Abstract: We studied the preparation and gas-sensing performance of a hybrid nanomaterial based on titania nanotubes and graphene derivatives. We fabricated the hybrid structure with tunable chemical-sensing properties, achieved by tailoring the structure and composition of graphene oxide and coupling it with titania nanotubes. The parameters of manufactured sensing structures were investigated for hydrogen and ammonia. Our experimental findings indicate that this research may demonstrate an efficient way to enhance the gas-sensing properties of metal oxide nanomaterials for health and safety applications.

Keywords: nanomaterials; titania; graphene; chemical sensor; gas sensor

1. Introduction

Modern gas-sensing systems based on nanotechnology may enable reliable and continuous detection of different gaseous compounds to control atmospheric pollutants and protect human health [1–5]. With their quantum-mechanical properties, wide-bandgap semiconductor nanostructures can affect the characteristics of functional devices [6–8]. Therefore, the application of semiconductor nanomaterials in the development of chemical gas sensors is of great interest [9–11]. Highly ordered transition metal oxide nanostructures have been considered as promising materials for applications in chemical gas sensors due to their good chemical stability and functional properties [12]. In this regard, well-ordered and highly aligned titania nanotubes, with their superior electron transport properties and large surface area, are very attractive structures for the fabrication of gas-sensing systems [13–17]. Herein, we report the preparation and investigation of sensing properties of titania-based nanotubular structures for their application in gas-detection devices. We studied the effect of the additive material on the functionalities of nanotubes to optimize their sensing performance. The morphology, structure, and composition of prepared materials were examined. The sensing properties of materials were studied for hydrogen (H₂) and ammonia (NH₃). We have analyzed the interaction mechanism between the prepared nanotubes and gaseous compounds, considering their structural and compositional modifications. The obtained results demonstrate that the fabricated sensing materials have potential for application in detection systems [17].

2. Materials and Methods

Titania nanotubes were prepared as follows: The metallic titanium films were deposited on alumina substrates by radio frequency magnetron sputtering. Then, metallic films were anodized in a two-electrode system Teflon cell at room temperature. We reported the detailed information on anodization procedure in our previous reports [16,18]. The prepared materials were crystallized via thermal treatment in a tubular furnace at 400 °C for 6 h. We reported the crystallization regimes and analysis of the samples in [19].
The morphological analysis of samples (Figure 1) was performed by means of a LEO 1525 scanning electron microscope (SEM) equipped with a field emission gun. In order to fabricate the hybrid material, we prepared an aqueous dispersion of graphene oxide. Then, we drop-casted the prepared dispersion on the surface of titania nanotubes. To carry out gas-sensing measurements, platinum electrodes and a heater were deposited on the surface of the sensing structures and on the backside of substrates by DC magnetron sputtering. The gas-sensing tests were performed in a test chamber and the measurements were controlled by a computer-controlled gas flow system. The sensor based on pure titania is denoted as S1 and the sensor based on the composite material is denoted as S2 (Figure 2).

![Figure 1. SEM images of the obtained samples. (a) The surface morphology of pristine titania nanotubes with different resolutions; (b,c) the morphologies of the fabricated composite material with different resolutions.](image)

![Figure 2. The dynamic response of obtained S1 and S2 sensors for different concentrations of H2 and NH3 at 200 °C.](image)

### 3. Results and Discussion

The results of the morphological analysis of samples are shown in Figure 1. The SEM observations confirmed that highly ordered titania nanotubes were successfully prepared. The tube diameter was 30 nm (Figure 1a). Figure 1b,c shows the surface morphology of the composite structure. As can be seen, the surface of the titania nanotubes was covered by graphene oxide sheets. Figure 2 presents the dynamic response of the fabricated S1 and S2 sensors for concentrations of 120, 240, and 480 ppm of H2 and 10, 20, and 30 ppm of NH3.
of NH$_3$. The sensing measurements were carried out at 200 °C. The graphene oxide significantly increased the response of the titania nanotubes towards H$_2$. Meanwhile, very small differences were observed between the sensing behavior of the S1 and S2 structures towards NH$_3$. The drastic enhancement in the response of the S2 sensor compared to S1 can be attributed to the depletion layer formed between the titania nanotubes and graphene oxide. In this case, the presence of more active centers improved the adsorption of H$_2$ on the surface of the hybrid material, which is important for its sensitivity.

4. Conclusions

We fabricated a hybrid structure based on titania nanotubes and graphene oxide. Then, we investigated its gas-sensing performance for H$_2$ and NH$_3$. Our experimental findings show that the depletion layer formed between two materials plays a crucial role in tuning the sensing response of the hybrid structure. The hybrid material exhibited a better sensing response towards H$_2$ compared to pristine titania nanotubes, indicating that this this is an efficient and promising way to enhance the sensing parameters of metal oxide gas sensors. Moreover, a noticeable difference between the responses of the composite structure and pristine nanotubes towards NH$_3$ was not observed, which indicates an enhancement in the selectivity of the composite.

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