Electronic Supplementary Material (ESI) for RSC Advances.

Silver nanoparticles decorated polyaniline-zeolite nanocomposite material based non-enzymatic electrochemical sensor for nanomolar detection of lindane

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Supporting Information

1. Materials and instruments used

All chemicals were of analytical reagent grade and used as received without further purification. Tetraethylorthosilicate (TEOS, 98%), tetrapropylammonium hydroxide (TPAOH), propyltriethoxy silane (PrTES, 97%), 3-aminopropyl trimethoxysilane, poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, Mw 5800) (hereafter designated as P123), and lindane were purchased from Sigma Aldrich, India. Aniline, ammonium peroxydisulphate (APS), and sodium borohydride were obtained from Spectrochem Pvt. Ltd., India. Silver nitrate ($AgNO_3$) was obtained from Fisher Scientific, India. Sodium dodecyl sulfate was obtained from S D Fine Chemical Ltd., India. Deionized water from Millipore Milli-Q system (Resistivity 18 MΩcm) was used in the electrochemical studies. Stock solution of lindane was prepared in methanol. 0.05 M tetra-n-butylammonium bromide (TBAB) solution (prepared in 60:40 (v/v) methanol-water) was used as the supporting electrolyte.

X-ray diffraction (XRD) patterns were recorded in the 2θ range of 5-90° with a scan speed of 2°/min on a PANalytical X'PERT PRO diffractometer, using Cu Kα radiation (λ=0.1542 nm, 40 kV, 40 mA) and a proportional counter detector. Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at 393 K for 3 h in the degas port of the adsorption apparatus. The specific surface area of zeolites was calculated from the adsorption data points obtained at P/P_0 between 0.05-0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using the Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV, to investigate the morphology of the materials. TEM investigations were carried out using FEI, Tecnai G^2 F30-S-T microscope operating at 300 kV. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used here using the same microscope, which was equipped with a scanning unit and a HAADF detector from Fischione (model 3000). The compositional analysis was performed using energy dispersive X-ray spectroscopy (EDS, EDAX Inc.) attachment on the Tecnai G^2 F30. The sample was dispersed in ethanol using ultrasonic bath, and dispersed sample was mounted on a carbon coated Cu grid, dried, and used for TEM measurement. Thermogravimetric analysis (TGA) was performed on a TGA/DSC 1 $STAR^e$ SYSTEM from Mettler Toledo instrument with temperature increments of 10 K/min in air stream.

2. Electroactive surface area

The $[Fe(CN)_6]^{3-/4-}$ is one of the most extensively studied redox couple in electrochemistry, which exhibits one-electron transfer (n = 1). The electroactive surface area of the modified electrodes was calculated according to the Randles-Sevcik equation (Eq. 1).[1]

$$I_p = (2.69 \times 10^5)\, n^{3/2}\, A D^{1/2}\, C\, \nu^{1/2} \qquad (1)$$

Where, I_p is the peak current of redox couple, n is the number of electrons participating in the redox reaction, A is the electroactive surface area (cm^2), D is the diffusion coefficient of $K_3[Fe(CN)_6]$ in the solution (cm^2/s), C is the concentration of $K_3[Fe(CN)_6]$ in the bulk solution (mol/cm^3), and ν is the scan rate (V/s).

3. Number of electrons transferred during lindane reduction

The number of electrons transferred during the reduction of lindane is calculated from the Randles-Sevcik equation for irreversible reduction processes by substituting the diffusion coefficient value of 0.89×10^{-5} cm^2/s for lindane as reported in the literature.[2, 3]

$$I_p = 2.99 \times 10^5 n(\alpha n_a)^{1/2} A C D^{1/2} \nu^{1/2} \qquad (2)$$

where I_p is the reduction peak current, n is the total number of electrons transferred, α is the charge transfer coefficient, n_a is the number of electron involved in charge transfer step, A is the area of electrode (cm^2), C is the concentration (mol/cm^3), D is the diffusion coefficient (cm^2/s), and ν is scan rate (V/s).

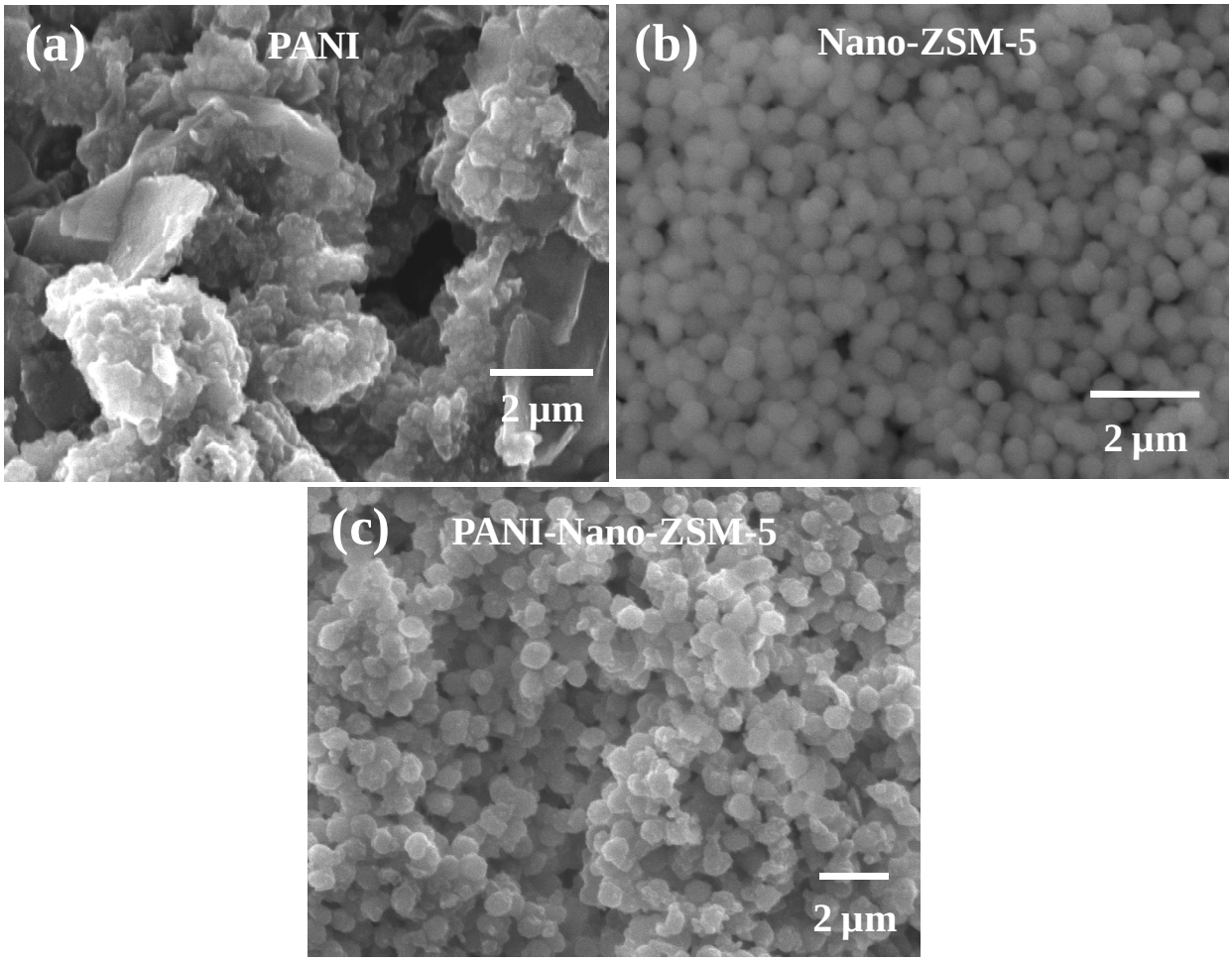


Figure S1. SEM images for PANI, Nano-ZSM-5, and PANI-Nano-ZSM-5 materials.

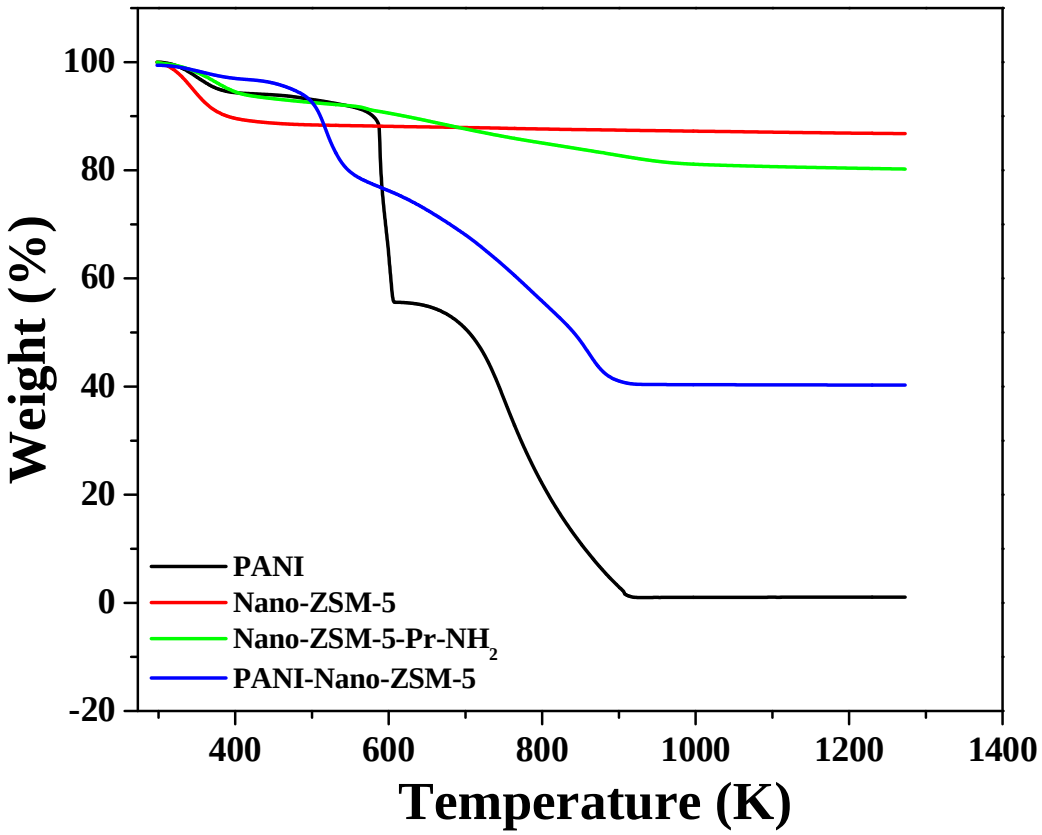


Figure S2. TGA thermograms of PANI, Nano-ZSM-5, PANI-Nano-ZSM-5-Pr-NH_2, and PANI-Nano-ZSM-5 materials at a heating rate of 10 K/min recorded in air stream.

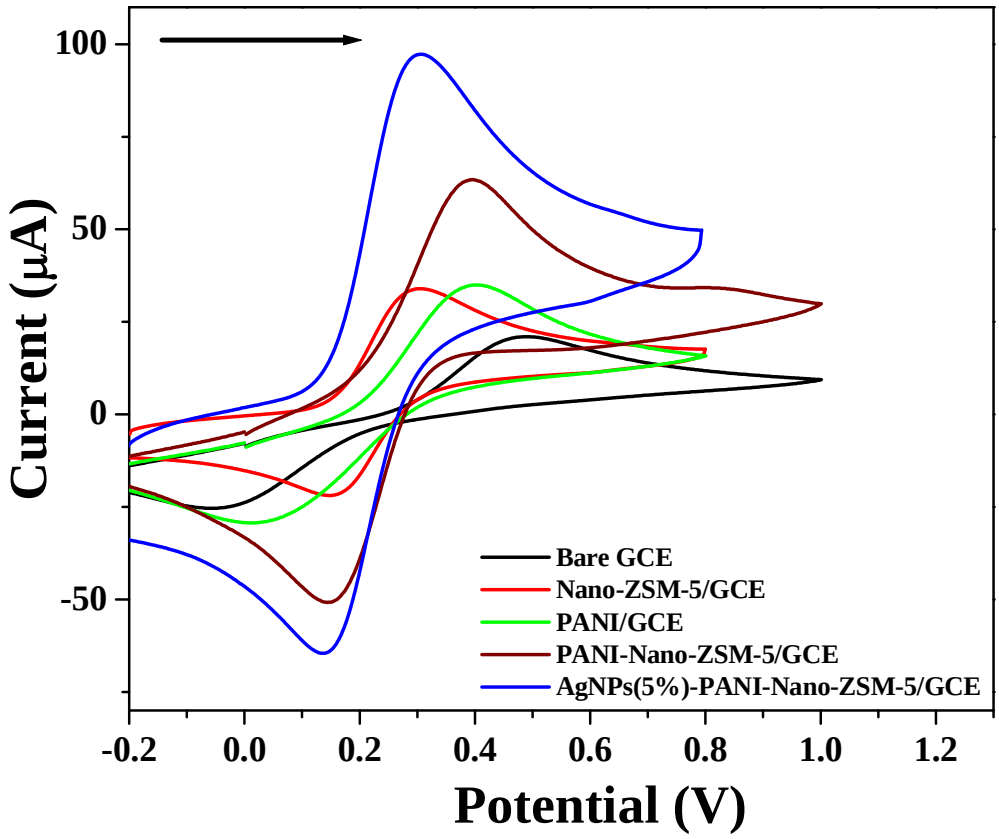


Figure S3. CV responses of various modified electrodes and bare GCE in 0.1 M KCl solution containing 1 mM of $[Fe(CN)_6]^{3-/4-}$ at a scan rate of 10 mV/s. Arrow indicates the starting point.

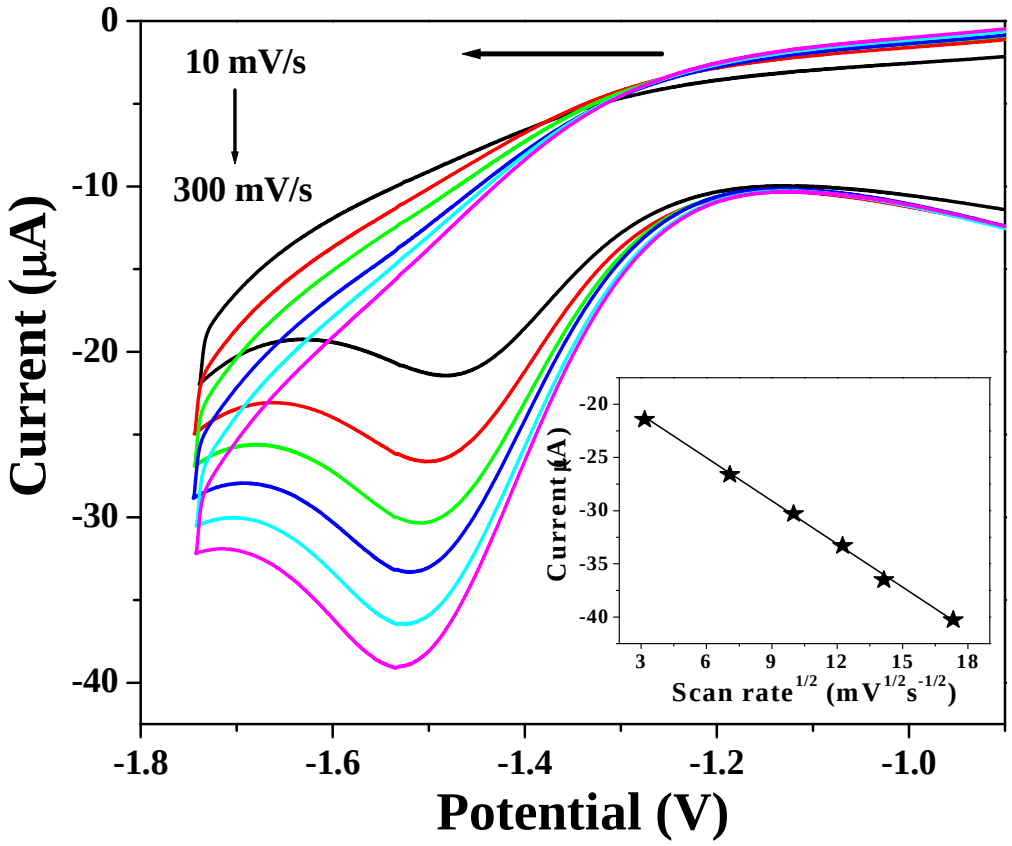


Figure S4. CVs of lindane (50 μM) at various scan rates (10-300 mV/s) at AgNPs(5%)-PANI-Nano-ZSM-5/GCE. Inset shows the plot of peak currents vs. square root of scan rates. Arrow indicates the starting point.

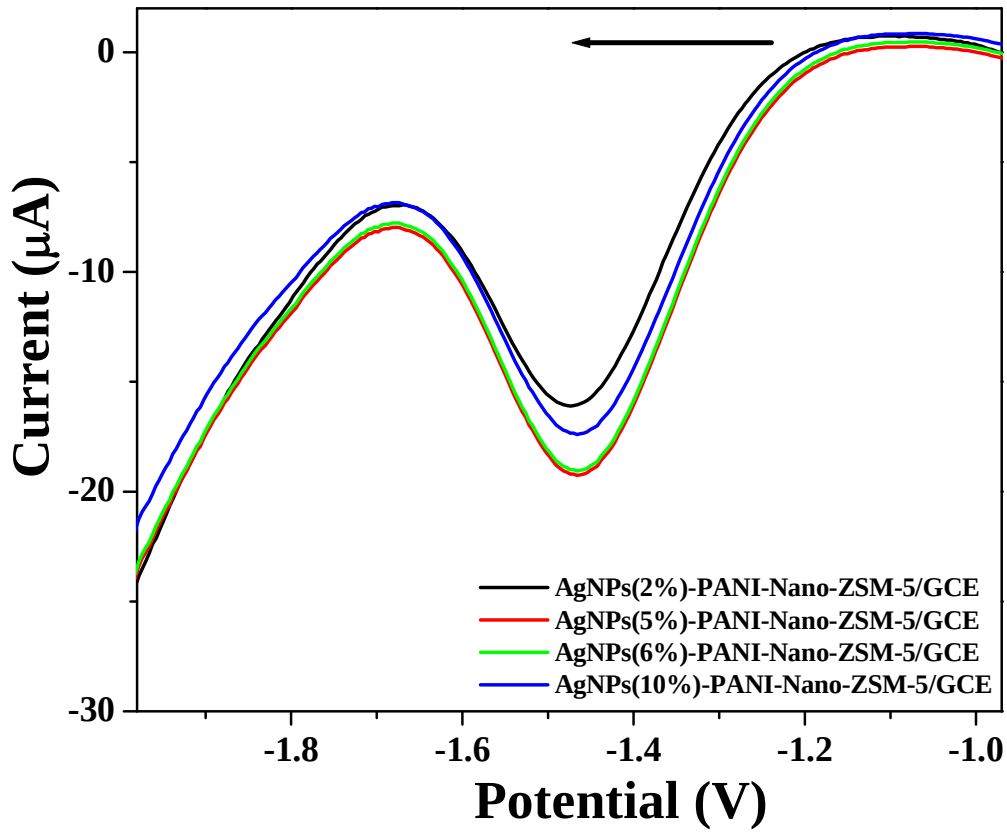


Figure S5. DPVs in the presence of lindane (60 μM) in 0.05 M TBAB solution in 60:40 (v/v) methanol-water (10 mL) at AgNPs-PANI-Nano-ZSM-5/GCE with different silver ratio. DPV parameters were selected as: pulse amplitude: 50 mV, pulse width: 50 ms, scan rate: 20 mV/s. Arrow indicates the starting point.

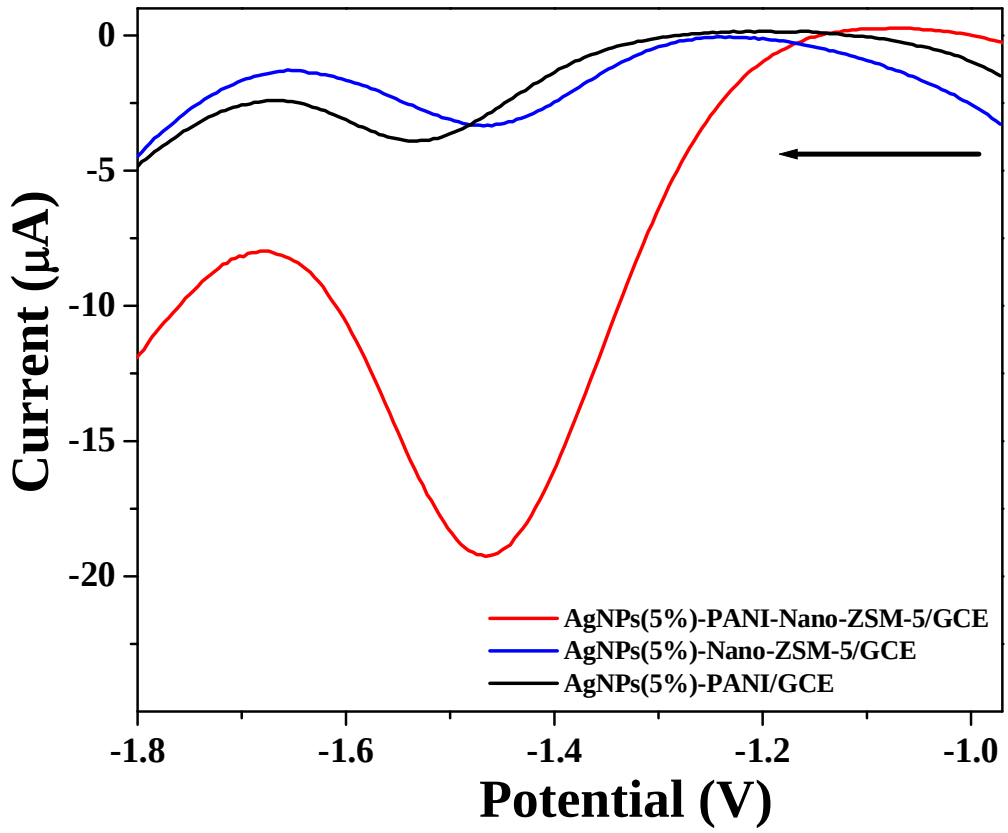


Figure S6. DPVs of lindane at AgNPs(5%)-PANI-Nano-ZSM-5/GCE, AgNPs(5%)-PANI/GCE, and AgNPs(5%)-Nano-ZSM-5/GCE in the presence of lindane (60 μM) in 0.05 M TBAB solution in 60:40 (v/v) methanol-water (10 mL). DPV parameters were selected as: pulse amplitude: 50 mV, pulse width: 50 ms, scan rate: 20 mV/s. Arrow indicates the starting point.

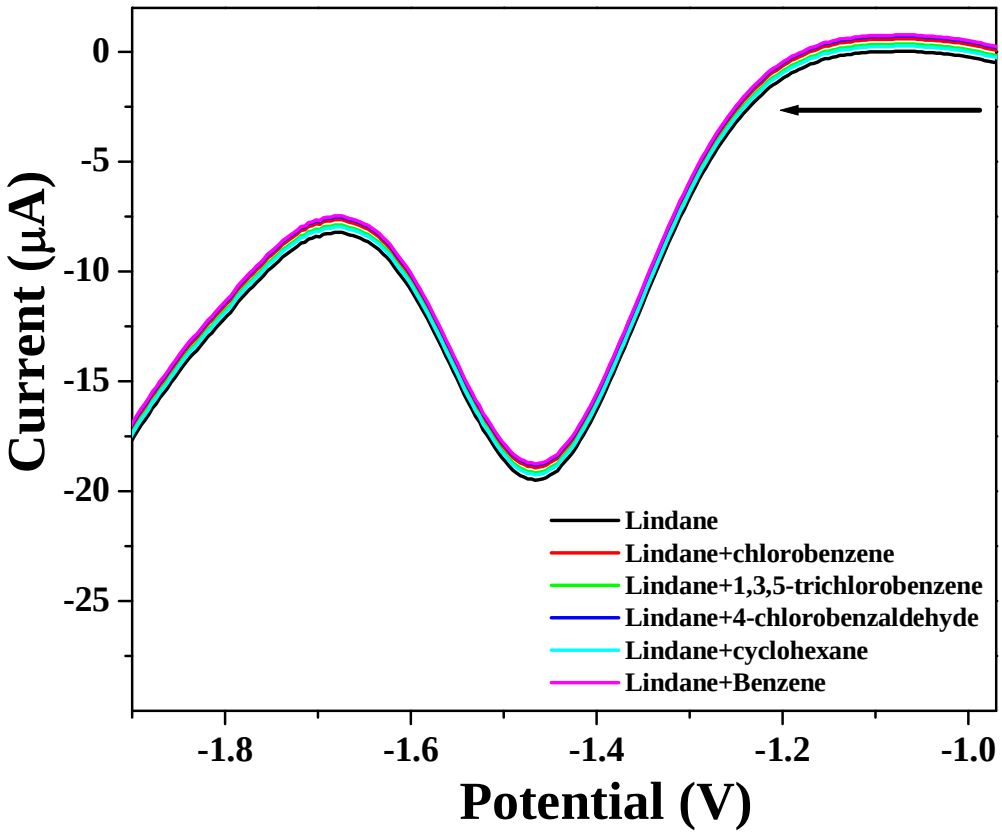
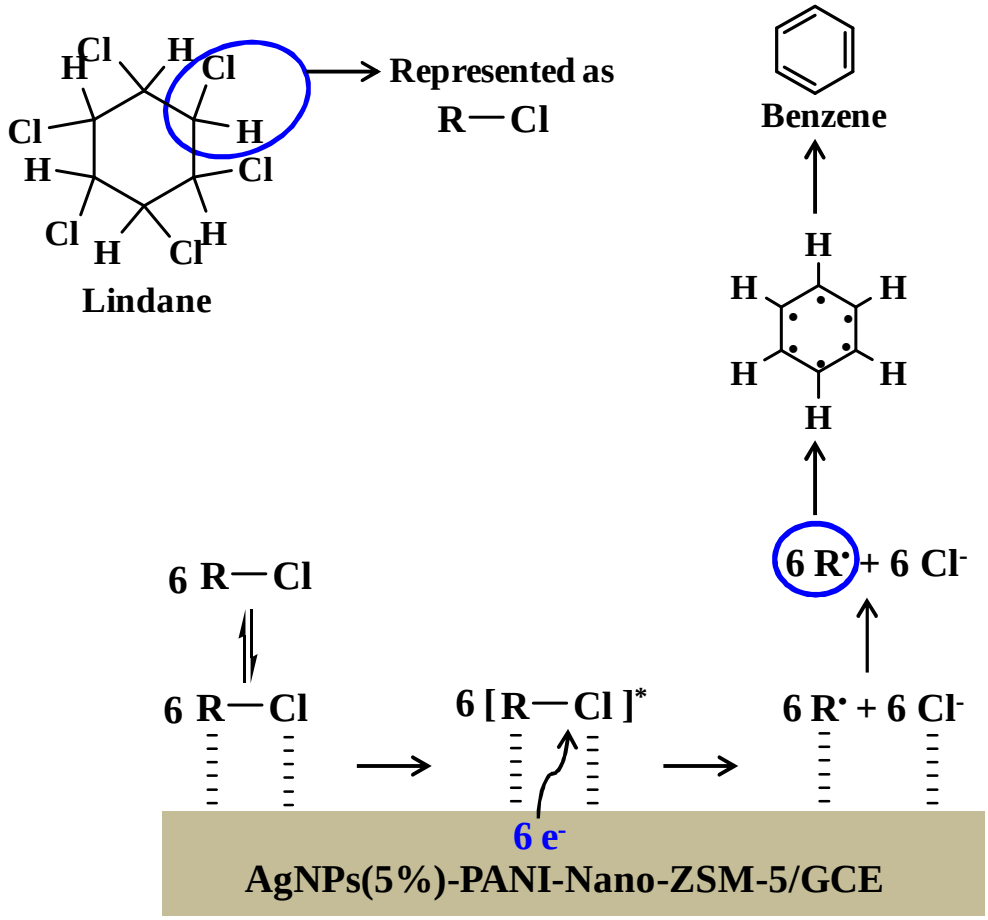


Figure S7. DPVs at AgNPs(5%)-PANI-Nano-ZSM-5/GCE in the presence of lindane (60 µM) and lindane (60 µM) with various interfering agents (5 µM) in 0.05 M TBAB solution in 60:40 (v/v) methanol-water (10 mL). DPV parameters were selected as: pulse amplitude: 50 mV, pulse width: 50 ms, scan rate: 20 mV/s. Arrow indicates the starting point.



Scheme S1. Mechanistic representation for the electrochemical reduction of lindane at AgNPs(5%)-PANI-Nano-ZSM-5/GCE.

Table S1 Voltammetric data for the reduction of lindane (50 μM) at AgNPs(5%)-PANI-Nano-ZSM-5/GCE at various scan rates.

S.No.	Scan Rate (mV/s)	$E_{p/2}$-E_p	α^c
1.	10	189	0.25
2.	50	178	0.26
3.	100	171	0.28
4.	150	165	0.29
5.	200	159	0.30
6.	300	152	0.31

[c] From $E_{p/2}$-E_p = 1.857 RT/αF = 47.7/α in mV at 298K

[α > 0.5 indicates a stepwise mechanism, whereas a α << 0.5 implies a concerted mechanism]

References

1. A. J. Bard and L. R. Faulkner, Electrochemical methods: Fundamentals and applications, Wiley New York, 1980, Vol. **2**.
2. P. R. Birkin, A. Evans, C. Milhano, M. I. Montenegro and D. Pletcher, *Electroanalysis*, 2004, **16**, 583-587.
3. M. U. Anu Prathap and R. Srivastava, *Electrochim. Acta*, 2013, **108**, 145-152.