Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Urease free Ni-microwires intercalated Co-ZIF electrocatalyst for rapid detection of urea in human fluid and milk samples in diverse electrolytes

P. Arul[a,b], N.S.K. Gowthaman[a], S. Abraham John[a]□, Sheng-Tung Huang[b*]

[a]*Centre for Nanoscience and Nanotechnology, Department of Chemistry, The Gandhigram Rural Institute, Gandhigram - 624 302, Dindigul, Tamilnadu, India.*
[b]*Institute of Biochemical and Biomedical Engineering, Department of Chemical Engineering and Biotechnology, National Taipei University of Technology,Taipei, 106, Taiwan.*

*Corresponding author: Tel: +91 451 245 2371; Fax : + 91 451 245 3031
E-mail: s.abrahamjohn@ruraluniv.ac.in [a*], *ws75624@mail.ntut.edu.tw*[b*]

1. Experimental

1.1. Chemicals and reagents

2-mercaptobenzimidazole (2-MBI), Cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) and hydrazine hydrate were purchased from Sigma-Aldrich. GC plates were purchased from Alfa Aesar. N,N-Dimethylformamide (DMF), disodium hydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$), nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$) and urea were purchased from Merck-India. All other chemicals used in this investigation were of high pure grade.

1.2. Instrumentation

Fourier transform infrared spectroscopy (FT-IR) measurements were carried out by using JASCO FT-IR 460 plus model, Japan. Crystalline nature of Co-ZIF-NiMWs was studied by using Rigaku X-ray diffraction (XRD) unit using Ni-filtered Cu Kα (λ = 1.5406) radiation. The scanning electron microscopy (SEM) measurements were performed by VEGA3 TESCAN, Czech Republic. The energy-dispersive X-ray spectroscopy (EDX) and elemental mapping were carried out by using Bruker Nano, Germany. The electrochemical and electrochemical impedance spectroscopy (EIS) measurements were carried out with CHI electrochemical workstation model 643B, Austin, TX, USA. Electrochemical measurements were performed in a three-electrode cell with GC (0.07 cm^2 area), NaCl saturated Ag/AgCl and Pt electrodes are used as working, reference and counter electrodes, respectively. All the electrochemical experiments were carried out at 27 °C under N_2 atmosphere.

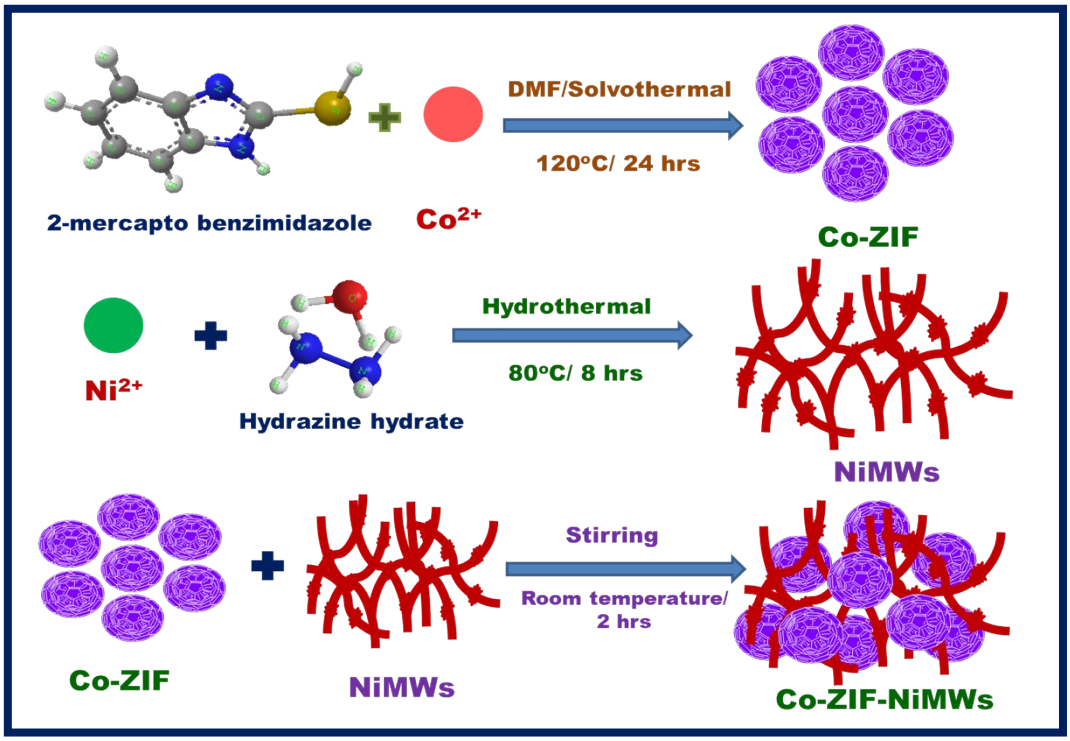
1.3. Fabrication of GC/Co-ZIF-NiMWs electrode

The GC electrode was cleaned based on the previous reported paper [1]. 4 mg of Co-ZIF-NiMWs was transferred into 1 mL of distilled water and sonicated for 15 min to make a homogeneous dispersion. Then, 7 µL of this dispersed solution was then coated on GC electrode and dried at room temperature followed by drop casting 7 µL of 0.5% Nafion over the modified electrode. The resulting electrode was dried at room temperature and then used for

electrochemical studies. The modified electrode is designated as GC/Co-ZIF-NiMWs electrode. Further, GC plate modified with identical procedure was used for ATR-FT-IR measurement. The experimental parameters used for differential pulse voltammetry (DPV) were: initial E (V) = -0.30, final (V) = +0.40, amplitude (V) = 0.05, plus width (sec) = 0.06, sampling width (sec) = 0.02, pulse period (sec) = 0.2 and quiet time (sec) = 2. For electrochemical impedance measurements, the parameters used were: DC potential = 0.356 V, high frequency (Hz) = 100000, low frequency (Hz) = 0.1 and amplitude (V) = 0.005, quiet time (sec) = 2.

References

1. Arul. P, John. S.A, *Electrochimi Acta* , 2017**, 235**, 680–689.



Scheme S1. Scheme showing the synthesis of Co-ZIF, NiMWs and Co-ZIF-NiMWs.

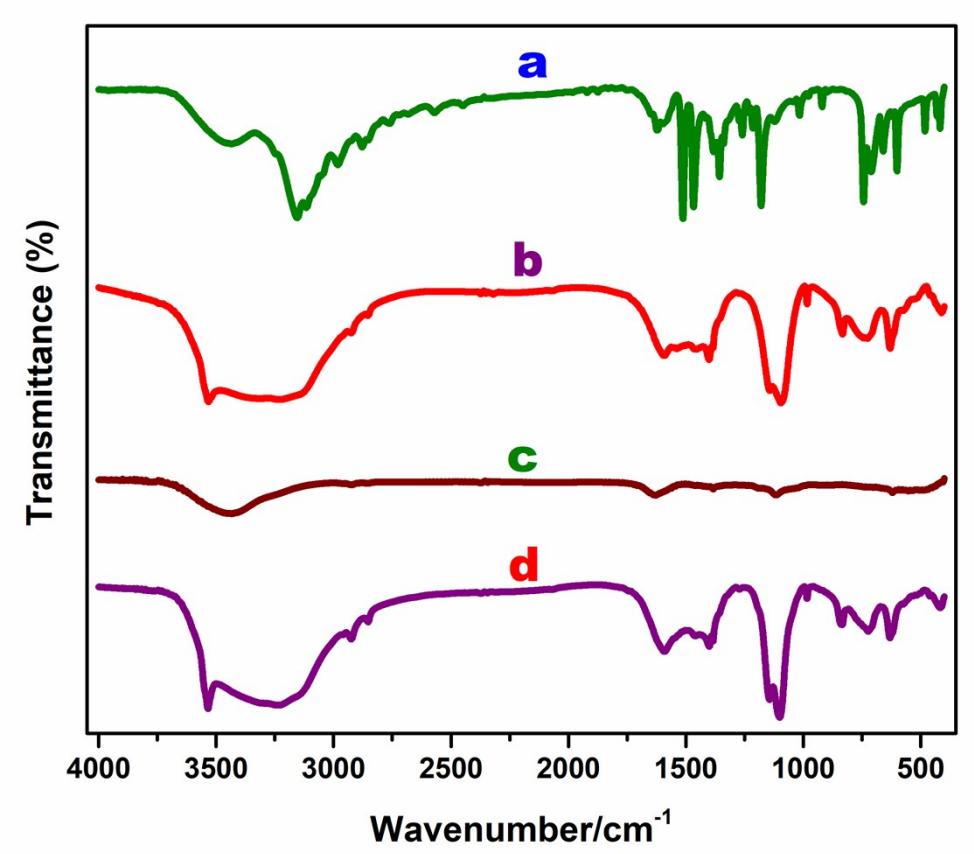


Fig.S1. FT-IR spectra for solid (a) 2-MBI, (b) Co-ZIF, (c) NiMWs and (d) Co-ZIF-NiMWs in KBr pellet.

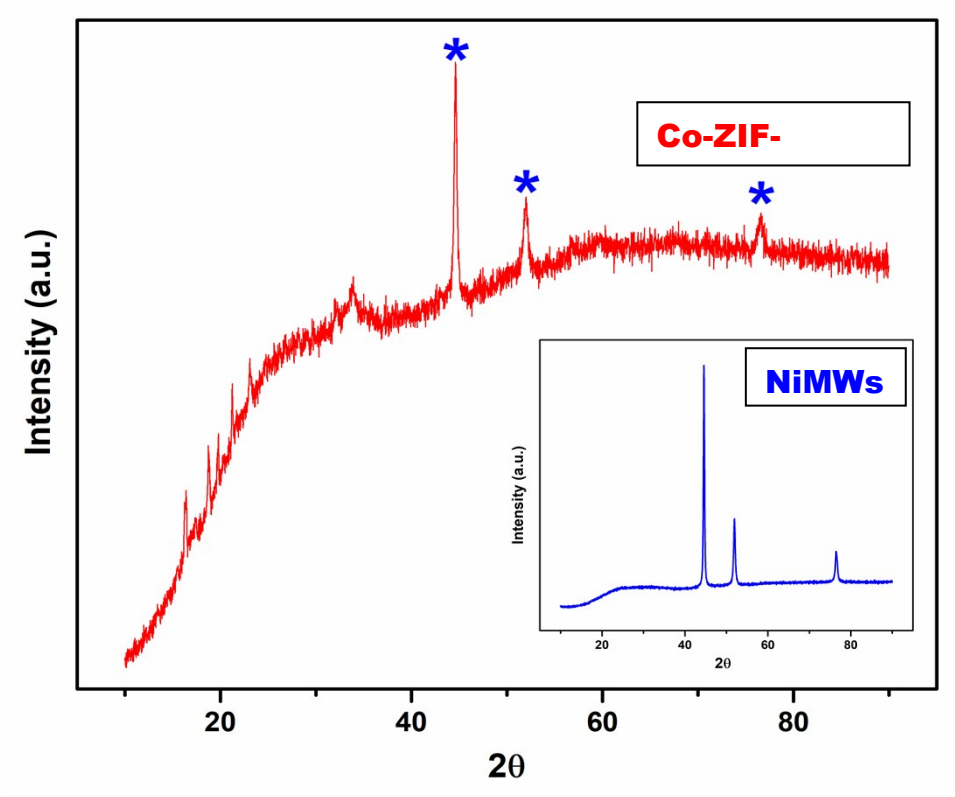


Fig.S2. X-ray diffraction pattern of powder Co-ZIF-NiMWs (*inset*: NiMWs).

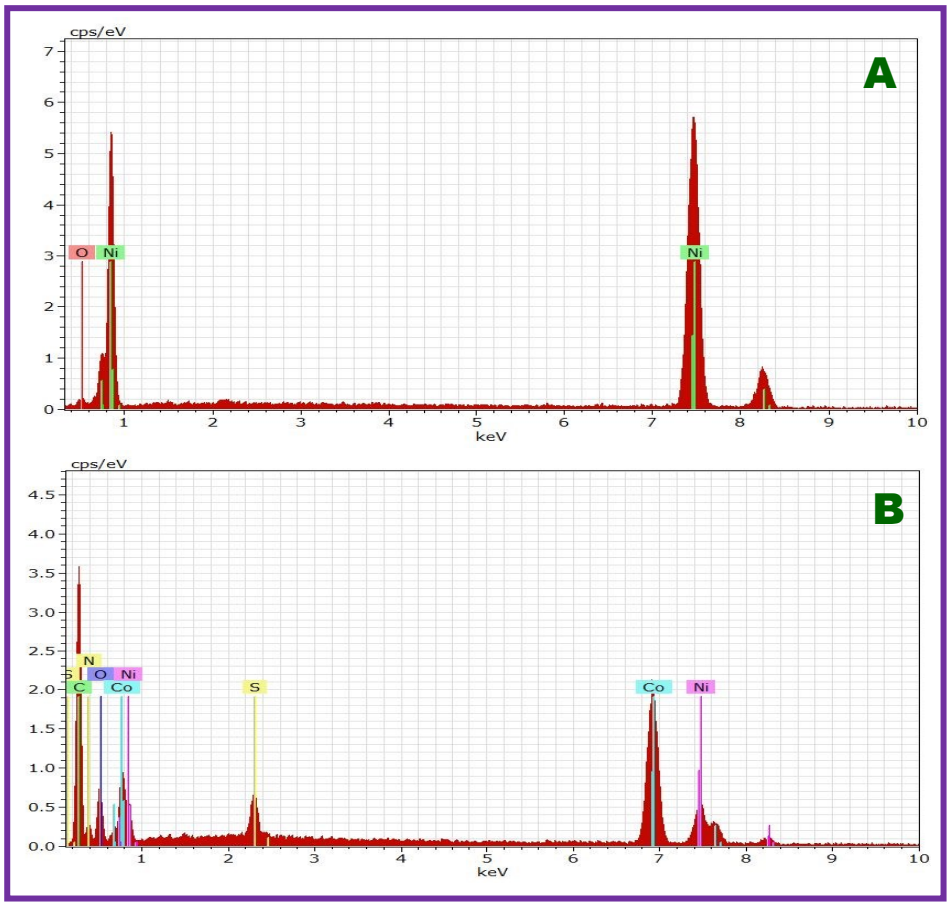


Fig.S3. EDX spectrum of NiMWs (A) and Co-ZIF-NiMWs (B).

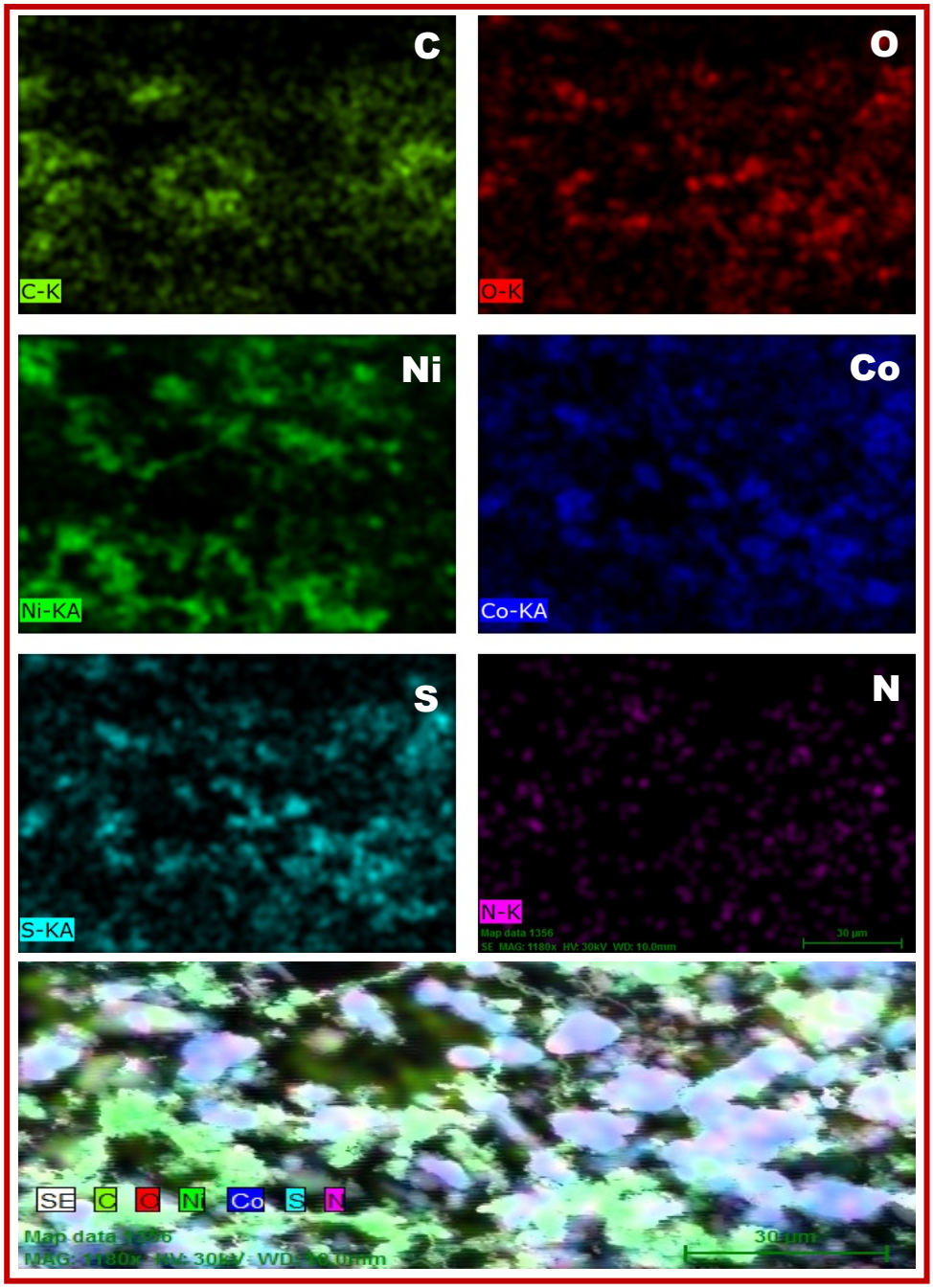


Fig.S4. Elemental mapping images of Co-ZIF-NiMWs.

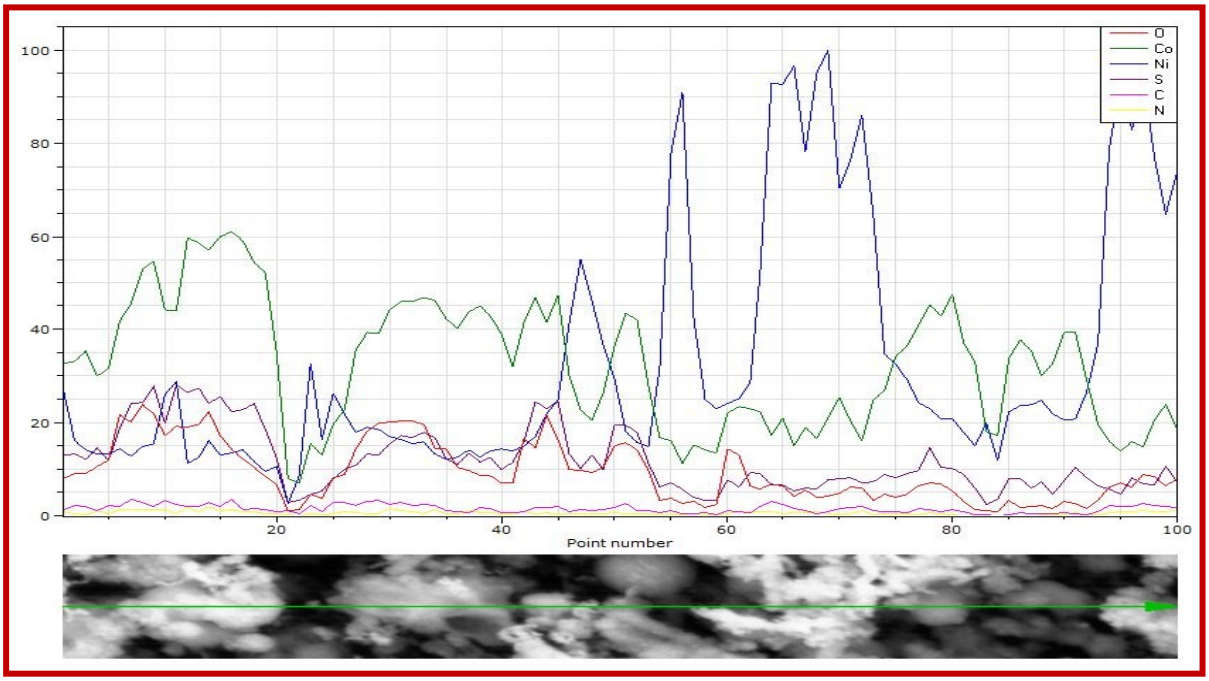


Fig.S5. Line scanning images of Co-ZIF-NiMWs

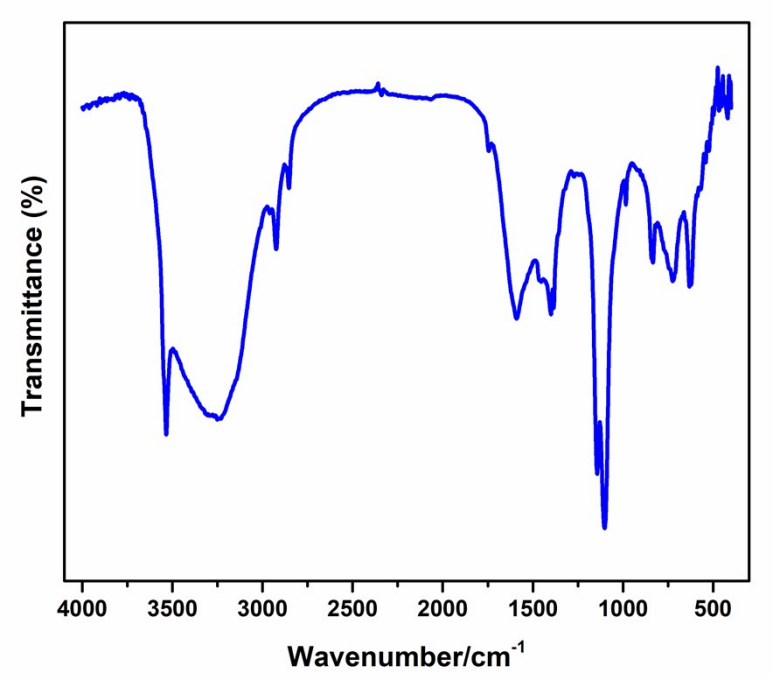


Fig.S6. ATR-FT-IR spectrum of Co-ZIF-NiMWs modified on GC plate.

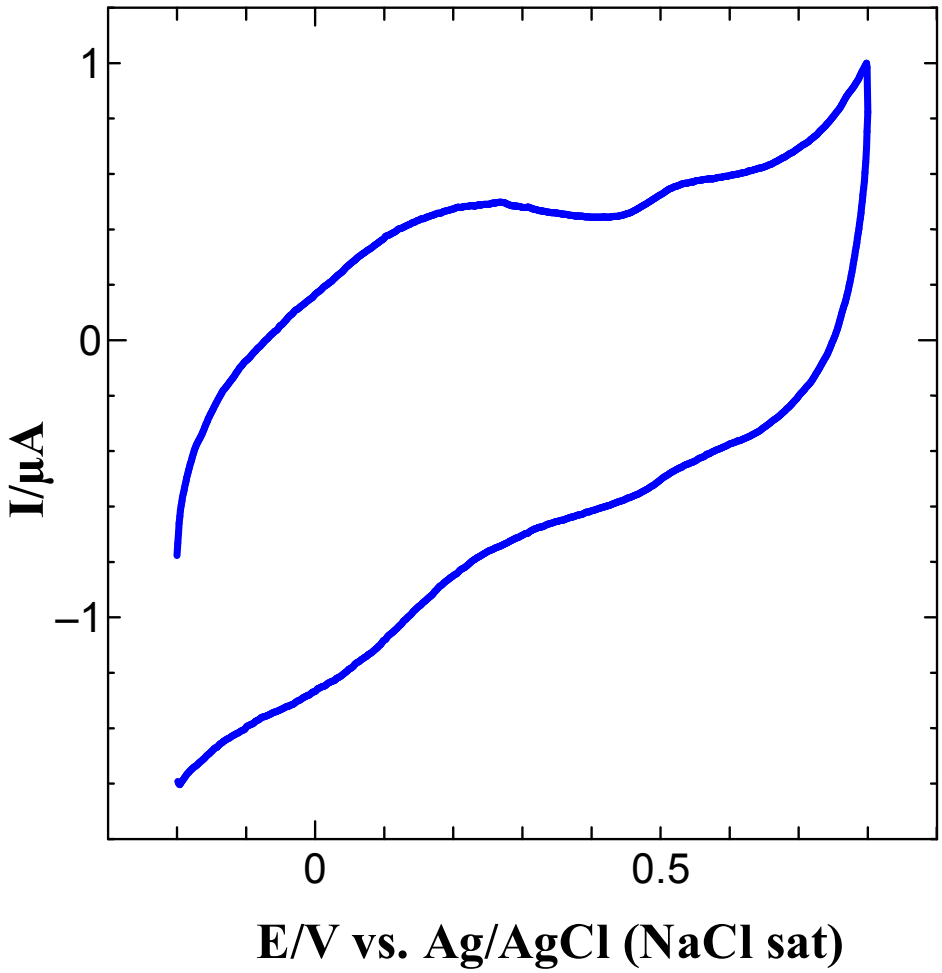


Fig.S7. CV obtained for Co-ZIF-NiMWs modified GC electrode at a scan rate of 50 mV s^{-1} in acetate buffer solution (pH 4).

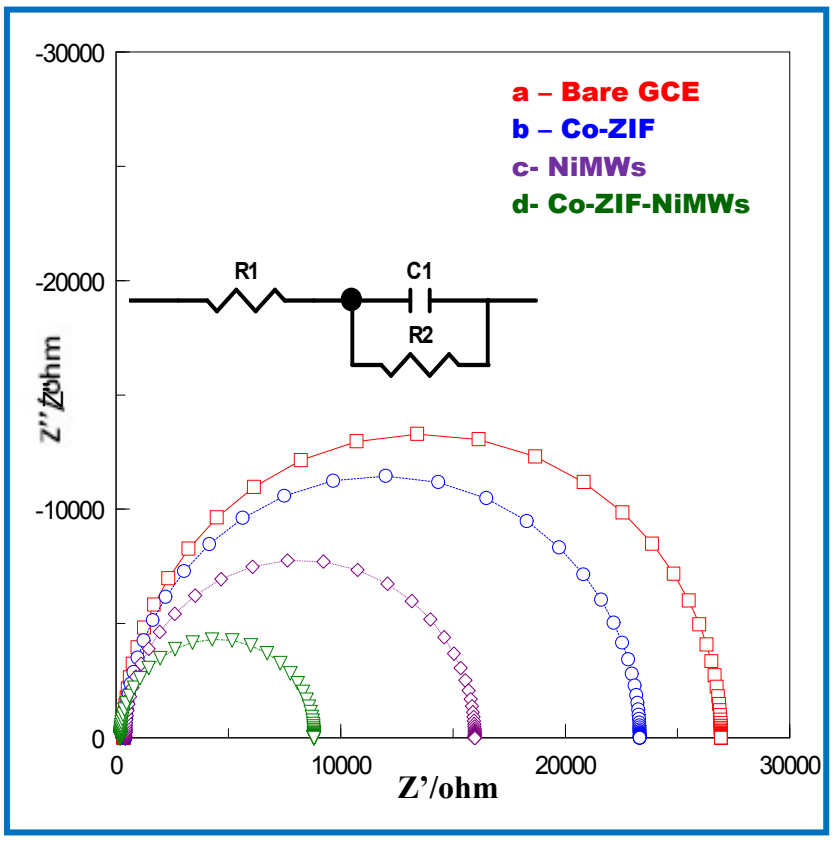


Fig.S8. Nyquist plots for bare GC, Co-ZIF, NiMWs and Co-ZIF-NiMWs modified GC electrodes in 1 mM $K_3[Fe(CN)_6]$ containing 0.1 M KCl at scanning frequencies from 0.01 to 100,000 Hz. ***Inset***: Equivalent electrical circuit used for fitting the impedance spectra.

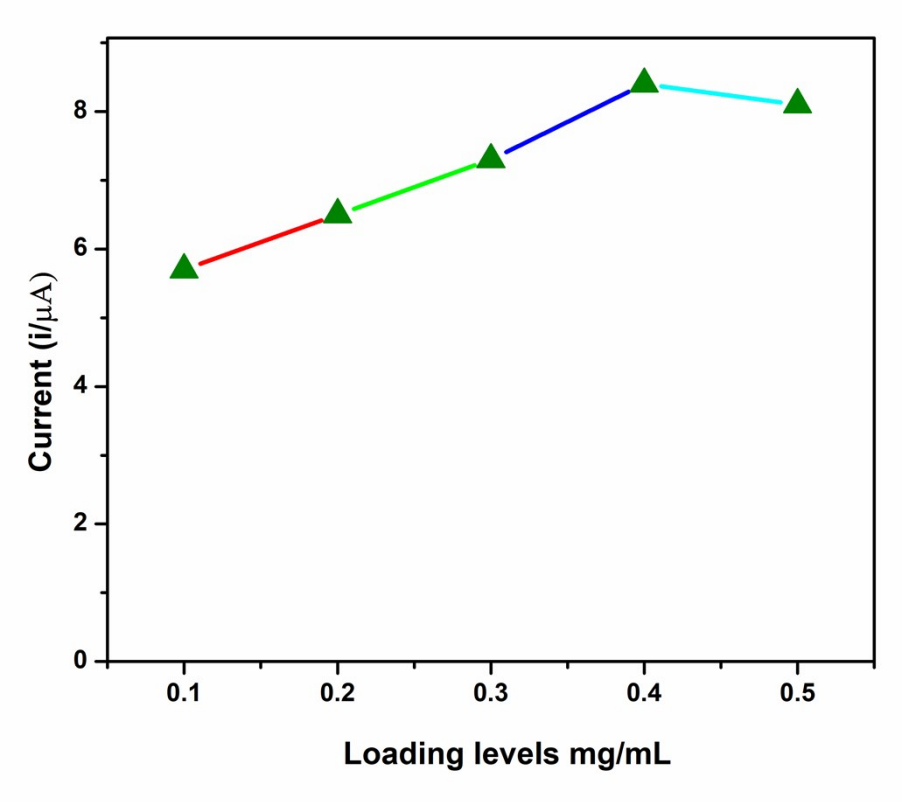


Fig.S9. Plot of oxidation current vs. effect of loading level in Tris-HCl buffer solution (pH 8.0).

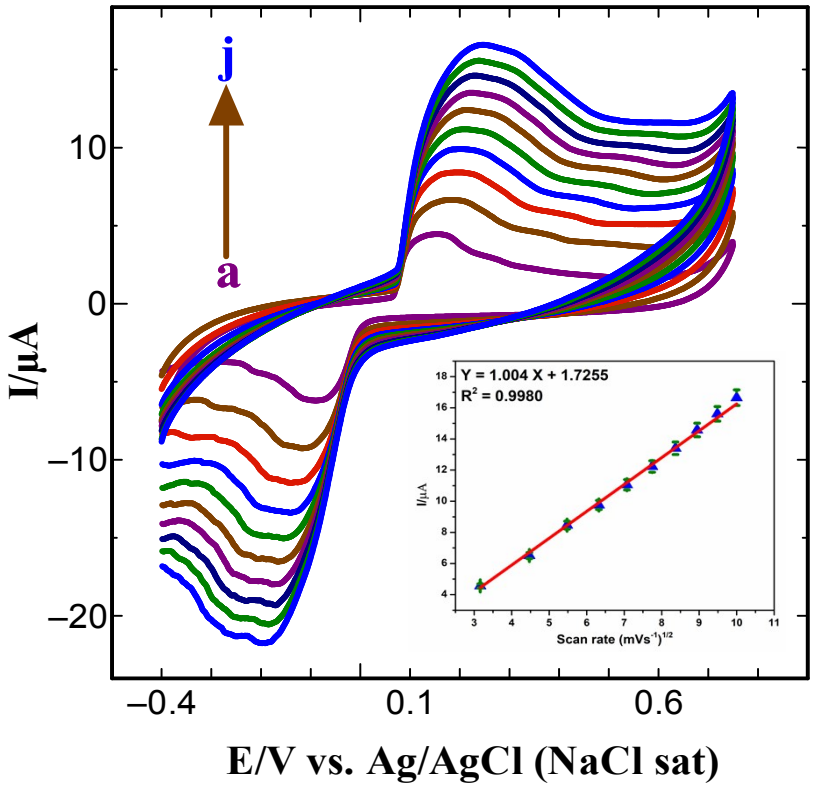


Fig.S10. CVs obtained for 2 mM urea at GC/Co-ZIF-NiMWs electrode in Tris-HCl (pH 8.0) at different scan rates: 10 to 100 mV s^{-1} (a-j). ***Inset*:** Plot of current vs. square root of scan rate.

Human urine sample	Spiked urine (mL)	Spiked urea (μM)	Found (μM)	Recoveries (%)
Sample 1	0.2	-	13.6	-
	-	20	33.2	98.80
	-	30	63.1	99.84
Sample 2	0.2	-	10.8	-
	-	20	30.5	99.02
	-	30	60.3	99.66

Table S1. Determination of urea in human urine sample using Co-ZIF-NiMWs/GC electrode in Tris-HCl buffer solution (pH 8.0).

Human urine sample	Urea level (mg/dL)	
	Proposed sensor	Clinical analysis
Sample 1	14.0	14.3
Sample 2	11.4	11.5

Table S2. Comparison of urea level determined from the proposed sensor and the clinical analysis in same human urine sample.

Milk Samples	Spiked milk (mL)	Spiked Urea (µM)	Found (µM)	Recoveries (%)
Sample 1	0.2		0.24	-
	-	20	20.21	99.85
	-	30	50.17	99.92
Sample 2	0.2	-	0.18	-
	-	20	20.07	99.45
	-	30	50.02	99.90

Table S3. Determination of urea in milk sample using Co-ZIF-NiMWs/GC electrode in Tris -HCl buffer solution (pH 8.0).