

Room-temperature chlorine gas sensor based on CdSnO₃ synthesized by hydrothermal process

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Abstract: The perovskite-structure CdSnO₃ was obtained by calcinating CdSnO₃·3H₂O precursor at 550 °C, which was synthesized by hydrothermal process at 170 °C for 16 h. The phase and microstructure of the obtained CdSnO₃ powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The CdSnO₃ powders exhibit uniformly cubic structure with side length of about 100 nm. The effects of working temperature and concentration of detected gas on the gas response were studied. The selectivity of chlorine gas against other gases and response–recovery time of the sensor were also investigated. The results reveal that the CdSnO₃ gas sensor has enhanced sensing properties to 1–10 ppm chlorine gas at room temperature; the value of gas response can reach 1338.9 to 5 ppm chlorine gas. Moreover, the sensor shows good selectivity and quick response behavior (23 s) to chlorine gas, indicating its application in detecting chlorine gas at room temperature in the future.

Keywords: chlorine gas sensor; room temperature; CdSnO₃; hydrothermal process

1 Introduction

Chlorine is widely used in many industrial processes, such as tap water treatment, paper making, printing and dyeing processes, and it is also used as disinfectant, bleacher, and raw material for producing hydrochloric acid and phosgene. However, chlorine may bring negative impact to human health when it emits into environment without proper treatment [1–3]. So it is necessary to detect chlorine gas in environment based on the human safeguards. Gas sensors play an important role in environmental monitoring. In recent years, some metal oxides and complex metal oxides have been reported to be used as chlorine gas sensors [3–12], but many of those sensors work at high

temperature [5–12]. For example, Wang *et al.* [7] synthesized mesoporous SnO₂-based sensor which was sensitive to chlorine gas at 370 °C. In₂O₃ sensor synthesized by Belysheva and Bogovtseva [9] showed better sensitivity to chlorine gas at 300 °C, and CdIn₂O₄ sensors [10] we prepared before showed faster response to chlorine gas at about 220–300 °C. Therefore, it is necessary to improve the property of chlorine gas sensors in order to decrease the working temperature.

In recent years, cadmium stannate (CdSnO₃), used as electrochemical material [13,14], has shown quite attractive gas sensitivity properties to various gases such as C₂H₅OH gas [15–18], butane [19], ammonia [20], CEES [21] and chlorine [2]. At present, CdSnO₃ is synthesized mainly by chemical coprecipitation [2,16–18,22]. It is well known that different synthesis methods may have different influences on the property

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or morphology of the products [18]. In this manuscript, CdSnO_3 of cubic perovskite structure was obtained by calcinating $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ precursor at 550°C , which was synthesized by hydrothermal process. The CdSnO_3 gas sensor shows enhanced sensing properties to 1–10 ppm chlorine gas at room temperature, and exhibits the best response and selectivity to chlorine gas in test gases. Good response, selectivity and short response time to chlorine gas at room temperature indicate that the sensor may be used to detect low concentration of chlorine gas at room temperature.

2 Experiment

2.1 Synthesis

$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (AR), SnCl_4 (AR) and NaOH (AR) were used as raw materials. $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and SnCl_4 (molar ratio of $\text{Cd}:\text{Sn} = 1:1$) were dissolved in distilled water. Then NaOH solution was added dropwise to the above mixed solution with constant magnetic stirring until the pH of the suspension reached to 9.5. The final mixture was transferred into a Teflon-lined stainless autoclave with 75% degree of fill, and the reaction was controlled at 170°C for 16 h. Then the autoclave cooled down to room temperature naturally. The precipitate was collected by centrifugation, washed with distilled water for several times and dried at 80°C for 10 h. Then the precipitate powders were calcined in air at 550°C for 2 h to get the final products.

2.2 Characterization

The crystal structure of the obtained sample was characterized by X-ray powder diffraction (XRD) using Bruker D8 Advance X-ray Powder Diffractometer employing $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) with 2θ scanning step of $0.02^\circ/\text{s}$ and covering the angle range of 10° – 70° . The shape and size of CdSnO_3 powders were analyzed by field-emission scanning electronic microscopy (SEM model JEOL JSM-6390LV) and transmission electron microscopy (TEM model JEOL JEM-2100).

2.3 Fabrication and measurement of sensors

The structure of the gas sensor belongs to side-heated type. The CdSnO_3 powders were mixed and ground with appropriate α -terpineol in an agate mortar to form a paste. Then, the paste was coated on an alumina

tubelike substrate on which a pair of Au electrodes had been previously printed, and subsequently calcined at 500°C for 1 h. Finally, a Ni–Cr heating wire was inserted into the tube to assemble a gas sensor. The structure and photograph of an as-fabricated sensor had been shown in literature [23]. The sensor was aged at 300°C for 240 h in air to improve its stability.

The properties of CdSnO_3 sensor were tested in a static test system made by Henan Hanwei Electronics Co. Ltd., Henan Province, China. When the sensor was tested, a given amount of test gas was injected into the chamber and mixed with air by a fan for 30 s (liquid reagents were injected by a sample injector on a heating apparatus in the back of the chamber and gasified quickly. Then they were mixed with air by a fan for 30 s). In the test process, the resistance response of the sensor for the test gas was measured by monitoring the voltage across the load resistor. Figure 1 shows the graph of testing principle. The heating voltage (V_h) is supplied to the coils for heating the sensor, the circuit voltage (V_c) is supplied across the sensor, and the load resistor (R_L) is connected in series. The signal voltage (V_{out}) across the load resistor, which changed with the type and concentration of the gas, is measured.

For reducing and oxidizing gases, the gas response of the sensor (S) is defined by Eqs. (1) and (2), where R_a and R_g are the resistances of the gas sensor in air and test gases, respectively:

$$S = \frac{R_a}{R_g} \quad (1)$$

$$S = \frac{R_g}{R_a} \quad (2)$$

The response time is defined as the time needed for the sensor resistance to change by 90% of the difference from the maximum value to the minimum after the test gas injection. The recovery time is the time required for the sensor resistance to change by 90% of the difference from the minimum value to the maximum after releasing the test gas.

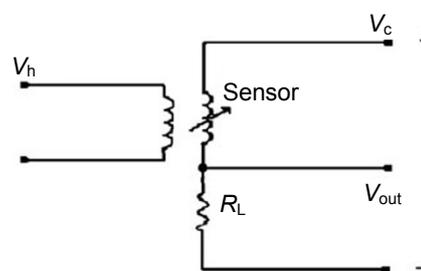


Fig. 1 Graphic of testing principle.

3 Results and discussion

3.1 Structural and morphological characterization

Figure 2 shows the XRD patterns of the samples before and after calcined at 550 °C. As shown in Fig. 2, after the hydrothermal reaction, a good crystalline of $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ precursor is obtained, which is consistent with the standard data file of $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ (JCPDS 28-0202). After the precursor is calcined, the perovskite structure of CdSnO_3 (JCPDS 34-0758) is obtained. There are few residual peaks indexed to Cd_2SnO_4 (JCPDS 34-0928), which are marked with black trigonal symbols. These residual peaks almost cannot be seen from Fig. 2, which indicates a very small quantity of Cd_2SnO_4 presented in the product. Figures 3(a) and 3(b) show the SEM images of CdSnO_3 powders. It is very remarkable that the samples are uniformly cubic structure in shape. A similar cubic-morphology was also observed by Sharma [14] and Tang *et al.* [24]. At the same time, TEM image (Fig. 3(c)) reveals that the side length of the cubic particle is about 100 nm. The high-resolution TEM (HRTEM) image of the sample is shown in Fig. 3(d). From Fig. 3(d), it can be observed that the lattice spacings of $d=0.274$ nm, 0.301 nm and 0.202 nm

correspond to the (110), (104) and (024) facets of the perovskite-structure CdSnO_3 . All the spacings are very close to the standard d values, confirming that as-synthesized CdSnO_3 is well-crystalline. The obtained HRTEM results exhibit full consistency with examined XRD observations.

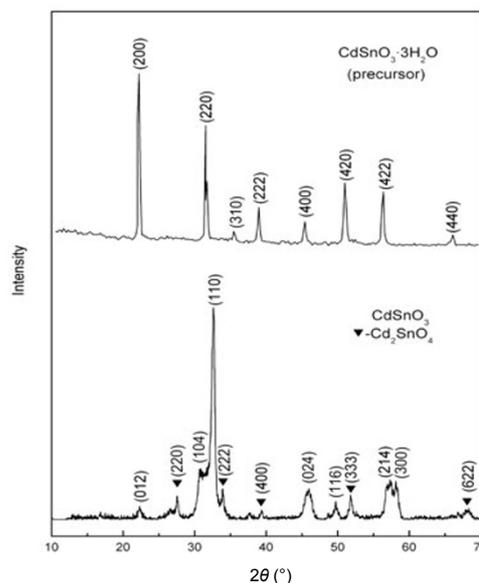


Fig. 2 XRD patterns of $\text{CdSnO}_3 \cdot 3\text{H}_2\text{O}$ (precursor) and CdSnO_3 powders.

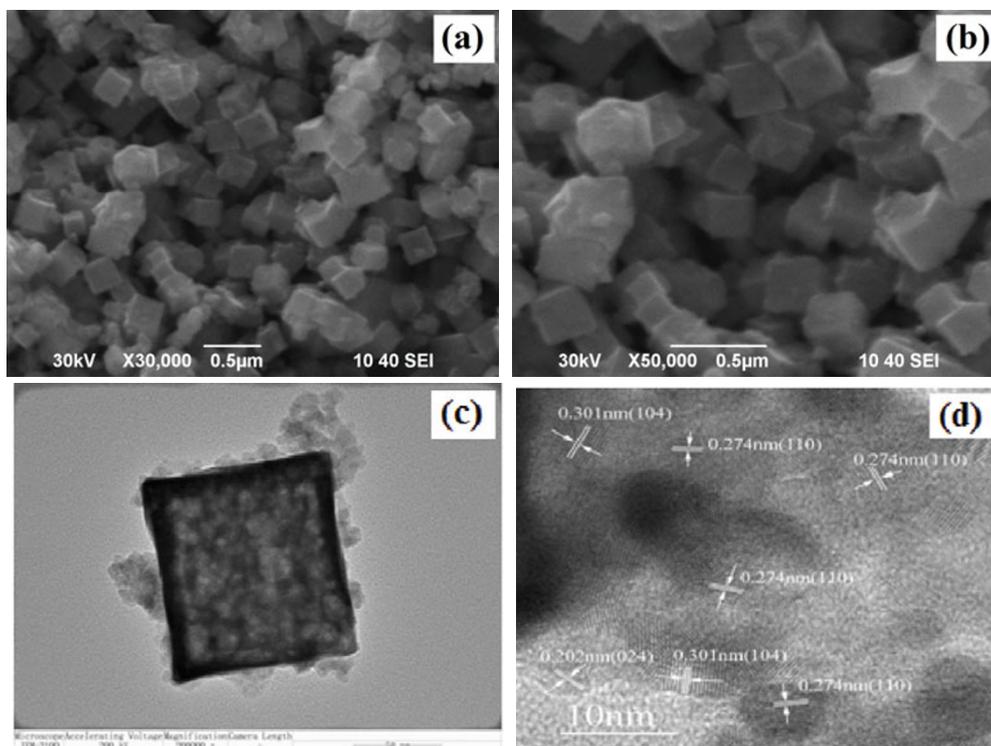


Fig. 3 The SEM (a), (b), TEM (c) and high-resolution TEM (HRTEM) (d) images of CdSnO_3 .

3.2 Gas-sensing properties

The working temperature has a great influence on the response of gas sensor. As shown in Fig. 4, the responses of CdSnO₃ sensor to 5 ppm chlorine gas were tested at different working temperature. With the working temperature varying from 25 °C to 350 °C, the gas response decreases. Room temperature (25 °C) is suggested to be the optimal working temperature to chlorine gas, because the sensor working at this temperature shows the maximum response of 1338.9. The comparison of working temperature among various material gas sensors to chlorine gas sensing is summarized in Table 1. From Table 1, it can be observed that CdSnO₃ sensor prepared in this work has higher response and lower working temperature to chlorine gas.

Selectivity is another important parameter of gas sensors. The selectivity coefficient (K) is defined as: $K = S_A/S_B$, where S_A and S_B are the responses of sensor to chlorine gas and B gas, respectively. Generally, the selectivity coefficient should be more than 5 [10]. As shown in Fig. 5, the responses of CdSnO₃ sensor to 5 ppm different gases were tested at room temperature. It can be seen that the response of the sensor to chlorine gas is much higher than to other test gases. The selectivity coefficients are 362 to NO₂, 383 to H₂S, 496 to SO₂, 536 to acetone, 570 to ethanol, 406 to formaldehyde, and 515 to ammonia, respectively. The results show that CdSnO₃ sensor has a high selectivity to Cl₂ at room temperature.

Response of the gas sensors depends on the concentration of the test gas, too. As shown in Fig. 6, different chlorine gas concentrations were tested at

room temperature. The response of CdSnO₃ sensor increases with increasing gas concentration in the range of 1–10 ppm. To our delight, the sensor shows a high response of 10.5 to chlorine gas even at 1 ppm, indicating that the sensor may be used to detect low concentration of chlorine gas at room temperature.

Figure 7 shows the response and recovery characteristics of CdSnO₃ sensor to 1 ppm and 5 ppm

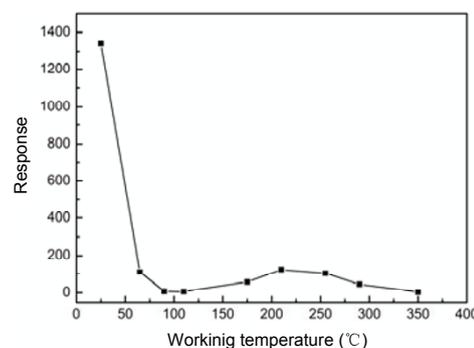


Fig. 4 Gas responses of CdSnO₃ sensor as a function of working temperature to 5 ppm chlorine gas.

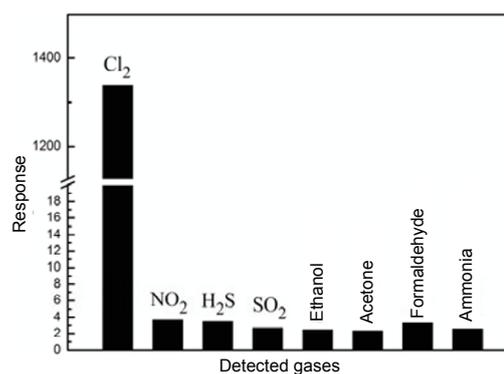


Fig. 5 Gas responses of CdSnO₃ sensor to different detected gases.

Table 1 Gas responses to chlorine gas of sensing materials in the present study and those reported in the literature [3–12]

Sensing materials (preparation)	Cl ₂ (ppm)	R_g/R_a	Working temperature (°C)	Reference
CdSnO ₃ (hydrothermal method)	5	1338.9	25	This work
ZnO(screen-printing technique)	300	195	25	[3]
SnO ₂ /W ₁₈ O ₄₉ (sequential thermal evaporation)	4	~12	25	[4]
CdS(sol-gel process)	10	–	200	[5]
CdIn ₂ O ₄ (co-precipitation method)	0.5	6000	250	[6]
SnO ₂ (hydrothermal method)	5	26.8	260	[7]
Cr ₂ O ₃ (sol-gel process)	10	–	300	[8]
NiO(thick-film technology)	0.7	~1.6	250	[9]
In ₂ O ₃ (thick-film technology)	0.7	~105	300	[9]
WO ₃ (thick-film technology)	0.7	~70	210	[9]
CdIn ₂ O ₄ (sol-gel process)	10	53000	255	[10]
CdIn ₂ O ₄ (flux method)	400	9.24	450	[11]
Cr ₂ O ₃ (electron-beam deposition)	5	–	220	[12]

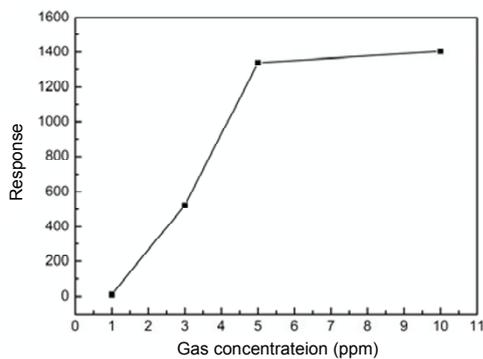


Fig. 6 Gas responses of CdSnO₃ sensor to different chlorine gas concentrations.

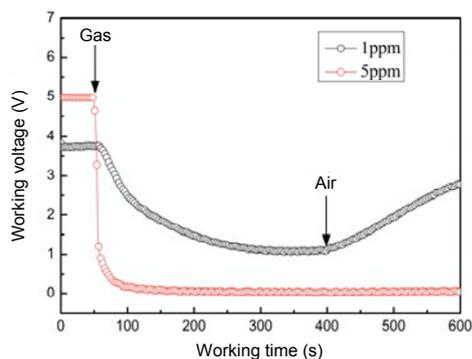
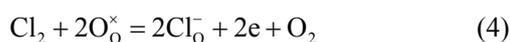
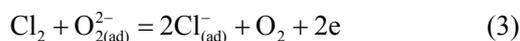


Fig. 7 Response and recovery characteristics of CdSnO₃ sensor to chlorine gas.

chlorine gas at room temperature. The response time are 88 s to 1 ppm chlorine gas and 23 s to 5 ppm chlorine gas, respectively, but the recovery time is sluggish, so it needs to improve the recovery time in our next work. It is also obvious that the response resistance decreases with the addition of chlorine gas and increases with the removing of chlorine gas and introducing of air, indicating the characteristic of n-type semiconductors of CdSnO₃ sensor.

3.3 Gas-sensing mechanism

There are four adsorption behaviors of chlorine on the oxide surface [2,3,25]:



where subscripts, ad and O, mean the species adsorbed on the surface and the species occupying lattice oxygen sites, respectively. V₀^{''} is an oxygen vacancy. In reactions (3) and (4), chlorine substitutes for

adsorbed oxygen and lattice oxygen to form Cl_(ad)⁻ and Cl₀⁻, respectively, inducing electron donation into the oxide. On the other hand, in reactions (5) and (6), chlorine is adsorbed on the surface and occupies the oxygen vacancy to form Cl_(ad)⁻ and Cl₀⁻, respectively. In these cases, electrons are drawn from the oxide, resulting in an increase in resistance.

In this work, the working temperature of CdSnO₃ sensor is room temperature. At room temperature, there would be no oxygen adsorption [3,25], so the oxygen adsorption-desorption mechanism is not employed to sense the chlorine gas. Thus, the reactions (5) and (6) of chlorine gas sensing response of the oxides' surface are favorable mechanism in the present case. When the sensor is exposed to chlorine gas, chlorine molecule will be adsorbed on CdSnO₃ surface or occupy the oxygen vacancy to form Cl_(ad)⁻ or Cl₀⁻ by attracting electrons from CdSnO₃. Since CdSnO₃ is an n-type semiconductor, the resistance of sensor will increase. On the other hand, the reverse reaction will take place after chlorine gas is off the sensor, and the trapped electrons will go back to the sensor, which will finally lead to an increase of electron concentration and a decrease in the resistance. This analysis is in accordance with the curves of the response and recovery time (Fig. 7).

4 Conclusions

In summary, after a simple hydrothermal process of 170 °C for 16 h, CdSnO₃·3H₂O precursor was obtained, and cubic perovskite-structure CdSnO₃ with side length of about 100 nm was obtained by calcinating CdSnO₃·3H₂O. The sensor based on CdSnO₃ shows enhanced response and selectivity to chlorine gas at room temperature. Especially, the sensor has a high response of 10.5 even to 1 ppm chlorine gas. Therefore, it will have good potential application to detect low concentration of chlorine gas at room temperature in the future. The work to improve the recovery time of the sensor and further detect chlorine gas in the concentration of ppb level is underway in our laboratory.

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