Investigation of NO_2 adsorption on WO_3 nanoparticles by DRIFT Spectroscopy

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(1) Introduction

Nitrogen dioxide (NO_2) released from combustion facilities and automobiles is toxic and deteriorates the environment through acid rain and photochemical smog. Therefore, the development of a sensor with high sensor response to low concentrations of NO_2 is necessary. Various metal oxide semiconductors, such as tin oxide, titanium oxide, and tungsten oxide, have been studied as materials for NO_2 sensors and shown good sensing properties. However, details of the interactions of semiconductors with NO_2 have not been fully understood. One method to gain valuable information in this respect is the Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). Thus, the aim of the present work is to investigate the adsorption of NO_2 on WO_3 nanoparticless with different diameters by DRIFTS.

(2) Experimental Methodology

WO_3 nanoparticles were prepared by resistive heating of a tungsten filament under an oxygen atmosphere at a low pressure. The diameter of nanoparticles was controlled by changing oxygen pressure and annealing temperature. In this study, the small nanoparticles with diameter of 36 nm was deposited at 1 kPa and annealed at 400°C; the large nanoparticles with diameter of 250 nm was prepared at 10 kPa and annealed at 600°C. FTIR spectroscopy was carried out with a IRPrestige-21 Spectrometer at a resolution of 8 cm^{-1} accumulation 150 scans. The sample was introduced into a cell allowing heat-treatments in flowing gas. Prior to all experiments, the sample was treated in situ at 400°C for 30 min in a flow of dry air (200 ml/min) and then cooled down to the reaction temperature. Keeping at 30 min, dry air was switched to reaction gas, with which 1000 ppm NO_2 was introduced into the reaction cell. FTIR-spectra were recorded after 10 min. The adsorption experiment was carried out in the temperature range between 25 and 300°C.

(3) Brief Summary of the obtained results

Figures 1(a) and (b) show the FTIR spectra of WO_3 nanoparticles with diameter of 36 and 250 nm at different temperatures in 1000 ppm NO_2 / dry air atmosphere. Various IR-bands appear and intensity depends on temperature and diameter of nanoparticles. Bands at 1631 and 1597 cm^{-1} in Fig. 1(a) and bands at 1630 and 1597 cm^{-1} in Fig. 1(b) can be attributed to bridging nitrate NO_3^- species and shows a maximum intensity at 150°C. Band at 1290 cm^{-1} in Fig. 1(a) and at 1293 cm^{-1} in Fig. 1(b) can be attributed to bidentate nitrite NO_2^- specie. A maximum intensity is observed at 50°C for small particles (see Fig. 1(a)), while it is observed at 150°C for large particles (see Fig. 1(b)).

A comparison between the electrical response of the sensor made with nanoparticles with diameter of 36 and 250 nm and the evolutions of the intensity of the various adsorbate bands strongly suggests that nitrites are responsible for the sensor response. Figures 2(a) and (b) show the response of nanoparticles versus operating temperature in a flux of 1 ppm NO_2 containing dry air, together with the intensity of the bands at 1290 and 1293 cm^{-1}. This band is indeed the only one having this behavior.

Therefore, we propose that the bidentate nitrite species are responsible for the electrical response of WO_3 nanoparticles.

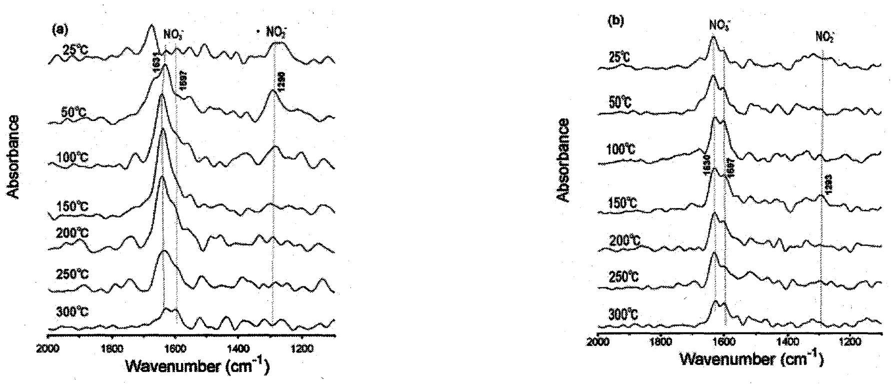

Fig. 1 FTIR spectra of WO_3 nanoparticles with diameter of 36 and 250 nm at different temperatures in 1000 ppm NO_2 / dry air atmosphere. (a) Small particles with diameter of 36nm and (b) large particles with diameter of 250 nm.

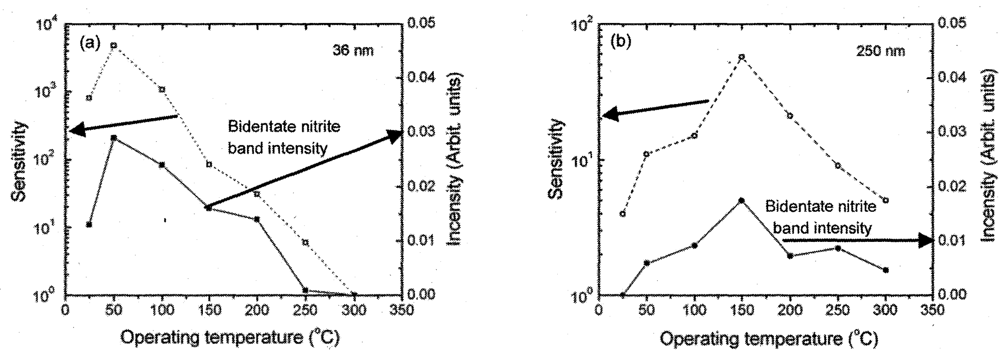

Fig. 2 Sensitivity of WO_3 nanoparticles to 1 ppm NO_2 and intensity of the bidentate nitrite band intensity as a function of the operating temperature. (a) Small particles with diameter of 36nm and (b) large particles with diameter of 250 nm.

(4) Conclusion

The adsorption of NO_2 on WO_3 nanoparticles has been observed in situ by DRIFTS. Various adsorbed species have been identified. The change in the intensity of adsorbed species has been followed as a function of temperature. By comparing electrical measurements to our spectral characterizations, we propose that bidentate nitrites are responsible for the WO_3 response to NO_2.