Synthesis and LPG-sensing properties of TiO₂ nanowires

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Abstract. TiO₂ nanowires were synthesized by a hydrothermal process in KOH solution at 190°C using TiO₂ powder as a source material. Characterizations indicate the high degree of crystallinity with diameter of ca. 10-20 nm and length in micrometer scale of the obtained TiO₂ nanowires. Multiple nanowires gas sensors were fabricated by dispersing the TiO₂ nanowires on an interdigit Pt-electrode. The TiO₂ nanowires sensors show a high sensitivity to Liquefied Petroleum Gas (LPG) at working temperature of 400°C. The results demonstrate the possibility of using TiO₂ nanowires for gas-sensing application.

Keywords: TiO₂, nanowires, LPG, gas sensors.

1. Introduction

The synthesis and characterization of one-dimensional (1D) nanostructures (nanowires, nanotubes, nanorods) have received considerable attention due to their unique properties and novel applications. Miniaturization may represent the trend in a range of novel technologies. It is clear that a wealth of interesting and new phenomena are associated with nanoscale structures, with the best established examples including size-dependent excitation or emission [1], quantized conductance [2], Coulomb blockade (or single-electron tunneling, SET) [3], and metal-insulator transition [4]. It is generally accepted that the 1D nanostructures provide a good system to investigate the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement). They are also expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical, and electromechanical devices with nanoscale dimensions. In comparison with quantum dots and wells, the advancement of 1D nanostructures has been slow until very recently and has been hindered by the difficulties associated with the synthesis and fabrication of these nanostructures with well-controlled dimensions, morphology, phase purity, and chemical composition.

Although 1D nanostructures can now be fabricated (in the setting of a research laboratory) using a number of advanced nanolithographic techniques, further development of these techniques into practical routes to large quantities of 1D nanostructures from a diversified range of materials, and at reasonably low cost, still requires great ingenuity. In contrast, unconventional methods based on chemical syntheses might provide an alternative and intriguing strategy for generating 1D nanostructures in terms of material diversity, cost, throughput, and the potential for high-volume production [5].

Many methods have been successfully developed for the fabrication of 1D nanostructures,
including VS (vapor-solid), VLS (vapor-liquid-solid), SLS (solution-liquid-solid), template-based synthetic approaches and laser ablation [6]. However, almost all of these methods used either catalyst materials or physical templates, which unavoidably brought some contamination to the products. Therefore, it is very interesting to explore a new approach to synthesize 1D nanomaterials without using preformed templates or catalyst materials. Recently, the reaction between different TiO$_2$ precursors and a concentrated alkaline solution under moderate hydrothermal method is observed to be an effective approach to prepare 1D nanostructures of titania. Among various technologies available today in advanced materials processing, the hydrothermal technique occupies a unique place owing to its advantages over conventional technologies. A simple and cost-effective hydrothermal method for the large scale production of pure titania nanotubes of small diameters was introduced by Kasuga et al [7, 8].

Much effort has been concentrated on the important metal oxides such as SnO$_2$, TiO$_2$, ZnO [9]. TiO$_2$ is an n-type wide band-gap oxide semiconductor used for variety of applications such as gas sensors, dyesensitized solar cells, environmental purification, nanodevices, and photocatalysts [10-15]. TiO$_2$ nanostructured materials are particularly interesting because of their high specific surface area. We adopt a simple wet chemical approach to synthesize single crystalline TiO$_2$ nanowires. Moreover, this is a simple and cheap approach which is suitable for domestic research conditions.

In this report, we present the synthesis, microstructure, and the Liquefied Petroleum Gas (LPG) sensing characteristics of TiO$_2$ nanowires.

2. Experimental

2.1. Synthesis of nanowires based on hydrothermal processes

The TiO$_2$ nanowires were synthesized by a hydrothermal process and using commercial TiO$_2$ powder (Merck, 98%) as source material. In detail, 1 g of TiO$_2$ powder and 25 ml of 10 M KOH solution are stirred at room temperature for 24 h. The mixture was put into a teflon-lined stainless autoclave which was heated at 190$^\circ$C for 24 h. After that, it was naturally cooled down to room temperature. A white mixture was washed by deionized water to reduce KOH concentration. The obtained precipitation was filtered and washed with 1 M HCl solution until a pH value near 7 for eliminating potassium ions. After treating by HCl solution, the mixture was filtered and washed by deionized water, all washing steps were carried out by using a centrifuge. The experimental procedures flow is shown in figure 1.

![Figure 1. Schematic diagram of experimental procedure.](image)

The obtained titanium oxide nanowires were annealed at 400$^\circ$C for 30 min with the temperature increasing at the rate of 100$^\circ$C/h. The collected TiO$_2$ nanowires were ultrasonically dispersed in
polyethyleneglycol and then deposited on Pt-interdigitated electrode by drop-coating. The electrode was fabricated using conventional photolithography method as previously reported [16]. Finally, the sensors were heat-treated at 600°C for 30 min.

2.2. Characterizations
The morphologies and crystal structures of the TiO2 nanowires were characterised using field emission scanning electron microscopy (FE-SEM, HITACHI S4800), transmission electron microscopy (TEM, JEM-100cx instrument with an accelerating voltage of 80 kV) and X-ray diffractometer (PANalytical-Philips X’pert Pro with Cu Kα radiation λ = 1.54056 Å).

The LPG sensing properties of TiO2 nanowires were studied through the resistance change under LPG vapour atmosphere, for LPG concentrations of 500, 1000, 2000, 4000 and 8000 ppm, and at operating temperatures of 400°C. The response and recovery characteristics were monitored and recorded by using a precision semiconductor parameter analyzer (HP 4156A). Herein, the response was defined as the ratio R_air/R_gas, where R_air is the sensor resistance in air and R_gas is the resistance in the presence of reducing gas.

3. Results and discussion

3.1. Microstructure characteristics
Figure 2 shows FE-SEM image of TiO2 nanowires after heat treatment at 400°C for 30 min. The presence of numerous TiO2 nanowires with diameter of ca. 10-20 nm and length of ca. 700-800 nm was observed (see figure 3). In comparison with Ref. [17], it can be seen that the obtained TiO2 nanowires are more uniform, longer and have a larger aspect ratio.

Figure 2. FE-SEM image of TiO2 nanowires annealed at 400°C.

Figure 3. TEM image of TiO2 nanowires annealed at 400°C.

3.2. The gas sensing characteristics
The gas sensing property of the TiO2 nanowires were evaluated upon exposure to LPG. The sensors show an obvious response to the target gas at operating temperatures of 400°C. Figure 4 shows the dynamic responses of the TiO2 nanowires gas sensor towards 500, 1000, 2000, 4000 and 8000 ppm LPG vapour. One can see that the electrical resistance of the material dramatically reduced from 78.6 MΩ to 20.07 MΩ in the presence of 500 ppm LPG with response time of 25.2 s. The corresponding sensitivity of 3.9 was obtained. The response curve shows that the resistance of the sensor varies over time with various cyclic tests for different LPG concentrations (500, 1000, 2000, 4000 and 8000 ppm). It can be seen that the resistance increases and returns to the original value upon exposure to air. Thus, the as-synthesized materials are potential candidate for gas sensor application.
These measurements highlight also the complete recovery of the signal when the air flux is stored after the gas test. The response time, $\tau_{\text{res}}$, is defined here as the time it takes for the conductance of the gas sensor to increase to 90% of the maximum conductance when the target gas is introduced into an environment of air. The recovery time, $\tau_{\text{rec}}$, is the time required for 70% reduction in conductance when the target gas is turned off and air is reintroduced into the chamber (i.e., the time to reach 30% of maximum conductance value in the presence of the target gas) [18]. Response time decreases rapidly with increased gas concentration, whereas the recovery time increases with increasing gas concentration (see Figure 5).

Figure 6 shows the relationship between sensitivity and LPG concentration for the sensor operating at 400°C. It can be seen that the response of the sensor to LPG increases rather steeply with increasing gas concentration, without showing a saturating tendency up to 8000 ppm because there are still sufficient numbers of available surface states to act on LPG vapour. Linearity of response in the low concentration (< 2000 ppm) range is properly suited for the use of these TiO$_2$ nanowires in checking the concentration of LPG in domestic applications.

4. Conclusion
TiO$_2$ nanowires have been successfully synthesized by a hydrothermal process at 190°C for 24 h. The obtained nanowires exhibited diameter of ca. 10-20 nm and length of ca. 700-800 nm. The obtained TiO$_2$ nanowires are uniform, long and have a large aspect ratio. The response of the obtained nanowires to LPG concentrations of 500, 1000, 2000, 4000 and 8000 ppm at operating temperature of 400°C has been characterized.
The obtained results open new perspectives on fabricating devices based on TiO$_2$ nanowires for detecting LPG using wet chemical approaches.

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Acknowledgements
We sincerely thank the financial support of the project B2008-01-218, State Research Programme under project KC.02.05/0610 and the Vietnam-Italy International Cooperation project for the period of 2006-2008.