.1 M PBS (pH=7.0) containing different Cl^- concentration of 0 mM, 20 mM, 40 mM, 60 mM, and 80 mM, respectively. (B) The impact of Cl^- concentration on the oxidation peak current ratio of I_{Cu}/I_{MB}.

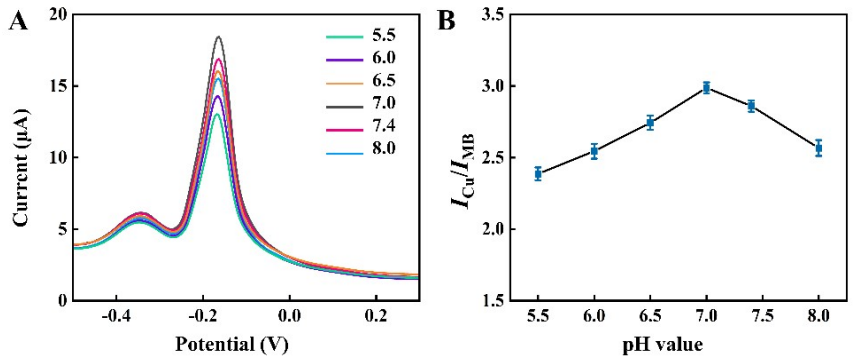

Fig. S6. (A) DPVs of GC/MWCNTs-Cu MOFs/MB electrode in 0.1 M PBS with different pH values. (B) The effect of pH value on the peak current ratio of I_{Cu}/I_{MB}.

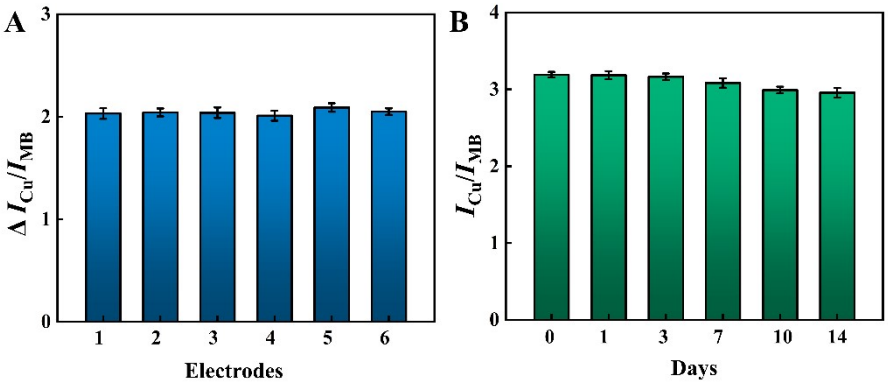

Fig. S7. (A) DPV responses of different GC/MWCNTs-Cu MOFs/MB electrodes towards 50 nM GLYP in 0.1 M PBS (pH=7.0) containing 40 mM Cl^-. (B) Stability test for GC/MWCNTs-Cu MOFs/MB.

Table S1. Comparison of analytical performance of different electrochemical methods for the detection of GLYP.

Methods	Linear range (mol L^{-1})	LOD (mol L^{-1})	Reference
Nanoporous copper (NPC)	$3.0 \times 10^{-8} – 6.5 \times 10^{-8}$	3.0×10^{-9}	[1]
Cu-TCPP/AuNPs/CP	$0.2 \times 10^{-6} – 1.2 \times 10^{-4}$	0.3×10^{-7}	[2]
MIPNs-based electrochemical sensor	$2.5 \times 10^{-6} – 3.5 \times 10^{-4}$	1.9×10^{-6}	[3]
graphite oxide paste electrode (GrO-PE)	$1.8 \times 10^{-5} – 1.2 \times 10^{-3}$	1.7×10^{-8}	[4]
CuAl–LDH/Gr NC	$2.96 \times 10^{-9} – 1.18 \times 10^{-6}$	1.0×10^{-9}	[5]
GC/MWCNTs-Cu MOFs/MB	$0.5 \times 10^{-9} – 4.0 \times 10^{-7}$	1.4×10^{-11}	This work

Table S2. Standard methods for GLYP analysis.

Method	Derivatization reagent	Sample preparation	Conditions	Linear range	LOD	Reference
LC-ESI-MS/MS	FMOC-Cl	SPE	2.0×50 mm I.D., Discovery®C18 MP：5 mM HAc/NH4Ac (pH 4.8)-ACN Flowrate: 1.0 mL/min	25-5000 ng/L	5 ng/g	[6]
LC- ESI-MS/MS	FMOC-Cl	SPE	2.0×30 mm I.D., XBridgeTM Premier BEH C18 MP: 5mM water buffered ammonium acetate (pH 9.0) -MeOH Flowrate: 0.2 mL/min	0.5-500 ng/L	0.2 ng/L	[7]
HPLC-FL	FMOC-Cl	−	4.6×150 mm I.D., ZORBAX SB-C18 MP: 5mmol/L ammonium acetate, pH 9.0 and MeOH Flowrate: 1.0 mL/min	0.8-10 μg/L 10-160 μg/L 160-6000 μg/L	0.24 μg/L	[8]
LC-MS/MS	−	SPE	3.0×100 mm I.D., Acclaim™ Trinity Q1 MP: 100 % water (A) and 100 % ammoniumformate/formic acid buffer (B) Flowrate: 0.7 mL/min	10-1000 ng/mL	19 ng/g	[9]
UHPLC-MS/MS	FMOC-Cl	QuEChERS	2.1×150 mm I.D., AccucoreTM aQ C18 Thermo Scientific MP: 95 % H_2O, 5 % MeOH, 5 mM NH_4HCO_2, 0.1 % CH_2O_2 (A); 95 % MeOH, 5 % H_2O, 5 mM NH_4HCO_2, 0.1 % CH_2O_2 (B) Flowrate: 0.3 mL/min	0.025-10 μg/L	0.025 μg/L	[10]

Reference

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