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Synthesis, characterization and gas sensitivity of MoO_3 nanoparticles

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Abstract. **Nanoparticles of molybdenum oxide were synthesized using the citrate sol–gel method and characterized using scanning electron microscopy and X-ray diffraction techniques. The sensitivity of the material to the presence of various gases was analysed and the particles showed higher sensitivity towards NO_2 gas.**

Keywords. **Sol–gel citrate; metal oxide; gas sensing; nanoparticles; SEM.**

1. Introduction

High sensitivity gas sensing assumes great importance in view of the plethora of health hazards related to poisonous gases that are associated with industrial and automobile exhausts. Thus, the requirement of gas sensors to sense such harmful gases is indubitable and with this requirement comes the demand for highly sensitive detection systems that detect trace levels of highly harmful gases.

One approach is the use of advanced materials technologies. The sensitivity of the sensing device is directly proportional to the surface area to the volume ratio of the exposed sensing surface. Hence, nano sized particles used as sensors would have the maximum ratio and provide the best possible response. For example, Rella *et al* (1999) demonstrated that by maintaining the grain size of SnO_2 particles in the 10–100 nm range increased their sensitivity towards CO. Ferroni *et al* (1999) demonstrated good response in the use of solid solutions of TiO_2 and WO_3 when the grain size was maintained at 60 nm. Chung *et al* (1999) showed that by increasing the firing temperature the response of WO_3 sensors to NO_x reduced. Rossinyol *et al* (2005) demonstrated the advantageous use of nanostructured cerium oxide and tungsten oxide in gas sensing. A number of nano structured materials are known to have been used as metal oxide gas sensors amongst which the following are a few: ZnO, Fe_2O_3, WO_3, SnO_2, ZrO_2, $SrTiO_3$ and the like (Hoffheins *et al* 1996). The sensing properties of resistive type of sensors were found to increase by reducing the size of the oxide particles (Gouma 2003). Nanocrystalline oxide-based sensors were found to be highly sensitive towards gaseous species that may have evolved from various chemical processes. It was thus thought pertinent to study the system of nanostructured molybdenum oxide in a continuous effort of improving gas sensitivity to NO_2.

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This paper involves the synthesis of nano structured molybdenum oxide particles using the citrate sol–gel method. The characterization of the samples prepared has been done with the help of an SEM micrograph and X-ray diffraction techniques. The relative sensitivity of the system obtained has been tested for the passage of different gases.

2. Experimental

Molybdenum oxide nanoparticles were synthesized using the citrate sol–gel method. Ammonium molybdate powder (1·16 g) was dissolved in de-ionized water to which was added citric acid crystals (0·38 g). The mixture was then stirred carefully using a magnetic stirrer while ammonium hydroxide was added to obtain a pH of 7. The mixture was then heated in a furnace to a temperature of 250°C for 1 h. Initially a zero gel and finally a powder was obtained. The powder was then heated to a temperature of 500°C for 90 min to obtain a pale yellow powder.

To carry out the characterization, the prepared sample was sonicated and then gold coated. MoO_3 synthesized by the sol–gel citration method was characterized using an SEM (JEOL JSM 5600LV instrument) and X-ray analysis done on a Philips X-ray diffractometer.

For carrying out the gas sensitivity studies, synthesized MoO_3 powder was converted to a paste using ethanol and mixed thoroughly. The prepared paste was then applied onto the micro-fabricated alumina substrate. The paste on the substrate was then allowed to dry. The gas sensitivity test was conducted by passing gas through a multi gas channel controller MKS 1251C with appropriate electrical circuitry to support it.

The 1251C multi gas controller from MKS system was used for the sensitivity/cross sensitivity tests for the sensor material. The sensor was exposed to $N_2 + O_2$ (80% + 20%) for 6 h at 300°C for curing. Different gases of desired concentrations were opened at different times to check the sensor material's sensitivity towards each of them.

The base gas was 99·999% ultra pure N_2 and the test temperature was 400°C. Before gas testing, the settings in the gas controller were programmed for all the gases for desired time period so that there is no human error during the test. The sequence of gas flow was N_2, NO, N_2, CO, N_2, O_2 (each gas for 5 min). The electronics to amplify and signal processing was a simple impedance match circuit and was set for gain '4' for all the gas adsorption signal outputs.

The impedance (resistance) of the sensor changed drastically as the NO and NO_2 gases were 'ON', whereas the change was minimal for CO and O_2 gases.

3. Results and discussion

3.1a *Scanning electron microscopy*: The SEM characterization was conducted using a JEOL JSM 5600 LV instrument. The type of electrons used was of the secondary type. Fairly spherical nano-crystallites were observed in the micrographs. It was also observed that the synthesis carried out at temperatures above 750°C led to agglomerated particles being formed while the synthesis carried out at lower temperatures (till 500°C) but for a longer duration yielded better results. The samples prepared have been found to be in the 10–100 nanometer range. The particle size and shape analysis were carried out by Quantimet software from Leica, UK (Cambridge instruments).

Figure 1 shows SEM micrograph of the oxide sample prepared using the above illustrated process.

3.1b *X-ray diffraction*: X-ray analysis of the oxide particles were performed using a Philips X-ray diffractometer.

Figure 2 represents the XRD patterns for MoO_3 powders. The wavelength used for the XRD analysis was CuK_α, –1·50546 Å. After the synthesis, it was found that the peaks corresponding to (0 2 0), (1 1 0), (0 4 0), (0 2 1) are of orthorhombic crystal structure of MoO_3. It is noted that all the XRD peaks are identified as MoO_3 peaks from the JCPDS card 35-0609.

Figure 2 shows the XRD pattern for the sample prepared. The peaks correspond to the orthorhombic crystal structure of MoO_3.

3.1c *Gas sensitivity*: Micro-fabricated sensor substrates consisting of 1 × 1 cm alumina with inter-digitized electrodes deposited on one side of them were used for gas detection and the set up consists of 2 electrodes and 2 heaters connected across the substrate-coating. The passage of gases was opened so that it passed through the sample. The time vs voltage plot shown in figure 3 is used in determining the gas sensitivity.

A characteristic graph of sensitivity would consist of a build up and a recovery phase as the channel is shut off. The heater voltage is set at 7·5 V and the input voltage at 5 V. Gas sensing studies were conducted by passing the gases in the following order: N_2, NO_2, N_2, NO, N_2, CO, N_2, O_2, N_2. The plot clearly indicates that the sample is not sensitive to N_2 gas (region 1 in figure 3), but as soon as NO_2 gas is passed, there is a deflection (region 2) in the voltage–time plot till the saturation is reached (point 3). This indicates that the sample is sensitive to the presence of NO_2 gas. Following this, the gas supply is shut off and the recovery phase is initiated (region 4). The recovery phase is followed by the sensing of NO gas (region 5). However, the sensitivity to NO is much lesser, as indicated by a smaller drop in the plot till the saturation is reached (point 6). Similarly the next recovery phase is followed by the sensing of CO gas till the saturation point (point 7). Thus the sensitivity is again much lower, when compared to the sensitivity to NO_2 gas (point 3). It is, therefore, evident that the sensitivity of the sample is more towards NO_2 than towards CO or N_2 gases. It is very important to observe the cross-sensitivity of the sensor to other gases like CO, CO_2, O_2. There was a flow of these cross sensitive gases for 5 min with 500 ppm concentration and the graph clearly indicates that the response was flat. Though the recovery of the sensor for the gases was relatively

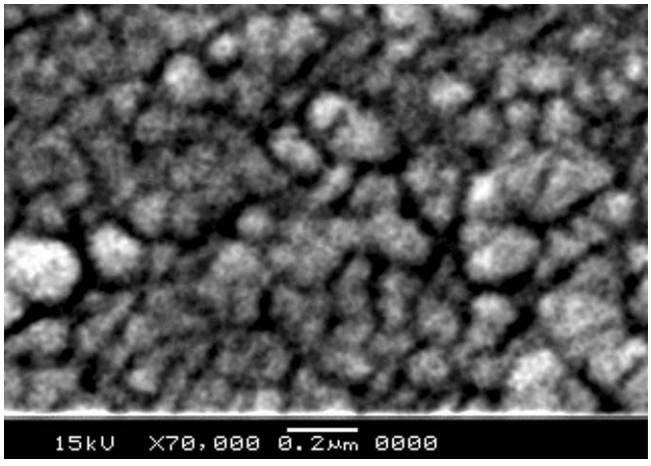

Figure 1. SEM micrograph of the oxide sample prepared.

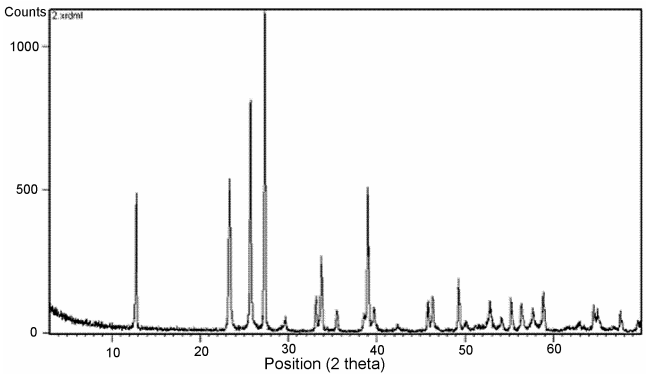

Figure 2. XRD pattern for the sample prepared.

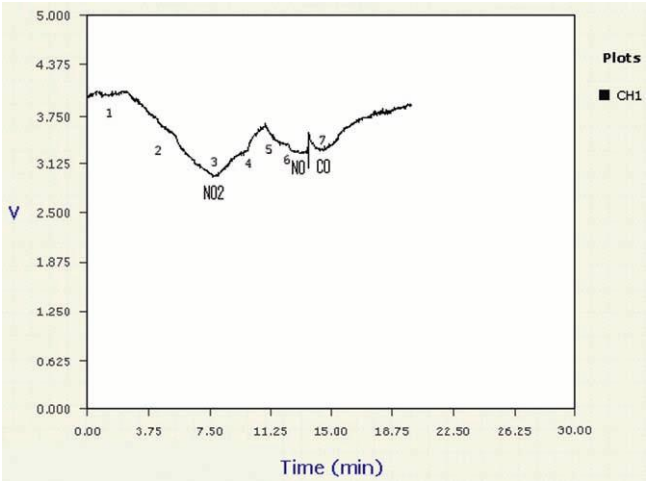

Figure 3. Sensitivity plot for various gases.

slow, the problem was overcome by using heater control techniques which switches the sensor temperatures to higher values for 15 s. It may also be noted that the sensitivity of gases is in the order of the thermal and electrical conductivity of the gases: $NO_2 > NO > CO > N_2$.

The underlying principle behind this behaviour is primarily the surface reaction that takes place between the gas molecules and the material sensing it. As the size of the material particles used for sensing tends towards nanometer scale, the particles can be considered to be as a continuous surface in three dimensions (Somarjai 1998) and this in turn increases the surface reactivity due to the higher surface area. The increase in reactivity can also be attributed to the fact that there is an increase in the number of defect sites which are responsible for the reactions taking place on the surface. Oxygen ions are adsorbed onto the surface, removing electrons from the bulk and creating a potential barrier, this process is responsible for the varied conductivity in the initial stages. When the gases to be sensed are passed over the surface, they combine with this oxygen, thus reducing the potential barrier created and hence change the conductivity. This change in the conductivity is a function of the characteristic properties of the gases and is indicative of the presence of gas being sensed.

The gas detection by chemical sensors based on semiconducting materials is due to the variation in conductivity. This is induced by the adsorption of gases on the semiconductor surface as mentioned earlier. When oxygen is adsorbed on the semiconductor surface, negatively charged oxygen ions are formed (Morrison 1994; Henrich and Cox 1993). This can be represented as

$$O_2 + 2e^- \rightarrow 2O^-.$$

The oxygen ionosorption causes electron transfer from the surface of the grain towards the adsorbed species thus leading to the formation of an electron depleted surface. This varies the electrical conductivity of the semiconductor.

When a gas such as CO is adsorbed in the presence of ionosorbed oxygen, a similar variation in conductivity is seen and the reaction can be represented by

$$2CO + O_2^- \rightarrow 2CO_2 + e^-,$$

$$CO + O_2^- \rightarrow CO_2 + e^-.$$

Figure 3 shows sensitivity data for the sol–gel based MoO_3 powder for different gases. The plot indicates that the sample has higher sensitivity towards NO_2 when compared to CO or other gases.

4. Conclusions

The present work provides a method for processing nanostructured MoO_3 with enhanced gas sensing capabilities. Nano-sized MoO_3 was synthesized using the citrate sol–gel method and the same was characterized using electron microscopy and X-ray diffraction techniques. The sample was then subjected to gas sensitivity tests using a multi gas channel controller. The sample showed exemplary sensitivity towards NO_2 gas while exhibiting lower sensitivity towards gases like NO, CO etc.

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