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Au/La Co-Modified In$_2$O$_3$ Nanospheres for Highly Sensitive Ethanol Gas Detection

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Abstract: In this paper, the gas-sensitive properties of co-doping the rare earth element La and noble metal Au in In$_2$O$_3$ nanospheres were investigated for ethanol detection. Through XRD and SEM characterization, the grain size of La-In$_2$O$_3$ and Au/La-In$_2$O$_3$ nanoparticles was smaller than that of pure In$_2$O$_3$. As expected, the smaller grain size sample has shown a higher response for ethanol vapor. Compared with the pure In$_2$O$_3$ nanoparticles, the 2 mol%Au/2 mol%La-In$_2$O$_3$ sample has shown better ethanol-sensing properties, including higher sensitivity ($S = 381$) and lower operating temperature (210 °C) for 100 ppm ethanol vapor. In addition, the Au/La-In$_2$O$_3$ sensor presented a fast response time (1 s). The enhancement mechanism of the ethanol response was discussed for Au/La-In$_2$O$_3$ nanoparticles. The obtained experimental results would provide a new road for designing higher response sensors.

Keywords: rare earth; noble metal; gas response; enhancement

1. Introduction

Ethanol (C$_2$H$_5$OH), a common volatile compound gas, is widely applied to industrial production, the food industries and the biomedical field. However, exposure to excess ethanol gas can bring about headaches, liver and kidney damage, central nervous system harm and breathing difficulties [1,2]. Moreover, many traffic accidents are induced by ethanol abuse at present, which has caused around 1.35 million people deaths per year globally. Hence, the quantitative investigation of ethanol has become a key role for protecting human health, ensuring food safety and avoiding drunk driving via breathing test [3,4].

Recently, a variety of ethanol sensors have been designed with different sensing principles [5–7], such as those based on a chemiresistive model [8], optical fiber [9] and electrical properties [10]. Among them, chemiresistive model sensors present lower power, fast response, compact size and high sensitivity, resulting in the best option for ethanol detection. The characteristics of the chemiresistive model sensor indicate that the resistance of the sensor changes with the target gas concentration variation because of the physical/chemical adsorption of the target gas. Different metal oxide semiconductor materials have been applied to the chemiresistive model ethanol sensor, such as ZnO, SnO$_2$, TiO$_2$, Fe$_2$O$_3$, In$_2$O$_3$ and so on [11–16]. Among these host materials, In$_2$O$_3$ is a wide bandgap (3.55–3.75 eV) n-type semiconductor, which is widely applied in gas sensors because of its simple preparation, good electrical conductivity, considerable chemical stability and environmentally friendly characters. However, the ethanol sensors designed with pure In$_2$O$_3$ as the base sensing materials have some disadvantages, such as lower sensing response, longer response/recovery time, poor selectivity and high operating temperature. Generally, the doping noble metal in In$_2$O$_3$ host induces a remarkable improvement of the gas sensing properties [17–22]. In addition, many papers have also
confirmed that the lattice defect induced by the impurity doping was an effective road to increase the gas-sensing properties of n-type semiconductor materials. At present, the trivalent rare earth (RE) ions have been applied in many fields due to their optical, magnetic and electrochemical performances based on 4f-4f electronic transitions. Particularly, the prominent catalytic property and large oxygen ion mobility for RE materials contribute to their chemical sensing applications. Many RE ions doping gas-sensing materials have been reported for improving the gas-sensing properties of metal oxide semiconductors, such as Ce/SnO$_2$, Eu/SnO$_2$, Sm/SnO$_2$ and Y/SnO$_2$ [23–26]. Anand et al. prepared Dy$^{3+}$-doped In$_2$O$_3$ gas sensors by the co-precipitation method with good sensitivity to 50 ppm ethanol at 300 °C and good response values to 50 ppm acetone at 350 °C [27]. Duan et al. have synthesized Ho-doped In$_2$O$_3$ gas-sensitive materials with a response value of up to 60 ppm for 100 ppm ethanol at 240 °C, which is three times higher than that of pure In$_2$O$_3$. In addition, the sensitivity of Ho-doped In$_2$O$_3$ to 200 ppb ethanol reached 2[S = Rg/Ra] [28]. Qin et al. prepared Er-doped In$_2$O$_3$ gas sensors by the carbon thermal reduction method and the Er doping significantly reduced the operating temperature of the sensors. Moreover, the response of the Er-doped In$_2$O$_3$ gas sensor for 100 ppm ethanol at 220 °C is 4.8[S = Rg/Ra], which is twice as high as that of the pure In$_2$O$_3$ gas sensor [29]. Therefore, designing an ethanol-sensing material through the codoping of noble metal and RE ions would become one of the feasible routes to enhancing the ethanol-sensing property.

In this paper, the La$^{3+}$ ions and noble metal Au co-doping of In$_2$O$_3$ nanomaterials were prepared through the hydrothermal method. The resistive-type sensor based on La/Au-In$_2$O$_3$ nanomaterials was designed to detect ethanol. The ethanol-sensing performances (sensitivity, selectivity and response/recovery time) of the fabricated sensor were investigated. It has been found that the remarkable enhancement of the response for ethanol was obtained, which is attributed to La/Au codoping in In$_2$O$_3$. The possible sensing mechanism was demonstrated based on the change of semiconductor conductance.

2. Experiment

2.1. Synthesis of La/Au-In$_2$O$_3$ Nanomaterials

The pure In$_2$O$_3$, 2 mol%La-In$_2$O$_3$ and x mol%Au/2 mol%La-In$_2$O$_3$ (x = 1, 2, 3) nanomaterials were prepared through a simple hydrothermal method. The main raw materials of indium nitrate (In(NO$_3$)$_3$·4.5H$_2$O), lanthanum nitrate (La(NO$_3$)$_3$·6H$_2$O) and chlorauric acid (HAuCl$_4$) were purchased from Sinopharm Chemical Reagent Co. All raw materials in the experiments were of analytical grade and did not require further purification. The synthesis process of 2 mol% La-In$_2$O$_3$ sample was as follows. According to the calculated amount, a certain amount of In(NO$_3$)$_3$·4.5H$_2$O, La(NO$_3$)$_3$·6H$_2$O and sodium citrate were dissolved in deionized water. First, the solution(A) of La(NO$_3$)$_3$ was added to the solution(B) of In(NO$_3$)$_3$ with a parting funnel. Then 10 mL of sodium citrate solution(C) was added to the above-mixed solution(A + B) with a separatory funnel and stirring continued for 30 min with a magnetic stirrer. The above-mixed solution was transferred to a PTFE-lined stainless steel reactor (50 mL) and kept at 200 °C for 4 h. The obtained white precipitate was washed repeatedly with deionized water and ethanol. Then, it was dried at 70 °C for 10 h. Finally, the samples were calcined at 500 °C in oxygen for 3 h. The preparation of La/Au-In$_2$O$_3$ sample was compounded with La-In$_2$O$_3$, HAuCl$_4$ and L-lysine. First, HAuCl$_4$ solution and L-lysine solution were added to La-In$_2$O$_3$ suspension sequentially with a separatory funnel and stirred for 10 min, then treated with ultrasound for 20 min. The precipitate was centrifuged and collected, followed by washing several times with ethanol and deionized water, then dried in a blast dryer at 60 °C for 12 h. Finally, the prepared material was calcined at 300 °C for 30 min, after which the La/Au-In$_2$O$_3$ nanomaterials were obtained.

2.2. Characterization
The crystalline phase of the prepared sample was characterized by X-ray diffraction (XRD, Rigaku Ultima IV) under an operating voltage and current of 40 kV and 40 mA. The Cu-Kα radiation was used with the wavelength \( \lambda = 1.54056 \text{ Å} \). The morphology of the samples was characterized by scanning electron microscopy (SEM, Quanta 450).

The gas sensor was prepared through sensing materials and ceramic tubes with gold electrodes. First, the appropriate amount of sample was ground into a homogeneous paste. Then the material is uniformly coated on ceramic tubes. Finally, the sensor was aged for 5 days at 200 °C in air using a chromium–nickel coil as a heating resistance wire. In addition, the gas-sensitive performance of the sensor was tested using the CGS-8 (Beijing Elite Tech Co., Ltd., China) intelligent gas sensing analysis system. The response of the gas sensor was usually defined as \( R_a/R_g \), where \( R_a \) was the resistance of the sensor in air and \( R_g \) was the resistance of the sensor in the gas to be measured [30,31].

3. Results and Discussion

3.1. Structural and Morphology

The crystalline structures of pure In\(_2\)O\(_3\), La-In\(_2\)O\(_3\), and Au/La-In\(_2\)O\(_3\) (Au = 1 mol%, 2 mol%, 3 mol%) samples were analyzed by XRD, and the results are shown in Figure 1. It can be seen that the main diffraction peaks of the five samples match well with hexagonal phase In\(_2\)O\(_3\)(JCPD#73-1809). However, three weak diffraction peaks at \( (2\theta = 35.35^\circ, 50.90^\circ, 60.60^\circ) \) are also presented, which belong to cubic phase In\(_2\)O\(_3\). This phenomenon may be the result of the combined effect of the surfactant sodium citrate, hydrothermal temperature and time, which is consistent with the results observed by Feng Chen et al. [32,33]. In addition, no diffraction peaks of La\(_2\)O\(_3\) and Au are detected because of their low doping amount. To further characterize the features of La/Au co-doped In\(_2\)O\(_3\), the lattice parameters of samples are calculated. The Scherrer formula can be used to estimate the grain size [34]:

\[
D = \frac{K\lambda}{B\cos\theta}
\]

where \( K \) is the Scherrer constant (\( K = 0.943 \) for cubic particles); \( B \) is the half height and width of the diffraction peak; \( (\lambda = 1.54056 \text{ nm}) \) is the x-ray wavelength; and \( \theta \) is the Bragg diffraction angle. The grain size of pure, 2 mol%La, 1 mol%Au/2 mol%La, 2 mol%Au/2 mol%La and 3 mol%Au/2 mol%La doping In\(_2\)O\(_3\) samples are listed in Table 1. It can be seen that the grain size of samples decreases significantly after doping with La and Au.

![Figure 1. XRD patterns of the pure In\(_2\)O\(_3\), 2 mol%La-In\(_2\)O\(_3\) and x mol%Au/La-In\(_2\)O\(_3\) (x = 1, 2, 3) samples.](image)
Table 1. Lattice parameters and crystallite size of pure In$_2$O$_3$, 2 mol% La-In$_2$O$_3$ and x mol% Au/La-In$_2$O$_3$ (x = 1, 2, 3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameters (Å)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure In$_2$O$_3$</td>
<td>a = 5.490, b = 5.490, c = 14.508</td>
<td>18.29</td>
</tr>
<tr>
<td>2%La:In$_2$O$_3$</td>
<td>a = 5.482, b = 5.482, c = 14.515</td>
<td>12.17</td>
</tr>
<tr>
<td>1%Au/2%La:In$_2$O$_3$</td>
<td>a = 5.490, b = 5.490, c = 14.520</td>
<td>13.18</td>
</tr>
<tr>
<td>2%Au/2%La:In$_2$O$_3$</td>
<td>a = 5.488, b = 5.488, c = 14.544</td>
<td>12.59</td>
</tr>
<tr>
<td>3%Au/2%La:In$_2$O$_3$</td>
<td>a = 5.489, b = 5.489, c = 14.491</td>
<td>13.11</td>
</tr>
</tbody>
</table>

The SEM images of pure In$_2$O$_3$, 2 mol%La-In$_2$O$_3$ and 2 mol%Au/2 mol%La-In$_2$O$_3$ are shown in Figure 2. As seen in Figure 2a,b, the particles of pure In$_2$O$_3$, 2 mol%La-In$_2$O$_3$ present porous aggregate state. The size of particle should belong to nanoscale. While the morphology of 2 mol%Au/2 mol%La-In$_2$O$_3$ shows the uniformly sized dispersed spheres about 3 nm. The formation of spheres may be due to the addition of L-lysine as a dispersant and sonication.

Figure 2. The SEM images of pure In$_2$O$_3$ (a), 2 mol%La-In$_2$O$_3$ (b) and 2 mol%Au/2 mol%La-In$_2$O$_3$ (c).

3.2. Ethanol-Sensitive Properties

To investigate the ethanol-sensing performances of Au/La-In$_2$O$_3$ nanomaterials, the ethanol (100 ppm) sensing responses of pure In$_2$O$_3$, 2%La-In$_2$O$_3$, 1%Au/2%La-In$_2$O$_3$, 2%Au/2%La-In$_2$O$_3$ and 3%Au/2%La-In$_2$O$_3$ were tested at different temperatures from 190 °C to 260 °C in Figure 3. The sensitivities of 2%La-In$_2$O$_3$, 1%Au/2%La-In$_2$O$_3$, 2%Au/2%La-In$_2$O$_3$ and 3%Au/2%La-In$_2$O$_3$ sensors first increase rapidly, then decrease and reach maximum value at 210–230 °C, which reveal a “pyramid” shape. This can be explained as follows: at low temperature the adsorbed ethanol molecules are not activated enough to overcome the activation energy barrier to react with the adsorbed oxygen species, while at high temperatures the gas adsorption is too difficult to be adequately compensated for the increased surface reactivity. That is, at lower operating temperatures, the activation energy of ethanol vapor molecules is weak, and the ethanol molecules are probably not absorbed by sensing material, which results in the lower response. With the operating temperature increasing, the activation energy of ethanol molecules is enhanced. The reaction of ethanol molecules and adsorbed oxygen is increased, which leads to the gas response improvement. However, when the working temperature is over a certain value, the escaping rate of ethanol molecules from the sensing materials is enhanced, which leads to the weak reaction between ethanol molecules and oxygen molecules. For this reason, the response value begins to decrease. As shown in Figure 3, the optimal operating temperature of the 2%Au/2%La-In$_2$O$_3$ sensor is 210 °C with a response of 381. In addition, 2%La-In$_2$O$_3$ sensors give at 230 °C a response of 43. However, the optimal operating temperature of pure In$_2$O$_3$ is over 260 °C. In addition, the 2% Au/2%La-In$_2$O$_3$ sensor shows the higher sensitivity (381) at the lowest optimal operating temperature (210 °C) to 100 ppm ethanol. Loading Au and La onto In$_2$O$_3$ helps to lower the optimum working temperature, because the Au can decrease the ac-
tivation energy barrier of the surface reaction due to its excellent catalytic property. It is noted that the decoration of Au and La can significantly enhance the response. Due to RE ions’ catalytic properties, the codoping La can increase the reaction rate. Amazingly, the Au doping can significantly increase the sensitivity, proving that noble metals play a catalytic role. The response of the La/Au-In₂O₃ sensing materials at first increases with increasing Au concentration, and reaches the maximum value for 2%Au/2%La-In₂O₃, then decreases. The 2%Au/2%La-In₂O₃ sensor has achieved a response of 381, about 14 times more than that of the pure In₂O₃ sensor and about 8.9 times that of the 2%La-In₂O₃ sensors. As mentioned above, the catalytic performance of Au will further increase the response of the La/In₂O₃. However, the overloading Au doping value will result in the decrease of the contact surface between the gas and the In₂O₃ host. This means that the response will decrease. This suggests that co-doping of RE ions and noble metals is an effective method for enhancing the semiconductor materials gas-sensing response.

The sensing response of 2%Au/2%La-In₂O₃ nanomaterials at 210 °C was measured. Figure 4a shows the four consecutive repeatability experiment results of 2%Au/2%La-In₂O₃ sensor toward 50 ppm. The results show that the sensor has a fast response time and good repeatability. The response–recovery times of the 2%Au/2%La-In₂O₃ sensor are investigated toward 50 ppm in Figure 4b. The response–recovery times of the sensor reached 1/394 s. This indicates that the sensor has a super-fast response for the application.
In Figure 5a the response-recovery curves of the sensor for different ethanol concentrations are investigated from 1 to 100 ppm. The results show that the sensor has a fast and increasing response amplitude at increasing concentrations of ethanol vapor, and then returns to the initial state after re-exposure to air, with a lower detection limit of 1 ppm (response value of 1.48). The linear fitting relationship between the response values of the Au/La-In2O3 sensor and different ethanol concentration is shown in Figure 5b. The response of the sensor increases linearly with increasing ethanol concentration in the range of 20–80 ppm. The relation is \( Y = 2.89X - 26.89 \), where the correlation coefficient is \( R^2 = 0.9785 \). It indicates that the \( R^2 \) is about 1 with better linear fitting. Therefore, the Au/La-In2O3 sensor can be applied to the quantitative detection of ethanol from 20 to 80 ppm.

3.3. Mechanistic Analysis

As reported, the possible gas-sensing mechanism of the metal oxide semiconductor is discussed with the “gas adsorption and gas desorption reaction”. Once the sensing materials are exposed to—oxygen in the air, the physical and chemical adsorption process of the oxygen will occur on the surface of the sensor, which generates the anionic
The surface of In$_2$O$_3$ materials will lose electrons, which reduces the resistance of the sensor. When the sensor is exposed to ethanol, the reaction of the ethanol and adsorbed oxygen anions will occur at the surface of the sensor. The electrons are released to the sensing materials and the result is a decreased resistance for the gas-sensing application. The process can be described by following equation.

\[
\begin{align*}
\text{O}_2 \text{(gas)} & \rightarrow \text{O}_2 \text{(ads)} \\
\text{O}_2 \text{(ads)} + e^- & \rightarrow \text{O}_2^- \text{(ads)} \quad (100 \degree C < T) \\
\text{O}_2^- \text{(ads)} + e^- & \rightarrow 2\text{O}^- \text{(ads)} \quad (100 \degree C < T < 300 \degree C) \\
\text{O}^- \text{(ads)} + e^- & \rightarrow \text{O}_2 \text{O}^- \text{(ads)} \quad (300 \degree C > T) \\
\text{C}_2\text{H}_5\text{OH(gas)} + 3\text{O}^- \text{(ads)} & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6e^- \\
\text{C}_2\text{H}_5\text{OH(gas)} + 6\text{O}^- \text{(ads)} & \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} + 6e^- 
\end{align*}
\]

Through the process, the electrons would be released back to the In$_2$O$_3$. So, the resistance of the sensing materials begins to decrease. In this paper, the ethanol gas response of 2%Au/2%La-In$_2$O$_3$ shows the best sensing performance, while that of 2%La-In$_2$O$_3$ also has a better sensing property than pure In$_2$O$_3$. The possible reasons for the remarkable enhancement for ethanol detection could be described as follows:

(1) The response of gas sensors is greatly influenced by the grain size based on the previous reports. The smaller grain size of the sensing material will result in larger specific surface area, which generates higher gas sensitivity [35,36]. For 2%La-In$_2$O$_3$ materials, the average grain size has been calculated to be 12.17 nm, which is smaller than that of pure In$_2$O$_3$. Therefore, the response of the 2%La-In$_2$O$_3$ sensor is larger than that of the pure In$_2$O$_3$ sensor. In addition, the doping La$^{3+}$ ions maybe replace the site of the In$^{3+}$ ions (Figure 7). The XRD results indicate that the doping of La$^{3+}$ leads to a structural disorder of In$_2$O$_3$, and even more lattice defects. It is well known that intrinsic defects or the non-stoichiometry mainly determine the sensing materials. So, the sensor can absorb more oxygen on the surface, and the 2%La-In$_2$O$_3$ sensor has much more chemisorbed oxygen than the pure In$_2$O$_3$ sensor. As proposed, the sensing response is expected to occur mainly via electron transfer and/or variation of chemisorbed oxygen species on the sensor surface, so the sensor performances can be improved with the increase of chemisorbed oxygen. Hence, the La-In$_2$O$_3$ sensor contains more chemisorbed oxygen to react with the ethanol and brings about the higher response to it, which agrees with the testing results of the ethanol-sensing properties [37].

Figure 7. Single cell structure of In$_2$O$_3$ and La$^{3+}$ replaces In$^{3+}$.

(2) The Au codoping in La-In$_2$O$_3$ material for ethanol response improvement can be explained from two aspects. First, the catalytic effect of Au significantly enhances the values of the absorbed oxygen, which results in the decrease of the optimal working temperature [38]. Second, the Shottky junction between Au and In$_2$O$_3$ will be formed on the In$_2$O$_3$ nanomaterials. As shown in Figure 8, it is known that the work function of In$_2$O$_3$ (4.8 eV) is lower than that of Au (5.1 eV), and electrons flow from the conduction band of
In$_2$O$_3$ to the surface of Au, which makes the energy band of In$_2$O$_3$ more curved, and the interface of Au-doped In$_2$O$_3$ has an increased width of the electron depletion layer and increased resistance compared to the pure In$_2$O$_3$ interface [39,40]. When the sensor is put into ethanol vapors, the ethanol molecules react with a large number of oxygen negative ions and release electrons into the conduction band of In$_2$O$_3$, the width of the electron depletion layer decreases and the resistance decreases. This results in a sensor with good gas-sensitive performance.

Figure 8. Energy level diagrams of (a) pure In$_2$O$_3$ and (b) Au/La-In$_2$O$_3$ in air.

4. Conclusions

The Au/La-In$_2$O$_3$ nanoparticles were prepared by a simple hydrothermal method and ultrasonic treatment. The structure and morphology of all the Au/La-In$_2$O$_3$ samples were characterized. The morphology of pure In$_2$O$_3$ and La-In$_2$O$_3$ showed porous aggregate state nanoparticles, while that of Au/La-In$_2$O$_3$ showed uniformly sized dispersed spheres of about 3 nm. The gas-sensing properties were investigated for ethanol vapor. The excellent gas-sensitive performance of Au/La-In$_2$O$_3$ sample was obtained for ethanol. Compared to the pure In$_2$O$_3$ materials, the 2%Au/2%La-In$_2$O$_3$ sensor achieved a highest response of 381, about 14 times that of the pure In$_2$O$_3$ sensor and about 8.9 times that of the 2%La-In$_2$O$_3$ sensors for 100 ppm ethanol. In addition, a fast response time (1 s), better selectivity and lower operating temperature were obtained for ethanol vapor. The enhancement mechanism of the ethanol response was discussed for Au/La-In$_2$O$_3$ nanoparticles. The above experimental results would provide a new road for designing higher-response sensors.

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