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Pure SnO_2 Gas Sensor with High Sensitivity and Selectivity towards C_2H_5OH

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Abstract

To observation, poisonous gases in the environment, Sensors with high selectivity, high response and low operating temperature are required. In this work, pure SnO_2 nanoparticles was prepared by using a simple and inexpensive technique (hydrothermal method) without a template. Various confirmatory tests were performed to characterize SnO_2 nanoparticles such as energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transition Electron Microscopy (TEM), during the detection of the gas, we found that pure SnO_2 nanoparticles has a high selectivity for ethanol to 100 ppm at a low temperature (180˚C) and a high response (about 27 s) and a low detection limit of 5 ppm, also it have response/recovery times about (4 s, 2 s) respectively. The distinctive sensing properties of SnO_2 sensor make it a promising candidate for ethanol detection. Furthermore, the gas-sensing mechanism have been examined.

Keywords

Hydrothermal Method, Nanoparticles, Ethanol, SnO_2, Gas Sensor

1. Introduction

Volatile organic compounds are considered a major component that participates in the formation of ozone, which are air pollutants, and their percentage increases from weakness in the outside air, due to their presence in many products in the home, as volatile organic compounds are now included in about 90% of the products that enter the home, Its sources include drinking water, carpets, paints, deodorants, cleaning methods, materials used for shoe polishing, cosmetics, dry cleaning clothes, moth repellents, air fresheners, and car exhaust [1] [2] [3]. One of the volatile organic compounds that must be detected is ethanol. Ethanol is an organic chemical compound that belongs to the alcohol family. It has the chemical formula: C_2H_5OH and it is called generalized alcohol [4]. Ethanol is a colorless, flammable substance formed from the fermentation of sugar. It is used in alcoholic beverages and in the manufacture of perfumes and is used as a fuel in mechanical engines prepared for ethanol [5]. Whereas, eating small to moderate amounts may lead to symptoms of toxicities, such as inconsistency in muscle work, poor vision, slurred speech … etc. As for eating large amounts, dampening of the bulb reflexes, such as drowsiness, forgetfulness, and memory impairment, amnesia, hypothermia, hypoglycemia, stupor, coma, respiratory depression may occur [6]. Therefore, it is necessary to find a high-efficiency and low-cost sensor material for the detection of ethanol [7]. TiO_2, Cr_2O_3, CuO, ZnO, and SnO_2, etc. are semiconducting metal oxides. Defined as high-efficiency and low-cost sensor materials for the detection of toxic and harmful gases [8] [9] [10] [11] [12]. Recently, different structures of MOS materials with a large specific surface area have been reported to improve the sensing response of sensors, for an example nanowires, nanoparticles, nanorods, hierarchical flower-like structure and hollow microspheres [13] [14].

The SnO_2 known as n-type semiconductor with band gap 3.6 eV. Also, it is promising for gas sensing materials in order to chemical stability, perfect thermal, excellent mobility of an electron and low cost [15]. To synthesis SnO_2 nanocrystal line, Different methods have been used such as chemical vapor deposition, sputtering, hydrothermal and sol-gel, among them hydrothermal method is simple and inexpensive method. Syntheses of pure SnO_2 nanoparticles by a hydrothermal method are still limited. In this work, pure SnO_2 nanoparticles were successfully synthesized by hydrothermal method without any template. The obtained sample was analyzed by SEM, TEM, EDX, and XRD. Moreover, the sensing performances and gas sensing mechanism were discussed.

2. Experimental

In a typical procedure, 1.6 g NaOH, 1.4 g $SnCl_2 \cdot 2H_2O$ and 1 g PVP were dissolved in mixed solution contained of 5 ml H_2O_2 and 35 ml DI under a magnetic stirring at 30˚C for 2 h. Then the above mixed solution was transferred to 50 ml Teflon-lined stainless-steel autoclave and reacted for 10 h at 180˚C, therefore, after the autoclave cooling down to room temperature naturally the precipitate was washed with deionized water and ethanol for serval time, finally the SnO_2 powders were obtained after dried in a furnace for 24 h. The crystal structure X-ray diffraction (XRD) of SnO_2 nanoparticles was tested by using an X-ray diffractometer (XRD, D/Max-2400) with Cu Kα1 radiation (λ = 0.15406 nm), Elemental composition was tested by (EDX) an energy-dispersive X-ray detector, surface morphological and microstructural of the sample was carried out on a scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, JEM-2010). The gas sensing properties were evaluated by the WS-30B gas sensing apparatus (Wei Sheng Electronics Science and Technology Co., Ltd., Henan Province, China). The sensor response (R) to gas was defined as Ra/Rg, where Ra and Rg were the initial sensor resistance in air and gas [16].

3. Results and Discussion

The X-ray diffraction (XRD) analysis was used to examine the crystal structure of the sample, in Figure 1(a). The peak positions of the sample displayed a rutile type tetragonal structure of SnO_2, which were matched well with a standard card (JCPDS, 41-1445) with $a = b = 4.736$ Å and $c = 3.185$ Å. No impurity phase detected which indicates the high purity of the prepared SnO_2 [17]. The crystallite size d is measured using Debye-Scherer's formula:

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

β is the Full Width at Half Maximum (FWHM) of the peak, θ is the Braggs angle, and λ is the wavelength of X-ray. After calculating by means of the above equation, he found that it is equal to 2.215 nm [18] [19]. (the EDX spectroscopy of SnO_2 nanoparticles) in Figure 1(b), indicating that our sample composed of Sn and O elements. Figure 2(a), Figure 2(b) showed the SEM images of SnO_2 nanoparticles, the nanoparticles are well crystallized, Figure 2(c) displays the TEM image of the as-synthesized product. It can be clearly seen that nanoparticles with rough surfaces, it is matched well with results of SEM, rough surfaces. It is very good to the desorption and adsorption of gas molecules [20] [21], the inner figure in Figure 2(c) is SAED pattern illustrated the polycrystalline nature of SnO_2 sample, the HRTEM image displayed in Figure 2(d), the lattice distance was calculated to be 0.175 nm. It corresponds to (211) crystallographic orientation, the optimum operating temperature was determined, the response values of

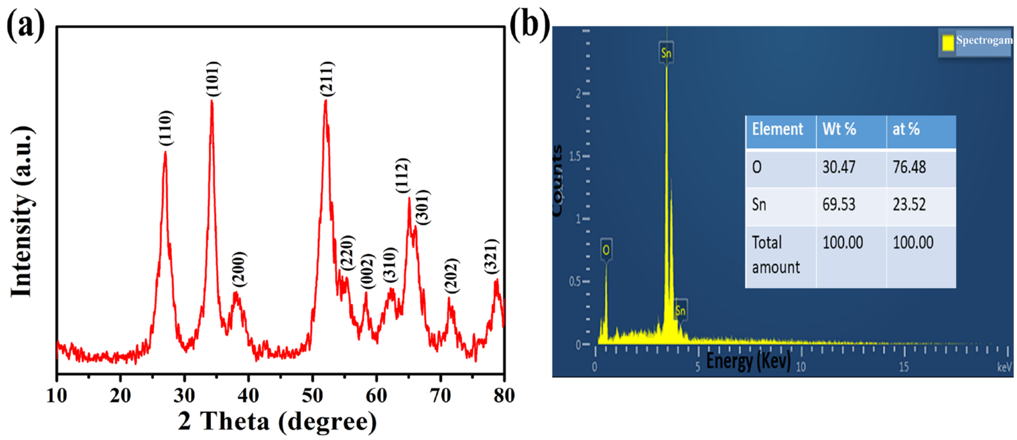

Figure 1. (a) The XRD pattern of SnO_2 nanoparticles; (b) showed EDS pattern of the SnO_2 nanoparticles.

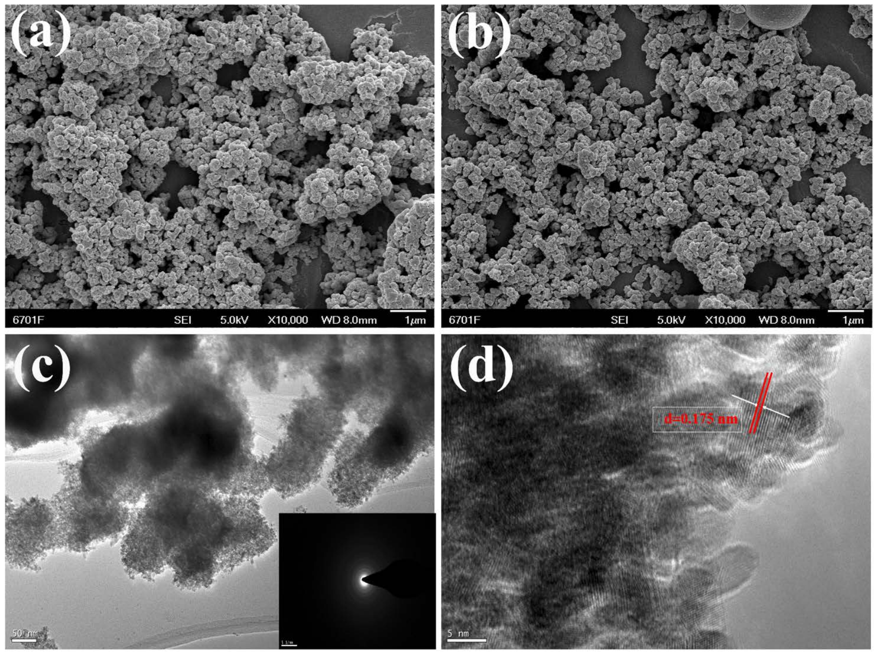

Figure 2. (a) (b) displayed the morphologies of SnO_2 nanoparticles; (c) showed the TEM picture of SnO_2 nanoparticles, the inner figure in (c) showed the SAED pattern; (d) displayed HRTEM picture of SnO_2 nanoparticles.

SnO_2 nanoparticles to 100 ppm ethanol under different operating temperatures in the range of 140˚C → 340˚C are evaluated and depicted in Figure 3(a), when the increase of ethanol concentrations from 5 → 1000 gas response increases progressively, Figure 3(b), when the concentration is above 150 ppm, the gas sensor nearly be stable. The responses of SnO_2 nanoparticles to 100 ppm different gasses at 180˚C determined in Figure 3(c). Our sensor exhibits high selectivity to ethanol. The response and recovery times are about 4 s and 2 s, respectively, Figure 3(d). In Figure 3(e) indicated the sensor nearly to be stable. The results indicate that the SnO_2 nanoparticles based sensor can successfully differentiate ethanol at 180˚C. Table 1 showed the Comparison between various SnO_2 based gas sensors to C_2H_5OH.

Experimental results of SnO_2 nanoparticles sensor have been compared with the results reported by the other workers on C_2H_5OH sensors and presented in Table 1. It can be seen that SnO_2 nanoparticles sensor can reach a relatively higher response toward C_2H_5OH at lower temperature. The obtained results indicate that the SnO_2 nanoparticles sensor is promising for C_2H_5OH gas sensing. In Figure 4 the gas-sensing mechanism of SnO_2 nanoparticles when the sample is exposed to air, oxygen molecules will be absorbed on the surface, trapping the conduction band's electrons and creating chemisorbed oxygen species (e.g. O^{2-}, O^- and O_2^-) through Eqs [30].

$$O_2 + e^- \rightarrow O_2^-(ads) \tag{1}$$

$$O_2^-(ads) + e^- \rightarrow O^-(ads) \tag{2}$$

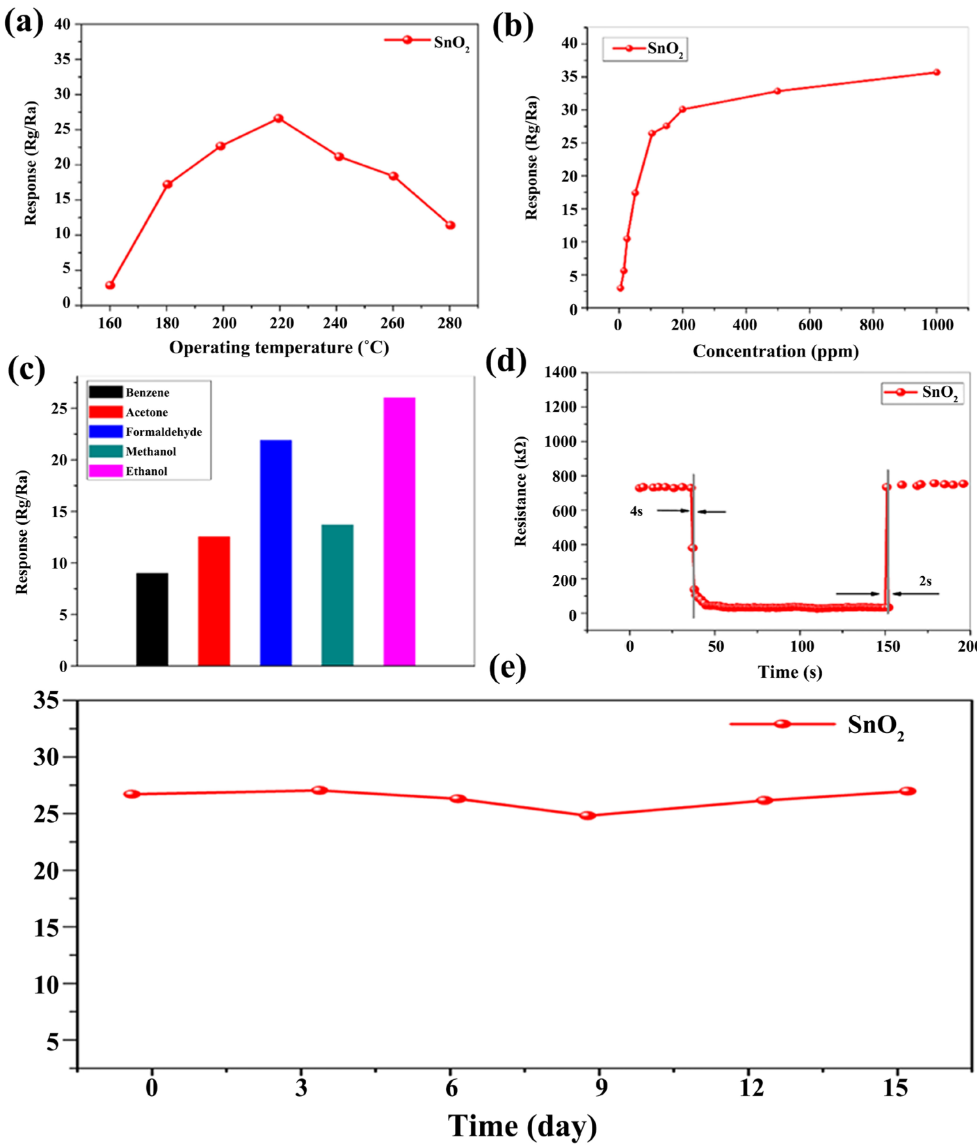

Figure 3. (a) displayed the gas sensor responses of sample to 100 ppm ethanol to different operating temperatures; (b) is gas sensor responses to different concentrations (5 - 1000 ppm) of ethanol; (c) displayed the response to 100 ppm ethanol at different gases; (d) is the response and recover time towards 100 ppm ethanol at 180˚C; (e) showed the stability of SnO_2 sample to 100 ppm ethanol at 180˚C.

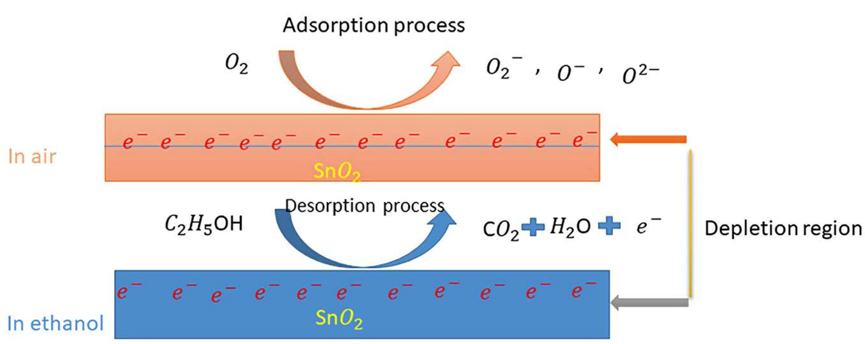

Figure 4. Demonstrated gas sensing mechanism of SnO_2 nanoparticles.

Table 1. The Comparison between various SnO_2 based gas sensors to C_2H_5OH.

Sensor materials	Con (ppm)	Selectivity	Gas response	Synthetic method	Ref.
3D porous flower-like SnO_2	500	ethanol	208	HM	[22]
α-Fe_2O_3/SnO_2	100	ethanol	22.46	ES	[23]
Porous SnO_2 nanowires	100	ethanol	~1.7	EF, HM	[24]
GO/SnO_2 nanosheets	100	ethanol	2.9	HM	[25]
WO_3-SnO_2nanosphere composites	1000	acetone	16.9	HM	[26]
La-doped SnO_2 nanoparticles	5	formaldehyde	4.2	BM	[27]
Porous flower-like SnO_2	100	formaldehyde, ethanol	24.8	HM	[28]
Hollow ZnO-SnO_2	100	ethanol	392.29	ES	[29]
SnO_2 nanoparticles	100	ethanol	27	HM	this work

Where: EF ≡ electrospinning followed; HM≡ hydrothermal method; BM ≡ ball-milling solid chemical reaction method; ES ≡ electrospinning.

$$O^{-}(ads) + e^{-} \rightarrow O^{2-}(ads) \tag{3}$$

which will generate an electron depletion layer on the surface, leading to high resistance of the material. When the sample is exposed to ethanol, the adsorbed ethanol molecules will react with the surface oxygen species. This process releases the trapped electrons back to the conduction band. Thus, the thickness of the electron depletion layer will decrease, resulting in low resistance of the sample. This progress can be described as follows [31]:

$$C_2H_5OH + 6O^{-}(ads) \rightarrow 2CO_2 + 3H_2O + 6e^{-} \tag{4}$$

$$C_2H_5OH + 6O^{2-}(ads) \rightarrow 2CO_2 + 3H_2O + 12e^{-} \tag{5}$$

4. Conclusion

In summary, SnO_2 nanoparticles have been successfully synthesized through a facile and low-cost hydrothermal method. The sensor exhibits excellent sensitivity about 27, fast response and recovery time (4 s and 2 s), long-term stability and the optimum operating temperate 180˚C. Thus SnO_2 nanoparticles can be used as a promising material for ethanol sensors.

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Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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