Sensors and Actuators B 228 (2016) 295–301

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Facile synthesis of In_2O_3 nanospheres with excellent sensitivity to trace explosive nitro-compounds

Yang-Yang He, Xu Zhao, Yang Cao, Xiao-xin Zou, Guo-Dong Li *

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, International Joint Research Laboratory of Nano-Micro Architecture Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China

ARTICLE INFO

Article history:
Received 24 September 2015
Received in revised form 9 January 2016
Accepted 12 January 2016
Available online 15 January 2016

Keywords:
In_2O_3
Explosives
Gas sensor
Nanospheres
Nitrocompounds

ABSTRACT

In_2O_3 nanospheres with excellent sensing ability to explosive nitro-compounds have been successfully synthesized via a two-step method including a mild solvothermal process and calcination at elevated temperature in air. The as-synthesized In_2O_3 nanospheres are of 200–300 nm in diameter and are composed of small nanoparticles with a size of around 5 nm. The structure, morphology and thermal stability are investigated by XRD, SEM, TEM, HRTEM, TG and XPS. At 140 °C, the responses of this sensor toward 100 ppm nitromethane, nitroethane and nitropropane are 163, 220 and 375, respectively. And what's more, the sensor also exhibits short response time of less than 1 s, good long-term stability, and low detection limits. The good sensing performance should be attributed to the strong electron-withdrawing effect of nitro group and low working temperature.

1. Introduction

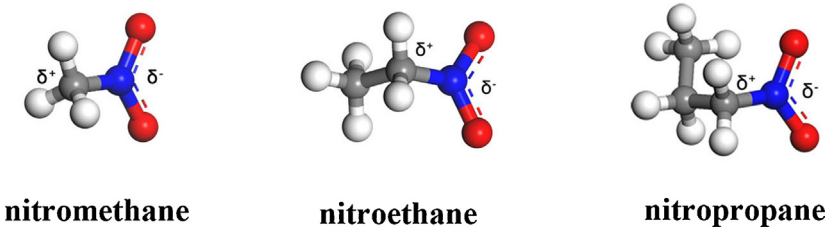
In recent years, the research interest in the detection of nitro-containing compounds, both Nitroaromatic and Nitroalkane, has increased greatly due to their highly explosive and toxic nature [1]. They can usually cause heavy headaches, sore throat, abdominal pain, cancer and even lead to death at a low concentration [2]. Nitroaromatics, including 2, 4-dinitrotoluene (2, 4-DNT), 2, 6-dinitrotoluene (2, 6-DNT), 2, 4, 6-trinitrotoluene (TNT) and picric acid (PA) etc., are widely used in the fields of synthesizing pesticides, explosive, dye and textile industries. Nitroalkanes, involving nitromethane, nitroethane, nitropropane and 2, 3-dimetheyl-2, 3-dinitrobutane etc., are important pharmaceutical intermediates, regents for explosive and excellent solvents for vinyls, polyamides, epoxies and acrylic polymers, and so on [3]. Moreover, nitromethane can be used as rocket fuel. For the safety concern, it is necessary to detect these nitro-containing compounds mentioned above at a low concentration. Thus, many methods have been developed for the monitor of nitro-containing compounds, including ion mobility spectrometry [4], fluorescence spectrophotometry [5], mass spectrometry [6] and electrochemical sensor [7]. Although some of these methods can give high response, good selectivity and accuracy, they are expensive, high energy consumption and not portable. Furthermore, most of the above methods are complicated and require professional experts to operate the equipment and analyze the data. Obviously, it is important to develop low cost, convenient and portable gas sensors to detect those nitro-containing explosives for practical application.

Metal oxide semiconductor (MOS) with different compositions and structures, including SnO_2, ZnO, In_2O_3, TiO_2 and Fe_2O_3 etc., have been widely investigated for reductive and oxidative gas detecting [8]. Among those MOS, In_2O_3, an important n-type semiconductor with a wide band gap of 3.6 eV and good conductivity, has been extensively studied in the area of solar cell, display, gas sensor, photocatalysis and so on [9–12]. Up to now, In_2O_3 materials with different structures and morphologies have been prepared, such as nanowires, nanorods, nanoparticles, nanocubes, nanofibers, nanoplates and nanospheres [11–17]. They showed excellent sensing ability to acetone, carbon monoxide, chlorine, ethanol, hydrogen sulfide, ammonia and/or other volatile organic compounds (VOCs) [18–31]. However, none of them was related to the detection of trace explosive nitrocompounds in air.

Herein, we report an In_2O_3 nanospheres based sensor with excellent sensing performance to the above nitroalkane at relatively low operating temperature of 140 °C. To verify the action of nitro group during the sensing process, methane, ethane and propane were also investigated. For the strong electron-withdrawing effect of nitro group, nitroalkane can be activated

* Corresponding author. Fax: +86 43185168624.
E-mail addresses: lgd@jlu.edu.cn, lifind@21cn.com (G.-D. Li).

http://dx.doi.org/10.1016/j.snb.2016.01.042
0925-4005/



Scheme 1. The schematic graphs of nitromethane, nitroethane and nitropropane.

(Scheme. 1) and react with oxygen species adsorbed on the surface of In_2O_3 at 140 °C, whereas, alkane such as methane, ethane and propane is inactive at this condition. Thus, we believe that it would promote the development of detecting nitro-explosive at low concentration levels.

2. Experimental

2.1. Synthesis of In_2O_3 nanospheres

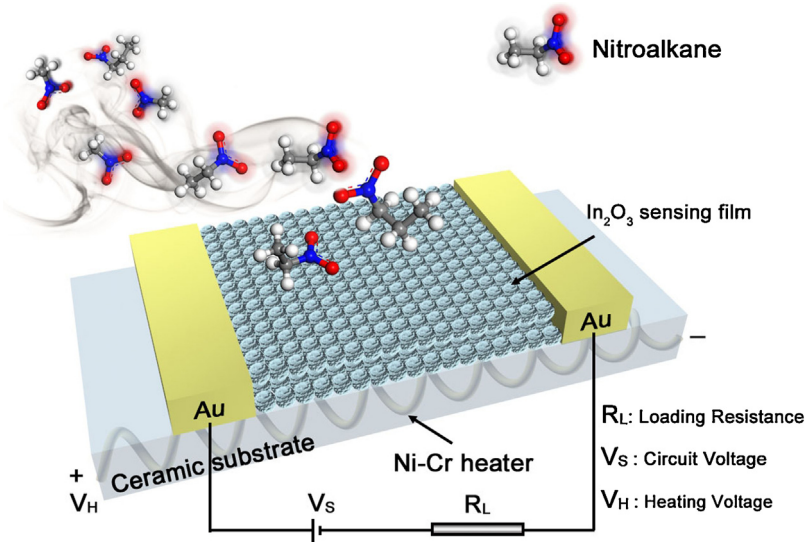
Firstly, indium alkoxide nanospheres were synthesized via a solvothermal process by using the mixture of ethanol, ethylene glycol and 1, 3-propanediol. Secondly, the final In_2O_3 nanospheres were obtained by calcining the indium alkoxide precursor at elevated temperature in air. 1, 3-propanediol was purchased from Shanghai Demand Chemical Co., Indium (III) nitrate hydrate was purchased from Sinopharm Chemical Reagent Co., Ltd. Ethylene glycol and ethanol were purchased from Beijing Chemical Works. All the reagents and chemicals used in our experiments are analytical grade and without further purification. In a typical synthetic procedure, $In(NO_3)_3{\cdot}4.5H_2O$ (0.30 g) was added into a mixture of ethanol (30 mL), ethylene glycol (5 mL) and 1, 3-propanediol (5 mL) and stirred till the formation of homogeneous colorless and transparent solution. Then, the solution was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 6 h. The obtained white indium alkoxide solid product was separated from the solution by centrifugation, then washed with absolute ethanol, and dried at 80 °C in air. The In_2O_3 nanospheres were prepared by the subsequent calcination of indium alkoxide at 300 °C, 400 °C, 500 °C in air for 2 h and the related products were denoted as S300, S400, S500, respectively.

2.2. Structural characterization

The X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/Max 2550 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å) operated at 200 mA and 50 kV. The scanning electron microscopic (SEM) images were taken on a JEOL JSM 6700F electron microscope, while the transmission electron microscopy (TEM) images were recorded with a Philips-FEI Tecnai G2S-Twin. The X-ray photoelectron spectroscopy (XPS) was measured on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic X-ray source (Al Kα hυ = 1486.6 eV). The thermal gravimetric analysis (TG) curve for the precursor was conducted in air on a NETZSCH STA 449C TG thermal analyzer from 25 to 800 °C at a heating rate of 10 °C min^{-1}.

2.3. Sensor fabrication and response testing

To assemble sensors, In_2O_3 nanospheres were dispersed in an appropriate amount of ethanol to form viscous slurry by milling. The gas sensor was fabricated by coating the slurry on the surface of a ceramic tube with a tiny brush. The length and diameter of this tube are 4 mm and 1 mm, respectively. And there are two gold electrodes and four platinum wires on both ends of the ceramic tube. A Nickel-chromium alloy coil was inserted into the tube and was used as a heating unit for tuning the operating temperature of the sensors (Scheme. 2). After ageing at 200 °C for 12 h, the sensing properties of the In_2O_3 sensor were tested on a commercial CGS-8 gas sensing measurement system (Beijing Elite Tech Company Limited) with a static gas sensing chamber. The sensor response value is depicted as the ratio of Ra/Rg, where Ra is the resistance in fresh air, Rg is the resistance in the desired concentration of target gas diluted with fresh air. Response and recovery time is defined as



Scheme 2. Schematic illustration of the sensor's structure.