

ELECTROCHEMICAL INSIGHTS INTO MANGANESE-COBALT DOPED α -Fe₂O₃ NANOMATERIAL FOR CHOLESTEROL DETECTION: A COMPARATIVE APPROACH

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1. Results and discussions:

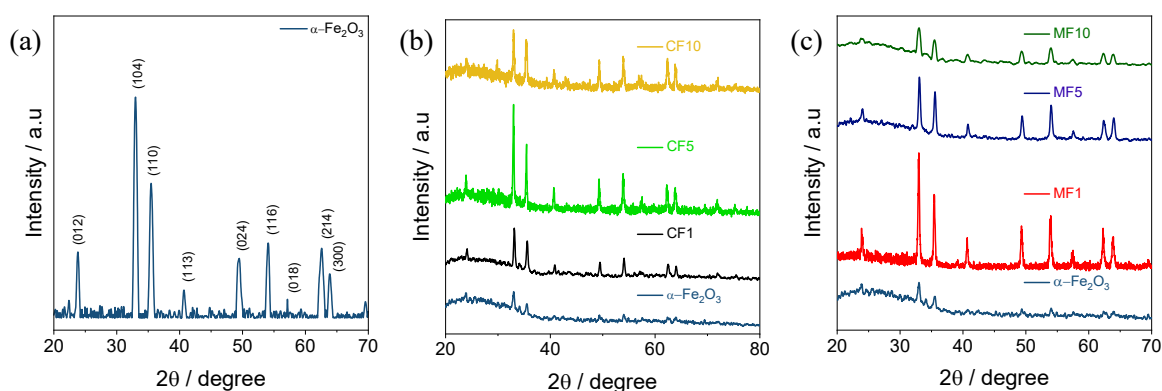


Figure. S1: XRD analysis of (a) α -Fe₂O₃; (b) α -Fe₂O₃ doped with cobalt; (c) α -Fe₂O₃ doped with manganese, respectively.

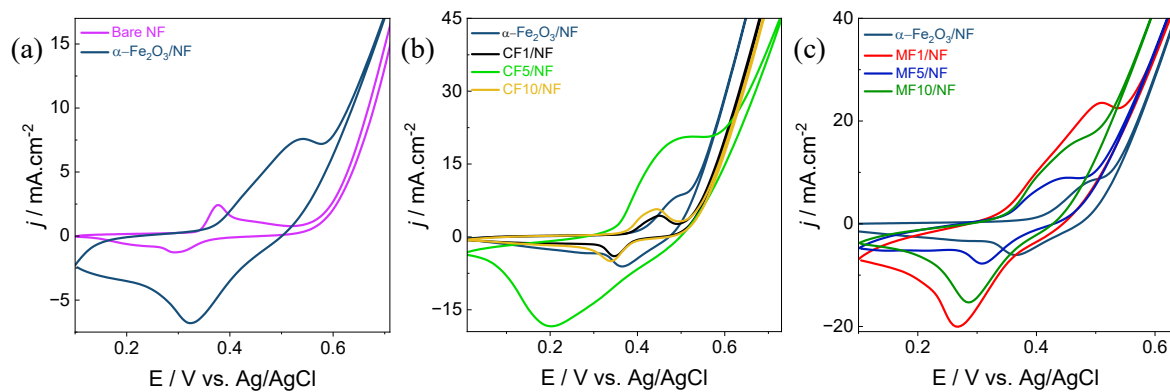


Figure. S2: Comparison of CVs of (a) bare NF and $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$; (b) $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$ with cobalt-doped nanocomposite; (c) $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$ with manganese-doped nanocomposite.

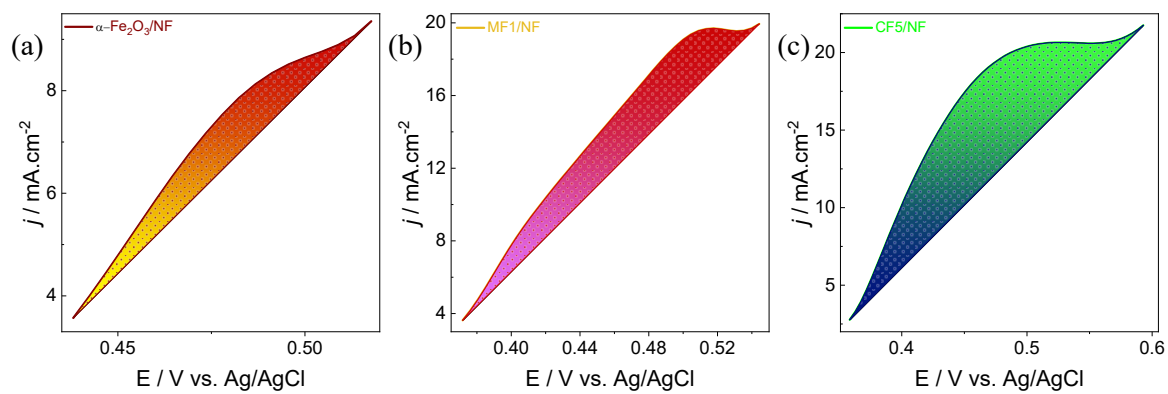


Figure. S3: Oxidation peak study of (a) $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$; (b) MF1/NF; (c) CF5/NF.

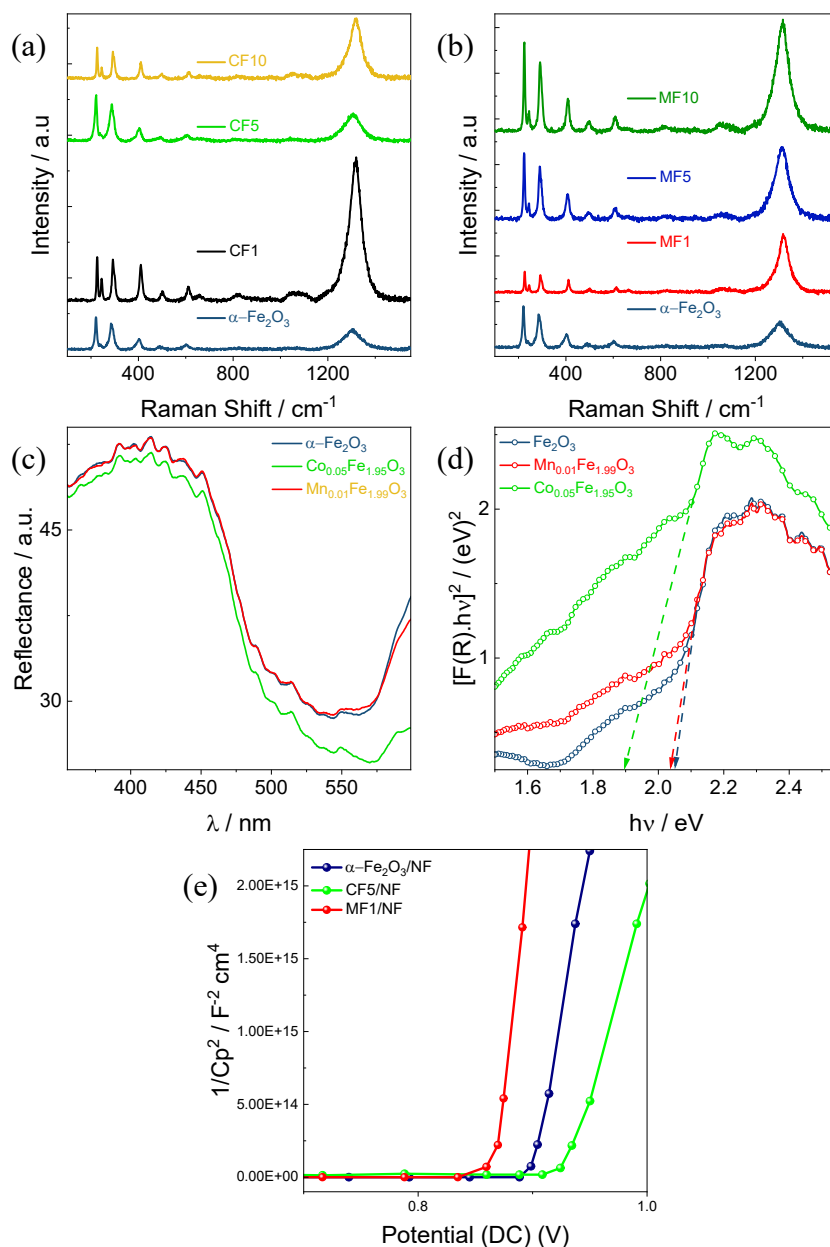


Figure. S4: Raman spectroscopy analysis of (a) Cobalt-doped α - Fe_2O_3 ; (b) Manganese-doped α - Fe_2O_3 ; (c) Reflectance spectra of α - Fe_2O_3 , CF5, and MF1, respectively; (d) Optical band gap plots obtained from UV spectra for α - Fe_2O_3 , CF5, and MF1; (e) Mott Schottky plot of α - $\text{Fe}_2\text{O}_3/\text{NF}$, CF5/NF, and MF1/NF respectively.

The Mott–Schottky (MS) analysis provides further clarification of the apparent discrepancy between the optical band gap and EIS results. In MF1, despite the marginal reduction in band gap, the steeper MS slope signifies a lower donor density and reduced concentration of mobile carriers. These defect-related states primarily function as trap centres, thereby accounting for the increased charge-transfer resistance. In contrast, CF5 exhibits a comparatively flatter MS

slope, indicative of a higher donor density arising from Co-induced oxygen vacancies, which enhance electronic conductivity. Collectively, the MS results underscore that interfacial charge-transfer kinetics are more strongly influenced by carrier density and defect chemistry than by band gap modulation alone.

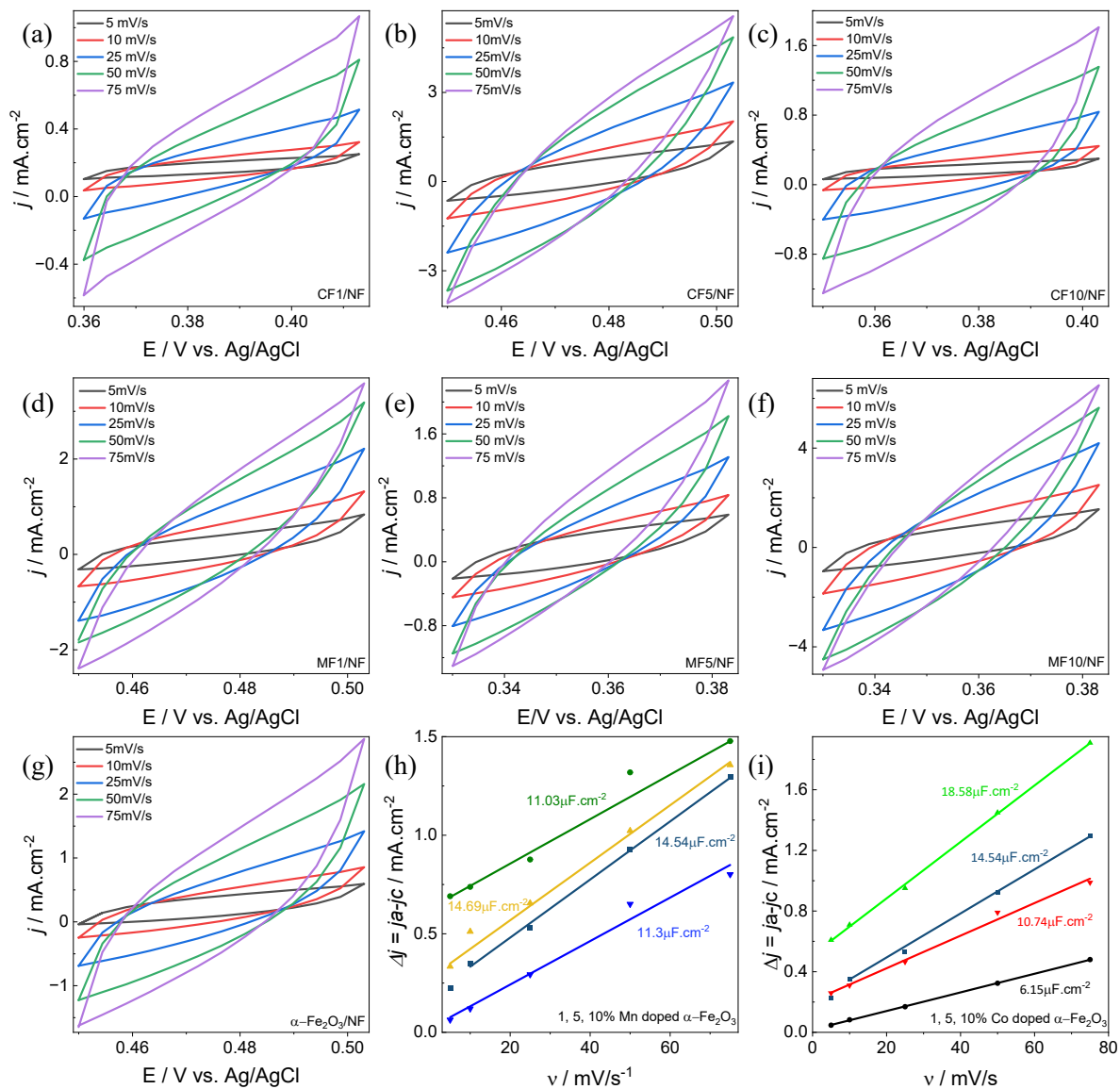


Figure. S5: ECSA analysis of (a) CF1/NF; (b) CF5/NF; (c) CF10/NF, (d) MF1/NF (e) MF5/NF (f) MF10/NF (g) α -Fe₂O₃/NF (h, i) Calibration plot of doped Mn and Co with α -Fe₂O₃, respectively.

Material	Slope ($\mu\text{F}.\text{cm}^{-2}$)	(Slope / 40×2) (cm^2)
$\alpha\text{-Fe}_2\text{O}_3/\text{NF}$	14.54	0.182
MF1/NF	14.69	0.184
MF5/NF	11.3	0.141
MF10/NF	11.03	0.138
CF1/NF	6.15	0.077
CF5/NF	18.58	0.232
CF10/NF	10.74	0.134

Table. S1: Surface Area Calculation

Parameter	$\alpha - \text{Fe}_2\text{O}_3/\text{NF}$	CF5/NF	MF1/NF
$R_s (\Omega)$	0.7395	0.7171	1.148
$R_{ct} (\Omega)$	1.791	1.637	3.995
$Q_{ct} (\mu\text{F})$	11.11	11.62	4.101
$R_{ce} (\Omega)$	80.4	126.1	120.6
$Q_{ce} (\text{mF})$	0.455	0.251	0.381

Table. S2: EIS parameters for the fitted Circuit

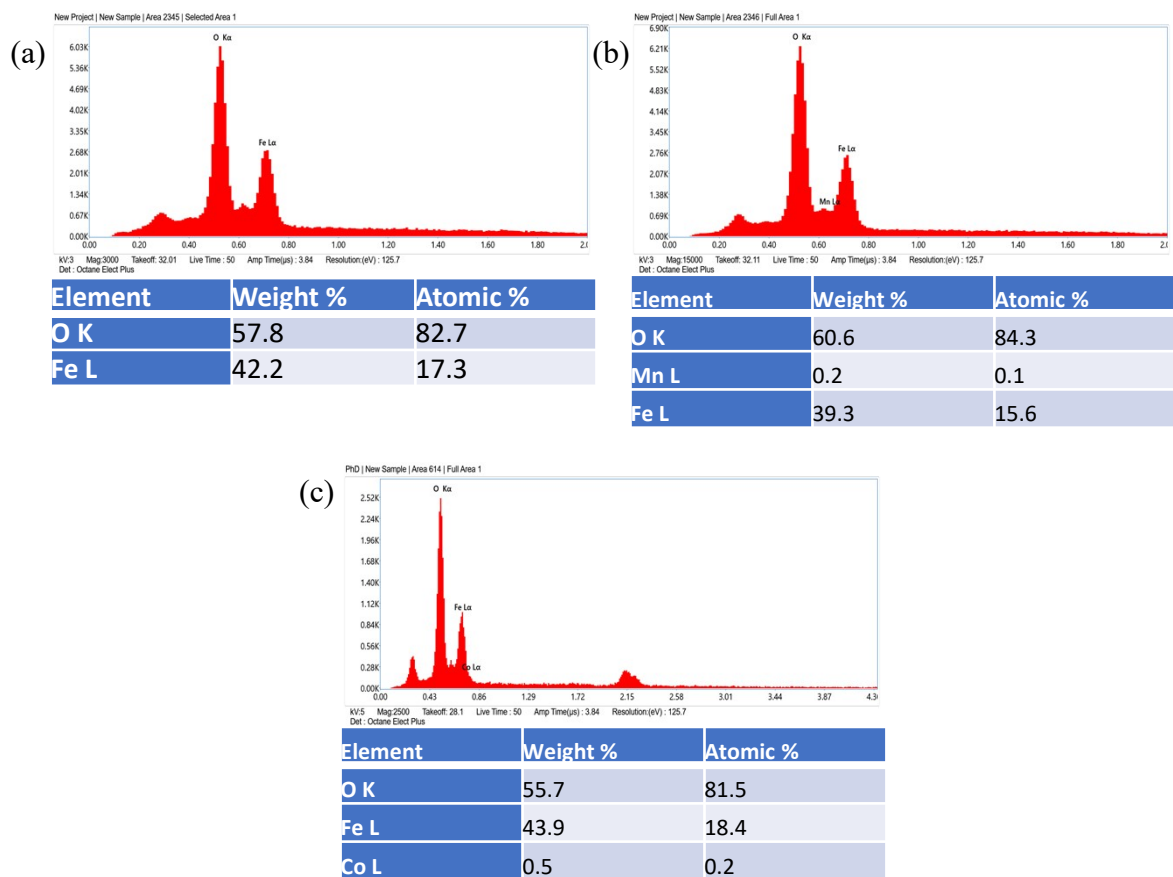


Figure. S6: EDAX analysis of (a) α - Fe_2O_3 ; (b) MF1; (c) CF5.

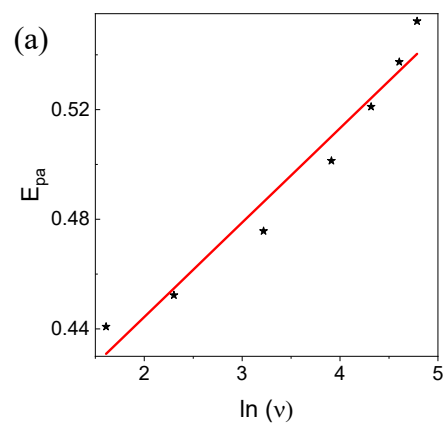


Figure. S7: (a) Laviron Equation for CF5/NF.

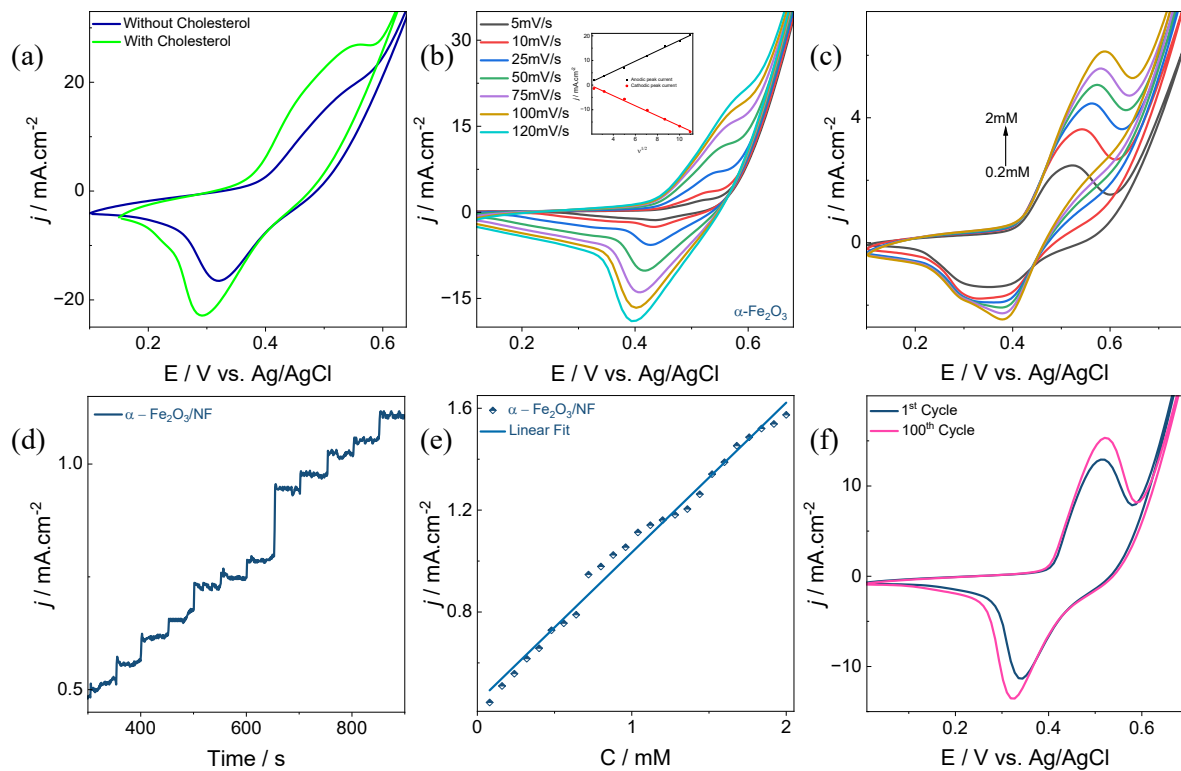


Figure. S8: (a) CV comparison of CF5/NF with and without Cholesterol. (b) Scan rate study of $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$; (c) Successive Addition of 2 mM Cholesterol in 0.5 M KOH; (d) CA study of $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$; (e) Calibration curve of $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$; (f) CVs of $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$ for 100 cycles in 0.5 M KOH with 2 mM Cholesterol.

(a)

No. of trials	Material	Sensitivity ($\mu\text{A.mM}^{-1}.\text{cm}^{-2}$)
1	CF5/NF	1364.17
2	CF5/NF	1364.23
3	CF5/NF	1364.20
Mean $\pm$ SD		1364.20 $\pm$ 0.03

(b)

No. of trials	Material	Sensitivity ($\mu\text{A.mM}^{-1}.\text{cm}^{-2}$)
1	$\alpha\text{-Fe}_2\text{O}_3/\text{NF}$	589.95
2	$\alpha\text{-Fe}_2\text{O}_3/\text{NF}$	590.05
3	$\alpha\text{-Fe}_2\text{O}_3/\text{NF}$	590.00
Mean $\pm$ SD		590.00 $\pm$ 0.05

Table. S3: Reproducibility of (a) CF5/NF and (b) $\alpha\text{-Fe}_2\text{O}_3/\text{NF}$ sensitivities over three trials, expressed as mean $\pm$ SD

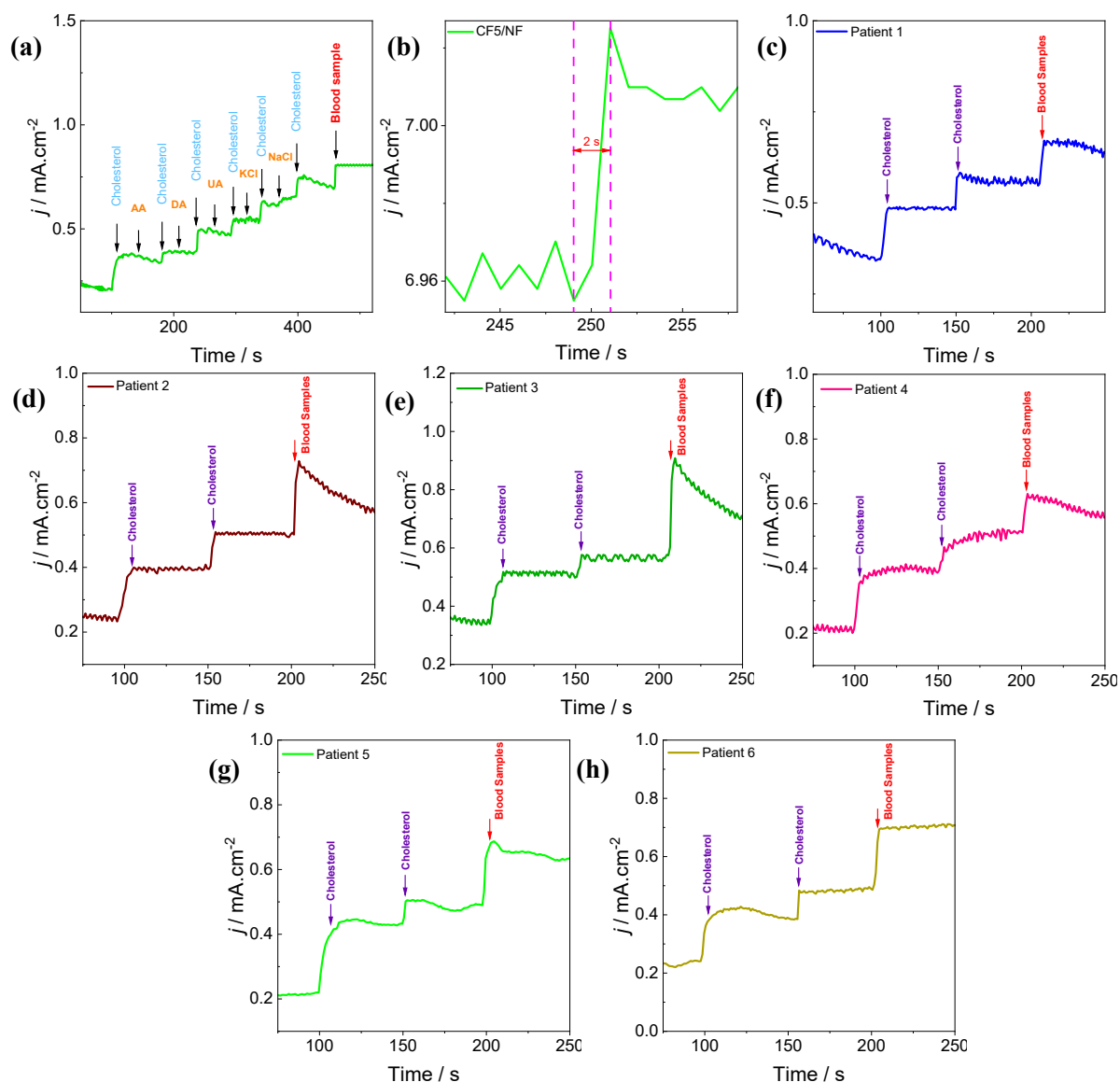


Figure. S9: (a) An interference study of CF5/NF in a 0.5 M KOH solution under stirring conditions to assess its reaction to various interfering species of 0.5mM at a potential of +0.55 V; (b) Response time plot using CA; (c-h) CA analysis of real human blood serum (Red) and synthetic cholesterol (Lavender) of 6 patients.

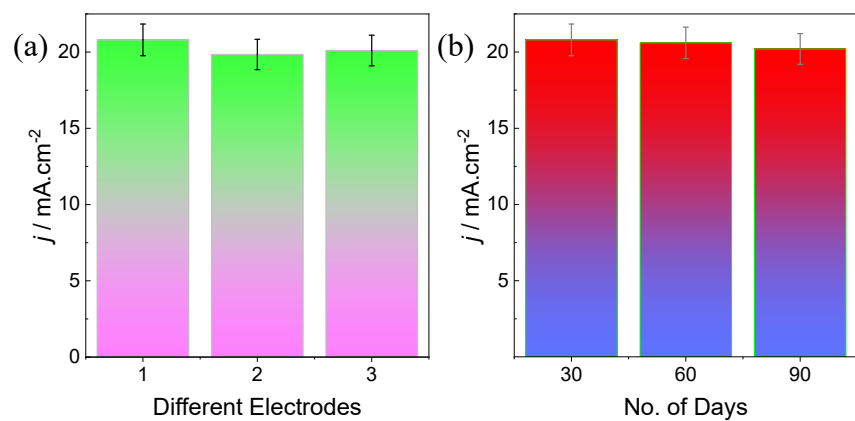


Figure. S10: (a) Reproducibility was assessed using three different CF5/NF electrodes; (b) The stability of the CF5/NF electrode was evaluated for 90 days.