Effect of flame-made metal (M=Pt, Nb, Ru)-loaded In_2O_3 on NO_2 gas sensing

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ABSTRACT

Unloaded In_2O_3 and M (M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles loaded with 0.25–1.00wt% M were successfully synthesized in a single step by the flame spray pyrolysis (FSP) technique. Indium nitrate, platinum (II) acetylacetonate, niobium ethoxide and ruthenium (III) acetylacetonate were used as In, Pt, Nb and Ru precursors respectively, dissolved in ethanol. The unloaded In_2O_3 and M-loaded In_2O_3 nanoparticles were characterized. The average diameter of the spherical nanoparticles were in the range of 10.2 to 15.2 nm under 5/5 (precursor/oxygen) flame conditions. All peaks can be confirmed to correspond to the cubic structure of In_2O_3 (JCPDS No. 03–065–3170). Gas sensing studies showed that Pt-loaded In_2O_3 gave an enhancement in NO_2 sensing in term of response and selectivity. 0.5wt% Pt/In_2O_3 exhibited good selectivity against H_2S and NO gases. When compared to other metal loading such as Nb and Ru, Pt-loaded In_2O_3 exhibited much better gas sensing against NO_2, H_2S and NO gases.

Keywords: unloaded and M (M=Pt, Nb and Ru)-loaded In_2O_3, , nanoparticles; flame spray pyrolysis (FSP); NO_2 gas sensors

INTRODUCTION

Semiconductive indium oxide (In_2O_3) [1] with a wide bandgap (around 3.6 eV at room temperature) has attracted much attention in recent years, owing mainly to its application in solar cell, field-emission display, lithium ion battery, nanoscale biosensor, gas sensor, optoelectronics, and photocatalysis.

Flame spray pyrolysis (FSP) has previously been employed to synthesize nanostructured particles [2]. FSP is a very promising technique for synthesis of high purity nano-sized materials with controlled size and high surface area in one step. The aim of this research is to apply this technique to synthesize the unloaded In_2O_3 and 0.25–1.00 wt% M (M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles. Characterization of the unloaded In_2O_3 and M-loaded In_2O_3 nanoparticles was also performed. Gas sensing of M (M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles towards NO_2, H_2S and NO gases were performed. The effect of metal loading on In_2O_3 towards NO_2 was also reported.

METHOD

Powder characterization

The unloaded In_2O_3 and 0.25–1.00 wt% M(M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM). The BET surface area (SSA_{BET}) of the nanoparticles was measured by nitrogen adsorption.

Sensingfilm fabrication

Sensing films were prepared from unloaded In_2O_3 and 0.25–1.00 wt% M (M=Pt, Nb and Ru)-loaded In_2O_3 by mixing 60 mg of the nanoparticles into an organic paste composed of ethylcellulose and terpineol (0.25 mL), which acted as a vehicle binder and solvent, respectively. The mixtures were spin coated on alumina substrates interdigitated with gold electrodes on the front site and then were annealed at 350°C for 2 h with a heating rate of 2°C/min for binder removal.

Gas-sensing measurement

For gas sensing measurements, unloaded In_2O_3 and M (M=Pt, Nb and Ru)-loaded In_2O_3 sensors were heated by the external NiCr heater to the operating temperatures at

200, 250, 300 and 350ºC in dry air before exposure to the test gases into a stainless steel chamber (the setup is reported in our previous work [3]). The gas sensing response (S) is given by $S = R_g/R_a$, where R_g and R_a are the electrical resistances of the sensor measured in the presence of oxidizing gas and pure dry air respectively. The response time (T_{res}) is the time required to reach 90% of the response signal.

RESULTS AND DISCUSSION

FSP is a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step of the unloaded In_2O_3 and 0.25–1.00 wt% M (M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles under 5/5 (precursor/oxygen) flame conditions. All peaks in the XRD spectrum can be confirmed to correspond to the cubic structure of In_2O_3 (JCPDS No. 03–065–3170). The SSA_{BET} was found to be in the range of 54.9 to 81.6 m^2/g corresponding to d_{BET} of 10.2–15.2 nm. The SEM result showed the presence of agglomerated nanospheres with an average diameter of 10–20 nm. TEM-bright-field images of the In_2O_3 nanoparticles revealed spherical and cubic morphologies of the synthesized nanoparticles with the crystallite size of 10–20 nm.

Figure 1 shows the change in resistance of In_2O_3 sensing films with different Pt loading concentrations under exposure to various NO_2 concentrations ranging from 0.125–5 ppm at the operating temperature of 200–350ºC.

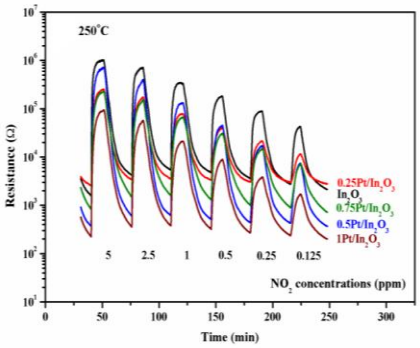

Fig.1 Change in resistance under exposure to NO_2 with the concentrations ranging from 0.125 to 5 ppm of 0–1wt% Pt-loaded In_2O_3 sensors at the operating temperature ranging from of 200–350°C.

The effect of operating temperature ranging from 200 to 350°C on NO_2 response of In_2O_3 with different Pt-loading concentrations is demonstrated in Figure 2.Among various Pt-loaded In_2O_3 sensing films, the gas sensing behaviorsare drastically declined with increasing operatingtemperature (300–350°C) and decreasing operating temperature (200°C) at all gas concentrations. The 0.5 wt% Pt-loaded In_2O_3 sensor exhibits the highest response of ~1904 to 5 ppm NO_2 at an optimal temperature of 250°C, which shows the highest response at 250°C. Figures 3 and 4 show various Nb-loaded In_2O_3 sensing films and Ru-loaded In_2O_3 sensing films, In_2O_3 sensor exhibits the highest response of ~ 643.1 to 5 ppm NO_2 at an optimal temperature of 250°C.

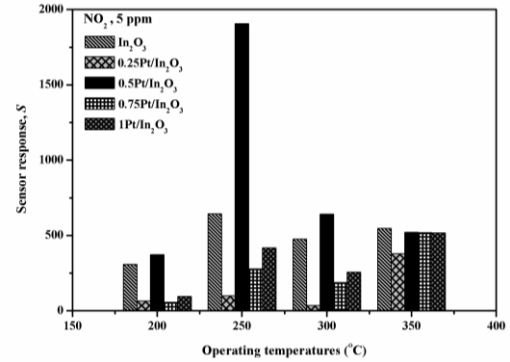

Fig.2 Sensor response of Pt-loaded In_2O_3 sensor to 5 ppm NO_2 vs. different operating temperatures ranging from 200 to 350°C.

(1)

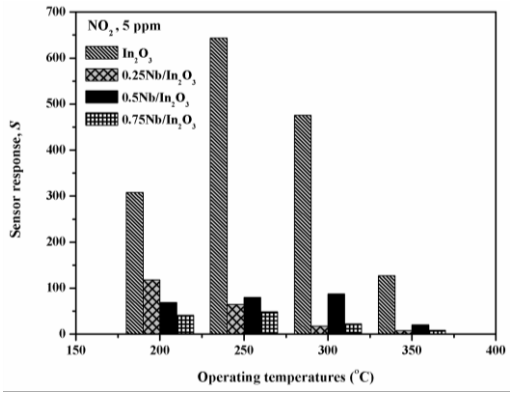

Fig. 3 Sensor response of Nb-loaded In_2O_3 sensor to 5 ppm NO_2 vs. different operating temperatures ranging from 200 to 350°C.

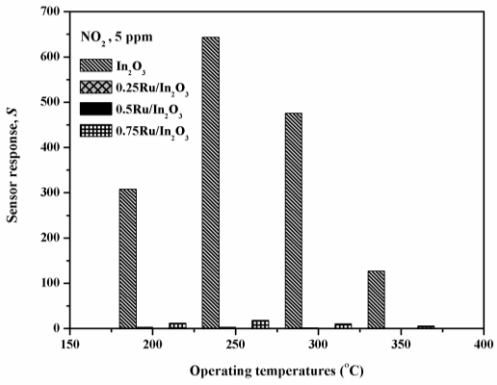

Fig.4 Sensor response of Ru-loaded In_2O_3 sensor to 5 ppm NO_2 vs. different operating temperatures ranging from 200 to 350°C.

When comparing the NO_2 response of Pt-loaded In_2O_3 with other semiconducting metal oxides, 0.5wt% Pt-loaded In_2O_3 shows the highest response compared to other metal oxides. Penza *et al.* [4] reported that the highest sensing behaviors of Pt-loaded WO_3 to 10 ppm NO_2 was about 3.45 at 150ºC. Stankova *et al.* [5] reported Pt-loaded microhotplates WO_3 sensors prepared by reactive rf. spluttering with response of 11.73 to 10 ppm NO_2 at 260ºC. Srivastava *et al.* [6] also reported the Pt-loaded WO_3 film prepared by screen-printing, and the sensing test at 450ºC with NO_2 at concentration ranging from 40–400 ppm. A sensor showed the highest sensor signal at 400 ppm (S= 4).

The gas sensing selectivity of Pt-loaded In_2O_3 gas sensors were characterized towards various toxic gases such as NO_2, NO and H_2S at their critical concentrations and operating temperature of 250°C as shown in Figure 5. It was found that In_2O_3 exhibit high response to NO_2, moderate response to NO and low response to H_2S. With the optimal Pt-loading concentration of 0.5wt% has good gas selectivity to NO_2, which increasing order of response to NO_2, NO and H_2S, respectively. The 0.5wt% Pt-loaded In_2O_3 sensors exhibits very high NO_2 response at high concentration and much less response to other gases including NO and H_2S. Therefore, Pt can improve NO_2 sensing selectivity againstof these two gases. The observed high NO_2 selectivity suggest specifically high reaction rate between NO_2 gas and interface between Pt-loaded In_2O_3 nanoparticles.

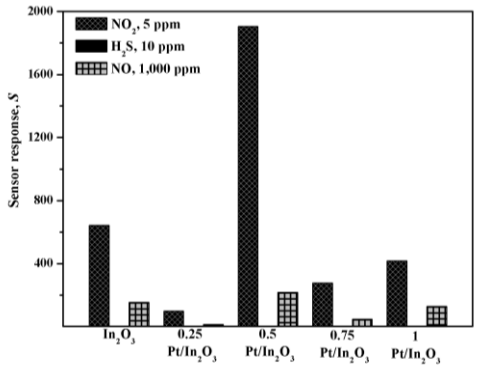

Fig.5 The selectivity histograms of sensor responses to 5 ppm NO_2, 10 ppm H_2S, and 1,000 ppm NO of 0–1wt% Pt-loaded In_2O_3 sensors at the optimal operating temperatures of 250°C.

To investigate the effect of noble metal catalyst on In_2O_3 towards NO_2 gas, other metals particularly Nb and Ru have also been investigated as the catalyst for NO_2 oxidation. Figure 6 shows the response change of samples under exposure to 5 ppm concentrations of NO_2 at 250°C. It can be clearly seen that the Pt-loaded In_2O_3 sensor shows the highest response compared with In_2O_3 sensor loaded with Nb and Ru. Therefore, Pt is confirmed to be the most effective catalyst for NO_2 oxidation on In_2O_3 support.

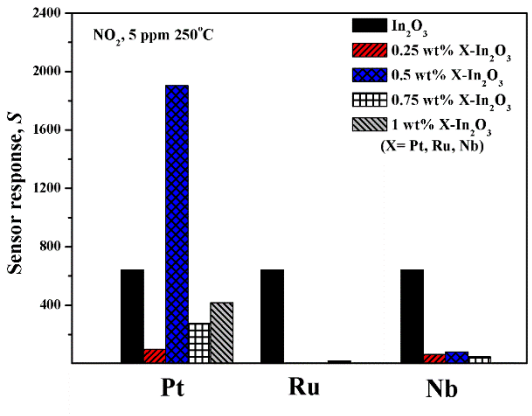

Fig.6 Effect of M-loading (M = Pt, Ru, Nb) on In_2O_3 sensors towards 5 ppm NO_2 gas at 250ºC.

CONCLUSION

In summary, we have shown that FSP is a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step of the unloaded In_2O_3 and 0.25–1.00 wt% M(M=Pt, Nb and Ru)-loaded In_2O_3 nanoparticles under 5/5 (precursor/oxygen) flame conditions. Gas sensing studies showed that Pt-loaded In_2O_3 gave an enhancement in NO_2 sensing in term of response and selectivity. When compared to other metal loading such as Nb and Ru, Pt-loaded In_2O_3 exhibited much better gas sensing against NO_2, H_2S and NO gases.

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