Physica B xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Structural transformation and enhanced gas sensing characteristics of TiO_2 nanostructures induced by annealing

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ARTICLE INFO

Keywords:
NO_2 gas sensing
TiO_2 nanotubes
Nanorods

ABSTRACT

The improved sensitivity and selectivity, and admirable stability are fundamental features required for the current age gas sensing devices to appease future humanity and environmental requirements. Therefore, herein, we report on the room temperature gas sensing behaviour of TiO_2 nanotubes with significance response and sensitivity towards 60 ppm NO_2 gas. Improved sensitivity of 29.44 ppm^{-1} and admirable selectivity towards NO_2, among other gases ensuring adequate safety in monitoring NO_2 in automobile and food industries. The improved sensitivity of TiO_2 nanotubes was attributed to larger surface area provided by the hollow nanotubes resulting to improved gas adsorption and the relatively high concentration of oxygen vacancies.

1. Introduction

To date, fabrication of low-cost, ultra-sensitive and selective chemiresistive sensors that are able to detect toxic, flammable and explosive gases have become indispensable for environmental monitoring, industrial and biomedical applications [1]. Some of the challenges are ultra-sensitive gas sensors that can operate at low temperature with high selectivity to detect the harmful gases. The current promising materials are semiconductor metal oxides (MOX) which have displayed a substantial potential by their noticeable change in their electrical resistance upon exposure to either reducing or oxidizing gases [2]. Moreover, MOX are very stable and they can be easily synthesized in various forms using different synthesis routes (e.g. chemically or in the vapour phase) [2–4].

TiO_2 nanotubes synthesized via hydrothermal method in alkali solution have attracted a number of researchers interest since the first demonstrated by Kasuga et al. in 1998 [5]. This is due to the improved photocatalytic properties; charge transport properties and the large specific surface area provided by the tube-like structure increasing the number of potential active sites for the gas adsorption as compared to their bulk form [6–8] enabling potential application in gas sensing [3], lithium ion battery [8], hydrogen storage [7] and environmental cleaning [9].

TiO_2 nanostructure can be achieved in different phases such as anatase, rutile, and TiO_2(B), all owing to the synthesis conditions such as post heat treatment by annealing at low (< 300 °C), to elevated temperatures (400–900 °C) [10,11]. These TiO_2 polymorphs have different effects on the performance of the sensor, such as the high photocatalytic activity of anatase than that of rutile [11,12]. From our previous studies we found that upon annealing at elevated temperature (700 °C), our nanoparticles prepared using 18 M NaOH transformed to "rod-like" structure. Moreover, the sensing properties toward NO_2 and CH_4 gases improved due to a transformation of morphology and phase (from pure anatase to 30% rutile) [3]. However, in the current work, we elucidate that a higher sensing response towards NO_2 gas is dependent on the morphology. Rengaraj et al. [13] has indicated that the performance of the inorganic materials can be significantly improved by controlling the size, morphology and structure. In addition, there are few studies who have reported high sensing response towards NO_2 gas at room temperature after annealing without assistance of UV light or dopants. Therefore, herein, we report on the effect of annealing temperature on the gas sensing properties of TiO_2 nanotubes prepared following the microwave assisted hydrothermal and annealing at various temperatures. Furthermore, the enhanced sensitivity and selectivity towards NO_2 gas are correlated with the morphology, crystal structure, and optical properties.

2. Experimental procedure

2.1. Synthesis

All the chemicals used were purchased from Sigma Aldrich and used without any further purification. To prepare the TiO_2 nanotubes the microwave assisted hydrothermal method was followed. As a

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http://dx.doi.org/10.1016/j.physb.2017.07.041
Received 20 April 2017; Received in revised form 28 June 2017; Accepted 18 July 2017

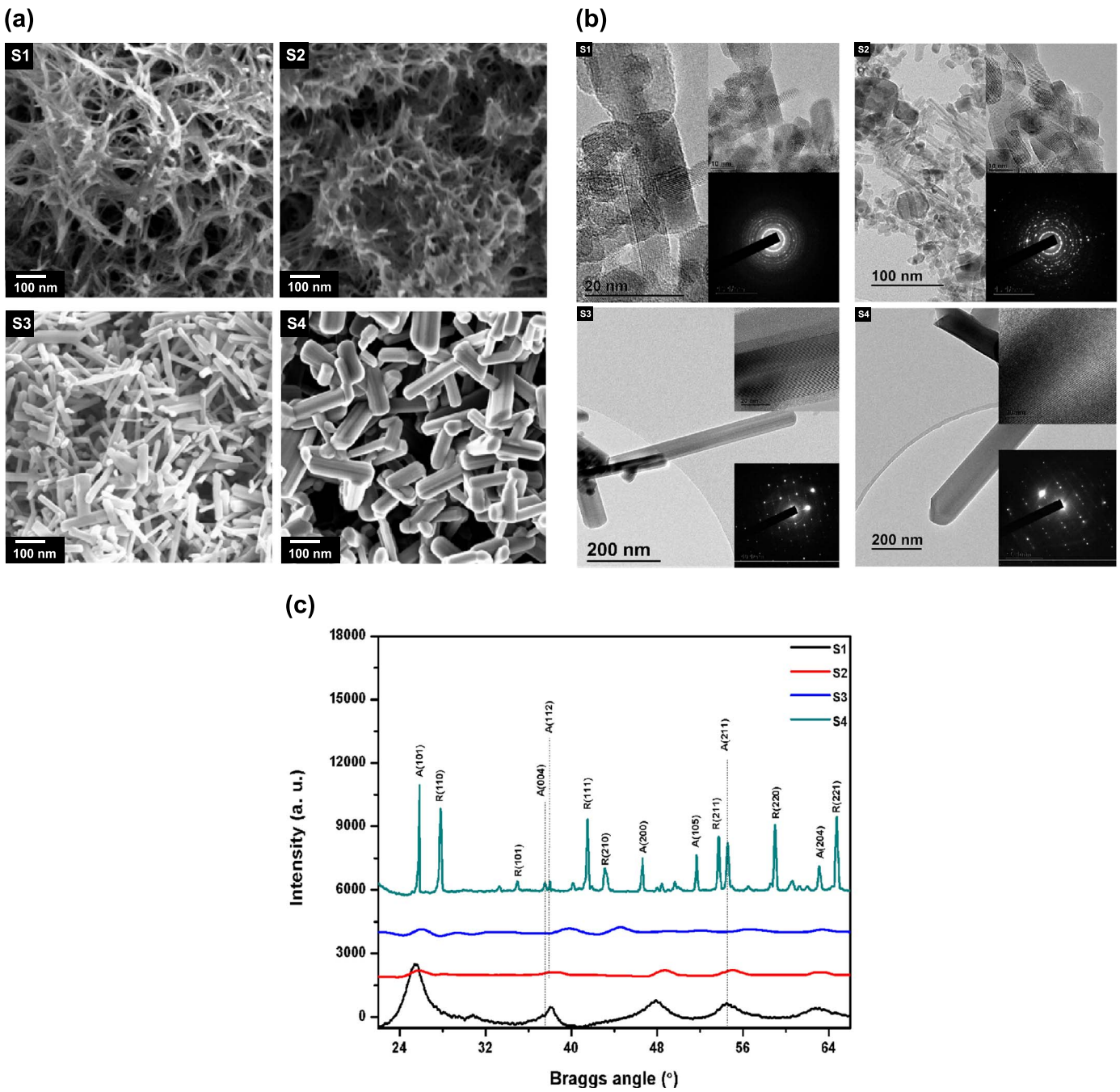

Fig. 1. (a) SEM micrographs, (b) HR-TEM with corresponding SAED patterns (inserts) and (c) XRD patterns of TiO_2 nanostructures.

starting material commercial TiO_2 powder, P25 Degussa (mixture of anatase and rutile) was dispersed in 100 ml of 10 M sodium hydroxide (NaOH, 99.9% purity) solution and stirred for homogeneity. The mixture was transferred into microwave Teflon vessels and microwave (Perkin Elmer/Anton Paar Multiwave 3000) irradiated at 150 °C for 15 min. After being cooled to room temperature the products were centrifuged and washed with 1.0 M hydrochloric acid (HCl) aqueous solution (37% purity) and distilled water till pH 7. The final powder was dried at 120 °C for 12 h. It should be pointed out that the samples were labelled as S1, S2, S3 and S4 for the as-prepared, 450 °C, 700 °C and 900 °C annealed samples for 4 h, respectively.

2.2. Characterization

The morphology and structure were confirmed using the ZEISS scanning electron microscope (SEM) and JOEL-2100 high resolution transmission electron microscope (HR-TEM) with monochromatic radiation source operated at 200 kV in conjunction with the X-ray diffraction (XRD) patterns obtained by a Panalytical X′ pert Pro PW 3040/60 diffractometer equipped with Cu Kα radiation operated at 45 kV and 40 mA. The specific surface area and the pore volume of the samples were measured by nitrogen (N_2) physisorption using a Micromeritics TRISTAR 3000. The photoluminescence (PL) measurements were characterized using a Horiba Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 325 nm. Gas sensing measurements were carried out by homogenously dispersing TiO_2 nanostructures in ethanol and drop-coated on alumina substrates. The response of the samples was examined by monitoring the variation of the electrical resistance of the sensors using a KSGAS6S gas sensing station (KENOSISTEC, Italy) under a constant flux of synthetic air of