Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Metal-Organic Framework Functionalized Sulphur doped Graphene: A Promising Platform for selective and sensitive Electrochemical Sensing of Acetaminophen, Dopamine and H_2O_2

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Figures and Tables:

Table-S1: Peak potential values (E_{pa} and E_{pc}) and peak current values (I_{pa} and I_{pc}) of 2 mM Acetaminophen and 2 mM Dopamine in 0.1M PBS (pH 7.0) over various electrodes systems viz. Bare GCE, Cu-MOF, S-Gr and Cu-MOF@S-Gr.

Table: S2-Peak potential values (E_{pa}) and peak width values of 0.5mM Acetaminophen and 0.5mM Dopamine in 0.1M PBS (pH 7.0) estimated from DPVs recorded over various electrode systems viz. Bare GCE, Cu-MOF/GCE and Cu-MOF@S-Gr/GCE and the Resolution (R) observed for the presence of these analytes from their mixtures.

Table: S3- Comparison of the different parameters regarding the electrochemical sensing of acetaminophen (AC) and dopamine (DA) as observed in the present work with those reported for the electrochemical sensing of these analytes over various so claimed state-of-art modified electrode materials.

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Fig-S1: DPVs recorded for 0.5mM Acetaminophen **[panel A]** and 0.5mM Dopamine **[panel B]** in 0.1M PBS (pH 7.0) over various electrode systems viz. Cu-MOF@S-Gr/GCE **(a)**, Cu-MOF/GCE **(b)** and Bare GCE **(c)**

Fig-S2: DPVs recorded for changing concentration of acetaminophen **[panel A]** and dopamine **[panel C]** in 0.1M PBS (pH 7.0) over Cu-MOF@S-Gr/GCE. Calibration plots between $[I_p]$ v/s [AC], I_p= -4.0443+0.1645[AC] (R^2=0.99) with linear behavior in the concentration range of 2µM -98 µM **[panel B].** Calibration plots between $[I_p]$ v/s [DA] with two linear ranges from 10µM-36µM,I_p= -1.3661+0.1121 [DA](R^2=0.99) and from 38µM- 80µM, I_p= 0.3677+0.07052 [DA](R^2=0.99) **[panel D].**

Fig-S3: DPVs recorded for acetaminophen and dopamine in 0.1M PBS (pH 7.0) over Cu-MOF@S-Gr/GCE in presence of ascorbic acid as an interfering agent.

Fig-S4: CV curves recorded for 2 mM H_2O_2 over different electrode systems viz. Bare GCE **(a)**, S-Gr/GCE **(b)**, Cu-MOF/GCE **(c)** and Cu-MOF@S-Gr/GCE **(d)[panel A]**; CVs recorded for changing concentration of H_2O_2 from 0 -3 mM over Cu-MOF@SGr modified GCE **[panel B]**.

1. Double-potential step Chronocoulometry

The electrochemically effective surface area (ECSA) of the Cu-MOF@S-Gr modified GCE was estimated from the slope of the plot (Q versus $t^{1/2}$) data recorded for the double step Chronocoulometric response of $Fc(CH_2OH)$ solution (2mM) as model complex following equation :

$$Q(t) = 2nFAC_o D^{\frac{1}{2}} t^{\frac{1}{2}} \pi^{\frac{-1}{2}} + Q_{dl} + Q_{ads}$$

where, A is the electrochemically active areas of the working electrode, n is the number of electron transfer, D is the diffusion coefficient of the redox probe, C is the concentration of substrate, Q_{dl} is the double layer charge which could be eliminated by background subtraction, Q_{ads} is the Faradaic charge and could be obtained by the intercept of the Anson's plot after the subtraction of background. The Chronocoulometric curve of the various electrode systems in $Fc(CH_2OH)$ solution (2mM, 0.1M KNO_3) is displayed in **Fig-6(A)**. The redox reaction $Fc(CH_2OH)/Fc^+(CH_2OH)$ involves one-electron transfer (n=1) and the diffusion co-efficient of $Fc(CH_2OH)$ is 7.5×10^{-6} cm^2s^{-1}.The electroactive surface area calculated is 0.104 cm^2 for bare GCE, 0.171cm^2 for Cu-MOF/GCE and 0.195cm^2 for Cu-MOF@S-Gr/GCE. The roughness factor of the bare GCE thus obtained is equal to 1.46. It is clear that the electroactive surface area (ECSA) follows the order: Cu-MOF@S-Gr/GCE> Cu-MOF/GCE> Bare GCE which can be attributed to the incorporation of S-Gr that significantly increases the ECSA of the nanocomposite modified electrode.

Table-S1: *Peak potential values (E_{pa} and E_{pc}) and peak current values (I_{pa} and I_{pc}) of 2mM acetaminophen and 2mM dopamine in 0.1M PBS (pH 7.0) over various electrode systems viz. Bare GCE, Cu-MOF/GCE, S-Gr/GCE and Cu-MOF@S-Gr/GCE.*

Electrode	**2mM AC**		**2mM DA**	
	E_{pa}(V)	**I_{pa}(μA)**	**E_{pa}(V)**	**I_{pa}(μA)**
Bare GCE	0.391	4.260	0.273	3.846
S-Gr	0.370	10.67	0.232	11.80
Cu-MOF	0.222	25.03	0.176	50.78
Cu-MOF@S-Gr	0.219	47.11	0.175	62.20

2. DPV analysis

In case of AC, the calibration plot confirms that AC oxidation peak current is linearly dependent over its concentration in the concentration range of 2μM to 98μM with linear regression equation of I_p= -4.0443+0.1645[AC] (R^2=0.99). The limit of detection for AC was found to be 0.012μM. Similarly, the calibration plot of DA confirms the linear increase in the oxidation peak current with increasing DA concentration. However, in this case, two linear segments with different slopes were observed in a total range of 10μM to 80μM. The linear regression equation for 10μM-36μM is, I_p= -1.3661+0.1121 [DA] (R^2=0.99) while the other one for 38μM- 80μM is Ip= 0.3677+0.07052 [DA] (R^2=0.99). The detection limit was calculated to be 0.0371μM. Besides, from the slope of the calibration plot and the electroactive area, the normalized sensitivity for electrochemical detection ability of Cu-MOF@S-Gr towards AC and DA was calculated from the slope of the calibration plot. Thus, the sensitivity of 0.85μA/μM/cm^2 and 0.58μA/μM/cm^2 for AC and DA was obtained respectively.

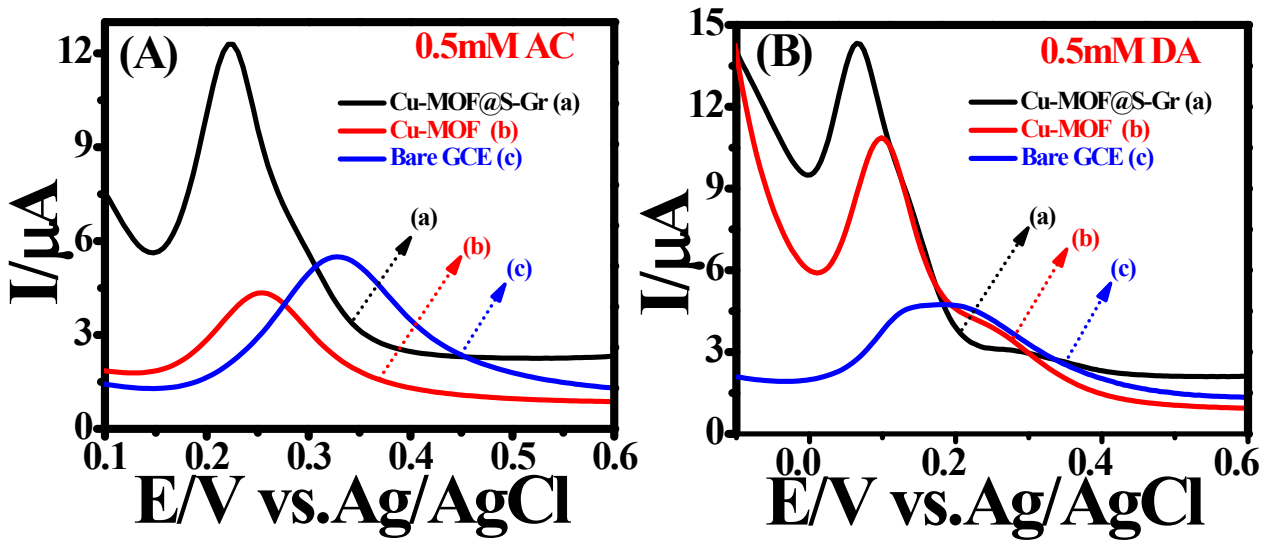

Figure: S1. *DPVs recorded for 0.5mM acetaminophen **[panel A]** and 0.5mM dopamine **[panel B]** in0.1M PBS (pH 7.0) over various electrode systems viz. Cu-MOF@S-Gr/GCE **(a)**, Cu-MOF/GCE **(b)** and Bare GCE **(c).***

Table: S2-*Peak potential values (E_{pa}) and peak width values of 0.5mM Acetaminophen and 0.5mM Dopamine in 0.1M PBS (pH 7.0) estimated from DPVs recorded over various electrode systems viz. Bare GCE, Cu-MOF/GCE and Cu-MOF@S-Gr/GCE and the Resolution (R) observed for the presence of these analytes from their mixtures.*

Modified	**0.5 mMDA**		**0.5 mMAC**		**Resolution (R)**
Electrode	**E_{pa}(V)**	**Peak Width**	**E_{pa}(V)**	**Peak Width**	$R = \frac{2[E_{p(AC)} - E_{p(DA)}]}{E_{pw(AC)} + E_{pw(DA)}}$
Bare GCE	0.391	0.251	0.501	0.220	0.47
Cu-MOF	0.127	0.164	0.294	0.189	0.95
Cu-MOF@S-Gr	0.140	0.151	0.468	0.144	2.22

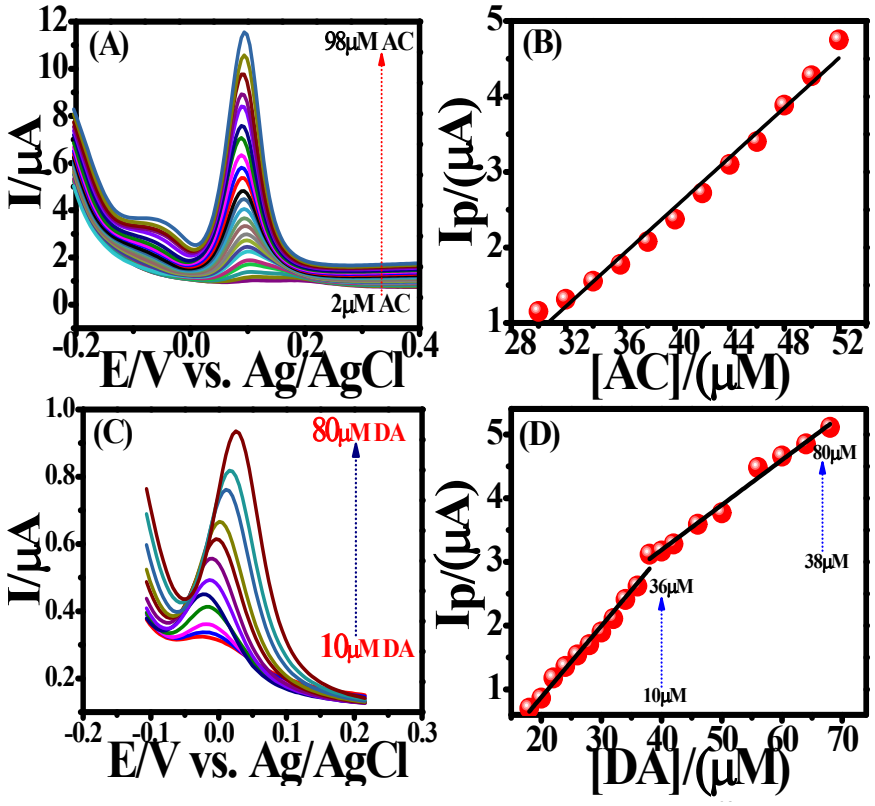

Figure: S2. *DPVs recorded for changing concentrations of acetaminophen **[panel A]** and dopamine **[panel C]** in 0.1M PBS (pH 7.0) over Cu-MOF@S-Gr/GCE. Calibration plots between [I_p] v/s [AC], I_p= -4.0443+0.1645 [AC] (R^2=0.99) with linear behaviour in the concentration range of 2μM -98 μM **[panel B].** Calibration plots between [I_p] v/s [DA] with two linear ranges from 10μM-36μM, I_p= -1.3661+0.1121 [DA] (R^2=0.99) and from 38μM- 80μM, Ip= 0.36766+0.07052 [DA] (R^2=0.99) **[panel D].***

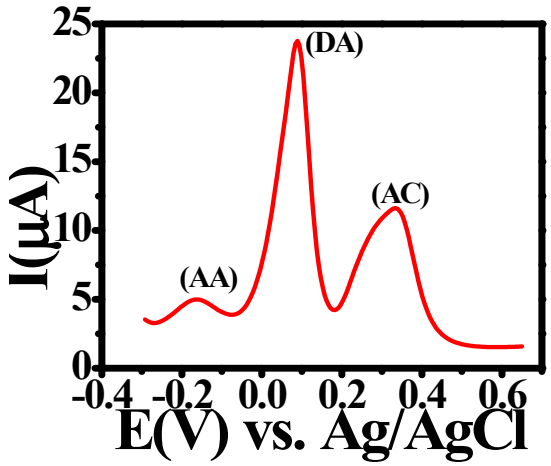

Figure: S3. *DPVs recorded for acetaminophen and dopamine in 0.1M PBS (pH 7.0) over Cu-MOF@S-Gr/GCE in presence of ascorbic acid as an interfering agent.*

Table.S3: *Comparison of the different parameters regarding the electrochemical sensing of acetaminophen (AC) and dopamine (DA)as observed in the present work with those reported for the electrochemical sensing of these analytes over various so claimed state-of-art modified electrode materials.*

	Acetaminophen (AC)		Dopamine (DA)			
Modified Electrode	**Linear Range**	**LOD (μM)**	**Linear range**	**LOD (μM)**	**Sensitivity (μA/μM/cm²)**	**Ref.**
Gold nanosheets/GCE	3-320	0.23	2-298	0.28	-	[1]
Ni-O-CuO/GR/GCE	4-100 100-400	1.33	0.5-20	0.167	0.618(AC) 1.12(DA)	[2]
[AgLn]/GCE	5-300	0.5	5-200	0.7	-	[3]
FC-S-Au/CNC/Graphene/GCE	0.5-46	0.1	0.2-2.5	0.05	-	[4]
Cu(tpa)-EGr/GCE	1-100	0.36	1-50	0.21	-	[5]
Cu MOFs/MWCNT	1-40	0.232	0.6-70	0.083	-	[6]
AG-NA/GCE	0.05-20	0.016	0.5-35	0.33	-	[7]
MWCNT/GO	0.5-400	0.05	0.2-400	0.02	0.938(AC) 1.53(DA)	[8]
Ag-ZIF-67p/GCE	0.5-160	0.2	0.2-150	0.05	0.798(AC) 1.11(DA)	[9]
Pt/CeO_2@Cu_2O-CPE	0.5-100	0.091	0.5-100	0.079	-	[10]
PXa/Au/Cu-TCPP/GCE	5-125	1.5	5-100	1.0	-	[11]
Cu MOF/ERGO	0.2-160	0.016	0.2-300	0.013	-	[12]
WP6-Pd-COF	0.1-7.5	0.03	0.2-8	0.060	-	[13]
3D-N-Gr	0.1-600	0.26	1-1000	0.02	-	[14]
Ce/Selenotungstate/CFMCN	8-600	2.03	4-100	0.053	-	[15]
AC/CPE	0.1-1000	0.0282	0.1-1000	0.0313	-	[16]
α-Fe_2O_3-en-CHIT-g-PANI	5-100	5.7	-	-	1.1(AC)	[17]
Au@Pd HNRs/BG/GCE	130-1010	6.35	50-275	4.58	-	[18]
ECG/FTO	-	-	0-100	0.26	-	[19]
Cu-MOF@S-Gr	**2-188**	**0.012**	**1-113**	**0.0371**	**0.85(AC) 0.58(DA)**	**Present Work**

H_2O_2 Sensing

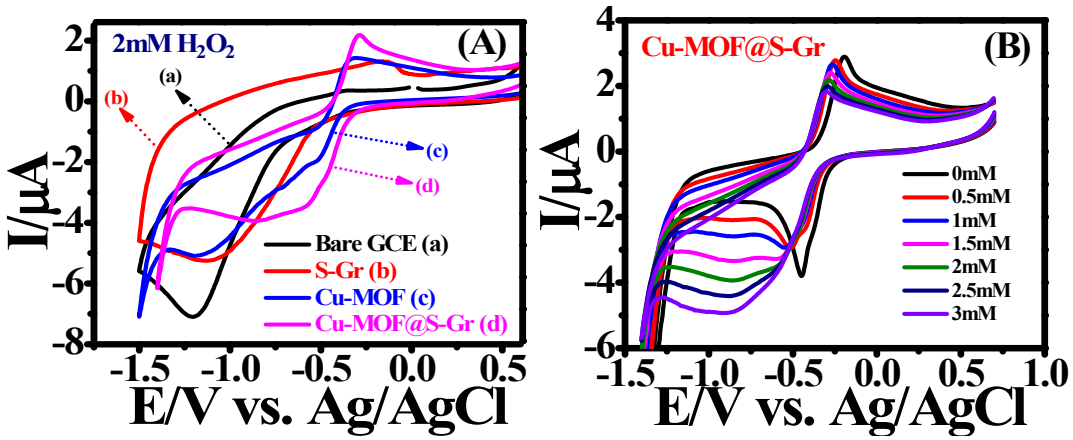

Figure: S4.*CV curves recorded for 2mM H_2O_2 over different electrode systems viz. Bare GCE* ***(a)****, S-Gr/GCE* ***(b)****, Cu-MOF/GCE* ***(c)*** *and Cu-MOF@S-Gr/GCE* ***(d)[panel A]****. CVs recorded for changing concentration of H_2O_2 from 0mM-3mM over Cu-MOF@S-Gr modified GCE* ***[panel B]****.*

Table.S4: *A Comparison of the different parameters regarding the electrochemical sensing of H_2O_2as observed in the present work with those reportedoverdifferent materials purposefully crafted for the said sensing.*

Hydrogen peroxide(H_2O_2) Electrochemical Sensing Specific Parameters				
Modified Electrode	**Linear Range(μM)**	**Detection limit(μM)**	**Sensitivity (μA/μM. cm^2)**	**References**
N-CNT	1.76-139	0.5	0.830	[20]
Cu_xO NPs@ZIF-8	1.5-21442	0.15	0.178	[21]
TOAB/ZnP(p)-C60/GCE	35 - 3400	0.81	-	[22]
Co_3O_4/MWCNTs/CPE	20–430	2.46	1.003	[23]
$Ni(OH)_2$/ERGO MWNT/GCE	10–9050	4.0	-	[24]
$[Cu(adp)(BIB)(H_2O)]_n$/GCE	0.1–2.75	0.068	–	[25]
Cu-MOF/MPC/GCE	10–11,600	3.2	-	[26]
Cu-CoTCPP/MWCNTs	0.5-1800	0.24	0.168	[27]
Pt NPs@UIO-66	5-14750	3.06	0.753	[28]
Co(III)/MWCNT/Nafion	0.05-100	0.05	–	[29]
AuPt/ZIF-8-rGO	0.1-18000	0.019	–	[30]
Ni(II)-MOF/CNTs	10-51600	2.1	–	[31]
Au NPs/UiO-66	200-23000	0.045	0.329	[32]
$ZnMn_2O_4$@rGO	0.03-6000	0.012	11.21	[33]
MnO-Mn_3O_4@rGO	4-1700	0.1	–	[34]
$NiCo_2S_4$/rGO	25-11250	0.19	0.118	[35]
MIL-53-Cr^{III}	25-500	3.52	11.9**(μA/mM)**	[36]
Cu-MOF@S-Gr	**0.1-3.0**	**0.0113(redn)**	**63.82(redn)**	**Present**
	1.0-10	**0.115 (oxdn)**	**8.13(oxdn)**	**Work**

Table: S5- *Estimation of recovery of spiked H_2O_2 in Tap water samples by the proposed DPV method over Cu-MOF@S-Gr nanocomposite modified GCE.*

$[H_2O_2]/(\mu M)$			
$[H_2O_2]/(\mu M)$	**Amount Recovered**	**Recovery (%)**	**RSD (%)**
1	0.97	97.0	0.39
2	1.97	98.5	0.65
3	2.89	96.33	0.50

References:

1. Q. L. Zhang, J.X. Feng, A.J. Wang, J. Wei, Z.Y. Lv and J.J. Feng. A glassy carbon electrode modified with porous gold nanosheets for simultaneous determination of dopamine and acetaminophen. *Michrochim. Acta*., **2015,***182,* 589-595.

2.B. Liu, X. Ouyang, Y. Ding, L. Luo, D. Xu and Y. Ning. Electrochemical preparation of nickel and copper oxides-decorated graphene composite for simultaneous determination of dopamine, acetaminophen and tryptophan. *Talanta*., **2016,***146,* 114-21.

3.H. Chiniforoshan, L. Tabrizi and N. Pourrahim. A new Ag-nanoparticle with 4-nitro phenylcyanamide ligand: synthesis characterization and application to the detection of dibucaine, naphazoline, dopamine, and acetaminophen.*J. Appl. Electrochem.,* **2015,***45,* 197-207.

4.L. Yang, N. Huang, Q. Lu, M. Liu, H. Li, Y. Zhang and S. Yao. A quadruplet electrochemical platform for ultrasensitive and simultaneous detection of ascorbic acid, dopamine, uric acid and acetaminophen based on a ferrocene derivative functional Au NPs/carbon dots nanocomposite and graphene. *Anal Chimica. Acta*., **2016,***903,* 69-80.

5.X. Wang, Q. Wang, Q. Wang, F. Gao, Y. Yang and H. Guo. Highly dispersible and stable copper terephthalate metal-organic framework-graphene oxide nanocomposite for an electrochemical sensing application. *ACS Appl. Mater. Interfaces*., **2014,** *6,* 11573-80

6.W. Yao, H. Guo, H. Liu, Q. Li, R. Xue, N. Wu, L. Li, M. Wang and W. Yang. Simultaneous Electrochemical Determination of Acetaminophen and Dopamine Based on Metal-Organic Framework/Multiwalled Carbon Nanotubes-Au@Ag Nanocomposites. *J. Electrochemical Society*., **2019,***166,* 1258-1267.

7. D. Kim, S. Lee and Y. Piao. Electrochemical determination of dopamine and acetaminophen using activated graphene-Nafion modified glassy carbon electrode.*J. Electroanal. Chem.,* **2017,***794,* 221-228.

8. S. Cheemalapati, S. Palanisamy, V. Mani and S. M. Chen. Simultaneous electrochemical determination of dopamine and paracetamol on multiwalled carbon nanotubes/graphene oxide nanocomposite-modified glassy carbon electrode. *Talanta*., **2013,***117,* 297-304.

9.J. Tang, Y. Liu, J. Hu,S. Zheng, X. Wang, H. Zhou and B. Jin. Co-based metal-organic framework nanopin as composite doped with Ag nanoparticles: A sensitive electrochemical sensing platform for simultaneous determination of dopamine and acetaminophen.*Microchemical Journal*., **2020,***155,*104759.

10. A.R. Rajamani and S. C. Peter. Novel Nanostructured Pt/CeO_2@Cu_2O Carbon-Based Electrode To Magnify the Electrochemical Detection of the Neurotransmitter Dopamine and Analgesic Paracetamol.*ACS. Appl. Nano. Mater.,* **2018,***1,* 5148-5157.

11. Z. Qiu, T. Yang, R. Gao, G. Jie and W. Hou. An electrochemical ratiometric sensor based on 2D MOF nanosheet/Au/polyxanthurenic acid composite for detection of dopamine. *J. Electroanal. Chem*., **2019,***835,* 123-129.

12. M.B. Gholivand and M. Amiri. Simultaneous detection of dopamine and acetaminophen by modified gold electrode with polypyrrole/aszophloxine film. *J. Electroanal. Chem*.,**2012,***676,* 53-59.

13. X. Tan, T. Mu, S. Wang, J. Li, J. Huang, H. Huang, Y. Pu and G. Zhao. Simultaneous determination of Acetaminophen and dopamine based on a water-soluble pillar[6]arene and ultrafine Pd nanoparticle-modified covalent organic framework nanocomposite. *Analyst.*, **2021,***146,*262-269.

14. J. Jiang, D. Ding, J. Wang, X. Lin and G. Diao. Three-dimensional nitrogen-doped graphene-based metal-free electrochemical sensors for simultaneous determination of ascorbic acid, dopamine, uric acid, and acetaminophen**.** *Analyst.,* **2021,***146,* 964-970.

15. J. Jiang, L. Liu, G. Liu, D. Wang, Y. Zhang, L. Chen and J. Zhao. Organic-Inorganic Hybrid Cerium-Encapsulated Selenotungstate Including Three Building Blocks and Its Electrochemical Detection of Dopamine and Paracetamol. *Inorg. Chem*., **2020,***59,* 15355-15364.

16. H. Hammani, A. Hrioua, S. Aghris, S. Lahrich, S. Saqrane, M. Bakasse and M.A. El-Mhammedi. Activated charcoal as a capture material for dopamine, paracetamol and salicylic acid in human blood and pharmaceutical formulations. *Mater.Chem. Phys.,* **2020,***240,* 122111.

17. C. S. Kushwaha and S. K. Shukla. Electrochemical Sensing of Paracetamol Using Iron Oxide Encapsulated in Chitosan-Grafted-Polyaniline. *ACS.Appl.Polymer Mater*., **2020,***2,* 2252-2259.

18. X. Chen, G. Zhang, Y. He, L. Shi, J. Zhang, G. Yang, H. Pan, W. Liu and S.A. Feng. Sensitive Electrochemical Sensor Based on Au@Pd Hybrid Nanorods Supported on B-doped Graphene for Simultaneous Determination of Acetaminophen, Dopamine and Tyrosine. *Int. J. Electrochem. Sci*., **2020,***15,* 5927-5944

19. Md. M. Rahman, D. Liu, N.S. Lopa, J-B. Baek, C-H. Nam and J-J. Lee, Effect of the carboxyl functional group at the edges of graphene on the signal sensitivity of dopamine detection, *J. Electroanal. Chem*., **2021**, *898*, 115628

20. J. M. Goran, E.N. H. Phan, C.A. Favela and K.J. Stevenson. H_2O_2 Detection at Carbon Nanotubes and Nitrogen-Doped Carbon Nanotubes: Oxidation, Reduction, or Disproportionation. *Anal. Chem*., **2015,***87,* 5989-5996

21. J. Yang, H. Ye, F. Zhao and B.A. Zeng. Novel Cu_xO Nanoparticles@ZIF-8 Composite Derived from Core–Shell Metal–Organic Frameworks for Highly Selective Electrochemical Sensing of Hydrogen Peroxide. *ACS Appl. Mater. Interfaces.,* **2016,***8,* 20407-20414.

22. H. Wu, S. Fan, X. Jin, H. Zhang, H. Chen, Z. Dai and X. Zou. Construction of a Zinc Porphyrin–Fullerene-Derivative Based Nonenzymatic Electrochemical Sensor for Sensitive Sensing of Hydrogen Peroxide and Nitrite. *Anal. Chem*., **2014,***86,*6285-6290.

23. H. Heli and J. Pishahang. Cobalt oxide nanoparticles anchored to multiwalled carbon nanotubes: Synthesis and application for enhanced electrocatalytic reaction and highly sensitive nonenzymatic detection of hydrogen peroxide. *Electrochim. Acta*., **2014,***123,* 518–526.

24. A. Gu, G.F. Wang, J. Gu, X.J. Zhang and B. Fang. An unusual H_2O_2 electrochemical sensor based on $Ni(OH)_2$ nanoplates grown on Cu substrate. *Electrochim. Acta*., **2010,***55,* 7182–7187.

25. C. Zhang, M.Y. Wang, L. Liu, X. Yang and X. Xu. Electrochemical investigation of a new Cu-MOF and its electrocatalytic activity towards H_2O_2 oxidation in alkaline solution. *Electrochem. Commun*., **2013,** *33,* 131–134.

26. Y. Zhang, X. Bo, C. Luhana, H. Wang, M. Li and L. Guo. Facile synthesis of a Cu-based MOF confined in macroporous carbon hybrid material with enhanced electrocatalytic ability. *Chem. Commun*., **2013,***49,* 6885–6887.

27. L.M. Shi, J.X. Pan, B. Zhou, X. Jiang. A New Bifunctional Electrochemical Sensor for Hydrogen Peroxide and Nitrite Based on a Bimetallic Metalloporphyrinic Framework. *J. Mater.Chem. B*., **2015**, *3*, 9340-9348

28. Z. Xu, L. Yang and C. Xu. Pt@UiO-66 Heterostructures for Highly Selective Detection of Hydrogen Peroxide with an Extended Linear Range. *Anal. Chem*., **2015**, *87*, 3438-3444

29. C. M. Parnell, F. Watanabe, U.B. Nasini, B. C. Berry, T. Mitchell, A.U. Shaikh and A. Ghosh. Electrochemical sensing of hydrogen peroxide using a cobalt(III) complex supported on carbonaceous nanomaterials. *J. Electroanal. Chem*., **2015,***740,* 37-44.

30. T. Zhang, Y. Xing, Y. Song, Y. Gu, X. Yan, N. Lu, H. Liu, Z. Xu, H. Xu, Z. Zhang and M. Yang. AuPt/MOF–Graphene: A Synergistic Catalyst with Surprisingly High Peroxidase-Like Activity and Its Application for H_2O_2 Detection. *Anal. Chem.,* **2019,***91,* 10589-10595.

31. M. Q. Wang, Y. Zhang, S.J. Bao, Y. N. Yu, C. Ye. Ni(II)-BasedMetal-Organic Framework Anchored on Carbon Nanotubes for Highly SensitiveNon-Enzymatic Hydrogen Peroxide Sensing. *Electrochim. Acta*.,**2016**, *190*, 365-370.

32. Q. Wang, X. Zhang, X. Chai, T. Wang, T. Cao, Y. Li, L. Zhang, F. Fan, Y. Fu and W. Qi. An Electrochemical Sensor for H_2O_2 Based on Au Nanoparticles Embedded in UiO-66 Metal–Organic Framework Films**.** *ACS Appl. Nano Mater*., **2021,***4*, 6103–6110

33. Y. Li, K. Huan, D. Deng, L. Tang, J. Wang and L. Luo. Facile Synthesis of $ZnMn_2O_4$@rGO Microspheres for Ultrasensitive Electrochemical Detection of Hydrogen Peroxide from Human Breast Cancer Cells.*ACS Appl. Mater. Interfaces*., **2020,***12,*3430-3437.

34. Y. Li, L. Tang, D. Deng, H. He, X. Yan, J. Wang and L. Luo. Hetero-structured MnO-Mn_3O_4@rGO composites: Synthesis and nonenzymatic detection of H_2O_2. *Mater.Sci. and Engg*., **2021,***118,*111443.

35. M. Wang, J. Ma, X. Guan, W. Peng, X. Fan, G. Zhang, F. Zhang, Y. Li. A novel H_2O_2 electrochemical sensor based on $NiCo_2S_4$ functionalized reduced graphene oxide.*J. Alloys Compd*., **2019**, *784,* 827–833.

36. N.S. Lopa, Md. M. Rahman, F. Ahmed, S.C. Sutradhar, T. Ryu, and W. Kim, A base-stable metal-organic framework for sensitive and non-enzymatic electrochemical detection of hydrogen peroxide, *Electrochim. Acta*., **2018**, *274*, 49-56.