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Supplementary data

Electrochemically functionalized graphene for highly sensitive detection of nitrofurazone

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Table S1. The ratios of different functional groups.

Sample	C-C%	-OH%	-COC%	-C=O%	O%
GS/GCE	74.58	15.27	5.33	4.82	25.42
EGS-1.0/GCE	54.14	31.16	7.16	7.54	45.86
EGS-1.4/GCE	40.75	43.25	8.07	7.92	59.25
EGS-1.6/GCE	39.34	30.63	16.43	13.60	60.66

Table S2. The fitting parameters of the Randles equivalent circuits of GCE, GCE-1.4, GS and EGS-1.4

Sample	R_e (Ω)	R_{ct}(kΩ)	C_{dl} (F)	Z_w (Ω)		
				W-R	W-P	W-T
GCE	177.0	70.26	2.95×10^{-7}	99963	0.50	0.30
GCE-1.4	180.1	60.26	1.56×10^{-6}	77770	0.50	0.67
GS	341.6	26.66	8.98×10^{-6}	66933	0.50	10.64
EGS-1.4	480.4	9.03	3.63×10^{-6}	39532	0.50	1.95

R_e: solution resistance; R_{ct}: charge transferred resistance; Z_w: Warburg impedance element; W-R: coefficient of Warburg impedance; W-P is fixed as 0.5; W-T: the diffusion interpretation.

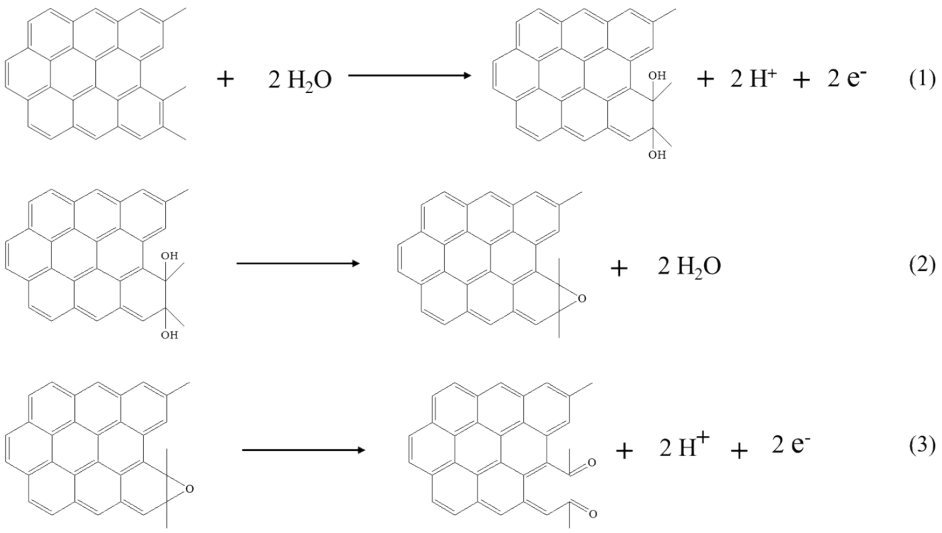
Table S3. The comparison of electrochemical sensors for NFZ

Sensing material	Detection signal	Linear range (μM)	Detection limit (nM)	Ref
DUT-67/T-PPY-2[a]	reduction	9.08-354.08	8.7	1
Polyfurfural/rGO[b]	reduction	1-50	25	2
dsDNA[c]	reduction	2.5-37.5	80	3
PACBK[d]	reduction	0.2-15.0	28	4
CMWCNTs[e]	reduction	1.0-5000	64.5	5
Hollow MIL-101[f]	oxidation	0.030-55	10	6
EGS-1.4/GCE	oxidation	0.01-0.8	2.1	This work

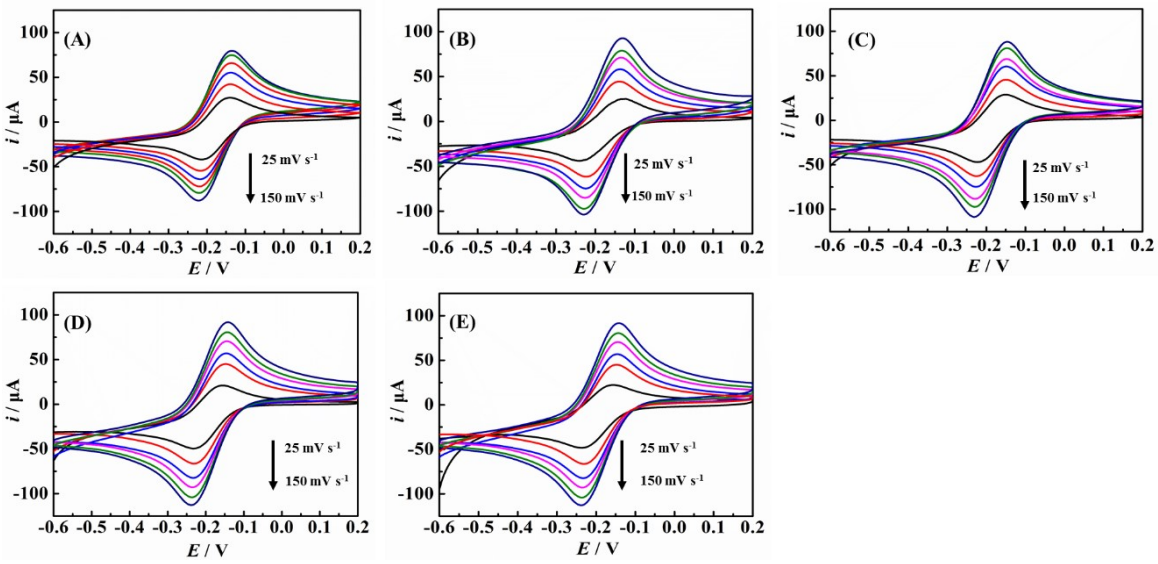
[a] DUT-67/T-PPY-2: Zirconium-based mental organic frameworks/tubular poly pyrrole;

[b] rGO : reduced graphene oxide; [c] dsDNA: double-stranded calf thymus DNA;
[d] PACBK: poly(acid chrome blue K); [e] CMWCNTs: carboxyl multi-walled carbon

nanotubes; [f] MIL-101: chromium(III) terephthalate MOF.



Scheme S1. The probable mechanism for the formations of oxygen-containing groups during electrochemical oxidation of graphene.



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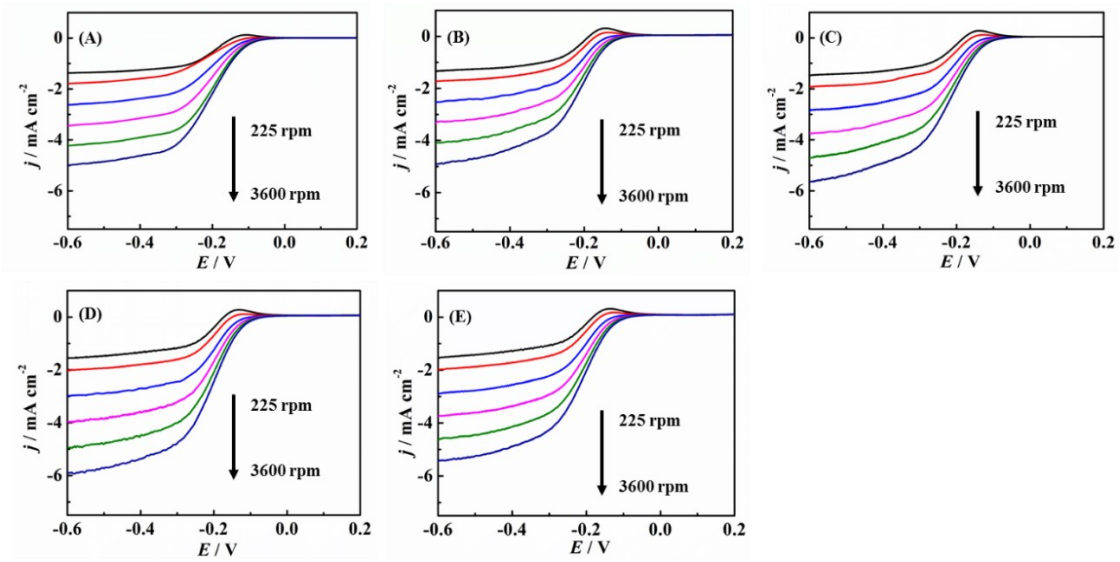

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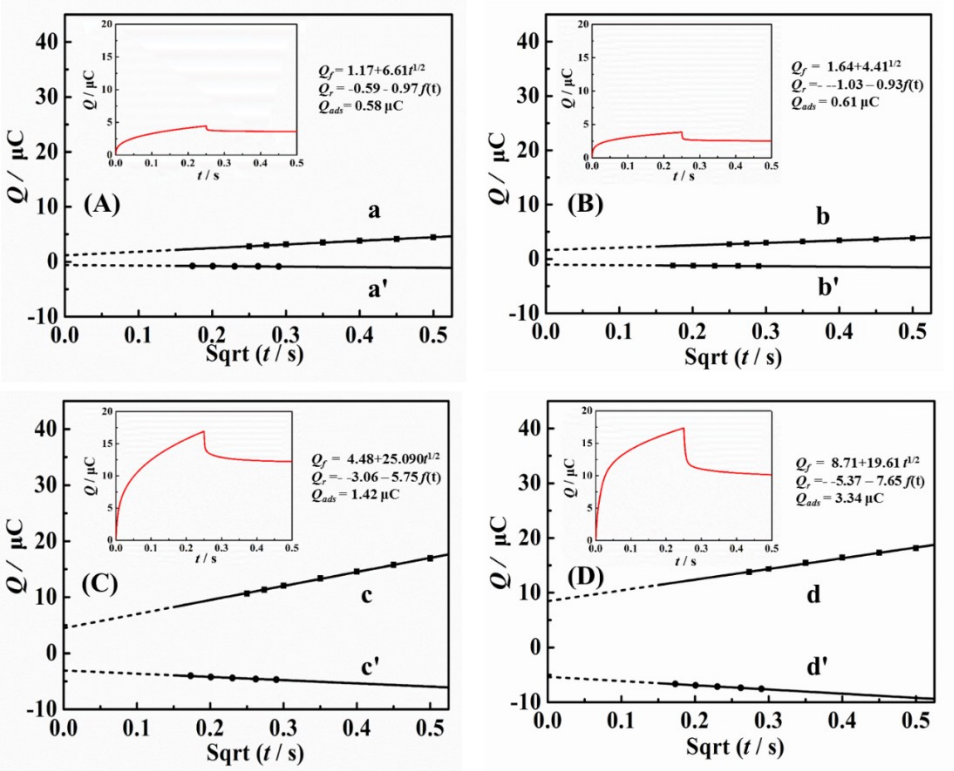

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Sample treatment

Fish meat was purchased from a local market, minced using a meat grinder, and soaked into NFZ standard solution with different concentrations for 20 min. The spiked fish meat samples were then treated as follows. Fish sample (10.00 g) was added into a 50 mL centrifuge tube, then 20.00 mL mixed solvent of acetone and dichloromethane (v/v 3:7) as well as 10.0 g Na_2SO_4 were successively added. The mixture was ultrasonicated for 15 min, centrifuged at 4500 rpm for 5 min, and the supernatant was collected. The extraction process was repeated, and the combined supernatant was distilled to near dryness in 45°C water bath under reduced pressure using a rotary evaporator. Finally, 2.00 mL of 50% acetonitrile aqueous solution was added to the reconstitute extract, and the obtained sample solution was filtered through 0.45 μm membranes for further detection.

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