

An aqueous phase TEMPO mediated electrooxidation of 2-thiophene methanol using MnO₂-Pi dispersed nanocarbon spheres on carbon fiber paper electrode

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Electronic Supplementary Information

ESI 1. Electrodeposition of MnO₂-Pi nanoparticles on NCS/CFP electrode

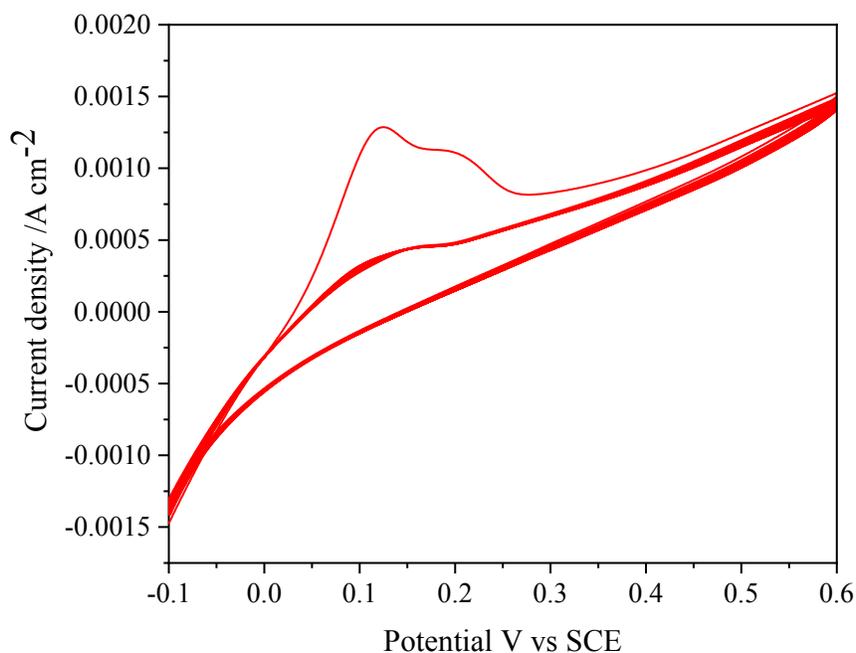


Fig. S1 Cyclic voltammograms corresponding to the electrodeposition of MnO₂-Pi on NCS/CFP electrode in 25 successive cycles, in the electrolyte solution containing KMnO₄ (0.025 M) and 0.1 M PBS (pH 7.0) with scan rate of 0.05 V s⁻¹.

ESI 2. EIS studies of modified and bare CFP electrodes

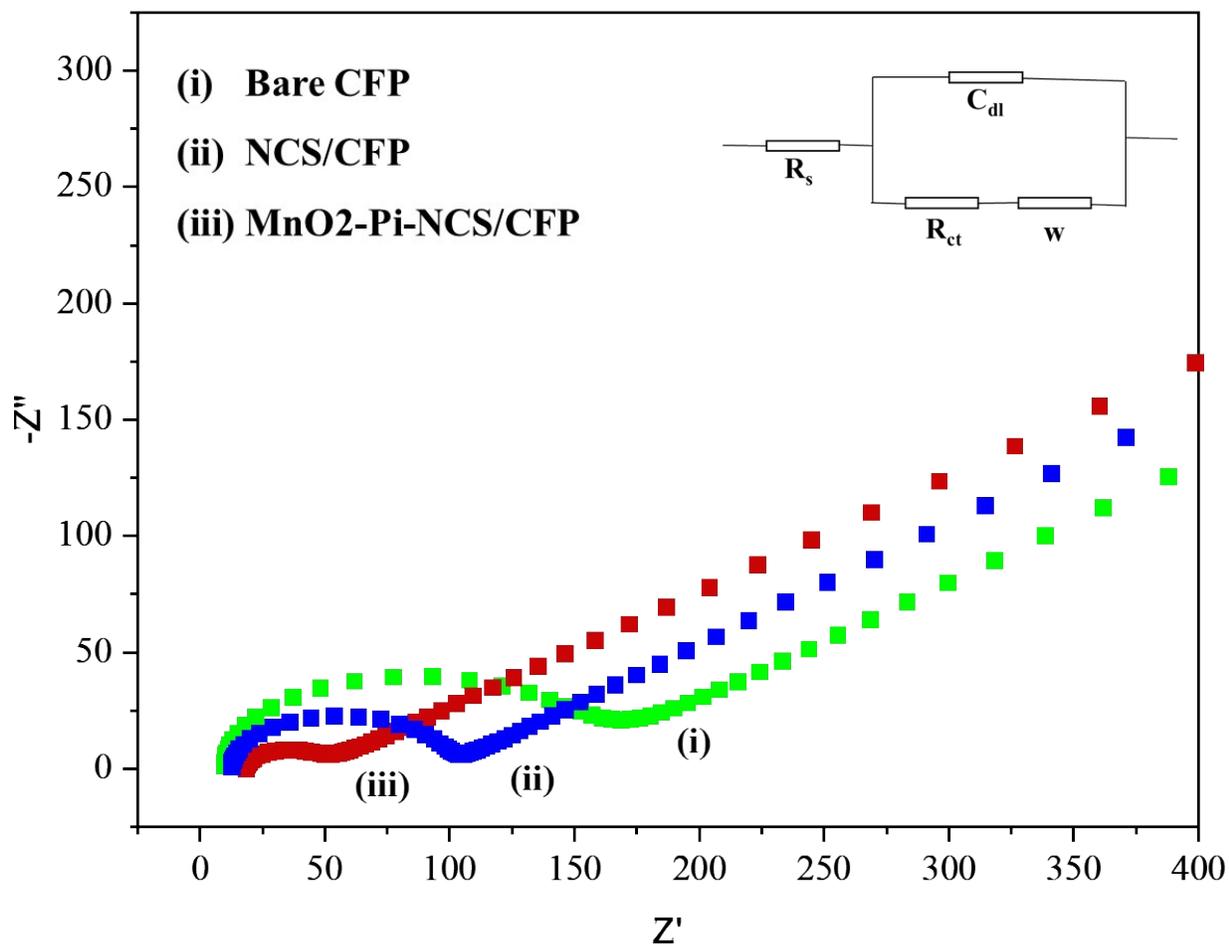


Fig. S2 Nyquist plots of (i) Bare CFP (ii) NCS/CFP and (iii) MnO₂-Pi-NCS/CFP electrodes in 5 mM K₄[Fe(CN)₆]/K₃[Fe(CN)₆] solutions containing 0.1 M KCl.

ESI 3. EDS Analysis

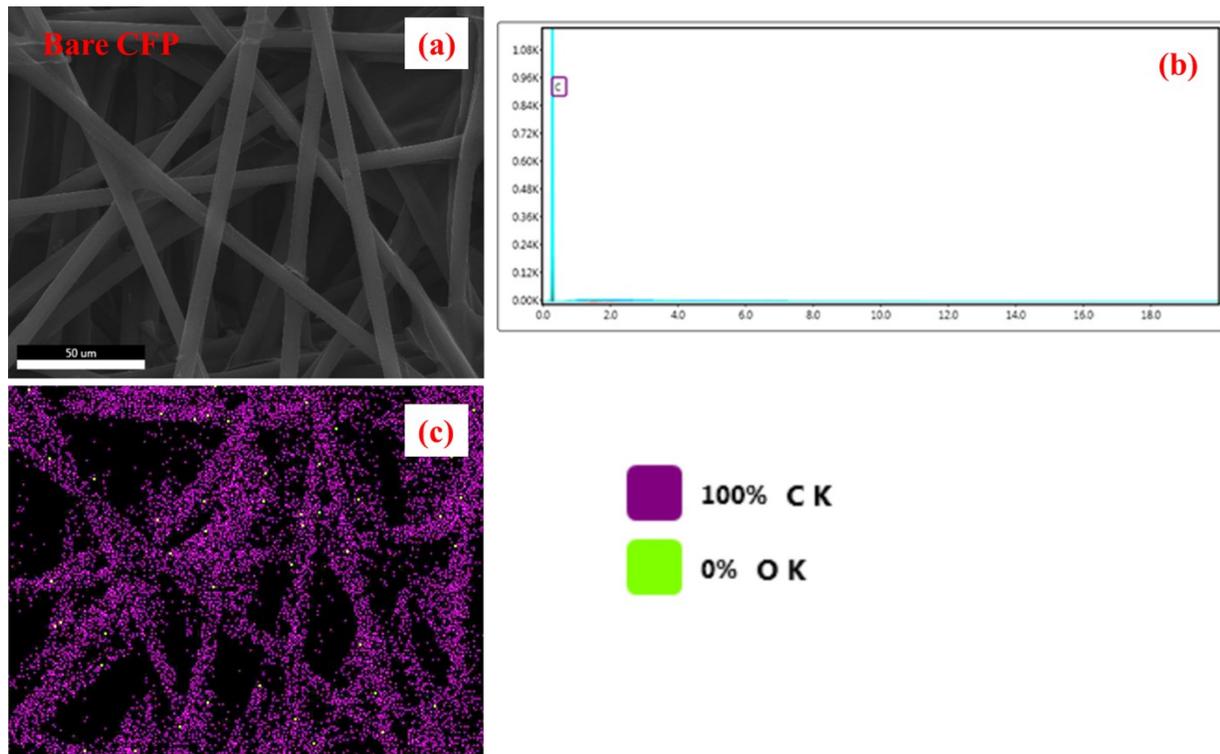


Fig. S3. EDS image and spectrum of the bare CFP (a and b), (c) Elemental mapping showing carbon element of bare CFP electrode.

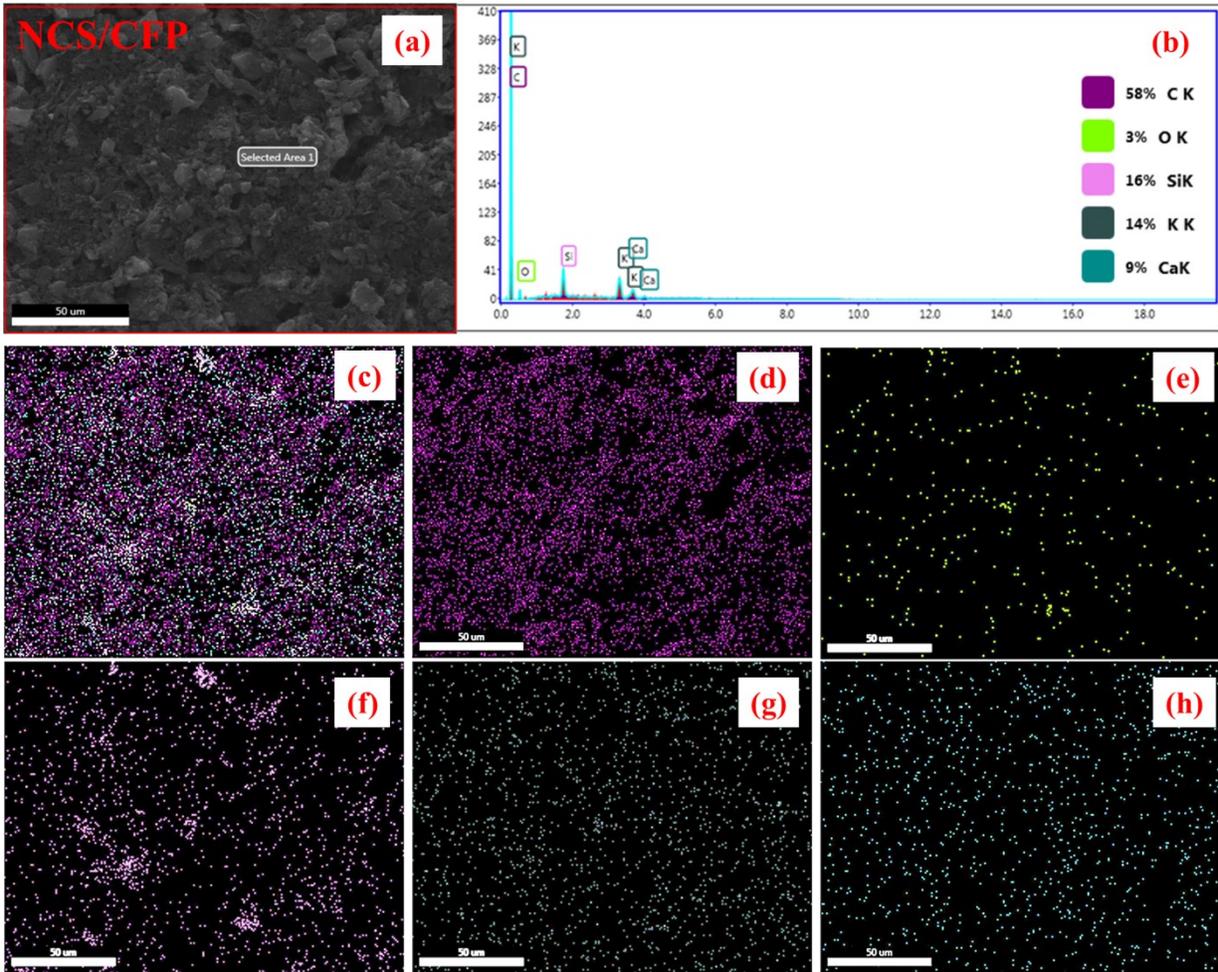


Fig. S4. EDS image and spectrum of the NCS/CFP electrode (a and b), (c) Elemental mapping showing all elements in the NCS/CFP electrode material; Elemental mapping of (d) carbon (e) oxygen (f) Silicon (g) Potassium (h) Calcium

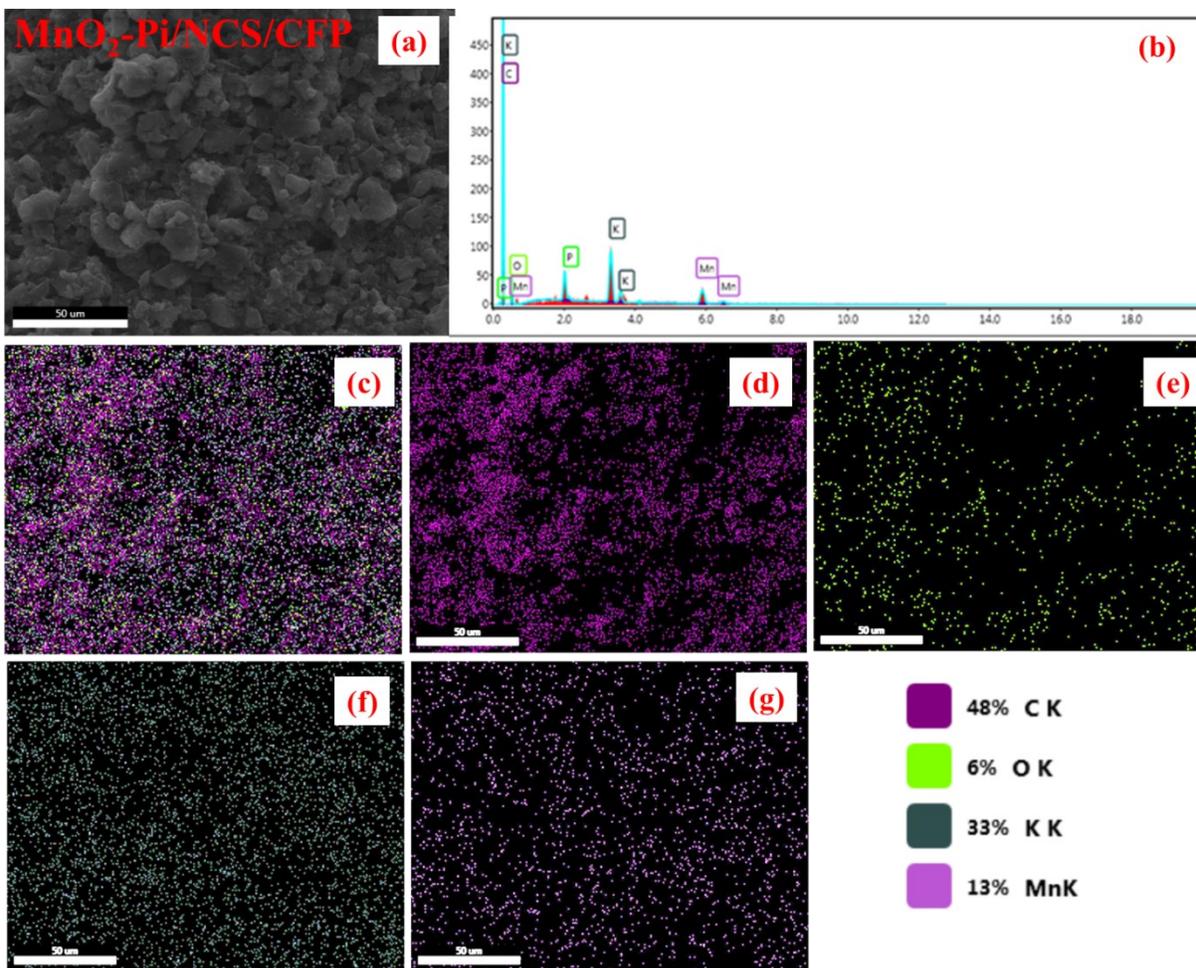


Fig. S5. EDS image and spectrum of the MnO₂-Pi/NCS/CFP electrode (a and b), (c) Elemental mapping showing all elements in MnO₂-Pi/NCS/CFP electrode; Elemental mapping of (d) carbon, (e) oxygen, (f) potassium and (g) manganese

ESI 4. TEM Analysis

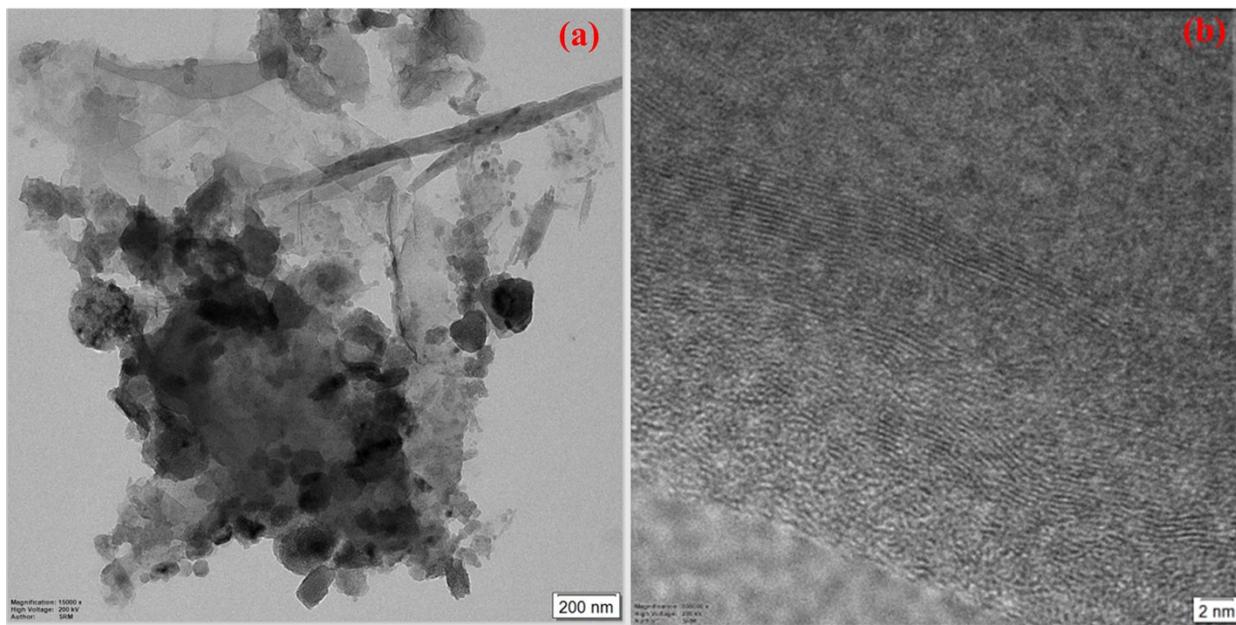


Fig. S6. (a) TEM image and (b) HRTEM image of MnO₂-Pi/NCS/CFP electrode

ESI 5. FTIR spectroscopic analysis of 2-thiophene methanol and 2-thiophenemethanal

The characteristic peak of O-H stretching at 3309 cm⁻¹ in reactant, 2-thiophene methanol (**Figure. S7a**) was found to be absent in the FTIR spectrum of the product, 2-thiophene methanal or 2-thiophene carboxaldehyde (**Figure. S7b**). The characteristic peak of C=O at 1666 cm⁻¹ in the isolated product confirms the formation of 2-thiophene carboxaldehyde.

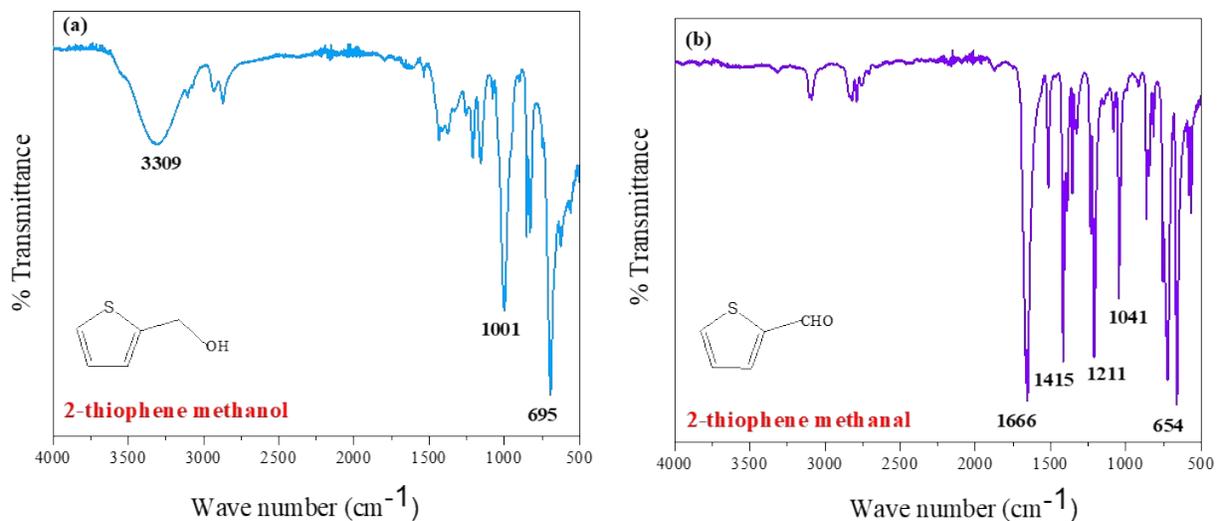


Fig. S7. FTIR spectra of (a) 2-thiophene methanol and (b) 2-thiophene methanal

ESI 6. ¹H NMR analysis of 2-thiophene methanal

The expected product 2-thiophene methanol has shown three signals in the ¹H NMR spectrum represented in **Fig. S8**. The characteristic signal at 9.929 ppm confirms the presence of aldehydic proton. This confirms the formation of 2-thiophene methanal as result of TEMPO mediated oxidation of 2-thiophene methanol. [2-thiophene methanal (colorless, yield 74%): ¹H-NMR (400 MHz, CDCl₃) δ 9.929(s, 1H), 7.746–7.781 (m, 2H), 7.194–7.215 (m, 1H).

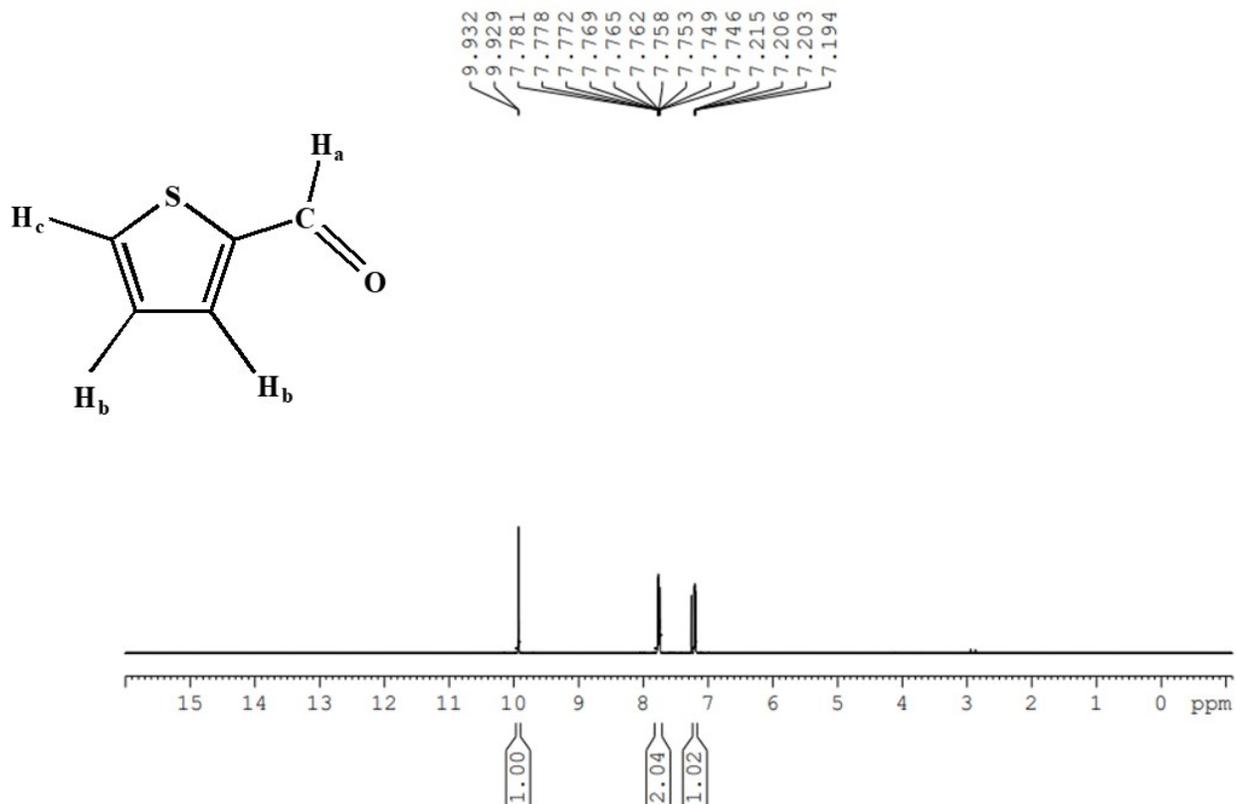


Fig. S8. ¹H NMR spectrum of the isolated product, 2-thiophenemethanal

ESI 7. Effect of number of MnO₂-Pi deposition cycles on the electrocatalytic oxidation of 2-thiophenemethanol

The effect of number of deposition cycles on the electrocatalytic oxidation was investigated by using electrodes, which are prepared by depositing MnO₂-Pi nanoparticles on NCS/CFP in different number of cycles such as 5, 10, 12, 14, 16, 18, 20, 22, 24 and 25. The study was conducted by varying the scanning potential cycles but keeping the concentration of 2-thiophenemethanol constant (10 mM). The redox peak current values, obtained from cyclic voltammetry (**Fig. S9**), show an increasing trend with increase in the number of scanning potential cycles. The potential was found to shift towards more negative values upto 25 cycles, after which it remained unchanged. Therefore, 25 cycles were considered as the optimum number of cycles for the deposition of MnO₂-Pi on NCS/CFP electrode to bring about oxidation of 2-thiophenemethanol in the TEMPO-medium.

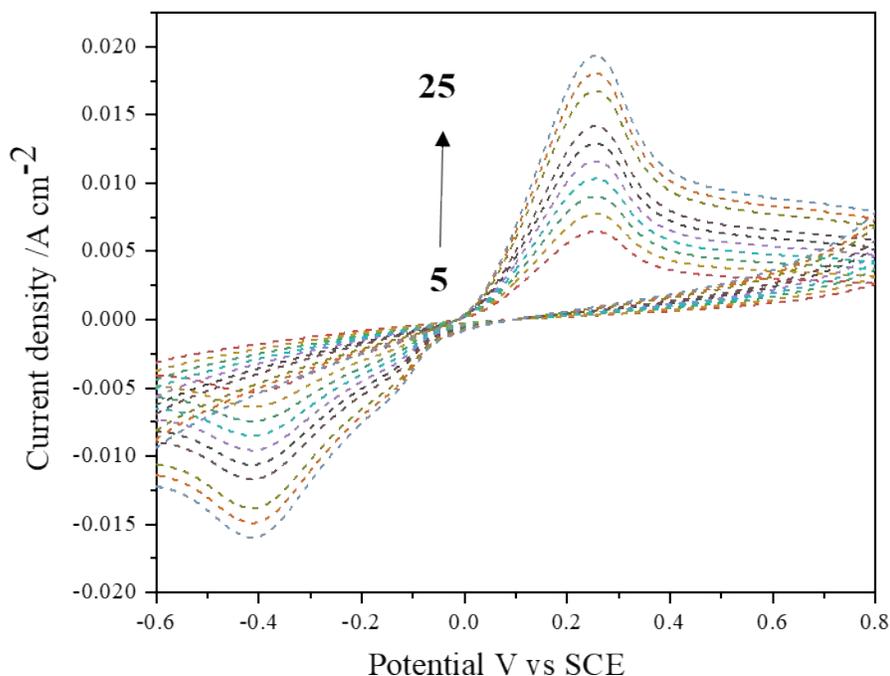


Fig. S9. Effect of the number of cycles on 0.01 M TEMPO in 0.01M H₂SO₄ at a scan rate of 0.05 Vs⁻¹, (in the presence of 10 mM 2-thiophenemethanol).

ESI 6. Effect of scan rate on electrocatalytic oxidation of 2-thiophenemethanol

The effect of scan rate on the electrocatalytic oxidation of thiophene carbinol was studied at MnO₂ Pi-NCS/CFP electrode in aqueous acidic medium. The cyclic voltammetric experiments were performed using 10 mM thiophene carbinol varying the scan rate (v) from 0.01 to 0.13 V/s. The resulted voltammograms are depicted in **Fig. S10a**. The effect of scan rates on the peak currents were considered to understand the kinetics of the electrode processes controlled by diffusion or adsorption.

The linear graph was obtained by plotting the logarithm of anodic peak currents ($\log i_{pa}$) against the logarithm of scan rates ($\log v$), as shown in **Fig. S10b**. The straight line equation is given below;

$$\log i_{pa} \text{ (A)} = -0.8471 \log v \text{ (V/s)} + 1.3151 \quad R^2 = 0.9994$$

The graph of logarithm of cathodic peak currents ($\log i_{pc}$) versus logarithm of scan rates ($\log v$) showed a linear plot (Fig. S4c); the corresponding straight line equation is given below;

$$\log i_{pc} (\text{A}) = 0.9261 \log v (\text{V/s}) - 1.1472 \quad R^2 = 0.9979$$

The results indicated that the processes at electrode surface were adsorption controlled rather than diffusion controlled. This could also be confirmed by the positive shift observed in the anodic and cathodic peak potentials with increase in the scan rate.

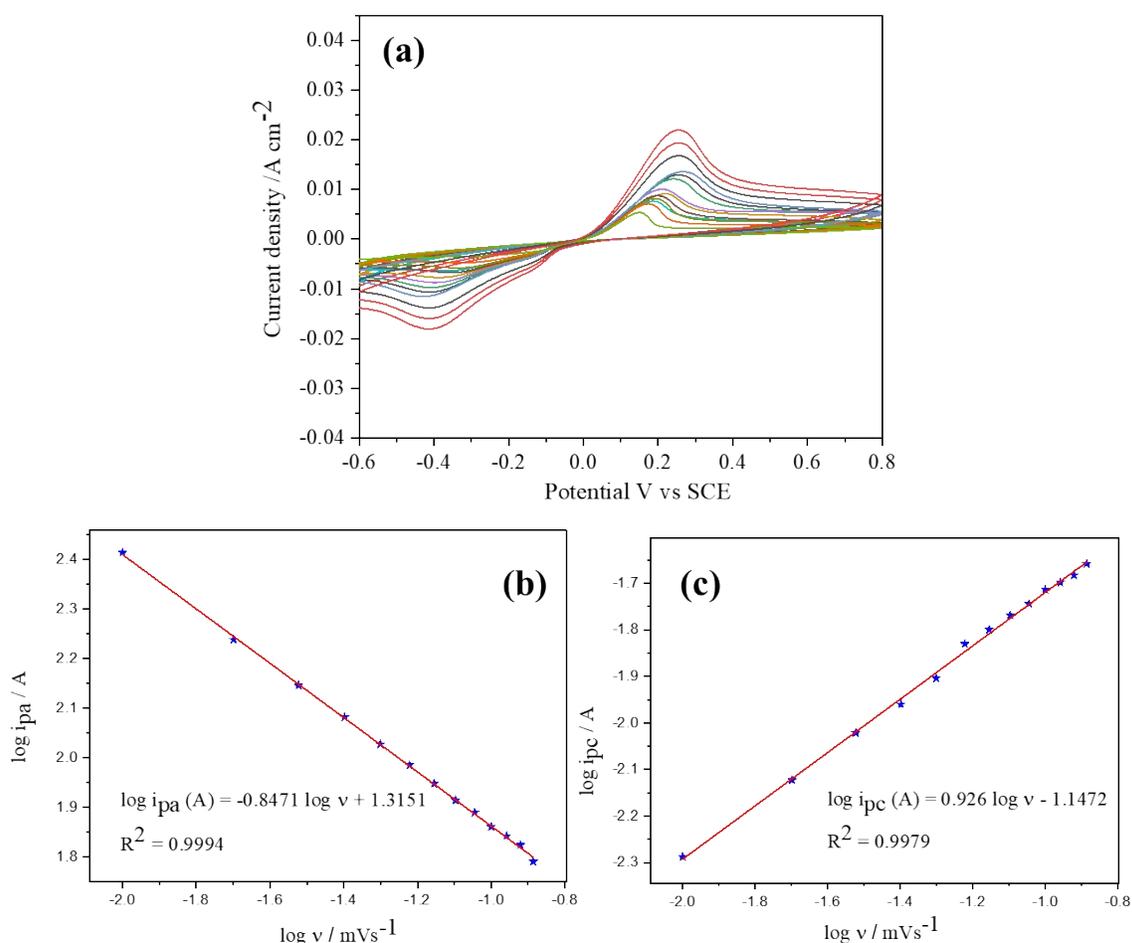


Fig. S10. (a) Cyclic voltammograms obtained for the TEMPO mediated oxidation of thiophene carbinol at MnO₂-Pi-NCS/CFP electrode by changing the scan rates from (i) 0.01 – (xii) 0.13 Vs⁻¹; (b) Plot showing the logarithm of anodic peak currents versus the logarithm of scan rates; (c) Plot showing the logarithm of cathodic peak currents versus the logarithm of scan rates.