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# Synthesis and gas sensing properties of $Fe_2O_3$ nanoparticles activated $V_2O_5$ nanotubes

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ABSTRACT

The $Fe_2O_3$ nanoparticles activated $V_2O_5$ nanotubes were achieved via a hydrolysis method. The TEM and SEM images of the nanotubes indicated that the $Fe_2O_3$ nanoparticles with the particle size of about 15 nm were dispersed on the surface of the $V_2O_5$ nanotubes. The activated nanotubes exhibited excellent response and selectivity towards the ethanol gas. The lowest detection limit for ethanol gas was about 10 ppm at 230 °C, which suggested that the $Fe_2O_3$ nanoparticles activated $V_2O_5$ nanotubes would be a potential candidate for practical detector for ethanol.



## 1. Introduction

The increasing concerns with air pollution and industrial safety stress the need of monitoring combustible and toxic gases in real time. A tremendous effort has been made to develop gas sensors to a high level. Recently, researches show that one-dimensional (1D) nanostructure semiconducting oxides have several advantages with respect to traditional thin- and thick-film sensors such as high surface-to-volume ratio, dimensions comparable to the extension of surface charge region. This region depleted of majority carriers extends approximately a few Debye lengths in to the bulk [1–6]. So it has been shown that the gas sensor response increases abruptly when the particle size becomes comparable or smaller than the Debye length (typically several nanometer) [7].

1D $V_2O_5$ nanomaterials are an attractive class of nanomaterials, and widely applied to the fields such as thermochromism, optics and electrochemistry [8–10]. Also many researchers reported that the nanostructured vanadium oxides are promising materials for gas sensing applications. Raible et al. reported that the gas sensor based on $V_2O_5$ nanofibers exhibited high selectivity and sensitivity to amines [11]. Liu et al. found that $V_2O_5$ nanobelts sensor presented good sensitivity to ethanol and the detection limit was about 10 ppm [12]. In order to enhance the reactions and improve detecting abilities, the metal oxide or noble metal nanoparticles were deposited on the surfaces of 1D nanomaterials [13,14]. $Fe_2O_3$ nanoparticles are known to be widely used materials as active element of thick-film gas sensor, which offered a high sensitivity to some gases without the application of noble metal catalysts [15–18]. Si et al. synthesized $Fe_2O_3$/ZnO core/shell nanorods, which exhibit a high sensitivity to some volatile gases, short response/recovery time and can work at relatively low temperatures [17]. Liu et al. reported the enhanced sensitivity of $V_2O_5$ nanobelts coated with nanosized metal oxides in comparison with the uncoated ones [18].

From the available references, it follows that modifying of a sensitive materials with $Fe_2O_3$ can significantly enhance the sensitivity. In this paper, we prepared $Fe_2O_3$ activated $V_2O_5$ nanotubes (VONTs) by a simple hydrothermal method starting from a mixture of VONTs and $Fe(NO_3)_3$ solution. These were evaluated for the detection of ethanol and toluene and the results showed that the activated nanotubes exhibited excellent response and selectivity towards the ethanol gas, and may be used for the detection of the gas in10 ppm at 230 °C.

## 2. Experimental

VONTs were prepared via a rheological phase reaction followed by a self-assembling process at 180 °C [19]. A desired amount of the as-prepared VONTs were dispersed in 30 ml ethanol and 10 ml deionized water by ultrasonication for 10 min (solution I). Then 1 ml $Fe(NO_3)_3$ ethanol solution (0.1 mol/L) was added to the solution I (solution II). The solution II was transferred into a Teflon-lined

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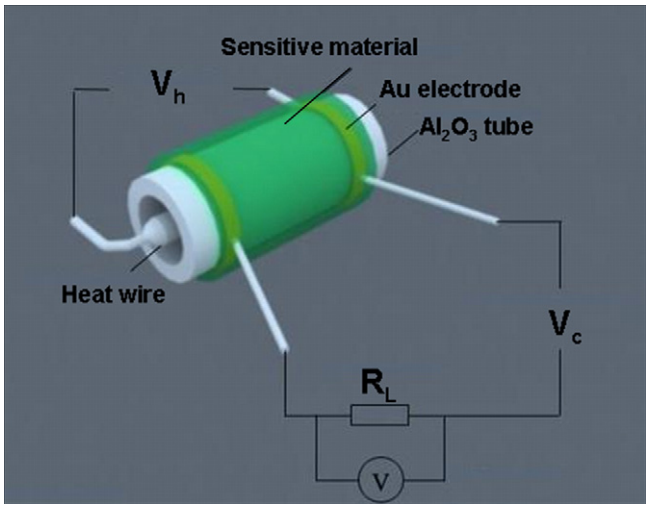


**Fig. 1.** Schematic diagram of the structure and the measuring circuit of a gas sensor.

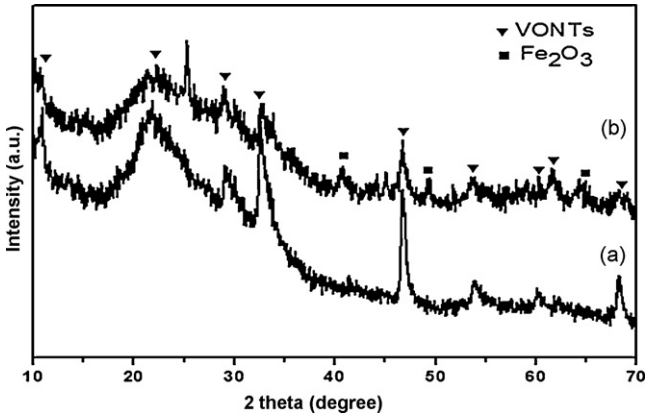


**Fig. 2.** XRD patterns of the samples: (a) VONTs and (b) $Fe_2O_3$ activated VONTs.

autoclave with a stainless steel shell and kept at 180 °C for 6 h. Finally, the mixture was cooled down to the room temperature and the precipitate was washed several times by ethanol to remove the residual $Fe_2O_3$, and dried in vacuum at 80 °C for 4 h.

The X-ray powder diffraction (XRD) measurement was performed on a D/MAX-III X-ray diffractometer with Cu $K_\alpha$ radiation and graphite monochromator. Scanning electron microscopy (SEM) images were collected with JSM-5610LV at 20 kV. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and energy-dispersive spectrometry (EDS) were recorded with a JEOL JEM-2010 FEF microscope operated at 200 kV.

The gas sensing properties of $Fe_2O_3$ activated VONTs were measured with a commercial gas sensing measurement system of WS-30A (Zhenzhou Winsen Technology Corp., LTD). As shown in Fig. 1, the sensor was prepared by coating a sensing layer, a black mixture of $Fe_2O_3$ activated VONTs and a small amount of terpineol, on a ceramic tube (8 mm in length, 2 mm in external diameter and 1.6 mm in internal diameter), on which an Au electrode and two Pt wires had been installed at each end. Then the as-prepared sensor was dried at 100 °C for 7 days in air. Finally, a Ni–Cr alloy was put in it as a heating unit to control the working temperature of the sensor. After fitting the sensor into the gas sensing measurement apparatus, adjusting the heating voltage to 2 V to give temperature of 250 °C to sensing film for 5 min for film strength enhancement and sensing property stability. Then a given mass of target gases was injected into the testing chamber by a microinjector. The sensor response ($S$) is defined as the ratio $R_a/R_g$, namely $S = R_a/R_g$, where $R_a$ and $R_g$ are the electrical resistance of sensors in air and in a test gas, respectively. The response time is defined as the time needed to reach 90% of the equilibrium value after injecting the test gas while the recovery time is defined as the time needed to return to 10% above the original response in air after stopping the flow of the test gas.

## 3. Results and discussion

The phases of the samples were characterized by XRD (Fig. 2). Compared with the pure VONTs, there were some additional diffraction peaks existed in the $Fe_2O_3$ activated VONTs, and all the additional diffraction peaks could be readily indexed to $Fe_2O_3$ (JCPDS 005-0637) and $V_{0.87}Fe_{0.13}O_{2.17}$ (JCPDS 035-0333). The presence of $V_{0.87}Fe_{0.13}O_{2.17}$ may be the result of atomic diffusion or doping at interfaces.

Fig. 3 presented the SEM, TEM images of the VONTs. The obtained nanotubes were 2–6 μm in length, 60–150 nm in outerdiameter, 20–30 nm in innerdiameter and about 3.2 nm of the layered distance. Fig. 4 shows the SEM, TEM images and the EDS results of the $Fe_2O_3$ activated VONTs. It should be noted that the 1D morphology totally remained. And the surface became rough, which implied the existence of the $Fe_2O_3$ nanoparticles on the surface. The TEM image further confirmed that the $Fe_2O_3$ nanoparticles were around the surface of the VONTs, and the average particles size was about 15 nm. EDS was also measured to determine the chemical composition of the $Fe_2O_3$ activated VONTs. The results showed that it only contained three types of elements V, O and Fe (the Cu

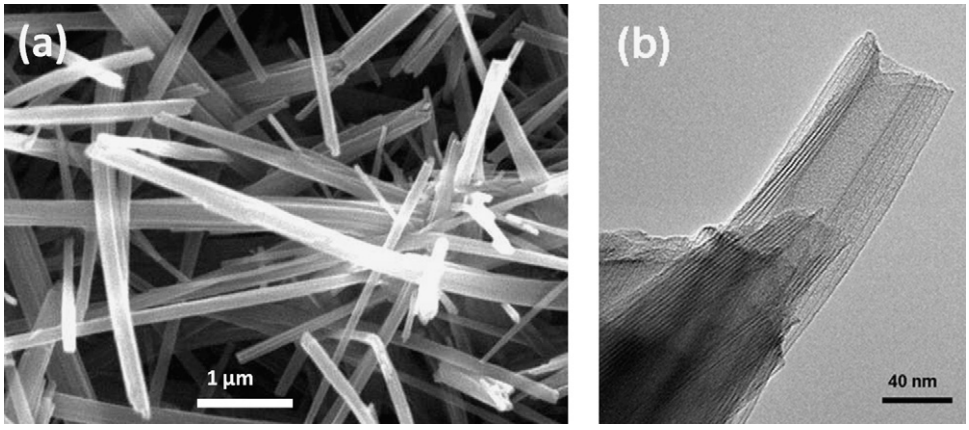


**Fig. 3.** SEM and TEM images of VONTs.

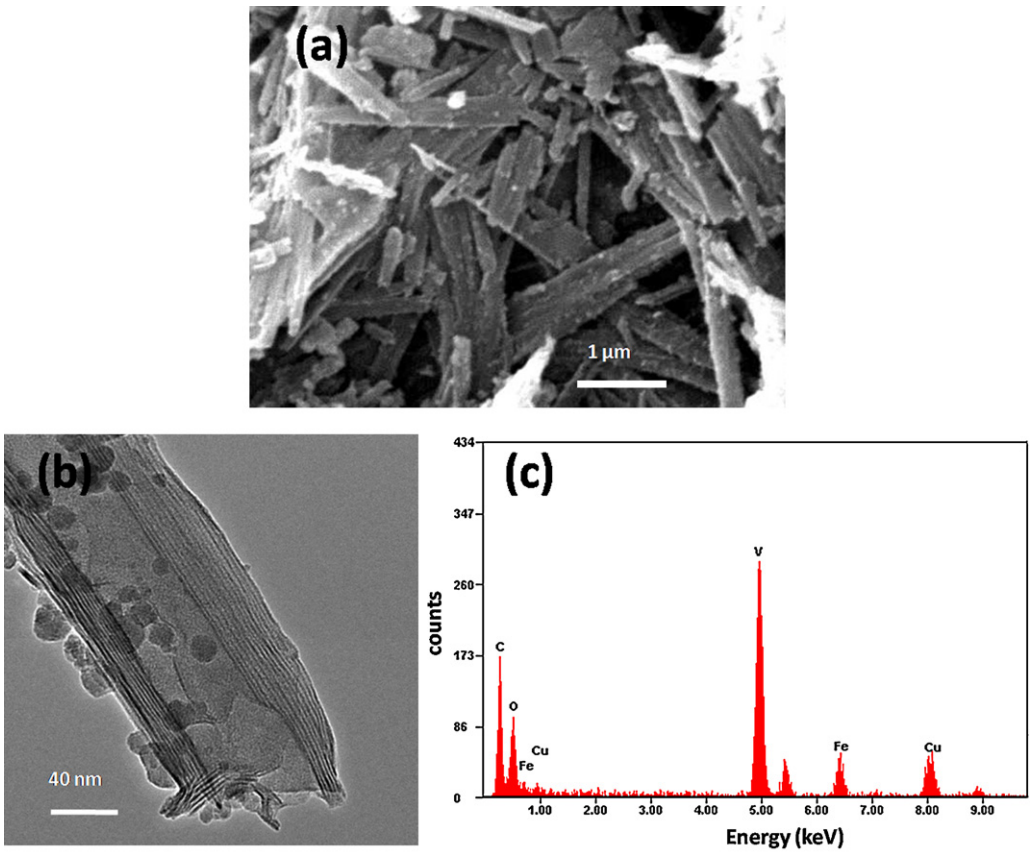


**Fig. 4.** $Fe_2O_3$ activated $V_2O_5$ nanotubes: (a) typical SEM image, (b) TEM image and (c) EDS spectrum recorded on an individual nanotube.

signal came from the copper TEM grid). All these evidences proved that the $Fe_2O_3$ activated VONTs were successfully synthesized.

The as-prepared gas sensor was tested under a relative humidity of about 30–40% in air at 25 °C and the working temperature ranged from 230 to 330 °C. Fig. 5(a) shows a typical isothermal response of the resistance as different concentration pulses of ethanol (from 10 to 1000 ppm) at a working temperature of 270 °C. The resistance underwent a drastic drop on the injection of ethanol and reached the equilibrium value within 15 s, exhibiting n-type semiconductor characteristic. Then it mostly restored its initial value after releasing the test gas. The lowest detection limit was about 10 ppm. During the cycling between increasing concentration of ethanol and ambient air, the resistance restored its initial value immediately after the test gas was released, which suggested that the stability of the sensor was good. However, with the increase of the gas concentration, the recovery time became longer, from 20 to 40 s at 270 °C. Fig. 5(b) shows the response to ethanol at different concentrations and operating temperatures. It could be seen that the change of resistance with the concentration of ethanol at different temperatures was non-linear. The response increased gradually with the increase of the gas concentration and operating temperature. When the operating temperature was at 330 °C, the sensor response to 1000 ppm ethanol gas could reach 3.37, which is about two times larger than that of pure VONTs (1.8) at the same condition, and also higher than that of $V_2O_5$ nanobelts reported in Ref [12].

For n-type semiconducting metal oxides, the gas sensing mechanism can be explained by the space-charge region mode [20]. At certain temperature, oxygen ionosorbs over metal oxides in different forms, such as $O^{2-}$, $O^-$, which is corresponding to a high

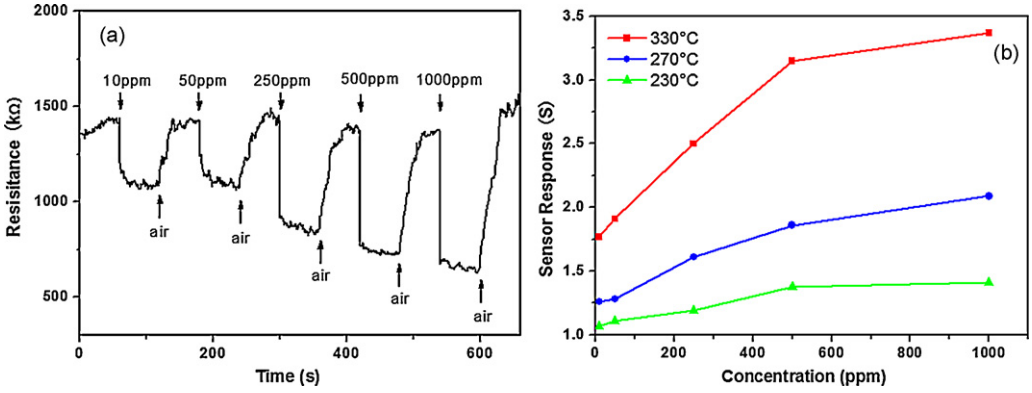


**Fig. 5.** (a) Typical resistance response curve on cycling between increasing concentration of ethanol and ambient air at 270 °C and (b) the sensor response to ethanol at different operating temperatures.

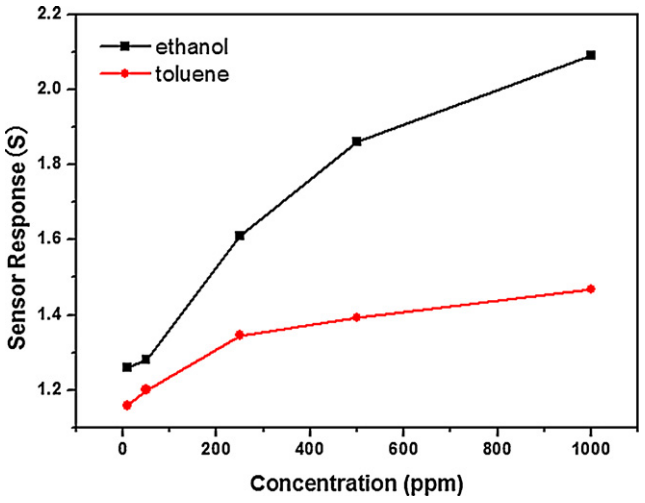


**Fig. 6.** The comparison of sensor response of $Fe_2O_3$ activated VONTs to (a) ethanol and (b) toluene at 270 °C.

resistance of the sensor. When the target gas comes into contact with the surface, it will react with the ionosorbed surface oxygen, releasing electrons from surface state to the conduction band, induce the decrease in the resistance of the sensor. The sensitivity of the sensor is affected by many factors, such as grain size and interface structures [21]. In Ref. [22], it was demonstrated that, when the grain size comparable to twice the Debye length, a space-charge region can develop in the whole crystallite, and the maximized conductance switch can be observed. For $Fe_2O_3$ activated VONTs structure, the diameter of pure VONTs is very large, about 60–150 nm, oxygen molecules deplete partially electrons in the VONTs, so the surface of VONTs is partially depleted. But the particles size of $Fe_2O_3$ is only about 15 nm, which is comparable to twice the Debye length, so oxygen molecules deplete completely electrons in the $Fe_2O_3$. It means that $Fe_2O_3$ nanoparticles increase the quantity of active sites on the surface of gas sensors, which is positive to the sensor response [23,24]. When the sensor is exposed to target gases, the extracted electrons of both $Fe_2O_3$ and VONTs will be released back, led to great change in resistance. Moreover, the $Fe_2O_3$ activated VONTs structure can well avoid the aggregation of particles, and provide a larger number of pores and a higher surface. All of these eventually led to the sharp improved gas sensing properties of the sensors made by $Fe_2O_3$ activated VONTs.

In practical applications the selectivity of gas sensor is also an important parameter. Therefore, toluene sensing properties of $Fe_2O_3$ activated VONTs were also measured under the same condition. Fig. 6 shows the comparison of sensor response of $Fe_2O_3$ activated VONTs to ethanol and toluene operating at 270 °C. It can be seen that the response to toluene was smaller than that to ethanol, and the change of response was very slight when the sensor exposed in different concentrations of toluene, which indicates that the sensor had very good selectivity to ethanol.

## 4. Conclusion

The $Fe_2O_3$ activated VONTs were synthesized and the average diameter of the $Fe_2O_3$ nanoparticles was about 15 nm. The $Fe_2O_3$ activated VONTs structure exhibited a dramatic improvement in ethanol sensing properties including sensor response and selectivity. The response of this material to ethanol increased with a rise of operating temperature and gas concentration. When the sensor worked at above 230 °C, the detection threshold could decrease to 10 ppm levels. These favorable gas sensing features made the $Fe_2O_3$ nanoparticles activated VONTs sensor to be the potential candidate for practical detector for ethanol.

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