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Preparation and Sensitivity of SnO_2 Grafted MCM-41 Sensor

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Abstract: SnO_2 grafted MCM-41 sensor was prepared by MOCVD in the pore of MCM-41. The sensor has high sensitivity for carbon monoxide at low temperature compared with commercially available low-surface-area tin dioxide.

Keyword: Sensor, mesoporous, SnO_2, CO, sensitivity.

Tin dioxide is one of the most widely used semiconductor gas sensor to detect reducing gases[1-3]. The sensing mechanism of SnO_2 is usually based on the change of the resistance of the sensor in different gas environment. In air, the surface-adsorbed oxygen species on the surface of SnO_2 act as surface acceptors of electrons, hence diminishing the conductivity of SnO_2. However, when reducing gases such as H_2, CO, or CH_4 are introduced in the air stream, the resistance of the SnO_2 sensor is decreased by the removal of adsorbed oxygen species from the lattice sites[4,5].

Due to this surface phenomena in controlling the sensitivity of a sensor, it has been reported that there is a linear relationship between the sensitivities to H_2 the surface area of tin dioxide sensors, which were prepared using surfactant hydrothermal treatment [6,7]. It has also been found that a mechanical mixture of the commercially available low surface area tin dioxide (about 3 m^2/g) and the recently discovered high surface area MCM-41 material (about 1,200 m^2/g) showed very high sensitivities to hydrogen and carbon monoxide[8]. The reason of substantial improvement of the gas sensing properties suggested that the partial coating of tin dioxide in the mesopores of MCM-41 probably forms the thin film of high surface area SnO_2. The results indicated that the property of the thin film on the high surface area SnO_2 was different from the bulk property of low surface area SnO_2. Here we report the use of metallorganic chemical vapor deposition (MOCVD) method to synthesize a uniform layer of SnO_2 grafted on the surface of the inner walls of MCM-41; the material is designated as SnO_2/MCM-41. The sensing properties of the SnO_2/MCM-41 sensor was tested for the detection of carbon monoxide.

MCM-41 was prepared by hydrothermal synthesis. $NaAlO_2$ (0.49 g) and H_2O (4.01 g) were added to 20% TEAOH solution (9.4 g) and stirred to dissolve. Colloidal silica

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(Ludox, 9.6 g) was added to the above solution and stirred for another 30 min. 20.2% CTMAOH solution (21 g) was added dropwise to the above mixture, the mixture was stirred for another 30 min. The resultant mixture was loaded in a teflon-lined autoclave and heated without stirring at 96^{o}C for 72 h. After cooling to room temperature, the solid product was recovered by filtration, washed with pure water for 3 times and dried at 40^{o}C overnight. The resulting powder was calcined in air at 600^{o}C for 15 h.

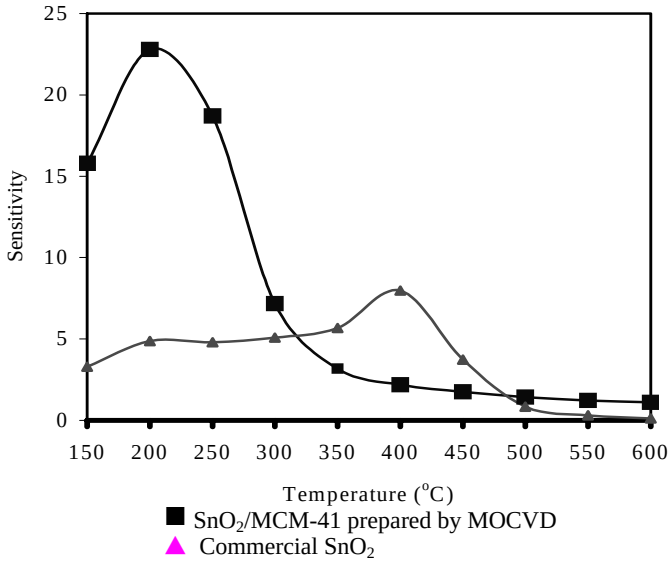
The grafting the thin film of SnO_2 on the surface of MCM-41 material was carried out *via* chemical vapor deposition. The metal organic precursor of tetramethyl tin was maintained at 0^{o}C and its vapor was transported by a helium-stream into a CVD reactor containing MCM-41, which had been previously degassed by purified helium flow at 500^{o}C for 2 h. Inert helium gas was used as a degassing gas in order to prevent the decomposition of tetramethyl tin by air oxidation or hydrolysis *via* surface adsorbed water. For uniform grafting of SnO_2 in the mesopores of MCM-41, the surface of MCM-41 should be kept water-free by degassing at high temperature so that only surface bound oxo and hydroxo groups were available to react with tetramethyl tin. The deposition of tetramethyl tin was carried out at 500^{o}C for 1 h. After the deposition was finished, a helium stream containing 10 % of oxygen was used to oxidize the surface attached organic tin at 500^{o}C (in order to oxidize organic tin to SnO_2).

The gas sensing properties of the synthesized SnO_2/MCM-41 sensor were measured by observing the change of the sensor's resistance in air and in reducing gases, recorded on a Keithley 6517 electrometer. The sensitivity (S) of a sensor is expressed as the ratio of the difference of the sensor's resistance in air (Rair) and in reducing gas (R_{gas}), *i.e.* $S = (R_{air} - R_{gas})/R_{gas}$. The SnO_2/MCM41 sensor for detecting CO contains 28.6 wt% tin.

The sensitivity of the SnO_2/MCM41 sensor prepared by MOCVD to carbon monoxide (3000ppm) is a function of temperature **Figure 1**. It showed that this SnO_2/MCM41 sensor has high sensitivity for carbon monoxide in the temperature range of 150 - 400^{o}C. As temperature increased, the sensitivity of the SnO_2/MCM-41 sensor for CO increased and then decreased. The highest sensitivity for CO is at 200^{o}C. Compared with the sensing performance of commercial available SnO_2 sensor, the newly prepared SnO_2/MCM-41 sensor has much higher sensitivity for carbon monoxide. With this system, the highest sensitivity of detecting CO is at much lower temperature (about 200^{o}C) than commercial SnO_2 sensor (about 400^{o}C). The high sensitivity at low temperature of the newly prepared sensor makes it possible for practical use. Further studies showed that the SnO_2 grafted MCM-41 sensor has sensitivity even in 100 ppm carbon monoxide. There is linear relation between the sensitivity and carbon monoxide concentration in the range of 100-3000 ppm.

In conclusion, a new semiconductor oxide sensor, SnO_2/MCM-41, has been successfully prepared by metallorganic chemical vapor deposition of tetramethyl tin in the mesopores of MCM-41 followed by high temperature oxidation in oxygen. The sensor was found to have a high sensitivity for carbon monoxide. The highest sensitivity for CO was at 200^{o}C. The sensor behaviors are different from the commercial SnO_2 sensor's.

Figure 1 Sensitivity for CO of SnO_2 grafted MCM-41 sensor



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