

A simple route to obtain TiO₂ nanowires by the sol–gel method

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Abstract In this work, titanium dioxide (TiO₂) nanowires were synthesized by the sol–gel method, without using any kind of templates, instead of that acetic acid was used as morphological modifier. In order to control crystalline phases and crystal size, TiO₂ was calcinated at 400, 500 and 600 °C during 1 h. The resulting morphology was nanowires, which diameter was maintained constant after calcination at different temperature (about 76 nm). Moreover, crystalline phases in order of predominance were anatase, anatase–rutile and rutile–anatase at 400, 500 and 600 °C, respectively. Additionally, the crystallite size increases with respect to temperature from 13 to 75 nm.

Keywords TiO₂ nanowires · Sol–gel method · Morphological modifier

1 Introduction

Among semiconductor materials, nanosized titanium oxide (TiO₂) is one of the most common materials for many applications such as, ceramic microporous membranes, sensors, solar cells, catalysis devices, etc. [1–3]. Also, it is known that TiO₂ is an excellent catalyst in the field of photocatalytic decomposition of organic materials [4]. TiO₂ has been synthesized with different morphologies, and especially one-dimensional TiO₂-related materials, such as nanotubes, nanowires, and nanofibers have attracted particular interest because of their unique microstructure and promising functions.

Although the nanotube structure is attractive due to its high surface area, titanate nanotubes with free-alkali ions are usually unstable at high temperatures (at 500 °C) and convert into anatase particles. Nevertheless, the solid nanowire form improves the stability at higher temperature (typically at 500–800 °C) to maintain the 1-D nanostructure [5, 6]. In order to prepare nanosized TiO₂ with advanced properties, several kinds of techniques have been employed, such as, hydrothermal synthesis [7, 8], mechanical milling [9], precipitation [10], chemical vapor deposition (CVD) [11] and glycothermal method [12]. Also a common technique that can result in TiO₂ with high surface area and reasonably good thermal stability is the sol–gel method [13–16], besides to obtain nanosized TiO₂ with different morphologies such as particles, rods, tubes, wires, sheets, mesoporous and aerogels. The use of acetic acid as modifier involves three basic steps: (1) exchange of isopropoxy groups with acetate groups, (2) esterification in solution resulting in gradual hydrolysis of the Ti precursors, and (3) ultimate precipitation of hexameric ring-structured titanium-oxo-acetate crystals [17]. Recently, Attar et al. [18] have reported the effect of modifier ligands (acetic acid and acetyl acetone) on the nano TiO₂ formation from titanium isopropoxide (TIP) by sol–gel method. The use of acetic acid (AcOH) as a TiO₂ sol modifier in alcohol solvent showed to be a successful synthesis route of Ti–O–Ti inorganic network with controlled properties. In another hand, several works [18, 19] studied the influence of acetic acid in the TiO₂ morphology, obtaining particles in “rice and grain shape” of anatase phase and “rod shape” of rutile phase.

In this work, a simple sol–gel route was employed to prepare TiO₂ nanowires, using acetic acid as morphological modifier. Also, the influence of calcination temperature on microstructural characteristics was investigated.

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2 Experimental

Nanocrystalline TiO₂ wires reported in this study were prepared by the sol–gel method, using TIP (Ti[OCH(CH₃)₂]₄, Aldrich Inc.), isopropanol (CH₃CHOHCH₃, Aldrich Inc.) and acetic acid (CH₃COOH, Fluka Inc.). First, 1 mol of TIP was mixed with 2 mol of isopropanol, after 10 min 4 mol of acetic acid were added. Finally, 20 min later, 2 mol of isopropanol were added and stirred in order to complete 1 h of reaction time. To obtain the xerogel, the sol was dried at 100 °C during 24 h. Finally, the xerogel was calcinated in a conventional furnace at normal atmosphere at 400, 500 and 600 °C during 1 h in order to densify and crystallize the material.

TiO₂ nanowires were characterized by means X-ray diffraction (XRD) using a Bruker D8 focus with CuK α radiation, high resolution scanning electron microscopy (HR-SEM) using a Quanta 3D dual beam microscope and transmission electron microscope (TEM) using a JEOL 2000FXII microscope. Crystallite size and nanowire thickness were measured from HR-SEM and TEM images using a commercial image analyzer.

3 Results and discussion

3.1 XRD study

Figure 1 shows the powder XRD pattern for xerogel condition and after calcination process at different temperature. From this figure, it can be seen that TiO₂ was not observed at xerogel condition due to its amorphous state. After calcination at 400 °C, only the characteristic peaks of anatase phase (JCPDS No. 89-4921) are present, while at 500 °C the emergence of the rutile phase is observed

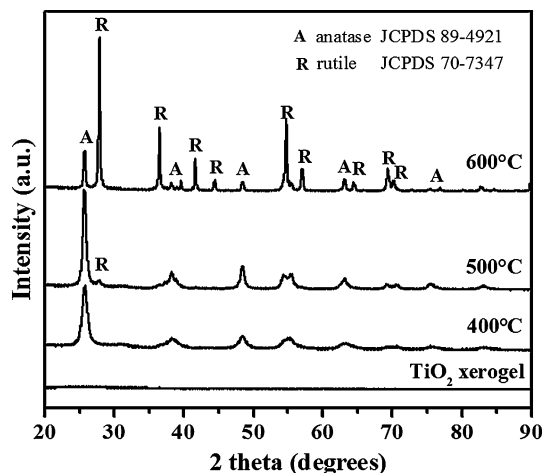


Fig. 1 XRD patters of TiO₂ calcinated at different temperature showing TiO₂ phases

(JCPDS No. 70-7347). In the sample of 600 °C, the reflections associated with the rutile phase are clearly defined, while the diffraction peaks of anatase phase decrease markedly. Additionally, it can be observed a reduction of XRD peak broadness as the calcinations temperature is increased. This fact has been associated with the increase of crystallite size [20].

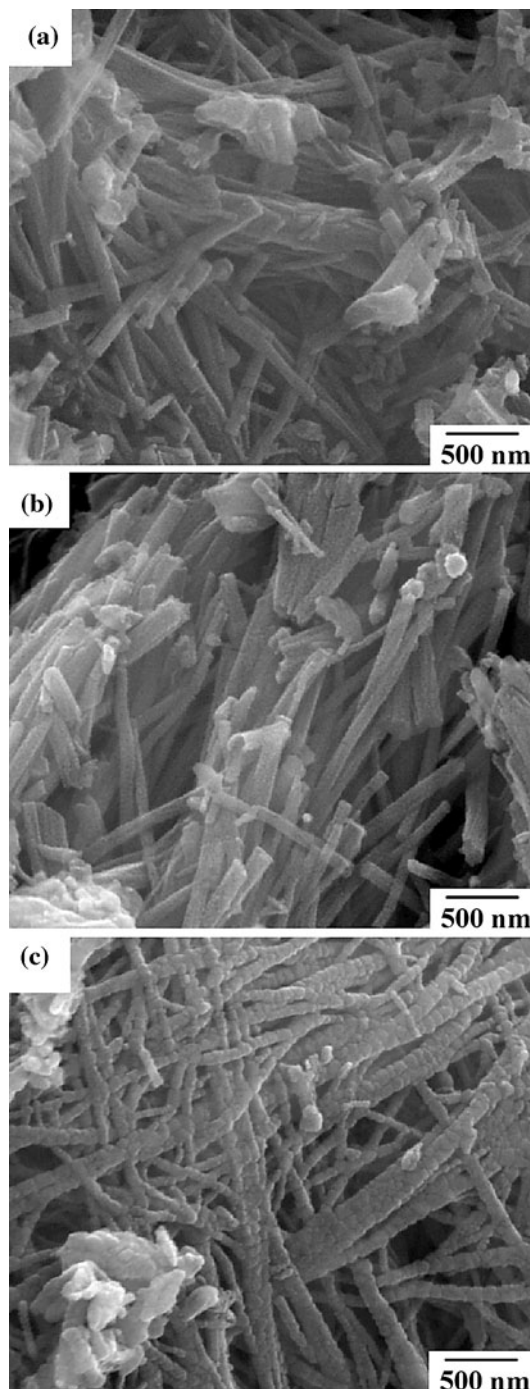


Fig. 2 HR-SEM images of TiO₂ calcinated at different temperature, a 400 °C, b 500 °C and c 600 °C

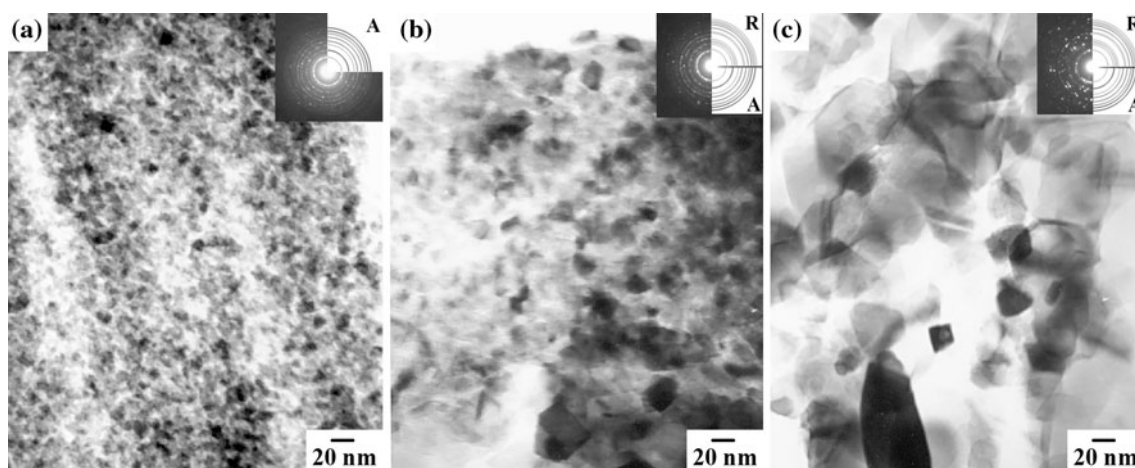


Fig. 3 TEM images and SAEDPs of TiO₂ calcinated at different temperature, **a** 400 °C, **b** 500 °C and **c** 600 °C

3.2 HR-SEM and TEM studies

Figure 2 shows HR-SEM images of TiO₂ heat treated at 400, 500 and 600 °C, respectively. It can be observed that after calcinations the samples showed nanowires morphology with an average nanowire thickness of about 76 nm for all samples. There's not markedly difference in size between materials heat treated at 400 and 500 °C. However is clear that at 600 °C, the fibers are longer, this may be related to the remarkable growth of crystallite size and the transformation of anatase–rutile phase.

Figure 3 shows TEM images in bright field mode with its corresponding selected area electron diffraction pattern (SAEDP). It can be observed that the nanowires are formed by nanometric crystals and the increasing calcination temperature lead to an increase in crystallite size, which agrees with the reduction of XRD peak broadness. The SAEDPs are shown as concentric rings, which also indicated that the crystallite size is in nanoscale. It is known that fine-grained polycrystalline samples gave diffraction pattern of continuous rings as the many small crystallites at random orientation produce a continuous distribution of hkl spots. The SAEDPs were indexed according with the JCPDS cards of anatase and rutile phases, and they are indicated by A and R in Fig 3, respectively.

Finally, Table 1 shows the microstructural characteristics of the TiO₂ nanowires reported in this work. Crystallite

Table 1 Microstructural characteristics of TiO₂ calcinated at different temperature

Calcination temperature (°C)	Average crystal size (nm)	Wire thickness (nm)
400	13	73
500	18	78
600	75	76

size was determined from TEM images and wire thickness from HR-SEM images, using a commercial image analyzer.

4 Conclusions

TiO₂ nanowires were obtained using a simple route by the sol–gel method. Phase composition, morphology and crystallite size were controlled by calcination at different temperatures. The apparent 1-D morphology of TiO₂-related nanowires was thermally stable from 400 to 600 °C, showing a similar diameter (about 76 nm), however crystallite size increases with respect to temperature from 13 to 75 nm. According to the XRD and TEM results, anatase phase begins to transform to rutile phase at about 500 °C.

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