

Review

Enhanced CO sensitivity and selectivity of gold nanoparticles-doped SnO₂ sensor in presence of propane and methaneB. Bahrami^{a,b}, A. Khodadadi^b, M. Kazemeini^a, Y. Mortazavi^{c,*}^a Department of Chemical and Petrochemical Engineering, Sharif University of Technology, Tehran, Iran^b Catalysis and Nanostructured Materials Research Laboratory, School of Chemical Engineering, University of Tehran, Tehran, Iran^c Nanoelectronics Center of Excellence, P.O. Box 11365/4563, University of Tehran, Tehran, Iran

ARTICLE INFO

Article history:

Received 11 November 2007

Received in revised form 23 February 2008

Accepted 25 February 2008

Available online 29 February 2008

Keywords:

Selective CO gas sensor

Au/SnO₂

Gold nanoparticles

Methane

Propane

ABSTRACT

We report the effect of gold nanoparticles on the sensitivity and selectivity of SnO₂-based sensors for detection of CO in the presence of methane and C₃H₈, a model compound representing liquid petroleum gas (LPG). 1.0 wt% Au/SnO₂ powder was prepared by a co-precipitation method. The powder formed was washed, dried at 150 °C, and calcined at 300 °C for 3 h. The BET surface area of SnO₂ and Au/SnO₂ was measured to be 210 and 110 m²/g, corresponding to 4 and 7.5 nm loose spherical particles, respectively. Responses of the Au/SnO₂ and SnO₂ sensors to 40–1000 ppm CO, 0.2–1.0% C₃H₈ and 1.0–3.0% CH₄ were studied at 170–300 °C in an automated gas sensing system. In this temperature range, the Au/SnO₂ sensor is about 4–17 and 7–20 times more selective to 0.1% CO in the presence of 1.0% propane and 3.0% methane, respectively. Highly dispersed gold nanoparticles may be responsible for the enhanced sensitivity and selectivity of the Au/SnO₂ sensor to CO.

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Contents

1. Introduction	352
2. Experimental	353
3. Results and discussion	353
4. Conclusions	356
References	356

1. Introduction

Tin oxide semiconductor sensors are widely used for detection of various pollutants and combustible gases. The advantages of these sensors are high sensitivity, simple design, and low weight and cost. However, the major problems associated with SnO₂ are its low selectivity. The sensitivity and selectivity of these sensors may be improved by using suitable additives such as noble metals (Pd, Pt) [1] and transition metal oxides (La₂O₃, Nd₂O₃ and SrO) [2–6]. For instance ceria has been used to increase the sensitivity to H₂S [7] and improve the CO selectivity [8]. Using noble metals and other types of dopants is a typical approach to improve the selectivity of chemical gas sensors [1].

Carbon monoxide is one of the most common and dangerous pollutants present in the environment due to emissions from

automated vehicles, incomplete oxidation of fossil fuels, industrial wastes, etc. Its poisonous effects on human life are well known. Thus, a selective CO gas sensor is required to prevent CO poisoning in residential and work areas. Fortunately the subject has attracted a great deal of attention.

Catalytic properties of Au nanoparticles have gained a lot of attention since Haruta et al. [9] reported that gold becomes active once its particle size is reduced to a few nanometers. Many investigations indicate that Au nanoparticles are active for several chemical reactions, such as CO oxidation, propylene oxidation, NO reduction by CO, water–gas shift reaction, and selective purification of CO from H₂-containing gases [10]. In most cases, to improve catalytic activities, Au nanoparticles are usually dispersed onto some metal oxides, including reducible (NiO or Fe₂O₃) [9] and irreducible (Al₂O₃) oxides [11]. Thus, the interaction between Au and the support plays an important role in improvement of the catalytic reaction. In this regard the proposed mechanisms can be classified in terms of support dependence. The first mechanism is based on the variable electronic structure induced by strain and

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charge transfer between support materials and Au nanoparticles [12]. The enhanced catalytic activities include the activations of both Au nanoparticles and support materials. The second mechanism considers that the support can provide active oxygen [13], or stabilize reactants and intermediates [12]. The main factors affecting reaction kinetics include the size of Au nanoparticles and the type of support. The Au nanoparticles in the range of 2–4 nm in size are found to be the most active for many catalytic applications [14]. There are several parameters affecting the size of Au nanoparticles: for instance, exposure of the Au nanoparticles to high temperatures leads to sintering, also high loading of gold on the support resulting in more severe sintering.

Preparation conditions have important effect on the activity of gold nanoparticles. For instance washing process and the poisoning effect of chloride have been investigated in detailed by Oh et al. [15]. The residual chloride has been reported to affect the activity of the compound in two different ways. It facilitates the agglomeration of Au particles during the heat treatment (calcination step) by formation of Au–Cl–Au bridges [16], and it inhibits the catalytic activity by poisoning the active sites. According to the reported results, the average gold particle size is larger for the catalysts with higher residual Cl⁻ content [15].

In this investigation we report the effects of gold nanoparticles on the sensitivity and selectivity of SnO₂-based sensors for detection of CO in the presence of C₃H₈ as a model compound for liquid petroleum gas (LPG) and methane, the main constituent of natural gas.

2. Experimental

Au/SnO₂ powder was prepared by a co-precipitation method using an aqueous solution of HAuCl₄ and SnCl₄. A 32% ammonia solution was added to the above solution while stirring (500 rpm) at 50 °C. The final pH value of the solution was controlled to be in the range of 9–10. After ageing for 1 h, the precipitate was washed several times with deionized water to remove chloride ions, then dried at 150 °C and calcined at 300 °C for 3 h. SnO₂ powder was prepared with the same recipe except that there was no solution containing the gold precursor.

The samples prepared as such were applied onto alumina ceramic tubes with previously deposited gold contacts with a 1.5-mm spacing. After calcination at 300 °C for 2 h, the samples were ready for the tests.

To study the responses of the sensors to different concentrations of CO, propane and methane, concentrated mixtures of the gases were prepared by mixing ultra-high-purity gases with zero dry air to make different concentrations in the range of 40–1000 ppm CO, 0.2–1.0% propane and 1.0–3.0% methane.

To study the performance of the sensors in the presence of different gases of various compositions at different temperatures, a testing setup was used. The experimental set up consisted of a gas manifold, a glass U-tube reactor (holding the sensors) immersed in a molten salt bath for a uniform temperature, and a data acquisition system for continuous monitoring of sensor responses. CO, propane and methane in air were mixed with different flow rates of air to adjust the concentration of the gases passing over the sensors. The temperature of the sensors was varied from 170 to 300 °C. Depending upon the operating temperature and the additive used, sensor resistance may vary from a few tens of ohms to a few mega ohms. The response of a sensor is defined as its resistance in air divided by that in the gas, i.e., $R_{\text{air}}/R_{\text{gas}}$.

The BET surface area measurement carried out by nitrogen adsorption after degassing of the samples at 300 °C for 1 h, using a CHEMBET 3000 apparatus. XRD analyses were done on a Philips-X'pert. XRD patterns were recorded using Cu K α radiation,

mounting powder samples on a Plexiglas sample holder. Transmission electron microscopy (TEM) image of Au/SnO₂ powder was taken using a CM 200 FEG TEM Philips-M.E.R.C. TEM images of Au/SnO₂ sample were obtained using finely ground powder dispersed on a copper mesh with a carbon micro-grid.

3. Results and discussion

The BET surface area of SnO₂ and Au/SnO₂ was measured to be 210 and 110 m²/g, corresponding to 4.0 and 7.5 nm loose spherical particles, respectively. It seems that Au incorporation increases the grain size of SnO₂ which in turn lowers the specific surface area. It has been reported that increasing the concentration of Au in SnO₂ samples increases the grain size of SnO₂ [14].

Fig. 1 presents the XRD patterns of SnO₂ and Au/SnO₂ calcined at 300 °C. Compared to the JCPDS (File No. 41-1445) standard pattern, the peaks well agreed with the tetragonal rutile structure of SnO₂ crystal, with no additional lines belonging to other phases such as SnO.

In the XRD pattern of Au/SnO₂ no diffraction peak of gold is observed. This is probably due to the low amount and small particle size of the gold, and therefore its diffraction peaks do not allow being distinguished from the background. At the same calcination temperature, diffraction peaks of SnO₂ in the Au/SnO₂ sample become sharper, indicating the size of SnO₂ particles has increased. The average diameters of SnO₂ and Au/SnO₂ particles, calculated by using Scherrer's equation based on the peak broadening analysis at the (1 1 0) peak, were found to be 4.0 and 7.5 nm, respectively. Fig. 2 presents the TEM micrograph of the Au/SnO₂ sample. The TEM analyses well agree well with the BET results. Fig. 2a and b presents the bright-field images of the Au/SnO₂ catalyst. It is observed that the gold nanoparticles have been dispersed effectively on the surface of SnO₂ without being agglomerated. The gold nanoparticles have crystallite sizes between 2 and 4 nm. Energy dispersive spectrum in Fig. 2c confirms the presence of Au element. It is also confirmed that there is no detectable chloride ions, indicating they were completely removed by washing during the catalyst synthesis. The selected area electron diffraction (SAED) pattern of the Au/SnO₂ (Fig. 2d) distinctly exhibits four diffraction rings, which correspond to the (1 1 0), (1 0 1), (2 1 1) and (1 1 2) planes of the tetragonal-phase of SnO₂ with rutile structure, respectively. This is in agreement with the XRD results, and indicates that the SnO₂ nanoparticles are well crystallized. The response of SnO₂ and Au/SnO₂ sensors to various concentrations of CO, propane and methane, measured at different temperatures, are presented in Fig. 3. The figure shows that the sensitivity of the sensor increases in the order of CH₄ < C₃H₈ < CO.

Fig. 3 also reveals that at the same concentration of various gases, the response magnitude of the Au/SnO₂ sensor is about 2–15

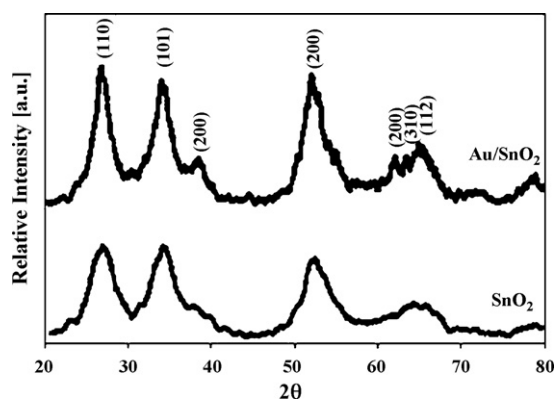


Fig. 1. XRD patterns of 1 wt% Au/SnO₂ and SnO₂ catalyst calcined at 300 °C.

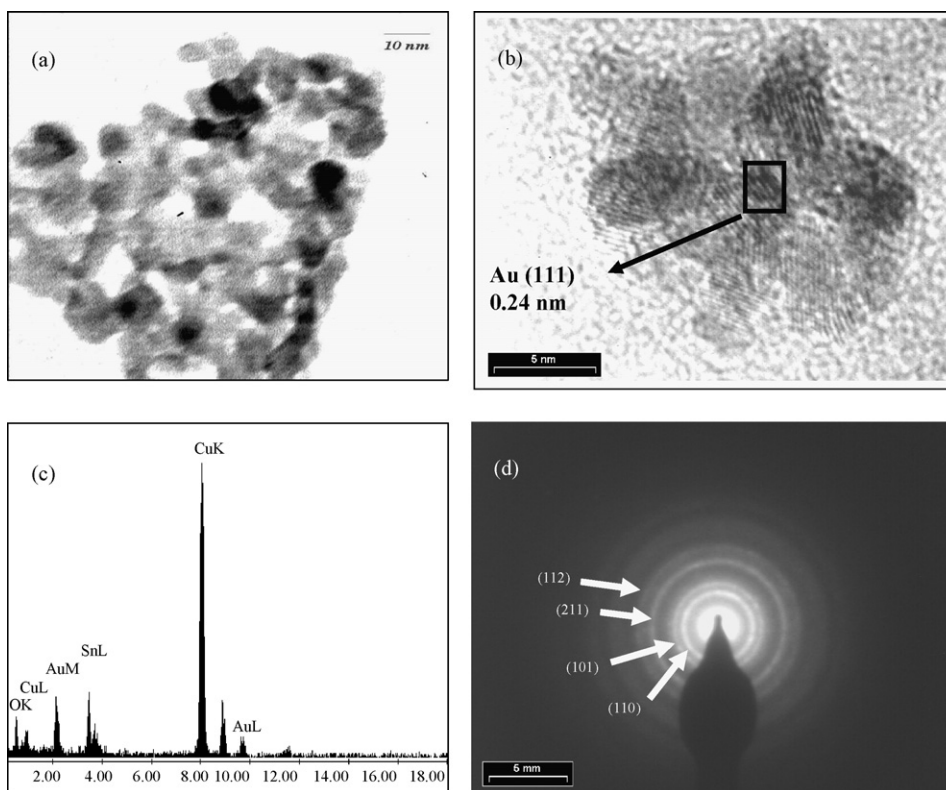


Fig. 2. (a and b) TEM micrographs, (c) EDS spectra and (d) an electron diffraction pattern of 1.0 wt% Au/SnO₂.

times higher than that of the SnO₂ sensor. Both sensors show the lowest response to methane. Furthermore, responses of both sensors increase with concentration. The extent of improvement of Au/SnO₂ to methane is much lower compared to those of CO and C₃H₈. It seems that methane as the most stable hydrocarbon has the least interaction with SnO₂ and Au/SnO₂ at the temperature range used in this study.

Fig. 4 presents the response of Au/SnO₂ and SnO₂ to different concentrations of CO in air at different temperatures. From Fig. 4, it can be observed that the response of Au/SnO₂ to CO is about one order of magnitude larger than that of SnO₂. At higher concentrations, the difference in response between Au/SnO₂ and SnO₂ becomes even larger.

For both sensors the response changes with temperature. Maximum sensitivity on Au/SnO₂ is obtained at 250 °C after which the response decreases with an increase in temperature. However, for the SnO₂ sample the maximum response occurs at 275 °C.

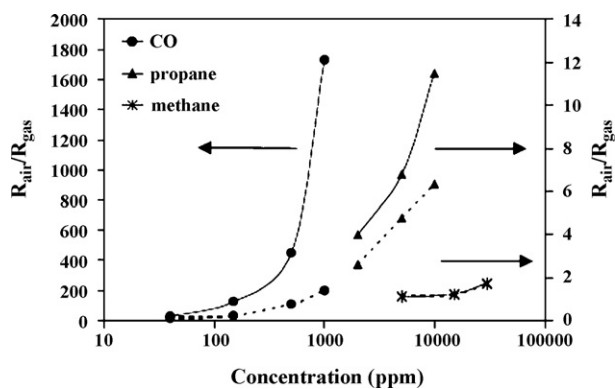


Fig. 3. Response of Au/SnO₂ (solid line) and SnO₂ (dashed line) to various gases at 250 °C.

The surface oxygen species have been evidenced with spectroscopic techniques on the surface of SnO₂. At low temperatures (<200 °C) oxygen adsorbs associatively on SnO₂ either in a neutral form, i.e. O_{2(ads)} or a charged form, i.e. O_{2(ads)}⁻. At higher temperatures, however, oxygen adsorbed dissociatively either in a neutral form, i.e. O_(ads) or a charged form, O_(ads)⁻ [16].

The following mechanism for the reaction of oxygen species on the surface with a target gas such as CO has been proposed [17].

At lower temperatures:



At higher temperatures:

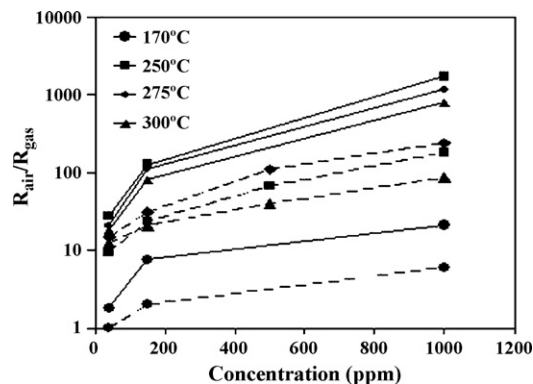


Fig. 4. Response of Au/SnO₂ (solid line) and SnO₂ (dashed line) to various concentrations of CO at different temperatures.

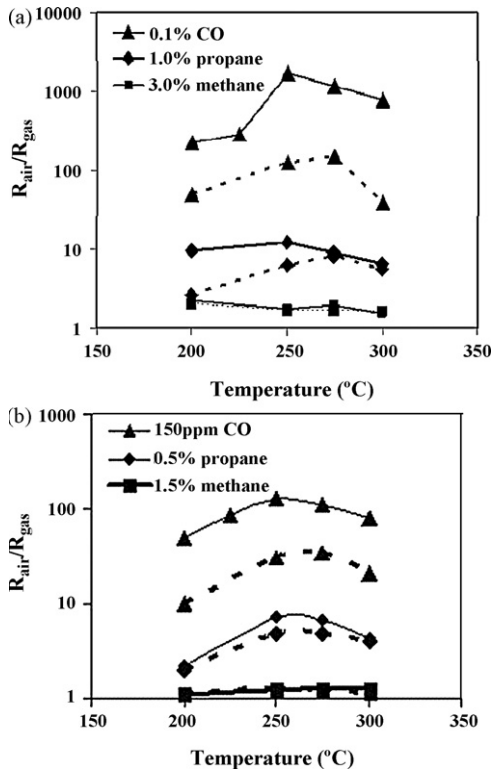


Fig. 5. Response of Au/SnO₂ (solid line) and SnO₂ (dashed line) to (a) 0.1% CO, 1.0% propane and 3.0% methane and (b) 150 ppm CO, 0.5% propane and 1.5% methane at various temperatures.

This mechanism predicts that at low temperatures for two CO molecules one electron is released (Eqs. (1a) and (2a)), whereas at higher temperatures for each CO molecule one electron is released (Eqs. (1b) and (2b)). Thus the sensor response is enhanced at higher temperatures.

In Au/SnO₂ sample the maximum response occurs at low temperature compared to SnO₂ sample, i.e. 250 °C compared to 275 °C. This difference is due to the promotion effect of Au nanoparticles.

The response decline at higher temperatures is likely due to the extent of adsorption of both the target gas and oxygen on the samples. Adsorption is an exothermic phenomenon, and thus at higher temperatures the extent of adsorption decreases which in turn leads to lower response of the sensors.

Fig. 5 shows the response of Au/SnO₂ to different concentrations of CO, propane and methane in the range of 200–300 °C. It can be observed that Au/SnO₂ is highly selective to CO in the presence of

propane and methane in both high- and low-concentration range. Figs. 3 and 4 also clearly demonstrate the selective performance of the Au/SnO₂ sensor.

Fig. 6 presents the selectivity of the sensors to 1000 ppm CO in the air in presence of 1.0% propane and 3.0% methane at different temperatures. Selectivity is defined as the ratio of the response of a sensor to different gases. As is observed at all temperatures, the selectivity of Au/SnO₂ sensor to the CO in presence of both propane and methane is significantly higher than that of SnO₂. Au/SnO₂ sensor shows the highest selectivity at 250 °C. It seems that the catalytic activity of Au/SnO₂ at this temperature for CO oxidation is the highest compared to C₃H₈ and CH₄. High activity of gold-containing catalysts involves catalysis on the boundary of small gold particles and the support [9]. The proposed mechanism involves reversible adsorption of CO on the surface and periphery of gold particles, irreversible adsorption of oxygen at the peripheral interface to produce oxygen species as a rate-determining step, and fast formation of a CO–Au–O intermediate to produce CO₂ on the peripheral interface [18]. The proposed mechanism has been further supported by FTIR studies performed by Bocuzzi et al. [19,20]. They reported that oxygen adsorption changes the CO-stretching frequencies, which may indicate the adsorption of CO and oxygen in the neighbourhood of each other on a gold particle.

The Au/SnO₂ sensor is about 4–17 and 7–20 times more selective to 0.1% CO in the presence of 1.0% propane and 3.0% methane, respectively.

In order to investigate the effects of Au on the response time and recovery time of the SnO₂-based sensors a transient experiment according to the following procedure was performed. Prior to the transient experiment air was passed over the sensors for a long period of time. At $t=0$, i.e. the onset of the transient experiment, the air was replaced by 1000 ppm CO in air and remained as such for several minutes. At $t=13$ min it was switched back to air again. Fig. 7 presents the sensors responses to 1000 ppm CO under transient conditions. Two important parameters affecting the response time are the operating temperature and preparation method. For instance Ahmad et al. [21] reported that according to these factors, the 90% response time of SnO₂ varied in the range of 10–75 s in a temperature range of 350–425 °C. Their results also revealed that with a 75 °C decrease in operating temperature, the response time increased between 30 and 50%. In our case the operating temperature is 250 °C and thus, it is acceptable to observe a longer response time. According to Fig. 7a the 90% response time of SnO₂ is about 120 s, which seems quite reasonable.

In Fig. 7, both sensors have almost similar response time. Both sensors take a longer time to return back to the initial response value when they are exposed to air after exposure to 1000 ppm CO in air. However, the Au/SnO₂ sensor has a longer recovery time than

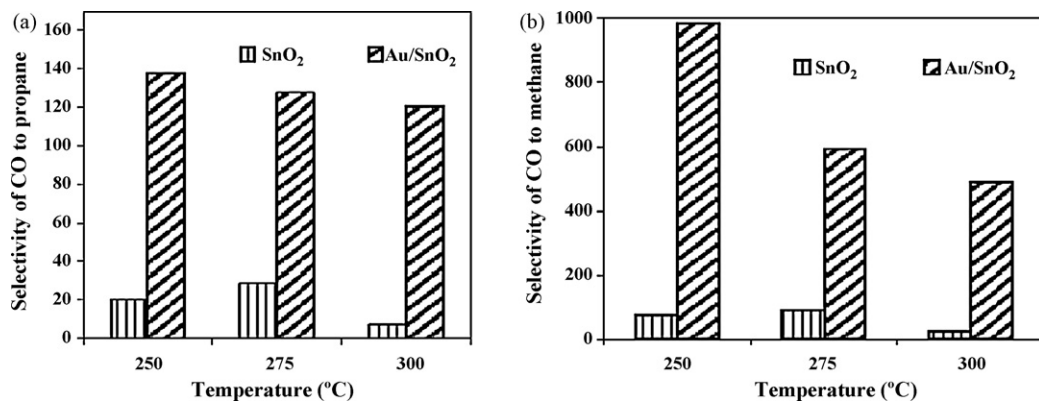


Fig. 6. Response of the sensors to 1000 ppm CO in the presence of (a) 1.0% propane and (b) 3.0% methane.

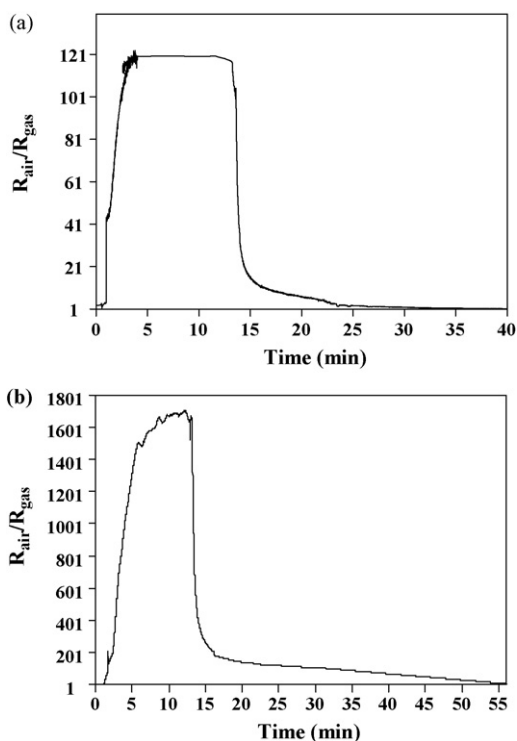


Fig. 7. Transient response and recovery time of (a) SnO_2 and (b) Au/SnO_2 sensors at 250°C . The air was replaced by 1000 ppm CO in air at $t=0$ and switched back to air again at $t=13$ min.

the SnO_2 sensor. Further investigation is underway to elaborate on the cause of long recovery and perhaps propose ways to shorten that.

4. Conclusions

The effects of gold nanoparticles as a dopant for SnO_2 -based sensors on the response and selectivity to CO in the presence of propane and methane were investigated. An Au/SnO_2 sample was prepared by a co-precipitation method and characterized by BET, XRD and TEM. It was demonstrated that the nanoparticles of gold were distributed on the SnO_2 surface with a size distribution mostly between 3 and 5 nm.

It was shown that in the temperature range of 170 – 300°C , the Au/SnO_2 sensor has much higher responses to CO and propane as compared to a SnO_2 sensor. Au/SnO_2 and SnO_2 show a maximum sensitivity at 250 and 275°C , respectively. For the Au/SnO_2 sensor, due to the promoting effect of Au, the maximum response to CO occurs at relatively lower temperature.

It was also shown that the selectivity of Au/SnO_2 sensor for CO in the presence of C_3H_8 and CH_4 was improved significantly. The Au/SnO_2 sensor is about 4–17 and 7–20 times more selective to 0.1% CO in the presence of 1.0% propane and 3.0% methane, respectively. Highly dispersed gold nanoparticles and small size of these particles are thought to be responsible for the enhancement of both sensitivity and selectivity.

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