Electronic Supplementary Information

Cobalt ions incorporated Nanocrystalline spinel cubic zinc ferrite for targeted magnetic hyperthermia and sensing applications

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Synthesis of cobalt doped and bare zinc ferrite nanoparticles

A standard chemical co-precipitation method was employed to prepare the doped and bare zinc ferrite nanoparticles.[1,2] The chemical composition of the as-synthesized ferrite nanoparticles was $Co_xZn_{1-x}Fe_2O_4$ (x = 0, 0.10, 0.30 and 0.50). High-purity chemicals, namely $Co(NO_3)_2.6H_2O$, $Zn(NO_3)_2.9H_2O$, and $Fe(NO_3)_3.6H_2O$ were used to fabricate ferrite nanoparticles without additional purification. In stoichiometric quantities, these chemicals were dissolved in 200 ml of distilled water. The resulting solution in the beaker underwent continuous stirring on a magnetic stirrer at 700 rpm to achieve homogeneity. The precipitating reagent, sodium hydroxide (NaOH) solution, was added further drop-wise under

identical stirring conditions to raise the mixture's pH to 11, facilitating precipitation. After reaching a pH of 11, the solution was digested for two hours at a constant temperature of 80°C with continuous stirring to certify the complete reaction. The mixture was then cooled to room temperature and washed multiple times with distilled water and methanol to achieve a neutral pH of 7. The resulting precipitate was air-dried and ground into a fine powder. Subsequently, the pure and doped powder samples underwent calcination at 500°C for 5 hours in a furnace to enhance nano-crystallinity. To prevent quenching effects during calcination, the furnace temperature was raised to 500°C, maintained for 5 hours, and then gradually lowered.[2] The prepared ferrite samples were named Co-00 (ZNF), Co-10 (ZNF), Co-30 (ZNF), and Co-50 (ZNF) corresponding to increasing percentages of Co ions. All the synthesized nanopowder samples were further subjected to various characterizations.

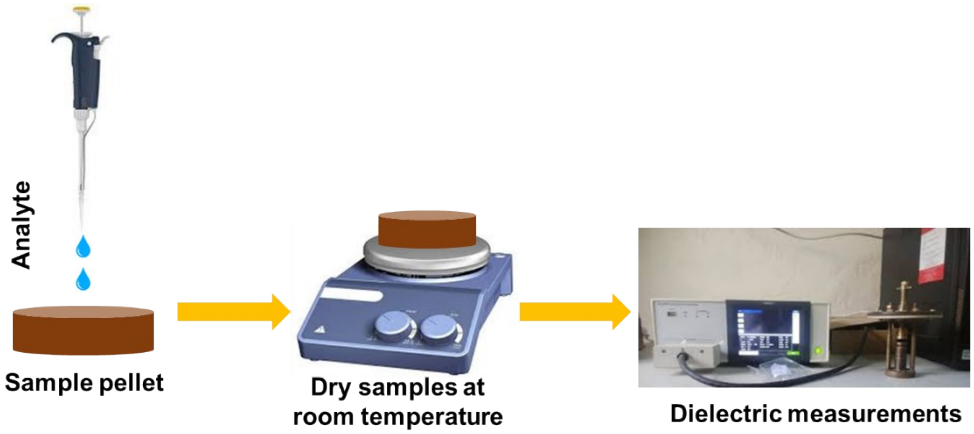
Measurement set-up for metribuzin sensing

Nanocrystalline undoped and cobalt doped zinc ferrite (ZNF) samples were synthesized and formed into thin circular pellets with a 13 mm diameter using hydraulic pressure for precise measurements.[3] Solutions with concentrations of 1 part per million (ppm) and 2 ppm were prepared for the following analytes: metribuzin, glyphosate, citric acid, and urea. The dielectric value of a control sample was initially determined. Then, the following process was repeated for each analyte concentration.

For metribuzin:

1. 100 µl of 1 ppm metribuzin solution was dropped onto the pellet
2. The pellet was dried and the dielectric measured
3. 100 µl of 2 ppm metribuzin solution was dropped onto a new pellet
4. The pellet was dried and the dielectric measured

This process was repeated for glyphosate, citric acid, and urea solutions for Co-00 (ZNF) and Co-50 (ZNF) samples. Values of the dielectric constant were recorded at room temperature for each sample to create the Cole-Cole plot.



Schematic drawing of the experimental setup

Characterization techniques

The physical characterization of Co-doped zinc ferrite (ZNF) samples was thoroughly conducted using various techniques. Room temperature XRD profiles were captured with a Bruker D8 Advance powder X-ray diffractometer utilizing Cu-Kα radiation (wavelength 1.5406 Å). The powder samples were scanned at a rate of 0.02°/sec over a range of 20° to 80°. The X-ray diffractometer operated at 40 kV and 40 mA. The morphology, shape, and mean size of both pristine and doped ferrite nanoparticles were investigated using HRTEM (JEM-2100F, JEOL, Japan), operating at an accelerating voltage of 200 kV. Raman spectra were recorded for each ferrite at 300 K using a Raman spectrometer (Renishaw, UK) and a laser source having 473 nm wavelength between 100 to 800 cm^{-1}. FTIR spectra for entire samples were registered at 300 K with Perkin-Elmer FTIR spectrophotometers. Magnetic properties at various temperatures were measured using a SQUID-VSM (Quantum Design) magnetometer. Absorption data, and optical properties were explored using a UV DRS

spectrometer (UV-2550, Shimadzu, USA). The dielectric properties along with sensing abilities at room temperature for all the prepared samples were examined using an LCR meter (HIOKI, IM 3536). Hyperthermia applications were tested for all the as-synthesized ferrite samples using an induction heating experiment with Ambrell equipment (Scottsville, USA).

Table S1: Represents refinement parameters, including goodness of fit (χ^2), reliability factors (R_P, R_{WP}, R_F^2) and unit cell parameters for all the samples.

Sample-Id	**Co-00 (ZNF)**	**Co-10 (ZNF)**	**Co-30 (ZNF)**	**Co-50 (ZNF)**
Space group	*Fd-3m*	*Fd-3m*	*Fd-3m*	*Fd-3m*
Unit cell parameters				
a (Å) ± 0.001	8.431	8.412	8.393	8.384
Density (g/cm^3)	5.343	5.386	5.436	5.468
D (nm) ± 0.1	9.7	10.5	20.1	12.7
Microstrain (X 10^{-3}) ± 0.01	-0.65	-0.66	5.06	3.89
Refinement parameters				
R_{wp} (%)	5.49	5.51	4.65	4.19
R_p (%)	4.45	4.34	3.70	3.32
χ^2	1.13	1.21	1.19	1.06

Table S2: Contains cationic distribution, ionic radii of cations and theoretical lattice constants of all the nanoferrites.

Sample Id	**Tetrahedral site (A)**	**Octahedral site (B)**	**r_A (Å)**	**r_B (Å)**	**a_{th} (Å)**
Co-00 (ZNF)	$Zn^{2+}_{1.0}$	$Fe^{3+}_{2.0}$	0.6000	0.6450	8.198
Co-10 (ZNF)	$Zn^{2+}_{0.9}Fe^{3+}_{0.1}$	$Co^{2+}_{0.1}Fe^{3+}_{1.9}$	0.6045	0.6500	8.218
Co-30 (ZNF)	$Zn^{2+}_{0.7}Fe^{3+}_{0.3}$	$Co^{2+}_{0.3}Fe^{3+}_{1.7}$	0.6135	0.6600	8.259
Co-50 (ZNF)	$Zn^{2+}_{0.5}Fe^{3+}_{0.5}$	$Co^{2+}_{0.5}Fe^{3+}_{1.5}$	0.6225	0.6700	8.299

Table S3: Represents oxygen position parameter and hopping lengths for all the prepared ferrite samples.

Sample Id	U	Δ (U - 0.375)	H_A (Å)	H_B (Å)
Co-00 (ZNF)	0.3852	0.0102	3.650	2.980
Co-10 (ZNF)	0.3852	0.0102	3.642	2.974
Co-30 (ZNF)	0.3852	0.0102	3.634	2.967
Co-50 (ZNF)	0.3851	0.0101	3.630	2.964

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85 Table S4: Raman active modes for each as-synthesized nanoferrites.

Sample Id	Raman active modes (cm^{-1})						
	$A_1(3)$	E_g	$T_{2g}(2)$	$T_{2g}(3)$	$B_2(3)$	$A_{1g}(2)$	$A_{1g}(1)$
Co-00 (ZNF)	302.2	334.3	479.5	515.1	-----	628.7	671.6
Co-10 (ZNF)	297.4	333.7	461.9	507.6	-----	630.4	676.4
Co-30 (ZNF)	296.6	332.9	459.5	539.9	-----	611.2	657.8
Co-50 (ZNF)	292.6	318.4	464.3	535.2	602.9	641.7	674.9

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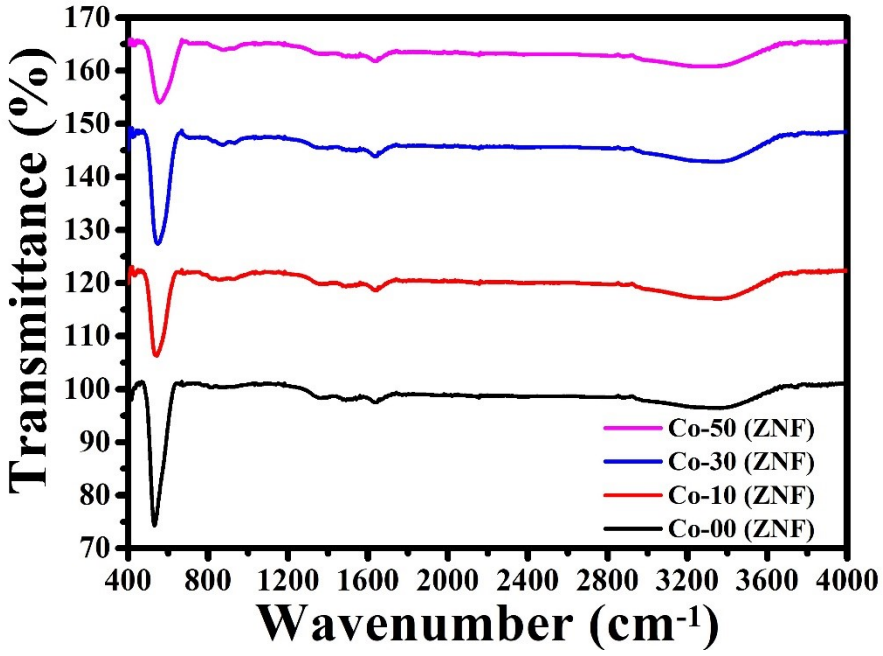

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88 Figure S1: Room temperature FTIR spectra of all the ferrite samples.

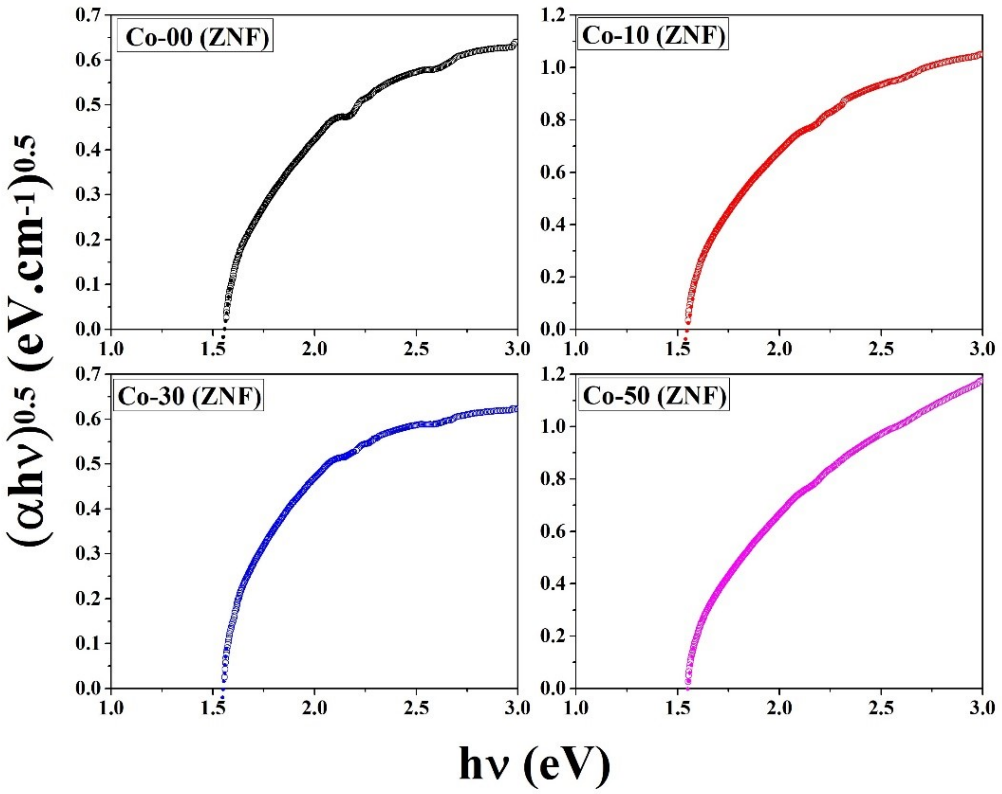


Figure S2: Tauc plots of all the as-synthesized samples.

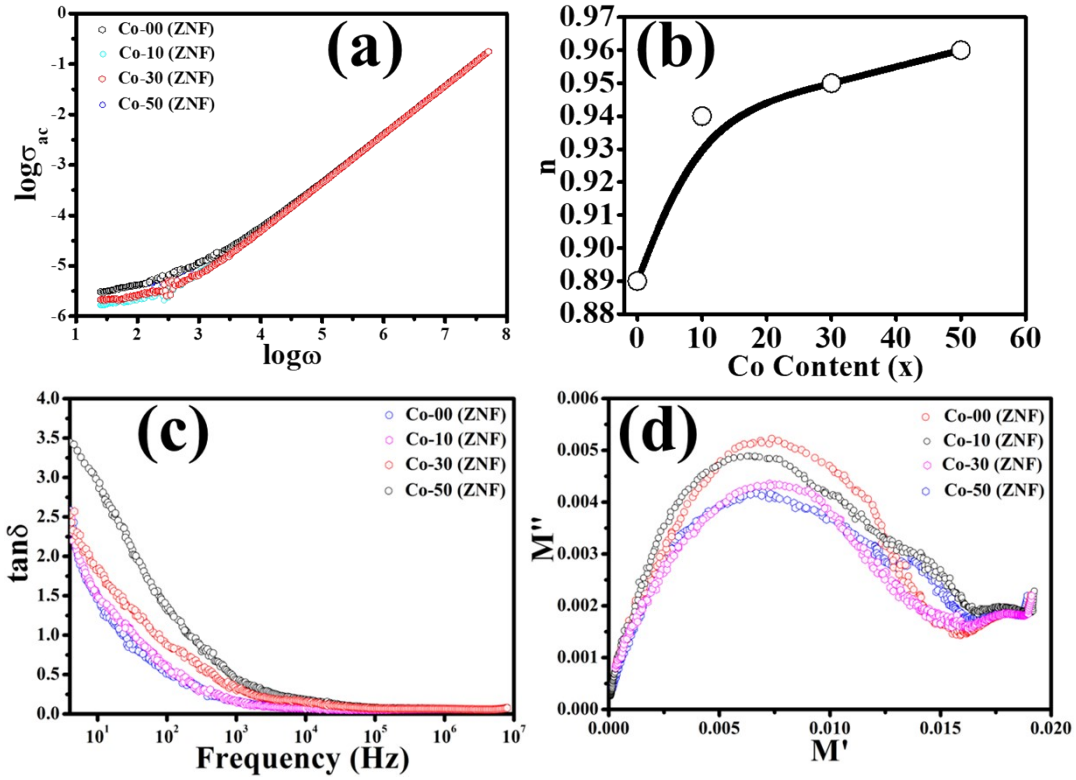


Figure S3: (a) Plot of AC conductivity against frequencies in logarithmic scale, (b) plot of exponent against cobalt ions concentration and (c) dielectric loss-tangent plots and (d) Cole-Cole plots of all the as-fabricated samples.

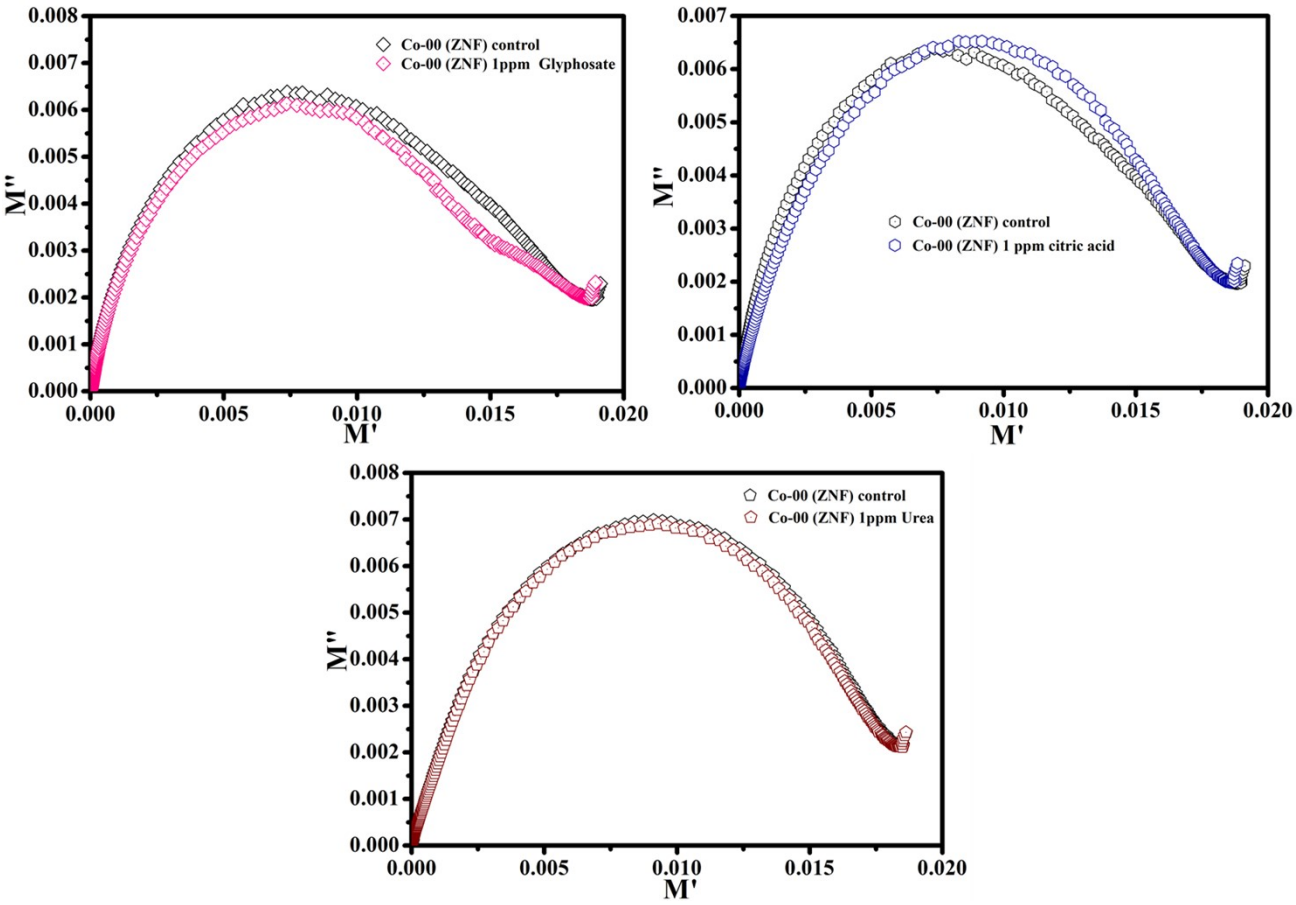
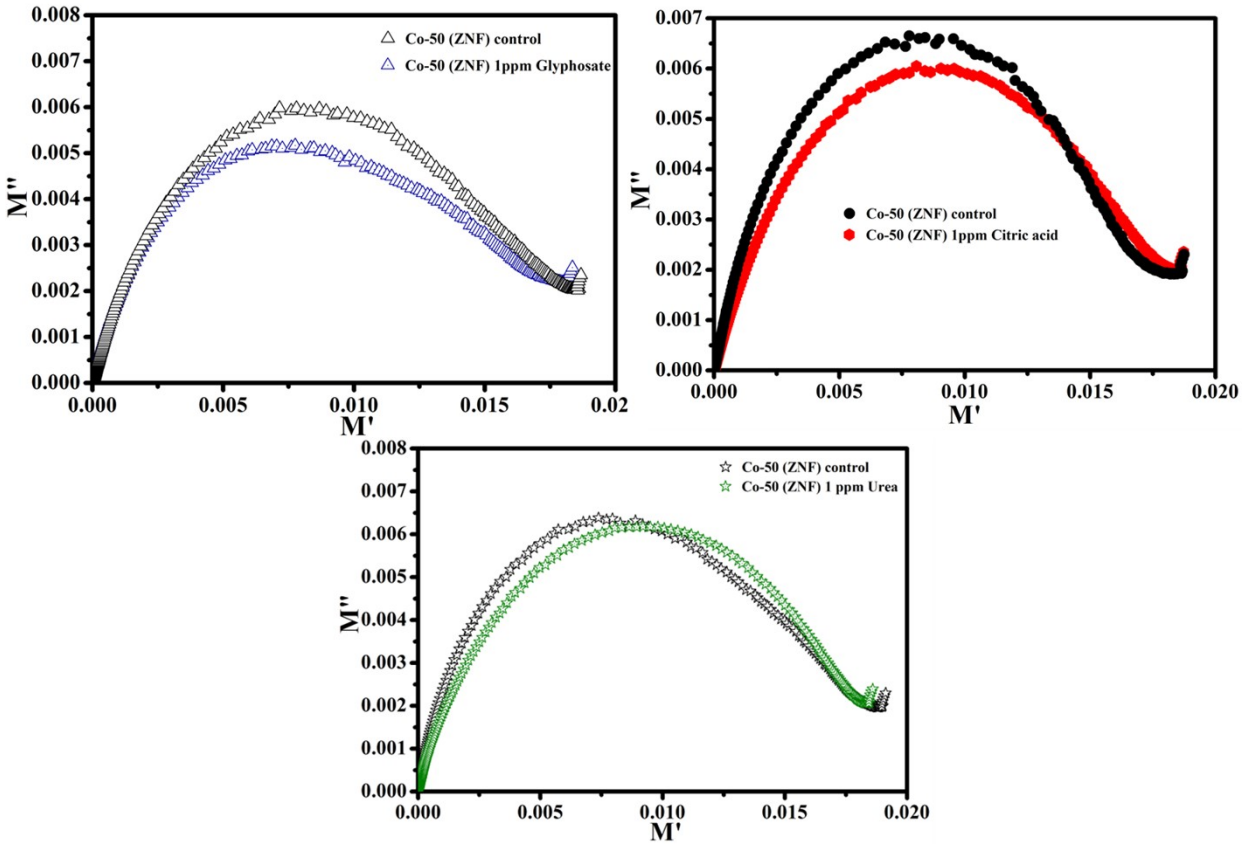


Figure S4: Selectivity of Co-00 (ZNF) sample over other analytes including Glyphosate, Citric acid, and Urea solution.



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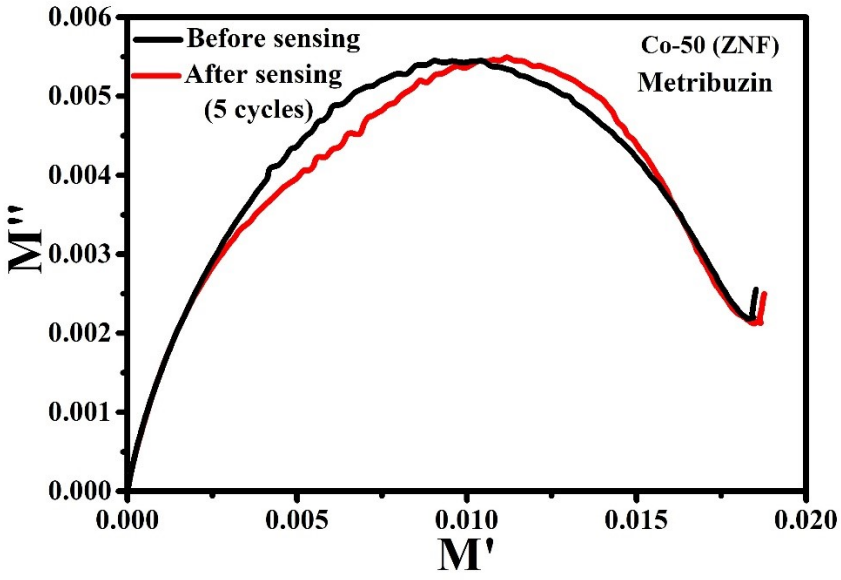
101 Figure S5: Selectivity of Co-50 (ZNF) sample over other analytes including Glyphosate,

102 Citric acid, and Urea solution.



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104 Figure S6: Cole-Cole plot of Co-50 (ZNF) sample before and after five consecutive cycles of

105 metribuzin sensing.

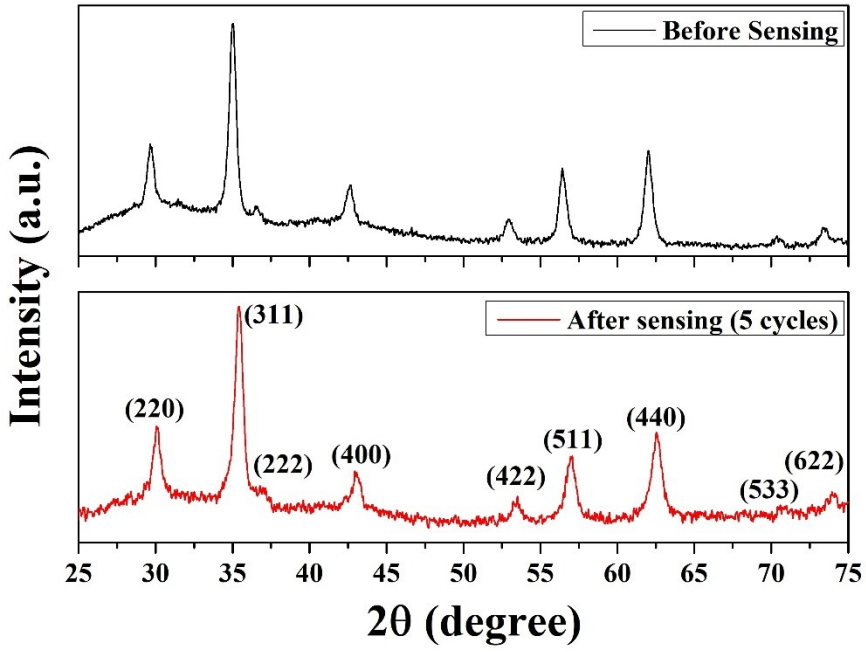

Figure S7: XRD pattern of Co-50 (ZNF) samples before and after five consecutive cycles of metribuzin sensing.

References

1 M. P. Ghosh and S. Mukherjee, *Journal of Materials Science Materials in Electronics*, 2020, **31**, 6207–6216.

2 N. J. Mondal, R. Sonkar, B. Boro, M. P. Ghosh and D. Chowdhury, *Nanoscale Advances*, 2023, **5**, 5460–5475.

3 R. Sonkar, N. J. Mondal, S. Thakur, E. Saikia, M. P. Ghosh and D. Chowdhury, *Nanoscale Advances*, 2023, **5**, 7042–7056.