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Hierarchically Assembled Titania Based Nanostructures: Innovative and Efficient Strategies for the Synthesis and the Improvement of Sensing Properties †

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Abstract: We have developed innovative and efficient strategy for the preparation and improvement of sensing performance of well-ordered titania nanotubes. We have synthesized different materials based on titania nanotubes using cost-effective techniques. The morphological and structural analyses of the prepared materials have been carried out. The sensing properties of the structures have been studied towards NO_2. Investigations have shown the functionalization process has crucial effect on sensing properties of titania nanotubes. The obtained results demonstrate that the prepared structures are promising for the potential applications in the area of chemical sensors for the environmental monitoring.

Keywords: titania; nanostructures; gas sensor

1. Introduction

Nowadays, environmental pollution is one of the major problems. Due to this reason the application of chemical gas sensors for air quality monitoring and control is very important. There are different toxic gases in the environment that are responsible for the pollution. Among these gases NO_2 plays major role in the atmospheric reaction that produces ground-level ozone. NO_2 is also generated during different combustion processes. NO_2 causes irritation of the throat and respiratory system. The presence of relatively higher concentrations of NO_2 causes severe respiratory diseases [1]. Metal oxide structures were used for fabrication of gas sensor devices due to their long time stability, good chemical and physical properties [2–4]. Metal oxides change their conductivity with exposure to oxidizing and reducing gasses. The working principles of the oxide materials based on this conductance change mechanism [5].

TiO_2 is a low cost oxide material with the unique properties. Recently, one-dimensional TiO_2 nanostructures with their large surface to volume ratio and variety of surface morphologies have been used in gas sensing application. This materials showed good response mainly to ethanol. acetone and hydrogen [3]. Different approaches have been developed to improve the sensing performance of TiO_2. Meanwhile, number of fabrication methods for preparation of one-dimensional

TiO_2 nanostructures, such as magnetron sputtering, hydrothermal synthesis, atomic layer deposition and electrochemical anodization have been developed [3].

Herein, we report synthesis and the improvement of sensing properties of well-ordered titania nanostructures. The fabricated material is based on niobium-mixed TiO_2 nanotubes (Nb-TiO_2). The structures were obtained by combination of magnetron sputtering and electrochemical anodization methods. The morphological and structural analysis of samples were carried out. The sensing properties of obtained materials were tested towards NO_2. Investigations have shown that we developed a cost-effective and easy synthesis method for the fabrication of high performance and small size chemical gas sensors for NO_2 detection.

2. Experimental

Nb-TiO_2 nanotube arrays were prepared by the electrochemical anodization of metallic Nb-Ti thin films deposited on alumina substrates. The deposition of the metallic films was performed by means of radio frequency (RF) magnetron sputtering. Then, the metallic films were anodized by potentiostatic mode using a two-electrode configuration. Anodization process was carried out at room temperature. Afterwards, the obtained samples were annealed at 400 °C. The formation and the growth mechanism of the prepaared materials were investigated. The morphological and the structural analyses of the nanotubes were carried out. To test the samples the platinum electrodes were deposited on the surface of the structures using RF magnetron sputtering. Then, the platinum heater was deposited on the backside of the substrates. The sensing properties of the samples have been studied toward NO_2 at 100 and 200 °C. The test chamber for gas sensing measurements is shown in Figure 1. Gas sensing tests were performed by means of the flow-through technique at atmospheric pressure. A constant synthetic airflow was used as carrier gas for the analyte dispersion. The gas mixtures for the sensing measurements were obtained by means of a computer controlled gas flow system. The relative humidity in the test chamber was 30%. The conductance of the obtained sensors was monitored by means of the volt-amperometric technique at constant voltage. Before the measurement at each temperature the samples were stabilized for 10 h.

Figure 1. The test chamber for the sensing measurements.

3. Results and Discussions

The morphological analysis of the samples were performed by means of scanning electron microscopy (SEM) using a LEO 1525 microscope equipped with field emission gun. The SEM images of the structures are reported in Figure 2. The average inner diameter of TiO_2 tubes is about 30 nm. The length of tubes, measured by cross-sectional SEM images, is ~900 nm. The obtained nanotubes arrays are debris free.

Figure 3 reports the the sensing properties of the structures towards NO_2. The sensing mechanism of the obtained n-type material depends on the adsorption/desorption reactions of gas molecules, that leads to the trapping of electrons and consequently a decrease in electrical conductance. The sensing tests were performed from 100 to 300 °C. The investigations showed that the kinetics increased slowly as a function of the operating temperature at 100 °C. The optimal operating temperature for the NO_2 gas was 200 °C. We have compared the conductance of the obtained material with our previous results obtained for titania nanotubes and find out that increase of concentration of Nb produces a clear improvement of titania conductance [6]. This is an important feature for application of titania in sensing devices.

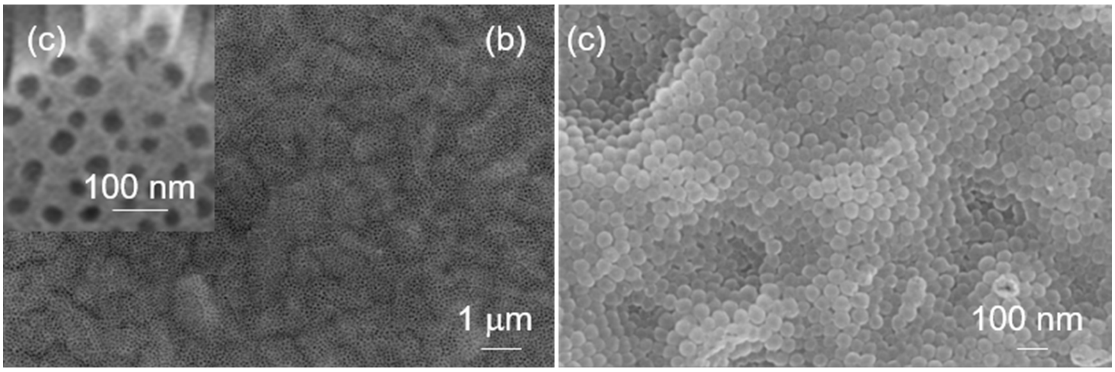

Figure 2. SEM images of the nanotube arrays: (**a**) morphology of nanotubes with the high resolution, (**b**) the top-view of nanotube array, (**c**) the bottom-view of nanotubes.

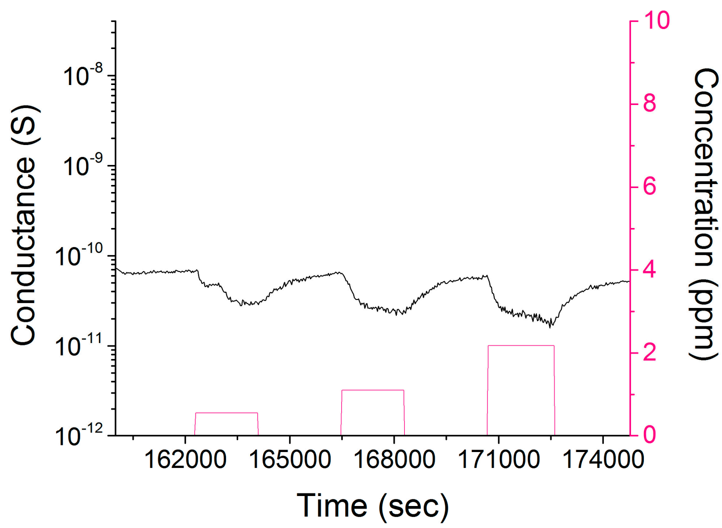

Figure 3. Variation of the sample conductance as a function of the introduction of different concentrations of NO_2 (0.5, 1 and 2 ppm) at 200 °C.

4. Conclusions

In summary, we have prepared Nb-TiO_2 nanotube arrays by low-temperature electrochemical anodization method for gas sensing applications. Morphological analysis have shown that well-aligned and highly ordered tubes with the large surface area have been obtained on alumina substrates. The gas sensing properties of the obtained structures have been investigated by exposing them to NO_2 gas. The prepared material have shown better gas sensing performance compared to the pure titania nanotubes for NO_2 at the relatively low working temperature. The obtained results show that Nb-TiO_2 tubular structures are promising for the development of gas sensing devices for the environmental monitoring.

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