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<th>A novel non-enzymatic lindane sensor based on CuO-MnO2 hierarchical nano-microstructures for enhanced sensitivity</th>
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In this work, we present new results about the non-enzymatic detection of lindane by using CuO/MnO$_2$ hierarchical nano-microstructure. The linear range for the determination of lindane is up to 700 μM with a limit of detection of 4.8 nM which is much lower than for other non-enzymatic lindane sensors.

In 1825, Michael Faraday reported to the Royal Society of London the synthesis and isolation of hexachlorocyclohexane (HCCH), otherwise known as benzene hexachloride. The reaction generates stereoisomers of HCCCH, among these isomers, only the Lindane (y-HCCH) exhibits insecticidal property. Lindane has been used worldwide as a general, broad-spectrum insecticide for a variety of purposes, including fumigation of stored grain products, pest control on domestic animals, mosquito control, to kill soil-dwelling and plant-eating insects. Many countries have been using HCCH as a topical treatment for head lice and scabies. Lindane is not bio-degradable; therefore, its accumulation has been detected in human blood, breast milk, and adipose tissue around the world. As a consequence of its toxic, carcinogenic, bioaccumulative and eating insects. Researchers have recognized that metal oxides composites always show excellent electrochemical performances over the single metal oxide alone. Therefore, a facile route for large-scale production of CuO/MnO$_2$ composites is still highly demanded.

In this communication, we report a facile method for the synthesis of CuO/MnO$_2$: hierarchical nano-microstructure. Further, we demonstrated the applicability of CuO/MnO$_2$: hierarchical nano-microstructure as an active electrocatalyst towards reduction of lindane. The CuO/MnO$_2$: sensors exhibited low detection limit, and wide linear range toward the detection of lindane, which can be ascribed to the novel structure of CuO/MnO$_2$: composites.
The textural properties of metal oxides were investigated by N\textsubscript{2} adsorption/desorption measurements (Fig. S2, ESI\textsuperscript{†}). \textit{CuO/MnO\textsubscript{2}} exhibits type IV isotherm with H3 hysteresis loop. The increase in slope at 0.45 corresponds to capillary condensation, typical of mesoporous materials, while the further increase at higher relative pressures indicates inter-particle porosity with slit-shaped pores.\textsuperscript{10a} BJH pore size distribution of \textit{CuO/MnO\textsubscript{2}} shows a pore size distribution centered at ~22.7 nm (Fig. S2, inset). The surface areas of 31.3, 55, and 77.6 m\textsuperscript{2}g\textsuperscript{-1} and pore volumes of 0.112, 0.15, and 0.157 cm\textsuperscript{3}g\textsuperscript{-1} were obtained for \textit{CuO}, \textit{MnO\textsubscript{2}}, and \textit{CuO/MnO\textsubscript{2}}, respectively. To investigate surface property of the composite, FT-IR spectrum analysis was conducted (Fig. S3, ESI\textsuperscript{†}). Samples show characteristic absorption bands in the range of 400 to 800 cm\textsuperscript{-1}, which can be assigned to Mn\textsubscript{2}O\textsubscript{4} stretching vibrations (Fig. S3, ESI\textsuperscript{†}).\textsuperscript{10b} The FT-IR spectra of \textit{CuO/MnO\textsubscript{2}} exhibited very weak signals corresponding to the vibrational modes of \textit{CuO} due to the high loading of \textit{MnO\textsubscript{2}}.\textsuperscript{10b} Diffused reflectance UV–visible investigation was used to determine the electronic structure and optical properties of \textit{CuO/MnO\textsubscript{2}} (Fig. S4, ESI\textsuperscript{†}). The band gap value for the \textit{CuO} was found to be 1.6 eV.\textsuperscript{11} The observed optical band gap for \textit{CuO/MnO\textsubscript{2}} was found to be 1.91 eV. Furthermore, the increase in the optical band gap in \textit{CuO/MnO\textsubscript{2}} materials can be explained on the basis of quantum size effect.\textsuperscript{11} The study suggests that \textit{MnO\textsubscript{2}} acted as a chemical modifier and caused a structural change or electronic effect.

\textit{CuO/MnO\textsubscript{2}} modified electrode was constructed to obtain the optimized analysis parameter for lindane reduction. Fig. S5 (ESI\textsuperscript{†}) shows cyclic voltammetric responses at the \textit{CuO/MnO\textsubscript{2}} modified electrode before and after the addition of lindane (200 µM). In the absence of lindane, no peak was observed. When lindane was added, a distinct peak at -1.5 V (vs Ag/AgCl) appeared, which is completely irreversible, imply that the reaction with lindane at \textit{CuO/MnO\textsubscript{2}} modified electrode is rapid (Fig. S5, ESI\textsuperscript{†}).\textsuperscript{8c} The effect of potential scan rate on the reduction peak currents was investigated in the range from 20 to 300 mV s\textsuperscript{-1} (Fig. S6, ESI\textsuperscript{†}). Reduction peak currents are linearly proportional to the square root of the scan rate, which shows that lindane undergoes a diffusion controlled reduction; the non-zero intercept can be explained as an adsorption process after diffusion to the electrode surface (Fig. S6, ESI\textsuperscript{†}).\textsuperscript{8b} The results of the voltammetric analyses are collected in Table S1. A survey of the data reported in Table S1 showed that the transfer coefficient (\(\alpha\)) value less than 0.5. It is well established that dissociative electron transfer (ET) which is concerted has a very small value of \(\alpha\) typically around 0.3.\textsuperscript{12} Moreover, there is no reverse peak obtained for a wide range of scan rates, which shows that the reduction process is irreversible.\textsuperscript{12} The removal of a chlorine atom by the reduction of polychlorinated benzenes always leads to a product that is more difficult to reduce.\textsuperscript{13} Incontrast, cleavage of carbon–chlorine bonds in lindane take place very fast and readily form fully reduced benzene.\textsuperscript{11} Differential pulse voltammetric (DPV) response at \textit{CuO/MnO\textsubscript{2}} modified electrode for different concentrations of lindane is shown in Fig. 2. The current obtained is proportional to the concentration of lindane in the reaction vessel (Fig. 2, inset).

A linear response was obtained between the peak current and lindane concentration (Fig. 2) with linear regression equation of, \(I(\mu A) = -4.18-0.022C (\mu mol L^{-1}) (R^2 = 0.9998)\) in the concentration range of 1 µM–700 µM with the sensitivity of 0.12 µA µM\textsuperscript{-1} cm\textsuperscript{-2} and a lower detection limit of 4.8 nM. DPV method was used to investigate the comparative electrocatalytic activity of various metal oxides modified electrodes investigated in this study with \textit{CuO/MnO\textsubscript{2}} modified electrode. \textit{MnO\textsubscript{2}} modified electrode showed sensitivity of 0.10 µA µM\textsuperscript{-1} cm\textsuperscript{-2} in the concentration range of 40 µM–250 µM (Fig. S7, ESI\textsuperscript{†}). The intercept of the calibration curve was not found to be zero, suggesting undesired non-Faradaic processes (Fig. S7 inset, ESI\textsuperscript{†}).\textsuperscript{15} However, when the similar study was performed at \textit{CuO} and bare glass carbon electrode in the presence of lindane, it did not show an increment in the reduction peak, suggesting no electrocatalytic activity for lindane reduction. The limit of detection was calculated by using IUPAC (International Union of Pure and Applied Chemistry) definitions, using standard approach of alternative (SA).\textsuperscript{15}

\[
\text{LOD}_{\text{SA}} = 3S/q \quad (1)
\]

where \(S\) is the standard deviation of the blank signal, and \(q\) is the slope of the calibration curve. Based on these observations, one can easily conclude that among the materials investigated in this study, \textit{CuO/MnO\textsubscript{2}} modified electrode exhibited the highest activity towards lindane reduction. Fig. S8 (ESI\textsuperscript{†}) shows a comparison of the DPVs obtained at \textit{CuO/MnO\textsubscript{2}} and \textit{MnO\textsubscript{2}} modified electrodes in the presence of 200 µM lindane. DPV measurements show that \textit{CuO/MnO\textsubscript{2}} modified electrode exhibits higher current response compared to \textit{MnO\textsubscript{2}} modified electrode. The current responses for 200 µM lindane at \textit{CuO/MnO\textsubscript{2}}, and \textit{MnO\textsubscript{2}} modified electrodes are...
-9.6 µA, and -8.4 µA, respectively (Fig. S8, ESI†). This improved analytical performance of CuO/MnOx is attributable to the synergistic contributions of the two nanostructured components in the composite. The sensing ability of the prepared CuO/MnOx-modified electrode towards lindane was compared with the reported nanostructures (Table S2). The analytical performance of CuO/MnOx-modified electrode is superior to the reported literature (Table S2), which are attributed to the greater number of catalytic active sites available in the CuO/MnOx.

The interference study was carried out using continuous amperometry. The possibility of the interference was evaluated against several inorganic ions and organic compounds (1 mM each) such as cyclohexane (CH), chlorobenzene (CB), and benzene (B) (Fig. 3). The results indicate that CuO/MnOx-based sensor is specific to lindane. No interference was observed for 20 fold excess of tricosane, 1,3,5-trichlorobenzene (1,3,5-TCB), 4-chlorobenzaldehyde (4-CBA). It may further be noted that the response current decreased by 13.8%, when 250 times higher concentration of 1,3,5-TCB was added. It should be noted that neither ethanol (1 mM), nor phenol (1 mM) elicited any response, these compounds being picked on the grounds of water solubility and structural features. The ion makeup of other anions likely to be present such as sulfate (1 mM) or nitrate (1 mM), and 100 fold of NH4+, K+, Na+, Ca2+, Mn2+, Fe3+ and Co2+ has no effect on the peak currents corresponding to the lindane reduction signal. The reproducibility of CuO/MnOx was evaluated by parallel DPV investigations of five numbers of identically fabricated CuO/MnOx electrodes. The sensor electrodes show relative standard deviations (RSD) of only ~ 2.4%, which is significantly lower. This essentially suggests very high reproducibility of the CuO/MnOx-modified electrode and the process of electrode fabrication, which may be crucial for the most precise estimation of lindane, which is attributed to the structural stability and non-deformation of the designed pore architecture. Stability of the sensor electrode for a longer duration is of paramount importance for better practical and economic viability. In this context, the CuO/MnOx-based sensor electrode was subjected to sensitivity assessment over a period of 21 days at a time interval of three days. The electrode was stored at room temperature when not in use and reactivated by dipping in supporting electrolyte for 30 minutes before sensitivity measurement. A minimal sensitivity loss of ~ 1.5 % over a period of 21 days of analysis clearly showing the exceptional stability of the CuO/MnOx electrode, which is highly suitable for longer duration applications. In order to verify the feasibility of the CuO/MnOx-modified electrode, this electrochemical method was applied to determine the concentration of lindane in tap water samples. Because the content of lindane in tap water was very low, therefore, samples containing a different amount of lindane were prepared in 60-40 (v/v) methanol–tap water (20 mL) (Table S3). The RSD and recovery calculations indicated the potential practical application of our proposed sensor.

In summary, we have presented a simple and well performing novel non-enzymatic sensor for lindane. CuO/MnOx nano-microstructure allows a detection concentration of lindane as low as 4.8 nM. This proposed electrochemical sensing methodology is thus expected to open opportunities for the detection of lindane in the ground water and other water bodies.

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Notes and references

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