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Two-Dimensional Titanium Oxide Nanosheets for NO_2 Gas Sensing at Room Temperature

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Abstract:
For the first time, we present NO_2 gas sensing performance of two-dimensional titanium oxide (2D TiO_x) nanosheets operating at room temperature. The TiO_x nanosheets have been synthesized via a wet chemical route. Material characterizations reveal TiO_x nanosheets with thickness of <1 nm. The developed sensor shows high and reversible response to NO_2 gas at room temperature. Sensing of NO_2 down to 600 ppb levels was measured.

Key words: 2D materials, titanium oxide nanosheets, gas sensor, room temperature, NO_2.

Introduction

Nitrogen dioxide (NO_2) is a highly poisonous gas produced as a byproduct in industrial applications such as internal combustion engines, food processing, petroleum refining, and thermal power stations. This gas is dangerous at concentrations greater than 1 ppm at which it can anesthetize a human's sense of smell, and therefore create a potential for overexposure [1]. Furthermore, NO_2 has a potential use as a biomarker in diagnostic processes [2]. Therefore, the realization of highly sensitive NO_2 gas sensors with low detection limit is of critical importance for different applications including health and environmental monitoring [3]. Room operating temperature for these sensors would enable them to be embedded in mobile systems for continuous monitoring of air quality.

Nanostructured titanium oxide materials have shown promising results for gas sensing applications [4]. To the best of authors' knowledge, NO_2 gas sensors based on nanostructured titanium oxide operating at room temperature (RT) have not yet been reported. In this work, we present a novel approach on the development of a room-temperature NO_2 gas sensor employing 2D TiO_x nanosheets.

Experimental

The 2D TiO_x nanosheets were prepared by a wet chemical method. Firstly, stoichiometric TiO_2 and K_2CO_3 (all chemicals from Sigma-Aldrich) powders were mixed and then heat-treated at 1073 K for 1 h in air, followed by another 20 h calcination at 1273 K. Note 3% excess of K_2CO_3 was used due to potassium volatilization. The obtained crystals ($K_{0.8}Ti_{1.8}O_4$) were then treated in 1 M HCl (1 g in 100 ml solution) at RT for 5 days with daily replacement of the HCl solution to convert the crystals into their protonic form. After that, the samples were washed thoroughly with pure water and centrifuged. The collected precipitates were dried and finally exfoliated into nanosheets by vigorous shaking for one week in a tetra-butylammonium hydroxide (TBAOH) solution (0.025 M) with a TBAOH/H^+ (H^+ in the protonic crystals) molar ratio of 1:1.

The synthesized TiO_x nanosheets were drop-cast on Au interdigitated electrodes (IDTs) with 200 µm gap, which were deposited on 10×10 mm^2 alumina substrate using electron beam evaporation system. The NO_2 sensing performance of the developed sensor at RT was investigated using a fully automated multi-channel gas testing system as shown in our previous work [5]. The response upon exposure

to the target gas was evaluated by measuring a change in the sensor's resistance while a bias voltage of 3 V was applied.

Results and Discussion

Fig. 1a shows the helium ion microscopy (HIM) image of the TiO_x film in a layer-by-layer structure made of <1 nm thick nanosheets. They provide a high surface area-to-volume ratio for gas adsorption.

Fig. 1b shows the size distribution of the TiO_x nanosheets under TEM. Though the contrast is low due to the extremely small thickness, the outline of the nanosheets can still be visualized. Fig. 1b inset is the selected area electron diffraction (SAED) pattern of a single TiO_x nanosheet being dropped onto the Cu grids. A few faint SAED rings with some bright spots are clearly observed, evidencing the single crystalline feature of the nanosheet and a high degree of exfoliation [5].

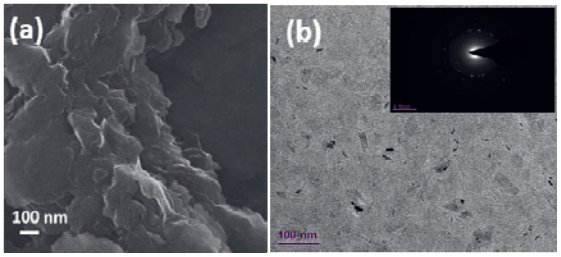

Fig. 1. (a) HIM image (b) TEM image of layered TiOx film on alumina substrate. Inset: SAED.

Fig. 2a shows the dynamic response of the developed conductometric sensor based on TiO_x nanosheet towards NO_2 gas with different concentrations at RT. A response of 28, 48.3, 55.3, 55.7 and 55% was recorded upon 10 min exposure to 0.6, 1.2, 2.5, 5 and 7.5 ppm NO_2, respectively. A plot of response magnitude as a function of NO_2 concentration is shown in Fig. 2b. Response time ($t_{90\%}$) decreased as the gas concentration increased. A response time of 6.9, 6.82, 5.25, 3.52 and 3.3 min was measured for 0.6, 1.2, 2.5, 5 and 7.5 ppm NO_2, respectively.

Conclusions

We successfully developed a novel NO_2 gas sensor based on TiO_x nanosheets operating at room temperature. The TiO_x nanosheets were synthesized using a simple and scalable wet chemical approach. The sensors showed high response to NO_2 with concentration as low as 600 ppb. A response of 28% was measured for 600 ppb NO_2. The sensor returned to the baseline after purging out the NO_2 gas at room temperature. The experimental results demonstrated that a TiO_x nanosheet is a promising material for gas sensing applications at room temperature, which characterized a p-type metal oxide semiconducting behaviour. Further investigations including surface functionalization will be conducted to improve the baseline stability and response and recovery time.

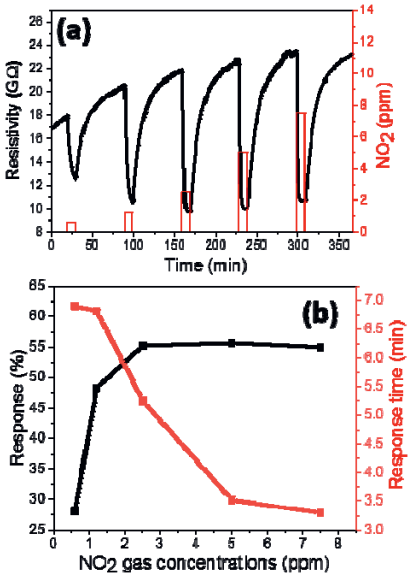

Fig. 2. (a) Dynamic response towards NO_2 and (b) response as a function of NO_2 concentration at RT.

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