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An Innovative Experimental and Mathematical Approach in Electrochemical Sensing on Mapping a Drug Sensor Landscape

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1 Experimental Procedure

1.1 Materials

The chemicals listed below were obtained from Sigma-Aldrich: Ethanol (70.0 % v/v), cerium nitrate hexahydrate (99.0 % w/w), chlorpromazine hydrochloride (98.8 % w/w), ethylene glycol (97.5 % v/v), sodium hydroxide (99.2 % w/w), sodium phosphate monobasic (99.1 % w/w) and dibasic anhydrous (99.2 % w/w), and zirconium oxychloride (98.0 % w/w). These chemicals were utilized in their original form. Deionized (DI) water was employed to create the necessary solutions for the entire study.

1.2 Synthesis of CeO₂/ZrO₂ nanocomposite

Zirconium oxychloride and cerium nitrate hexahydrate, at doses of 0.5 mg and 1.5 mg respectively, were dissolved in 50 mL of deionized water in a beaker and stirred for 1 hour at room temperature. The solution was stirred for one hour prior to introducing additional substances in order to ensure uniform distribution and achieve homogeneity¹. The solution in the beaker underwent a slow introduction of 16.65 g of ethylene glycol while being stirred continuously for 20 minutes. Subsequently, a suspension was formed by adding 5.0 mL of N/10 sodium hydroxide to the mixture mentioned above, and it was stirred for an additional hour. To eliminate any unreacted precursors, the resulting precipitate was centrifuged with water initially, and later with ethanol. The resultant colloidal suspension was dried overnight at 50°C, yielding a crude powder. Finally, the powder underwent calcination at 550°C for a duration of 4 hours.

1.3 Fabrication of modified electrodes

The GCE underwent initial polishing with alumina powder before modification. Subsequently, the GCE was subjected to ultrasonic cleaning using a mixture of water and ethanol. A quantity of 1.0 mg of CeO₂/ZrO₂ was dispersed in water and sonicated for 30 mins. Then, 5.0 μL of the dispersed CeO₂/ZrO₂ was drop-casted onto the surface of the GCE. The modified GCE, referred to as CeO₂/ZrO₂/GCE, was then dried in an air oven. All subsequent electrochemical sensing experiments utilized the aforementioned modified electrode. For the CV studies, a potential window ranging from -0.2 to 1.0 V was employed, with a scan rate of 50.0 mVs⁻¹ in 0.1 M phosphate buffer (PB).

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Table S1 List of parameters used in stochastic modelling

Parameter	Description	Model value	Reference
C_{CPH}^*	Initial reactant concentration	0.01 [mmol/L]	Experiment
D_{CPH}	Reactant diffusion coefficient	2.15e-12 [m ² s ⁻¹]	2
$D_{CPH^{2+}}$	Product diffusion coefficient	(1/3)*2.15e-12 [m ² s ⁻¹]	2
F	Faraday constant	96485.3365 [C/mol]	-
R	Universal gas constant	8.3144621 [J/mol*K]	-
T	Temperature	304.15 [K]	Experiment
E_f^0	Formal potential	0.6 [V]	Experiment
E_i	Start potential	-0.2 [V]	Experiment
E_v	End potential	1.0 [V]	Experiment
v	Scan rate	50 [mVs ⁻¹]	Experiment
n	Number of electron transferred	2	Experiment

Notes and references

- 1 S. K. Ponnaiah, P. Periakaruppan, B. Vellaichamy, New electrochemical sensor based on a silver-doped iron oxide nanocomposite coupled with polyaniline and its sensing application for picomolar-level detection of uric acid in human blood and urine samples, *The Journal of Physical Chemistry B* 122 (2018) 3037–3046.
- 2 R. D. Crapnell, H. S. Alhasan, L. I. Partington, Y. Zhou, Z. Ahmed, A. A. Altalhi, T. S. Varley, N. Alahmadi, G. H. Mehl, S. M. Kelly, et al., Electrochemically induced mesomorphism switching in a chlorpromazine hydrochloride lyotropic liquid crystal, *ACS omega* 6 (2021) 4630–4640.

Table S2 Details regarding the instruments used for characterization of the nanocomposite

Instrument	Make/Model	Study
UV-VIS spectroscopy	Jasco (V- 770) spectrometer	Qualitative analysis
FT-IR spectroscopy	4600 Plus FT-IR spectrometer (JASCO)	Identification of functional groups
X-ray diffraction	JEOL JDX 8030 X-ray diffractometer	Crystalline structure
Raman Spectroscopy	WI Tec Alpha-300RA Raman Spectrometer	Study of vibrational and rotational modes of molecules
FE-SEM measurements/EDX	ZEISS-EVO 18 Research	Structure and surface morphology
HR-TEM analysis/SAED	FEI TECNAI T20 G2	Structure and surface morphology
Electrochemical experiments	CHI (Model 660E, Austin, TX, USA) (Bare GCE/modified electrodes as working electrodes and Pt wire and Ag/AgCl with internal KCl as auxiliary electrode and reference electrode)	CV and LSV

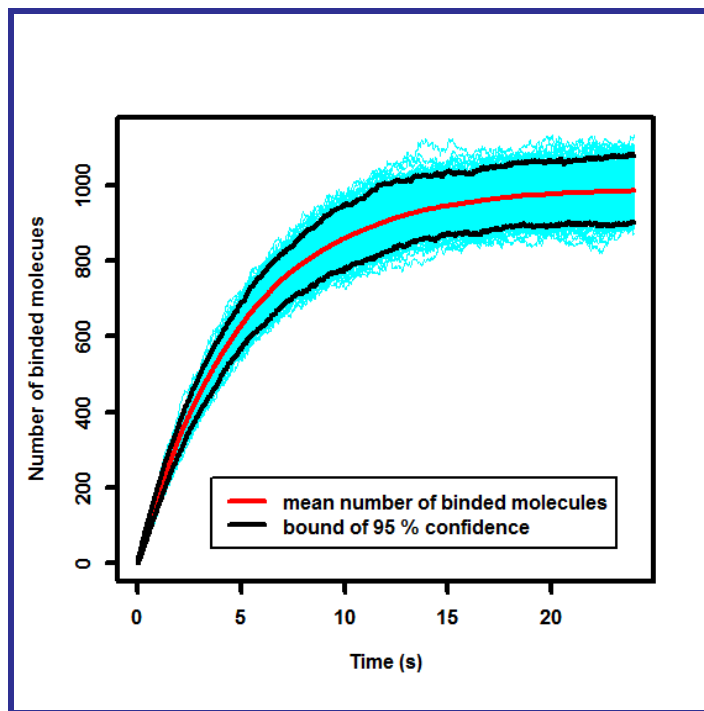


Fig. S1 Fluctuation in binding and unbinding of CPH molecules during CV process

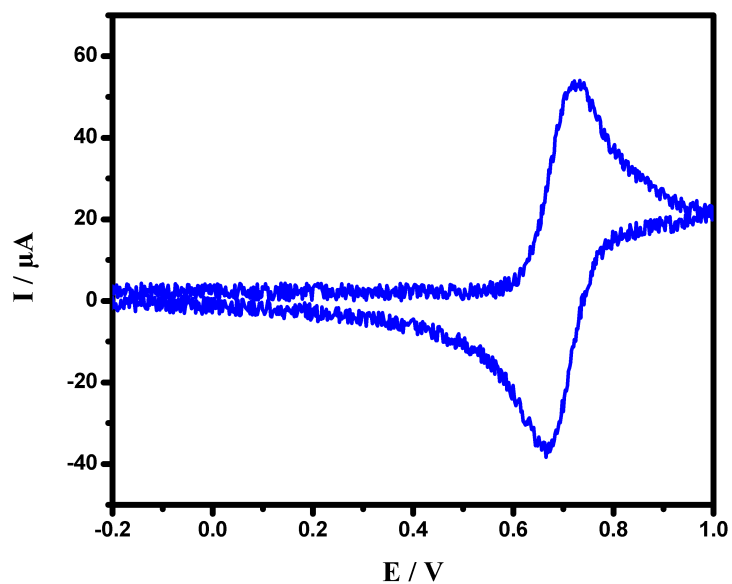


Fig. S2 Outcome of the CV process derived from the stochastic model using R software and OriginPro

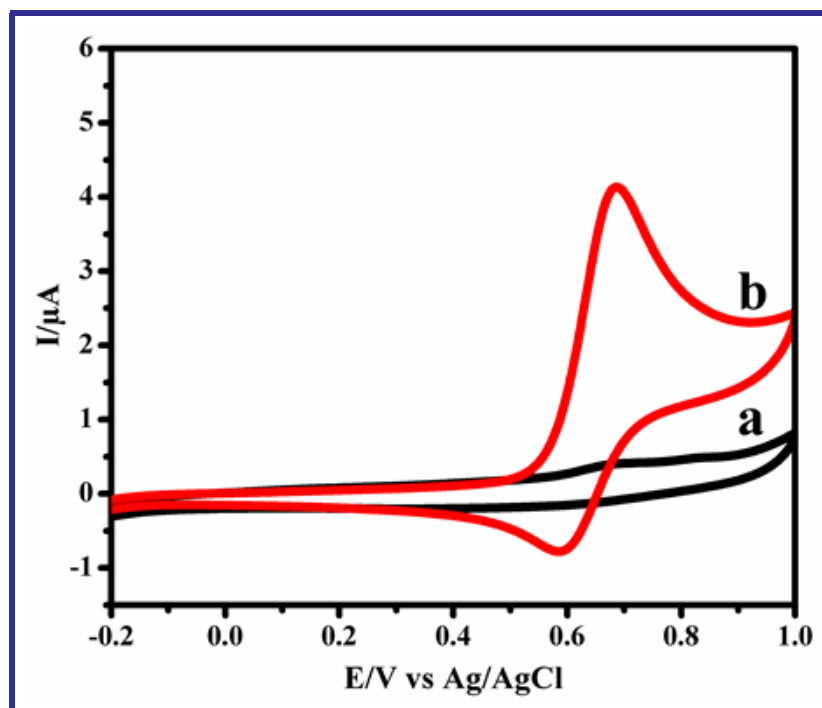


Fig. S3 CVs for bare GCE (a) and $\text{CeO}_2/\text{ZrO}_2/\text{GCE}$ (b) in the presence of CPH ($10 \mu\text{M}$)

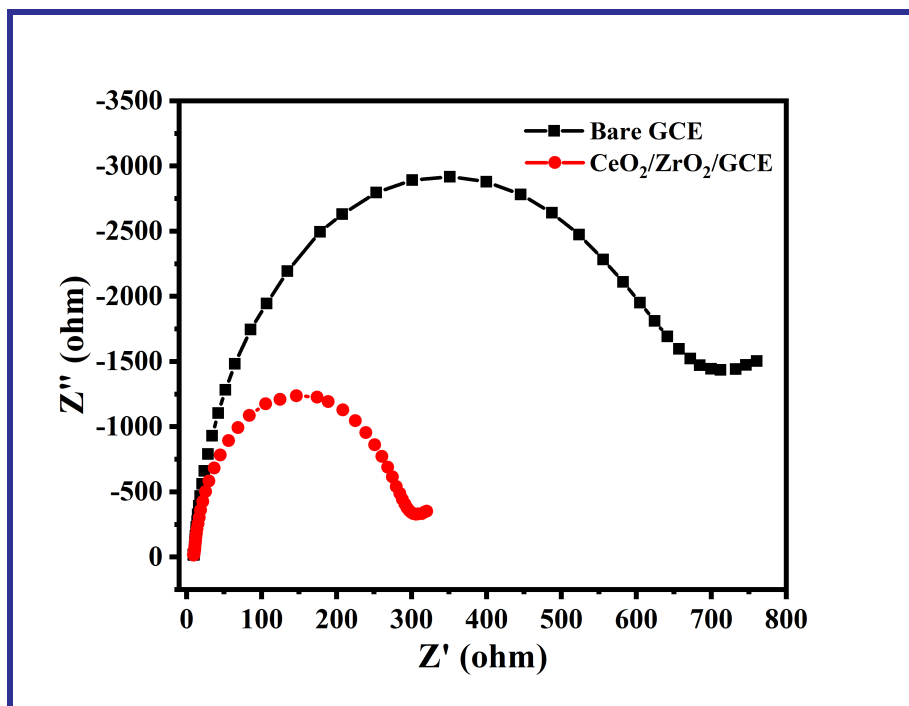


Fig. S4 EIS-Nyquist plot and CV response for bare GCE, CeO₂/ZrO₂/GCE in 0.1 M KCl in the presence of [Fe(CN)₆]^{3-/4-} solution

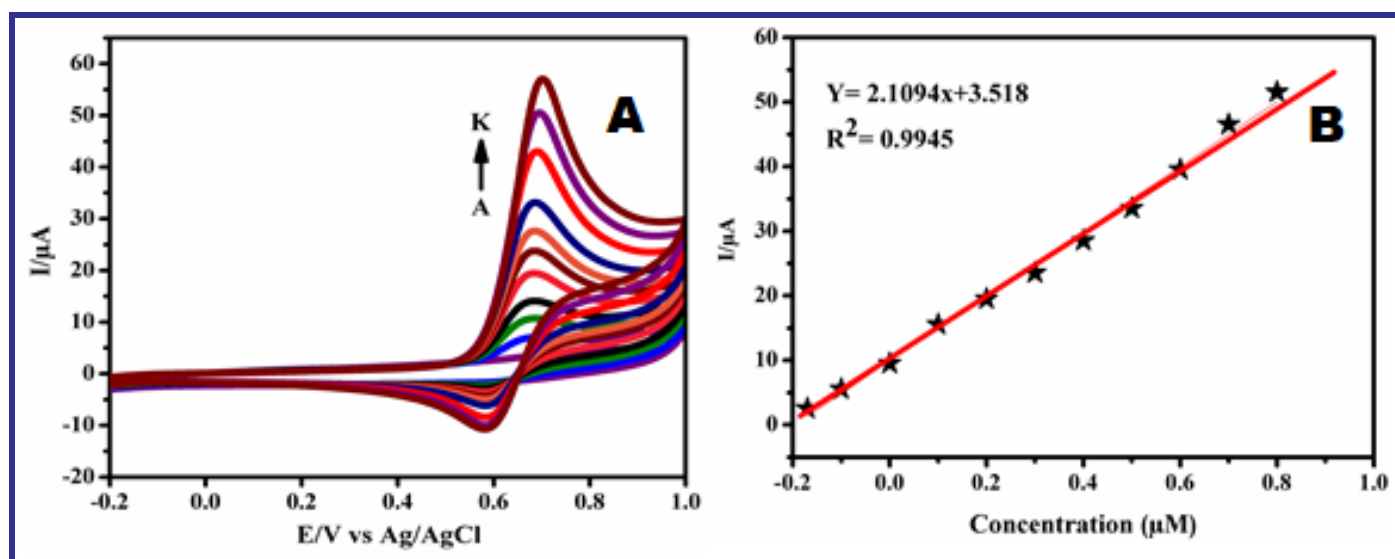


Fig. S5 (A) CV curves for CeO₂/ZrO₂/GCE in the presence of CPH in different addition of CPH (from 10 to 110 μM) in 0.1M PB (pH 7.0) at scan rate 50mVs⁻¹, and (B) the calibration plot for the linear dependence of CPH vs I/μA

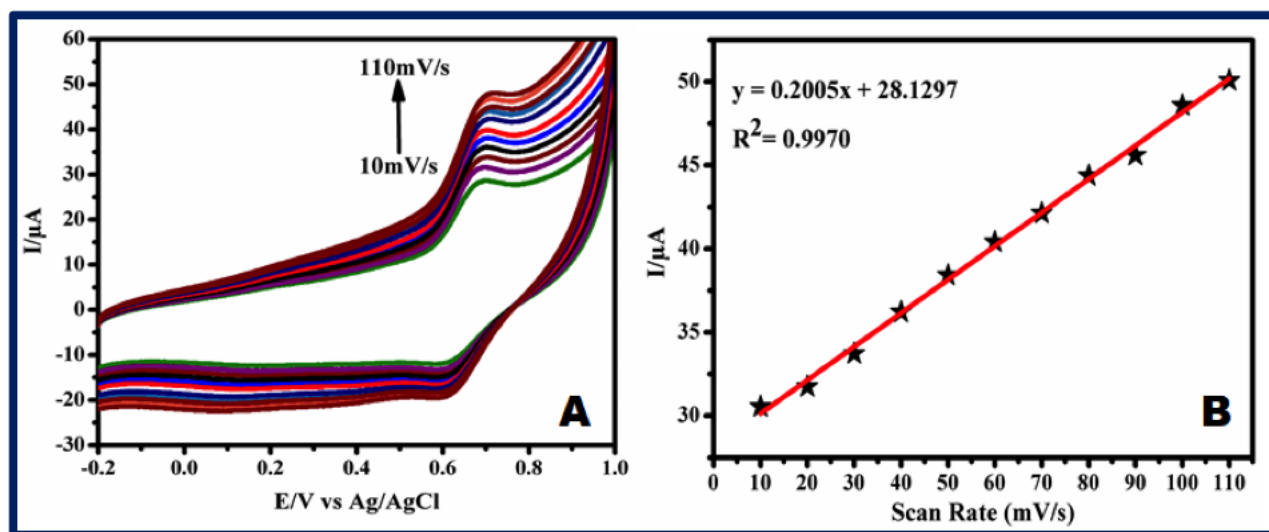


Fig. S6 CV curves for CeO₂/ZrO₂/GCE at different scan rates (from 10 to 110 mV⁻¹) in the presence of 50 μM concentration of CPH (A), the calibration plot for the linear dependence of peak current vs square root of scan rate (B)

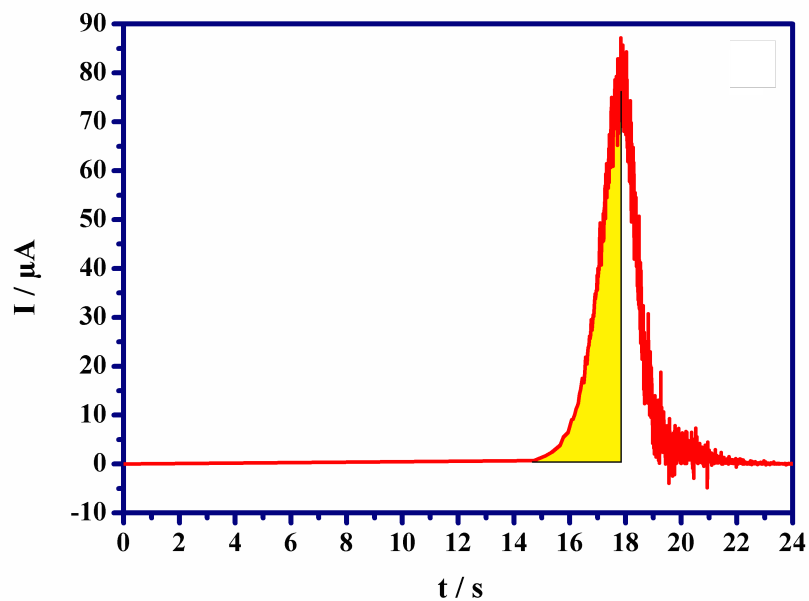


Fig. S7 Peak integration of LSV using stochastic model at 1.9 μM in 0.1M PB at a scan rate 50 mVs⁻¹