α-MnO₂ Nanowires as Potential Scaffolds for a High-Performance Formaldehyde Gas Sensor Device

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Abstract: Herein, we report a chemi-resistive sensing method for the detection of formaldehyde (HCHO) gas. For this, α-MnO₂ nanowires were synthesized hydrothermally and examined for ascertaining their chemical composition, crystal phase, morphology, purity, and vibrational properties. The XRD pattern confirmed the high crystallinity and purity of the α-MnO₂ nanowires. FESEM images confirmed a random orientation and smooth-surfaced wire-shaped morphologies for as-synthesized α-MnO₂ nanowires. Further, the synthesized nanowires with rounded tips had a uniform diameter throughout the length of the nanowires. The average diameter of the α-MnO₂ nanowires was found to be 62.18 nm and the average length was ~2.0 μm. Further, at an optimized temperature of 300 °C, the fabricated HCHO sensor based on α-MnO₂ nanowires demonstrated gas response, response, and recovery times of 19.37, 18, and 30 s, respectively.

Keywords: α-MnO₂; nanowires; formaldehyde; gas sensor; high-performance

1. Introduction

Formaldehyde (HCHO) is classified as one of the dangerous gases and is supposed to generate indoor and outdoor pollution. Formaldehyde is widely used in the chemical and textile industries, including the manufacturing of adhesives and the processing of wood products, paper, synthetic polymers, and more. It is also used as a preservative in various biological and industrial applications, long-term exposure to formaldehyde can cause cancer, asthma, leukemia, and other diseases. It has been reported that formaldehyde can cause nasal and throat irritation in a very low concentration level of 0.08 ppm [1]. The International Agency for Research on Cancer (IARC) has identified it as a first class carcinogenic substance [2,3].

The past few decades have witnessed a great exploration of gas sensors based on metal oxide semiconductors. Such semiconducting metal-oxides-based gas sensors have generated extensive research interest due to their remarkable features, such as high gas response at low working temperature, high selectivity, ease of operation, portability, bio-compatibility, and low fabrication costs [4]. Additionally, new physical and chemical
properties appear when the semiconducting metal oxides are reduced to nanometer scales. Extensive studies have been carried out for the synthesis of nanostructured metal oxides with customizable structure, surface area, and surface defects [5,6]. The size, morphology, surface defect density, crystallinity, and bandgap energies of metal oxide nanostructures determine the movement of electrons and holes, electronic properties, and, hence, the gas sensing responses [7].

To date, many metal oxides have been explored as gas sensors for HCHO. Bouchikhi et al. [8] examined the gas-sensing parameters of pristine and metal nanoparticles decorated WO$_3$ nanowires under UV light irradiations. Choi et al. [9] found a very short response (1.4 s) and recovery time (2.9 s) for a 2D-layered MoS$_2$-based HCHO gas sensor. Enhanced HCHO sensing was observed for microsphere resonator coupled glass-coated ZnO nanorods [1]. Through an in situ reduction method, the prepared PdAu/SnO$_2$-nanosheets exhibited temperature-dependent dual selectivity for HCHO sensing with a low detection limit of 45 ppb [10]. NiO nanowires with cubic phase showed a shorter response time (17 s) and recovery time (19 s) toward 200 ppm HCHO gas [11]. Additionally, ZnO nano/microrods [12], Ag-loaded ZnO [13], TiO$_2$ nanotubes [14], tubular SnO$_2$ [15], MnO$_2$ nanoparticles [16], SnO$_2$ nanosheets [17,18], and many more have been reported as gas sensors for HCHO.

Due to the intermediate +4 oxidation state, the reduction potential of 1.23 V, and the capability to exhibit a redox reaction, MnO$_2$ has emerged as a promising chemi-resistive material for the fabrication of gas sensor devices [19]. MnO$_2$ has a high structural flexibility and exists in different crystallographic phases, i.e., α-MnO$_2$, β-MnO$_2$, γ-MnO$_2$, and δ-MnO$_2$ [20]. Several morphologies of MnO$_2$, such as nanoparticles [16], nanowires [21], nanowires [22], nanospheres [23], hollow micro-spheres [24], thin films [25], rectangular pyramid [26], nano-micro-flowers [27], nanoflakes [28], and many more, have been synthesized through different synthetic methods. Recently, Umar et al. explored the ethanol gas sensing applications of the α-MnO$_2$ nanoparticles synthesized hydrothermally [16]. Barreca et al. [29] reported synthesis of β-MnO$_2$ nano-systems through physical plasma enhanced chemical vapor deposition and analyzed the gas-sensing behavior toward acetonitrile and ethylene. High aspect ratio β-MnO$_2$ nanowires synthesized via a facile greener technique exhibited a sensitivity of 0.5 at 300 °C and a short response time of 10 s for 20 ppm H$_2$ gas.

A detailed literature survey revealed that α-MnO$_2$ nanowires have been rarely reported as HCHO gas sensor materials. Keeping this in mind, we hydrothermally synthesized α-MnO$_2$ nanowires and used them to fabricate an HCHO gas sensor. Prior to sensor fabrication, α-MnO$_2$ was characterized through different techniques. Finally, a gas sensing mechanism was also proposed for the α-MnO$_2$ nanowires-based gas sensor toward HCHO.

2. Materials and Methods

2.1. Synthesis of α-MnO$_2$ Nanowires

Entire chemicals were procured from Sigma-Aldrich (St. Louis, MO, USA) and utilized as received without being further purified. In a typical facile hydrothermal process, potassium permanganate (KMnO$_4$) and concentrated hydrochloric acid (HCl) were mixed well in 1:4 molar ratios in 50 mL deionized (DI) water. The resulting solution was then vigorously stirred (30 min) before being moved to a Teflon-lined stainless-steel autoclave and heated to 150 °C for 15 h. The autoclave was cooled to room temperature after the reaction was completed in the desired time. Black-colored precipitate was centrifuged and washed with DI water and dried in air. The dried powder was calcined at 450 °C for 5 h and finally characterized in terms of morphological, structural, compositional, and gas-sensing properties.

2.2. Characterizations of the Synthesized α-MnO$_2$ Nanowires

As-synthesized α-MnO$_2$ nanowires were analyzed through X-ray diffraction for determining the polymorphic form and crystal size (XRD; PANanalytical XpertPro., Malvern, UK, Cu-Kα; λ = 1.542 Å). Field emission scanning electron microscopy (FESEM; JEOL-JSM-
7600F, Hitachi, Tokyo, Japan) combined with energy dispersive spectroscopy (EDS) analysis was conducted to elaborate the morphology and compositional analysis. The electron mapping technique associated with FESEM was analyzed for evaluating the homogeneity of the constituent elements. Transmission electron microscopy and high-resolution TEM (HRTEM; JEOL JEM JSM 2010; Hitachi, Tokyo, Japan) techniques were used to investigate the structural features and the lattice interplanar angles of the synthesized nanostructures. Vibrational and scattering properties were examined using Fourier transform infrared (FTIR; Perkin Elmer-FTIR Spectrum-100, Waltham, MA, USA) spectroscopy and Raman spectroscopy (Perkin Elmer-Raman Station-400 series, Waltham, MA, USA), respectively.

2.3. Fabrication of Formaldehyde Gas Sensor Based on α-MnO$_2$ Nanowires

To fabricate the working electrode, a thin α-MnO$_2$ nanowire paste was prepared in ethylene glycol and pasted on alumina substrate (Active surface area = 1 cm$^2$) with Platinum printer digital patterns. It was finally annealed in air at 300 $^\circ$C for 2 h. The complete sensor set up consisted of an electrometer, mass-flow controllers, a gas cylinder, and a data acquisition system with a PC interface. The gas responses at different operating conditions were calculated from the ratio of the resistances of the α-MnO$_2$ nanowires-based sensor in the presence of HCHO ($R_g$) and in air ($R_a$).

\[
\text{Gas Response} = \frac{R_g}{R_a}
\]  

3. Results and Discussion

3.1. Characterizations and Properties of Synthesized α-MnO$_2$ Nanowires

The XRD pattern of the synthesized MnO$_2$ nanowires exhibited characteristic peaks corresponding to the α-MnO$_2$ crystal phase. The diffraction peaks at $12.95^\circ$, $18.32^\circ$, $28.82^\circ$, $37.67^\circ$, $42.1^\circ$, $49.91^\circ$, $56.30^\circ$, $60.27^\circ$, $65.22^\circ$, $69.46^\circ$, and $71.34^\circ$ correspond to (110), (200), (310), (211), (301), (411), (600), (521), (200), (541), and (312) diffraction planes, respectively [30,31]. These patterns are in excellent agreement with those reported in the literature [16,32] and JCPDS-44-0141 (Figure 1). The high crystallinity and purity of the α-MnO$_2$ nanowires were also confirmed from the sharpness of the diffraction peaks and the absence of any diffraction peak corresponding to any impurity.

![Figure 1. XRD diffraction pattern of α-MnO$_2$ nanowires.](image_url)
In Figure 2a,b, FESEM images for the hydrothermally synthesized α-MnO$_2$ nanowires are shown. These images indicate a very high-density growth of the nanowires. The formation of α-MnO$_2$ nanowires of variable lengths and diameters can be confirmed from FESEM images. FESEM images further confirmed a random orientation and smooth-surfaces for the α-MnO$_2$ nanowires. The average diameter of the α-MnO$_2$ nanowires was found to be 62.18 nm, calculated using ImageJ software. A standard deviation of 15.99 was calculated. The corresponding statistical data are shown in Table S1. An average length of ~2.0 µm was observed.

The qualitative element composition and the distribution of the hydrothermally synthesized α-MnO$_2$ nanowires were analyzed through EDS spectrum and elemental mapping images, respectively (Figure S1). Selected area electronic FESEM image (Figure S1a) and EDS spectrum (Figure S2b) with inset representing the atomic and weight percentages of Mn and O in the sample indicate the presence of only Mn and O signals. The presence of only Mn and O elements in the EDS spectrum provides strong evidence for the successful formation of the MnO$_2$ as well as the excellent purity of the sample. EDS element mapping images for the MnO$_2$ nanowires are shown in Figure S1c,d, which indicate the homogeneous distribution of the constituent elements evenly throughout the matrix of the MnO$_2$ nanowires.

Figure 3a–c shows the characteristic panoramic TEM images for as-synthesized α-MnO$_2$ nanowires. As mentioned in FESEM images, the TEM images also confirm the formation of nanowire-shaped morphologies with smooth surfaces throughout the length of the nanowires. The diameters of the α-MnO$_2$ nanowires ranged from ~60 to 65 nm with lengths up to ~2.0 µm. The HRTEM image of part of an individual rod demonstrates that the nanowire has uniform lattice fringes as shown in Figure 3d. The lattice spacing of 0.69 nm was obtained, which corresponds to the (110) diffraction plane of α-MnO$_2$ (JCPDS No. 44-0141). Similar lattice spacing was observed by Wang et al. [33] for single-crystal α-MnO$_2$ nanowires synthesized hydrothermally from single KMnO$_4$ under acidic conditions.

The FTIR spectrum demonstrates a broad peak at 3430 cm$^{-1}$ and a short peak at 1633 cm$^{-1}$ (Figure 4a). These peaks correspond to the O–H stretching and bending vibrations, respectively, for physisorbed H$_2$O [34]. The weak FTIR peaks appearing at 611 and 517 cm$^{-1}$ are because of the stretching vibration of the metal-oxygen (Mn–O) bond, and they confirm the formation of MnO$_2$ [16,35]. Raman spectrum shows three prominent peaks at 308, 370, and 651 cm$^{-1}$ (Figure 4b). The strongest peak at 652 cm$^{-1}$ is because of the Mn–O symmetric stretching vibration bond of the MnO$_6$ octahedron [36]. The weaker Raman peaks at 308 and 370 cm$^{-1}$ are assigned to the lattice vibrations on the Mn–O bond and bending vibrations of Mn–O–Mn in MnO$_2$, respectively [37,38].
Figure 3. (a,b) Low resolution TEM images, (c) high resolution TEM image, and (d) HRTEM image for α-MnO₂ nanowires.

Figure 4. (a) FTIR spectrum and (b) Raman spectrum for α-MnO₂ nanowires.
3.2. Formaldehyde Gas Sensing Properties of Synthesized α-MnO₂ Nanowires

The response of the gas sensor depends on several temperature-related factors, including the oxygen adsorption, adsorption/desorption rate of gas molecules, and the carrier concentration [39]. Thus, the response of the α-MnO₂ nanowire-based gas sensor was analyzed for 200 ppm HCHO to find the suitable working temperature (Figure 5a). The gas response increased as the temperature was increased from 100 to 300 °C. As the temperature is increased, thermal activation results in the movement of more carriers in the form of electrons and holes onto the surface of MnO₂ nanowire, which increases the effective adsorption and oxidation of O₂ and analyte gas molecules [40,41]. At lower temperatures (<300 °C), the reactions between the adsorbed O₂ and HCHO gas molecules were sluggish due to insufficient activation energy [42]. At very high temperatures (>300 °C), the gas response was found to decrease, which was attributed to the enhanced rate of desorption of the adsorbed O₂ and HCHO gas molecules from the surface of the gas sensor according to previously reported results [43,44]. At the optimum temperature of 300 °C, a gas response of 19.37 s was observed. In addition to the aforementioned factors, the operating temperature for a gas sensor also depends upon multiple other significant factors, such as the grain size, porosity, and surface–volume ratio of the gas sensor material. The gas diffusion rate is still another factor affecting the operating temperature [45–47]. Factors related to gas sensing material can be controlled by the calcination conditions during synthesis. It has been reported that sensor materials with a smaller grain size show better gas sensing performances as compared to larger-grain-sized materials [48]. Small grain size favors the formation of large number of potential barriers at the grain boundaries, which results in significantly large resistance modulations. Thus, the grain size, porosity, and crystallinity of the α-MnO₂ nanowires can be controlled by either calcination temperature or calcination time. A thorough investigation is still required to optimize the grain size, porosity, and crystallinity for efficient adsorption of the analyte gases on the surface of the sensor materials; hence, by controlling the synthetic parameters, the working temperature can be optimized as well.

The gas response of the gas sensor showed a direct correlation with the HCHO concentration, which is indicated by the high value of the determinant coefficient ($R^2 = 0.99544$) for the linear fit plot obtained by plotting the gas response against the concentration of the HCHO (Figure 5b). The experimental results clearly show that the α-MnO₂ nanowire-based gas sensor produces HCHO concentration-dependent gas sensing results.

Long-term stability of the as-fabricated HCHO gas sensor was adjudged from the dynamic repeatable response-recovery curves for 200 ppm HCHO gas at an optimized 300 °C temperature. When exposed to HCHO gas, the sensor response increased rapidly and dropped to the baseline value immediately after the restriction of gas supply. This further demonstrates the repeatability of the fabricated gas sensor in the form of reversible response–recovery curves after each cycle (Figure 5c). The enhanced response–recovery curve for 200 ppm HCHO gas at an optimized temperature was examined for the estimation of the response and recovery times. Very short response ($\tau_{\text{res}}$) and recovery ($\tau_{\text{rec}}$) times of 18 s and 30 s, respectively, were observed (Inset Figure 5c). The cutting-edge status of the present work is evidenced in the very low response and recovery times of the fabricated α-MnO₂ nanowire-based gas sensor compared to other recently reported sensors for HCHO (Table 1).
3.3. Sensing Mechanism for the Fabricated Formaldehyde Gas Sensor

The gas sensing mechanism is based on variations in the chemo-resistive properties of α-MnO₂ nanowires. Initially, when the surface of the α-MnO₂ nanowires is exposed to air, O₂ molecules undergo adsorption followed by reduction to various ionized oxygenated species under working temperature conditions by capturing electrons from the conduction band of n-type MnO₂ semiconductor (Equations (2) and (3)). As a result, an outer electron depletion layer (EDL) is formed near the surface which has lower conductivity than the core region [16,59].

In the presence of HCHO, EDL thickness is further increased because of the reducing nature of HCHO [60]. Finally, HCHO molecules are oxidized to CO₂ and H₂O with the help of oxygenated ionizable species (Equations (4)–(6) (Figure 6)).

\[
\begin{align*}
\text{O}_2(\text{g}) + e^{-} & \rightarrow 2 \text{O}^{2-}(\text{g}) \quad \text{(2)} \\
\text{HCHO}(\text{g}) + 2 \text{O}^{2-}(\text{g}) & \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + 2 e^{-} \quad \text{(4)}
\end{align*}
\]

Table 1. Sensing parameters for various gas sensor materials toward HCHO.

| Sensor Material                      | Conc. (ppm) | Gas Response | Response Time (s) | Recovery Time (s) | T (°C) | Refs. |
|--------------------------------------|-------------|--------------|-------------------|-------------------|--------|-------|
| SnO₂ nanosheets                      | 10          | 20.5         | 36                | 238               | 200    | [17]  |
| Porous SnO₂                          | 10          | 50.0         | 50                | 350               | 200    | [55]  |
| Mesoporous InOCl                     | 50          | 45.0         | 18                | 47                | 200    | [56]  |
| Ag-In₂O₃ Nanowires                   | 85          | 152.0        | 135               | 160               | 300    | [57]  |
| Er-doped In₂O₃ nanotubes            | 20          | 12.0         | 5                 | 38                | 260    | [49]  |
| rGO/ZnSnO₂ microspheres             | 10          | 12.8         | 87                | 31                | 103    | [50]  |
| Fe-Doped ZnO/rGO Nanocomposite      | 5           | 12.7         | 34                | 37                | 120    | [51]  |
| NiO/ZnO Microflowers                | 200         | 26.2         | 18                | 30                | 100    | [58]  |
| SnO₂/In₂O₃ hetero-nanofibers         | 10          | 7.5          | 26                | 37                | 375    | [52]  |
| Ag-functionalized In₂O₃/ZnO         | 100         | 10.0         | 20                | 4                 | 300    | [53]  |
| CaFe₄O₉ nanocubes                    | 300         | 16.5         | 153               | 54                | 300    | [54]  |
| α-MnO₂ Nanowire                      | 200         | 19.37        | 18                | 30                | 300    | This work |

Figure 5. (a) Gas response vs. operating temperature for 200 ppm HCHO gas, (b) variations of gas response as a function of concentration of HCHO gas, (c) dynamic repeatable response–recovery curves for 200 ppm HCHO gas at optimized 300 °C temperature (Inset: response–recovery curve for the calculation of response and recovery times), and (d) sensor stability test for 7 days using α-MnO₂ nanowire-based gas sensor toward 200 ppm HCHO gas at 300 °C.
For potential and practical applications, the long-term stability of the gas sensors is critical. The fabricated α-MnO2 nanowire-based gas sensor showed consistent long-term gas response stability toward 200 ppm HCHO gas at 300 °C for seven consecutive days; an insignificant change in gas response was observed (Figure 5d). Gas-sensing parameters for gas sensors based on α-MnO2 nanowires were found to be superior to the previously reported literature (Table 1). Overall, the fabricated α-MnO2 nanowire-based gas sensor showed high HCHO gas sensor responses compared to some recently reported sensors [49–54]. Although the sensors [55–58] showed higher gas responses compared to our sensor, they have the limitations of very high response and recovery times.

3.3. Sensing Mechanism for the Fabricated Formaldehyde Gas Sensor

The gas sensing mechanism is based on variations in the chemo-resistive properties of α-MnO2 nanowires. Initially, when the surface of the α-MnO2 nanowires is exposed to air, O2 molecules undergo adsorption followed by reduction to various ionized oxygenated species under working temperature conditions by capturing electrons from the conduction band of n-type MnO2 semiconductor (Equations (2) and (3)). As a result, an outer electron depletion layer (EDL) is formed near the surface which has lower conductivity than the core region [16,59].

In the presence of HCHO, EDL thickness is further increased because of the reducing nature of HCHO [60]. Finally, HCHO molecules are oxidized to CO2 and H2O with the help of oxygenated ionizable species (Equations (4)–(6) (Figure 6)).

\[
\begin{align*}
\text{O}_2(\text{g}) + 4e^- &\rightarrow 2\text{O}^2-_\text{ads} \quad (2) \\
\text{O}_2(\text{g}) + 2e^- &\rightarrow \text{O}^2-_\text{ads} \quad (3) \\
\text{HCHO}_{\text{ads}} + 2\text{O}^-_{\text{ads}} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2e^- \quad (4) \\
\text{HCHO}_{\text{ads}} + 2\text{O}^2-_\text{ads} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} + 4e^- \quad (5) \\
\text{HCHO}_{\text{ads}} + 2\text{O}^2-_\text{ads} &\rightarrow \text{CO}_2 + \text{H}_2\text{O} + 4e^- \quad (6)
\end{align*}
\]

Figure 6. Proposed mechanism for HCHO sensing by α-MnO2 nanowire-based gas sensor.

4. Conclusions

α-MnO2 nanowires were synthesized using a single-step hydrothermal method and were explored as a dynamic chemi-resistive sensor material for the sensing of HCHO gas. Gas response behavior was analyzed as a function of temperature, concentration, and time. The as-fabricated sensor proved an excellent HCHO gas sensing activity with high gas responses, low recovery and response times, excellent repeatability, and a remarkable long-term stability of 7 days to 200 ppm HCHO gas at the low operating temperature of
300 °C. These properties of the fabricated gas sensor may thus make α-MnO2 nanowires suitable candidates for the fabrication of future gas sensors toward highly toxic gases.

**Supplementary Materials:** The following are available online at [https://www.mdpi.com/article/10.3390/coatings11070860/s1](https://www.mdpi.com/article/10.3390/coatings11070860/s1), Figure S1: (a) Selected area electronic FESEM image, (b) EDS spectrum (Inset: Atomic and weight percentages of Mn and O in sample) and (c,d) Elemental mapping images for Mn and O, respectively for α-MnO2 nanowires, Figure S2: Diameter size distribution for the α-MnO2 nanowires, Table S1: Descriptive Statistics Data for measuring diameter of the α-MnO2 nanowires.

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