

A facile route to synthesize titanium oxide nanowires via water-assisted chemical vapor deposition

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Received: 19 April 2010 / Accepted: 16 July 2010 / Published online: 10 August 2010
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Abstract Single crystalline rutile titanium oxide nanowires have been synthesized in bulk yield based on commercial metal titanium by a facile water-assisted chemical vapor deposition method. The morphology, crystallinity, and phase structure of the nanowires have been characterized by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and X-ray diffraction (XRD). This growth strategy is applicable for commercial metal titanium substrate with different spatial dimensions, such as powder, network mesh, and flat foil. The as-synthesized nanowires are found to be mainly composed of single crystalline rutile TiO₂ nanowires in spiral shape with a small amount of hexagonal Ti₂O nanowires with zigzag form. A growth mechanism has been proposed to explain the novel spiral and zigzag types of titanium oxide nanowires under moderate temperature (850 °C). This method promises an alternative way for industrialization of titanium oxide nanowires which may serve as a good candidate for

various industrial applications such as optoelectronic, electronic, and electrochemical nanodevices.

Keywords Chemical vapor deposition · Titanium oxide · Nanowires · Water vapor · Optoelectronic applications

Introduction

Since Fujishima and Honda (1972) reported that n-type titanium dioxide (TiO₂) could be used as a photo anode for a photo electrochemical cell, titanium oxide has been comprehensively investigated owing to its great applications in many fields. Titanium oxide possesses superior photo electrochemical conversion properties, excellent chemical and thermal stability, good electrical and optical properties, which make it a suitable candidate for solar cells (O'Regan and Grätzel 1991; Stergiopoulos et al. 2002), photo-degradation (O'Neill et al. 2003) and photocatalysis (Sung et al. 2006), optical (Wijnhoven and Vos 1998; Richel et al. 2002; Appell 2002) and electronic (Masumoto et al. 2001; Chambers et al. 2001) devices, gas sensors (Varghese et al. 2003; Rothschild et al. 2005), wastewater purification and self-cleaning coatings (Diebold 2003; Bonhote et al. 1999). With the research marching into nanoscale regime, anisotropic titania nanostructures, such as nanofilms (Damiriu et al. 2002), nanorods (Lan et al. 2005; Xiong and Balkus 2005; Peng and Chen 2004, 2005; Wu and Yu

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2004; Pradhan et al. 2003), nanowires (Miao et al. 2002; Lei et al. 2001; Wang et al. 2006; Xiang et al. 2005; Wu et al. 2005; Lee et al. 2006; Liu and Huang 2005), nanowalls and nanotubes (Lan et al. 2005; Wang et al. 2006; Liu et al. 2002; Kasuga et al. 1999; Yao et al. 2003), have stimulated great interest due to their high specific surface area, large sensitivity and high catalytic activity, which promise their significantly enhanced applications.

Recently, the potential of rutile titanium oxide as a non-platinum catalyst for fuel cells application has been reported (Kim et al. 2007), in which (110) plane of the titanium oxide shows highest catalytic activity for the oxygen reduction reaction.

Generally, the techniques of synthesizing nanostructured titanium oxide can be divided into two categories: (1) wet-chemical methods such as sol–gel (Miao et al. 2002; Lei et al. 2001; Liu et al. 2002), hydrothermal or solvothermal method (Lan et al. 2005; Xiong and Balkus 2005; Lei et al. 2001; Kasuga et al. 1999; Yao et al. 2003; Peng and Chen 2006); (2) “dry” methods such as physical vapor deposition (PVD) (Damiriu et al. 2002; Xiang et al. 2005), chemical vapor deposition (CVD) (Peng and Chen 2004, 2005; Wu et al. 2005; Lee et al. 2006), metal-organic chemical vapor deposition (MOCVD) (Wu and Yu 2004; Pradhan et al. 2003). The wet-chemical processes, with the advantage of easy scaling up, generally require post treatment and they are difficult to be integrated with semiconductor device fabrication (Xiong and Balkus 2005; Lei et al. 2001). In addition, further heat treatment is required to improve the crystallinity of the titanium oxide nanostructures, which adds to the complexity of the synthesis. “Dry” methods, on the other hand, have drawn more attention in synthesizing titanium oxide nanostructures with the advantage of high purity and crystallinity, as well as superior compatibility with conventional wafer processing. Xiang et al. (2005) fabricated TiO₂ nanowires using PVD method, Wu et al. (2005) manufactured TiO₂ nanowires using CVD method using O₂ as the oxygen sources and Wu and Yu (2004) made both TiO₂ nanorods and nanowalls using MOCVD method. However, all these methods need a vacuum at 10⁻³ Torr. Lee et al. (2006) manufactured TiO₂ nanowires using CVD method with the help of Au catalyst particles as well as vacuum. Peng and Chen (2004, 2005) produced TiO₂ nanorods by oxidizing the titanium metal directly with acetone or

dibutyltin dilaurate (DBTDL) as the oxygen sources. Although TiO₂ nanowires have been synthesized by several methods as mentioned above, it is still a big challenge to offer a facile way to synthesize TiO₂ nanowires with oriented growth in large scale and realized commercial manufacture of TiO₂ nanowires. In this paper, we have developed a facile template-, catalyst- and vacuum-free, medium temperature (850 °C) CVD method to obtain high yield rutile titanium oxide nanowires by simply introducing water vapor into a metal titanium-containing system. It has been found that oriented growth of the nanowires along [110] crystal direction dominates the growth process. The growth is applicable for metal titanium with different geometric shapes such as titanium powder, titanium mesh and titanium foil, and the results indicate that the titanium with a high surface area may benefit the growth of titanium oxide nanowires. Structural characterization indicates that the products are composed of majority spiral-shaped TiO₂ nanowires and minority zigzag-shaped Ti₂O nanowires. Growth process and possible growth mechanism of the products are systematically discussed. This method makes it possible for industrialization of synthesizing titanium oxide nanowires in a well-controlled and cost effective way.

Experimental methods

Three kinds of substrates were employed in this experiment. When either Ti foil or Ti mesh was employed, the substrate was pretreated by 37% w/w hydrochloric acid at 80 °C for 5 min then metal titanium powder, pretreated titanium foil or mesh was put in an Al₂O₃ boat placed inside a quartz tube of a horizontal quartz tube furnace. Before heating up, the furnace was firstly purged with pure argon (99.999%) for about 2 h at a flow rate of 400 sccm to exclude the air in the system. Meanwhile, water vapor was introduced into the system by passing the argon through a water bubbler. Subsequently, the furnace was heated to 850 °C with a ramping rate of 60 °C/min and argon flow rate of 400 sccm. Then the temperature was held at 850 °C for 2 h before cooling down to room temperature under flowing argon gas and water vapor.

The samples were characterized by Hitachi S-4500 field-emission scanning electron microscope (SEM)

operated at 5.0 kV, a JEOL 2010 FEG transmission electron microscope (TEM) at 200 kV for high-resolution imaging and selected area electron diffraction determination, and Rigaku-Miniflex X-Ray diffractometer using Cu K α (λ for K α = 1.54059 Å) radiation operated at 30 kV and 15 mA.

Results and discussion

Figure 1 shows general morphology of titanium oxide nanowires grown on Ti foil (Fig. 1a, b), Ti mesh (Fig. 1c, d) and Ti powder (Fig. 1e, f) by SEM. Although one-dimensional growth was observed on

the Ti foil substrate, the size and the structure of the product is significantly different from the ones obtained on Ti mesh and powder substrates. The latter features high density and uniform size distribution of the one-dimensional products. High magnification pictures in Fig. 1d and f show that the diameter of a single nanowire varies along the direction from base to tip, showing a needlelike shape. The low magnification SEM image in Fig. 1e shows that the nanowires are very dense and it is hard to distinguish the size of starting Ti particles as shown in Fig. 1f. The length of the nanowires reaches more than 20 μ m.

Figure 2a is a typical XRD pattern of the prepared sample. All peaks except the first one (arising from the

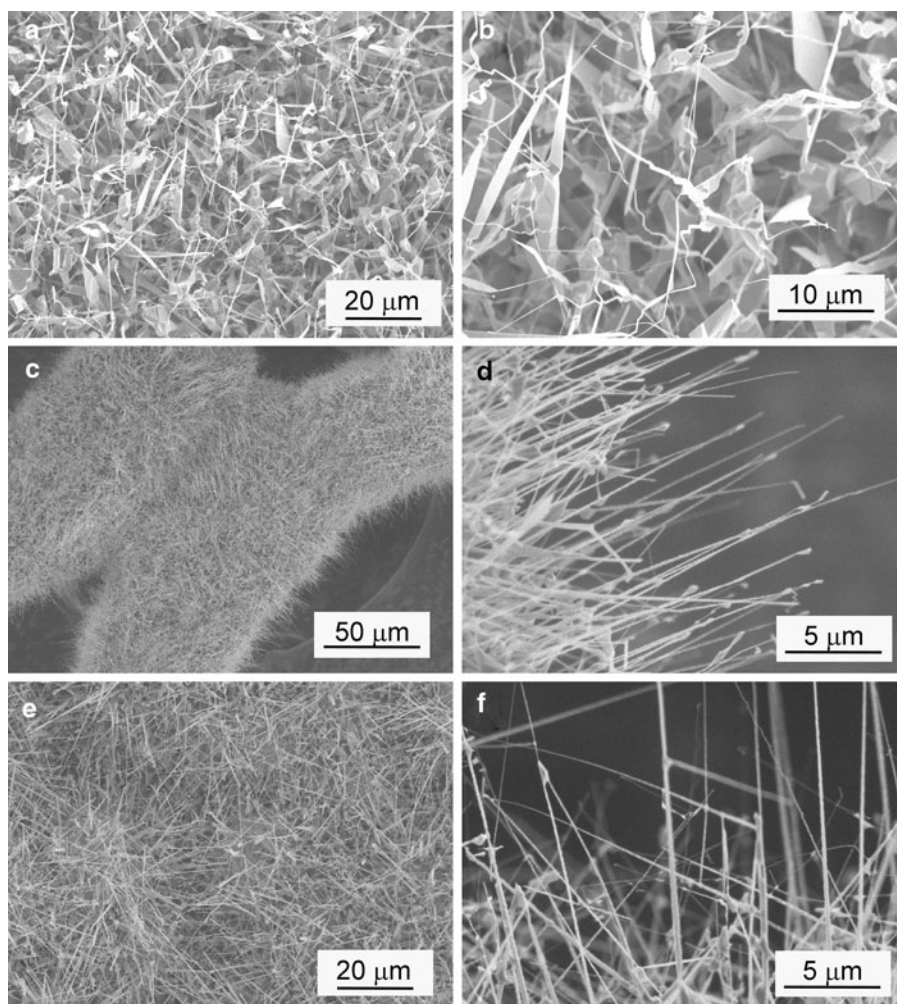


Fig. 1 SEM images of TiO $_x$ nanowires on (a, b) Ti foil, (c, d) Ti mesh, and (e, f) Ti powder

sample supporter) are indexed to TiO_2 rutile crystal structure [JCPDS 21-1276], indicating that TiO_2 rutile nanowires have been successfully synthesized by water-assisted CVD method. Although the diffraction peaks of different crystal planes appear in the pattern, the strongest peak of (110) plane indicates preferentially oriented growth of the nanowires in the [110]

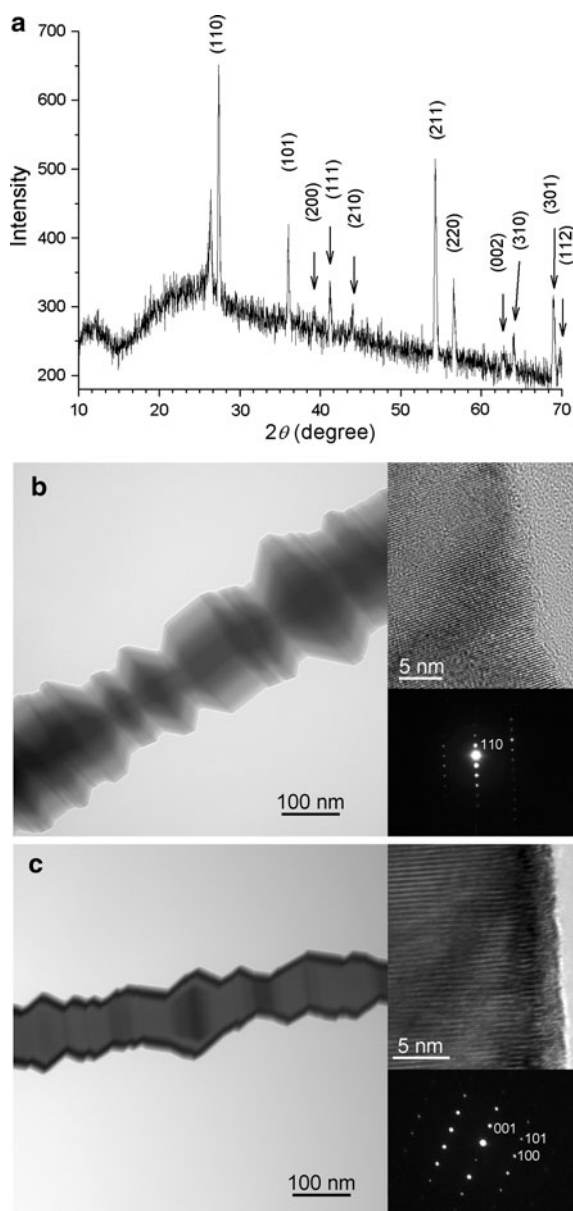


Fig. 2 **a** XRD pattern of titanium oxide nanowires on carbon paper. HRTEM images and SEAD pattern of two kinds of nanowires structure **b** and **c**

direction. Figure 2b and c show TEM characterization of these nanowires. As shown on the left panel of Fig. 2b, the diameter of a typical nanowire is changing continually along the length direction. The diameter of the thinner end of the nanowire is larger than 100 nm. Besides the majority spiral nanowires, some minority nanowires were also found as shown on the left panel of Fig. 2c. Although the diameter of this type of the nanowires is also changing incessantly, the shape of the nanowire exhibits a zigzag form, which is significantly different from the one shown in Fig. 2b. In addition, the diameter of zigzag-shaped nanowires is surely smaller than 100 nm, which is thinner than that of the spiral nanowires.

To understand the difference between these two kinds of structures, high-resolution transmission electron microscopy (HRTEM) observation and selected area electron diffraction (SAED) were conducted to obtain detailed structure information. The figure at the upper right corner in Fig. 2b shows the HRTEM image of a spiral nanowire, revealing a crystalline structure with an inter-planer spacing of 0.328 nm, in agreement with the d value of the (110) planes of the tetragonal rutile TiO_2 crystal structure whose lattice constants are $a = 4.593 \text{ \AA}$, $c = 2.959 \text{ \AA}$ and the space group is $P42/mnm$ (136) [JCPDS 21-1276]. The corresponding SAED of (110) plane shown at the lower right corner of Fig. 2b was recorded perpendicular to the lattice fringes, revealing that [110] is the favorable growth direction of TiO_2 nanowires. This suggests a faster growth rate along the [110] direction than that in other crystal directions, resulting in one-dimensional nanowires. The figure at the upper right corner of Fig. 2c shows the HRTEM image of a zigzag nanowire with an inter-planer spacing of 0.489 nm, in agreement with the d value of the (001) plane of the hexagonal Ti_2O crystal structure whose lattice constants are $a = 2.9593 \text{ \AA}$, $c = 4.8454 \text{ \AA}$ [JCPDS 11-0218]. The corresponding SAED pattern in the lower right corner of Fig. 2c matches well with the HRTEM image, revealing that [001] is the favorable growth direction of these Ti_2O nanowires.

The combination of XRD and HRTEM characterization reveals that the nanowires are mainly composed of rutile TiO_2 nanowires with spiral shape, along with a small amount of hexagonal Ti_2O nanowires with zigzag form. However, the amount of Ti_2O nanowire is too small to be detected by XRD.

Growth mechanism

To achieve the controlled growth of the titanium oxide nanowires, it is important to understand the growth mechanism of these nanowires. Since there are no catalysts employed in this growth process, vapor–liquid–solid (VLS) or solid–liquid–solid (SLS) mechanism can be excluded. In addition, due to the low probability of forming titanium vapor species at the processing temperature of 850 °C in this work it is also unlikely for the nanowires to grow by VS mechanism. It is well known that titanium oxide thin films can be effectively prepared through high temperature oxidation, which relates to the diffusion of titanium ions via interstitial sites and the diffusion of oxygen ions via vacancy sites. In our study, TEM investigation indicates that the nanowires are mainly composed of TiO₂ nanowires grown along [110] crystal direction, which is perpendicular to *c*-axis, implying an oriented growth of the nanowires induced by anisotropic diffusion. From the understanding of oxygen diffusion kinetics in the rutile titanium oxide, oxygen diffuses faster in the direction perpendicular to *c*-axis than that of parallel with the *c*-axis (Haul and Dumbgen 1965), while titanium diffuses much faster along the *c*-axis (Huntington and Sullivan 1965).

As reported by Shannon (1964), presence of hydrogen and/or water vapor can greatly promote the formation of oxygen vacancies, which increases the diffusivity of oxygen ions and reduces the diffusivity of titanium interstitials. This is in consistent with our finding that water vapor plays a crucial role in triggering the much higher growth rate (10–15 μm/h) of titanium oxide nanowires as compare to previously reported rate of 1–2 μm/h (Peng and Chen 2004). In addition, Badescu and Mormirlan (1996) reported the diffusion of oxygen dominates at the temperature of 850 °C, which is the temperature applied in our study. Based on the above analysis, we propose a growth mechanism governed by oxygen diffusion. The schematic diagram is shown in Fig. 3. In a metal titanium-containing CVD chamber (Fig. 3a) at high temperature, water vapor was introduced to act as the oxygen source. With the dissolution of water vapor, oxygen species diffuse into the titanium metal until the oxygen is saturated, as shown in Fig. 3b. Titanium oxide nucleates on the surface due to the supersaturation of the oxygen on the surface, then the newly formed titanium oxide attaches at the base of the

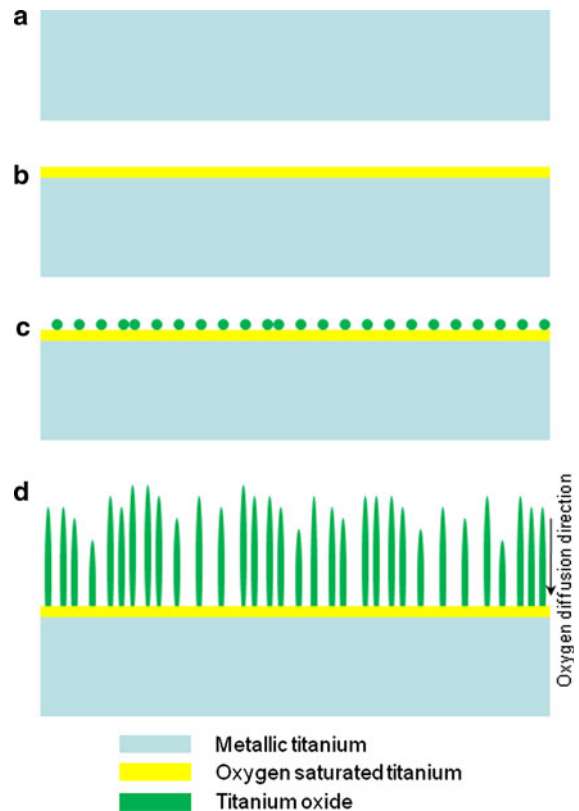


Fig. 3 Schematic graph of the proposed growth mechanism

existing nuclei, as shown in Fig. 3c. Because of the volume expansion caused by the oxidation, compressive stress was generated in the oxide layer acts as the diffusion driving force and meantime pushes the nuclei upwards (Barsoum et al. 2004).

Driven by the stress, oxygen diffuses along [110] crystal direction within the lattice, which results in an oriented growth of titanium oxide nanowires along [110] crystal direction as shown in Fig. 3d. On the other hand, the nanosized grain boundaries and the high density of defects provide a network for short circuit diffusion paths, which accelerates the oxygen ion's diffusion. From SEM and TEM observations, the as-synthesized nanowires show spiral-shaped (Fig. 2b) and zigzag-like (Fig. 2c) structure rather than typical nanowires with smooth surface, indicating large strain generated during the nanowire growth. As a result of oxygen introduced defects, spiral or zigzag-shaped nanowires are formed to reduce the strain built-up during the nanowire growth (Johansson et al. 2006; Fang et al. 2005). In our experiments, titanium substrates with three different morphologies

including titanium mesh, titanium powder, and titanium plate were employed as the titanium source. When we propose the solid phase diffusion growth mechanism working in the three cases, the morphology and size difference of the nanowires grown from different substrates have to be addressed. The mesh substrate favors the growth of high density nanowires with more uniform size, while the plate substrate gives low density nanowires with wide diameter distribution. This phenomenon may be due to different specific surface areas of the different substrates. The mesh substrate possesses a large specific surface area which provides more effective diffusion tunnels of oxygen species and increases the possibility of the nanowire nucleation and thereby promotes the growth of the high density nanowires with uniform size. In the case of the plate substrate, limited effective reaction area between the plate and the oxygen species restricts the oxygen diffusion into the substrate and results in the growth of non-uniform nanowires with low density. The growth on the powder substrates can be considered as an intermediate case between the two cases mentioned above. Although the majority of TiO₂ nanowires grew along [110] direction, a few Ti₂O nanowires grown along [001] direction were also observed. Since both Ti and Ti₂O have hexagonal structures, and a small amount of oxygen could drive the Ti to Ti₂O transformation owing to the similarity in their crystal structures and the small lattice mismatch (Liu et al. 2004). In addition, the preferential diffusion direction of titanium in rutile titanium oxide is along [001] direction. Therefore, the generation of Ti₂O nanowires may be ascribed to the epitaxial growth of the titanium oxide on titanium metal governed by titanium diffusion along *c*-axis.

Further work is underway in our group by exploring the TiO₂ nanowires with the oriented growth direction as the catalyst and electrode material for proton exchange membrane fuel cells applications.

Conclusions

In this paper, high yield TiO₂ nanowires mixed with a small amount of Ti₂O nanowires have been successfully synthesized from metal titanium by chemical vapor deposition method with the assistance of water vapor. SEM, TEM, SAED, and XRD are employed to investigate the morphology and structure of produced

nanowires. Based on our observation, a diffusion growth mechanism is proposed. This method makes it possible for cost effectively synthesizing large scale titanium oxide nanowires with well-controlled morphology. The as-synthesized single crystal TiO₂ nanowires are expected to be a good candidate for various industrial applications.

Acknowledgments This research was supported by General Motors of Canada, the Natural Science and Engineering Research Council of Canada (NSERC), Canada Research Chair (CRC) Program, Canadian Foundation for Innovation (CFI), Ontario Research Fund (ORF), Early Researcher Award (ERA), and the University of Western Ontario. We are in debt to David Tweddell, Fred Pearson and Ronald Smith for their kind help and fruitful discussions.

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