Electronic Supplementary Material (ESI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022
Please do not adjust margins

ARTICLE

Supporting Information

Melamine Functionalised Multiwalled Carbon Nanotubes (M-MWCNTs) as metal-free Electrocatalyst for Simultaneous Determination of 4-Nitrophenol and Nitrofurantoin.

Raviraj P. Dighole [a,b], Ajay V. Munde[a,c], Balaji B. Mulik[a], Sanjio S. Zade[c] and Bhaskar R. Sathe[a]*

a- Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431 004 (MS) India.

b- Arts, Science & Commerce College, Badnapur 431202.

c- Department of Chemical Sciences and Centre for Advanced Functional Materials, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia 741246, West Bengal, India.

*Corresponding author:

Dr. Bhaskar R. Sathe; Email: bhaskarsathe@gamil.com; bsathe.chemistry@bamu.ac.in

Professor Sanjio S. Zade; Email: sanjiozade@iiserkol.ac.in.

List of supporting information

S-1. Characterisation detail

Please do not adjust margins

Please do not adjust margins

The product was analyzed via. Fourier transform infrared spectroscopy (FTIR). Its phase and structure were characterized using X-ray diffraction (XRD, Siemens D-5005 diffract meter) equipped with an X-ray tube (Cu Ka; l ¼ 1.5418 nm, 40 kV, 30mA, Raman spectroscopy was performed using a microscope with Raman optics (Seki Technetronic Corporation, Tokyo) with a 532 nm LASER. For EDAX analysis, the samples were prepared on Au films. X-ray photoelectron spectroscopy (XPS) on a SPECS HSA-3500 with a monochromatic Al Ka X-ray Radiation X-ray source and hemispherical analyser was used to investigate the elemental states of the sample. Quantachrom Instruments- All electrochemical studies to perform on connected to CHI 660C electrochemical work station CHI Instrument660E, (USA) with three electrodes System. A glassy carbon electrode (GC, 3 mm dia.) was used as the working electrode to support the catalysts. A piece of Pt foil and SCE in 0.5M H2SO4 were used as the counter and reference electrodes respectively.

S-2. Linear fitting plots of Nitrophenol (4-NP)

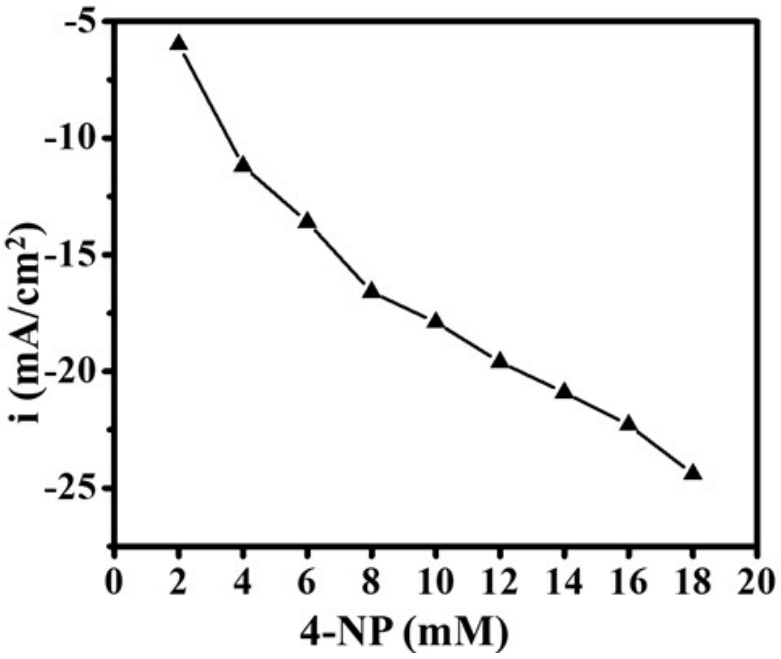


Figure S1. Depicts the liner fit plot for the concentration of 4-NP vs. peak current density.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

S-3. Linear fitting plots of Nitrofurantoin (NFT):

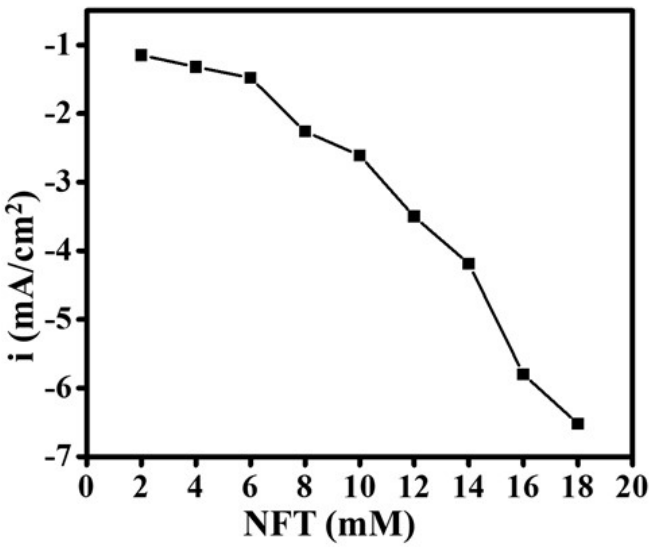


Figure S2. Depicts the liner fit plot for the concentration of NFT vs. peak current density.

S-4) Effect of H_2SO_4 on 4NP and NFT:

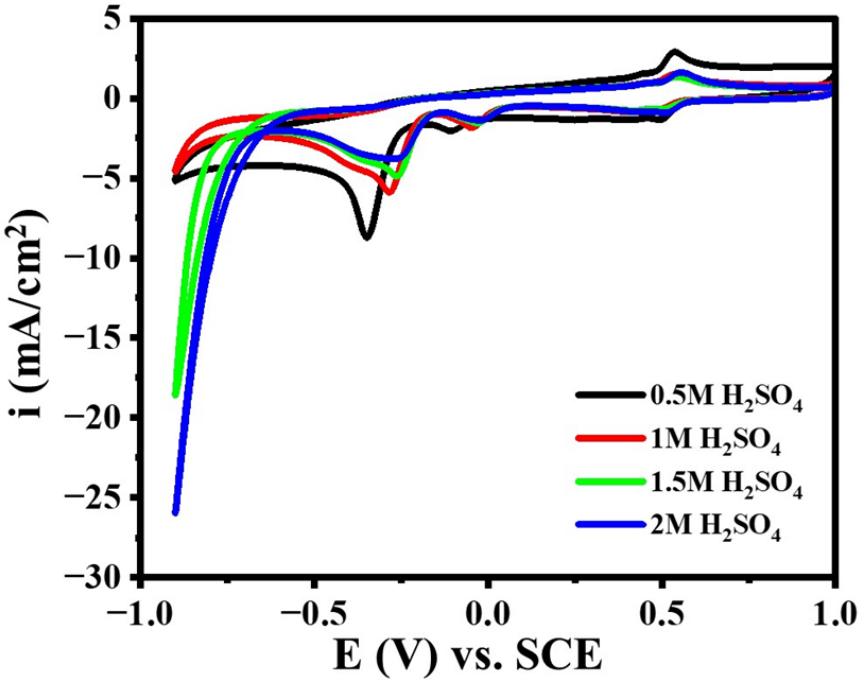


Figure S3. Effect of Electrolyte concentration on electroreduction of 4-NP and NFT in 0.5M, 1M, 1.5M and 2M respectively at M-MWCNTs at scan rate of 50 mV/s.

S-5) Stability test of 4NP and NFT

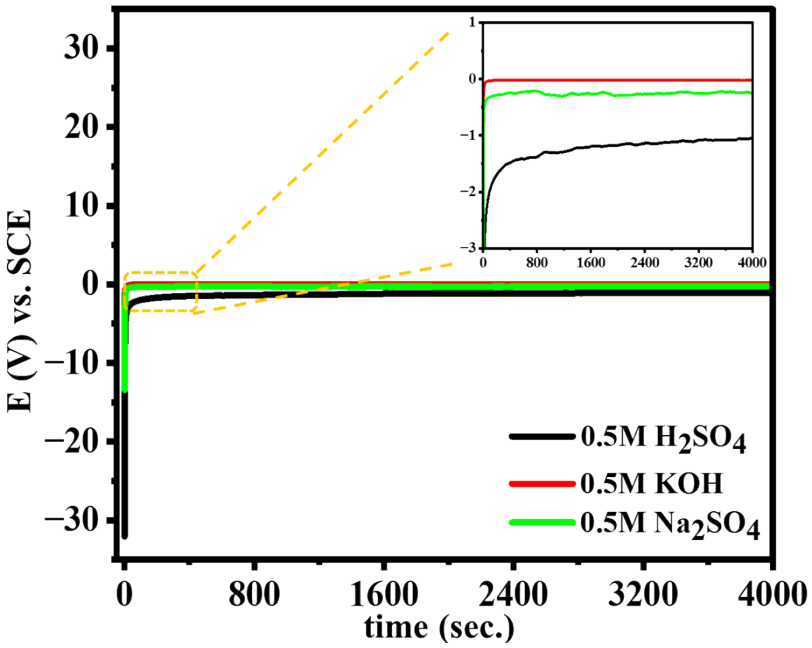
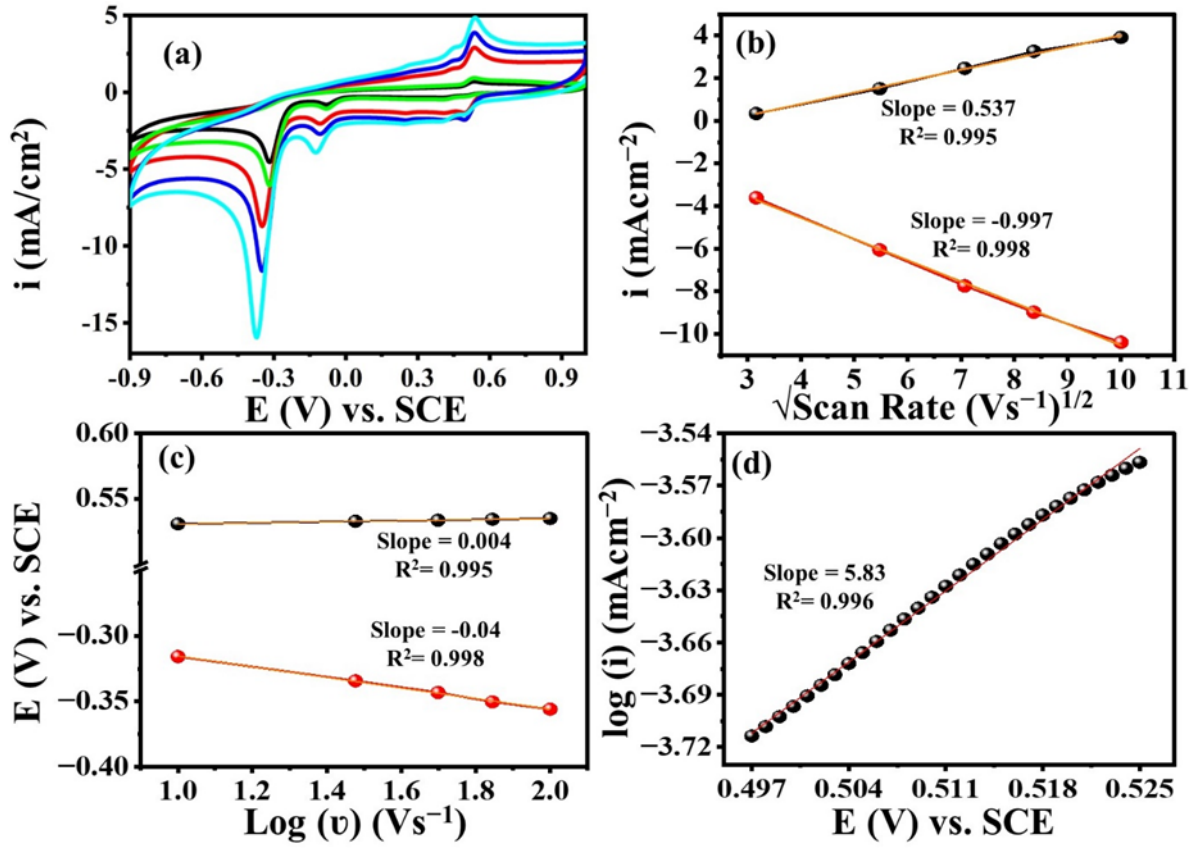


Figure S4. i-t stability tests in acidic, basic and neutral medium for 4mM 4-NP and NFT respectively vs SCE for 4000s.

S-6) Electrochemical Studies:



This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Figure S5. (a) Cyclic voltammograms of M-MWCNT in 0.5M H2SO4 with 4mM drug + 4mM 4-NP, at different scan rates: (a) 10, (b) 30, (c) 50, (d) 70, and (f) 100 mVs −1; **(b)** Anodic and cathodic peak currents (Ipa/c) versus square root of the scan rate ($v1/2$) recorded in 0.5M H2SO4 with 4mM drug + 4mM 4-NP; **(c)** Anodic and cathodic potentials (Epa/c) vs. log v. recorded in 0.5M H2SO4 with 4mM drug + 4mM 4-NP; **(d)** The plot of anodic peak current Ipa in mA vs square root of scan rate in Vs−1 for the M-MWCNT in 0.5M H2SO4 with 4mM drug + 4mM 4-NP in the scan rate range from 10 to 100 mVs^{-1}.

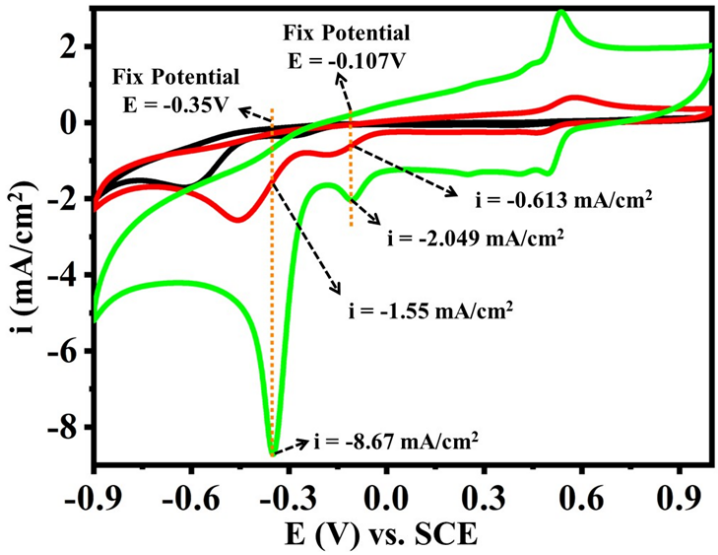


Figure S6. CV curves of Bare, CNT & CNT-Mel on 4mM drug + 4-NP at a scan rate of 50 mV/s

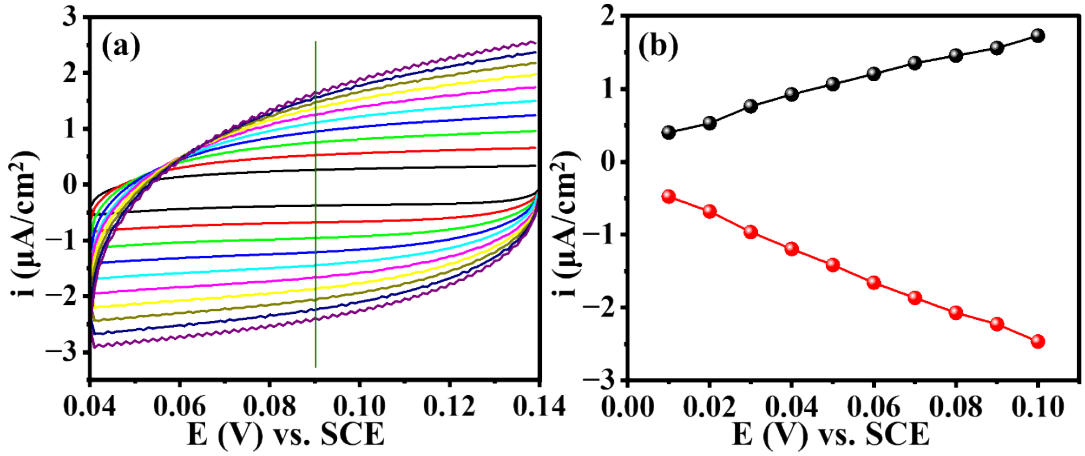


Figure S7-CV curves of the M-MWCNTs/GCE electrode in a non-Faradic area 4mM 4-NP and NFT in 0.5M H2SO4 at the scan rates of 10, to 100 mV/s. (b) corresponding capacitive currents plotted as a function of the scan rate.

Calculation for electrochemical active surface area:

Capacitive currents plotted as a function of the scan rate. *Cdl* was calculated:

$$Cdl = (\text{Slope anodic} - \text{Slope cathodic})/2$$

ECSA was calculated over by the *Cdl* using the specific surface capacitance (*Cs*) of the electrode

Please do not adjust margins

surface:

$$ECSA = Cdl / Cs$$

Table S-1. Comparative electroanalytical parameters for the determination of NFT at M-MWC/GCE with previous reports.

Sr. No.	Electrocatalyst	Methods	Linear range (µM)	LOD (µM)	Reference
1.	AgSAE	LSV	80.3–320.2	47.9	[1]
2.	CNF/SPCE	DPV	0.2–100	81	[2]
3.	NSO/GCE	i-t	0.006–466.67	3	[3]
4.	dsDNA/PAMT	CV	6-100	0.6	[4]
5.	rGO/Fe3O4NRs/GCE	DPV	0.1–100	0.083	[5]
6.	AHD-McAb/GCE	CV	0.198–211.0	0.198	[6]
7.	**M-MWCNT**	**LSV**	**2-18**	**0.167**	**This Work**

Table S-2. Comparative electroanalytical parameters for the determination of 4-NP at M-MWC/GCE with previous reports.

Sr. No.	Electrocatalyst	Methods	Linear range (µM)	LOD (µM)	Reference
1.	Reduced graphene oxide (rGO)/GCE	DPV	50-800	42	[7]
2.	DTD/Ag NPs/GCE	CV	1-100	0.25	[8]
3.	rGO- Ag/GCE	Amprometry	0.5-5.6	0.32	[9]
4.	FeOx/TiO2@mC/GCE	Amperometry	5-310	0.183	[10]
5.	CeO2-CuO/GCE	CV	74-300	2.03	[11]
6.	CoOxNS/GCE	CV	20-240	0.3	[12]
7.	Zeolite/c–PANI–SSA/GCE	CV	1-100	1.27	[13]
8.	**M-MWCNT**	**LSV**	**2-18**	**0.165**	**This Work**

References:

[1] P. Salgado-Figueroa, P. Jara-Ulloa, A. Alvarez-Lueje, J.A. Squella, Sensitive determination of nitrofurantoin by flow injection analysis using carbon nanofiber screen printed electrodes, Electroanalysis. 25 (2013) 1433–1438. https://doi.org/10.1002/elan.201300065.

[2] Z. Krejčová, J. Barek, V. Vyskočil, Voltammetric determination of nitrofurantoin at a mercury meniscus modified silver solid amalgam electrode, Electroanalysis. 27 (2015) 185–192. https://doi.org/10.1002/elan.201400410.

 This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Please do not adjust margins

[3] M. Annalakshmi, S. Sumithra, S.M. Chen, T.W. Chen, X.H. Zheng, Facile synthesis of ultrathin NiSnO3nanoparticles for enhanced electrochemical detection of an antibiotic drug in water bodies and biological samples, New J. Chem. 44 (2020) 10604–10612. https://doi.org/10.1039/d0nj01375g.

[4] G. Aydoğdu, G. Günendi, D.K. Zeybek, B. Zeybek, Ş. Pekyardimci, A novel electrochemical DNA biosensor based on poly-(5-amino-2-mercapto-1, 3,4-thiadiazole) modified glassy carbon electrode for the determination of nitrofurantoin, Sensors Actuators, B Chem. 197 (2014) 211–219. https://doi.org/10.1016/j.snb.2014.02.083.

[5] B. He, J. Li, A sensitive electrochemical sensor based on reduced graphene oxide/Fe3O4 nanorod composites for detection of nitrofurantoin and its metabolite, Anal. Methods. 11 (2019) 1427–1435. https://doi.org/10.1039/c9ay00197b.

[6] Q. Wang, Y.C. Liu, Y.J. Chen, W. Jiang, J.L. Shi, Y. Xiao, M. Zhang, Development of a direct competitive chemiluminescent ELISA for the detection of nitrofurantoin metabolite 1-amino-hydantoin in fish and honey, Anal. Methods. 6 (2014) 4414–4420. https://doi.org/10.1039/c4ay00487f.

[7] P. Wiench, B. Grzyb, Z. González, R. Menéndez, B. Handke, G. Gryglewicz, pH robust electrochemical detection of 4-nitrophenol on a reduced graphene oxide modified glassy carbon electrode, J. Electroanal. Chem. 787 (2017) 80–87. https://doi.org/10.1016/j.jelechem.2017.01.040.

[8] G. Rounaghi, R.M. Kakhki, H. Azizi-Toupkanloo, Voltammetric determination of 4-nitrophenol using a modified carbon paste electrode based on a new synthetic crown ether/silver nanoparticles, Mater. Sci. Eng. C. 32 (2012) 172–177. https://doi.org/10.1016/j.msec.2011.10.014.

[9] Y. Tang, R. Huang, C. Liu, S. Yang, Z. Lu, S. Luo, Electrochemical detection of 4-nitrophenol based on a glassy carbon electrode modified with a reduced graphene oxide/Au nanoparticle composite, Anal. Methods. 5 (2013) 5508–5514. https://doi.org/10.1039/c3ay40742j.

[10] M. Wang, Y. Liu, L. Yang, K. Tian, L. He, Z. Zhang, Q. Jia, Y. Song, S. Fang, Bimetallic metal–organic framework derived FeOx/TiO2 embedded in mesoporous carbon nanocomposite for the sensitive electrochemical detection of 4-nitrophenol, Sensors Actuators, B Chem. 281 (2019) 1063–1072. https://doi.org/10.1016/j.snb.2018.11.083.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

Please do not adjust margins

[11] S.B. Khan, K. Akhtar, E.M. Bakhsh, A.M. Asiri, Electrochemical detection and catalytic removal of 4-nitrophenol using CeO2-Cu2O and CeO2-Cu2O/CH nanocomposites, Appl. Surf. Sci. 492 (2019) 726–735. https://doi.org/10.1016/j.apsusc.2019.06.205.

[12] A. Noorbakhsh, M.M. Mirkalaei, M.H. Yousefi, S. Manochehri, Electrodeposition of cobalt oxide nanostructure on the glassy carbon electrode for electrocatalytic determination of para-Nitrophenol, Electroanalysis. 26 (2014) 2716–2726. https://doi.org/10.1002/elan.201400386.

[13] A. Jović, A. Đorđević, M. Čebela, I. Stojković Simatović, R. Hercigonja, B. Šljukić, Composite zeolite/carbonized polyaniline electrodes for p–nitrophenol sensing, J. Electroanal. Chem. 778 (2016) 137–147. https://doi.org/10.1016/j.jelechem.2016.08.025.

 This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins