Sensors and Actuators B 262 (2018) 350–358

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

2D TiO_2 nanosheets for ultrasensitive humidity sensing application benefited by abundant surface oxygen vacancy defects

Miaomiao Gong[a,b,1], Yushu Li[a,1], Yanan Guo[a,*], Xu Lv[a], Xincun Dou[a,*]

[a] Xinjiang Key Laboratory of Explosives Safety Science, Laboratory of Environmental Science and Technology, Xinjiang Technical Institute of Physics & Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 25 October 2017
Received in revised form
30 December 2017
Accepted 23 January 2018

Keywords:
2D TiO_2 nanosheets
Humidity sensor
Surface defects
Specific surface area

ABSTRACT

To realize the sensitive and rapid sensing of humidity, 2D as-prepared TiO_2 nanosheets (hereafter shorted as TiO_2 nanosheets) with characteristics of surface oxygen vacancy defects and large surface area were designed and synthesized. The TiO_2 nanosheets-based sensor exhibit superior humidity sensing performance with an ultrahigh sensitivity evidenced by the dramatic impedance variation of more than four orders of magnitude from relative humidity (RH) 11% to 95%, fast response (3 s) and recovery (50 s) process, as well as a small hysteresis (~4.6%). Additionally, a systematic study of the sensing performances of sensors fabricated from TiO_2 nanosheets and two counterparts calcined in N_2 and O_2 with decreased specific surface area and controlled surface defects, namely TiO_2-400 (N_2) and TiO_2-400 (O_2), has been conducted. The results show that at low RH level of 33% and 54%, TiO_2-400 (N_2) with highest surface oxygen vacancy defects concentration exhibits the highest response of 6.26 and 34, respectively, while at high RH range of 85% to 95%, the TiO_2 nanosheets with largest specific surface area shows the highest response which is almost 10 times higher than that of the calcined counterparts. Combining the complex impedance analysis, the overall ultrahigh humidity sensing performance of TiO_2 nanosheets-based sensor is attributed to the dissociating promotion by the abundant surface defect and enhanced electrolytic conduction by the large specific surface area.

1. Introduction

Humidity monitoring has attracted considerable research attention due to their key technical applications in various fields, such as industrial processing, agriculture, food and medicine storage [1,2]. Up to now, nanostructured metal oxides such as ZnO [3], TiO_2 [4,5], SnO_2 [6], and ABO_3-type [7,8] compounds were the most studied humidity sensitive materials due to the controllable specific surface area and porosity, as well as facilely modified properties. Among them, TiO_2 is known as a superior humidity sensitive material [9] with the preferably hydrophilic property resulting from the surface defects, namely the Ti^{3+} defect sites or oxygen vacancies sites, which could readily adsorb the water molecules in the atmosphere [10]. Besides, the oxygen vacancies could also enhance the dissociation of the adsorbed water molecules, producing an hydroxyl group at the vacancy and also a second hydroxyl group at a nearby bridging-bonded oxygen site [11], which has been widely investigated through various methods such as temperature-programmed desorption, vibrational spectroscopy, photoelectron diffraction, scanning tunneling microscopy, and density functional theory calculations on rutile TiO_2 [10,12,13] and anatase TiO_2 [14–16], respectively. The enhanced water dissociation triggered by oxygen vacancies is beneficial for improving the humidity sensing performance of TiO_2-based sensors, especially at low humidity level [17]. Moreover, another ideal characteristic for excellent humidity sensor in general is large specific surface area, which could afford sufficient sites for physisorption of water molecules to participate into the conduction and hence result in a large response value [4,18]. However, the reported TiO_2-based humidity sensors generally suffered from the limited sensitivity caused by low surface/volume ratio [19,20], or the high resistance and poor charge transfer process of pure TiO_2 sensing material. Hence, many efforts have been made to conquer these problems from one aspect or another. For instance, the sensitivity of TiO_2 sensing material was enhanced by increasing the specific surface area via incorporating graphene on the expense of longer response/recovery process [21]. Besides, another effective method to improve the

---

* Corresponding authors.
E-mail addresses: guoyn@ms.xjb.ac.cn (Y. Guo), xcdou@ms.xjb.ac.cn (X. Dou).
[1] Miaomiao Gong and Yushu Li contribute equally to this work.

https://doi.org/10.1016/j.snb.2018.01.187
0925-4005/

sensing performance of TiO_2 with enhanced sensitivity and reduced response/recovery time is doping with dopants to accelerate the charge transfer process, such as ions [22,23] and inorganic salts [24,25], which, however, tend to migrate and drain leading to decreased sensitivity and therefore a deteriorating sensor stability at high RH level. Therefore, the pure TiO_2 nanostructure with abundant surface defects along with high specific surface area and good charge-transfer ability is a kind of highly desirable material design for humidity sensing application with boosted sensitivity, reduced response/recovery time, and possibly, a small hysteresis.

The state-of-art studies of TiO_2-based humidity sensitive materials are mainly focused on 0D nanomaterials (fine LiCl-doped TiO_2 nanoparticles [26]), 1D nanomaterials (TiO_2-B nanowires [9], TiO_2 nanotubes [27], and nitrogen doped TiO_2 nanotubes [28]) and 3D nanomaterials (interconnected porous ceramic [29]). While, unlike other 2D semiconducting layered materials such as transition metal dichalcogenides [30–32] and black phosphorus [33,34], the TiO_2 nanosheets with anisotropic 2D nanostructure are barely studied as humidity sensing material probably due to the challenges in the preparation of the homogeneous 2D nanosheets by exfoliation [35], although the nanoscale thickness and infinite lateral dimensions endow TiO_2 nanosheets with unique intrinsic characteristics such as large specific surface area, increased surface defects and good electronic conductivity [36–38], which would be greatly beneficial for humidity sensing application.

In this work, ultrathin 2D TiO_2 nanosheets with high specific surface area and sufficient surface defects were synthesized through a facile surfactant-assisting self-assembly method [39]. The impedance-type humidity sensor based on the as-synthesized TiO_2 nanosheets exhibits outstanding sensing performance with dramatic impedance variation of more than four orders of magnitude from RH 11% to 95%, short response time (3 s) and recovery time (50 s), as well as a small hysteresis (~4.6%). According to the surface protonic/ionic conducting mechanism for humidity sensors, the superior sensing performance of TiO_2 nanosheets-based humidity sensor could be attributed to the enhanced dissociation of water and the abundant adsorption sites, induced by the abundant surface defects and large surface area respectively. The important role of surface defects and specific surface area in humidity sensing property is verified by two designed counterparts of TiO_2-400 (N_2) and TiO_2-400 (O_2) with controlled defect concentration and specific surface area. To the best of our knowledge, this is the first trial on the ultrathin TiO_2 nanosheets for humidity sensing application.

2. Experimental

2.1. Chemicals and reagents

Titanium isopropoxide (TTIP), Hydrochloric acid (HCl), Ethanol (EtOH, CH_3CH_2OH), Polyethylene oxide-polypropylene oxide-polyethylene oxide (P123, PEO_{20}-PPO_{70}-PEO_{20}), Ethylene glycol (EG, $(CH_2OH)_2$), Lithium chloride monohydrate ($LiCl{\cdot}H_2O$), Magnesium chloride hexahydrate ($MgCl_2{\cdot}6H_2O$), Sodium chloride (NaCl), Potassium chloride (KCl), Potassium nitrate (KNO_3) and Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$) were purchased from Sigma Aldrich.

2.2. Synthesis of TiO_2 nanosheets

TiO_2 nanosheets were synthesized via a facile surfactant self-assembly method. In a typical procedure, 1.05 g TTIP was dissolved in 1.48 ml concentrated HCl under vigorous stirring for 15 min at room temperature (solution A); while 0.8 g P123 was dissolved in 6.0 g EtOH during stirring for 15 min at room temperature (solution B). Solution B was added into solution A slowly and stirred for another 30 min. Finally, 5 ml mixture solution was added to 20 ml EG and transferred into a 50 ml autoclave and heated at 150 °C for 20 h. After the reaction was completed, the reaction mixture was cooled down to room temperature and the precipitate was washed with ethanol and deionized water for three times with assistance of centrifuge, followed by drying at 80 °C overnight to yield the ultrathin TiO_2 nanosheets product. The counterparts of TiO_2-400 (N_2) and TiO_2-400 (O_2) were obtained by calcining the ultrathin TiO_2 nanosheets at 400 °C in N_2 and O_2 atmosphere for 2 h, respectively.

2.3. Device fabrication

Initially, the prepared material was mixed with deionized water with a weight ratio of 10:1 and ground in a mortar to form a paste. The paste was then coated on a ceramic substrate by a thin brush to form a sensing film on which silver interdigitated electrodes with both finger-width and inter-finger spacing of about 200 μm was previously printed. The thickness of the film was controlled by the brushed cycles. The sample was dried naturally in air for overnight before testing.

2.4. Humidity sensing evaluation

As the humidity generation sources, the six different saturated salt solutions, including LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl and KNO_3, were separately kept in six closed 250 ml conical flasks for at least 12 h to give approximate relative humidities of 11%, 33%, 54%, 75%, 85% and 95%, respectively [40]. For humidity sensing test, the sensor was inserted into the humidity chamber and the complex impedance was measured by electrochemical workstation (CIMPS-2, ZAHNER) with applied voltage of 1 V and varied frequency from 100 Hz to 100 kHz at room temperature (25 ± 2 °C). After the sensor impedance reached a new constant value, the sensor was then inserted into the humidity chamber with relative humidity of 11% to recover. The relative response of the humidity sensor in impedance is defined as, Response = R_L/R_H, where R_L and R_H are the electrical impedance of the sensor in low and high humidity respectively. The response time is defined as the period in which the sensor impedance reaches 90% of the response value upon exposure to the target humidity, while the recovery time is defined as the period in which the sensor impedance changes to 10% of the response value after the target humidity is removed.

2.5. Characterization

X-ray diffraction (XRD) measurement was conducted using powder XRD (Bruker D8 Advance, with Cu-K_α radiation operating at 40 kV and 40 mA, scanning from $2\theta = 10$ to $80°$). Field-emission scanning electron microscope (FESEM, ZEISS SUPRA 55VP) and transmission electron microscope (TEM, JEM-2011) were applied to characterize the morphology of the samples. The nitrogen adsorption-desorption isotherms, the corresponding pore size distributions and the Brunauer-Emmett-Teller (BET) specific surface area of the samples were determined by a mesoporous method on the NOVA 2200e (Quantachrome, USA) physical adsorption instrument. The X-ray photoelectron spectroscopy (XPS) measurement was conducted on an Esca Lab 250Xi spectrometer (Thermo Scientific) using monochromatic Al Kα X-ray source (anode HT = 15 kV) operating at a vacuum higher than 2×10^{-9} mbar to quantitatively evaluate the surface electronic state of the Ti and O elements. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker Elexsys E500 spectrometer by applying an X-band (9.43 GHz, 1.5 mW) microwave with sweeping magnetic field at room temperature in cells that can be connected to a conventional high-vacuum apparatus.