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The sensing behavior of semiconductor metal oxides based on SnO_2 thick film for detection of chlorinated VOCs in low concentration

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Abstract

A SnO_2-based semiconductor thick film gas sensor was fabricated for detection of chlorinated VOCs such as dichloromethane (DCM) and trichloroethylene (TCE) at concentrations of 10 and 20 ppm respectively in the temperature range of 100–400°C. Other semiconductors such as ZnO, CuO and Sm_2O_3 were added in 5.0% wt to SnO_2 by co-precipitation method. The samples were characterized by TEM, XRD and BET. Characterization results showed that presence of dopants causes an increase in surface area and a decrease in the particle size of the sensing materials. Moreover, the TEM micrographs confirmed that the size of synthesized materials is less than 20 nanometers. It was found that SnO_2-Sm_2O_3 has the highest sensitivity to DCM, especially at low temperatures. Also sensitivity is quite high for this sensor even at a concentration as low as 0.1 ppm. However, presence of promoters suppressed the sensitivity to TCE.

Key words: Gas sensor, volatile organic compounds, VOC, SnO_2.

Introduction

It is a fact that in the modern world people spends about 90% of their times indoors [1]. Recent findings have demonstrated that indoor air is often more polluted than outdoor air because of poor ventilation. Thus, monitoring indoor air quality has attracted an increasing interest. There are various volatile organic compounds (VOCs) in indoor air which originates from various sources. Chlorinated organic such as DCM and TCE, are classified as an indoor pollutant. These VOCs are emitted from furnishings and if the concentration of them exceeds exposure limits they cause problems such as irritation, nausea, headache and even cancer.

Chen et al. Used an electrodeposited Pb-modified electrode to sense TCE in high concentrations [2]. Choi et al. have studied on various additives to SnO_2 for detection of DCM in low concentration and have seen that added promoters do not always increase the sensitivity of pure SnO_2[3]. In the present study we investigated the effects of several metal oxides as promoters on the sensitivity of SnO_2-based sensors.

Experimental

Pure SnO_2 was prepared from $SnCl_4$ solution (Merck) by a precipitation method. Addition of promoters was performed by co-precipitation method. The powders obtained were dried and calcined at 450°C. The powders were characterized by XRD, TEM and BET surface area.

The thick-film sensors were fabricated on the alumina substrate with Au electrodes. The sensors were exposed to 10 ppm DCM and 20 ppm TCE and the changes in the resistances vs temperature were measured. Following the sensitivity measurements, the sensitivity of the sensors vs concentration at the temperature of the maximum sensitivity was obtained.

Results

The specific surface areas (BET) of SnO_2, SnO_2-5wt% ZnO, SnO_2-5wt% CuO and SnO_2-5wt% Sm_2O_3 were measured to be about 37.5, 59.9, 64.1 and 61 $m^2.g^{-1}$ respectively. The XRD spectra of the powders are presented in Figure 1. As is observed there is no indication of the presence of ZnO, CuO and Sm_2O_3. Due to the low calcination temperature these compounds

are either amorphous or crystalline with very small crystallite size. The peaks of SnO_2 in the samples with promoters have smaller intensities and more broad, indicating that the promoters act as crystal growth inhibitor.

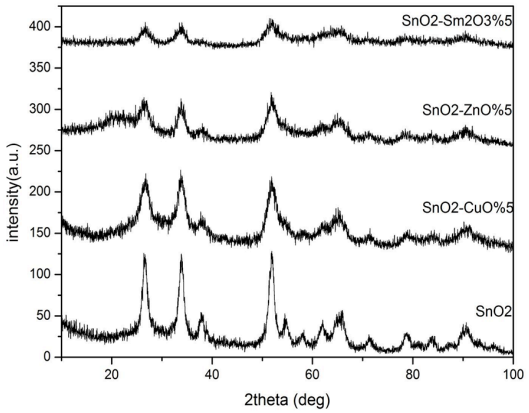

Fig. 1. XRD patterns of sensors calcined at 450°C.

The TEM micrographs in Fig. 2. show the microstructure of the pure SnO_2 and SnO_2-5 wt% Sm_2O_3 samples. The nanoparticles of samples are nearly spherical with average grain sizes around 15 nm and 12 nm, respectively.

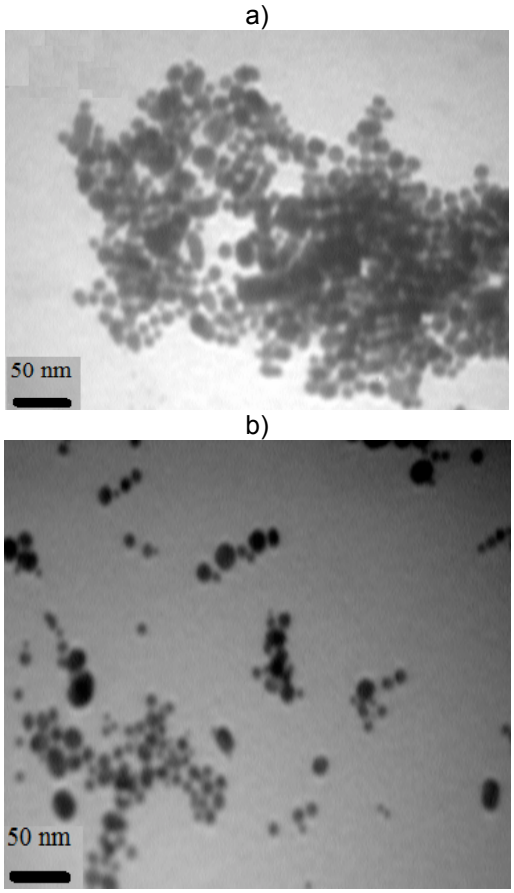

Fig. 2. TEM micrograohs of a) Pure SnO_2 b) SnO_2-5wt% Sm_2O_3.

The sensitivity of the sensors, i.e. R_a/R_g, vs temperature is presented in Fig. 3.

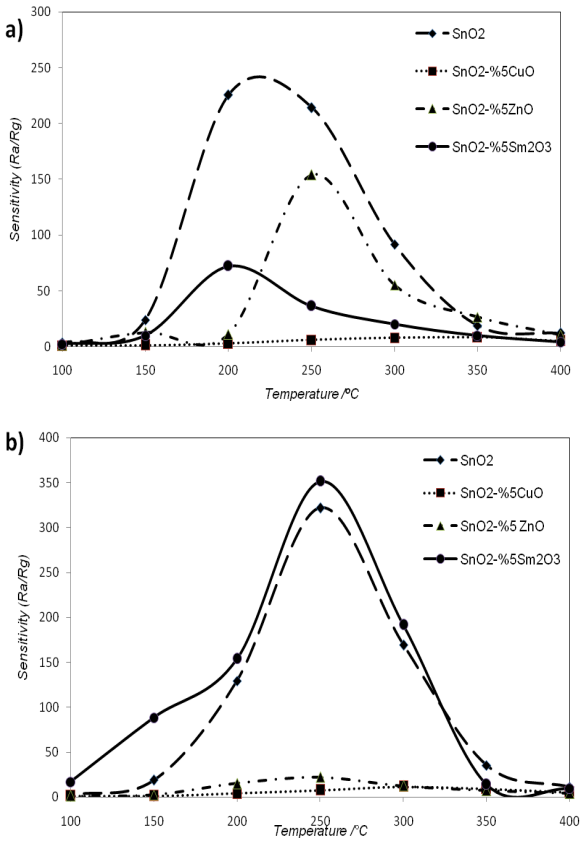

Fig. 3. Sensitivity towards a) TCE 20 ppm and b) DCM 10 ppm at different operating temperatures for pure SnO_2, SnO_2-5 wt % CuO, SnO_2-5 wt % ZnO and SnO_2- 5wt%Sm_2O_3.

As is shown in Figure 3(a) by doping metal oxides to SnO_2 , sensitivity to TCE decreases. In case of DCM (Fig. 3(b)) sensitivity of SnO_2-5 wt%Sm_2O_3 is larger than pure SnO_2 for the temperature range examined. However, this effect is more pronounced at lower temperature, for instance the sensitivity of SnO_2-5wt% Sm_2O_3 becomes 4-5 times larger than that of pure SnO_2 at 150°C. Other dopants supperess the sensitivity to the target gas. The catalytic activity of SnO_2-5 wt% CuO, SnO_2-5 wt% ZnO for oxidation of DCM are presented in Fig. 4. As is evident the low sensitivity of these sensing matrials are mostly due to their high catalytic activity in the temperature range similar to the operating temperature of the sensors.

The sensitivity of SnO_2-5 wt% Sm_2O_3 to various concentrations of DCM at 250ºC is shown in Fig. 5. It is interesting that the sensitivity is quite high even at a concentration as low as 0.1 ppm.

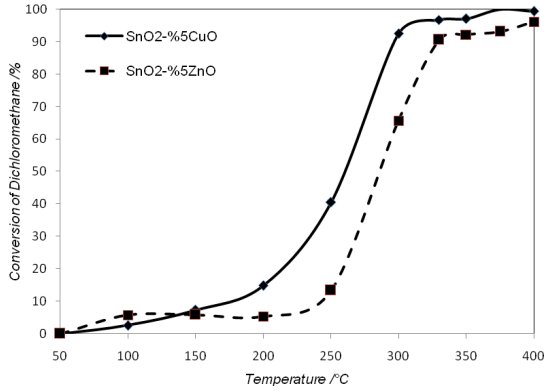

Fig. 4. The catalytic reaction of 10 ppm DCM in air over the ZnO and CuO-doped SnO_2.

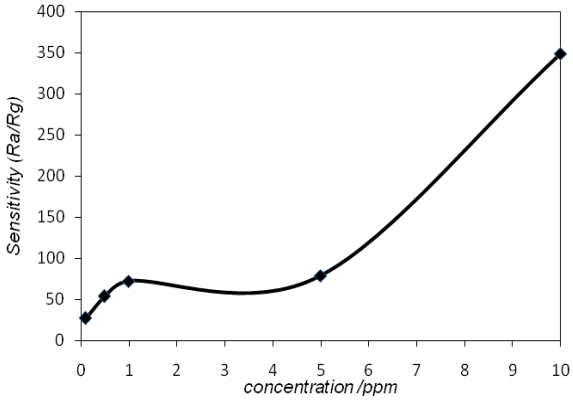

Fig. 5. Correlation between DCM concentrations and sensitivity of SnO_2- 5.0wt%Sm_2O_3 film at 250°C.

Conclusion

In this study, we tried to find suitable dopants for SnO_2-based sensors for sensing low concentration of chloric volatile organic compounds. SnO_2 samples doped with copper oxide, zinc oxide and samarium oxide were synthesized through co-precioitation method and characterized by XRD, TEM and BET techniques. Characterization results showed that presence of dopants causes an increase in surface area and a decrease in the particle Size. Then these synthased materials are used for sensing trichloroethylene and dichloromethane. The results revealed that 5.0 wt%Sm_2O_3 doped SnO_2 sample has higher sensitivity and lower operating temperature than that of pure SnO_2 and other sensing materials used in this study. This sensor showed good sensitivity to target gases even at low concentrations. The catalytic activity studies revealed that the low sensitivity for other sensors such as 5.0 wt%CuO and 5.0 wt%ZnO are mostly due to high catalytic activity in temperature range similar to the operating temperatures of the sensors.

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