Design of Nanoscaled Surface Morphology of TiO$_2$–Ag$_2$O Composite Nanorods through Sputtering Decoration Process and Their Low-Concentration NO$_2$ Gas-Sensing Behaviors

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Abstract: TiO$_2$–Ag$_2$O composite nanorods with various Ag$_2$O configurations were synthesized by a two-step process, in which the core TiO$_2$ nanorods were prepared by the hydrothermal method and subsequently the Ag$_2$O crystals were deposited by sputtering deposition. Two types of the TiO$_2$–Ag$_2$O composite nanorods were fabricated; specifically, discrete Ag$_2$O particle-decorated TiO$_2$ composite nanorods and layered Ag$_2$O-encapsulated TiO$_2$ core–shell nanorods were designed by controlling the sputtering duration of the Ag$_2$O. The structural analysis revealed that the TiO$_2$–Ag$_2$O composite nanorods have high crystallinity. Moreover, precise control of the Ag$_2$O sputtering duration realized the dispersive decoration of the Ag$_2$O particles on the surfaces of the TiO$_2$ nanorods. By contrast, aggregation of the massive Ag$_2$O particles occurred with a prolonged Ag$_2$O sputtering duration; this engendered a layered coverage of the Ag$_2$O clusters on the surfaces of the TiO$_2$ nanorods. The TiO$_2$–Ag$_2$O composite nanorods with different Ag$_2$O coverage morphologies were used as chemoresistive sensors for the detection of trace amounts of NO$_2$ gas. The NO$_2$ gas-sensing performances of various TiO$_2$–Ag$_2$O composite nanorods were compared with that of pristine TiO$_2$ nanorods. The underlying mechanisms for the enhanced sensing performance were also discussed.

Keywords: sputtering; surface decoration; nanostructured surface; composite nanorods

1. Introduction

The development of chemosensors made from semiconductor oxides has recently become a key research topic [1,2]. Therefore, the development of highly responsive sensing oxide devices toward specific harmful gases has attracted interest in industry. For the gas sensor applications, one-dimensional (1D) metal oxides usually show better performance in comparison with their thin-film or bulk counterparts because of their high surface-to-volume ratio [3–6]. In particular, gas sensors based on 1D titanium dioxide (TiO$_2$) nanostructures have received considerable attention because they can be fabricated with diverse chemical and physical methods; moreover, TiO$_2$ has been shown to be favorable for the detection of diverse harmful gases and volatile organic vapors at elevated temperatures [5,7,8].

Recently, combining n-type oxides with p-type semiconductor oxides to form a heterogeneous structure has attracted great attention due to this combination’s enhanced gas-sensing performance toward target gases [9–11]. The existence of the interfacial potential barrier at the p–n junctions of the heterogeneous structure play an important role in improving the gas-sensing performance of the constituent oxides. Several p–n junction-based sensors made from different material systems and configurations have been proposed. For examples, Woo et al. reported a discrete configuration of
p-type Cr2O3 nanoparticles on the surfaces of ZnO nanowires; this p–n heterostructure enhances gas selectivity and sensitivity toward trimethylamine [11]. The decoration of NiO nanoparticles in porous SnO2 nanorods remarkably enhances the gas-sensing response to ethanol as compared with pristine SnO2, which can be attributed to the formation of NiO–SnO2 p–n heterojunctions [12]. P-type Ag2O phase-functionalized In2O3 nanowires shows an improved gas-sensing performance toward NO2 gas [13]. However, reports on the incorporation of p-type oxides into n-type TiO2 nanostructures to form a p–n junction gas sensor are limited in number.

In this study, 1D TiO2–Ag2O p–n heterogeneous structures are synthesized through the combination of hydrothermal growth and sputtering methods. Ag2O is a p-type semiconductor oxide; it has previously been used as a gas-sensing material [13]. Moreover, Ag2O crystals with various morphologies can be synthesized through chemical or physical routes [14–16]. Notably, Ag2O particles are mostly synthesized through chemical routes but, using such chemical routes, it is hard to control the decoration morphology of the Ag2O crystals on 1D nanostructures [15]. By contrast, the fabrication of Ag2O through a physical method (sputtering) is advantageous concerning the control of the Ag2O content, crystalline quality, and coverage morphology on 1D TiO2. In this study, two types of TiO2–Ag2O composite nanorods are synthesized. By controlling the sputtering duration of the Ag2O, discrete Ag2O particle-decorated TiO2 nanorods and Ag2O layers encapsulating TiO2 nanorods are fabricated. The Ag2O coverage morphology effects on the low-concentration NO2 gas-sensing performance of the TiO2–Ag2O p–n composite nanorods are systematically investigated in this study.

2. Materials and Methods

In this study, TiO2 nanorods were grown on fluorine-doped SnO2 (FTO) glass substrates. First, 0.25 mL of TiCl4 and 19 mL HCl were added to 11 mL deionized water and then stirred to obtain a transparent solution for the hydrothermal growth of TiO2 nanorods. The hydrothermal reaction was conducted at 180 °C for 3 h. For the preparation of TiO2–Ag2O composite nanorods, Ag2O crystals were decorated onto the surfaces of the TiO2 nanorod template via sputtering. Radiofrequency magnetron sputtering of Ag2O was conducted using a silver metallic target in an Ar/O2 (Ar:O2 = 5:2) mixed ambient. The sputtering deposition temperature of the Ag2O was maintained at 200 °C. The gas pressure during sputtering deposition was fixed at 20 mTorr and the sputtering power was fixed at 50 W for the silver target. Two sets of TiO2–Ag2O composite nanorods with Ag2O sputtering durations of 130 s and 270 s were prepared; these were represented as TiO2–Ag2O-1 and TiO2–Ag2O-2, respectively, in this study. The sample configurations of the TiO2–Ag2O-1 and TiO2–Ag2O-2 composite nanorods are shown in Figure 1.

An X-ray diffractometer (XRD; D2 PHASER, Bruker, Karlsruhe, Germany) was used to analyze the crystal structures of the TiO2–Ag2O composite nanorods. Scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan) and transmission electron microscopy (HRTEM; JEM-2100F, JEOL Tokyo, Japan) were used to characterize the morphology and detailed microstructures of the composite nanorod samples. The attached energy dispersive X-ray spectroscopy (EDS) of TEM was used to investigate the composition and composition distribution of the nanorod samples. Moreover, X-ray photoelectron spectroscopy (XPS; ULVAC-PHI XPS, ULVAC, Chigasaki, Japan) was used to characterize the elemental binding states of the synthesized samples.

The response of pure TiO2 nanorods and the TiO2–Ag2O nanocomposites to NO2 was tested in a vacuum test chamber. Silver electrodes were laid on the surfaces of the samples to form electric contacts for measurements. An Agilent B2911A meter measured the resistance variation of the nanorod sensors at a constant potential of 5 V as a function of time. Constant dry air was used as the carrier gas and the desired concentration of NO2 gas (0.5, 1.5, 3.0 ppm) was introduced into the test chamber. A direct heating approach was used to operate the sensors at elevated temperatures in the range of 200–300 °C.
3. Results and Discussion

X-ray diffractometer (XRD) patterns of TiO$_2$–Ag$_2$O composite nanorods with various Ag$_2$O thin-film sputtering durations are shown in Figure 2. The distinct Bragg reflections centered at 27.46°, 36.05°, 41.22°, and 54.33° correspond to the crystallographic planes (110), (101), (111), and (211) of the rutile TiO$_2$ phase, respectively (JCPDS no. 00-004-0551). Moreover, the Bragg reflections centered at 32.72° and 37.98° are assigned to the crystallographic planes of cubic Ag$_2$O (111) and (200), respectively (JCPDS no. 00-012-0793). The XRD results reveal that highly crystalline rutile TiO$_2$-cubic Ag$_2$O composite nanorods were formed through the sputtering deposition of Ag$_2$O thin films onto the surfaces of the TiO$_2$ nanorods, and no other impurity peak was observed. As expected, the intensity of the Ag$_2$O Bragg reflections peaks increased with the increase of the Ag$_2$O thin-film sputtering duration, revealing an increased Ag$_2$O phase content in the composite nanorods.

![Figure 1. Sample configurations of the TiO$_2$–Ag$_2$O-1 and TiO$_2$–Ag$_2$O-2 composite nanorods synthesized with various sputtering durations of Ag$_2$O.](image)

![Figure 2. XRD patterns of various composite nanorods: (a) TiO$_2$–Ag$_2$O-1, (b) TiO$_2$–Ag$_2$O-2.](image)
Figure 3a shows the scanning electron microscopy (SEM) image of the as-synthesized TiO$_2$ nanorods. The TiO$_2$ nanorods had a rectangular cross-section crystal feature with an average diameter of approximately 100 nm; the side facets of the nanorods were smooth. Figure 3b presents the SEM image of the TiO$_2$–Ag$_2$O-1 composite nanorods. The surface morphology of the composite nanorods reveals that a small amount of nanoparticle-like crystals was decorated onto the surfaces of the TiO$_2$ nanorods. The nanoparticle-like crystals dispersed separately on the surfaces of the TiO$_2$ nanorods. Figure 3c shows the SEM image of the TiO$_2$–Ag$_2$O-2 composite nanorods. The TiO$_2$ nanorods were homogeneously encapsulated by the aggregation of massive Ag$_2$O nanoparticles, resulting in the irregular-shaped cross-section crystal feature of the composite nanorods. Detailed TEM analyses were performed to further confirm the morphology change of the TiO$_2$–Ag$_2$O composite nanorods prepared at various Ag$_2$O sputtering durations.

![Figure 3. SEM images of various nanorods: (a) TiO$_2$, (b) TiO$_2$–Ag$_2$O-1, (c) TiO$_2$–Ag$_2$O-2.](image)

Figure 4a shows the low-magnification transmission electron microscopy (TEM) image of a TiO$_2$–Ag$_2$O-1 composite nanorod. A small amount of Ag$_2$O particles was dispersedly decorated on the surface of the TiO$_2$ nanorod via the sputtering growth of the Ag$_2$O. The high-resolution TEM images shown in Figure 4b,c indicate distinct lattice fringes in the Ag$_2$O particle. Moreover, the lattice fringe distance of approximately 0.24 nm was assigned to the crystallographic plane spacing of cubic Ag$_2$O (200). Figure 4d exhibits the selected area electron diffraction (SAED) pattern of several TiO$_2$–Ag$_2$O-1 composite nanorods. Several clear diffraction rings associated with (111) and (200) planes of the Ag$_2$O and (110), (111), and (211) planes of the rutile TiO$_2$ were observed in the SAED pattern. This demonstrates the good crystallinity of the composite nanorods and indicates that these composite nanorods have a polycrystalline nature. Figure 4e presents the EDS spectrum of a TiO$_2$–Ag$_2$O-1 nanorod. In addition to carbon and copper signals originating from the TEM grid, Ti, Ag, and O elements were detected in the selected heterostructure and no other impurity atom was detected. The EDS elemental mapping images taken from the TiO$_2$–Ag$_2$O-1 nanorod are presented in Figure 4f. The Ti signals were homogeneously distributed over the region of the nanorod template. By contrast, the Ag signals were mainly distributed on the outer region of the composite nanorod; the distribution of Ag signals was discrete and randomly decorated on the TiO$_2$ surface. A good Ag$_2$O particle-decorated TiO$_2$ nanorod with a dispersive particle decoration feature was obtained in the TiO$_2$–Ag$_2$O-1 composite nanorods.
Figure 4. TEM analysis of the TiO$_2$–Ag$_2$O-1 composite nanorods: (a) Low-magnification TEM image of the TiO$_2$–Ag$_2$O-1 composite nanorod. (b, c) High-resolution TEM images taken from various regions of the composite nanorod. (d) Selected area electron diffraction (SAED) pattern of several TiO$_2$–Ag$_2$O-1 composite nanorods. (e) Energy dispersive X-ray spectroscopy (EDS) spectrum of the composite nanorod. (f) Ti, Ag, and O elemental mapping images taken from the selected composite nanorod.

Figure 5a shows the low-magnification TEM image of the TiO$_2$–Ag$_2$O-2 composite nanorod. In comparison with Figure 4a, the distribution density of the Ag$_2$O particles on the surface of the TiO$_2$ nanorod was denser and many particles were clustered, resulting in a rugged surface feature of the composite nanorod. The tiny Ag$_2$O particles aggregated together and fully encapsulated the surface of the TiO$_2$ nanorod. A clear heterointerface was observed between the TiO$_2$ and Ag$_2$O (Figure 5b, c). The distinct lattice fringes in the inner and outer regions of the composite nanorod in Figure 5b, c demonstrated a good crystallinity of the composite nanorod. The SAED pattern in Figure 5d supports the good crystallinity of the composite nanorods, as revealed in the high-resolution TEM images of the selected composite nanorod, and is also in agreement with the XRD result. Figure 5e shows the corresponding EDS spectrum of the TiO$_2$–Ag$_2$O-2 composite nanorod. Besides the carbon and copper signals and the elements of Ag, Ti, and O, no other impurity atom was detected from the selected composite nanorod. Notably, the relative intensity of the Ag signal was more intense than that of the TiO$_2$–Ag$_2$O-1 nanorod in Figure 4e, revealing a higher Ag content in TiO$_2$–Ag$_2$O-2 due to the prolonged sputtering duration of Ag$_2$O.
The O1s spectrum of the composite nanorods is shown in Figure 6d. The asymmetric O1s spectrum indicates the possible presence of oxygen vacancies in the surfaces of the as-synthesized TiO2. The distinct two features were deconvoluted into four subpeaks. The subpeaks centered at 529.2 and 531.2 eV existed in the Ag2O nanoparticles on the composite nanorods studied herein. The presence of the mixed Ti4+/Ti3+ valance state indicates the possible presence of oxygen vacancies in the surfaces of the as-synthesized TiO2 nanorods [5,8]. The O1s spectrum of the composite nanorods is shown in Figure 6d. The asymmetric O1s spectrum was deconvoluted into three subpeaks centered at 532.5, 531.2, and 529.2 eV. Notably, the subpeaks centered at 529.2 and 531.2 eV correspond to the lattice oxygen in Ag2O and TiO2, respectively [18,19]. Moreover, the external absorbed –OH groups or water molecules on the surfaces of the composite nanorods are reflected by a subpeak at approximately 532.5 eV [20].
Figure 6. XPS analysis of the TiO$_2$–Ag$_2$O-1 composite nanorods: (a) Survey scan spectrum. (b) Ag 3d narrow scan spectrum. (c) Ti 2p narrow scan spectrum. The red curve is associated with the contribution of the Ti$^{4+}$ valance state and the blue curve originated from the Ti$^{3+}$ valence state. (d) O1s narrow scan spectrum. The blue and pink curves are ascribed to the lattice oxygen in Ag$_2$O and TiO$_2$, respectively. Moreover, the green curve is ascribed to external absorbed –OH groups or water molecules on the surfaces of the composite nanorods.

Figure 7 shows the temperature-dependent gas-sensing responses to NO$_2$ (1.5 ppm) of gas sensors made from TiO$_2$, TiO$_2$–Ag$_2$O-1, and TiO$_2$–Ag$_2$O-2 composite nanorods. For the NO$_2$ target gas, the n-type gas-sensing response of nanorod-based sensors is defined as $R_g/R_a$ and the p-type gas-sensing response of nanorod-based sensors is defined as $R_a/R_g$, where $R_g$ is the sensor resistance under target gas exposure and $R_a$ is the sensor resistance with the removal of the target gas. The optimal operating temperature of oxide sensors to obtain the highest gas-sensing response is highly associated with the balance between the chemical reactions and the gas diffusion rate of the oxide surfaces [5]. The maximum responses of the TiO$_2$–Ag$_2$O-1 and TiO$_2$–Ag$_2$O-2 sensors to NO$_2$ were obtained at the operating temperature of 250 °C in this study. Meanwhile, a relatively high operating temperature of 275 °C was needed for the TiO$_2$ nanorods to obtain the maximum gas-sensing response under similar gas-sensing test conditions. Notably, the gas-sensing response versus operating temperature curve of TiO$_2$–Ag$_2$O-1 showed a distinct summit at 250 °C, differing substantially from the curves of the TiO$_2$ and TiO$_2$–Ag$_2$O-2 nanorod sensors. This result might be a sign of different gas-detecting mechanisms operating among the various nanorod-based sensors. Therefore, the optimal gas-sensing temperature of the fabricated composite nanorod sensors toward NO$_2$ was chosen as 250 °C in this study.
An approximate increase of the gas-sensing response by 2.4 times was observed with an increase in A similar conduction type variation due to the p-type crystal coverage TiO resistance upon exposure to the target gas, while the recovery time is the duration in which the sensor nanorod-based sensors is defined as the duration required for an occurrence of a 90% change in sensor aggregations on the surfaces of TiO response value larger than 2.0, revealing that the decoration of discrete or layered Ag TiO2–Ag2O-1 nanorods meant that, upon exposure to the NO2 target gas, the n-type conduction dominated the material’s gas-sensing behavior. By contrast, the TiO2–Ag2O-2 nanorods demonstrated a thick, full-coverage layer of Ag2O clusters or aggregations on the surfaces of the TiO2 nanorods. This morphology feature might account for the conduction and chemoresistive variation in the TiO2–Ag2O-2 sensor, which was dominated by p-type Ag2O shell layers of the composite nanorods. A similar conduction type variation due to the p-type crystal coverage effect on the p–n heterogeneous oxides has been demonstrated in a ZnO–Cr2O3 system [11]. Comparatively, the TiO2–Ag2O-1 sensor exhibited the largest degree of sensor resistance variation before and after the introduction of the NO2 gas under the given test conditions. Notably, the pristine TiO2 sensor demonstrated the lowest sensor resistance variation size upon exposure to NO2 gas. The plot of NO2 gas-sensing response versus NO2 concentration for various TiO2 nanorod-based sensors is shown in Figure 8d. The NO2 gas-sensing response of the TiO2–Ag2O-1 sensor was approximately 3.1 upon exposure to 0.5 ppm NO2. Moreover, the gas-sensing response of the TiO2–Ag2O-2 sensor increased to 7.6 upon exposure to 3.0 ppm NO2. An approximate increase of the gas-sensing response by 2.4 times was observed with an increase in NO2 concentration from 0.5 ppm to 3.0 ppm by the TiO2–Ag2O-1 sensor. By contrast, the TiO2–Ag2O-2 sensor exhibited gas-sensing responses of approximately 2.2 and 3.1 upon exposure to 0.5 ppm and 3.0 ppm NO2, respectively; these response values are lower than those of the TiO2–Ag2O-1 sensor under similar test conditions. A concentration-dependent increment of the gas-sensing response for a low concentration range of 0.5–3.0 ppm NO2 was less visible for the TiO2–Ag2O-2 sensor. Notably, the gas-sensing response of the pristine TiO2 sensor at the same operating temperature did not show a response value larger than 2.0, revealing that the decoration of discrete or layered Ag2O particles or aggregations on the surfaces of TiO2 nanorods to form a p–n heterogeneous system is beneficial to the enhancement of the NO2 gas-sensing response of TiO2 nanorods. The gas-sensing response time of the nanorod-based sensors is defined as the duration required for an occurrence of a 90% change in sensor resistance upon exposure to the target gas, while the recovery time is the duration in which the sensor resistance drops by 90% from the maximal steady-state value, following the removal of the target gas.
The response times for the TiO$_2$, TiO$_2$–Ag$_2$O-1, and TiO$_2$–Ag$_2$O-2 nanorods upon exposure to 0.5–3.0 ppm NO$_2$ gas ranged from 85 to 93 s. No substantial difference in the response times of various nanorod sensors exposed to different concentrations of NO$_2$ gas was observed. By contrast, a marked improvement in the recovery time of the TiO$_2$ nanorods sputtered with a coating of Ag$_2$O particles was visibly demonstrated. The recovery times of the pristine TiO$_2$ nanorod sensor ranged from 405 to 820 s after exposure to 0.5 to 3.0 ppm NO$_2$. Decreased recovery times were shown in the TiO$_2$–Ag$_2$O-2 nanorod sensor, which ranged from 191 to 280 s after exposure to 0.5 to 3.0 ppm NO$_2$. Notably, the TiO$_2$–Ag$_2$O-1 nanorod sensor exhibited a substantial decrease in the recovery time upon the removal of NO$_2$ gas; the recovery times ranged from 97 to 136 s in the NO$_2$ concentration range of 0.5 to 3.0 ppm. The size of the Ag$_2$O particles (or clusters) and their dispersibility are vital factors affecting gas-sensing performance, which lead to the highly effective desorption of surface-adsorbed ions with the removal of the target gas at elevated temperatures [21]. The TiO$_2$–Ag$_2$O-1 nanorod sensor exhibited the superior gas-sensing performance among the various nanorod sensors in this study. The cycling gas-sensing tests of the TiO$_2$–Ag$_2$O-1 nanorod sensor exposed to 1.5 ppm NO$_2$ at 250 °C are shown in Figure 8e. The result indicates that the TiO$_2$–Ag$_2$O-1 nanorod sensor had good reproducibility during multiple cycles of response and recovery. Figure 8f shows the across selectivity profiles of the TiO$_2$–Ag$_2$O-1 sensor upon exposure to 100 ppm H$_2$, 50 ppm C$_3$H$_6$OH, and 50 ppm NH$_3$ gases, as well as 3.0 ppm NO$_2$. The TiO$_2$–Ag$_2$O-1 sensor exhibited a highly selective gas-sensing response toward the low-concentration NO$_2$ gas as compared to the other various target gases.

The NO$_2$ gas-sensing performances of the sensors based on several TiO$_2$-based composite oxides are summarized in Table 1. Compared to previous works [22–25], the TiO$_2$–Ag$_2$O-1 nanorod sensor herein showed superior NO$_2$ gas-sensing performance under similar test conditions. The gas-sensing test results herein demonstrated that the TiO$_2$–Ag$_2$O composite nanorods decorated with discrete Ag$_2$O particles have potential for applications as NO$_2$ gas sensors at low concentrations.
surface chemisorption reactions occurring during the gas-sensing process of the TiO$_2$–Ag$_2$O composite nanorods upon exposure to NO$_2$ gas are described below:

\[
\text{NO}_2 + e^- \rightarrow \text{NO}_2^-,
\]

(1)

\[
\text{NO}_2 + \text{O}_2^- + 2e^- \rightarrow \text{NO}_2^- + 2\text{O}^-.
\]

(2)

The NO$_2$ molecules capture electrons from the oxide surface to form NO$_2^-$ ions; this engenders the electron density variation of the oxides. By contrast, the surface-adsorbed NO$_2^-$ ions are desorbed with the removal of the NO$_2$ gas and, consequently, in this process the recovery of the initial conditions takes place. Notably, the contact of the TiO$_2$–Ag$_2$O oxides form p–n junctions at the hetero-interfacial regions. This additionally formed potential barrier in the TiO$_2$–Ag$_2$O composite nanorods explains the superior gas-sensing responses of the composite nanorods compared to that of the pristine TiO$_2$ nanorods. A similar formation of heterogeneous p–n junctions improves the gas-sensing responses of composite nanorods, as has been demonstrated in ZnO–ZnCr$_2$O$_4$, ZnO–Mn$_3$O$_4$, and ZnO–Cr$_2$O$_3$ p–n composite structures [9–11]. Furthermore, the reasons for the NO$_2$ gas-sensing response of the TiO$_2$–Ag$_2$O-1 sensor being higher than that of the TiO$_2$–Ag$_2$O-2 sensor at the given test conditions are explained by the schematic mechanisms exhibited in Figure 9. The schematic of the gas sensor device is also shown in Figure 9a. When the Ag$_2$O particles are coated on the surfaces of the TiO$_2$ nanorods in a discrete configuration, the randomly distribution of the depletion region at the interface of the p-Ag$_2$O and n-type TiO$_2$ will initially narrow the space of the conducting channel along the radial direction of the TiO$_2$ (Figure 9a). Moreover, the exposure of the free surfaces of the Ag$_2$O particles and TiO$_2$ rods in ambient air also initially lead to a surface hole accumulation layer and depletion layer, respectively. Furthermore, following the decoration of the Ag$_2$O particles in a continuous layer configuration on the surfaces of the TiO$_2$ nanorods, the conducting channel in the TiO$_2$ will also be narrowed (Figure 9b). After introducing NO$_2$ gas into the test chamber, the depletion region size at the TiO$_2$–Ag$_2$O hetero-interfacial region of the TiO$_2$–Ag$_2$O-1 sensor varies due to the surface-adsorbed NO$_2^-$ ions. Moreover, the surface depletion region of the TiO$_2$ nanorods is also thickened. The variation of the depletion size at different regions, further narrowing the conduction channel size of the TiO$_2$ nanorods, results in the increased sensor resistance of the TiO$_2$–Ag$_2$O-1 nanorod sensor. By contrast, the TiO$_2$–Ag$_2$O-2 nanorod sensor exhibits a p-type conduction gas-sensing behavior in this study. This reveals that the conduction channel size in the TiO$_2$ nanorod of the composite nanorod no longer plays a vital role affecting the chemoresistive variation upon exposure to NO$_2$ gas. It has also been shown that in core–shell ZnO–ZnMn$_2$O$_4$ and ZnO–Cr$_2$O$_3$ nanostructures, the p–n contact regions at the hetero-interfaces no longer play significant roles in the gas-sensing reaction [10,11]. The conduction path in the Ag$_2$O layer, by contrast, dominates the gas-sensing response of the TiO$_2$–Ag$_2$O-2 nanorod sensor. Notably, when the TiO$_2$–Ag$_2$O-2 nanorod is exposed to NO$_2$ gas, the accumulation layer in the Ag$_2$O layer thickens. This increases the carrier number in the p-type Ag$_2$O layer; therefore, a decreased sensor resistance is expected. However, the surface Ag$_2$O layer-dominated chemoresistive variation size of the TiO$_2$–Ag$_2$O-2 nanorod sensor is expected to be lower than that of the TiO$_2$–Ag$_2$O-1

### Table 1. NO$_2$ gas-sensing performance of various TiO$_2$-based composites prepared using various methods in the operating temperature range of 200–300 °C [22–25].

| Composite Nanorods | Synthesis Method | Operating Temperature (°C) | Concentration (ppm) | Response (Ra/Rg) | Detection Limit (ppm) | Response/Recovery Time (s) |
|-------------------|------------------|-----------------------------|---------------------|-----------------|-----------------------|--------------------------|
| TiO$_2$–Ag$_2$O (this work) | Hydrothermal and solvothermal method | 250 | 1.5 | 5.5 | 0.5 | 87/112 |
| TiO$_2$–Er$_2$O$_3$ | Sol-gel method | 200 | 10 | 4.5 | 0.5 | N/A |
| TiO$_2$–V$_2$O$_5$ | Sol–gel and solvothermal method | 200 | 2 | 0.8 | N/A | N/A |
| TiO$_2$–Mo$_2$O$_3$ | Sol–gel method | 300 | 2 | 2.3 | 0.5 | 120/180 |
| TiO$_2$–Ga$_2$O$_3$ | Sol–gel method | 200 | 2 | 2.25 | N/A | 150/270 |

- The NO$_2$ molecules capture electrons from the oxide surface to form NO$_2^-$ ions; this engenders the electron density variation of the oxides. By contrast, the surface-adsorbed NO$_2^-$ ions are desorbed with the removal of the NO$_2$ gas and, consequently, in this process the recovery of the initial conditions takes place.
nanorod sensor, which is dominated by the rugged conduction channel size in the TiO$_2$ core region upon exposure to NO$_2$ gas. Therefore, the superior NO$_2$ gas-sensing performance was obtained by the TiO$_2$–Ag$_2$O-1 nanorod sensor in this study.

![Schematic illustrations for possible gas-sensing mechanisms of (a) TiO$_2$–Ag$_2$O-1 and (b) TiO$_2$–Ag$_2$O-2 toward NO$_2$ gas.](image)

**Figure 9.** Schematic illustrations for possible gas-sensing mechanisms of (a) TiO$_2$–Ag$_2$O-1 and (b) TiO$_2$–Ag$_2$O-2 toward NO$_2$ gas.

4. Conclusions

In summary, TiO$_2$–Ag$_2$O composite nanorods were synthesized through the combination of hydrothermal growth and sputtering methods. The structural analysis reveals that the as-synthesized TiO$_2$–Ag$_2$O composite nanorods have a high crystallinity. The electron microscopy analysis results demonstrate that a shorter Ag$_2$O sputtering duration causes the formation of TiO$_2$–Ag$_2$O composite nanorods decorated with discrete Ag$_2$O particles. Meanwhile, a prolonged Ag$_2$O sputtering process engenders the aggregation of numerous Ag$_2$O particles, which form a layered configuration on the composite nanorods. The formation of p–n junctions in the composite nanorods enhances their NO$_2$ gas-sensing performance as compared to pristine TiO$_2$ nanorods. Moreover, different gas-sensing mechanisms of the TiO$_2$–Ag$_2$O nanorods with various Ag$_2$O coverage morphologies account for the superior NO$_2$ gas-sensing responses of the TiO$_2$–Ag$_2$O-1 sensor at a low concentration range in this study.

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