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Nanocarving of titania (TiO_2): a novel approach for fabricating chemical sensing platform

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Abstract

A simple, inexpensive method for producing titania (TiO_2) surfaces comprised of nanofibers has been discovered. These nanofibers are formed via the reaction of dense polycrystalline TiO_2 in a H_2/N_2 environment at 700 °C for 8 h. The nanofibers formed by this process have diameters of 15–50 nm and lengths of 1–5 μm. The preferred crystallographic orientation for this "nanocarving" process is the [0 0 1] direction and the nanofibers are single crystal TiO_2. Several processing variables are found to affect the nanofiber formation. The sintered state before the nanocarving treatment plays a critical role in the formation of nanofibers. The flow rate of H_2/N_2 gas during the treatment also influences the rate of nanofiber formation. Preliminary results show enhanced gas sensitivity, though the response is sluggish.

Keywords: D. TiO_2; E. Sensors; Nanofiber; Nanomaterials

1. Introduction

Recently, nanometer scale oxides have received significant attention because of their attractive electronic, photonic, catalytic, chemical, and bio-chemical properties. Titania (TiO_2) is one of the important engineering materials which has been used in chemical sensors [1,2], catalytic supports [3,4], and dye-sensitized solar cells [5]. Since the chemical events take place at the titania surface, the surface morphology and surface area play important roles in such applications. For example, it has been reported that the chemical sensitivity and catalytic activity of semiconductor sensors depend linearly on the surface area [6,7], because larger surface area provides more active sites for gas–solid interaction, resulting in large change of conductivity, or high sensitivity.

Many approaches have been explored for tailoring the surface morphology of titania by several researchers. Pan et al. reported ultra-long nano-belts of zinc, tin and indium oxide by evaporating commercial metal oxide powder at high temperatures [8]. A different approach was used by Imhof and Pine [9], where they produced porous titania structure by emulsion templating with ordered pores of about 50 nm diameter. Sugiura et al. [10] used photoelectrochemical etching for fabricating honeycomb-type channels on titania grains. In their experiments, they applied photo (UV light), electro (electrical potential) and chemical (aqueous solution) stimulants to produce the honeycomb nano-channels. However, the widespread utilization of advanced nanostructured materials is often complicated by the conflicting demands for precise control of fine features and for large-scale mass production. Therefore, novel methods for fabricating well-organized oxide nanostructures that are simple and that can be readily scaled up need to be identified to allow for rapid and low-cost manufacturing.

Recently, the authors developed a novel and very inexpensive method for the fabrication of titania surfaces with crystallographically-oriented nanofibers [11,12]. This paper reports the effect of the processing conditions on fiber formation as well as preliminary results on gas sensing using this structure.

2. Experimental

The starting material was commercial anatase TiO_2 powder (Alfa Aesar, 99.9% pure) having an average particle size

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of 32 nm. Preweighed powder of 0.3 g was pressed under a pressure of 392 MPa in a stainless-steel die by single-end compaction. The sintering was done in the temperature range of 1100–1400 °C for 8 h in air. The sintered pellet was 1 mm thick and 10 mm in diameter. Sintered titania samples were then exposed to an atmosphere of 5% H_2/N_2 at 700 °C for 8 h. Two gas flow rates were used, 100 and 500 ml/min. The surface impurity was detected by inductively-coupled plasma (ICP) with a laser ablation method. Although the sample contained ppm level impurities of Cu, Al, Ni, Cr, Fe and V, they did not play any role in the fiber formation.

A Philips XL-30 scanning electron microscope (SEM) was used to observe the surface morphology of nanofibers. The structure and chemistry of the titania nanofibers were examined with a Philips CM200 transmission electron microscope (TEM). The nanofibers were removed from the specimen surface by exposure to ultrasonic energy during immersion in methanol. The nanofibers were then collected onto a carbon-coated copper grid for TEM analyses involving bright field imaging and selected area electron diffraction (SAED). XPS (Perkin-Elmer Model 550 ESCA/Auger spectrometer) was used to determine the oxidation state of titanium.

The sensing measurement was done at 400 °C inside a sealed quartz tube fitted with an inlet and an outlet for gas flow. To fabricate a sensor device, two strips of conductive gold paste were painted on the nanofiber-covered surface and gold lead wires were attached by heat treating the assembly at 700 °C for a few hours. Gas flow through the test tube was controlled by a mass flow controller (MKS instruments, Austin, TX). The test gas concentrations were created by mixing (regulated by the mass flow controller) H_2 gas balanced with N_2. The sensing signal was recorded by a computer as a change in the electrical resistance of the sensor measured using a HP digital multimeter.

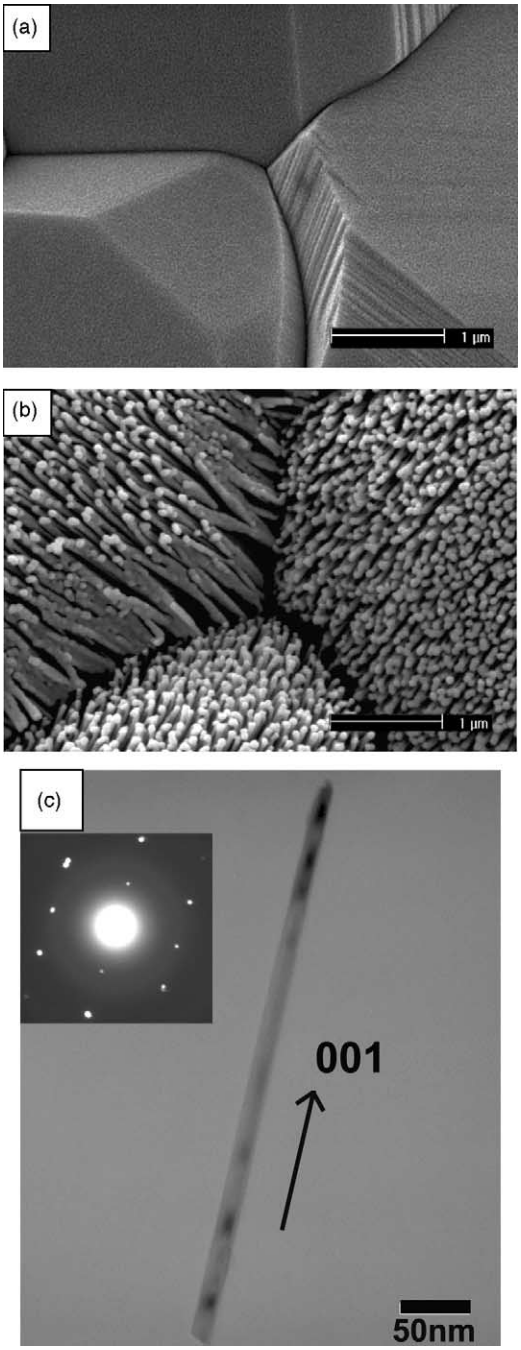

Fig. 1. Electron micrographs of titania surfaces showing the dramatic morphological change resulting from the H_2/N_2 treatment: (a) SEM image of rutile grains on the surface after the sintering heat treatment at 1200 °C for 6 h in air; (b) nanofibers formed on titatnia surfaces after exposure to a flowing 5% H_2/95% N_2 mixture for 8 h at 700 °C and (c) TEM image and selective area diffraction pattern (SAED) of a nanofiber.

3. Results and discussion

Before the nanocarving process, the sintered polycrystalline titania were composed of faceted grains that resulted

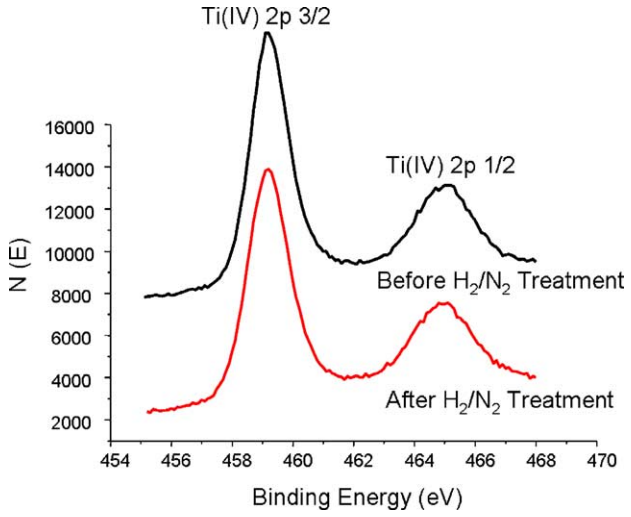

Fig. 2. X-ray photoelectron spectroscopy (XPS) of titania before and after the nanocarving treatment. The binding energy of the peaks represent Ti (IV) 2p and the peak position did not shift after the H_2/N_2 treatment.

from sintering at 1200 °C for 6 h (Fig. 1(a)). The average size of the rutile grains was 4.0 μm. The sintered pellets were exposed to a flowing 5% H_2/95% N_2 gas mixture at 700 °C for 8 h. An SEM image of the external surface of the specimen after the H_2/N_2 treatment is shown in Fig. 1(b). Fine fibers, with diameters of 15–50 nm and lengths of up to 5 μm, were observed to have formed on the external specimen surface.

As reported by the authors in an earlier publication [12], the nanofiber arrays formed as a result of an etching process (not a deposition process) that is selective to a specific crystallographic orientation. Fig. 1(c) shows a TEM image of a nanofiber along with its selective area diffraction (SAD) pattern. SAED patterns obtained at various positions along the length of a given nanofiber indicated that each nanofiber was comprised of a single rutile crystal. Such SAED analyses also revealed that the long dimension (fiber axis) of each nanofiber was parallel to the [0 0 1] crystallographic direction of rutile. When titania single crystals were heat treated in H_2/N_2, rectangular shape etch-pits were observed along the [0 0 1] direction with their walls pointed along <1 1 0>, though well developed fiber formation was not visible.

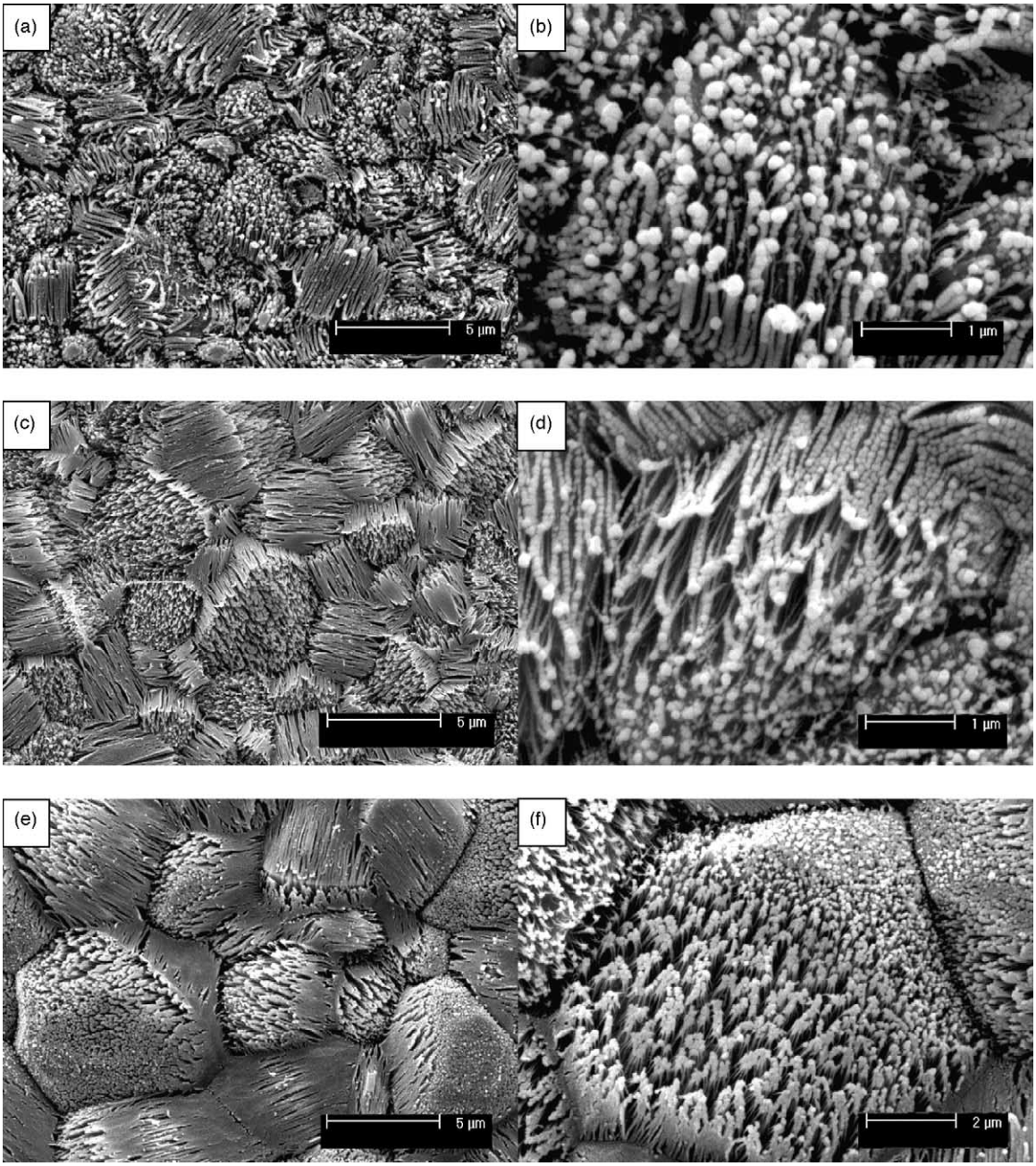

Fig. 3. Scanning electron micrographs after the nanocarving treatment of titania, which was sintered at: (a, b) 1100 °C; (c, d) 1200 °C; (e, f) 1300 °C and (g, h) 1400 °C. The left and right images are low and high magnifications, respectively.

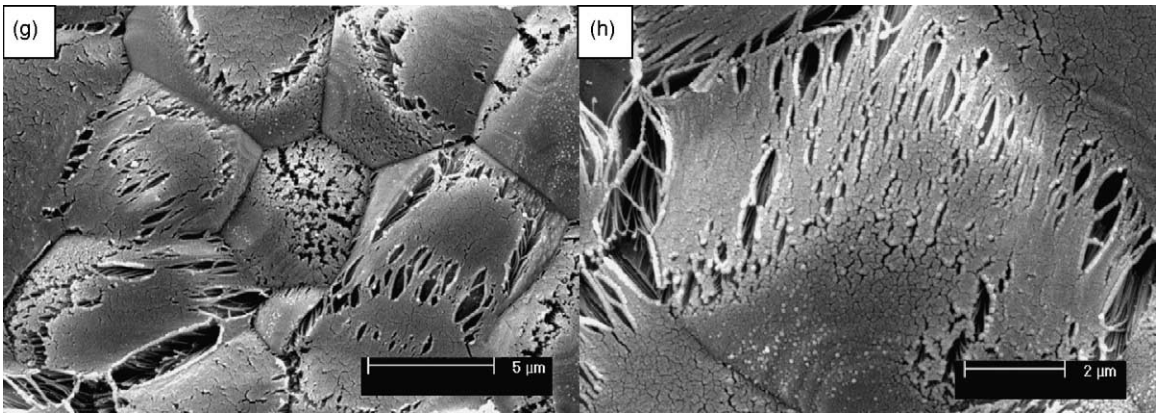

Fig. 3. (*Continued*).

The oxygen partial pressure established by the flowing 5% H_2/95% N_2 gas mixture at 700 °C was measured to be 10^{-19} Pa with a commercial oxygen sensor. The phase stability diagram reported for the Ti–O system indicates that a slightly reduced form of titanium oxide, TiO_{2-x} with $x = 0.02$, should be stable under these conditions [13]. Such a TiO_{2-x} stoichiometry could, in principle, be achieved by the generation of point defects (e.g., titanium interstitials and oxygen vacancies) or extended defects (e.g., shear planes and stacking faults) such as are present in the so-called Magneli phases [14]. Extended defects were not observed in the nanofibers by high-resolution TEM analyses, which suggested that the nanofibers were comprised of slightly-reduced rutile containing primarily point defects. Fig. 2 shows X-ray photoelectron spectroscopy (XPS) of specimens before and after the H_2/N_2 treatment. The binding energy of the peaks represent Ti (IV) 2p and the peak position did not change after the H_2/N_2 treatment indicating no change in the oxidation state of titanium.

Although the nanofiber formation requires only a two-step process (sintering in air and H_2/N_2 treatment), there are a few important requirements that must be met to obtain well-developed titania nanofibers. First, sintered samples with high density and large grain size (a few μm) seem to be needed. Several attempts to produce fibers in powder compact or samples with low density and small grain size were unsuccessful.

Second, sintering conditions (temperature and time) play critical role in creating faceted grains, and hence need to be optimized for a given batch of TiO_2 powder (Fig. 3). For this study, sample sintered at 1200 °C for 6 h showed well-developed nanofibers on the surface. For samples sintered below 1200 °C, titania surface seemed to be severely etched out and nanofibers couldn't be formed during the reduction treatment. Also, for samples sintered above 1200 °C, the degree of faceting diminished and consequently fibers were not well-developed.

The third condition for well-developed nanofibers is the control of gas flow rate during the H_2/N_2 treatment. Fig. 4 shows the gas flow rate dependence on the nanofiber formation. Nanofibers were formed in the whole grain at a high flow rate (~500 ml/min), while nanofibers were partially formed at a low flow rate (~100 ml/min). The dependence of nanofiber formation on the gas flow rate suggests that the

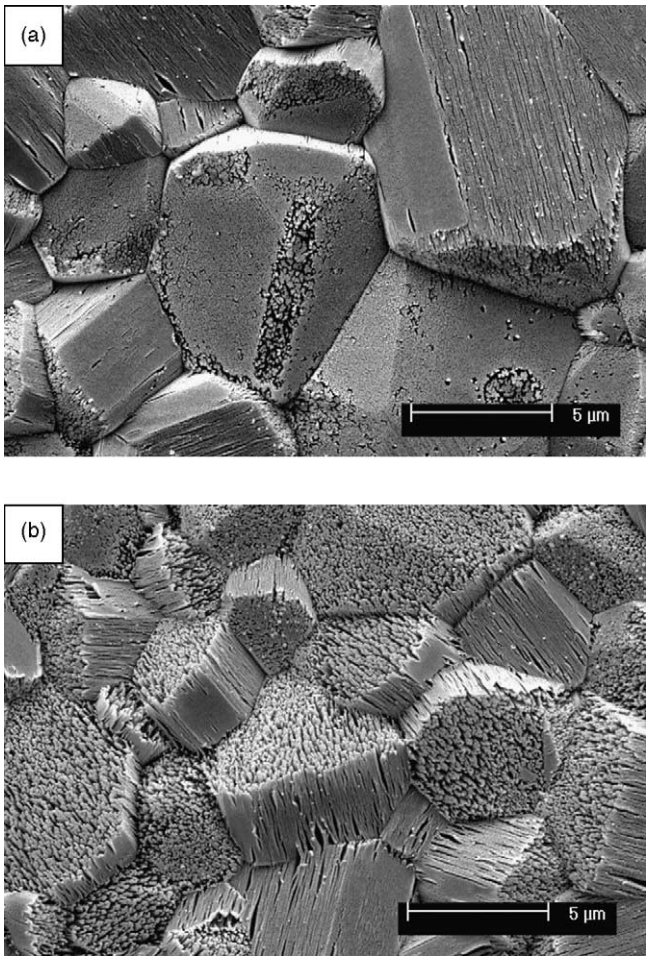

Fig. 4. Scanning electron micrographs of heat-treated titania at 700 °C in the H_2/N_2 atmosphere at a flow rate of (a) 100 ml/min and (b) 500 ml/min. The sample was sintered at 1200 °C for 8 h.

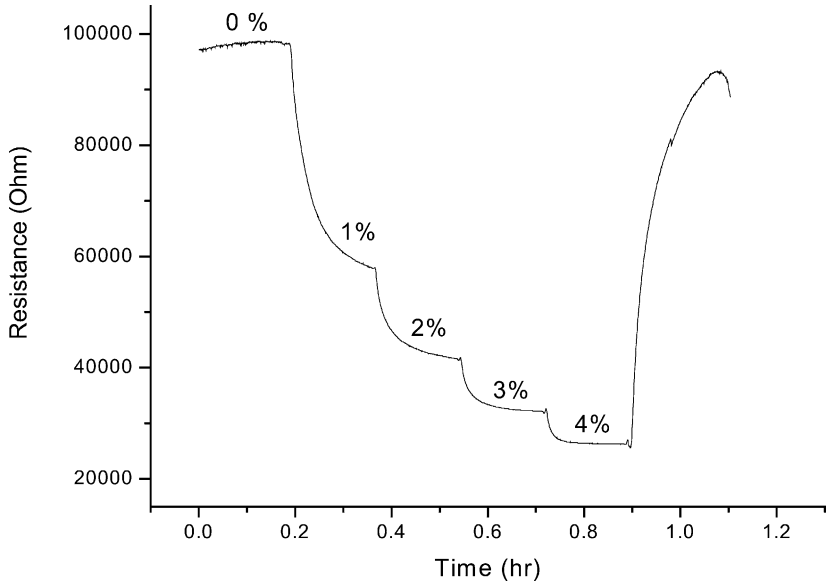

Fig. 5. Dynamic response changes in the electrical resistance of nano-fibrillar titania when exposed to 0–4% H_2 gas at 400 °C. The sample was sintered at 1200 °C for 8 h.

process depends on the diffusion of the reactant gas through a gaseous boundary layer or evaporation of products.

One of the potential applications of titania nanofibers is in the area of chemical sensors. As shown in Fig. 5, the resistance of the TiO_2 sample changed when it was exposed to H_2 gas and gradually saturated. Fig. 6 shows the sensitivity (R/R_0) of the sensor versus concentration of H_2. Sensitivity is defined as the resistance of the sensor at a given concentration of the target gas (saturated R values in Fig. 5) normalized by the resistance in the absence of the target gas (R_0). Comparing with sintered titania which showed practically no response, the nanofiber-based sensor exhibited good response due to increased surface area. Although the sensitivity is high, the response time seems to be a little longer (of the order of 10 min) than those of powder-based sensors.

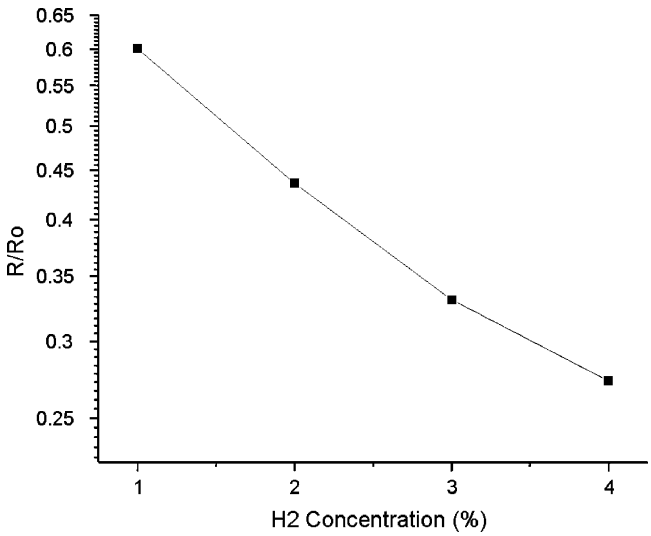

Fig. 6. Sensitivity (R/R_0; resistance of the sensor at a given H_2 concentration normalized by the resistance in the absence of H_2) vs. H_2 concentration.

4. Conclusions

A simple, modest-temperature gas–solid reaction-based "nanocarving" process has been developed for fabricating titania nanofibers. The nanofibers have diameters ranging between 15 and 50 nm and lengths of 1–5 μm. The arrays of nanofibers are oriented in the [0 0 1] direction and are single crystal TiO_2. Sintering conditions (temperature and time) play critical role in creating faceted grains and need to be optimized. Moreover, the gas flow rate during the H_2/N_2 heat treatment affects the process. For this study, samples sintered at 1200 °C for 8 h with a gas flow rate ∼500 ml/min during the nanocarving process show well-developed fibers. Preliminary sensing tests show enhanced sensitivity toward H_2, though the response is a bit sluggish. This reaction-based, nanocarving process can be readily scaled up (by continuous operation of controlled-atmosphere furnaces) to yield large quantities of low-cost, high-surface area titanium oxide nanofiber arrays with potential for catalytic, gas-sensing, electronic, and/or antimicrobial functions for a variety of environmental, biomedical, transportation, and chemical manufacturing applications.

Acknowledgements

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