Electronic Supplementary Information

An electrochemical sensor based on anti-fouling membrane for determination of histamine in fish samples

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Purification of MWCNTs

0.5 g MWCNTs was accurately weighed, then 15 ml HNO_3 and 45 ml H_2SO_4 added in MWCNTs sample in sequence to obtain a suspension of MWCNTs. The suspension was heated and stirred in a 70 °C oil bath to reflux for 5 h. After the reaction was completed, it was diluted with deionized water and cooled to room temperature. The carboxylated MWCNTs were collected by centrifugation and washed continuously with deionized water until neutral. The collected MWCNTs were dried in a vacuum oven at 50 ℃, and finally ground with agate to obtain purified MWCNTs powder.

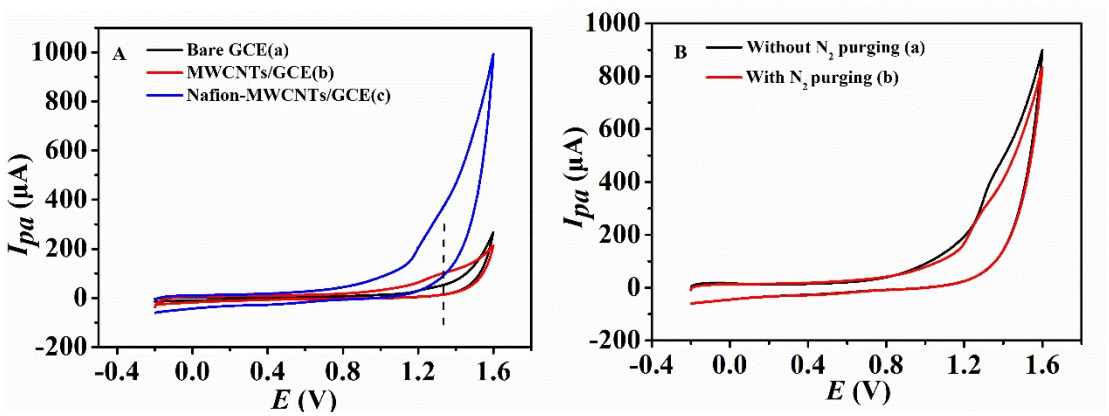


Fig. S1 (A) CV curves of the background solution of 0.1 mol·L^{-1} phosphate buffer solution (pH 7.0) on bare GCE (a), MWCNTs/GCE (b), Nafion-MWCNTs/GCE (c). (B) CV curves of the background solution of 0.1 mol·L^{-1} phosphate buffer solution (pH 7.0) on Nafion-MWCNTs/GCE with and without N_2 purging.

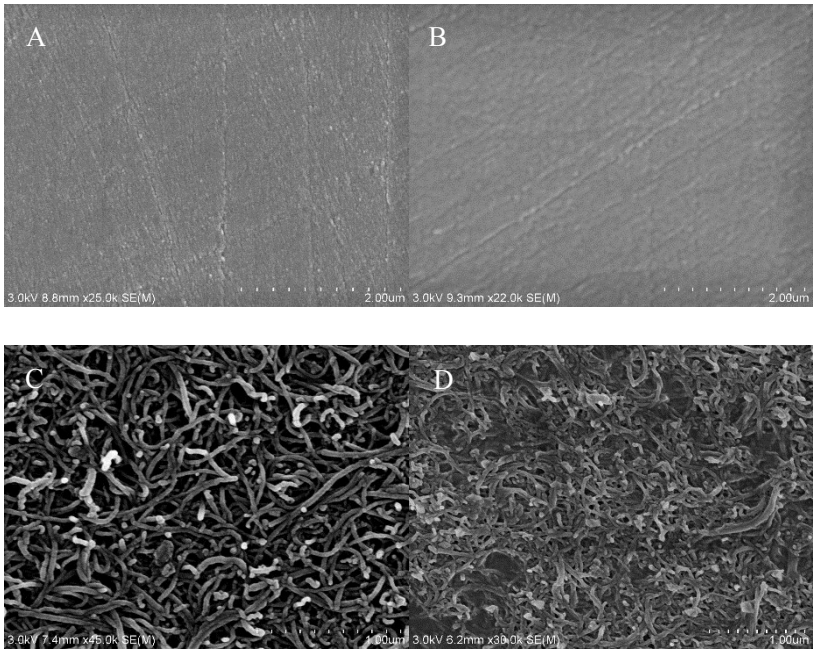
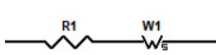
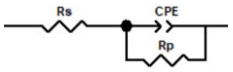


Fig. S2 SEM photographs of bare GCE (A), Nafion/GCE (B), MWCNTs/GCE (C) and Nafion-MWCNTs/GCE (D).

Table S1 The equivalent circuit models for electrochemical impedance spectroscopy (EIS) of different electrodes

	Bare GCE		Nafion-MWCNTs/GCE	Nafion-MWCNTs/GCE	Nafion/GCE
	Bare GCE	Bare GCE after scan in HA solution			
The equivalent circuit model					

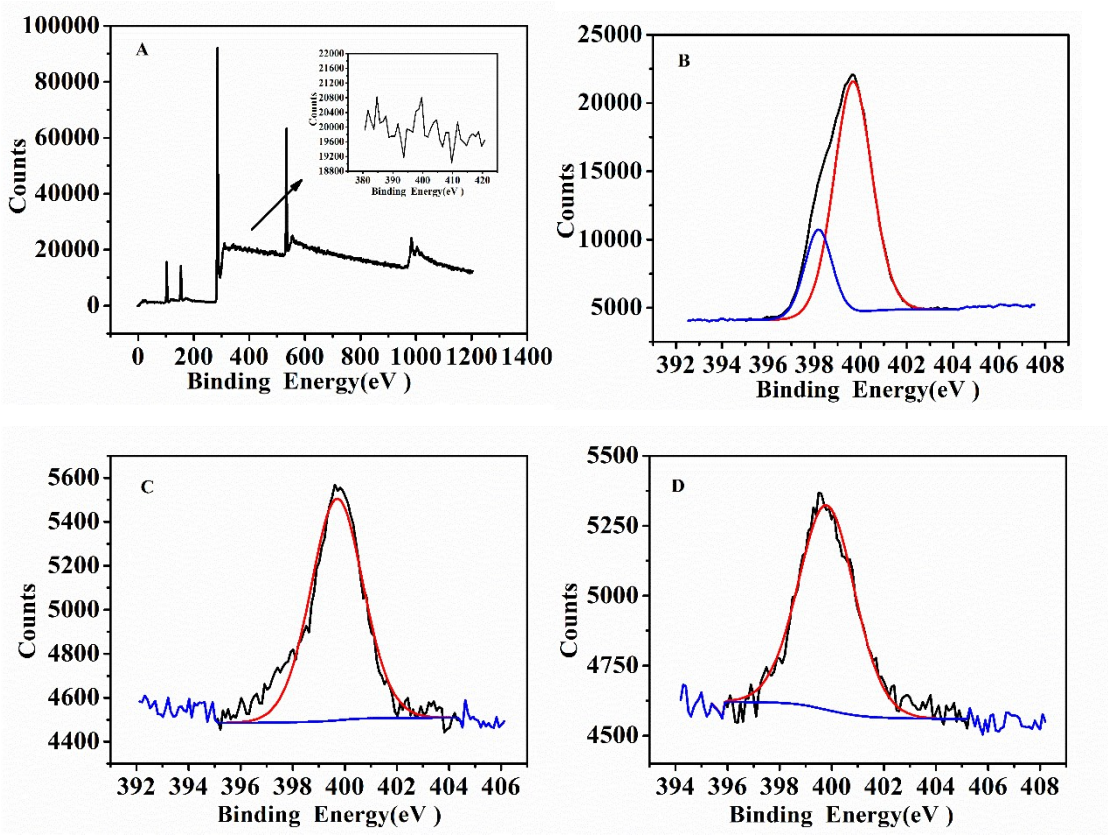


Fig. S3 XPS Spectra of bare GCE (A), N 1s peaks fitting of bare GCE after scanned in 1 mmol·L^{-1} HA from - 0.2 to + 1.6 V (B), Nafion-MWCNTs/GCE (C), Nafion-MWCNTs/GCE after scanned in 1 mmol·L-1 HA from - 0.2 to + 1.6 V (D).

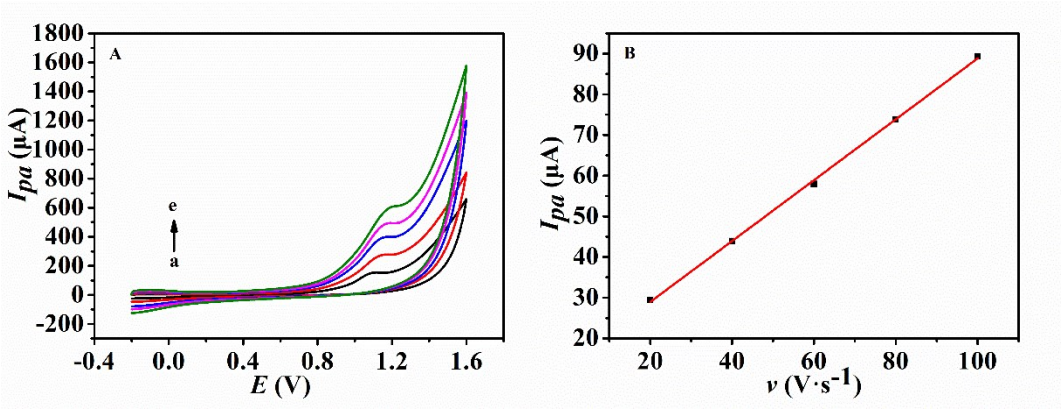


Fig. S4 (A) CV curves of 100 μmol·L^{-1} HA at different scan rates. Scan rates (a-e)：20, 40, 60, 80, 100 mV·s^{-1}; (B) The linear relationship between peak currents and scan rates. CV conditions: scan range from -0.4 V to -1.6 V, phosphate buffer solutions (0.1 mol·L^{-1}, pH 7.0).

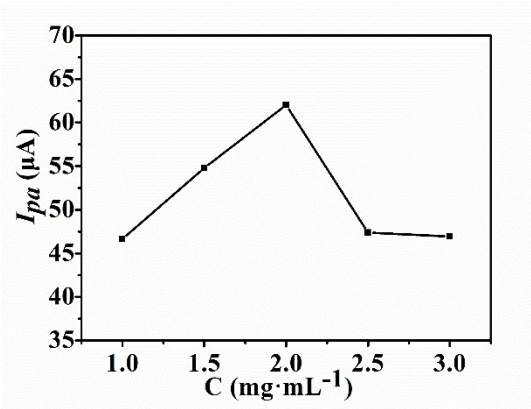


Fig. S5 Optimization of MWCNTs concentration in Nafion-MWCNTs dispersion. HA concentration: 100 μmol·L^{-1}, Nafion concentration: 0.3%, adsorption time: 5 min and 0.1 mol·L^{-1} phosphate buffer solution (pH 7.0). DPV conditions: scan range from 0.4 V to 1.6 V, pulse amplitude of 0.1 V, pulse width of 0.05 s and pulse period of 0.25 s.

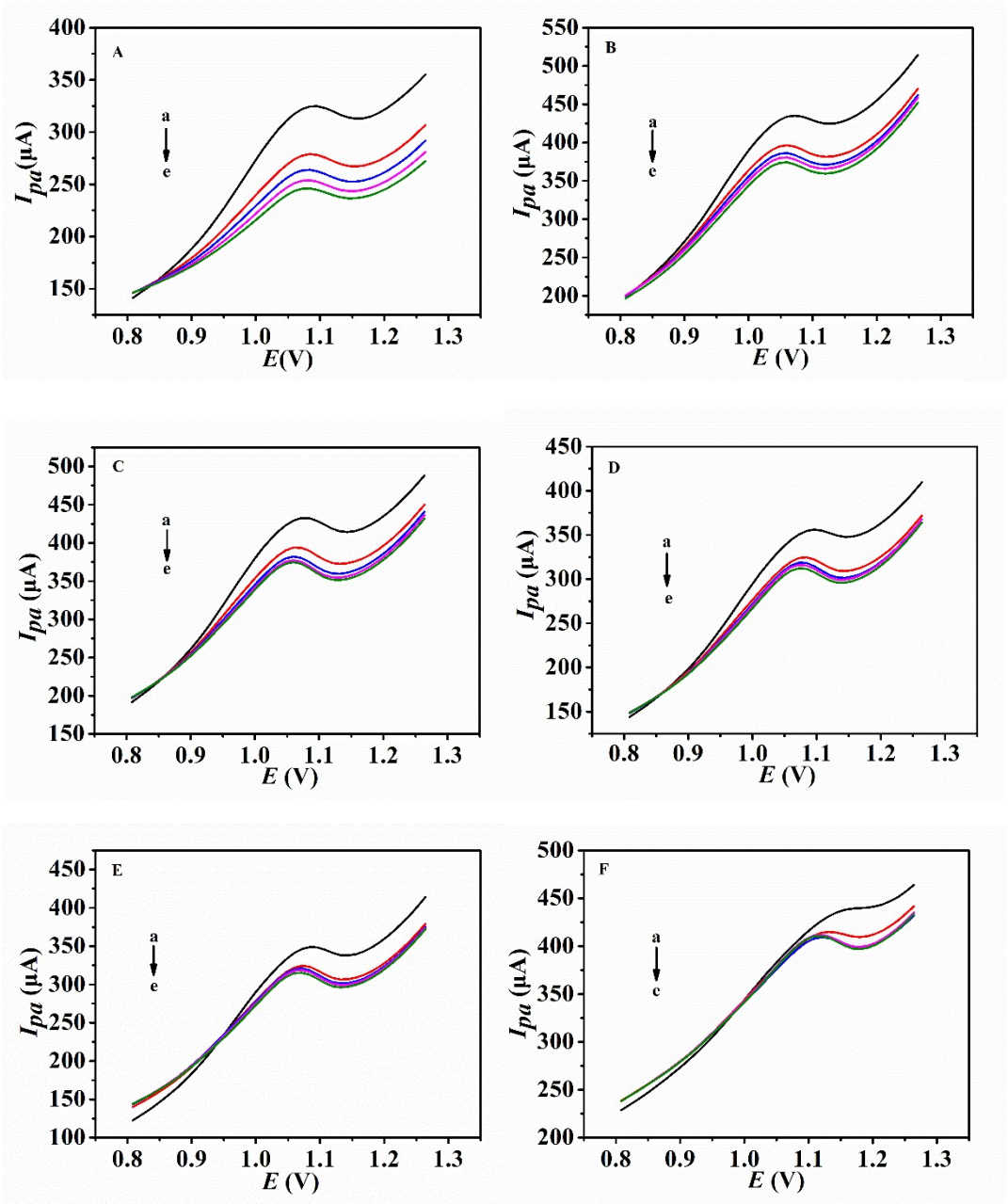


Fig. S6 DPV of 100 μmol·L^{-1} HA in 0.1 mol·L^{-1} phosphate buffer solution (pH 7.0) by continuous scanning for five times recorded on Nafion-MWCNTs/GCE with 0.05% Nafion (A), 0.1% Nafion (B), 0.15% Nafion (C), 0.2% Nafion (D), 0.3% Nafion (E), 0.4% Nafion (F) in Nafion-MWCNTs dispersion, MWCNTs concentration: 2mg·mL^{-1}; a-e: run 1- run 5. The DPV conditions were the same as in Fig. S2.

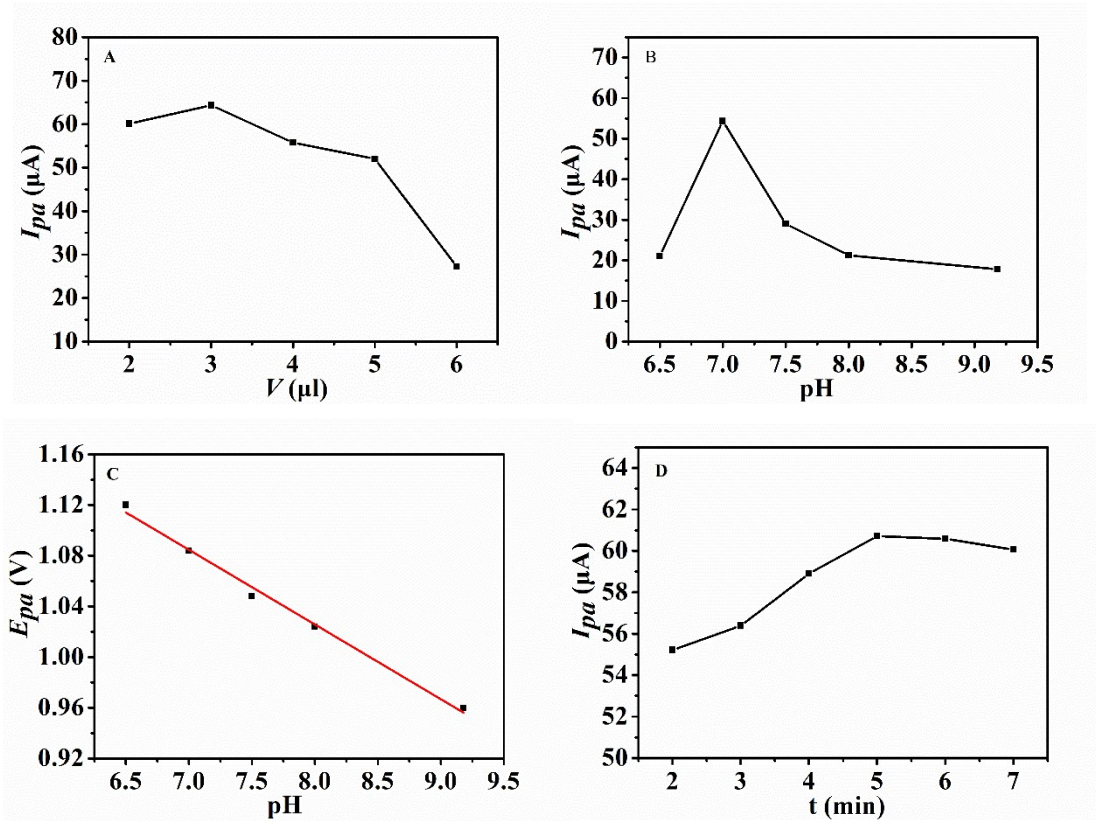
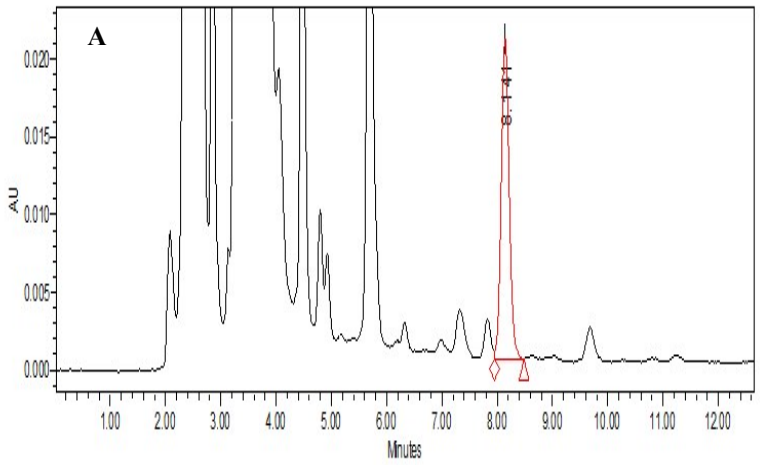


Fig. S7 The effect of Nafion-MWCNTs dispersion volume on I_{pa} (A); the effect of pH of phosphate buffer solutions on I_{pa} (B); the linear relationship between E_{pa} and pH of phosphate buffer solutions (C); the effect of the adsorption time on I_{pa} (D). The DPV conditions were the same as in Fig. S2.



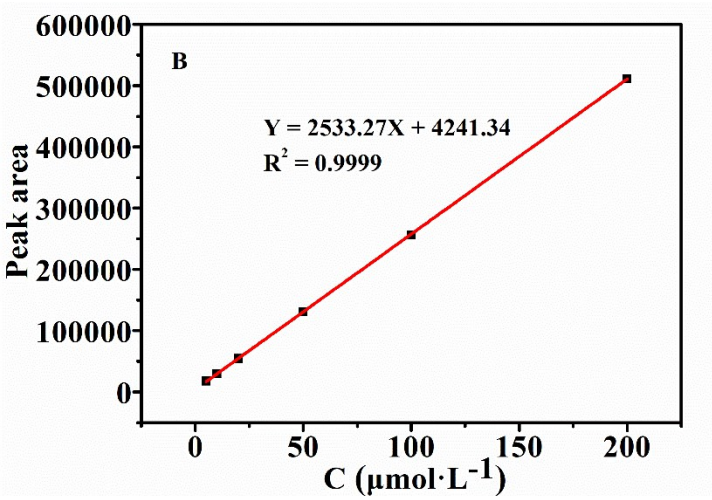


Fig. S8 Chromatogram of the fish sample stored at 4 ℃ for 3 days (A) and the linear relationship between peak area and HA concentrations (B). HPLC chromatographic conditions: Agilent 5 HC-C_{18} column (250 mm×4.6 mm, 5 μm), acetonitrile and 0.1mol·L^{-1} ammonium acetate (V/V = 80/20) as mobile phase, flow rate of 1 mL/min, and UV detection at 254 nm.