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Electrical characterization of TiO_2-based ceramics for VOCs

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Abstract Cr doped TiO_2 and TiO_2/Cr_2O_3 powders are prepared by sol–gel technique and solid state reaction respectively. The structural and electronic properties of these powders are investigated. The responses of the materials made from the powders to benzene and formaldehyde vapors are studied. The research results show that Cr^{3+} can enter into the lattice as substitutional metal dopant by sol gel route at lower temperature. The segregation of Cr_2O_3 happens when Cr content exceed 8 at.%. The resistance of TiO_2 can be remarkable decreased by doping Cr^{3+} as substitutional metal dopant. Besides Cr^{3+}, the segregation of Cr_2O_3 also contributes to the alteration of conduction from n- to p-type. With some other catalyzer, both of Cr doped TiO_2-based and Cr_2O_3/TiO_2-based ceramics can detect benzene and formaldehyde vapors at 21 ppm.

Keywords Cr_2TiO_2 ceramics · Volatile organic compounds · Gas sensing

1 Introduction

In recent years, the demand of sensors for safety control and environmental monitoring has been expanded enormously. Especially, Aromatic hydrocarbons such as benzene, have been found to be responsible for the leucocythemia and lung cancer. And they are frequently encountered in every day life. For example, they exist in unleaded gasoline, paint, etc. In past years, different techniques have been developed and used to detect and measure these kinds of substances in the air. At present the devices capable of achieving this purpose include some electronic sensors and all sorts of gas chromatographs. However, they are not only expensive but also have many detection limits. For example usually they detect only one family of compounds, and are not as portable as desired. Furthermore, some of those sensors can only be used one time.

Recently researches on TiO_2-sensors for detection of VOCs are reported [1, 2]. It is identified that a variety of gaseous compounds have been oxidized with TiO_2, including formaldehyde, pyridine, trichloroethylene, benzene, toluene, ethylene, etc. The results from these researches have shown effective removal and conversion of the above organics into less toxic compounds. Nevertheless, some problems prevent the TiO_2 sensors being used as a portable miniature system. The fact is that TiO_2 based sensing materials exhibit high resistance in the air and need long time to recover from the former reaction. This paper reports our research work on improving the gas sensing properties of TiO_2 based sensing materials, particularly on decreasing the initial resistance of the materials.

2 Experiment

Cr doped TiO_2 powder was prepared using sol–gel route. Chromium salt is dissolved to get Cr ethylene glycol solution. Titanium butoxide was dissolved in the solution of ethylene glycol and acetic acid (volume rate 1:1). The precursor sol was obtained by adding Cr^{3+} solution into Ti–sol. The complex was well stirred for about an hour at

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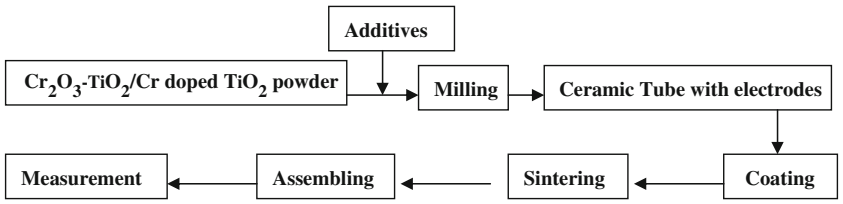

Fig. 1 Flow chart of the ceramic sensor fabricated in present research [3]

353 K to produce a clear, homogenous solution. The sol was dried to form gel. The gel was calcined to form Cr-doped TiO_2 powder at 923 K, 1023 K, and 1123 K respectively. The Cr doped TiO_2 powders with different mol ratio from 3% to 32% (atomic percent of Cr_2O_3 in the mixture of Cr_2O_3 and TiO_2) were prepared in the same way.

The Cr_2O_3/TiO_2 powder was prepared by conventional solid state reaction of TiO_2 and Cr_2O_3. The starting materials TiO_2 and Cr_2O_3 are prepared respectively by sol–gel method described above. They were mixed in appropriate mol ratio to get 3%, 8%, 14%, 25%, and 32% (atomic percent of Cr_2O_3 in the mixture of Cr_2O_3 and TiO_2). The mixture was ground for about 4 h to get fine and well homogeneous powder. The powder was sintered at 923 K, 1023 K, and 1123 K respectively.

Two kinds of powders described above were used to prepare gas sensing ceramic sensors with some metal oxides as the additives, and the catalyst used is $PdCl_2$ or $AuCl_3$. The processing flow chart of the gas sensor is shown in Fig. 1 [3]. The materials were finally sintered in the air at 923 K. The structure of the sensor is given in Fig. 2 [4].

The structural characteristics of the powders were examined by X-ray technique. The gas sensing properties of the sensors were measured using a computerized multimeter system. The detected gas was introduced in a sealed test chamber (300 mm×300 mm×240 mm) with a pipette. A blender was used to keep the well-distributed atmosphere for measurement. The gas response S is defined as S=Ra/Rg, where Rg is the resistance of sensors at different detected gas concentrations and Ra is the resistance of the sensors in the air.

3 Results and discussion

3.1 Structural characteristic

XRD patterns of the Cr doped TiO_2 and Cr_2O_3/TiO_2 powders calcined at 923 K and 1123 K are shown in Fig. 3.

In our case, TiO_2 exist as rutile phase in both of the two kinds of powders after sintered at 923 K. The diffraction peaks of Cr_2O_3 in Fig. 3(a) indicate that the Cr_2O_3 exist as the second substance even 3 at.% Cr_2O_3 mixed for the powder prepared by solid state reaction. According to Ref. [5], the temperature for Cr doped into the lattice of TiO_2 is 1300 K by solid state reaction because of the good stability of TiO_2. For the powder prepared through sol–gel route, no Cr_2O_3 diffraction peak is detected in 3 at.% Cr doped powder sintered at 923 K (see Fig. 3(b)). Whereas, the appearance of Cr_2O_3 diffraction peaks reveal the segregation of Cr_2O_3 in 8 at.% doped powder sintered at 923 K. The experimental result is closed to that in Ref. [6]. It is suggested that the soft solution route make it easier for Cr^{3+} getting into the lattice of TiO_2 at lower temperature. Figure 4 shows the XRD patterns of the two kinds of powders with 8 at.% Cr_2O_3 sintered at 1123 K. There is no difference observed in the diffraction patterns between the two sorts of powders. It seems that the amount of Cr incorporation is limited.

3.2 Electronic characteristics

Resistance measurements of the ceramic sensors fabricated with the two sorts of powders were carried out. Figure 5 gives the variations of resistance values of Cr doped TiO_2

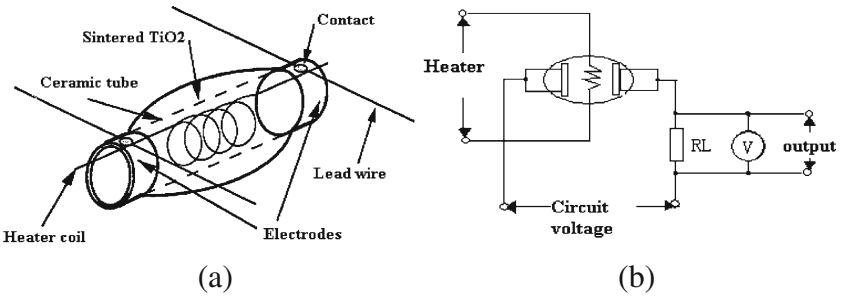

Fig. 2 Schematic drawing of the sensor structure (**a**) and the working principle (**b**) [4]

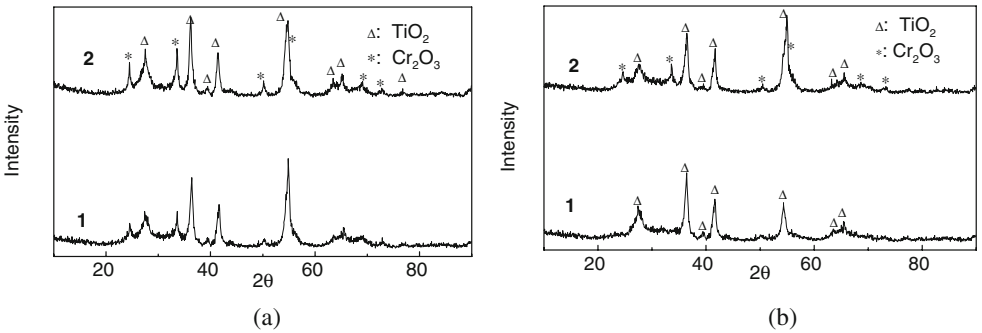

Fig. 3 XRD patterns of TiO_2 powder calcined at 923 K (curves *1* and *2* respond to 3 and 8 at.% Cr in the powder respectively) (**a**) Cr_2O_3/TiO_2; and (**b**) Cr doped TiO_2

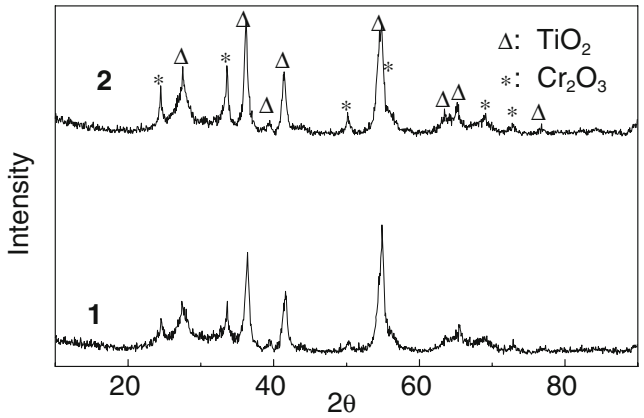

Fig. 4 XRD patterns of the powder sintered at 1123 K. (*1*) Cr doped TiO_2; and (*2*) Cr_2O_3/TiO_2

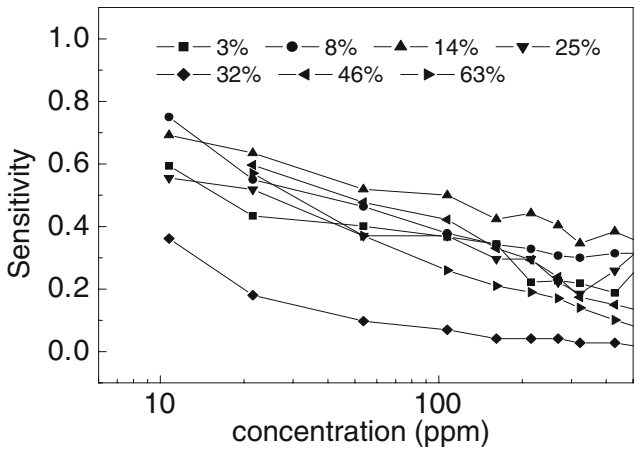

Fig. 6 Sensitivity dependence on benzene concentration for Cr_2O_3/TiO_2 based sensors with different Cr contents

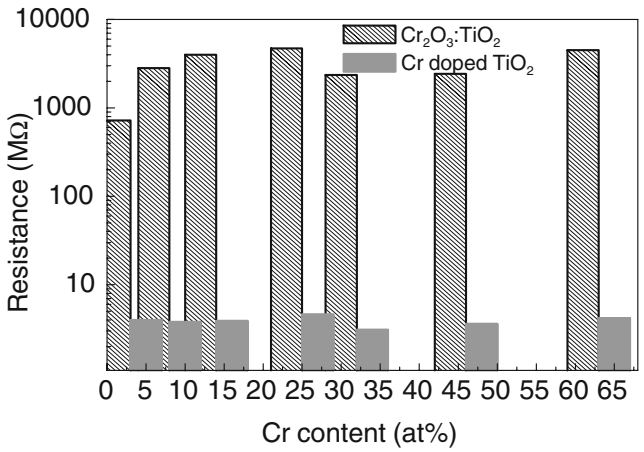

Fig. 5 Resistance of Cr doped TiO_2 and Cr_2O_3/TiO_2 based sensors with the different Cr content respectively

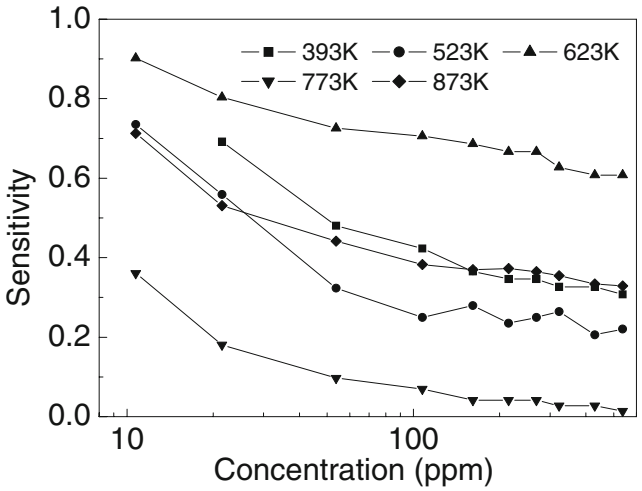

Fig. 7 Sensitivity dependence on benzene concentration for Cr_2O_3/TiO_2 based sensors with 32 at.% Cr at different temperature

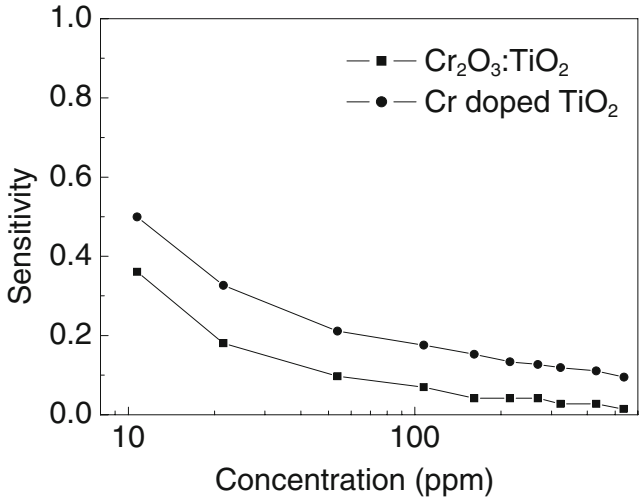

Fig. 8 Sensitivity dependence on benzene concentration for Cr_2O_3/TiO_2 and Cr doped TiO_2 based sensors with 32 at.% Cr at 773 K

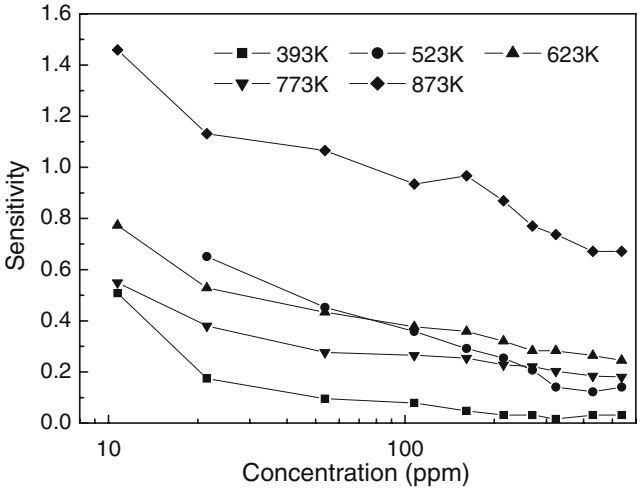

Fig. 10 Sensitivity dependence on formaldehyde concentration for Cr_2O_3/TiO_2 based sensors with 8 at.% Cr at different temperature

and Cr_2O_3/TiO_2 based sensors with the different Cr content respectively. Evidently, a sharply decrease in the resistance values of the sensors is obtained by Cr incorporation. The change of resistance value with the Cr content is not remarkable in our experiment for both of the two kinds of sensors. The electrical characteristics of the response to benzene and formaldehyde (shown in Figs. 6, 7, 8, 9, 10 and 11) indicate the p-type nature of both Cr contained TiO_2 ceramics. It is well known that Cr^{3+} acts as a accepter in Cr doped TiO_2 [7]. It results in the alteration of TiO_2 conduction from n to p type. In our experiment, Cr_2O_3/TiO_2 based ceramics, with only 3 at.% Cr contained, display p-type conduction characterization. It may be evident that the segregation Cr_2O_3 is also contributing to the conduction type alteration of TiO_2.

3.3 Gas sensing properties

Gas sensing properties are measured and analyzed for all sensors with respect to the vapor of benzene and formaldehyde. The response of the sensors to the benzene and formaldehyde are measured at different operating temperatures from 393 K to 873 K. Figure 6 shows the variations of sensitivity depend on benzene concentration for Cr_2O_3/TiO_2 based sensors with different Cr content. It shows that, for Cr_2O_3/TiO_2 based sensor, the best response to benzene is obtained from the sensors containing 32 at.% Cr. The dependences of the response versus operating temperature are shown in Fig. 7. One can see that the largest response to benzene occurs at the operating temperature 773 K. Working at this temperature, the sensors have good response even at 21 ppm. With the results of measurement, the sensing char-

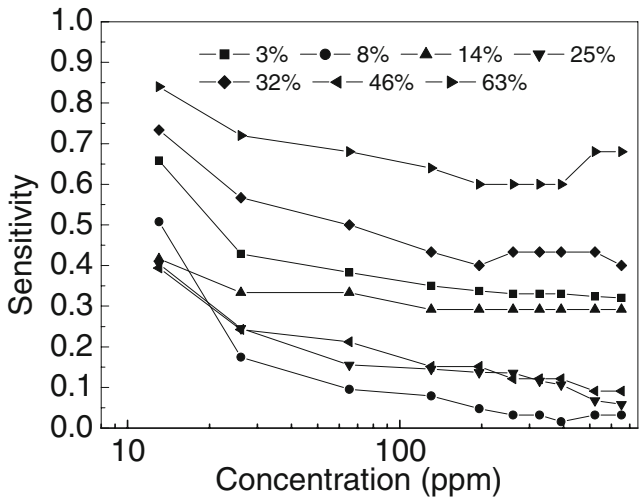

Fig. 9 Sensitivity dependence on formaldehyde concentration for Cr_2O_3/TiO_2 based sensors with different Cr contents

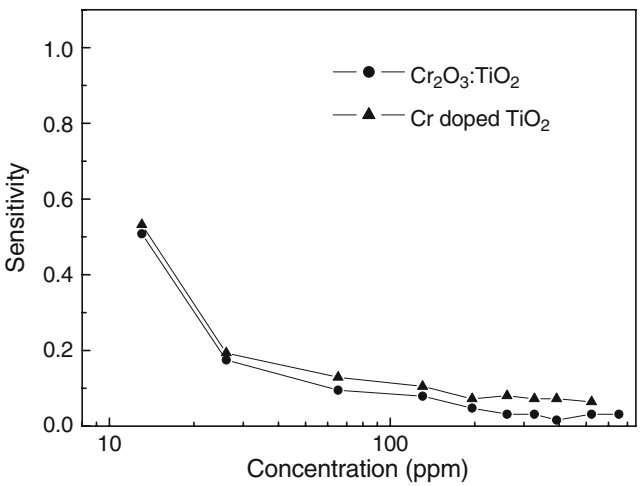

Fig. 11 Sensitivity dependence on formaldehyde concentration for Cr_2O_3/TiO_2 and Cr doped TiO_2 based sensors with 8 at.% Cr at 393 K

acteristic of Cr doped TiO_2 based sensors are similar to that of Cr_2O_3/TiO_2 based sensor in sensing to vapor of benzene. The best response to benzene vapor can also be achieved by the sensors containing 32 at.% Cr at the operating temperature of 773 K. The Cr doped sensors have smaller initial resistances and responses than the Cr_2O_3/TiO_2 based sensors with the same amount of Cr contained (see Fig. 8).

Figure 9 gives the response of the Cr_2O_3/TiO_2 sensors with different Cr content to formaldehyde at the operating temperature of 393 K. It reveals that the sensors with 8 at.% Cr_2O_3 have the largest response. Figure 10 indicates that the operating temperature associated with the best response is 393 K for the sensors with 8 at.% Cr_2O_3. For formaldehyde concentration as low as 21 ppm the detection of the sensors can still be available. With the results of the measurement of Cr doped TiO_2 sensors, the best response can also be obtained from the sensors with 8 at.% Cr_2O_3 at the temperature of 393 K. And the responses of Cr doped sensors are smaller than those of the Cr_2O_3/TiO_2 based sensors (see Fig. 11).

By comparing the sensing characteristics of the two sorts of sensors, Cr doped TiO_2 based sensors process lower initial resistance than Cr_2O_3/TiO_2 based sensors, and the former is less sensitive than the latter to benzene and formaldehyde. This may be explained by the difference of surface adsorption between two kinds of sensors. According to R.K. Sharma et al. [5], Cr doped TiO_2 ceramics have lower porosity and larger grain size. The gas sensing properties of the sensor are mainly controlled by surface reaction. High porosity is helpful to the increase the amount of adsorbed oxygen and detected gas species. So, the lower porosity of Cr doped TiO_2 ceramics may be responsible for the lower response for the sensors.

4 Conclusion

TiO_2 Powders contained Cr_2O_3 are prepared through two techniques respectively. The structural characterizations show that Cr^{3+} can enter to the lattice as substitutional metal dopant by sol–gel route at a lower temperature. The segregation of Cr_2O_3 happens when Cr content exceeds 8 at.%. The powder prepared using solid state reaction is the mixture of TiO_2 and Cr_2O_3 in our experiments. The origin of the p-type conduction is discussed. The resistance of TiO_2 can be decreased remarkable by doping Cr^{3+} into the lattice of TiO_2. Besides Cr^{3+}, the segregation of Cr_2O_3 contributes also to the alteration of conduction from n- to p-type. Both Cr doped TiO_2-based and Cr_2O_3/TiO_2-based ceramics with some other catalyzer can detect benzene and formaldehyde vapors respectively at the gas concentration as low as 21 ppm.

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