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Gas sensing enhancing mechanism via doping-induced oxygen vacancies for gas sensors based on indium tin oxide nanotubes

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ABSTRACT

It's demonstrated that the defects induced by doping can greatly influence the sensing properties of oxide-based gas sensors. In this work, the authors have designed indium tin oxide nanotubes (ITO NTs) with different Sn doping concentrations. Results showed that the walls of ITO NTs are comprised of the formed ITO and redundant In_2O_3 nanoparticles (NPs) at low doping concentration, and the doping-induced oxygen vacancies ($V_o^{\cdot}$S) can be tuned by Sn concentrations. Series of sensing tests to formaldehyde gas indicated that the ITO-7 NTs show the lowest working temperature (160 °C) and the highest specific response. Here, It is noted that to eliminate the influence of the coating amount of sensing performances, a concept of specific response was proposed i.e., $R_{air}/(m–R_{gas})$, where R_{air} and R_{gas} respectively stand for the resistances of gas sensors in the reference gas (in air this case) and in the test gas ambience, and m stands for the mass of the coated sensing materials. The decreased working temperature could be attributed to the formed In_2O_3 NPs/ITO tubular structure, and the enhanced specific response might be mainly associated with the $V_o^{\cdot}$S. Furthermore, a possible gas sensing enhancing mechanism via $V_o^{\cdot}$S for ITO-based gas sensors was proposed based on our results and analysis. This research would give some instructive advice to design high-performances oxide-based gas sensors via tuning the $V_o^{\cdot}$S.

1. Introduction

In_2O_3 is one n-type oxide semiconductor and has been frequently used to detect various flammable/toxic dangerous gases [1–3]. In spite of its advantages in gas sensing response, the In_2O_3-based gas sensors often suffer from high working temperatures [4,5]. In order to solve this problem, metal element doping has been demonstrated to be one simple and effective approach, and can be roughly divided into noble and common metal doping. For doping noble metal such as Pt and Ag, it can lower down the working temperature via improving catalytic activities of gas or directly interacting with electrons on the surface of semiconductors [6,7]. Alternatively, the common metal doping can also lower down the working temperature via introducing defects into the crystalline lattice of the matrix, and has attracted much more interest due to the cost issue [8–12].

Taking Sn doping for instance, the Sn doped In_2O_3 materials (i.e. indium tin oxide, ITO), known for use in transparent conductive films, have been often employed to detect methanol, formaldehyde, ethanol, CO_2, NH_3, NO_2, and etc [13–17]. Sberveglieri et al. first employed the sputtered ITO thin films to detect NO_2 gas, obtained the response (R_{gas}/R_{air}, where R_{air} and R_{gas} stand for the resistances of gas sensors in air and in the test gas ambience, respectively) to 250 ppm NO_2 is 8.5 at 300 °C [18]. The ITO sensors also showed fast response to NO_2 (response time (t_{res}) of less than 0.7 s, recovery time (t_{rec}) of 1–2 min), which could be the high conductance of ITO materials [19]. Jiao et al. prepared ITO thin films by sol–gel method, obtained the enhanced response of 15.8 to the 100-ppm NO_2 gas at 280 °C [20]. This enhancement in response is often assigned to the formed nanoscale morphology in

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the samples [21–25], but the working temperatures are still very high. More recently, Xu et al. have employed the electrospun ITO nanofibers to detect NO_2 gas, and found that the optimal working temperature can be lowered down to 160 °C, which is much lower than those of ITO thin films [14]. Qi et al. used the electrospun SnO_2 NPs-In_2O_3 composite nanofibers to detect 1 ppm NH_3 even at room temperature [22]. They have empirically contributed these great decreases in working temperatures to the small grain size and the one-dimensional conductive paths. While, it is known that those electrospun nanofibers should be post-annealed in air to remove the organic components in them before use. Thus these post annealing processes will often result in a type of oxygen-deficient samples [26–29]. Du et al. observed that the SnO_2/In_2O_3 composite nanofibers treated with oxygen plasma exhibit highly improved gas responsivity to formaldehyde vapor, and contributed this improvement to the conducting electron concentrations caused by oxygen defects [30]. Ahn et al. also demonstrated that the oxygen vacancies ($V_O^{\cdot\cdot}$S) show great influence on the response of the gas sensors [31]. Thus, tuning the concentration of $V_O^{\cdot\cdot}$S in the materials is another effective way to enhance the response of gas sensors. And few literatures have given a deep investigation on the relation between defects and performances of ITO-based sensors. Therefore, it is still important and instructive to explore how the $V_O^{\cdot\cdot}$S can affect the sensing behaviours of ITO-based sensors.

In this work, the authors have designed a type of high-surface-area ITO nanotubes (NTs) with various Sn content (3, 5, 7, 10, 12, and 15 mol%) by single-nozzle electrospinning technique. The morphologies of the samples can be well controlled by controlling the heating rate at 3 °C min^{-1}, and the concentration of $V_O^{\cdot\cdot}$S can be well tuned by doping concentration. As designed, the obtained ITO NTs were assembled into gas sensors to detect formaldehyde gas. Here, it is noted that a concept of specific response was proposed to eliminate the influence of the coating amount of sensing performances, i.e., $R_{air}/(m\,R_{gas})$, where R_{air} (R_{gas}) is the resistance in air (target gas) and m stands for the mass of the coated sensing materials. Series tests indicated that the gas sensors based on 7 mol% ITO NTs exhibit its maximum response at low operating temperature of 160 °C, and can quick respond to 100 ppm formaldehyde even at temperature less than 100 °C. Furthermore, a type of gas sensing mechanism via $V_O^{\cdot\cdot}$S was proposed and partially proved by our designed atmosphere annealing processes.

2. Experimental section

2.1. Preparation of ITO NTs

First, a type of precursor solution was prepared by dissolving 0.2 g of indium nitrate ($In(NO_3)_3{\cdot}4{\cdot}5H_2O$) and certain amount of $SnCl_2{\cdot}2H_2O$ into 2.5 mL of absolute ethanol, following by vigorous stirring. After the precursor solution became homogeneous, 0.4 g of polyvinylpyrrolidone (PVP, $M_w \approx 1{,}300{,}000$, Sigma-Aldrich, USA) and 2.5 mL of N,N-dimethylformamide (DMF) were further added. And the resultant solution was stirred for 2 h before sending to electrospinning processes. In the typical electrospinning process, a high DC voltage of 14 kV and a distance of 15 cm were applied between the collector and the metal needle. Finally, the collected composite fibers were heated to 600 °C with rate of 3 °C min^{-1} and kept at 600 °C for 2 h in air.

To tune the performances in the samples, different Sn doping concentrations (Sn/(Sn + In)) in the precursor solution were designed, i.e., 1, 3, 5, 7, 10, 12, and 15 mol%; and the resultant samples were labeled as ITO-3, ITO-5, ITO-7, ITO-10, ITO-12, and ITO-15, respectively. $SnCl_2{\cdot}2H_2O$ and $In(NO_3)_3{\cdot}4{\cdot}5H_2O$ were purchased from Alfa-Aesar Inc., USA; ethanol and DMF from Tianjin Chemical Corp., China. All chemical regents used analytical purity and used without further purification.

2.2. Assembly and gas-sensing measurements of sensor devices

Firstly, a proper amount of organic binder (made by dissolving 10 wt% ethylcellulose in α-terpineol) was mixed with the annealed ITO NT powder, forming a type of homogeneous paste. And then the paste was coated onto a type of commercial alumina ceramic tubes for sensing tests, which can be heated at operating temperatures between 100 °C and 300 °C in air via a Ni-Cr coil through their interior (as shown in Fig. S1(a)). After dried at 80 °C in a drier for several hours, the coated ceramic tubes were sent to a tube furnace and annealed at 400 °C in air for 2 h to remove the organic binder. Finally, the annealed ceramic tubes were fixed on a type of test bakelite base via two pairs of Pt wire electrodes (as shown in Fig. S1(b)). Ethylcellulose and α-terpineol were purchased from Alfa-Aesar Inc., USA.

The gas-sensing properties of the devices were tested on a WS-30A gas sensor instrument (Wei-Sheng Electronics Co. Ltd., Zhengzhou, China) under a relative humidity less than 30% RH. And, a type of standard dry helium-diluted 500 ppm formaldehyde gas was purchased Chengdu Taiyu Industrial Gases Co. Ltd., China, and used for target gas. In order to eliminate the effect of materials' mass on the devices, the specific response (response per mass) was proposed, and defined as $R_{air}/(m{\bullet}R_{gas})$, where R_{air} and R_{gas} are the resistance values measured in the air and reducing-gas ambiences, respectively; and m stands for the mass of the coated sensing materials. The response time t_{res} was defined as the time required for the variation in resistance to reach 90% of the equilibrium value after injection of a test gas, and the recovery time (t_{rec}) was the time necessary for the sensor to 10% of its original resistance in air.

2.3. Material characterizations

The morphologies and microstructures of the samples were investigated using field-emission scanning electron microscopy (FE-SEM, MIRA3, TESCAN) and high-revolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30, operated at 300 kV) equipped with energy dispersive X-ray spectroscopy (EDX) system. The crystal structures of the samples were recorded by X-ray diffraction (XRD, Philips X' Pert Pro, Cu-Ka, 0.154056 nm). Chemical bonds were studied by a multifunctional X-ray photoelectron spectroscope (XPS, PHI-5702, Mg KR X-ray, 1253.6 eV). Surface area was determined from N_2 gas-adsorption data via Brunauere-Emmette-Teller (BET, Micrometrics, ASAP 2010) system. And the photoluminescence (PL) spectra were recorded on a spectrophotometer (Shi-Madzu, RF-5301PC, 15 mW He–Cd laser, 325 nm).

3. Results and discussion

3.1. Morphology and microstructure characterizations

In this work, ITO NTs with different Sn loadings were designed to control the concentration of $V_O^{\cdot\cdot}$S, and the effect of $V_O^{\cdot\cdot}$S on the sensing performances of gas sensors was investigated in detail. Fig. 1 demonstrates the control processes of ITO NTs with different concentrations of $V_O^{\cdot\cdot}$S. On the base of our previous experimental and theoretical analysis [32–34], the formation of $V_O^{\cdot\cdot}$S in ITO NTs could be described as following: At first, the as-spun composite nanofibers are comprised with well-dispersed $SnCl_2$ and $In(NO_3)_3$ molecules. During the heating processes, the $SnCl_2$ and $In(NO_3)_3$ molecules in the composite nanofibers would usually be forced to immigrate out to the fibers' surface due to their lower diffusion velocities in organic solvent compared to PVP molecules'. And then, the migrated molecules will decompose, react with each other, and