Designing SnO$_2$ Nanostructure-Based Sensors with Tailored Selectivity toward Propanol and Ethanol Vapors

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1. INTRODUCTION

The intensification of environmental pollution due to industrialization, fuel burning, agriculture, and leakage of poisonous gases is a threat to human life. A timely discovery and the monitoring of toxic and harmful gases are essential for the environmental protection. Recently, gas sensors based on semiconductor metal oxides (SMOs) have become one of the most dominant research topics owing to their resistance to environmental pollution due to industrialization, fuel burning, agriculture, and leakage of poisonous gases. The sensors comprising SnO$_2$ hollow spheres, nanoparticles, nanorods, and fishbones with tunable morphologies were synthesized with a simple hydrothermal one-pot method. The SnO$_2$ hollow spheres demonstrated the highest sensing response (resistance ratio of 20) toward C$_3$H$_7$OH at low operating temperatures (75 °C) compared to other tested interference vapors and gases, such as C$_2$H$_5$OH, C$_2$H$_6$OH, CO, NH$_3$, CH$_4$, and NO$_2$. This improved response can be associated with the higher surface area and intrinsic point defects. At a higher operating temperature of 150 °C, a response of 28 was witnessed for SnO$_2$ nanorods. A response of 59 was observed for SnO$_2$ nanoparticle-based sensor toward C$_3$H$_7$OH at 150 °C. This variation in the optimal temperature with respect to variations in the sensor morphology implies that the vapor selectivity and sensitivity are morphology-dependent. The relation between the intrinsic sensing performance and vapor selectivity originated from the nonstoichiometry of SnO$_2$, which resulted in excess oxygen vacancies (V$_{O}$) and higher surface areas. This characteristic played a vital role in the enhancement of the target gas absorptivity and the charge transfer capability of SnO$_2$ hollow sphere-based sensor.

ABSTRACT: The application of metal oxide-based sensors for the detection of volatile organic compounds is restricted because of their high operating temperatures and poor gas sensing selectivity. Driven by this fact, we report the low operating temperature and high performance of C$_3$H$_7$OH and C$_3$H$_6$OH sensors. The sensors comprising SnO$_2$, hollow spheres, nanoparticles, nanorods, and fishbones with tunable morphologies were synthesized with a simple hydrothermal one-pot method. The SnO$_2$ hollow spheres demonstrated the highest sensing response (resistance ratio of 20) toward C$_3$H$_7$OH at low operating temperatures (75 °C) compared to other tested interference vapors and gases, such as C$_2$H$_5$OH, C$_2$H$_6$OH, CO, NH$_3$, CH$_4$, and NO$_2$. This improved response can be associated with the higher surface area and intrinsic point defects. At a higher operating temperature of 150 °C, a response of 28 was witnessed for SnO$_2$ nanorods. A response of 59 was observed for SnO$_2$ nanoparticle-based sensor toward C$_3$H$_7$OH at 150 °C. This variation in the optimal temperature with respect to variations in the sensor morphology implies that the vapor selectivity and sensitivity are morphology-dependent. The relation between the intrinsic sensing performance and vapor selectivity originated from the nonstoichiometry of SnO$_2$, which resulted in excess oxygen vacancies (V$_{O}$) and higher surface areas. This characteristic played a vital role in the enhancement of the target gas absorptivity and the charge transfer capability of SnO$_2$ hollow sphere-based sensor.

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core–shell hollow spheres by galvanic replacement, the gas selectivity could be tuned by varying the amount of SnO2 shells (14.6, 24.3, and 43.3 at. %) and operating temperatures. According to Motaung et al.,21 Co3O4 sensors retain a capability to selectively distinguish ethanol vapor at 275 °C. By increasing the amount of SnO2 shells to 14.6 and 24.3 at. %, very selective detection of xylene and methylbenzenes (xylene + toluene) was realized at 275 and 300 °C, respectively. Previous reports21−23 have indicated that VO has a crucial impact on the gas sensing properties. By enhancing the relative concentration of VO (i.e., providing more active sites), superior sensing performances can be achieved. The VO surface defects can considerably improve the absorptivity for the target gas and the charge transfer capability of SnO2.22

Despite the amount of work existing on the SnO2 hollowsphere gas sensing, however, to the best of our knowledge, no reports exist on the C2H5OH sensing properties of SnO2 hollow spheres at low operating temperatures (75 °C). Few or no studies exist, showing a clear correlation between the vapor gas sensing and point defects extracted using electron spin resonance. Accordingly, we report for the first time the unique C2H5OH sensing characteristics of SnO2 hollow sphere nanostructures prepared via a hydrothermal method. Moreover, the C2H5OH gas sensing properties were investigated for a SnO2 nanoparticle-based sensor. In a controlled manner, nanostructures with different morphologies such as hollow spheres, nanoparticles with two different sizes, nanoplatelets, nanorods, and fishbones were prepared. More importantly, this study explains how to determine the organic vapor sensing characteristics of these nanostructures in detail. Further, the relation between the defect type, SnO2 structure, and vapor selectivity was studied. The intrinsic sensing performance of the SnO2 hollow spheres was investigated via X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR). The EPR, XPS, and photoluminescence (PL) analyses reveal that VO is the dominant structure defects. Extraordinarily, the intensity of the paramagnetic signal related to VO is enhanced for the hollow spheres, which is in good agreement with the sensing response.

2. RESULTS AND DISCUSSION

2.1. SnO2 Nanostructure Characterization. Scanning electron microscopy (SEM) was used to determine the morphology and structure of the as-prepared SnO2 nanostructures. Figure 1 shows the SEM images of the SnO2 nanostructures prepared with sodium hydroxide (NaOH) and hexamethylenetetramine (HMT). At lower temperatures (Figure 1a), the nucleation stage occurred, Sn (OH)6 2− nuclei were created, and the greatest number of nuclei were formed in the solution in which the nuclei attracted species and other surrounding nuclei to form bigger spheres (hollow spheres). Between 24 and 48 h at 200 °C, the hollow spheres decomposed to small nanoparticles (Figure 1b), which later agglomerated to form bigger clusters of nanoparticles (Figure 1c).

Because of the size of the nanoparticles, we, therefore, labeled them as less agglomerated (LA) nanoparticles and more agglomerated (MA) nanoparticles. The addition of HMT as a surfactant at 200 °C for 12 h resulted in self-assembled nanoparticles, that is, the formation of flower-like SnO2 nanorod bundles (Figure 1d) disclosing a square-shaped structure. The width of the nanorods is approximately 120 nm. When the time was increased from 12 to 24 h at 200 °C, the formation of fishbone structures was observed (Figure 1e), which resulted from the growth of the flower-like nanorod bundles.

To validate the SEM results, low-resolution transmission electron microscopy (TEM) analyses were conducted. As shown in Figure 2a, hollow spheres with average diameters of 150 nm and wall thicknesses of approximately 20−40 nm are observed. Figure 2b,c reveals tiny and slightly bigger nanoparticles. Nanorods with flower-like structures are presented in Figure 2d, and fishbone-like structures exist in Figure 2e. The trunk diameter is approximately 80 nm, and the rod connected to the trunk has a diameter of approximately 20 nm.

The high-resolution (HR)-TEM images and selected area electron diffraction (SAED) patterns of various synthesized SnO2 nanostructures are shown in Figure 3a−e. The Debye rings of the hollow spheres and LA nanoparticles are more diffused compared to those of the other nanostructures. However, with increasing particle sizes, the Debye rings become brighter according to Figure 3c. Moreover, the nanorods exhibit single-crystal properties in Figure 3d. By contrast, the nanostructures of the fishbones and nanoplatelets are highly polycrystalline. The observed d-spacing of approximately 0.3347 nm is attributed to the (110) plane of tetragonal rutile SnO2.

The crystallite structure and phase purity of the products were determined with the X-ray diffraction (XRD) technique. The crystal orientation plays an imperative role in surface-related applications such as gas sensing owing to the high density of atomic steps, edges, and ample unsaturated coordination sites. In Figure 4, the XRD patterns of the samples obtained under different hydrothermal conditions display the peak positions that match well with the standard
data with $a = b = 0.4738$ nm and $c = 0.3188$ nm (JCPDS card no. 041-1445). No other phases can be observed for SnO$_2$. Hence, the as-prepared nanomaterials had a pure rutile SnO$_2$ structure. All diffraction peaks can be indexed to the tetragonal rutile SnO$_2$ phase with $a = b = 0.4748$ nm and $c = 0.3817$ nm. The most prominent peaks of these nanostructures correspond to the (110), (101), and (211) crystal lattice planes. It is further evident in Figure 4b that XRD patterns shift depending on the structure of SnO$_2$.

Regarding the tetragonal rutile structure of SnO$_2$, the interplanar space $d_{(hkl)}$ is related to the lattice parameter via

$$\frac{1}{d_{(hkl)}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

(1)

With $a$ and $c$ being lattice constants. The lattice constants can be calculated with

$$a = \frac{\lambda}{\sqrt{2} \sin \theta}$$

(2)

As listed in Table 1, various nanostructures depending on the morphology show different sizes of the crystallites, where then nanoparticle reveals smaller crystallites compared to the rest of the samples.

It is well known that the gas sensor properties are also dependent on the surface area and porosity of the SMO. Thus, nitrogen adsorption—desorption analyses were carried out. The results are shown in Figure 5. According to the IUPAC classification, the nitrogen adsorption—desorption isotherms of the hollow spheres and MA nanoparticles exhibit type IV isotherms.$^{27}$ The LA nanoparticles and nanorods have typical type III isotherms. At a relative pressure ($P/P_0$) of 0.5–1.0, the presence of large mesopores or macropores is observed. The amount of absorbed N$_2$ increases with increasing pressure.
Hence, the nanostructures possessed mesoporous structures. It evident that the desorption curves are slightly lower than the adsorption curve, especially for the fishbones, and such behavior could be due to poor pore volume. The pore size distribution investigated with the Barrett–Joyner–Halenda (BJH) method is shown in the insets of Figure 5. The pore sizes differ for the different morphologies of the nanostructures. Regarding the hollow spheres, high specific surface areas of 195.86 m² g⁻¹ and pore volumes of approximately 0.2625 cm³ g⁻¹ are observed. These findings suggest that the higher surface area and pore volume found for hollow spheres make them possible candidates for use in gas sensors.

The HR XPS spectra for Sn 3d in Figure 6 exhibit two peaks at approximately 486.9–4877 and 495.4–496.1 eV, which are assigned to Sn 3d₃/₂ and Sn 3d₅/₂, respectively. The single peak observed in the Sn 3d₅/₂ region (486.9–4877 eV) of all different nanostructures indicates that the samples have a Sn(IV) (Sn⁴⁺) state with no visible Sn³⁺, which is anticipated to appear at 485.8 eV. The observed peak shift is related to the morphology change as observed in Figure S1a (Supporting Information).

The XPS spectra were produced to determine the chemical composition of the materials. Figure 7 illustrates the HR XPS spectrum of oxygen. Based on the measured binding energy, the asymmetric shape of the spectrum indicates several chemical states. Therefore, the O 1s peaks can be deconvoluted into three peaks, as shown in Figure 7. For instance, the hollow spheres have three peaks at 531.4, 532.4, and 533.1 eV, whereas other morphologies including the nanoparticles and nanorods have three peaks centered at 530.9, 531.4, and 532.5 eV. The lower binding energies of 530.9 and 531.4 eV, respectively, correspond to O²⁻ ions in the SnO₂ lattice (O₁), and O²⁻ ions in the oxygen deficiency region within the SnO₂ matrix (O₂), which corresponds to V_O. From the Supporting Information, Figure S1b, it is observed that O 1s peaks shift depending on the structure of SnO₂, and such shifting was previously observed from the XRD patterns in Figure 4b.

Table 1. 2θ, Crystal Size, and d-Spacings of Various Nanostructures for the (110) Diffraction Peak

| Nanostructures | 2θ (deg) | D (nm) | a = b (nm) | c (nm) |
|----------------|---------|--------|------------|--------|
| hollow spheres | 26.684  | 10.80  | 0.4720     | 0.3346 |
| LA particles   | 26.566  | 6.80   | 0.4692     | 0.3123 |
| MA particles   | 26.849  | 7.73   | 0.4680     | 0.3155 |
| rods           | 26.711  | 19.60  | 0.4715     | 0.3170 |
| fishbones      | 26.701  | 12.60  | 0.4737     | 0.3188 |

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Figure 4. (a) XRD patterns of various as-prepared SnO₂ nanostructures. (b) Magnified at the (101) diffraction peak. LA nanoparticles, less agglomerated nanoparticles; MA nanoparticles, more agglomerated nanoparticles.

To further confirm the creation of the V_O and oxygen deficiency centers in the sensing and response mechanism of SnO₂, an EPR analysis was conducted (Figure 8). The hollow spheres, LA nanoparticles, MA nanoparticles, and fishbones in Figure 8 show a single broad resonance peak located at the g-factors of 1.8991, 2.0041, and 2.0161, respectively. The nanorods show two peaks located at the g-factors of 2.0023 and 2.1418. The signal at approximately 2.1 is related to superoxide radical O₂⁻, which forms owing to the transfer of electrons trapped in V_O to the adsorbed oxygen molecules in the SnO₂ surface. The observed resonances at 1.8991–2.0 are attributed to unpaired electrons trapped in singly ionized V_O. The hollow spheres show the highest signal. Thus, they possess high quantities of defects, as confirmed by the PL (see the Supporting Information, Figure S2) and XPS measurements. Such higher defect concentrations could be beneficial for gas sensing applications.

2.2. Electrical and Gas Sensing Properties. The MO gas sensor response is predominantly governed by the interaction between the analyte gas and oxygen species on the sensor surface. Therefore, the morphology, surface area, and defect states severely impact the sensing properties. Moreover, the responses of gas sensors based on MO materials are intensely affected by the operating temperature. To determine the optimal operating temperature, the performance of various SnO₂ nanostructures was tested with various gases (e.g., CO, CH₄, NO₂, and NH₃) and volatile organic compounds (e.g., C₃H₇OH, C₂H₅OH, and C₆H₅O) at 75°C, 150°C, and 225°C.

Among the tested sensors, the hollow spheres have the strongest response toward C₃H₇OH at a low operating temperature (75°C). The hollow spheres exhibit a response
The resistance change of the various SnO₂-based sensors with respect to C₂H₅OH is shown in Figure 9. All sensors display the typical n-type gas sensing behavior. The different morphologies have substantial effects on the baseline resistance of the gas sensors. The resistances of the nanorods and fishbones are higher in the air in comparison to those of the other nanostructures. Furthermore, regardless of the C₂H₅OH concentration, the resistance of the SnO₂-based sensors recovers to the baseline level after the C₂H₅OH flow stops. The response and recovery times of 110 and 90 s were noticed for the hollow spheres toward C₃H₇OH, while the response and recovery times of 105 and 100 s were witnessed for the LA nanoparticles toward C₂H₅OH, respectively.

Figure 10 shows the responses versus the C₃H₇OH and C₂H₅OH gas concentrations at 75 and 150 °C, respectively. The SnO₂ hollow spheres exhibit an exponential increase in the

Figure 5. Nitrogen adsorption–desorption isotherm and BJH pore size distributions (insets) of various SnO₂ nanostructures. (a) Hollow spheres, (b) LA nanoparticles, (c) MA nanoparticles, (d) fishbones, and (e) nanorods.

value of 15, which is five times higher than those of the others at this temperature. Previous studies have indicated that alcohols with increased −CH₂− groups are effortlessly decomposed and oxidized compared to those with lesser one. Consequently, C₃H₇OH containing the maximum number of −CH₂− groups is simply decomposed. Therefore, it reacts efficiently with the adsorbed oxygen molecules, resulting in a release of electrons, consecutively, enhancing the sensing response. This explains the high response of the film in the presence of propan-2-ol, followed by ethanol and methanol, respectively. To the best of our knowledge, a response value of 15.8 of pure SnO₂ for C₃H₇OH vapor at 75 °C is one of the highest response values that have ever been reported. The sensors with low operating temperatures not only reduce costs but also increase the life span of sensors without compromising stability. However, for an operating temperature of 150 °C, the nanorod-based sensor reveals a higher response toward C₂H₅OH. This clearly indicates a shift in the optimal temperature among sensors with varying morphologies. Thus, the optimal temperature is morphology-dependent. As a result, the operating temperatures of 75 and 150 °C were selected for SnO₂ hollow spheres and nanorod-based sensors for various concentrations of C₃H₇OH and C₂H₅OH vapors.

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Figure 10 shows the responses versus the C₃H₇OH and C₂H₅OH gas concentrations at 75 and 150 °C, respectively. The SnO₂ hollow spheres exhibit an exponential increase in the
response to 10−40 ppm of C₃H₇OH. It is well known that SnO₂ exhibits a great response at elevated temperatures (>200 °C). Nonetheless, the presented performance of the pure SnO₂ hollow spheres at 75 °C is even better than in other reports (Table 2). Tan et al. reported response values of approximately 19 for pure SnO₂ nanoparticles at 300 °C toward 100 ppm ethanol.

Table 2 compares the results of the current study with those reported in the literature for SnO₂ sensors tested on C₃H₇OH and C₂H₅OH, respectively. Please note that most reported SnO₂-based sensors were prepared via the hydrothermal method, which allows a clear comparison with our results. The gas response of the SnO₂ hollow spheres and nanoparticles toward C₃H₇OH and C₂H₅OH is higher than those of the sensors listed in Table 2 for a low operating temperature.

The selectivity of the SnO₂ sensors with respect to various target vapors and gases (e.g., C₃H₇OH, C₂H₅OH, CO, NH₃, CH₄, and NO₂) is shown in Figure 11. All sensors were tested with similar gas concentrations (40 ppm) and at two different working temperatures (75 and 150 °C). At 75 °C, the SnO₂ hollow sphere-based sensor exhibits a significantly higher response to C₃H₇OH compared with the other sensors (see Figure 11a). However, at 150 °C, the SnO₂ nanoparticle-based sensor reveals an improved response toward C₂H₅OH vapor. Thus, the operating temperature affects the selectivity of the MO gas sensor (Figure 11b). The high response to C₃H₇OH might be due to the highest number of (−CH₂−) groups, which decompose more easily and result in greater changes in the free-carrier density within the SnO₂ structure.

For quantification, the cross selectivity was calculated using the equation: $S = S_a/S_b$, where $S_a$ and $S_b$ are the responses of a sensor toward a target and the interfering gases, respectively. Figure 11c,d illustrates the cross selectivity of the SnO₂ hollow sphere- and LA nanoparticle-based sensors for C₃H₇OH and C₂H₅OH with respect to the interference gases, respectively. The response ratios of the hollow spheres of C₃H₇OH to C₂H₅OH and of the LA-nanoparticles of C₂H₅OH to NO₂ are relatively large (1450 and 1140, respectively). In this study, NH₃ and NO₂ act as prospectively strong interfering agents.

Figure 6. Sn 3d spectra of various SnO₂ nanostructures: (a) hollow spheres, (b) LA nanoparticles, (c) MA nanoparticles, (d) nanorods, and (e) fishbones.
Figure 7. O 1s XPS spectra of various SnO$_2$ nanostructures: (a) hollow spheres, (b) LA nanoparticles, (c) MA nanoparticles, (d) nanorods, and (e) fishbones.

Figure 8. (a) Electron spin resonance spectra of various SnO$_2$ nanostructures and (b) magnified spectra.
Figure 9. (a) Response vs operating temperatures of SnO$_2$-based sensors exposed to 40 ppm of C$_3$H$_7$OH and C$_2$H$_5$OH. (b) Dynamic resistance curves of various SnO$_2$-based sensors upon exposure to 10$^-1$00 ppm C$_2$H$_5$OH at 150 °C. (c) Real-time response of various SnO$_2$-based sensors toward C$_2$H$_5$OH vapor.

Figure 10. Response vs gas concentrations of (a) C$_3$H$_7$OH and (b) C$_2$H$_5$OH at 75 and 150 °C, respectively.

Table 2. Comparison of Gas Sensing Performances of SnO$_2$-Based Sensors for C$_3$H$_7$OH and C$_2$H$_5$OH

| sensing element          | synthesis method       | gas     | gas concentration (ppm) | operating temperature (°C) | response | refs |
|--------------------------|------------------------|---------|-------------------------|----------------------------|----------|------|
| SnO$_2$ hollow spheres   | hydrothermal           | C$_3$H$_7$OH | 40                       | 75                         | 20.1     | this work |
| SnO$_2$ LA nanoparticles | hydrothermal           | C$_2$H$_5$OH | 40                       | 150                        | 59.6     | this work |
| SnO$_2$ nanoparticles    | hydrothermal           | C$_3$H$_7$OH | 500                      | 100                        | 9.8      | 43   |
| SnO$_2$ nanoparticles    | hydrothermal           | C$_2$H$_5$OH | 17                       | 220                        | 32       | 44   |
|                         |                        |         | 1.7                     |                             | 6        | 6    |
| SnO$_2$ nanoparticles    | hydrothermal           | C$_2$H$_5$OH | 500                      | 100                        | 14.6     | 45   |
| SnO$_2$ nanoparticles    | quasi-molecular cluster| C$_2$H$_5$OH | 100                      | 300                        | 8.9      | 40   |
| SnO$_2$ nanowires        | quartz tube method     | C$_2$H$_5$OH | 50                       | 400                        | 7.1      | 46   |
gases. Therefore, the respective response ratios are considered as the influence parameters to evaluate the cross selectivity of the hollow spheres.

To study the stability of the hollow sphere- and nanorod-based sensors, repeatability and long-term stability analyses were carried out. Figure 12a shows the repeatability performance of the sensor for eight successive cycles toward 40 ppm C₃H₇OH for three weeks. On day one, the fresh sensor exhibits evident repeatability of six consecutive periods for 40 ppm C₃H₇OH. However, after seven days, the repeatability performance remains constant, whereas the response decreases, as confirmed by the stability plot in Figure 12b. This behavior is also observed after 23 days, where the response decreases by 88.1% with respect to the original value. It is further observed that the LA nanoparticle response decreases rapidly by 37% after 7 days, while after 23 days, the response dropped by 86.7%. However, we have found that upon incorporating the p-type NiO on the surface of the hollow spheres, the stability improved, and such results are not shown here because they fall under our future work.

The responses of the sensors exposed to 40 ppm C₃H₇OH in the presence of 40 and 60% relative humidity (RH) are shown in Figure 12c,d. The responses of both sensors decrease with RH. The performance of the SnO₂ hollow sphere-based sensor decreases by 87.3% toward 40 ppm C₃H₇OH in the presence of 60% RH. The response of the SnO₂ LA nanoparticle-based sensor decreases by 91.8% toward C₃H₇OH in the presence of 60% RH. Based on the above findings, it is evident that the current sensors are not stable either in an actual environment or in dry air after long exposure to C₃H₇OH or C₂H₅OH vapor.

Usually, the gas sensing mechanism of an n-type SnO₂ SMO can be determined according to the radial modulation in the electron depletion layer and the potential barrier modulation. The oxygen species that are adsorbed on the SnO₂ surface capture the electrons in the conduction band, thereby increasing the resistance because of the increasing electron depletion layer. When the sensor is exposed to a target gas (e.g., C₃H₇OH), the gas molecules interact with the preadsorbed oxygen species (O₂⁻). The electrons that are captured are released back into the SnO₂ conduction band, thereby decreasing the electron depletion layer and the resistance.51

To determine the reason for the different sensitivities and selectivities of the gas sensors, we analyzed different types of paramagnetic defects existing on the nonstoichiometric layers of the SnO₂ sensors and compared them with the sensing responses. According to the EPR, PL, and XPS analyses, VO is the dominant defect on the SnO₂ surface. VO is considered as an active site for oxygen adsorption. Therefore, the hollow spheres exhibit improved oxygen adsorption. To relate the paramagnetic defects to the gas sensing response, we calculated the number of spins (Figure 13a). Remarkably, the sensing response fluctuates with the EPR intensity. Therefore, a clear constructive relationship between the electrical response and paramagnetic VO is revealed, which is also confirmed by the PL and XPS results (see the Supporting Information). These results agree well with those reported in previous studies.
Thus, the quantity of paramagnetic VO identified via ESR is related to the number of electrons reaching the SnO₂ conduction band. This result agrees well with the improved sensing performance. From the XRD analysis, the hollow spheres displayed higher lattice strain, which resulted in the formation of more structural defects within the system as validated by PL, EPR, and XPS analyses.

Furthermore, to understand the sensing behavior occurring on the current sensing layer, we correlated the response versus the active surface area of various nanostructures, and the results are presented in Figure 13b. As shown in Figure 13b, as the surface area increases, the response also increases, whereby the hollow spheres reveal higher surface area, correlating well with the higher response they revealed. Remarkably, the hollow sphere structure containing the inner and outer shell layer can broaden the contact area existing between the sensing layer and analyte gases as observed in the current work. The high surface to volume ratio and density of surface active sites are supportive of the adsorption and desorption of C₃H₇OH gas molecules and surface interaction. The hollow sphere structure reduces the path of gas diffusion and enables the penetration of gas molecules.

Besides, Morazzoni et al. proposed new radical Sn⁴⁺−O₂ −, which is paramagnetically active and plays a vital part in the gas sensing mechanism.

\[
\begin{align*}
O_2^- & \rightleftharpoons V_0^+ + \frac{1}{2}O_2 + e^- \\
O_2^- & \rightleftharpoons V_0^{**} + \frac{1}{2}O_2 + 2e^- \\
Sn^{4+} - O_2^- & \rightleftharpoons Sn^{3+} + V_0^{**} + O_2 + 3e^-
\end{align*}
\]

When the SnO₂ hollow sphere- and nanoparticle-based sensors are exposed to C₃H₇OH (see Scheme 1) and C₂H₅OH at 75 and 125 °C, respectively, they will react with the adsorbed oxygen species (O₂ −), while, at temperatures of <300 °C, they will react with the adsorbed oxygen species (O −) through the following reactions and thereby resulting in a decrease in the sensor resistance.

\[
\begin{align*}
2C_3H_7OH + 9O_2(\text{ads}) & \rightarrow 8H_2O + 6CO_2 + 9e^- \\
\left(T_{up} < 100 \, ^\circ C\right) \\
C_2H_5OH_{(\text{gas})} + 6O_2(\text{ads}) & \rightarrow 3H_2O + 2CO_2 + 6e^- \\
\left(T_{up} < 300 \, ^\circ C\right)
\end{align*}
\]

3. CONCLUSIONS

Various SnO₂ nanostructures were successfully synthesized using a simple hydrothermal one-pot method. In a controlled
relative concentration of VO is morphology-dependent. The
and C2H5OH) at various operating temperatures. The SnO2
surface area. Fundamentally, each VO offers two electrons. Therefore,
a larger concentration of VO in the hollow spheres results in a higher
number of electrons, which can be absorbed.36,54,55

4. EXPERIMENTAL SECTION

4.1. Materials. All reagents were of analytical grade and used
without further purification. Tin chloride dihydrate (SnCl2·2H2O), sodium hydroxide (NaOH), HMT [H2N(CH2)6NH2], and absolute ethanol were purchased from Sigma-Aldrich, Johannesburg, South Africa.

4.2. Synthesis of SnO2 Nanostructures. The SnO2 hollow spheres were produced by mixing 0.4 g SnCl2·2H2O and 0.5 g NaOH in 20 mL deionized water and 0.5 M HNO3, under magnetic stirring for 20 min. Next, 40 mL ethanol was slowly added to the solution to form a white precipitate. The mixture was stirred for 24 h, washed with distilled water and ethanol, and dried at 80 °C for 24 h. The SnO2 nanoparticles were synthesized using 0.4 g SnCl2·2H2O and 0.5 g NaOH in 20 mL deionized water and 0.5 M HNO3. The solution was stirred for 20 min and transferred into a 45 mL Teflon-lined stainless-steel autoclave, which was sealed tightly and kept at 200 °C in an oven for 12–48 h. After the hydrothermal step, the autoclave was allowed to cool down to room temperature. The flower-rod bundle, fishbone platelet, and hierarchical flower-like platelet nanostructures were synthesized by mixing 0.4 g SnCl2·2H2O, 0.5 g NaOH, and 0.84 g HMT in 20 mL deionized water under continuous magnetic stirring. Next, 60 mL ethanol was added slowly to the white precipitate. The mixture was transferred into a 45 mL Teflon-lined stainless-steel autoclave and kept at 200 °C for 12–48 h. We should point out that to form different morphologies, different synthesis times had to be adopted. While with the MA nanoparticles, the synthesis reaction time prolonged in order to form larger sizes of the nanoparticles to have a comparison with smaller ones. Finally, the white precipitates were collected through centrifugation and washed thoroughly with distilled water and ethanol. Afterward, they were dried at 80 °C for 24 h.

4.3. Characterization. The SnO2 crystal structure was analyzed with a PANalytical X’pert PRO PW 3040/60 X-ray diffractometer with Cu Kα radiation and λ = 0.154178 nm at an acceleration voltage of 45 kV and a current of 40 mA (PANalytical, the Netherlands). The nanostructures and surface morphologies were determined with a scanning electron microscope (SEM, Zeiss Auriga, Germany) and JEOL-2100 transmission electron microscope (TEM, JEOL, Japan). The analysis of the pores, surface area, and nitrogen adsorption−desorption isotherms were conducted with the Brunauer−Emmett−Teller (BET) and BJH methods with a Micromeritics TRISTAR 3000 instrument, USA. The point defects and crystal quality were investigated with a Jobin-Yvon NanoLog PL spectrometer (Jobin-Yvon, France). Further, the chemical state of the nanostructures was studied via XPS with a PHI 5000 VersaProbe Scanning ESCA Microprobe (USA). To study paramagnetic defects, a JEOL X-band EPR spectrometer (JEOL, Japan) was used. The analyses were carried out at 25 and 75 °C to mimic the sensing conditions.

4.4. Sensor Fabrication and Sensing Characterization. The vapor and gas sensing properties were measured using the KSGAS6S gas sensing station (Kensios, Italy). In the typical sensor fabrication procedure, an appropriate

Figure 13. Gas sensing response toward 40 ppm C3H7Oa at 23 °C vs (a) number of spins related to paramagnetic defects and (b) BET surface area. Fundamentally, each VO offers two electrons. Therefore, a larger concentration of VO in the hollow spheres results in a higher number of electrons, which can be absorbed.36,54,55

Scheme 1. Schematic Diagram of the Oxygen Chemisorption and the Reaction between C3H7OH Gas and the Preadsorbed Oxygen Species

manner, nanostructures with different morphologies such as hollow spheres, nanoparticles with two different sizes, nanoplatelets, nanorods, and fishbones were synthesized. The defect analyses via EPR, PL, and XPS revealed that the hollow spheres contained the most defects (e.g., VO). Further, the relative concentration of VO is morphology-dependent. The SnO2 nanostructure-based gas sensors were fabricated and characterized for different gases (CO, NH3, CH4, and NO2) including volatile organic compounds (C3H7OH, C3H5OH, and C2H4OH) at various operating temperatures. The SnO2 hollow spheres exhibited an improved sensing response for C3H7OH gas at a low operating temperature (75 °C). At a high operating temperature (150 °C), the SnO2 nanoparticle-based sensor showed the highest response value. This variation in the optimal temperatures among sensors with different morphologies implied that the gas selectivity and sensitivity are morphology-dependent.
amount of sample powder was placed in an agate mortar and ground adding terpineol to form slurry. Afterward, the paste was carefully coated onto alumina substrates. The sensor units were placed in a sealed chamber at a controlled temperature under different conditions (i.e., in dry air and under RH values of 40 and 60%). The gas sensing studies were conducted exposing the fabricated sensors to different concentrations (10–100 ppm) of various reducing gases (e.g., CO, CH₄, and NH₃), volatile organic compounds (C₆H₅OH, C₆H₆O, and C₆H₅OH), and an oxidizing gas (NO₂) in a background of synthetic dry air. The gas/organic compound concentrations in the test chamber were precisely mixed with synthetic air. The measurements were carried out at various operating temperatures 25 °C (i.e., room temperature), 75, 150, and 225 °C. The sensor resistance was continuously monitored using a Keithley 6487 picocammeter/voltage source meter. We define the gas response as \( R/R_g \) − 1 for reduced gas and \( R/R_Rg \) − 1 for oxidized gas, where \( R_g \) and \( R_Rg \) are the resistances of the sensors in air and gas/organic vapor, respectively. The response recovery times were calculated as the time intervals between the time at which the response has achieved 90% of its maximum and the time at which it has decreased to 10% of its maximum.²

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01079.

Additional X-ray photoelectron spectroscopic results and PL spectra of various SnO₂ nanostructures (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Qi, Q.; Zhang, T.; Wang, S.; Zhang, X. Humidity Sensing Properties of KCl-doped ZnO Nanotubes with Super-rapid Response and Recovery. Sens. Actuators, B 2009, 137, 649–655.
(2) Ivanov, P.; Llobet, E.; Vilanova, X.; Brezmes, J.; Hubalek, J.; Correig, X. Development of High Sensitivity Ethanol Gas Sensors Based On Pt-doped SnO₂ Surfaces. Sens. Actuators, B 2004, 99, 201–206.
(3) Vander Wal, R. L.; Hunter, G. W.; Xu, J. C.; Kulis, M. J.; Berger, G. M.; Ticich, T. M. Metal-Oxide Nanostucture and Gas-Sensing Performance. Sens. Actuators, B 2009, 138, 113–119.
(4) Röck, F.; Barsan, N.; Weimar, U. Electronic Nose: Current Status and Future Trends. Chem. Rev. 2008, 108, 705–725.
(5) Zhou, X.; Zhang, J.; Jiang, T.; Wang, X.; Zhu, Z. Humidity Detection by Nanostructured ZnO: A Wireless Quartz Crystal Microbalance Investigation. Sens. Actuators, A 2007, 135, 209–214.
(6) Li, T.; Xu, L.; et al. A high heating efficiency two beam microplate for catalytic gas sensors. In Proceedings of the IEEE International Conference on Micro Electronic and Mechanical Systems MEMS; Kyoto: Japan, 2012; pp 65–68.
(7) Chougule, M. A.; Sen, S.; Patil, V. B. Fabrication of nanostructured ZnO thin film sensor for NO₂ monitoring. Ceram. Int. 2012, 38, 2685–2692.
(8) Ng, Z.-N.; Chan, K.-Y.; Tohosoph, T. Effects of Annealing Temperature on ZnO and AZO Films Prepared by Sol–Gel Technique. Appl. Surf. Sci. 2012, 258, 9604–9609.
(9) Cavicchi, R. E.; Walton, R. M.; Aquino-Class, M.; Allen, J. D.; Panchapakesan, B. Spin-on Nanoparticles Tin Oxide for Microhotplate Gas Sensors. Sens. Actuators, B 2001, 77, 145–154.
(10) Zhang, J.; Liu, X.; Neri, G.; Pinna, N. Nanostructured Materials for Room-Temperature Gas Sensors. Adv. Mater. 2016, 28, 795–831.
(11) Chi, W. S.; Lee, C. S.; Long, H. O.; Oh, M. H.; Zettl, A.; Carraro, C.; Kim, J. H.; Maboudian, R. Direct Organization of Morphology-Controllable Mesoporous SnO₂ Using Amphiphilic Graft Copolymer for Gas-Sensing Applications. ACS Appl. Mater. Interfaces 2017, 9, 37246–37253.
(12) Lee, S.-H.; Galstyan, V.; Ponzonii, A.; Gonzalez-Juan, I.; Riedel, R.; Dourges, M.-A.; Nicolas, Y.; Toupane, T. Finely Tuned SnO₂ Nanoparticles for Efficient Detection of Reducing and Oxidizing Gases: The Influence of Alkali Metal Cation on Gas-Sensing Properties. ACS Appl. Mater. Interfaces 2018, 10, 10173–10184.
(13) Ma, N.; Suematsu, K.; Yuasa, M.; Shimanoe, K. Pd Size Effect on the Gas Sensing Properties of Pd-Loaded SnO₂ in Humid Atmosphere. ACS Appl. Mater. Interfaces 2015, 7, 15618–15625.
(14) Hyodo, T.; Urata, K.; Kamada, K.; Ueda, T.; Shimizu, Y. Semiconductor-type SnO₂-based NO₂ Sensors Operated at Room Temperature under UV-light Irradiation. Sens. Actuators, B 2017, 253, 630–640.
(15) Hu, J.; Wang, T.; Wang, Y.; Huang, D.; He, G.; Han, Y.; Hu, N.; Su, Y.; Zhou, Z.; Yang, Z. Enhanced Formaldehyde Detection Based on Ni Doping of SnO₂ Nanoparticles by one-step Synthesis. Sens. Actuators, B 2018, 263, 120–128.
(16) Zhang, Z.; Xu, M.; Liu, L.; Ruan, X.; Yan, J.; Zhao, W.; Yun, J.; Wang, Y.; Qin, S.; Zhang, T. Novel SnO₂@ZnO hierarchical Nanostructures for Highly Sensitive and Selective NO₂ Gas Sensing. Sens. Actuators, B 2018, 257, 714–727.
(17) Wang, Z.; Zhang, T.; Han, T.; Fei, T.; Liu, S.; Lu, G. Oxygen Vacancy Engineering for Enhanced Sensing Performances: A case of SnO₂ Nanoparticles-Reduced graphene Oxide Hydrides for Ultra-sensitive ppb-level Room-Temperature NO₂ Sensing. Sens. Actuators, B 2018, 266, 812–822.
(18) Ju, D.-X.; Xu, H.-Y.; Qiu, Z.-W.; Zhang, Z.-C.; Xu, Q.; Wang, J.-Q.; Cso, B.-Q. Near Room Temperature, Fast-Response, and Highly Sensitive Triethylamine Sensor Assembled with Au-Loaded ZnO/ SnO₂ Core-Shell Nanorods on Flat Alumina Substrates. ACS Appl. Mater. Interfaces 2015, 7, 19163–19171.
(19) Kim, B.-Y.; Cho, J. S.; Yoon, J.-W.; Na, C. W.; Lee, C.-S.; Ahn, J. H.; Kang, Y. C.; Lee, J.-H. Extremely Sensitive Ethanol Sensor Using Pt-doped SnO₂ Hollow Nanospheres Prepared by Kirkendall Diffusion. Sens. Actuators, B 2016, 234, 353–360.
(20) Jeong, H.-M.; Kim, J.-H.; Jeong, S.-Y.; Kwak, C.-H.; Lee, J.-H. Co3O4–SnO₂ Hollow Heteronanostructures: Facile Control of Gas Selectivity by Compositional Tuning of Sensing Materials via Galvanic Replacement. ACS Appl. Mater. Interfaces 2016, 8, 7877–7883.
(21) Motaung, D. E.; Mhlongo, G. H.; Makgware, P. R.; Dhonge, B. P.; Cummings, F. R.; Swart, H. C.; Ray, S. S. Ultra-high Sensitive and
Selective H2 Gas Sensor Manifested by Interface of n–n Heterostructure of CeO2-SnO2 Nanoparticles. Sens. Actuators, B 2018, 254, 984–995.

(22) Pan, J.; Ganesan, R.; Shen, H.; Mathur, S. Plasma-modified SnO2 Nanowires for Enhanced Gas Sensing. J. Phys. Chem. C 2010, 114, 8245–8250.

(23) Ilyasukan, N.; Kohler, H.; Trautmann, T.; Schwotzer, M.; Pillai, V. P. M. Enhanced Ethanol Sensing Response from Nanostructured MoO3-ZnO Thin Films and Their Mechanism of Sensing. J. Mater. Chem. C 2013, 1, 3976–3984.

(24) Li, Y.; Zhu, B.; Guo, Y.; Li, K.; Zeng, H.; Dou, X. Surface Superoxide Complex Defects-Boosted Ultrasensitive ppb-level NO2 Gas Sensors. Small 2016, 12, 1420–1424.

(25) Xu, J.; Chen, Y.; Shen, J. Ethanol Sensor Based on Hexagonal Indium Oxide Nanorods Prepared by Solvothermal Method. Mater. Lett. 2008, 62, 1363–1365.

(26) Talebani, N.; Jafarinezhad, F. Morphology-controlled synthesis of nanostructures using hydrothermal method and their photocatalytic applications. Ceram. Int. 2013, 39, 8311–8317.

(27) Liu, Z.; Yamazaki, T.; Shen, Y.; Kikutake, T.; Nakatani, N.; Kawabata, T. Room temperature gas sensing of p-type TeO2 nanowires. Sens. Actuators, B 2011, 160, 448–454.

(28) Zheng, Y.; Wang, J.; Yao, P. Formaldehyde Sensing Properties of Electrospun NiO-Doped SnO2 Nanofibers. Sens. Actuators, B 2011, 156, 723–730.

(29) Lee, S.-H.; Galstyan, V.; Ponzo, A.; Gonzalez-Juan, I.; Riedel, R.; Dougeres, M.-A.; Nicolas, Y.; Toupance, T. Finely Tuned SnO2 Nanoparticles for Efficient Detection of Reducing and Oxidising Gases: The Influence of Alkali Metal Cation on Gas-Sensing Properties. ACS Appl. Mater. Interfaces 2018, 10, 10173–10184.

(30) Wang, Z.; Zhang, T.; Han, T.; Fei, T.; Liu, S.; Lu, G. Oxygen Vacancy Engineering for Enhanced Sensing Performances: A Case of SnO2 Nanoparticles-Reduced Graphene Oxide Hybrids for Ultra-sensitive ppb-Level Room-Temperature NO2 Sensing. Sens. Actuators, B 2018, 266, 812–822.

(31) Liu, J.; Dai, M.; Wang, T.; Sun, P.; Liang, X.; Lu, G.; Shimano, K.; Yamazoe, N. Enhanced Gas Sensing Properties of SnO2 Hollow Spheres Decorated with CeO2 Nanoparticles Heterostructure Composite Materials. ACS Appl. Mater. Interfaces 2016, 8, 6669–6677.

(32) Chhetri, P.; Choudhury, B.; Choudhury, A. Room Temperature Ferromagnetism in SnO2 Nanoparticles: An Experimental and Density Functional Study. J. Mater. Chem. C 2014, 2, 9294–9302.

(33) Acciari, M.; Canevalli, C.; Mari, C. M.; Mattoni, M.; Ruffo, R.; Scotti, R.; Morazzoni, F.; Barrea, D.; Armelao, L.; Tondello, E.; Bontempi, E.; Depero, L. E. Nanocrystalline SnO2-Based Thin Films Obtained by Sol–Gel Route: A Morphological and Structural Investigation. Chem. Mater. 2003, 15, 2646–2650.

(34) Acciari, M.; Canevalli, C.; Mari, C. M.; Mattoni, M.; Morazzoni, F.; Nosari, L.; Russo, U.; Ruffo, R.; Scotti, R. J. Ruthenium (Platinum)-Doped Tin Dioxide Inverted Opals for Gas Sensors: Synthesis, Electron Paramagnetic Resonance, Mossbauer, and Electrical Investigation. Chem. Mater. 2005, 17, 6167–6171.

(35) Epifani, M.; Prades, J. D.; Comini, E.; Pellicer, E.; Avella, M.; Siciliano, P.; Faglia, G.; Cirera, A.; Scotti, R.; Morazzoni, F.; Morante, J. R. The Role of Surface Oxygen Vacancies in the NO2 Sensing Properties of SnO2 Nanocrystals. J. Phys. Chem. C 2008, 112, 19540–19546.

(36) Canevalli, C.; Mari, C. M.; Mattoni, M.; Morazzoni, F.; Nosari, L.; Russo, U.; Ruffo, R.; Scotti, R. Interaction of NO with Nanostructured Ru, Pd, and Pt-doped SnO2: Electron Paramagnetic Resonance Mossbauer, and Electrical Investigation. J. Phys. Chem. B 2005, 109, 7195–7202.

(37) Prapatpatis, C. S.; Sahay, P. P. Alcohol-Sensing Characteristics of Spray Deposited ZnO Nano-particle Thin Films. Sens. Actuators, B 2011, 160, 1043–1049.

(38) Islam, M. R.; Kumazawa, N.; Takeuchi, M. Titaniumdioxide Chemical Sensor Working with AC Voltage. Sens. Actuators, B 1998, 46, 114–119.

(39) Kumazawa, N.; Rafiqul Islam, M.; Takeuchi, M. Photoreponse of a Titanium Dioxide Chemical Sensor. J. Electroanal. Chem. 1999, 472, 137–141.

(40) Pan, J.; Ganesan, R.; Shen, H.; Mathur, S. Plasma-modified SnO2 Nanowires for Enhanced Gas Sensing. J. Phys. Chem. C 2010, 114, 8245–8250.

(41) Li, Y.; Zhu, B.; Guo, Y.; Li, K.; Zeng, H.; Dou, X. Surface Superoxide Complex Defects-Boosted Ultrasensitive ppb-level NO2 Gas Sensors. Small 2016, 12, 1420–1424.

(42) Wang, S.; Xu, Y.; Cheng, C.; Zhang, T.; Ge, M.; Sun, Y.; Dai, N. Fabrication of Mesoporous SnO2 Nanocubes with Superior Ethanol Gas Sensing Property. Mater. Res. Bull. 2017, 89, 267–272.

(43) Huang, J.; Yu, K.; Gu, C.; Zhai, M.; Wu, Y.; Yang, M.; Liu, J. Preparation of Porous Flower-Shaped SnO2 Nanostructures and Their Gas-Sensing Property. Sens. Actuators, B 2010, 147, 467–474.

(44) Choi, H.-C.; Yeh, C. S. Hydrothermal Synthesis of SnO2 Nanoparticles and Their Gas-Sensing of Alcohol. J. Phys. Chem. C 2007, 111, 7256.

(45) L.; Ruffo, R.; Russo, U.; Scotti, R. Interaction of NO with Nanosized Siciliano, P.; Faglia, G.; Cirera, A.; Scotti, R.; Morazzoni, F.; Morante, F.; Toupance, T. Finely Tuned SnO2 Nanoparticles-Reduced Graphene Oxide Hybrids for Ultra-sensitive ppb-Level Room-Temperature NO2 Sensing. Sens. Actuators, B 2011, 160, 1043–1049.
(58) Karthikeyan, P. S.; Dhivya, P.; Deepak Raj, P.; Sridharan, M. V$_2$O$_5$ Thin Film for 2-Propanol Vapor Sensing. Mater. Today: Proc. 2016, 3, 1510−1516.

(59) Navale, S. T.; Yang, Z.; Liu, C.; Kumar, A.; Sharma, G.; Cao, P.; Patil, V. B.; Stadler, F. J. Solid-State Synthesis Strategy of Hierarchically-Structured BiOCl Desert-Roses for the Selective Detection of C$_2$H$_5$OH. J. Alloys Compd. 2019, 778, 532−541.