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Highly sensitive ethanol sensor based on Ce-doped WO₃ with raspberry-like architecture

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Abstract

This work reported a highly sensitive ethanol sensor assembled from raspberry-like hierarchical Ce-doped WO₃ nanoparticles. The Ce-doped WO₃ nanoparticles doped with different contents (0, 2, 4 and 8 at%) of Ce were synthesized by a facile hydrothermal method. The crystalline structure and the micromorphology of Ce-doped WO₃ nanoparticles were measured by x-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM), respectively. The x-ray photoelectric spectroscopy (XPS) and transmission electron microscopy (TEM) attached with energy-dispersive spectroscopy (EDS) confirmed the elemental distribution and the chemical state of surface elements. Comparison between the pristine and Ce-doped WO₃ samples revealed that the doping of Ce on WO₃ can powerfully improve the response ability to ethanol. As the doping content of Ce element was 4 at%, the sensor exhibited optimal response to ethanol in the range of 0.1–50 ppm at the working temperature of 350 °C. The response can achieve a high value of 12.3 for detecting 1 ppm ethanol with a fast response/recovery (6s/6s). Impressively, the sensor still maintained a good response (8.1) to ethanol even at sub-ppm level (0.1 ppm ethanol). This work will pave a platform for design and development of highly sensitive ethanol sensors.

1. Introduction

More and more sensors are used in today’s industry and life for safe, analysis and monitor [1–7]. Gas sensors, as one of the sensitive electronic devices, have been widely utilized in versatile applications of human health detecting [8, 9], toxic/inflammable gases alarming, environmental pollution gas monitoring [10, 11]. Some eminent gas detecting devices have been developed, such as metal oxide semiconductor (MOS) gas sensors [12, 13], solid electrolyte gas sensors [14], catalytic combustion gas sensors [15], surface acoustic wave gas sensors [16], perovskite gas sensors [17], quartz crystal microbalance devices [18] and micro-electrical mechanical system gas sensors [19]. Based on the demands of low-cost, easy processing and excellent sensing performances, MOS gas sensors have attracted intensive attention in both science and industry. MOSs can be divided into two types according to conductive mechanism: n-type MOSs conduct via electrons while p-type MOSs conduct via holes. The n-type MOSs gas sensing materials include ZnO [20, 21], SnO₂ [22], In₂O₃ [23], TiO₂ [24, 25], WO₃ [26]. The mainly p-type MOSs sensing materials contain NiO [27], Co₃O₄ [28], and CuO [29]. The n-type MOSs commonly have high response, while the p-type MOSs possess higher selectivity and superior humid resistance [30, 31].

WO₃, as one of the typical n-type MOSs, with a direct bandgap of 2.4–2.8 eV, is popular for the ability of photocatalysis, and has been widely used in the fields of super capacity [32], catalyst [33], electrochromic device [34] and gas sensor [35, 36]. For a long time, the tungsten oxide has been researched as sensing materials for detecting H₂ [37], NOₓ (NO and NO₂) [38], H₂S [39] and so on. Up to now, various WO₃ with different
morpheologies were developed to enhance their sensing performances. Chen et al fabricated nanoplates WO\textsubscript{3}\textsuperscript{−}\textsubscript{2} and nanoparticles WO\textsubscript{3} and discovered that the nanoplates WO\textsubscript{3} displayed higher acetone response resulting from the high surface areas\textsuperscript{[40]}. Wang et al prepared flower-like WO\textsubscript{3} assembled by nanosheets, which exhibited sensitive response to ppb-level NO\textsubscript{2} as low as ~40 ppb\textsuperscript{[41]}. Lu et al synthesized the monoclinic WO\textsubscript{3} nanocrystallines with remarkable sensitivity to acetone at the concentration of 0.25–100 ppm\textsuperscript{[35]}. In addition, doping with other metal elements is an effective strategy to improve the sensing performance of WO\textsubscript{3}. Introduction of novel metals as Pt, Ag and Ru on the surface of WO\textsubscript{3} nanoparticle is capable of improving sensing performance arising from the electron sensitization and catalyze function of the novel metals\textsuperscript{[42–44]}. Meanwhile, the heterostructure and oxygen defects formed during the doping process are also beneficial for enhancing the gas sensitivity of MOS. Some efforts have done to enhance the gas sensitivity of WO\textsubscript{3} by doping. For example, the WO\textsubscript{3} doped with In, Cu, Co, and Gd exhibited improved acetone sensing characteristics\textsuperscript{[45–48]}, while the Sn and Fe doped WO\textsubscript{3} displayed increase response to alcohol\textsuperscript{[49, 50]}. Besides, Upadhyay et al prepared Cr-doped WO\textsubscript{3} nanosheets which exhibited selective high response to formaldehyde\textsuperscript{[51]}. Consequently, simple doping treatment on WO\textsubscript{3} can readily achieve excellent gas sensing performance.

Although many metal elements have been doped in WO\textsubscript{3}, Ce-doped WO\textsubscript{3} still lacked enough attention. Ce is frequently used as the dopant and plays an important role on the improvement of pristine MOSs\textsuperscript{[52–54]}. There are few reports about the sensing characteristics of Ce-doped WO\textsubscript{3}. As previously reported, Ce doping can increase the amount of the vacancy in host material via the transformation of chemical valence (Ce\textsuperscript{4+} → Ce\textsuperscript{3+}), which is very beneficial for enhancing the response to reducing gases\textsuperscript{[54, 55]}. In this work, we synthesized a series of Ce-doped WO\textsubscript{3} with raspberry-like architecture by a simple hydrothermal method and investigated the ethanol sensitivity of WO\textsubscript{3} doped with different contents (0, 2, 4 and 8 at\%). Due to the doping of Ce element, the sensor exhibited superior response capacity to ethanol. Especially, when the Ce doping content was 4 at\%, the prepared sensor displayed optimal response to ethanol at the concentrations of 0.1–50 ppm. The sensor also exhibited fast response/recovery and excellent selectivity. We believe this work will pave a way to develop functional gas sensors and broaden their applications.

2. Experimental

2.1. Synthesis process

The different Ce-doping content WO\textsubscript{3} samples were prepared by the typical hydrothermal method without any surfactants. The raw materials were analytically pure and used without further purification. During the synthesis process, 0.396g WCl\textsubscript{6} (purchased from Macklin Inc.) was dissolved in 40 ml ethanol. Ce was added into the solution with different contents (0, 2, 4 and 8 at\%) by using Ce(NO\textsubscript{3})\textsubscript{3} · 6H\textsubscript{2}O (Macklin Inc.). After stirred for 1 h at room temperature, the homogeneous solution was transferred into a 50 ml Teflon-lined stainless autoclave and maintained in a constant temperature oven at 180 °C for 10 h. Then the autoclave naturally cooled to room temperature, and the sediment was obtained by centrifugation. The products were washed by pure water and alcohol several times, respectively, and further dried at 70 °C for 10 h in a vacuum oven. The dried products were annealed in muffle furnace at 450 °C for 2 h in air. The prepared WO\textsubscript{3} doped with 0, 2, 4, and 8 at\% were labeled as W0, C2W, C4W and C8W, respectively.

2.2. Characterization of structure and morphology

The crystallinity of the synthesized Ce-doped WO\textsubscript{3} samples were investigated by a Rigaku D/max-2500 x-ray diffraction (XRD, with Cu Kα radiation, λ = 1.5418 Å) in the scanning range of 20–60°. The morphologies and elements distribution in samples were observed by the FEI Quanta 250FEG field-emission scanning microscope (FESEM) and the JEOL JEM-2100 transmission electron microscope (TEM) attached with the energy-dispersive x-ray spectroscopy (EDS). The surface elements states of the prepared samples were recorded by a Thermo ESCALAB 250XI x-ray photoelectron spectrometer (XPS).

2.3. Devices preparation and measurement

The gas sensing characteristics were measured by the familiar Al\textsubscript{2}O\textsubscript{3} tubular–device as reported\textsuperscript{[56–58]}. The prepared Ce-doped WO\textsubscript{3} powder was pasted on an Al\textsubscript{2}O\textsubscript{3} ceramic tube and a Ni-Cr spiral heating coil was inserted in the ceramic tube. The prepared ceramic tube was welded on a hexagon base and maintain in the gas sensing test system. The humidity in the test environment was about RH 40%. The resistance variation of the device was recorded by a digital multimeter (Fluke, 8846A). The sensor’s response (S) was defined as the ratio of resistance in air (R\textsubscript{a}) to resistance in test gas (R\textsubscript{g}): S = \frac{R\textsubscript{a}}{R\textsubscript{g}}.
3. Results and discussion

3.1. Characterizations

As shown in figure 1, the crystal phases of 0, 2, 4 and 8 at% Ce-doped WO₃ samples were measured. All the peaks of the prepared samples are consistent with monoclinic structured WO₃ from the JCPDS-43-1035. The peaks of 0, 2 and 4 at% Ce-doped WO₃ are sharp, while the peaks of 8 at% Ce-doped WO₃ become weaken. As the doping amount of Ce increases, the intensity of the triplet peaks of (002), (020) and (200) gradually reduces. It can be attributed to the lattice distortion resulted from the substitution of Ce⁴⁺ ions for W⁶⁺ ions: the radius of doping ion (Ce⁴⁺ radius: 87 pm) is larger than the host (W⁶⁺ radius: 67 pm) [45, 47]. The mean crystalline sizes of pure, 2 at% and 4 at% Ce-doped WO₃ calculated by the Scherrer equation are 47.7, 36.0 and 31.2 nm, which indicates that the incorporation of Ce hinder the WO₃ nanocrystal growth during the hydrothermal synthesis process. Moreover, no peak pertaining to either Ce or cerium oxide can be found. Similar phenomena have been reported in the Gd-doped, Cr-doped and In-doped WO₃ [45, 47, 51]. Furthermore, the presence and element states of Ce were investigated by EDS and XPS.

The FESEM was used to investigate micro-morphology of synthesized WO₃ with different contents of Ce doping. In figure 2, it can be found that the as-prepared samples show a 3D microsphere structure. Figure 2(a) exhibits the panoramic view of the pure WO₃, which is composed of many particles. Analogously, the samples of Ce-doped WO₃ are also composed of spherical architectures as shown in figures 2(c), (e) and (g). However, compared to pure WO₃, the Ce doped WO₃ spheres are more uniform and smaller. Figure 2(b) shows the amplifying FESEM images of pure WO₃ with raspberry-like architecture. The sphere’s diameter is about 1.5 um and its surface is rough. As shown in figures 2(d), (f) and (h), the diameters of the Ce-doped WO₃ particles

![Figure 1. XRD patterns of the pristine and Ce-doped WO₃ samples.](image1)

![Figure 2. FESEM pictures of the as-prepared (a), (b) pristine, (c), (d) 2 at%, (e), (f) 4 at% and (g), (h) 8 at% Ce-doped WO₃ nanoparticles.](image2)
decrease. For 2 at% and 4 at% Ce content the particle size is around 0.8 μm, while the 8 at% Ce-doped WO₃ particle’s diameter is approximate 0.4 μm. This agrees with the XRD result that the Ce doping impedes the growth of WO₃ crystal. When the Ce content is 8 at%, the protuberances on the sphere’s surface become less.

Figure 3 exhibits the TEM images of the 4 at% Ce-doped WO₃ spherical architecture. As shown in figure 3(a), the particle is a condense sphere structure with uneven surface, which is consistent with the SEM result. Figure 3(b) shows the HRTEM figure of C₄W and the recognized crystal lattice planes. The interplanar distance of 0.375 nm corresponds with (020) crystallographic plane of monoclinic structured WO₃ (JCPDS-43-1035). Besides, the interplanar spacing of 0.387 nm belongs to (002) plane of WO₃. Furthermore, to confirm the existence and distribution of the elements, the EDS mapping images are presented in figures 3(c)–(f). It can be seen that the O, Ce and W are all dispersed on the holistic microstructure. Moreover, the density of Ce is lower than that of W because of the fewer content of Ce.

To further investigate the composition and chemical state of the surface elements, the XPS analysis was taken, as shown in figure 4. The survey spectra of pure WO₃ and 4 at% Ce-doped WO₃ are shown in figure 4(a). It shows the presence of W and O in both samples, and the additional peaks in the spectra of Ce-doped WO₃ can be assigned to Ce element, which indicates Ce has been successfully doped. Furthermore, to demonstrate the chemical state of doped Ce, the Ce 3d spectrum of 4 at% Ce-doped WO₃ is de-convoluted into a total of eight peaks (figure 4(b)). The peaks labeled a₀, a’, and a”, situated at 881.97, 883.82, 885.14, and 886.48 eV.

Figure 3. (a) TEM picture and (b) HRTEM picture of 4 at% Ce-doped WO₃ nanoparticle. (c)–(f) TEM picture of the 4 at% Ce-doped WO₃ nanoparticle and its corresponding elemental mapping images.
respectively, are assigned to Ce 3d\(_{3/2}\). Besides, the peaks labeled b\(_0\), b\(',\) b\(''\) which position at 900.19, 901.70, 903.49 and 905.13 eV respectively are attributed to 3d\(_{5/2}\). As reported, the Ce\(^{4+}\) can scavenge electrons and traps the electronics at high temperature:

\[
2\text{Ce}^{4+} + \text{O}_\text{O}^X \rightarrow 2\text{Ce}^{3+} + V'_\text{o} + \frac{1}{2}\text{O}_2
\]  

(1)

herein, the O\(_\text{O}^X\) is the O\(^{2-}\) while V\(_\text{o}\) is the oxygen vacancy with two negative charges [59, 60]. According to literatures, the peaks of a, a\(',\) b\(_0\), b\(',\) b\(''\) are related to Ce\(^{4+}\), while the peaks of a\(_0\), a\(''\) and b are related to Ce\(^{3+}\) [61, 62]. Figure 4(c) shows the W 4f spectra of pure and 4 at% Ce-doped WO\(_3\). For the pure WO\(_3\), the two peaks at 36.36 and 34.26 eV belong to W 4f\(_{5/2}\) and W 4f\(_{3/2}\), respectively. Whereas, the W 4f peaks of 4 at% Ce-doped WO\(_3\) exhibit evident blue shifts compared to the pure WO\(_3\) sample, which is due to the electron migration from WO\(_3\) to cerium oxide [44].

Figures 4(d)–(e) show the two samples’ O 1s spectra which both can be de-convoluted into three peaks. According to reports, the fitted peaks of 529.12, 530.20 and 531.67 eV are the characteristic peaks of lattice oxygen (O\(_\text{lat}\)) in metal oxides, adsorbed oxygen (O\(_\text{ads}\)) species and the oxygen bound (O\(_\text{bound}\)) in H\(_2\)O adsorbed on the surface, respectively [63, 64]. The amount of H\(_2\)O components adsorbed on the surface is relevant to the density of surface adsorption sites [44]. As shown in figure 4(e), the O 1s spectrum of 4 at% Ce-doped WO\(_3\) is
similar to that of the pure WO3. Comparing the two figures, it can be found that the total content of O_{ads} and O_{bou} of the Ce-doped WO3 is larger than that of the pure WO3. It suggests the Ce doping can improve the reaction of gas molecules and oxygen species absorbed on the surface of metal oxides.

### 3.2. Gas response and discussion

The as-prepared samples were constructed to be gas sensors and their sensing performances were measured by gas test system. Firstly, the operating temperature was measured, because it was an import factor that affected the sensors’ performance. We measured the prepared sensors’ response to 2 ppm ethanol at different operating temperatures as shown in figure 5. The best working temperature is 350 °C for all the prepared sensors. As previous reports, the increasing working temperature can provide the energy for gas molecules to overcome the barrier of surface reaction. However, if the temperature is elevated too high, the gas molecules tend to desorption from the surface of the MOSs [65, 66]. Besides, at too high temperature, the oxidation of the surface of WO3 proceeds faster than the reduction caused by the ethanol [39, 67]. Thus, with the working temperature increasing, the response value initially went up and then down.

The dynamic response curves of as-prepared sensors to ethanol with various concentrations at 350 °C were recorded in figure 6(a). For all prepared sensors, the response values raised as the concentration of ethanol increased in the range of 0.1–50 ppm. The C4W sensor exhibited the largest response to ethanol over the test concentration scope. The C2W and C8W sensors also showed larger responses to ethanol compared to the W0 sensor. It demonstrates that the Ce doping can enhance the gas sensitivity of WO3 to ethanol. The response of C8W sensor is lower than that of C4W sensor, probably because the excessive Ce ions take up the active sites on the surface [65].

Figure 6(b) shows the gas response of the sensors as a function of ethanol concentrations at 350 °C. The gas responses of C4W sensor are 8.1, 8.6, 10.7, 12.3, 16.7, 23.7, 31.7, 41.2 and 62.4 to 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 ppm ethanol gas, respectively. It can be seen that the response increase slowly after 10 ppm, because the absorbed gas on the surface is becoming to saturate at high ethanol concentration [47]. Figure 6(c) exhibits the linear relationship of gas response and ethanol concentration at the range of 0.1–2 ppm, which indicates the excellent sensing properties at low concentration.

The depletion layer model can be used to explain the gas sensing mechanism of WO3 sensor [40]. The gas response processes of pure and Ce-doped WO3 sensors are shown in figure 7. When the sensor is exposed to air, the oxygen could absorb on the surface of the metal oxide in the term of O_{2}^{-}, O^{-} or O_{2}^{2-} depended on the surrounding temperature. The absorbed oxygen species always deprive electrons from the semiconductor, resulting in a depleted layer on the surface. However, when the sensor is exposed to ethanol, the electrons will be released from absorbed oxygen species because of the surface reaction of ethanol and absorbed oxygen species [68]:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \text{O}^-_{\text{(ads)}} & \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O} + e^- \\
\text{CH}_3\text{CHO} + 5\text{O}^-_{\text{(ads)}} & \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + 5e^- 
\end{align*}
\]

As an n-type MOS, WO3 uses electrons as carriers, so the depleted layer decrease can reduce the resistance. In the case of Ce-doped WO3, the electron concentration decrease for the host ion is replaced by the doped ion,
which leads to the increase of the resistance. Similarly, the cases of resistance change caused by doping have been reported, such as Cu, Gd and Ru doped WO₃ [42, 47, 48]. As shown in figure 8, the $R_a$ of the Ce-doped WO₃ samples is higher than that of the pure WO₃ sample. The elevated resistance is good for the response improvement [61]. What’s more, the change of ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$) can occurred in reducing atmosphere at elevated temperature by capturing electrons, which resulting in plenty of vacancies. It can increase the amount of chemisorbed oxygen [54]. The change of Ce valence states may also promote the ethanol dissociation.

Figure 6. (a) Dynamic gas response curves and (b) response-concentration curves of different Ce contents doped WO₃ sensors to 0.1–50 ppm ethanol under 350 °C. (c) response-concentration curves at low concentrations (0.1–2 ppm).

Figure 7. The schematic illustration of ethanol gas sensing mechanism of pristine and Ce-doped WO₃ nanoparticles.
accompanied by the spillover effect according to the chemical sensitization and results in large resistance change [69, 70].

The response and recovery time is one of the important indexes that should be considered in practical application. Figure 9 shows the C4W sensor’s response transients to 1 ppm ethanol. Both the response and the recovery times of the C4W sensor to 1 ppm ethanol are about 6s. Compared to some ethanol sensors based on metal oxides, the as-prepared Ce-doped WO3 sensor shows excellent response and recovery rate as well as the higher response value (table 1).

Figure 10 shows the selectivity of the C4W sensor at the optimal working temperature of 350 °C. It can be clearly observed that the C4W sensor has larger response to 2 ppm ethanol in comparison with other test gases in the same concentration. This suggests that the 4 at% Ce-doped WO3 sensor has superior selectivity to ethanol. Figure 11 shows the 4-time response transient of C4W sensor to 2 ppm ethanol at 350 °C. The response test was taken every three days. It can be observed that the response and recovery curve could be repeated very well, which indicated that the C4W sensor had excellent reliability.

Figure 8. Response transient of different Ce contents doped WO3 sensors to 0.1 ppm ethanol at 350 °C.

Figure 9. Response and recovery time of 4 at% Ce-doped WO3 to 1 ppm ethanol at 350 °C.
4. Conclusion

In summary, a set of WO₃ hierarchical nanoparticles were prepared with different contents of Ce doping. The morphology characterization results revealed the raspberry-like structure. The chemical state of elements measured by XPS demonstrated the existence of Ce³⁺/Ce⁴⁺. The gas sensing test suggested the Ce doping enhanced the response to ethanol gas. What’s more, the 4 at% Ce-doped WO₃ showed the largest response to ethanol among the prepared doped WO₃ samples with different amount of Ce. The sensor exhibited good response to ethanol at sub-ppm level (to 0.1 ppm ethanol, the response is 8.1). Meanwhile, the sensor exhibited fast response and recovery (6s/6s), together with excellent selectivity. The simple fabrication and remarkable sensing performance make the Ce-doped WO₃ an ideal candidate as ethanol sensor.

Figure 10. Response of 4 at% Ce-doped WO₃ sensor towards 2 ppm of different gases at 350 °C.

Figure 11. Four times response transient of C4W sensor to 2 ppm ethanol at 350 °C. They were tested every three days.

| Materials                              | Temp. (°C) | Conc. (ppm) | Res. (Rₑ/Rₒ) | Res./Rec. time (s/s) | References |
|----------------------------------------|------------|-------------|---------------|----------------------|------------|
| Hollowed-out Co₃O₄ microspheres        | 220        | 100         | 38.2          | 0.1/0.2              | [71]       |
| SnO₂/Zn₂SnO₄ Porous spheres            | 250        | 100         | 30.5          | —                    | [72]       |
| Er-doped SnO₂                          | 240        | 100         | 48            | 35/40                | [73]       |
| ZnO nanorods                           | 300        | 100         | 44.9          | 6/31                 | [74]       |
| Cu-doped SnO₂ nanofibers               | 300        | 5           | 3             | 1/10                 | [75]       |
| Hollow and mesoporous ZnO microspheres | 420        | 5           | 2.2           | 4/6                  | [76]       |
| Rod-like CuO                           | 275        | 1           | 2.3           | —                    | [77]       |
| Ce-doped WO₃                           | 350        | 1           | 12.3          | 6/6                  | This work  |

Table 1. Gas sensitivity of metal oxides sensors to ethanol in previous reports.
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