Chapter 22
Synthesis, Characterization and Sensing Applications of Nanotubular TiO_2-Based Materials

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Abstract TiO_2-based nanotubular materials have been synthesized by different methods, i.e. anodic oxidation of Ti foils, hydrothermal process and atomic layer deposition of titania on carbon nanotubes. The effect of the different synthesis methods on the final characteristics of the nanotubular materials obtained have been evaluated by a detailed morphological and microstructural investigation carried out by SEM, TEM and XRD. Films of the synthesized nanotubular TiO_2, deposited on QCM substrates, have shown a promising potential for the monitoring of hydrogen at room temperature.

22.1 Introduction

Nanotubular materials are characterized by extraordinary electrical properties providing prototypical systems to study physics at the nanoscale. They also promise exciting new opportunities and challenges for potential applications in electronic devices, photocatalysis, electrodes for fuel cells and batteries,

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dye-sensitized solar cells and sensors. Among the nanotubular materials, carbon nanotubes (CNTs) have shown an impressive impulse since their first synthesis in 1991. In recent years, research on nanotube materials have developed into new areas, comprising inorganic and organic/inorganic hybrid nanotubes [1].

Metal oxide-based nanotubes, such as SnO_2, V_2O_5 or TiO_2 are particularly interesting in view of their application in chemical sensors [2]. In this communication we focused our attention on the preparation of TiO_2-based nanotubular materials by different approaches. Specifically, TiO_2 nanotubes have been prepared either by a hydrothermal process and anodic oxidation of Ti foils [3]. Hybrids TiO_2/CNTs nanotubular composites have been also prepared by a novel atomic layer deposition (ALD) process, which allows the coating of CNTs at low temperature, with a precise thickness control at nanometer level, smooth surface, and excellent conformality [4, 5].

The nanostructure of the synthesized TiO_2-based materials was then investigated by SEM, TEM and XRD, with aim to study the effects of the different synthesis conditions on the characteristics of final products. At last, films of the synthesized TiO_2-based nanotubular materials were investigate regarding their hydrogen sensing properties at room temperature.

22.2 Experimental

TiO_2 nanotubes-based materials have been prepared by the following approaches: (1) anodic oxidation of Ti foils; (2) hydrothermal process; (3) coating of CNTs.

Anodic oxidation of Ti foils has been carried out in a stirred electrochemical cell, at room temperature and atmospheric pressure. An Autolab PGSTAT30 potenziostat in a two electrode set-up was used to apply different anodizing voltages: 50 V for times of about 3 h 1/2 in ethylene glycol electrolyte with 0.3 wt% NH_4F and H_2O 2% vol. A platinum electrode served as a cathode.

The synthesis of TiO_2 nanotubes has been performed by a hydrothermal process in a Teflon-lined autoclave at temperatures ranging from 90 to 190°C for 3 days. The starting material, consisting in 0.5 g of tanium dioxide powder, was dispersed in 13 ml, 10 M NaOH aqueous solution pH 6 with deionized water under vacuum. After the synthesis the resulting suspension was washed until and the powders finally dried at 300°C for 20 h in air.

The synthesis of TiO_2/CNTs was done in an ALD reactor working in exposure mode from titanium isopropoxide and acetic acid. Applied Science nanotubes were used as support and treated with concentrated HNO_3 at 100°C for 2 h before deposition. By using carboxylic acids as oxygen source instead of the more traditionally used ones (e.g. water, ozone, oxygen, etc.) titania coating can be grown from the metal alkoxide precursor even at low temperatures.

The morphology and microstructure of the samples were investigated by SEM, TEM and XRD.

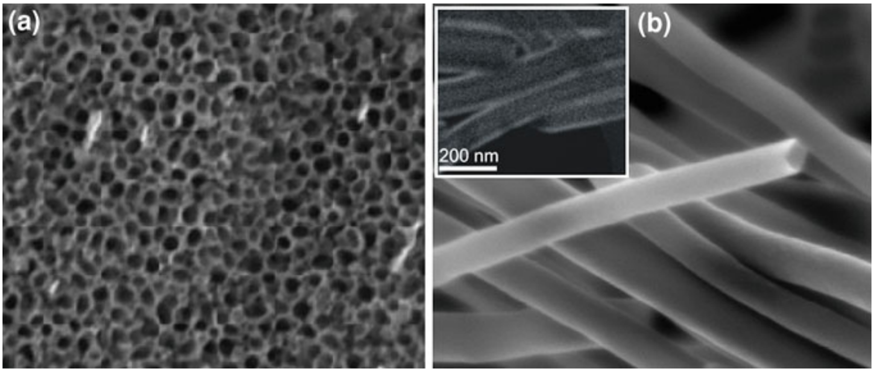

Fig. 22.1 SEM images of nanotubular TiO_2 prepared by: **a** anodic oxidation; **b** atomic layer deposition. Inset shows a TEM image of the same sample

22.3 Results and Discussion

The morphological study carried out by SEM and TEM, has shown the effects of the different synthesis approaches on the final characteristics of the nanotubular materials obtained. The morphology of the prepared TiO_2 nanotubes by anodic oxidation of Ti foils is characterized by an ordered array of vertically aligned 1D nanostructures, as shown in Fig. 22.1a. Hybrids TiO_2/CNTs nanotubular composites prepared by a novel ALD process, are shown in Fig. 22.1b. It can be observed that an homogeneous coating of titania is deposited onto the surface of functionalized carbon nanotubes. TEM clearly prove that the tubes are coated not only on the outer surface but also on the inside (see inset in Fig. 22.1b).

Due to the nanotubular structure with open ends, the synthesized samples show a high surface area (for example, BET give 260 m^2/g for nanotubes prepared by the hydrothermal process at 150°C).

As the morphological and structural features above illustrated can favour the adsorption of gaseous molecules, we decided to investigate the capability of these nanostructures to monitor hydrogen by means of quartz crystal microbalance (QCM) sensors. Hydrogen is largely used in the chemical, petrochemical and semiconductor industry, therefore the development of reliable hydrogen sensors is strongly demanded.

Preliminary hydrogen sensing tests were carried out with a gravimetric QCM sensor, coated with a sensing layer of TiO_2 nanotubes prepared through anodic oxidation of Ti foils, operating at room temperature. As shown in Fig. 22.2, the frequency of the QCM device decreases after a pulse of hydrogen in the nitrogen carrier, due to the mass increase consequently to hydrogen adsorption. The sensor response is fast (around 200 s), suggesting a strong adsorption of the hydrogen on the TiO_2 tubular nanostructure. The recovery time observed is instead longer. Moreover, a partial irreversibility of the desorption process is also noted, likely related to the well known ability of titania to bind strongly hydrogen molecules.

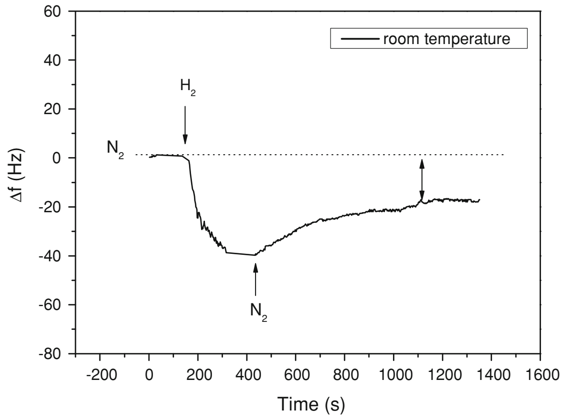

Fig. 22.2 Transient response of a QCM sensor coated with TiO_2 nanotubes prepared through anodic oxidation during a hydrogen pulse

Further experiments are in progress with aim to better understand the phenomena observed.

22.4 Conclusion

Different nanotubular titania structures have been synthesized and widely characterized. Preliminary sensing tests have shown the promising properties of these nanostructures for hydrogen detection at room temperature by means of micro-gravimetric sensors. Further work is in progress in order to investigate the adsorption mechanism of hydrogen and enhance the performance of the QCM sensor, for example by a suitable metal doping of the TiO_2-based nanotubular structure.

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