Electronic Supplementary Information

A novel non-enzymatic lindane sensor based on CuO/MnO₂ hierarchical nano-microstructures for enhanced sensitivity

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Part I: Experimental Details

***Materials*:** All chemicals were analytical grade and used without further purification. $Cu(NO_3)_2 3H_2O$, PEG200, NaOH, $KMnO_4$, NaOH, γ-HCCH (Lindane), ethanol, phenol, cyclohexane, chlorobenzene, benzene and tetra-n-butyl ammonium bromide (TBAB) were obtained from Sigma-Aldrich. Deionized water from Millipore Milli-Q system (Resistivity 18.2 MΩ cm) was used in the electrochemical studies. Solutions for all electrochemical experiments were deoxygenated with zero-grade argon.

Preparation of solution: Stock solution of lindane was prepared in methanol. 0.05 M tetra-n-butyl ammonium bromide (TBAB) solution was prepared in 60:40 (v/v) methanol–water. It was used as the supporting electrolyte.

Synthesis of CuO nanoleaves: 5 mM of $Cu(NO_3)_2 3H_2O$ was dissolved in 300 mL deionized water. 10 mL of PEG200 was poured into the aqueous $Cu(NO_3)_2 3H_2O$ solution. After the

PEG200 was uniformly dispersed in the solution, followed by addition of 40 mL NaOH solution (1.25 M), the blue suspension was left under agitation for 24 hours until the blue suspension totally transformed to a black suspension at room temperature. Product was filtered, washed with water and ethanol, dried in an oven at 353 K for 24 h.

Synthesis of δ-MnO₂ microspheres: 15 mmol of $KMnO_4$ was dissolved in 200 mL of distilled water. 5 mL hydrochloric acid was added to the above solution, and the reaction mixture was stirred for 0.5 hours and then transferred to a teflon-lined stainless steel autoclave, and put in an electric oven at 353 K for 15 hours, and after cooled to room temperature. Product was filtered, washed with water and ethanol, dried in an oven at 353 K for 24 hours.

Synthesis of CuO/MnO₂ core-shell nanostructures: In a typical synthesis, the as-synthesized CuO (60 mg) was dispersed into the $KMnO_4$ solution (30mL;50 mM). After sonication, the mixture was transferred to a teflon-lined stainless steel autoclave, and put in an electric oven at 433 K for 24 hours. Product was filtered and washed several times with pure water followed by ethanol. The product was dried at 323 K in air for 24 hours.

Materials characterizations: The as-prepared materials were characterized with X-ray powder diffractometer (XRD; Shimadzu XRD-6000, Cu Kα radiation) at a scan rate of $1°$ min^{-1}. Scanning Electron Microscopy (FESEM, JSM-7600F) and transmission electron microscopy (TEM; JEOL, JEM-2100F) operated at 200 kV was used to observe the morphological features. Nitrogen adsorption measurement at 77 K was performed by Tristar-3000 surface area analyzer. Samples were out-gassed at 423 K for 4 h in the degas port of the adsorption apparatus. The specific surface area was determined by Brunauer–Emmett–Teller (BET) method using the data points of P/P_0 in the range of about 0.05–0.3. The ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS) was obtained on a UV-visible spectrophotometer (Shimadzu UV-2501PC). FTIR spectroscopic tests were conducted on FTIR Frontier from Perkin Elmer.

Electrochemical measurements: Cyclic voltammetry (CV), Differential pulse voltammetry (DPV) and chronoamperometric studies were performed by using a computer-controlled Pine Instrument. A three electrode electrochemical cell was employed with Ag/AgCl as the reference

electrode (3M KCl), metal oxide mounted glassy carbon electrode (GCE) (0.196 cm^2) as the working electrode, and Pt foil as the counter electrode. Before modification of GCE, the polished electrode was ultrasonicated in ethanol and deionized water for 5 minutes, respectively. The working electrodes were prepared as follows: 10 μL aliquot of metal oxide suspension (a homogenous sonicated solution of 10 mg of metal oxide and a mixture of 0.1 mL of Nafion and 0.9 mL of water) was placed onto the electrode surface, the electrode was dried in air leaving the material mounted onto the GCE surface.
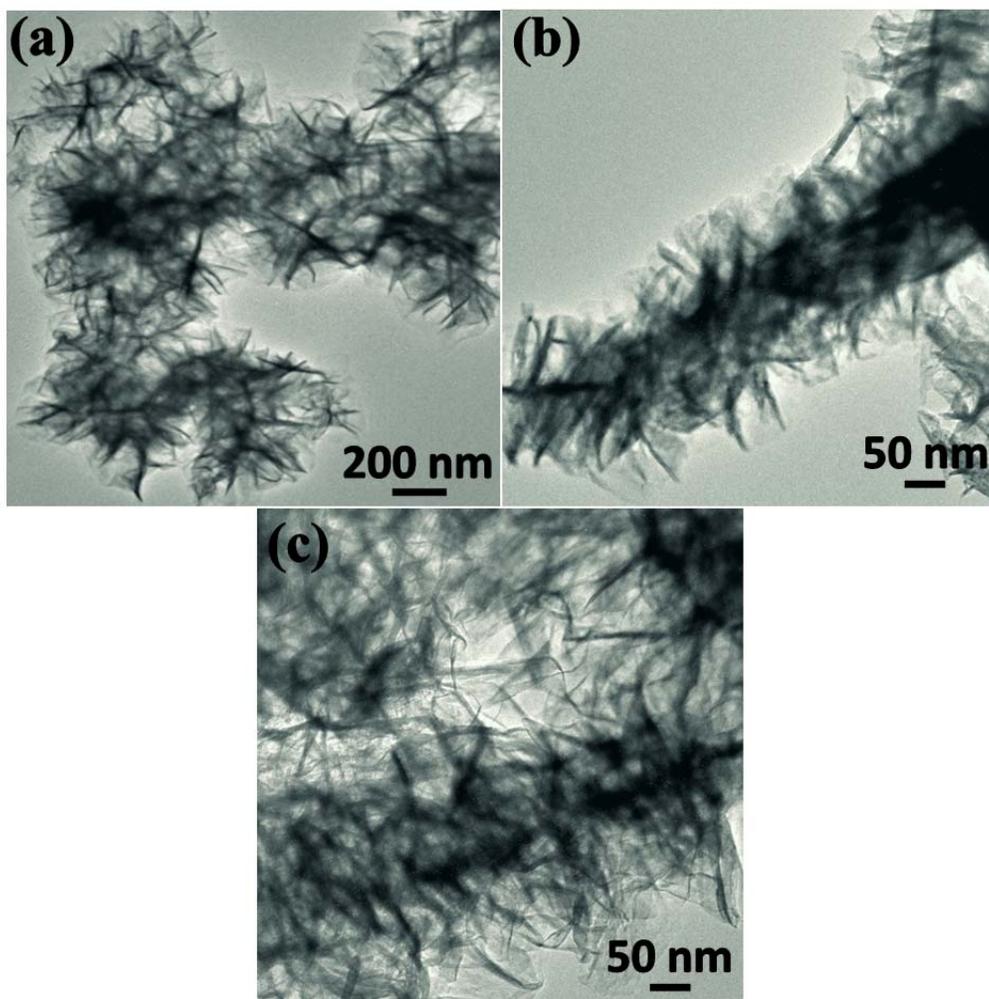
Part II: Supplementary Figure
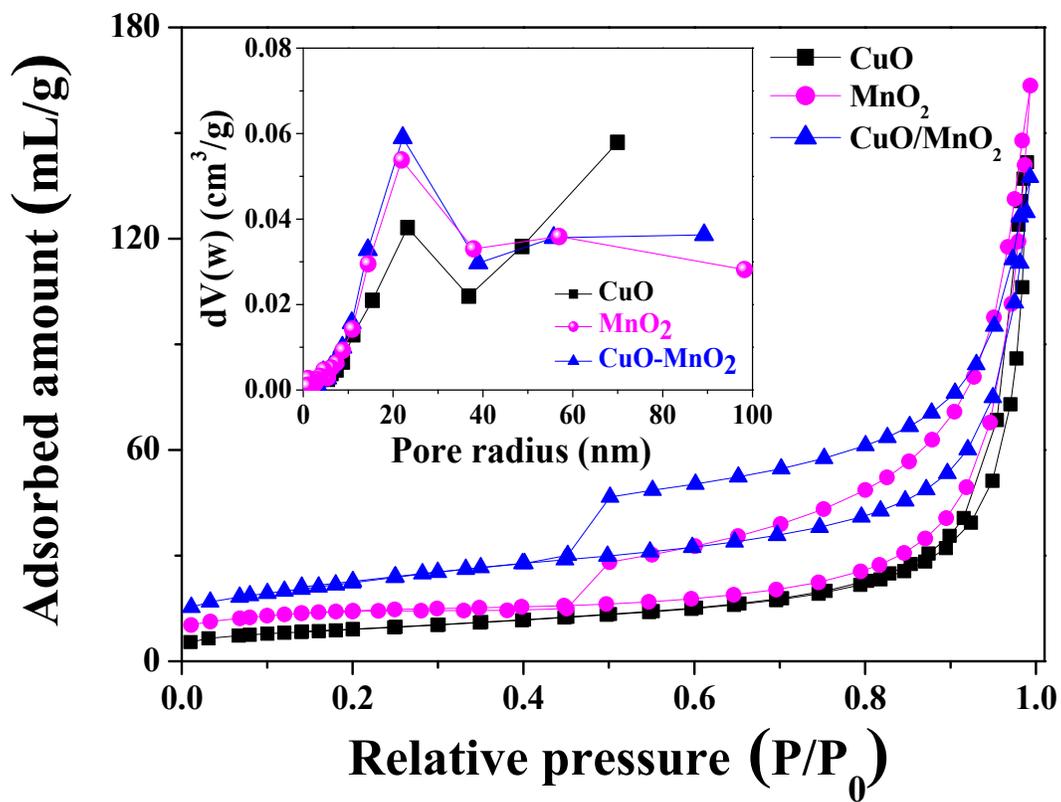

Figure S1 HRTEM images of CuO/MnO$_2$.

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Figure S2 N$_2$ adsorption–desorption isotherms of materials synthesized in this study. Inset shows pore size distribution.
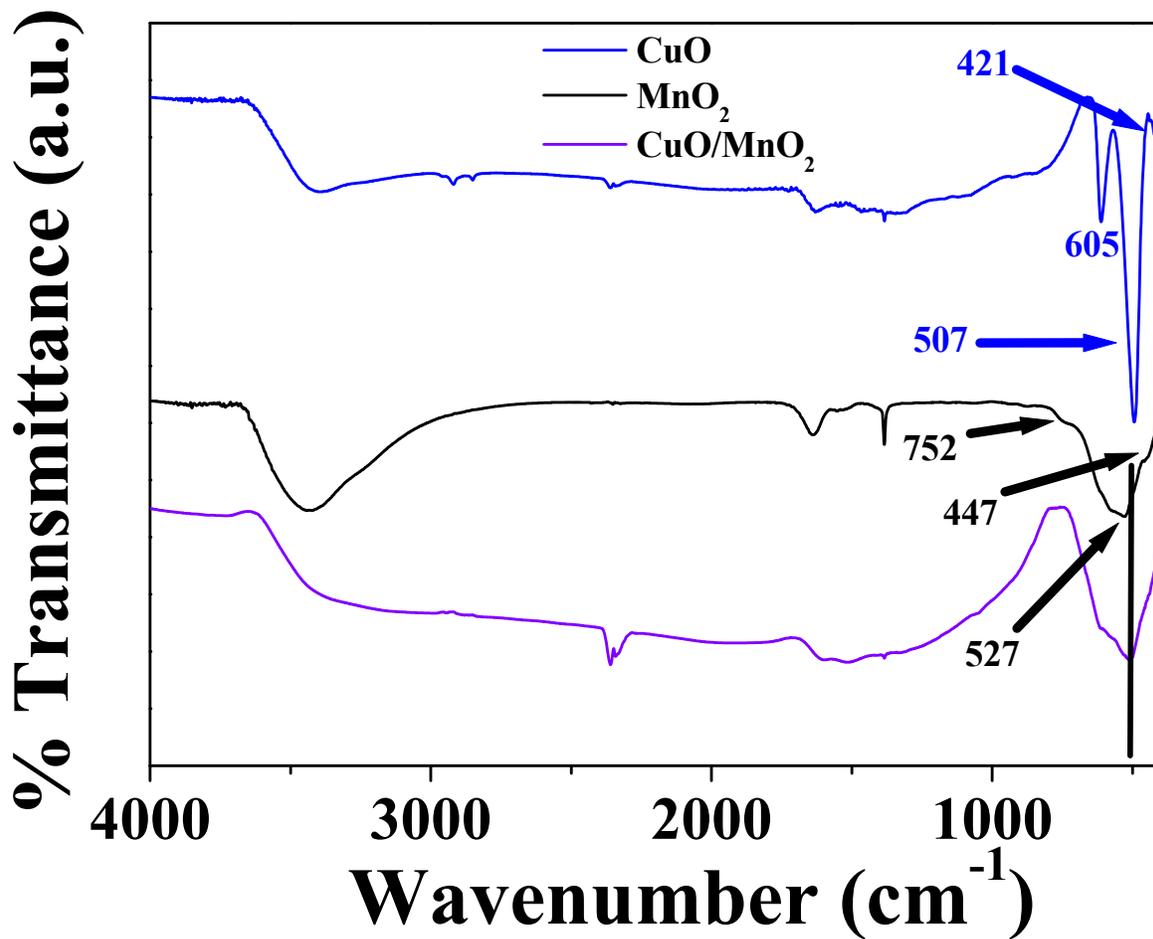
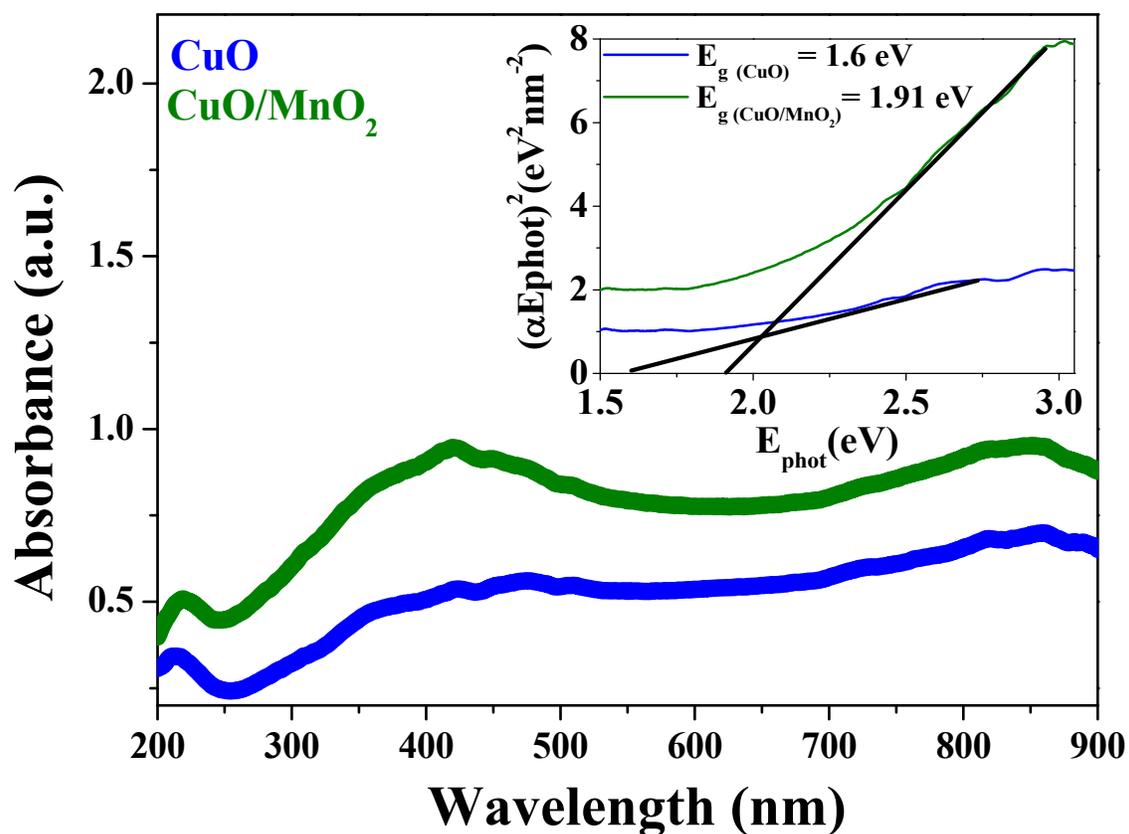**Figure S3** FTIR spectra of materials synthesized in this study.

Figure S4 DRUV-visible spectrum of CuO and CuO/MnO$_2$. Inset shows the plot of $(\alpha E_{photon})^2$ vs. Ephoton for CuO and CuO/MnO$_2$.

The plot of $(\alpha E_{photon})^2$ vs E_{photon} based on the direct transition is shown for these materials (Fig. S4). Equation, $(\alpha E_{photon})^2 = K (E_{photon} - E_g)$ can be used to calculate the band gap of the materials, where α is the absorption coefficient, E_{photon} is the discrete photon energy, K is a constant, and E_g is the band-gap energy.[1] The extrapolated value (the straight lines to the x axis) of E_{photon} at $\alpha = 0$ gives an absorption edge energy corresponding to E_g.
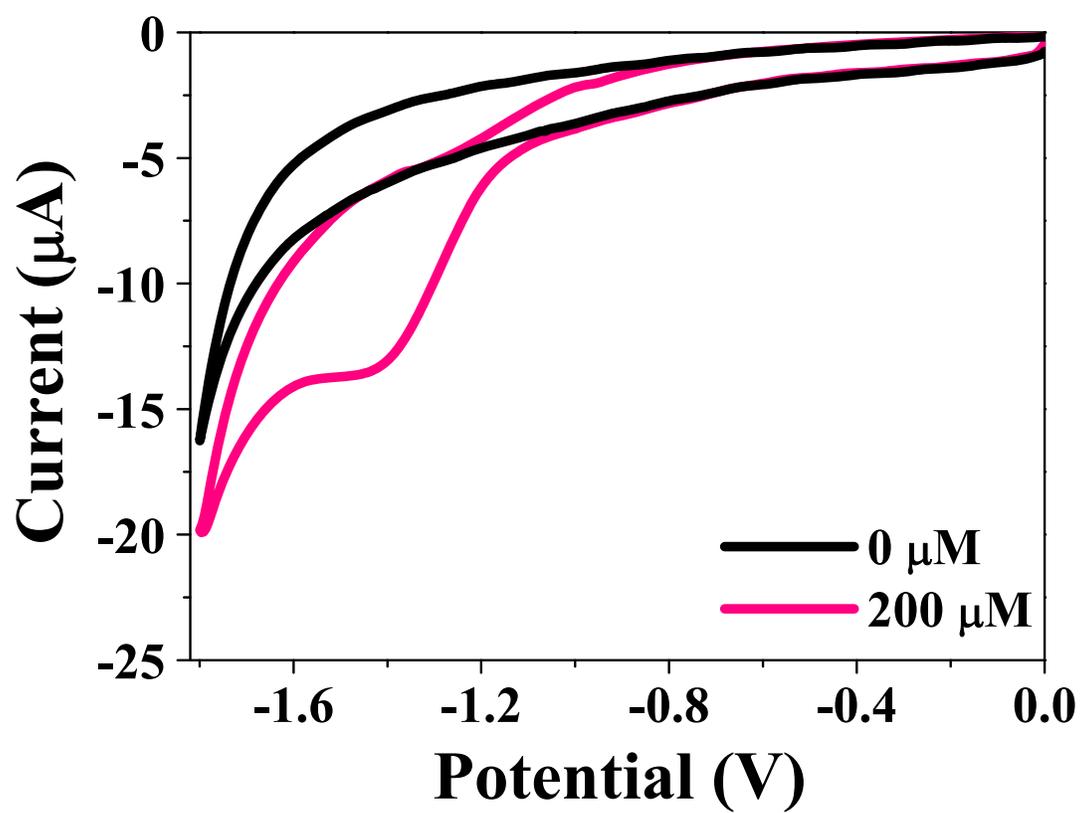
Figure S5 Cyclic voltammograms obtained at CuO/MnO$_2$ modified electrode in the absence and in the presence of 200 μM lindane at a scan rate of 50 mVs^{-1}. All scans go from 0 V to -1.8 V to 0 V.
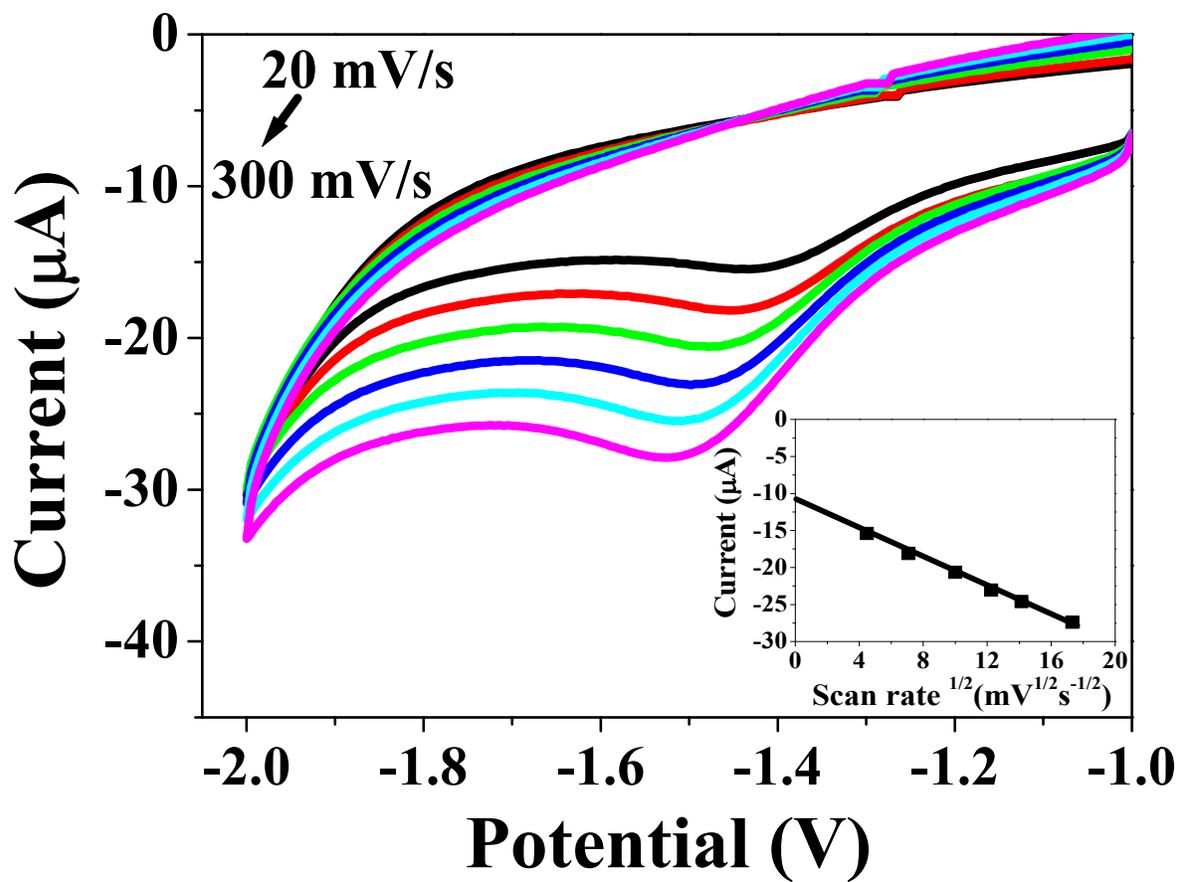
Figure S6 CVs of lindane (300 μM) at various scan rates (20-300 mVs^{-1}) at CuO/MnO$_2$ modified electrode. Inset shows the plot of peak currents vs. square root of scan rates.
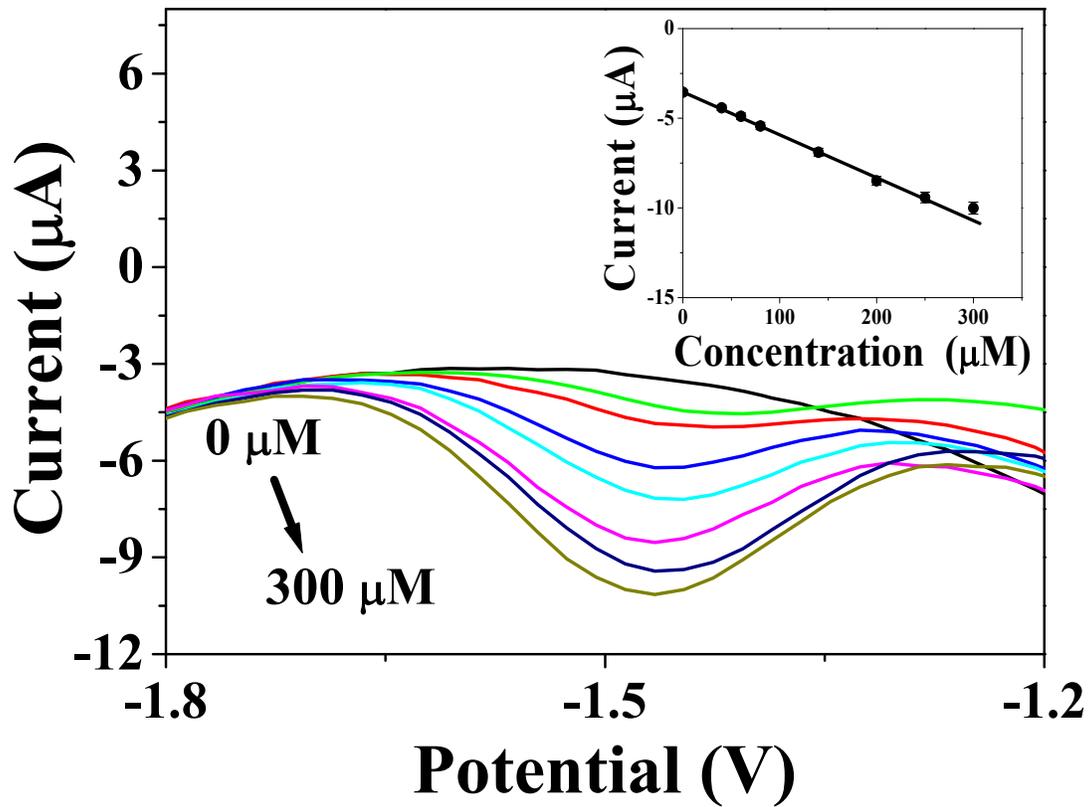
Figure S7 DPVs of lindane at varying the concentrations at the MnO_2 modified electrode using 0.05 M TBAB solution in 60:40 methanol–water (20 mL). Inset shows the calibration plot. DPV parameters were selected as: peak height = 50 mV; peak width = 200 ms; peak period = 400 ms; increment = 20 mV; pre and post-pulse width = 3 ms.

Figure S8 DPVs of lindane at CuO/MnO$_2$, and MnO$_2$ modified electrodes in the presence of 200 μM lindane. DPV parameters were selected as: peak height = 50 mV; peak width = 200 ms; peak period = 400 ms; increment = 20 mV; pre and post-pulse width = 3 ms.
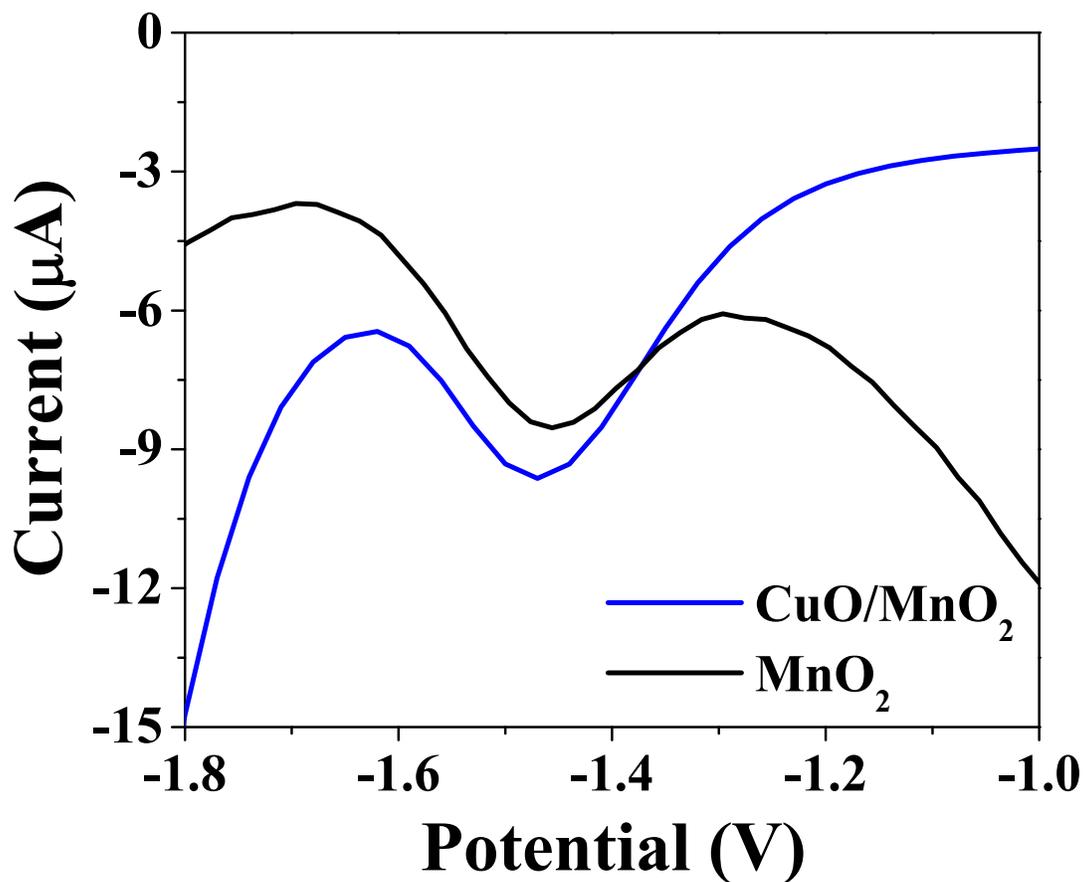
Table S1. Voltammetric data for the reduction of lindane (300 μM) at CuO/MnO$_2$ modified electrode at various scan rates (20-300 mVs^{-1}).

Scan rate (mV/s)	$E_{\frac{p}{2}} - E_P$	α [c]
20	205	0.25
50	190	0.27
100	178	0.28
150	170	0.30
200	160	0.32
300	155	0.34

[c] From $E_{\frac{p}{2}} - E_P = \dfrac{1.857\, RT}{\alpha F}$

Analysis of the voltammetric data recorded in a wide range of scan rates (20-300 mVs^{-1}) yields the high slopes values (Table S1). These high slopes indicate that the reduction process is electrontransfer (ET). In fact, it is well known that the concerted ET mechanism is characterised by small values of α.[2]

Table S2. Comparison of analytical performance of CuO/MnO_2 modified electrode with enzymatic and non-enzymatic sensors reported for electrocatalytic detection of γ-HCCH.

Electrode	Linear range	Detection limit	References
Enzymatic Sensors			
Polyaniline-gene *linA2* microbial biosensor	2–45 pM	2 pM	3
Non Enzymatic sensor			
$NiCo_2O_4$	10 –170 μM	3.6 μM	4
Cellulose acetate modified glassy carbon electrode	50–180 μM	9.18 μM	5
MIP Coated TiO_2 Nanotubes	0.1–10 μM	0.03 μM	6
DPA	40–100 μM	-	7
MIP	0.001–1 μM	0.0001 μM	8
CuO/MnO_2	1 μM–700 μM	4.8 nM	Present study

pM = picomolar; **DPA** = 9,10-diphenylanthracene; **MIP** = Molecular imprinted polymer; **μM** = micromolar; **nM** = nanomolar

Table S3. Determination of lindane dissolved in 60:40 (v/v) methanol–tap water (20 mL) samples at CuO/MnO_2 modified electrode.

Sample	Compound	Added/10^{-6} M	Found[a]/10^{-6} M	Recovery (%)
		0.8	0.81	101.3
Tap water	lindane	50	49.7	99.4
		100	99.8	99.8

[a]Average value of five determination.

References

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