<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Electrochemical sensor highly selective for lindane determination: a comparative study using three different α-MnO2 nanostructures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Anu Prathap, Mylamparambil Udayan; Sun, Shengnan; Xu, Zhichuan Jason</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Anu Prathap, M. U., Sun, S., &amp; Xu, Z. J. (2016). An electrochemical sensor highly selective for lindane determination: a comparative study using three different α-MnO2 nanostructures. RSC Advances, 6(27), 22973-22979.</td>
</tr>
<tr>
<td><strong>Date</strong></td>
<td>2016</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/10220/40521">http://hdl.handle.net/10220/40521</a></td>
</tr>
<tr>
<td><strong>Rights</strong></td>
<td>© 2016 The Royal Society of Chemistry. This is the author created version of a work that has been peer reviewed and accepted for publication by RSC Advances, The Royal Society of Chemistry. It incorporates referee’s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<a href="http://dx.doi.org/10.1039/c5ra26771d">http://dx.doi.org/10.1039/c5ra26771d</a>].</td>
</tr>
</tbody>
</table>
This article can be cited before page numbers have been issued, to do this please use: M.U. A. Prathap, S. Sun and Z. J. Xu, RSC Adv., 2016, DOI: 10.1039/C5RA26771D.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Electrochemical sensor highly selective for lindane determination: A comparative study using three different α-MnO₂ nanostructures

M.U. Anu Prathap, Shengnan Sun, and Zhichuan J. Xu*

Here we describe a simple, highly reproducible ultra-sensitive electrochemical sensor for lindane based on α-MnO₂ nanostructures. The results showed that the α-MnO₂ nanostructures effectively catalyzed the electrochemical reduction of lindane. A good linearity was obtained in the range of 1.1 to 510 μM with a detection limit of 114 nM. The proposed lindane sensor was successfully employed for determining lindane in tap water samples with good recoveries. Negligible amperometric currents are observed in the control experiments using triclosan (T), chlorobenzene (CB), benzene (B), 1,3,5-trichlorobenzene (1,3,5-TCB), and 4-chlorobenzaldehyde (4-CBA), suggesting sensing specificity to lindane. The proposed sensor also exhibited good stability and reproducibility for lindane determination.

Introduction

Lindane (gamma isomer of hexachlorocyclohexane) is an organochlorine insecticide named after Dutch chemist Teunis van der Linden who was the first to isolate α-, β-, and γ-isomers of hexachlorocyclohexane in 1912.1,2 The insecticidal properties of lindane were first demonstrated by Ulmann, 1972.1,2 Lindane has been used to treat food crops and to forestry products, as a seed treatment, a soil treatment, and to treat livestock and pets.1,3 Lindane is reported to be a central nervous system stimulant. Symptoms of acute exposure include mental and motor retardation, central nervous system excitation, tonic-clonic convulsions, respiratory failure, pulmonary edema and dermatitis.2,3 Lindane enters animal tissues through food chain, respiration or dermal contact.2,3 After being under review for nearly 30 years, the pesticide lindane was finally withdrawn by the Environmental Protection Agency (EPA) for use in agriculture.3,4 Lindane is recognized by EPA as one of the most toxic, persistent, bio-accumulative pesticides ever registered.5 Despite a recent global ban on its agricultural use, the pesticide is still used and approved by the Food and Drug Administration (FDA) as a second-line therapy for topical treatment of pediculosis capitis (head lice), pediculosis pubis (pubic lice), or scabies in patients greater than two years of age who cannot tolerate or have failed first-line treatment.5 Therefore, quantitative analysis of lindane is a paramount area in the context of the environmental bulwark. New methods, for lindane detection includes more sophisticated analytical approaches, such as gas chromatography, liquid chromatography or gas chromatographic-massspectrometry.6,7 Although chromatographic methods are accurate, they are expensive and time consuming.6,4 Among the various biosensing approaches, available to date, electrochemical sensors are emerging to be a technology of choice due to the rapid and sensitive response, low fabrication cost and operational convenience.5,8 An excellent study discusses the reductive dechlorination of lindane catalyzed by bioreceptor probe.9 It was found that the specificity of dechlorination depended on the enzyme stability, pH and temperature, which is the major limitation.7 Lindane has very low aqueous solubility and has a very high overpotential for reduction, as a result the direct reduction of lindane using the aqueous medium is a challenging task. Recent publications discuss on dechlorination of lindane in ethanol/water and lindane gave only one reduction wave and benzene as the reduction product with 100 % yield.10-15 The results of other researchers show chloride ion was liberated from lindane structure more rapidly than hydrogen or carbon atom fragments.10-15 Few studies have been dedicated to the non-enzymatic sensing of lindane using metal oxide, and it appears to be more effective.12,15 Thus, it is important to pursue a suitable modified electrode for the efficient reduction of lindane.

In recent years, the application of nanoscaled metal oxides has received great attention in biotechnology and bio-analytical chemistry.16-20 Transition metal element; manganese can exist as a variety of stable oxides (MnO, Mn₃O₄, Mn₂O₃, MnO₂) and crystallize in various types of crystal structures. Among them, α-MnO₂ has been widely investigated and extensively used in adsorption, catalysis, sensors, rechargeable lithium batteries.
and ion exchanges owing to the existing unique layers or tunnels in crystal lattices.\textsuperscript{21-23} It is generally accepted that the physicochemical properties of MnO\textsubscript{2} are greatly affected by the crystallographic structure, morphology, and surface area.\textsuperscript{21}

In this work, we report three synthetic pathways for the preparation of α-MnO\textsubscript{2} nanostructures, (e.g., NW (nanowire), NT (nanotube), and MS (microsphere); designated as: α-MnO\textsubscript{2}-NW, α-MnO\textsubscript{2}-NT, and α-MnO\textsubscript{2}-MS). We further demonstrated α-MnO\textsubscript{2} nanostructures exhibit excellent electrocatalytic activity for lindane reduction. The prepared sensor was characterized by electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV), cyclic voltammetry (CV), pulsed amperometry (PA) and chronoamperometry. Under the optimized conditions, the prepared sensor exhibited selective recognition and a highly sensitive detection toward lindane.

**Experimental Materials**

All chemicals were analytical grade and used without further purification. KMnO\textsubscript{4}, urea, γ-HCCH (Lindane), cyclohexane, chlorobenzene, 4-chlorobenzaldehyde, triclosan, 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 α-MnO\textsubscript{2} microspheres (α-MnO\textsubscript{2}-MS)**

α-MnO\textsubscript{2}-MS was synthesized by a hydrothermal approach with a modified procedure first reported by our group.\textsuperscript{25} 1.5 mmol (0.237 g) of KMnO\textsubscript{4} was dissolved in 100 mL of deionized water (DW), followed by the addition of 5 mL hydrochloric acid (11.65 M, 35% (w/w)), forming a solution. The resulting mixture was stirred for 0.5 hr; the solution was transferred to a Teflon-lined autoclave (50 mL capacity). The hydrothermal process was conducted at 353 K for 12 hr. Product was filtered, washed with water and ethanol, dried in an oven at 353 K for 8 h.

**Synthesis of α-MnO\textsubscript{2} hollow nanotube (α-MnO\textsubscript{2}-NT)**

α-MnO\textsubscript{2}-NT was synthesized by a hydrothermal approach by modifying the recipe.\textsuperscript{25} 15 mmol (2.37 g) of KMnO\textsubscript{4} was dissolved in 200 mL of deionized water (DW), followed by the addition of 5 mL hydrochloric acid (11.65 M, 35% (w/w)), forming a solution. The resulting mixture was stirred for 0.5 hr; the solution was transferred to a Teflon-lined autoclave (50 mL capacity). The hydrothermal process was conducted at 383 K for 15 hr. Product was filtered, washed with water and ethanol, dried in an oven at 353 K for 8 h.

**Materials characterization**

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\textsuperscript{-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\textsubscript{0} in the range of about 0.05–0.3.

**Electrochemical measurements**

Cyclic voltammetry (CV), Differential pulse voltammetry (DPV), Pulsed amperometry (PA) and Continuous amperometric 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\textsuperscript{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 MnO\textsubscript{2} suspension (a homogenous sonicated solution of 10 mg of MnO\textsubscript{2} 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.

**Results and discussion**

XRD analysis was primarily used to determine the structure of the α-MnO\textsubscript{2}-NW (Fig. 1a). All the diffraction peaks can be indexed to a tetragonal α-MnO\textsubscript{2} (JCPDS, file No.: 44-0141). Similar XRD observation was also noticed for α-MnO\textsubscript{2}-NT and α-MnO\textsubscript{2}-MS prepared in this study (Figure not shown). Fig. 1b-h shows the SEM and HRTEM images with different magnifications of α-MnO\textsubscript{2}-MS, α-MnO\textsubscript{2}-NT, and α-MnO\textsubscript{2}-NW. The SEM morphology of α-MnO\textsubscript{2}-MS is spherical with a flower-like morphology (Fig. 1b,e). The higher magnification image shows that the petal structure of microspheres is assembled by many nanosheets (Fig. 1c). Figs. 1(d-f) is the representative SEM and HRTEM images of the as-prepared α-MnO\textsubscript{2}-NT. Evidently, each MnO\textsubscript{2} nanotubes are of high quality; they are open-ended and have a length of hundreds of
nanometer. Figs. 1(c,f). Fig. 1g shows the low magnification image of the α-MnO₂-NW; it can be found that the product consists of nanowires. The MnO₂ nanowires are further investigated by HRTEM (Fig. 1h). The diameters of the presented MnO₂ nanowire are within 50 nm (Fig. 1h). The N₂ sorption isotherm of the α-MnO₂-NW sample shows a type IV curve with a sharp capillary condensation step in the relative pressure range of 0.6–1 and H₁ hysteresis loop, indicative of uniform cylindrical mesopores (Fig. 2a). The α-MnO₂-NT nanostructures synthesized in this study exhibited type IV isotherm with H₁ hysteresis, which is characteristic of the mesoporous materials. High uptake of N₂ adsorption at a low relative pressure (~ 0.4) reveal abundant micropores located in the α-MnO₂-NT (Fig. 2a). Textural properties for various materials obtained from the N₂-adsorption study is provided in Table S1, ESI†. The specific BET surface area for α-MnO₂-MS, α-MnO₂-NW, α-MnO₂-NT, and α-MnO₂-MS were found to be 124.2 m²/g, 79.3 m²/g and 12.2 m²/g, respectively. From the SEM images it can be seen that α-MnO₂-MS has thinner short fiber lengths and diameters ~ 50 nm, while α-MnO₂-NT has a diameter of ~ 110 nm and α-MnO₂-MS has higher diameter (sub-micrometer size), the decrease of the lateral dimensions (diameter) to the nanoscale offers a high specific surface area and a high surface site density to α-MnO₂-NW (Fig. 1). Fig. 2 XRD pattern (a) of α-MnO₂-NW. FE-SEM images (b,c) of α-MnO₂-MS, FE-SEM images (d,e) and TEM image (f) of the a-MnO₂-NT, and FE-SEM image (g) and TEM images (h) of the α-MnO₂-NW. The inset of (h) is a close view of α-MnO₂-NW.

The electrochemical behavior of different modified electrodes was investigated using potassium ferricyanide as the electrochemical probe by CV. Study was performed in 0.2 M KCl solution containing 50 mM K₃[Fe(CN)₆] and 20 mM K₄[Fe(CN)₆] at a scan rate of 20 mV/s at different modified electrodes. The CV of various modified electrodes exhibited a pair of well-defined redox peaks corresponding to Fe(CN)₆³⁻⁴⁻ redox couple (Fig. 2b). Among the various modified electrodes investigated in this study, α-MnO₂-NW exhibited the highest current response. The electroactive surface area of various electrodes was calculated according to the Randles-Sevčik equation (Eq. 1).

\[ I_p = \left(2.69 \times 10^5\right) n^{3/2} A D^{1/2} C^{1/2} \]

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 (cm²), \( D \) is the diffusion coefficient of K₃[Fe(CN)₆] in the solution (cm²/s), \( C \) is the concentration of K₃[Fe(CN)₆] in the bulk solution (mol/cm³), and \( v \) is the scan rate (V/s). The effective surface area of different modified electrodes was calculated as 0.403, 0.305, and 0.259 cm² for α-MnO₂-NW, α-MnO₂-NT, and α-MnO₂-MS, respectively. The high electroactive surface area of α-MnO₂-NW significantly eases the electron transfer rate at the electrode-electrolyte interface. Fig. 2c displays typical Faradaic impedance spectra (presented as Nyquist plot) of the α-MnO₂-NW electrode before and after additions of different concentrations of the lindane. Electrochemical impedance spectra were recorded in the frequency range from 1 MHz to 10 mHz with the AC signal amplitude of 10 mV. It can be clearly observed that the electron-transfer resistance (semicircle diameter) decreases as the lindane concentration is elevated. In EIS, the diameter of the semicircle portion at higher frequencies corresponds to the electron-transfer resistance (Rₑ). The change of Rₑ value at high frequencies was associated with the blocking behavior of the modified layer at the electrode surface. The collected data show that the Rₑ values are significantly smaller after the addition of lindane, e.g., decreasing from 7.02 kΩ to 3.12 kΩ, upon increasing the lindane concentration from 0 to 180 µM. The smaller semi-circle diameter (i.e. lower value of Rₑ) indicates faster electron-transfer kinetics of lindane (reduction) at the α-MnO₂-NW modified electrode.

α-MnO₂-NW modified electrode was constructed to obtain the optimized analysis parameter for lindane reduction. The electrochemical behaviour of lindane was first investigated using cyclic voltammetry in the absence and presence of 300 µM lindane. In the absence of lindane, no peak was observed. When lindane was added, a distinct peak at ~1.45 V (versus Ag/AgCl) was appeared, which is completely irreversible (Fig. S1, ESI†). The effect of scan rate (range of 20–200 mV s⁻¹) was investigated to predict the reaction kinetics process using cyclic voltammetry as shown in Fig. 2d. The results reveal that the reduction peak current of lindane was directly proportional to the square root of scan rate up to 200 mV s⁻¹, the negative intercept suggests that the electrode reaction is not a pure diffusion-controlled process (Fig. 2d, inset). The Randles-Sevčik equation for a reduction process with a zero intercept suggests a complete diffusion control process, thus, the negative intercept from the plot of peak current versus square root of scan rate can be explained as an adsorption of the lindane molecule after diffusion to the electrode surface. The results of the voltammetric analyses are collected in Table S2. The electron transfer coefficient \( \alpha \) was calculated from the peak width (\( \Delta E_{p/2} = E_p - E_0 \)). For all scan rates, a very low value of \( \alpha \) is obtained less than 0.5, showing that the rate-determining...
step of the electrode process is dissociative electron transfer (ET), which is concerted with the cleavage of the carbon–halogen bond. Dechlorination or displacement of chloride of polychlorinated cyclohexanes is different from the dechlorination of polychlorinated benzenes. Earlier workers reported that the elimination of a chlorine atom by the reduction of polychlorinated benzenes always leads to a product that is more difficult to be reduced. In contrast, breaking of carbon-chlorine bonds in lindane occur very fast and readily form fully reduced benzene.

Under the optimized conditions, pulsed amperometry and differential pulse voltammetry were used to determine lindane concentration. The Fig. 3a shows the pulsed amperometric response of $\alpha$-MnO$_2$-NW modified electrode to lindane. At the constant potential -1.45 V (vs Ag/AgCl), the measured current response is linear vs. the lindane concentration (Fig. 3a). $\alpha$-MnO$_2$-NW modified electrode can detect lindane in the concentrations range from 1.1 to 510 µM in the amperometric mode with a linear regression equation of, $J(\mu A) = -4.64\times10^{-4}C$ ($\mu$mol L$^{-1}$) ($R^2 = 0.9989$) with the sensitivity of 0.18 $\mu$A µM$^{-1}$ cm$^{-2}$ and a lower detection limit of 114 nM. The intercept of the calibration curve was not found to be zero, suggesting undesired non-Faradaic processes (Fig. 3a, inset).  

DPV measurements were also carried out containing different lindane concentrations to obtain an analytical curve. Fig. 3b shows that the cathodic peak current was linearly dependent on the lindane concentration in the range from 2 to 520 µM with a linear regression equation of, $I(\mu A) = -6.208-0.022C$ ($\mu$mol L$^{-1}$) ($R^2 = 0.9983$) with the sensitivity of 0.14 $\mu$A µM$^{-1}$ cm$^{-2}$ and a lower detection limit of 517 nM (Fig. 3b, inset). Similarly, linear relationship between oxidation peak currents and lindane concentrations was observed in the range of 4–500 µM, and 15–350 µM for $\alpha$-MnO$_2$-NT and $\alpha$-MnO$_2$-MS modified electrodes (Fig. S2 and Fig. S3, ESIF). To obtain the limit of detection (LOD), we used an IUPAC (International Union of Pure and Applied Chemistry) recommended methodology, using the standard approach of alternative (SA).

$$\text{LOD}_{\text{SA}} = 3S/q \quad (2)$$

Where S is the standard deviation of the blank signal, and q is the slope of the calibration curve. A comparison of the modified electrodes toward electrocatalytic reduction of lindane is presented (Fig. 4a). Based on the experimental evidence, one can conclude that $\alpha$-MnO$_2$-NW modified electrode exhibited superior sensing ability and current sensitivity compared to other modified electrodes investigated in this study. The high electrocatalytic response observed for the $\alpha$-MnO$_2$-NW can be correlated with the large surface area, excellent site accessibility and a low mass-transfer resistance for lindane.
Nanoscale

Fig. 3 (a) Pulsed amperometric response of the α-MnO₂-NW modified electrode to different concentrations of lindane at the specified voltage values. The inset shows the calibration plot. (b) DPVs of lindane at varying the concentrations at the α-MnO₂-NW modified electrode using 0.05 M TBAB solution in 60:40 methanol-water (20 ml). The 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.

The sensing ability of the prepared α-MnO₂-NW modified electrode towards lindane was compared with the reported nanostructures (Table S3, ESI†). The performance of α-MnO₂-NW nanostructures modified electrode is comparable if not superior to those reported in the literature Table S3, ESI†. For the practical use of non-enzymatic lindane sensors, specificity is another important factor that needs attention. Under a rational design, the lindane sensor should have minimal interferences from water and soil samples from industrial areas and agricultural land. In the present work, interfering compounds were picked based on structural similarity and solubility in water and soil. Therefore, interfering compounds, electroactive organic compounds and organic compounds containing chlorine groups were chosen which may potentially interfere with determination of lindane. The amperometric response of the α-MnO₂-NW modified electrode to the stepwise addition of lindane in the presence of 1 mM each of various interfering species such as cyclohexane (CH), triclosan (T), chlorobenzene (CB), and benzene (B) at an applied potential of -1.45 V is shown in Fig. 4b. The α-MnO₂-NW modified electrode shows excellent anti-interference behaviour towards interfering species (Fig. 4b). It may further be noted that when 150 times higher concentration of 4-CBA (0.5 M) and 1,3,5-TCB (0.5 M) interfered with the determination of lindane (Fig. 5a,b)). The results also showed that 1 mM concentrations of inorganic ions (Ca²⁺, Co²⁺, Mg²⁺, Mn²⁺, Ni²⁺, and Zn²⁺) did not interfere with the detection of lindane (Fig. 5c).

Fig. 4 (a) Comparison of the sensitivity for lindane at different modified electrodes investigated in this study. (b) Continuous amperometric response at the α-MnO₂-NW modified electrode in the presence of high concentration of interfering species, such as chlorobenzene (1 mM), benzene (1 mM), triclosan (1 mM), and cyclohexane (1 mM) as compared to the successive addition of lindane.

Fig. 6a illustrates a pulse amperometric response for series of injections of standard lindane solution at a fixed potential (pulse sequence (n)=5). Fig. 6a shows that when a fixed potential was applied (-1.45 V) the signal current increased relatively fast and no decrease of the signal was observed during the pulse length (relative standard deviation ~ 1.02%), suggesting very high reproducibility. After each measurement, the electrode was rinsed thoroughly with deionized water and was stored at room temperature when not in use and reactivated by dipping in the supporting electrolyte for 30 minutes before measurement. Furthermore, α-MnO₂-NW modified electrode could be used more than 13 times after subsequent cycles of washing and measuring operations. On the other hand, three fresh fabricated α-MnO₂-NW modified electrodes were also used for determining 50 µM lindane. The RSD was calculated to be 2.71%. Therefore, our proposed lindane electrochemical sensor has a satisfactory repeatability. We examined the current stability for α-MnO₂-NW modified electrode by recording amplitude of the pulse currents correspond to the addition of lindane (200 µM) (Fig. 6b). The amplitude of the 40 pulse currents display insignificant changes (<0.5%), indicating a good stability of the α-MnO₂-NW modified electrode. The storage stability was tested by storing the α-MnO₂-NW modified electrode for two weeks. The result showed that the reduction peak potential of lindane had no shift and the current response only showed 4.3% decrease compared with the original test.
To demonstrate the feasibility of sensor in practicable application, the proposed sensor was applied to the determination of lindane in tap water samples. No voltammetric response corresponding to lindane was observed in tap water, thus different quantity of lindane was added to the tap water samples. Spiking method was adopted to evaluate the lindane content of three samples. The standard addition methodology was used to determine the average recovery of lindane as well as to validate the proposed method. The results were summarized in Table S4, ESI†. As can be seen from Table S4, ESI†, the recoveries were from 98.5% to 102.0%. The recovery calculations indicated the potential practical application of our proposed sensor.

Conclusions

In summary, we demonstrate a novel electrocatalyst for the non-enzymatic reduction of lindane based on α-MnO₂ nanostructures. The sensors fabricated from the α-MnO₂-NW exhibited the highest performance among the studied materials with lower detection limit, high sensitivity, and wide linear range, making this novel sensing methodology an extremely promising one. We envision that this methodology reported here for the lindane reduction recommends a broad research in that direction.

Acknowledgements

This work was supported by MOE Tier 1 Grants (RGT13/13 and RG131/14) of Singapore and the Singapore National Research Foundation under its Campus for Research Excellence And Technological Enterprise (CREATE) programme. Authors thank the Facility for Analysis, Characterisation, Testing and Simulation (FACTS) in Nanyang Technological University for materials characterizations.

Notes and references
