Supplementary Information

Ionic Liquid Wrapped Co_3O_4 Embedded N Doped Porous Carbon for the Precise Monitoring of Salbutamol from Urine Sample for Dope Test

Muhammad Usman Ur Rehman[a], Gaber A. M. Mersal[b], Muhammad Farhan Farid[a], Azza A. Al-Ghamdi[c], Ahlam I. Al-Sulami[c], Muhammad Waseem Fazal[a], Mohamed M. Ibrahim[b], Saadat Majeed[a]*, Naeem Akhtar[a]*

[a] Institute of Chemical Sciences, Bahauddin Zakariya University (BZU), Multan 60800, Pakistan

[b] Department of Chemistry, College of Science, Taif University, P.O. Box 11099, Taif 21944, Saudi Arabia

[c] University of Jeddah, College of Science, Department of chemistry, Jeddah 21589, Saudi Arabia

Corresponding Author:

Naeem Akhtar: naeemakhtar@bzu.edu.pk

Saadat, Majeed: saadat.majeed@bzu.edu.pk

Section S1:

Synthesis of benzimidazolium-1-acatate ionic liquid (IL)

The benzimidazolium-1-acatate ionic liquid was synthesized through a neutralization reaction of acetic acid with benzimidazole. Briefly, a two-neck boiling flask was taken and poured with 16.9 mmol of benzimidazole and 10 mL of methanol while this mixture was strongly stirred at 64 °C. Subsequently, acetic acid (0.965 mL) was dropwise added, while this solution was kept under reflux for 10-12 h. Light-yellow mixture liquid was obtained through heating reaction at 100 °C by rotary evaporator S[1]. Moreover, liquid was also characterized through Fourier transform infrared (FTIR) analysis and Nuclear Magnetic Resonance spectroscopy (NMR) (Figure S1-S3).

Working electrode fabrication

All the electrochemical experiments were performed with the AMEL-2553 instrument, which was controlled by VA peak software at room temperature measurements. The electrochemical cell used was a conventional three-electrode system, which consisted of a lead pencil graphite (LPG) electrode (dimensions of LPG: 0.5 mm in diameter and 40 mm in length) modified with our synthesized material as working electrode, a platinum wire as counter electrode and Ag/AgCl as a reference electrode. Copper wire was connected to one end of the LPG to maintain the electrical contact. Cyclic voltammetry (CV), chronoamperometry, and electrochemical impedance spectroscopy (EIS) were carried out using Metrohm Autolab (Sr. #AUT50296) instrument, which was controlled by Nova 1.11 software. Rigaku D/max-2550 instrument

equipped with a Cu Kα radiation source (λ=1.5418 Å) was used for XRD measurements. Renishaw in Via-reflex spectrometer was used to record Raman spectra. The SEM images were attained employing the JEOL JSM-6360 LV instrument. FTIR spectra of IL were recorded using a Nicolet 6700 (Thermo-Fisher) spectrometer having a resolution of 4 cm^{-1} and in the range of 400–4000 cm^{-1} using KBr (ratio 5/95 wt. %) pellets. ^{1}H NMR and ^{13}C NMR spectra of IL were recorded at 600MHz in CD_3OD as a solvent and TMS as an internal standard.

Section S2:

FTIR analysis

In order to analyze the chemical structure of as-synthesized IL, FTIR spectroscopy has been employed. The stretching bands present at 2972 cm^{-1} and 3123 cm^{-1} are assigned to the alkyl group and alkenyl C—H stretching respectively. The bands at 1734 cm^{-1} and 1602 cm^{-1} correspond to C=O bonds and C=N, respectively. Also, The absence of stretching vibrations around 3046 cm^{-1} (O—H) verifies the presence of acetate ion S[2].

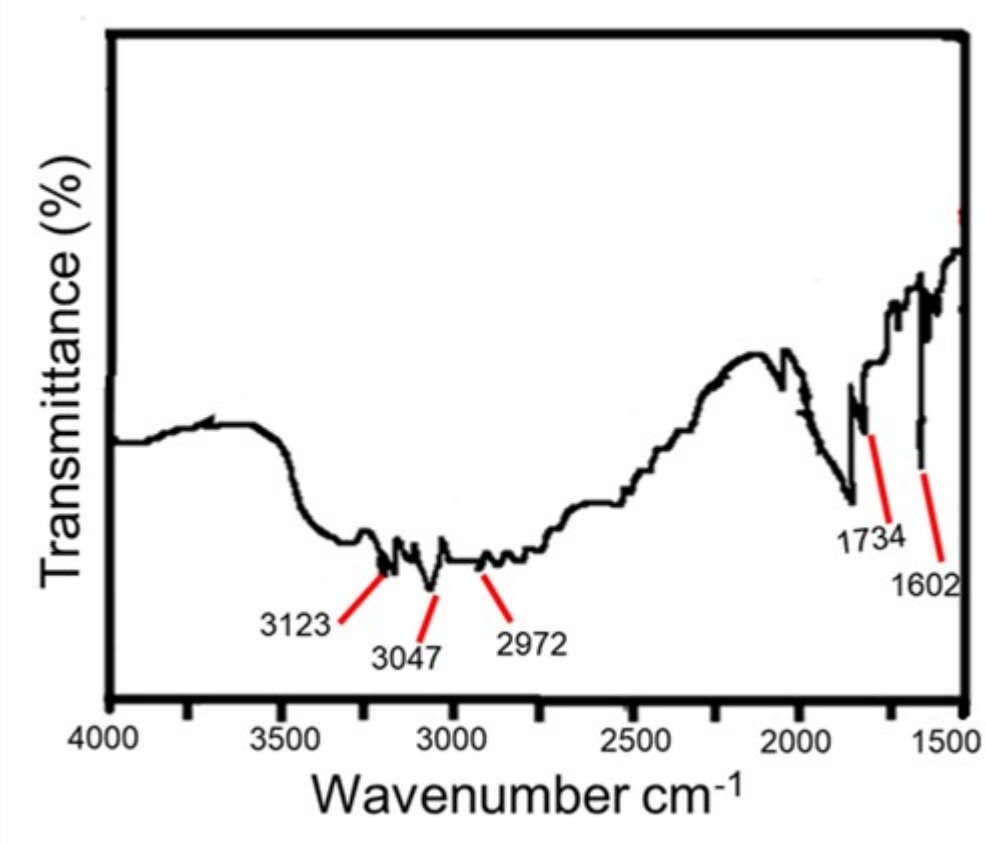

Figure S1 Representing FTIR analysis of IL.

NMR analyses

The purities of IL were verified by NMR.

^{1}H NMR: δ = 1.97 (s, 3H), 7.23 –7.25 (m, 2H), 7.58 –7.6 (m, 2H), 8.23 (s, 1H).

13C NMR: 21.5 (methyl peak), 115.7, 122.1, 138.4, 142.3, 172.5 (carbonyl carbon of acetate ion)

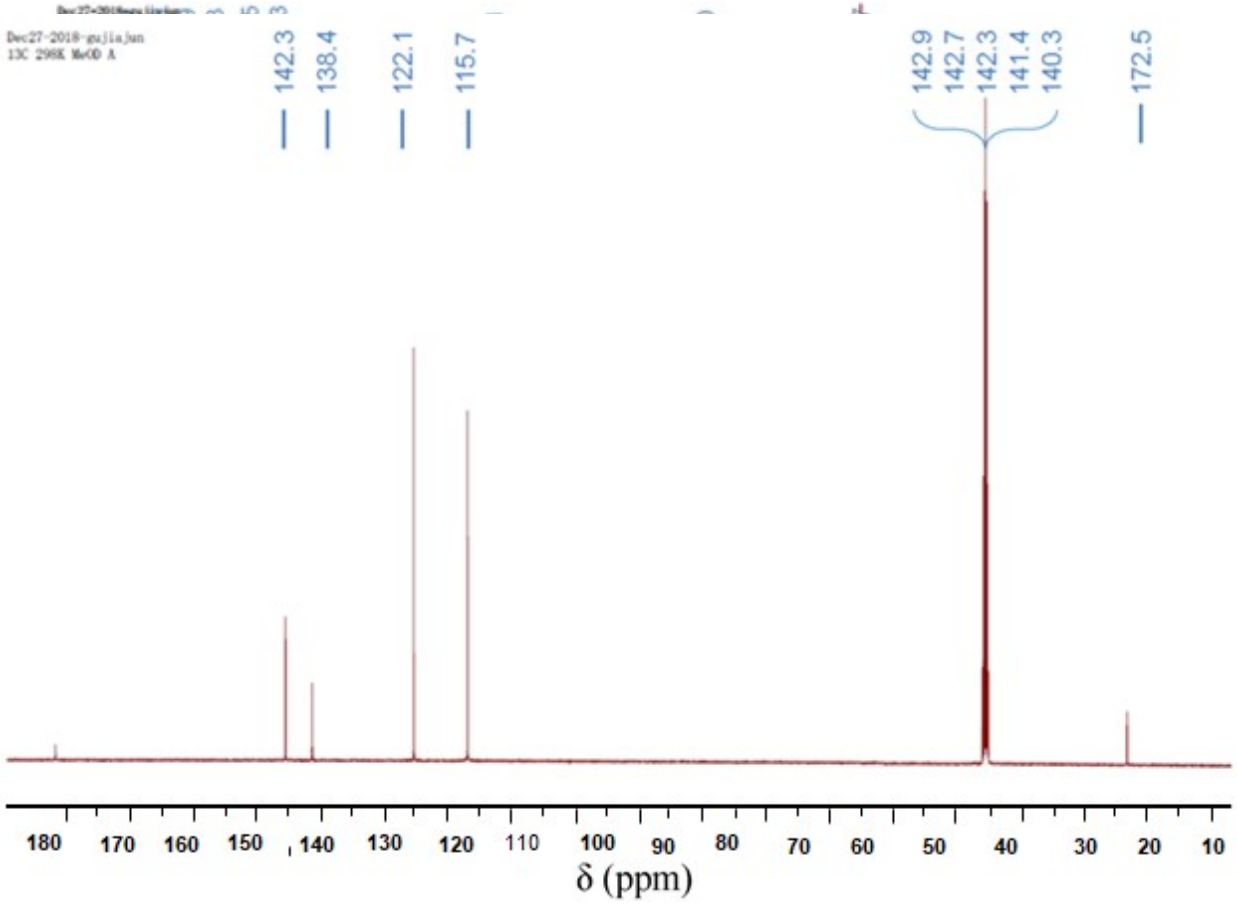

Figure S2. ^{13}C NMR of IL.

^{13}C NMR: 21.5 (methyl peak), 115.7, 122.1, 138.4, 142.3, 172.5 (carbonyl carbon of acetate ion) (Figure S2).

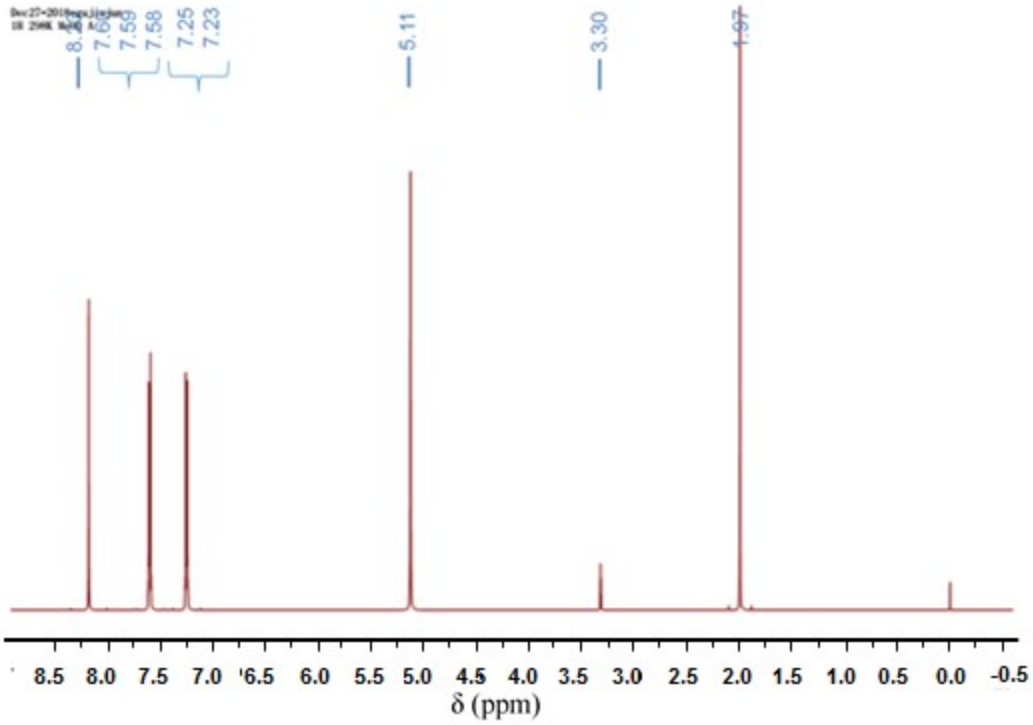

Figure S3. ^{1}H NMR of IL.

^{1}H NMR: δ = 1.97 (s, 3H), 7.23 –7.25 (m, 2H), 7.58 –7.6 (m, 2H), 8.23 (s, 1H) (Figure S3).

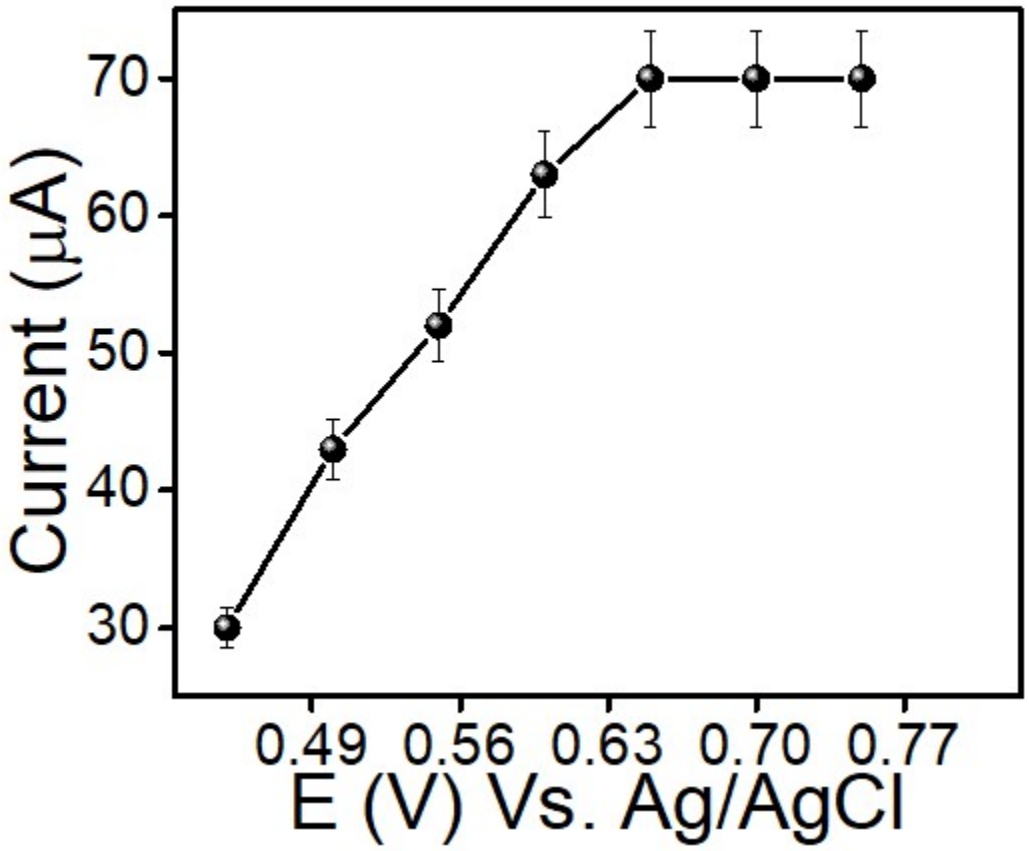

Figure S4. Linear plot drawn from DPV result for IL@NC-Co for optimization of potential.

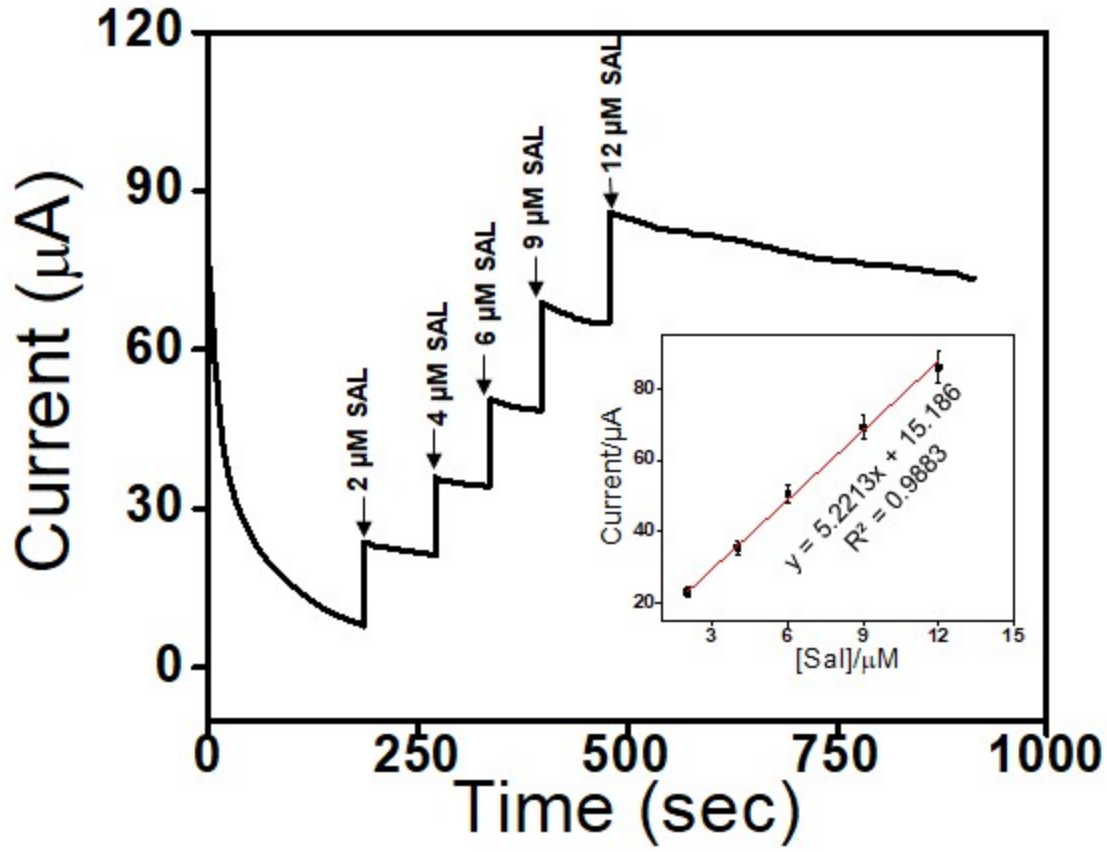

Figure S5. Amperometric response of IL@NC-Co electrode towards SAL with increasing concentrations. (Inset, calibration plot derived from Figure 5 as function peak current (μA) vs SAL concentration (μM))

Limit of detection calculated by using equation S1 by following the already reported literature S[3].

LOD = F x SD/*b*…….. (S1)

Where

F: Factor of 3.3, SD: Standard deviation of the blank, standard deviation of the ordinate intercept, or residual standard deviation of the linear regression, b: Slope of the regression line

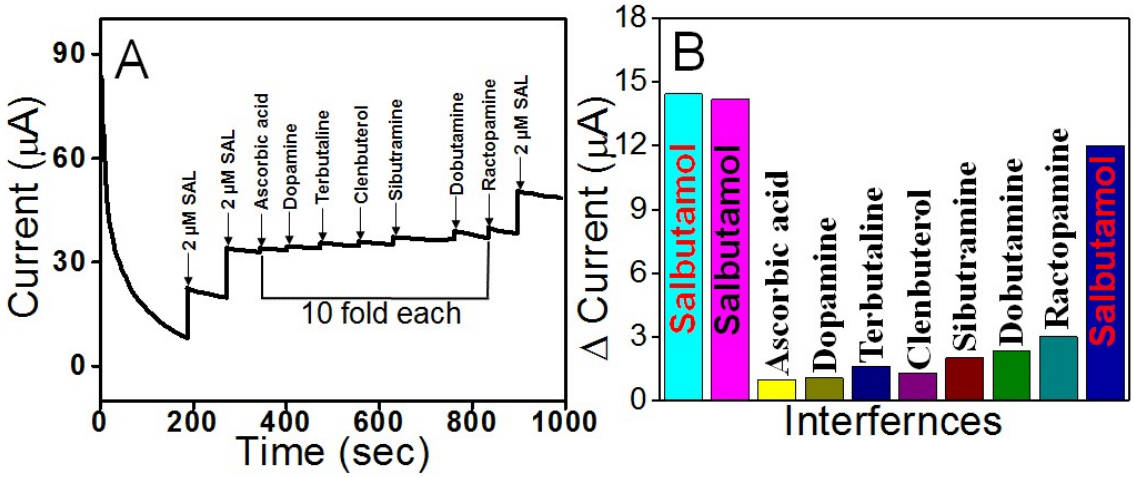

Figure S6 (A) Amperometric response of IL@NC-Co electrode toward SAL with interfering species. Whereas, (B) derived from (Figure S5A) shows the current difference of interfering species with SAL,

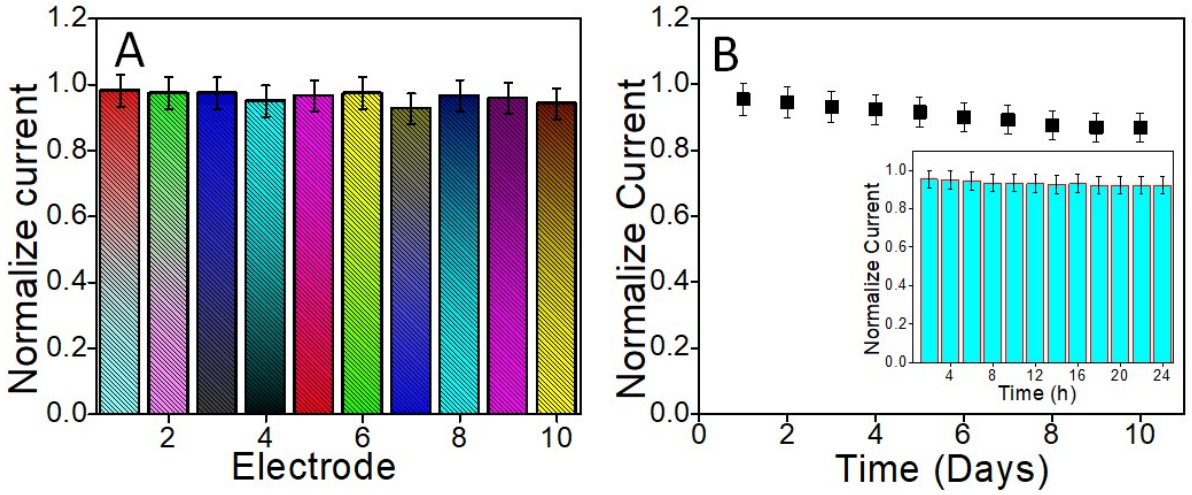

Figure S7. (A) The normalized current representing reproducibility of the 10 different IL@ NC-Co electrodes toward continuous monitoring of 2 μM SAL in 0.1 M PBS solution at applied potential of 0.66 V. Whereas, (B) normalized current response indicating reusability of the IL@ NC-Co electrode toward continuous 2 μM SAL monitoring for 10 days; inset of (B) shows the corresponding histogram of the average response current vs time/h.

Table S1 of comparison of different electrodes along with their linear range and LOD towards SAL

Sr.No	Electrode Name	Linear Range (µM)	Limit of Detection (nM)	Cost-effectiveness	Reference
1	graphene/PEDOT:PSS modified SPCE.	0.001-1.2	1×10^5	Expensive	S[4]
2	Poly(amino sulfonic acid)/GCE	2–100	600	Expensive	S[5]
3	Chitosan-MWCNT/GCE	0.5–40	80	Expensive	S[6]
4	Hybrid carbon nanotubes/GCE	0.1–33	100	Expensive	S[7]
5	CNTs/GCE	1-90	350	Expensive	S[8]
6	MIP/Ag–*N*-RGO-modified GCE	0.3-20	7	Expensive	S[9]
7	IL@NC-Co	2-2500	0.0014	Cost-effective	Our Work

References

S1. Shakeel, F., et al., *Melamine-derived N-rich C-entrapped Au nanoparticles for sensitive and selective monitoring of dopamine in blood samples.* RSC advances, 2022. **12**(40): p. 26390-26399.

S2. Hayat, K., et al., *H2O2 Screening from Saliva of Gum Diseased-patient through CN-dot Wrapped Cu2O Nano-frogspawns Ionic Liquid Nanocomposite.* Electroanalysis, 2020. **32**(8): p. 1664-1670.

S3. Khan, F., et al., *Carbon-dot wrapped ZnO nanoparticle-based photoelectrochemical sensor for selective monitoring of H 2 O 2 released from cancer cells.* Microchimica Acta, 2019. **186**: p. 1-9.

S4. Dechtrirat, D., et al., *An electrochemical MIP sensor for selective detection of salbutamol based on a graphene/PEDOT: PSS modified screen printed carbon electrode.* Rsc Advances, 2018. **8**(1): p. 206-212.

S5. Lijun, L., et al., *The determination of salbutamol sulfat based on a flow-injection coupling irreversible biamperometry at poly (aminosulfonic acid)-modified glassy carbon electrode.* Analytical letters, 2007. **40**(17): p. 3290-3308.
S6. Cao, Z., et al., *Determination of salbutamol sulfate based on chitosan multi-wall carbon nanotubes film modified glassy carbon electrode.* Sensor Letters, 2011. **9**(5): p. 1985-1989.
S7. Lin, K.-C., C.-P. Hong, and S.-M. Chen, *Simultaneous determination for toxic ractopamine and salbutamol in pork sample using hybrid carbon nanotubes.* Sensors and Actuators B: Chemical, 2013. **177**: p. 428-436.
S8. Bai, L., *Electrochemical behavior of salbutamol, clenbuterol, ractopamine and albuterol at CNTs/GCE.* International Journal of Electrochemical Science, 2022. **17**(5): p. 220567.
S9. Li, J., et al., *Ag/N-doped reduced graphene oxide incorporated with molecularly imprinted polymer: An advanced electrochemical sensing platform for salbutamol determination.* Biosensors and Bioelectronics, 2017. **90**: p. 210-216.