Sensors and Actuators B 205 (2014) 322–328

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A novel sensor for fast detection of triethylamine based on rutile TiO_2 nanorod arrays

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ARTICLE INFO

Article history:
Received 26 May 2014
Received in revised form 26 August 2014
Accepted 30 August 2014
Available online 16 September 2014

Keywords:
TEA sensing
Gas sensor
TiO_2
Nanorod arrays
In situ growth
Sensing mechanism

ABSTRACT

A TiO_2 nanoparticle (TP) film is employed as a seed layer for the hydrothermal growth of single crystalline rutile TiO_2 nanorod arrays on the substrate. The TP films were prepared by dip coating method from the TiO_2 sols. The TiO_2 nanorods are smooth with the average diameter of ~65 nm and the length of ~1 μm. The nanorods consist of parallel tiny nanotips about 3–5 nm in diameter on the top surface of the stem nanorod. Morphological evolutions *versus* reaction time were explored in detail through a series of SEM and XRD characterizations. The results indicated that the size of the rods increased with the reaction time increasing. A thin film sensor was formed from different sizes of single crystalline rutile TiO_2 nanorod arrays growing on a ceramic tube *in situ* and exhibited an improved triethylamine sensing performance with a fast response of 2 s and a detection limit of 0.1 ppm. The experiment results show that the TiO_2 nanorod arrays are a kind of promising material for detecting trace TEA.

1. Introduction

One-dimensional (1D) TiO_2 nanomaterials, such as nanorod, nanowire and nanotube, *etc.* [1–8], have triggered more and more research enthusiasms because of their distinctive physicochemical properties. They have been widely applied in fields of photovoltaic material, gas sensor, solar cell, *etc.* [9–15]. In recent years, 1D TiO_2 nanomaterial array attracts tremendous attention due to its higher surface-to-volume ratio, higher electron transportation and diverse applications [16–27]. Because 1D metal oxide nanomaterial arrays such as SnO_2 [28] and ZnO [29] have shown good sensing performance, the TiO_2 nanomaterial array is a remarkable candidate for gas detection. However, the application of the TiO_2 nanomaterial array in sensors remains unexplored [30].

Triethylamine (TEA), as one of the toxic gases released from petrochemicals, harvested fish and other seafood with aging, has caused a serious threat to environment and human beings. The development of highly sensitive sensors for accomplishing rapid and real-time detection of trace TEA is necessary. Various TEA sensors, such as optical sensors [31], conducting polymer sensors [32], semiconductor sensors [33–36], and cataluminescence gas sensors [37], have been reported. Among the above TEA sensors, semiconductor metal oxide sensors such as $NiFe_2O_4$ [33], $CoFe_2O_4$ [34], Fe_2O_3 [35] and V_2O_5 [36] have been developed for triethylamine detection due to their high sensitivity, stability and low cost. Recently, Chu et al. [38] reported the single-crystalline SnO_2 nanorods with an improved response to trimethylamine. Lv et al. [39] reported that a well-crystallized ZnO nanorods gas sensor was very sensitive to TEA with quick response/recovery characteristics at 150 °C. These results indicate that 1D metal oxide nanostructures could contribute to the improvement of gas sensing performance. However, several drawbacks, such as poor selectivity and stability, and long response and recovery times, limit previously studied materials in the practical application. Therefore, it is desirable to develop high performance gas-sensing materials. The development of TEA sensors with high selectivity and quick response still remains a challenge.

Herein, we report that single crystalline rutile TiO_2 nanorod arrays could grow on a TiO_2 particle (TP) film which was previously coated on ceramic tube or other solid substrates by dip coating method. The gas-sensing properties of such TiO_2 nanorod arrays were measured. The results indicated that the small size TiO_2 nanorod arrays exhibited an improved sensing performance to TEA.

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http://dx.doi.org/10.1016/j.snb.2014.08.092
0925-4005/

2. Experimental

All chemical reagents (analytical grade) were obtained from Beijing Chemical Reagents Company and used without further purification. Tetrabutyl titanate (8.5 mL) was diluted with 33.6 mL of ethanol, followed by the addition of 2.45 mL of diethanolamine (DEA) under vigorously stirring for hydrolysis at room temperature. After continuously stirring for 2 h, ethanol (5 mL) and deionized water (0.45 mL) was dropwised in above solution under vigorously stirring. After continuously stirring for 2 h, the mixed solution was aged at room temperature for 24 h, resulting in a clear and homogeneous sol.

2.1. Preparation of TiO_2 nanorod array films

The TP films were fabricated by dipping hydrophilic glass and Al_2O_3 substrates in the above coating sol with speed of 35 mm min^{-1} and kept in air for 10 min at room temperature. Then the films were annealed at 500 °C for 2 h. In a typical procedure, the above TP films were placed in a 50 mL Teflon-lined stainless steel autoclave which contained a mixture of tetrabutyl titanate, HCl (36–38%) and deionized water, with volume ratio of 1:40:40. The autoclave was heated at 150 °C for 4 h and then cooled down to room temperature. The films were washed with water and ethanol, respectively, and then dried in air. Finally, the TiO_2 nanorod arrays were obtained after calcined at 500 °C for 2 h.

2.2. Characterization of TiO_2 nanorod array films

The phase and crystal structure of the as-synthesized samples were characterized by X-ray powder diffractometer (XRD, Rigaku, D/MAX-3B) with Cu Kα1 radiation ($\lambda = 1.54059$ Å). The morphology and structure of the arrays were observed by field emission scanning electron microscope (FESEM, Hitachi, S-4800) and the transmission electron microscope (TEM, Jeol Jem-2100). The surface morphology of the prepared films was investigated by tapping-mode using atomic force microscope (AFM, DI, nanoscope IIIa), with glass as the substrate. The sample was also analyzed by X-ray photoelectron spectroscope (XPS) (VG Scientific, ESCALAB 250) with Al Kα radiation ($h\nu = 1486.6$ eV) within ±0.2 eV deviation in the binding energy position. The C 1s peak of the C—(C, H) component at 284.6 eV was used as an internal standard. The XPS peaks were fitted by a Gaussian and Lorentzian sum function using XPS Peak 4.1 Freeware [40].

2.3. Fabrication and gas sensing measurement of the TiO_2 nanorod array sensors

The structure of the sensor device and the measurement system is identical with those in our previous report [41]. A stationary state gas measurement method was used for testing the gas response in air with 40 ± 5 RH%. The sensor resistance was measured with a JF02E sensor measurement system (Sino-Platinum Metals CO. Ltd., China). In a typical sensing measurement procedure [41], a 10 L glass chamber was first evacuated, followed by injection of the target gas with the required quantity by a micro syringe. Then air was allowed to pass into the container to balance the inner-outer pressure of the test chamber. After the resistance of the sensor reached a steady value in air, the sensor was immediately transferred into the chamber. When the resistance of the sensor reached a steady value in the chamber, the sensor was taken out of the chamber again. The response of the sensor is defined as: R_a/R_g, where R_a is the sensor resistance in air, and R_g is the resistance in the test gas. The time required for a sensor to reach 90% of the resistance change ($R_a - R_g$) was defined as the response time in the case of adsorption, and the recovery time for desorption.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 is the typical FESEM images of TiO_2 nanorod arrays on a TP film synthesized at 150 °C for 4 h and then calcined at 500 °C for 2 h. These nanorods are tetragonal in shape with uneven top facets as shown in Fig. 1a. The side-view (Fig. 1b) clearly shows that the surface of nanorods is smooth with an average diameter of ~65 nm and the length of ~1 μm. The TEM image of one TiO_2 nanorod is shown in Fig. 1c. The nanorods are separated by gaps and there are numerous parallel tiny nanotips about 3–5 nm in diameter grown vertically on the top of the stem nanorod. The nanorods are single crystalline, as evidenced by the sharp SAED pattern of a nanorod examined along the [$\bar{1}$ 1 1] zone axis (the inset of Fig. 3c). The HRTEM (Fig. 1d) confirms that each nanotip is a [1 0 1]-oriented single crystal.

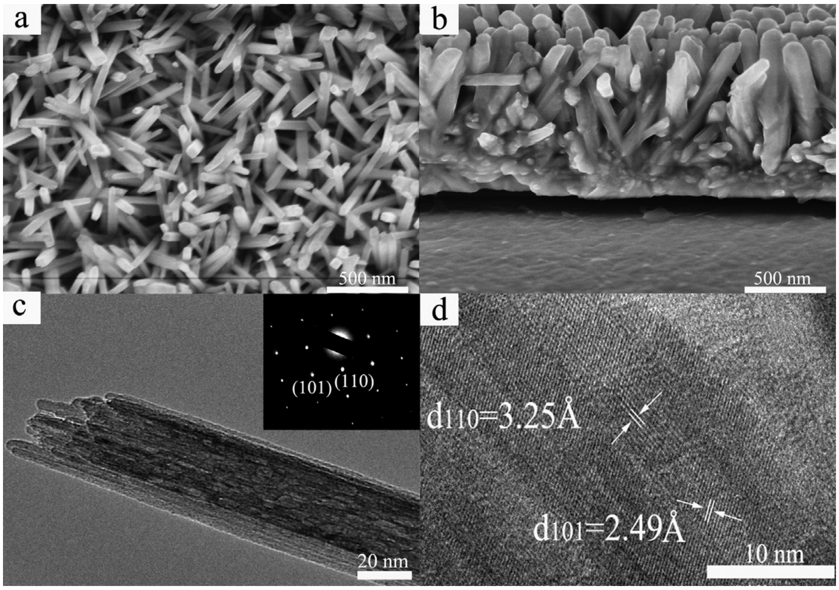

Fig. 1. SEM images of the TiO_2 nanorod array: top view (a) and side view (b). TEM (c), HRTEM (d) image and SAED (e) pattern of the TiO_2 nanorod.