Concomitant In Situ FTIR and Impedance Measurements To Address the 2-Methylcyclopentanone Vapor-Sensing Mechanism in MnO₂–Polymer Nanocomposites

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ABSTRACT: Polymer nanocomposite-based sensors were prepared using cellulose acetate (CA), carbon nanoparticles (CNPs), and manganese dioxide (MnO₂) nanorods to detect and to understand the sensing mechanism of 2-methylcyclopentanone vapor. A sensor with a mass ratio of 1:1.5:3 of MnO₂/CNPs/CA as well as MnO₂/CA and MnO₂/CNP composite and MnO₂ sensors were prepared. The sensor with the three sensing materials combined exhibited an enhancement of response for 2-methylcyclopentanone vapor, ascribed to a synergistic effect between MnO₂/CNPs/CA. An in situ Fourier-transform infrared (FTIR)-combined online LCR meter setup was used to understand the sensing mechanism of the sensor. The sensing mechanism involved a deep oxidation decomposition of the analyte to CO₂. This was confirmed from the in situ FTIR-combined online LCR meter results, where a new distinct CO₂ bending mode IR band was recorded. To optimize the performance of the sensor, the composites were prepared by varying the amount of metal oxide added into the composites; sensor A (composition of mass ratio 1:1.5:3), sensor B (composition of mass ratio 2:1.5:3), and sensor C (composition of mass ratio 2.5:1.5:3); their compositions are MnO₂/CNPs/CA. The performance of sensor B was higher than that of the other two sensors. The sensors also show relatively good response—recovery time. All fabricated sensors were found to have the sensing ability regenerated after the analyte was removed from the system without losing its sensing and recovery abilities. The structural and morphological features of the samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy.

1. INTRODUCTION

Volatile organic compounds (VOCs) are organic chemicals that are released from environmental pollutions or living organisms at high vapor pressure.¹ There are toxic gases (like H₂S, NO₂, CO, SO₂, NH₃, and O₃), flammable gases (H₂, CH₄, and so forth), and VOCs such as ethanol, acetone, methanol, and explosive gases.² VOC detection is very crucial in various applications and needs to be detected at a very low concentration (ppm or ppb).³ Some of these gases can cause lasting health defects. 2-Methylcyclopentanone is one of the VOCs identified in freesia flower essential oil.⁴ It is a cyclic ketone that appears as clear, colorless liquid with a boiling point of about 139 °C.⁵ Diebold⁶ reported that 2-methylcyclopentanone is stable under normal temperature and pressure but it can cause chemical pneumonitis in the lung if ingested, and inhalation of the vapor might lead to drowsiness/dizziness. Therefore, the fabrication of sensitive and user-friendly gas sensors is very important to monitor 2-methylcyclopentanone concentrations in the cosmetic industry as well as in environmental applications to protect the human health.

The increasing demand for the detection of different vapors and disease-related VOCs has lead researchers to fabricate a quick, low-cost, and sensitive gas sensor at room temperature.⁷,⁸ However, understanding the sensing mechanism of the sensor is very important in improving the performance and development of specific sensors. Gas sensors developed for room-temperature sensing have advantages over elevated temperature sensors such as low power consumption and low ignition risks when detecting flammable or explosive analytes.⁹ A typical gas sensor contains sensing materials which can respond to test analytes and a transducer that converts this
change into electrical signals.\textsuperscript{23} The nanostructured material-based gas sensors are well known to exhibit good sensing performances.\textsuperscript{7} Nanostructured metal oxide semiconductors such as MnO\textsubscript{2}, SnO\textsubscript{2}, ZnO,\textsuperscript{10} α-FeO\textsubscript{x},\textsuperscript{11} and In\textsubscript{2}O\textsubscript{3}\textsuperscript{12} have been widely studied for sensing various types of gases because of their large surface to volume ratio, stability, high sensitivity, low-cost, and small size.\textsuperscript{13}

MnO\textsubscript{2} exists in different polymorphic crystallographic forms regarded as \(α\), \(β\), \(γ\), \(δ\), and \(λ\).\textsuperscript{14,15} Zhang et al., and Subramanian et al.\textsuperscript{16,17} reported that MnO\textsubscript{2} has excellent chemical and physical characteristics at room temperature and is recommended as one of the most stable manganese oxides. Several methods have been devised to improve the electrical conductivity of MnO\textsubscript{2}, such as doping with conductive materials like carbons [carbon nanoparticles (CNPs), graphene, carbon nanotubes, and so forth.] or polymers. However, because of the high surface area and electric conductivity, CNPs are used extensively with MnO\textsubscript{2} for making composites.\textsuperscript{18} CNPs are recognized as an important class of carbon because of their important qualities such as low toxicity, optical and fluorescence intensity, stability, biocompatibility, and simple synthesis.\textsuperscript{19} They possess an sp\textsuperscript{2}-conjugated core with multiple oxygen-containing species enriched with carboxyl and hydroxyl including aldehyde.\textsuperscript{20} Different methods are adopted in synthesizing CNPs such as laser ablation, electrochemical exfoliation, acidic oxidation, incomplete combustion oxidation, hydrothermal pyrolysis, and so forth.\textsuperscript{21} Cellulose acetate (CA) is an insulating biopolymer that was used instead of conducting polymers in this study. This is because of its significant properties like low-cost, availability, good film-forming capability, nontoxicity, biocompatibility, and biodegradability, but the major drawback is its high melting point and poor mechanical properties.\textsuperscript{22,23}

The 2-methylcyclopentanone sensors reported in this study show a simple impedance response and sensors were fabricated and tested at room temperature using nanocomposites. Moreover, the in situ Fourier-transform infrared (FTIR)-combined with online LCR meter used to confirm that indeed the sensing mechanism of the fabricated sensors is due to the deep oxidation of the VOCs into CO\textsubscript{2} and also the electrical response is due to the deep oxidation of the analyte. To the best of our knowledge, this is the first report of detection of 2-methylcyclopentanone vapors using nanocomposites and understanding the sensing mechanism using the in situ FTIR-online LCR meter.

2. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of all the synthesized products and the corresponding diffractograms are shown in Figure 1. The main peaks corresponding to \(2θ = 12.7°, 18.1°, 25.7°, 28.8°, 37.4°, 41.9°, 49.8°, 56.3°, 60.2°,\) and 65.0°, correspond to crystal planes of the MnO\textsubscript{2} nanorods (NRs) \((110), (200), (220), (310), (211), (301), (141), (600), (251),\) and \((002)\)\textsuperscript{14} (reference code: 01-081-1947c and cross-reference ICSD: 073363). The characteristic diffraction peaks of CA appeared near \(2θ = 8°, 17°,\) and \(21.6°\).\textsuperscript{24} The two broad peaks \((002)\) and \((101)\) observed in CNPs can be attributed to the presence of amorphous carbon and graphitic structures present in CNPs.\textsuperscript{25} (ICDD: 04-018-7559, LPF: 1933772). All CNPs and MnO\textsubscript{2} peaks correspond to hexagonal and tetragonal crystal systems. No diffraction peaks of CNPs and CA were seen in the nanocomposite peaks, the reason could be that the intense peaks from MnO\textsubscript{2} NRs, shifted or suppressed

\begin{equation}
Dp = \frac{K\lambda}{\beta \cos \theta}
\end{equation}

where Dp is the average crystal size, \(λ\) is the X-ray wavelength \((\lambda = 0.1540 \text{ nm})\) for Cu K\textsubscript{α}, \(K = 0.89\), \(θ\) is the Bragg’s angle \((12.6°)\), and \(β\) is the full width at half-maximum using \((110)\). The average crystalline size of MnO\textsubscript{2} NRs in the composite was estimated to be 15.7 nm.

Figure 2 presents the Raman spectra obtained to examine the structural characteristics of the prepared samples. The structural and graphitic nature in CNPs is shown in Figure 2a. The Raman spectrum depicts a very strong D mode at 1356 cm\textsuperscript{-1} and the G band located at 1583 cm\textsuperscript{-1}. These peaks can be correlated to the presence of defects and cluster of graphitic nature in carbon in CNPs. The ratio of D and G (\(I_D/I_G\)) band was estimated to be 0.85. The spectrum for the CA is shown in Figure 2b. The characteristic Raman peaks for CA were observed at 2940 and 1139 cm\textsuperscript{-1} which corresponded with C–H and C–O stretch glycosidic linkage, respectively. The characteristic peaks observed at 1737, 1439, and 1377 cm\textsuperscript{-1} can be associated with C=C=O, C=C= and −C=H bond respectively. The strong absorption peaks at 658, 915, 1083 and 1257 cm\textsuperscript{-1} can be attributed to C–Cl, =C–H, =C–H and C–O respectively.\textsuperscript{26} The Raman spectrum for MnO\textsubscript{2} NRs was depicted in Figure 2c. The broad peak located at 643 cm\textsuperscript{-1} is associated with the MnO\textsubscript{2} octahedral in α-MnO\textsubscript{2} NRs while the peaks at 354 and 175 cm\textsuperscript{-1} correspond with the metal–oxygen chain distortion mode of Mn−O–Mn in the octahedral MnO\textsubscript{2} lattice.\textsuperscript{27} The Raman spectrum for the nanocomposite as shown in Figure 2d showed few peaks. This could be due to shift or overlap in the composite.

Figure 3 shows the surface morphologies for CA, CNPs, MnO\textsubscript{2} NRs, and MnO\textsubscript{2}/CNPs/CA nanocomposites that was examined using scanning electron microscopy (SEM). The image of CA is shown in Figure 3a. It was observed that CA has fibre-like structures that are densely packed with the relatively rough surface. As shown in Figure 3b, the MnO\textsubscript{2} morphology appears like NRs with a diameter between 1 and 2.5 μm. The SEM image in Figure 3c revealed the degree of the corrugation of CNPs. It was observed that the CNPs were aggregated and interconnected to each other. The morphology of the MnO\textsubscript{2}/CNPs/CA composite is depicted in Figure 3d, showing the CNPs and MnO\textsubscript{2} wrapped in CA bulk. Comparing the two images, the morphology of CNPs changed tremendously after the formation of the composite.
The morphologies of the as-prepared samples and the nanocomposite were confirmed by transmission electron microscopy (TEM) as shown in Figure 4. As observed in Figure 4a, when viewed at a higher magnification, CA appeared like an adhesive sheetlike structure. From the image, it seems that CA has a binding capacity. As observed in Figure 4b, the CNPs were aggregated in structure and appeared like spherical chain-linked nanoparticles. The diameter of the CNPs was between 30 and 55 nm. As confirmed by TEM presented in Figure 4c, the morphologies of the MnO2 NRs consist of long rod nanostructures with diameters ranging between 21 and 58 nm. The energy-dispersive spectroscopy (EDS) analysis in Figure 4d showed that the as-synthesized MnO2 NRs are composed of Mn, O, and K elements. Peaks of Cu and C are from the copper grid on which the sample was deposited while Fe is one of the components that cannot be avoided when using TEM.

Figure 2. Raman spectra for (a) CNPs, (b) CA, (c) MnO2 NRs, and (d) MnO2/CNPs/CA composite.

Figure 3. SEM micrographs of (a) CA, (b) CNPs (c) MnO2 NRs, and (d) MnO2/CNPs/CA nanocomposites.
4e, the planar spacings of 0.31 and 0.48 nm correspond to (301) and (200), respectively. The TEM image of the nanocomposite in Figure 4f revealed that CA formed an adhesive layer that binds MnO₂ NRs and CNPs to avoid aggregation. We also observed that MnO₂, CNPs, and CA are well dispersed in the composite, which was very crucial to improve electrical conductivity.

2.1. Application of the Synthesized Materials in the Detection of 2-Methylcyclopentanone. The active materials for fabricated sensors were a metal oxide, CNPs, and a biopolymer, in this case, CA, and variable mass ratios were mixed in 10 mL of dimethylformamide. Although, we tried another biopolymer such as chitosan, the noise to signal ratio was very high. The mixture (10 μL) was drop-cast on the gold-plated interdigitated electrode. After the cast, the active material was left to dry at room temperature and then subjected to vacuum to completely remove the organic solvent from the active materials. It can be seen from the image (see Figure 5) that the film of the sensing material almost homogeneously covers the electrode. Three sets of sensors were prepared, each sensor prepared in duplicate, by varying the mass ratio of MnO₂ in the polymer composites to study the effect of metal oxide in the detection of organic analytes, in terms of response, sensitivity, and recovery time. During the study, we used a minimum of 22.0 ppm and maximum of 112.5 ppm of the analyte vapor at a time. All the sensor performances were conducted at room temperature, atmospheric pressure, and 42% relative humidity.

2.2. Sensor Performance. In addition to the sensor containing the three sensing materials, MnO₂/CNPs/CA with mass ratio 2.5:1.5:3, we prepared two sensors by mixing each of the two sensing materials: sensor D (MnO₂/CNPs, mass ratio of 1:1.5), sensor E (MnO₂/CA, mass ratio of 1:3), and sensor F (MnO₂ NRs only). Because the three sensors were fabricated by mixing MnO₂, CNPs, and CA at different ratios, it is important to identify which combination of the components was responsible for the sensing of the analyte. Interestingly, the relative impedance response of sensor D and E was very low as compared to sensor C (see Figures 6 and 7).

For sensor F, the relative response showed a slight decrease as the analyte concentration increases. The response for the sensor C is very high and increases as the concentration of the analyte vapor increases with a linear relationship. The sensors never reached a plateau or saturation value. This might be because of the analyte that has a high boiling point and low vapor pressure (5.8 mm/Hg @ 25.00 °C).

A comparison (see Figure 7) reveals that the sensor based on the three sensing materials (MnO₂/CNPs/CA) is 2.5 times more responsive than the sensor based on MnO₂ only, 15 times more responsive than the sensor based on only MnO₂/CNPs, and over 200 times more responsive than the sensor based on MnO₂/CA. This indicates that incorporating the three sensing materials in a sensor leads to an enhancement of response for 2-methylcyclopentanone vapor sensing, which
oxide as a consequence of the charge capture. Interestingly, because the synthesized MnO₂ is an semiconductor metal oxide would facilitate more reactions on the surface of the sensing materials. The amount of the adsorbed oxygen molecules adsorb on the bare surface of n-type semiconductor metal oxides, it captures charge carriers to form chemisorbed oxygen species (O₂⁻, O₂⁻⁻, and O³⁻⁻). A depletion region is created on the surface of the semiconductor metal oxide as a consequence of the charge capture. Interestingly, when the analyte vapor molecules interact with surface oxygen species, it results in induced sorption from the surface, which facilitates injection of captured electrons back to n-type semiconductor metal oxides and the resistance of the n-type of semiconductors decreases. The amount of the adsorbed oxygen species also determines the response characteristics; a large amount of oxygen adsorbed on the surface of the semiconductor metal oxide would facilitate more reactions on the surface. Interestingly, because the synthesized MnO₂ is an n-type semiconductor metal oxide, after being incorporated with CNPs and CA the interaction with a reducing vapor (2-methylcyclopentanone), one would expect the resistance (and impedance) to decrease during sensing. However, we observed impedance as increase in all cases. This indicates that the composite containing the three active materials behaves like showing p-type conductivity.

Generally, the behavior of the p-type conductivity is first due to the coverage of the surface of the sensing materials with oxygen chemisorbed from the atmosphere. The oxygen molecules that adsorb on the sensing materials capture electrons and ionize into oxygen species (O⁻), resulting in the formation of a hole-accumulation layer. When the sensing materials are exposed to a reducing gas (such as 2-methylcyclopentanone gas), the analyte gas reacts with the surface oxygen species, as a consequence of the electron transfer from the reacting analyte vapor to the sensing materials. The electrons that are injected into the sensing materials recombine with the holes; this leads to a reduction of the concentration of the charge carriers and increasing resistance of the sensing materials.

It is common to observe that n-type sensing materials behave like p-type ones and vice versa during sensing. Such changes can be promoted either because of changes in temperature or in concentration. Hao et al. reported that n-type sensing materials changed to p-type at high temperatures. The reason is that at low temperatures, the adsorbed oxygen species are O₂⁻⁻ species. However, at high temperatures, O⁻ and O₂⁻⁻ species coexist and these oxygen species can capture more electrons than those at low temperatures. Similarly, Xue et al. observed temperature-dependent sensing behavior for Pt@SnO₂ NR sensing materials. At low temperatures, they observed an abnormal p-type conductivity. However, the expected n-type conductivity was observed at a high temperature of 300 °C; however, this unusual p-type behavior was explained because of Pt-catalyzed morphological changes of ion-sorbed oxygen. As such, an abnormal observation was not only due to the temperature change but also due to change in concentration of the analyte vapor. A study by Siciliano et al. indicated that depending on the concentration of the analyte, the sensing materials change from n-type at low concentrations to p-type conductivity at high concentrations.

Moreover, like the metal oxides, all types of oxygen species do exist on carbon nanomaterials surfaces, except 2O2⁻⁻. A study by Atamny et al. revealed that particularly on defect sites or at edges, below 873 K, carbonaceous materials convert O₂ molecules to electrophilic oxygen species, O⁻ (oxides), O₂⁻⁻ (superoxides), and O₂⁻⁻ (peroxides). These are electron-deficient species with a tendency to attack the electron-rich regions of hydrocarbon molecules and form degradation products. The existence of oxygen species (O⁻ or O₂⁻⁻) on the sensing materials leads to the formation of an inversion layer near the surface that contributes to the p-type sensing response. The sensing mechanism involves total oxidation to carbon dioxide and water. The proposed reactions of oxygen molecules with 2-methylcyclopentanone are described as follows (eqs 2–5).40

\[
\begin{align*}
O_2 \text{ (gas)} & \rightarrow O_2 \text{ (ads)} \\
O_2 \text{ (gas)} + e^- & \rightarrow O_2^- \text{ (ads)} \\
O_2^- \text{ (ads)} + e^- & \rightarrow 2O^- \text{ (ads)} \\
C_6H_{12}O\text{ (gas)} + 16O^- & \rightarrow 6CO_2 + 5H_2O + 16e^- 
\end{align*}
\]

2.3. In Situ FTIR-Combined Online LCR Meter Measurement. To confirm the sensing mechanism whether it involved deep oxidation, we set up an in situ FTIR-LCR meter while a freshly prepared sensor exposed to the analyte vapor (see the sensor setup in Figure 14). The FTIR spectra were taken every 2 min for 16 min and we did focus on specific IR bands that can give us an insight into the sensing mechanism: vibrational modes that are not saturated during the measurement and do not overlap other IR bands.

The in situ FTIR results indicate that a new distinct IR band was detected. The IR band at 668 cm⁻¹ is assigned to the CO₂ bending mode, the CO₂ bending mode intensity increases as the analyte molecules were exposed to the sensor (see Figure 8 inset) The CO₂ IR band is the result of deep oxidation of the 2-methylcyclopentanone on the surface of the sensing materials and then desorption of the carbon dioxide gas molecule from the surface of the sensors. At the same time, the electrical response of the sensor was recorded using an LCR meter. As the exposure time increased, the intensity of the CO₂ peaks increases with the electrical response. At time t
In situ FTIR spectra of sensor B at a variable time in a narrow range.

≈ 0 min, no intensity of the CO2 peaks was detected. The ΔZ, impedance variation, increased from the low value to the highest value in less than 1 min and become stable until the experiment was terminated (see Figure 9). The increase in ΔZ is clearly an indication and therefore, it confirms that the sensor sensing mechanism involves deep oxidation of the exposed analyte molecules, which release CO2 gas molecules.

2.4. MnO2 Concentration Effect on the Performance of the Sensors. To optimize the performance of the sensor, three sensors prepared by varying the amount of metal oxide added into the MnO2/CNPs/CA composites were exposed to 2-methyl-cyclopentanone vapor; sensor G (mass ratio 1:1.5:3), sensor H (mass ratio 2:1.5:3), and sensor I (mass ratio 2.5:1.5:3).

After the injection of the analyte, all the sensors, sensor G, sensor H, and sensor I, responded very well, increasing the relative impedance variation (ΔZ) response linearly as the analyte vapor concentration increases (Figure 10). All the three sensors retained their sensing ability after the analyte vapor was removed from the chamber. This trend was observed repeatedly.

The sensitivity of the fabricated sensors was determined by taking the derivative of the sensor response [dΔZ/(d[A])] with respect to the analyte concentration [A], that is, the linear coefficient of the fitted curve of each sensor. As shown in Table 1 and Figure 11, sensor G has very low sensitivity, about 3 mΩ ppm−1. Sensor H, however, showed relatively high sensitivity toward the 2-methylcyclopentanone vapor with 40 mΩ ppm−1 and sensor I displayed 20 mΩ ppm−1. The relative comparative sensitivity of sensor H is about 15 times more sensitive than sensor G and twice more sensitive than sensor I.

| MnO2/CNPs/CA | sensitivity (kΩ/ppm) | response time (min) | recovery time (min) |
|--------------|-----------------------|---------------------|---------------------|
| sensor G     | 0.00029               | 4.5                 | 2.1                 |
| sensor H     | 0.04                  | 4.3                 | 1.8                 |
| sensor I     | 0.02                  | 5                   | 4.2                 |

Real-time sensor response and recovery time for sensors I using 45 ppm of the analyte.

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the sensor responds in the presence of the analyte vapor and how fast it can recover back to the baseline (after exposure to the analyte is terminated). Therefore, response time was referred as the time for the sensor to achieve 90% of the maximum response (saturation) after the injection of the test gas and; the time for the sensor to recover 90% of the response after the test gas is removed is the recovery time (see Figure 11). Accordingly, generally, the response and recovery times of the three sensors were similar and there was no correlation between the amount of MnO₂ in the active material composition and either the response time or recovery time. The fastest response time of 4.3 min and the recovery time of 1.8 min were recorded for sensor H (see Table 1), which is also the sensor with higher sensitivity. Consequently, this sensor is also suitable for application in sensor arrays used to overcome the absence of sensor specificity to analytes when discrimination of 2-methylcyclopentanone is aimed.

The stability of the sensor was determined on a newly prepared sensor I toward 45 ppm of the analyte vapor concentration. As shown in Figure 12, the stability test was conducted over five cycles; after five cycles, the sensor maintained the original sensing ability without losing sensitivity.

3. CONCLUSIONS

Sensors based on binary or ternary composites of MnO₂ CNPs and CA responded very well when exposed to a variation in the concentration of 2-methylcyclopentanone vapor in a closed chamber. The use of all the three sensing materials in the active sensor material composite leads to an enhancement of response for 2-methylcyclopentanone vapor, which should be ascribed to a synergistic effect among MnO₂ CNPs, and CA. This was confirmed by preparing three sensors as a control, and by combining each of the two components [MnO₂/CNPs (sensor D), and MnO₂/CA (sensor E)]. The impedance response of sensor D and sensor E was very low as compared to the sensor C. The in situ FTIR-combined online LCR meter confirmed that the sensing mechanism involved a deep oxidation decomposition of the analyte molecules to CO₂ and H₂O. In terms of the sensitivity and response and recovery time, sensor B displayed higher sensitivity and faster response and recovery. All fabricated sensors regenerated the sensing ability after the analyte was removed from the system without losing sensitivity.

4. MATERIALS AND METHODS

4.1. Chemical. In this study, all the chemicals were used as purchased from Sigma-Aldrich (South Africa). Candlesticks (Lighthouse Candles) used to obtain CNPs were purchased from the local shop in Johannesburg, South Africa.

4.2. Collection of CNPs. The CNPs, also known as carbon quantum dots, were synthesized for this study by following a very simple method. The CNPs were collected by combustion of candlesticks with a crucible placed on top of the candle to trap the CNPs formed on the surface during several hours. After enough material has been collected for the experiments, a clean spatula was used to scrape CNPs out from the crucible, purified in ethanol using a centrifuge, and after drying at 60 °C, the sample was stored in a vial.

4.3. Synthesis of MnO₂ NRs. The synthesis of MnO₂ NRs was performed via the reactive-template method as reported by Zhang et al. with minor modification. In a typical synthesis, 0.6 g of KMnO₄ and 0.25 g of MnSO₄·H₂O were dissolved in 40 mL of deionized water. The solution was sonicated for 20 min and stirred for 5 min to form a homogeneous solution. The mixture was then transferred into a 100 mL Teflon-lined stainless steel autoclave. Hydrothermal treatment was carried out at 160 °C for 12 h. After reacting, the autoclave was naturally cooled down to room temperature. Dark brownish precipitates were collected by centrifugation and washed with deionized water and ethanol several times to remove impurities. Finally, the solid product was dried at 65 °C for 24 h.

4.4. Methodology. Three composites were prepared by weighing 10, 20, and 25 mg of MnO₂ NR powder in three different solutions containing CNPs (15 mg) and CA (30 mg) dissolved in 10 mL of dimethylformamide to obtain composites of MnO₂/CNPs/CA. Another three composites with MnO₂/CNPs, MnO₂/CA, and MnO₂ NRs were also prepared to use as controls. All the six prepared nanocomposites were sonicated for 15 min and then stirred continuously for 48 h to obtain uniform solutions. Then, approximately 10 μL of each composite was deposited onto six different gold-plated interdigitated electrodes composed of 0.1 mm width and 0.1 mm gap between metal lines of 18 pairs of 7.9 mm length. The three sensors containing 10, 20, and 25 mg of MnO₂ NRs were labeled sensor A, B, and C, while the control sensors containing MnO₂/CNPs, MnO₂/CA, and MnO₂ were labeled sensor D, E, and F, respectively. The sensors were left to dry at room temperature and kept under moderate vacuum for few days prior to use.

4.5. Electrical Characterization of the Sensor. The gas-sensing system setup was constructed by connecting an ISO-TECH LCR meter (LCR 831, 20 Hz–200 kHz) to the computer system (see Figure 13). The LCR meter, computer, and diaphragm vacuum pump were connected to the power supply. The sensors were placed into the sealed 20 L round bottle to interact with the vapor. The sensors work as transducers by converting chemical interaction with the sensor active material into an electrical signal which was measured by the LCR meter. When the exposure time of the sensor, which was for 15 min, elapsed the analyte vapor was removed by vacuuming using a diaphragm pump for 5 min at atmospheric pressure. The sensor was then left to recover for 3 min. This
process was repeated by injecting 22.5, 45, 67.5, 90, and 112 ppm of the analyte vapor. The concentration of 2-methylcyclopentanone was calculated in ppm using the following equation.47

$$C = \frac{22.4 \times TV}{273MV} \times 1000$$  \hspace{1cm} (6)

where \(C\) is the vapor concentration required, \(\rho\) is the density of the liquid (\(\text{g mL}^{-1}\)), \(T\) is the temperature (K), \(V\) is the volume of the liquid analyte (\(\mu\text{L}\)), \(M\) is the molecular weight of the liquid analyte (\(\text{g mol}^{-1}\)), and \(V\) is the volume of the test chamber (L). All experiments were carried out at room temperature. The obtained data were measured and recorded using alternating current (ac) voltage with an amplitude of 0.5 V and a suitable frequency of 25 kHz.48 The impedance responses of the modified nanocomposite-based sensors were investigated using a sweep rate of 7.4 points per second. ac was used to avoid a continuous drift of electrically active impurities of the active sensor layer and potential electrode deterioration. The impedance variation was used as sensor response because we applied a constant frequency of 25 kHz (in which the noise is negligible) and impedance is then the simplest quantity to be measured because it is the quotient between applied potential and measured current. The use of the impedance avoids the need for an LCR meter or impedance analyzer to determine the resistance and capacitance separately, simplifying the use of sensors in field applications because impedance can be determined using simple circuits.49,50 If necessary, it can be determined with help of a simple portable multimeter in case of practical measurements outside of the laboratory.

4.6. In Situ FTIR-Online LCR Meter Setup and Testing. IR spectra were recorded using the FTIR instrument (PerkinElmer Spectrum 100) with a resolution of 4 cm\(^{-1}\), taking an average of 16 successively collected scans. A cylindrical gas cell (approx. 110 mL volume) fitted with two KBr windows at both ends. The cell was placed at the center in such a way that the IR beam passes through the windows. The inserted sensor is positioned to the upper wall of the cell. The sensor was connected to the LCR meter through two electrically insulated wires (see Figure 14). During the measurement, the sensor was exposed to approximately 110 ppm 2-methylcyclopentanone vapor and the cell was kept in a closed system so that no leaks are experienced until the measurement is completed. Both the FTIR instrument and LCR meter were started concomitantly. FTIR spectra were taken every 2 min, while the impedance measurements were taken continuously for each sensor to a total maximum time of 16 min.

5. CHARACTERIZATION TECHNIQUES

The crystalline phases of all the prepared samples were characterized by using XRD (PANalytical X'pert, Netherlands) with Cu K\(\alpha\) radiation operated at a current of 40 mA and a voltage of 40 kV in 2\(\theta\) range 10°–90°. Raman analyses were carried out on using an alpha 300R (WITec) confocal laser Raman microscope configured with a frequency-doubled Nd:YAG laser (wavelength 532 nm). The Brunauer–Emmett–Teller surface area was measured by nitrogen adsorption–desorption isotherms in Micromeritics ASAP 2020. The samples were degassed for 12 h at 100 °C before analysis. The morphologies of the samples were investigated using TEM (JOEL-2010, 200 kV, HRTEM 200 V) with the samples deposited on coated copper grids and SEM (TESCAN Vega TC using VEGA 3 TESCAN XMU).

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Notes
The authors declare no competing financial interest.

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