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Ultrasensitive room-temperature detection of NO_2 with tellurium nanotube based chemiresistive sensor

Lei Guan[a], Shun Wang[a,b,*], Wen Gu[c], Jinxia Zhuang[a], Huile Jin[a], Weiming Zhang[a], Ting Zhang[c,*], Jichang Wang[d,*]

[a] Nano-materials & Chemistry Key Laboratory, Wenzhou University, Wenzhou 325035, Zhejiang, China
[b] State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027, China
[c] i-Lab, Suzhou Institute of Nano Tech and Nano Bionics, Chinese Academy of Sciences, Suzhou 215123, Jiangsu, China
[d] Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4

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ABSTRACT

Te nanotubes were synthesized through a microwave reflux method that employed a mixture of polyethylene glycol and water as solvent. The water content was used to manipulate the boiling temperature of the solvent. Characterizations of the Te products with scanning electron microscopy, transmission electron microscopy, energy dispersive spectroscopy and X-ray diffraction spectroscopy indicate that the growth of Te nanotubes is governed by both diffusion-limited depletion at the surface of seeds and dissolution–crystallization process. A chemiresistive sensor constructed with the as-prepared Te nanotubes exhibits excellent sensitivity and selectivity to trace amount of NO_2 at room temperature, where the low detection limit is found to near 500 ppt. The response of the gas sensor is totally reversible with the assistance of UV irradiation, in which increasing the UV exposure reduces the sensor recovery time to less than 5 min. The great performance of this Te-based gas sensor is attributed to the large surface-to-volume ratio and high crystallinity of these Te nanotubes.

1. Introduction

When fossil fuels such as coal and natural gas burn at a high temperature, NO_2, one of the six widespread air pollutants, is produced as a by-product through the combination of nitrogen and oxygen molecules. Because NO_2 correlates to the formation of acid rain, photochemical smog and respiratory diseases such as emphysema and bronchitis, in recent years a great deal of attention has been paid to its detection [1–7]. Tellurium-based sensors such as Te film [8], Te microtube [9], Te hollow nanofibers [10] and Te-SWNT hybrid structure [11] have shown promising results. To reduce the overall energy cost endured in the measurements and improve the sensitivity and selectivity of the sensor, Te crystals with new microstructures are constantly sought.

Te is a p-type semiconductor with a structure consisting of helical chains parallel to the *c* axis. These chains are bound through weak van der Waals interactions and form hexagonal lattices. According to literature the gas sensing of Te is connected to the concentration of electronic hole at the surface. Therefore, finding a way to increase the specific surface area of Te crystal is crucial in building a highly sensitive gas sensor. Meanwhile, studies have demonstrated that the size and morphology of materials also have great influences on their concomitant physical and chemical properties [12–18]. Hollow structure of a nanotube allows gas molecules to adsorb on both the inside and outside surface, significantly increasing the useful surface area. In the past two decades, a great deal of effort has been made toward the synthesis of tubular microstructures with materials having layered structures such as C [12], BN [13], and WS_2 [14]. Recently, nanotubes were also successfully prepared using materials having non-layered structures such as Te [15], Si [16], In_2O_3 [17] and GaN [18].

Methods used for synthesizing Te micro- and nano-tubes include physical vapor deposition (PVD). Through controlling the super-saturation of Te vapors by suitably tailoring the source, deposition temperatures, pressure and carrier gas flow rate, multitude of Te micro- or nano-tubes could be fabricated [9,19–22]. For example, Li's group used Te powder to synthesize Te microtubes in argon atmosphere [22]. Yakhmi's group heated Te powder and chunks to obtain Te nanotubes as well as other forms of

* Corresponding authors at: College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, Zhejiang, China. Tel.: +86 577 86689357; fax: +86 577 88373111.
E-mail addresses: shunwang@wzu.edu.cn (S. Wang), tzhang2009@sinano.ac.cn (T. Zhang), jwang@uwindsor.ca (J. Wang).

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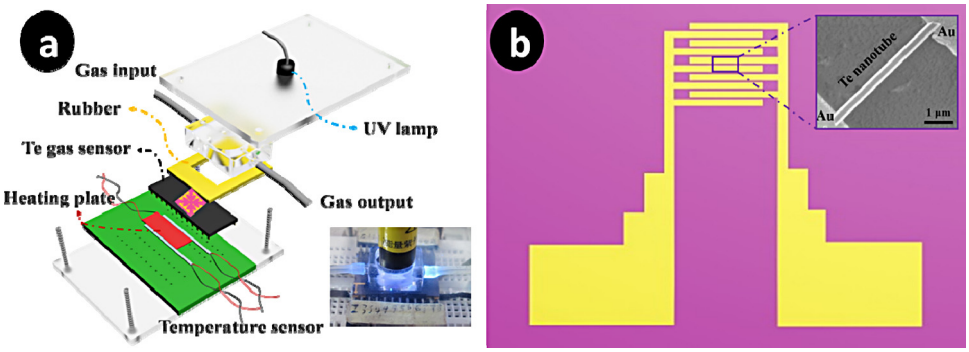

Fig. 1. (a) the schematic and photographs (inset) of a customized sensing test instruments, and (b) the schematic of an independent interdigitated electrode. Inset in (b) is a SEM picture of one Te nanotube on an interdigitated electrode.

nanostructures [20]. Solution routes, including hydrotherm, solvotherm and polyol reflux method [15,23–36], have also been extensively used to obtain Te nanotubes. Qian's group synthesized, for example, Te nanotubes with open ends and a common cylindrical morphology by using a hydrothemal method [34]. Zhu's group obtained the shuttle-like scrolled nanotubes of Te with the assistance of amino acid in an autoclave [30]. Using polyol reflux method, Xia and co-workers synthesized Te nanotubes with open ends and a cylindrical seed in the middle of each tube [15].

In this work, we prepared a NO_2 gas sensor using single crystalline Te nanotubes that were fabricated through a new synthetic approach. More specifically, diethyldithiocarbamato tellurium (TDEC) was reduced in a mixture of ethylene glycol and water, in which the presence of water allowed us to lower the reflux temperature from 197 to 160 °C. The chemiresistive sensor constructed with the as-prepared Te nanotubes has a low detection limit of NO_2 and good selectivity toward various gases such as CH_4, NH_3, CO and H_2. A fast recovery time could be achieved with the assistance of UV light irradiation.

2. Experimental details

2.1. Materials

Diethyldithiocarbamato tellurium(IV) (Zhejiang Ultrafine Powders & Chemicals Co. Ltd.) was recrystallized twice with high purity chloroform prior to its usage. The following analytical grade chemicals were used as received: ethylene glycol was purchased from Aldrich, ethanol and acetone were purchased from Shanghai Chemical Reagent Co. Deionized water was prepared with a Milli-Q purity system (18.2 MΩ).

2.2. Preparation of Te nanotubes and gas sensors

In a typical procedure, 0.14 mmol TDEC, 48.0 ml glycol, and 2.0 ml deionized water were added to a 50 ml round bottom flask. After that, the suspension was microwave-heated to 90 °C for 5 min at a power setting of 200 W and then to 160 °C for 1 min at a power setting of 500 W. After 6 min, the suspension solution turns from yellow to dark blue, indicating the formation of element Te. The resulting solid products were collected through centrifugation at 9000 rpm for 5 min and were washed with deionized water and ethanol several times. Afterwards, they were stored in ethanol.

To conduct NO_2 gas sensing, a customized sensing test instrument is made in our lab, which consists of heating plate, rubber gasket, and a quartz cell (see Fig. 1a). Te nanotubes based gas sensor is made of an interdigitated electrode (IDE, electrodes gap distance is 5 μm) that was patterned on top of a 500 nm SiO_2 layer on p-type Si substrate with micro-fabrication technology. To construct the IDE electrodes, a layer of 5 μm photoresistor (AZ4620, Hoechst Celanese Corporation, Somerville, NJ, US) was first spin-coated on the Si/SiO_2 substrate at 4000 rpm for 30 s, and then pre-baked at 100 °C for 3 min. The IDE pattern was subsequently transferred from the photolithography plate to a Si/SiO_2 substrate by exposing to 365 nm light for 23 s at 10 mW cm^{-2} (Karl Suss MA6 contact aligner, Germany) and developed for 1 min (AZ400 K:H_2O = 1:300, Hoechst Celanese Corporation). In the last step, a Ti layer (30 nm) and an Au layer (150 nm) were sputtered at 1 kW for 40 s and 200 W for 137 s (3.7×10^{-7} mbar, FHR, Germany), respectively. The IDE microelectrodes were finally formed by a lift-off method.

Schematic design of the IDE microelectrode is presented in Fig. 1b, in which the inset demonstrates how one Te nanotube connects the electrode gap (5 μm). Here, aqueous dispersion of Te nanotubes was drop-deposited with a microsyringe onto the IDE electrodes and dried in a vacuum oven at 120 °C for 1 h. After that, the sensor chips were bonded to a 24-pin CERDIP (Ceramic Dual Inline Package) chip carrier with Au wires (50 μm, West Bond 747677E, Los Angeles, USA) to form the gas sensing device.

2.3. Instruments

The microwave system used in the synthesis is a Shanghai SINEO MAS-microwave synthesizer (2450 MHz, maximum power 1000 W). X-ray diffraction (XRD) was conducted on a Bruker D8 Advance diffractometer using Cu $K\alpha$ radiation (λ = 0.15406 nm), where the data was collected in the 2θ range of 20–80° at a step size of 0.02°. The morphology was observed by scanning electron microscopy (SEM) on a FEI Nova Nanosem 200 microscope operated at an acceleration voltage of 10–15 kV. Transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (EDS) were taken on a JEOL 2010 high-resolution transmission electron microscope performed at 200 kV.

2.4. Detection of NO_2

All the measurements (I–V curves) were performed at room temperature (20 ± 2 °C) unless otherwise stated. Real-time response of the sensor was monitored with a custom lab view program under 2 V DC (National Instruments, Austin, TX, USA). Different concentrations of the analyte gas were achieved by mixing stoichiometric amounts of a target gas and nitrogen using mass flow controllers (MFCs, sevenstar CS200). The gas sensing experiment was typically conducted under a pressure of 1 atm. The sensor sensitivity (S) is defined as:

$$S = \frac{R_g - R_0}{R_0} \times 100\%$$