Chapter 3
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Synthesis and Characterization of Low Temperature LPG Sensing Palladium Doped Tin Oxide Nanospheres.

In this chapter synthesis of Pd/SnO$_2$ nanospheres with modified Pechini citrate route has been reported. Their application as a low temperature LPG sensor material has also been studied.
3.1 Why hydrocarbon gas sensor?

Although different hydrocarbons are widely used for domestic and industrial applications to provide a clean source of energy for burning, these gases are potentially hazardous because they can cause explosion if they leak out accidentally. Liquefied petroleum gas (LPG), the chief component of which are butane (70-80%), propane (5-10%), propylene, butylenes, ethylene and methane (1-5%) is known to cause accidents. Besides this, there are many other hydrocarbons (methane, butane, benzene etc.) which are frequently used as fuel as well as starting product for organic synthesis. Hence there is a great deal of worldwide interest in developing reliable and efficient hydrocarbon sensors having good sensitivity and selectivity.

3.2 Results and Discussions.

Tin oxide doped with various catalytic additives has been used as a sensor material for various gases like LPG [315], CO, NO2, ethanol, H2 [316, 317], H2S [204], NH3 [318], volatile organic compounds in air [319] etc. Along with the surface modification with different catalytic additives the particle size and the surface adsorbed oxygen plays a significant role in the interaction of gas with metal oxide surface.

Tin dioxide is an n-type wide band gap semiconductor. The conductivity of SnO2 is very sensitive to the surface state just in the 300 – 800 K temperature range [126]. The surface of SnO2 exhibits good absorption properties and reactivity due to the presence of free electrons in the conduction band, the presence of surface and bulk oxygen vacancies and active chemisorbed oxygen [320]. Hence SnO2 serves as a unique material for gas sensors. However, SnO2 based chemical sensors have low selectivity [321]. Selectivity allows to separate the contribution made by a particular type of molecule in the gas phase to the total electrical signal. The sensitivity of SnO2 may be improved by introducing dopants in the SnO2 matrix. The dopants have strong effect on catalytic and electronic properties of the surface. Transition metals or their oxides are generally used as the dopants into a highly dispersed oxide matrix to improve its selectivity.

Catalytic dopants (Pt, Pd, Ru, and Rh) have attracted the most attention [322-324]. It is assumed that these dopants catalyze specific chemical interaction of SnO2 with gases according to chemical or electronic mechanism. In the chemical mechanism adsorption of gas molecules on the dopant is followed by their interaction
with the SnO$_2$ matrix. This rapid transfer of the adsorbed molecule mediated by the metal dopants is known as a spillover effect [325]. Spill-over effect leads to the increase in the interaction of SnO$_2$ with the gas phase. Thus concentration of free charge carriers in SnO$_2$ correlates with the partial pressure of molecules in the gas phase. In the electronic mechanism there is direct chemical reaction of molecules from the gas phase with the dopant nanoparticles on the surface of SnO$_2$ resulting in a change in the oxidation state of dopant metals (for example, reduction of PdO to Pd) [326]. This process is accompanied by a change in the electron work function of the SnO$_2$ surface. Thus the conductivity of SnO$_2$ depends on the redox properties of the gas phase. The Pd/SnO$_2$ was chosen as a case study since it is one of the most widespread materials in commercial chemoresistive sensors. The addition of Pd in SnO$_2$ resulted in a remarkable improvement of the gas sensing properties allowing the selective detection of LPG at low temperature as compared to Ethanol, CO and H$_2$. Low concentration of 20ppm of LPG could be detected.

In the present chapter nanocrystalline pristine and Pd doped SnO$_2$ (Pd:SnO$_2$) with various mole% Pd has been synthesized by modified Pechini citrate route. The response of the pristine SnO$_2$ and Pd:SnO$_2$ was studied towards different reducing gases. The 1.5 mole% Pd doping shows an enhanced response of 75 and 95% towards LPG at as low as 50 and 100$^\circ$C respectively, which is quite a high value as compared with pristine SnO$_2$ (38 and 35% at 50 and 100$^\circ$C, respectively). Structural characterization reveals that Pd doping reduces crystallite size of SnO$_2$ and helps in the formation of distinct spherical nanospheres at a calcinations temperature of 500$^\circ$C. Thus increase in LPG response can be correlated with the spherical morphology, decrease in the crystallite size (~11nm) due to doping with Pd as compared with the pristine SnO$_2$ (~26nm) and mainly role of Pd as catalyst.

3.2.1 X-Ray diffraction analysis.

The structural and morphological properties of SnO$_2$ have a significant role on the electrical and gas sensing properties, hence structural and grain size measurements were performed. The XRD patterns of pristine and Pd:SnO$_2$ with various mole% Pd are shown in Figure 3.1.
All the diffraction patterns show characteristic tin oxide peaks with rutile structure [327] without presence of any impurity phase or peaks corresponding to PdO, indicating formation of single phase tin oxide structure. After incorporation of Pd, there is a broadening and drop off in the intensity of the peaks thereby supporting the reduction in the crystallite size; initially on doping with 1.5% Pd the intensity decreases while on further addition (2.5 and 3.5% Pd) no significant difference in the peak intensity is observed. It is well known that high surface to volume ratio due to nanostructures is one of the important criteria to increase the sensitivity towards a particular test gas. Thus 1.5% is the optimum concentration of Pd to get a very low crystallite size in the present method.

**Figure 3.1** XRD patterns of (a) pure and SnO₂ doped with (b) 1.5, (c) 2.5 and (d) 3.5 mol% Pd.
The effect of Pd incorporation on the crystallite size as calculated by Scherrer formula has been illustrated in Fig.3.2. Pure SnO$_2$ has a crystallite size of ~26 nm while SnO$_2$ with 1.5% Pd has a reduced crystallite size of ~11 nm; however, with further increase in the Pd concentration the crystallite size is found to increase marginally. As compared with the JCPDS data where $a = b = 4.738$ Å, $c = 3.188$ Å (Card No. 41 - 1445) the lattice parameters calculated from the spectrum of pristine SnO$_2$ match well. The variations in lattice parameters as a function of Pd are shown in Figure 3.3.

**Figure 3.2** Crystallite size of SnO$_2$ as a function of Pd concentration as calculated by Scherrer equation.

**Figure 3.3** Lattice parameters ($a = b$, $c$) of SnO$_2$ as a function of mole% Pd.
It is seen that on doping of Pd a marginal decrease in the lattice parameters is observed in all the concentrations, however, the reduction in 1.5% Pd is comparatively more than that of 2.5 and 3.5% Pd. The ‘a’ parameter remains same for 2.5 and 3.5% Pd while the ‘c’ parameter slightly decreases. Whereas on addition of 1.5 mole% Pd, a slight decrease in the ‘a’ parameter \( (a = b = 4.729 \text{ Å}) \) takes place while ‘c’ \( (c = 3.187 \text{ Å}) \) remains almost the same.

### 3.2.2 Transmission Electron Microscopy (TEM).

The particle shape and size distribution of the nanostructures can be determined by TEM. Fig. 4 shows typical TEM images of the pristine SnO\(_2\) (Figure 3.4a) and Pd:SnO\(_2\) (3.5% Pd) nanospheres (Figure 3.4b, c) prepared by modified Pechini citrate route.

It is observed that pristine tin oxide particles are larger than Pd-doped and do not have definite geometric shape. Besides, they are not separated. However, SnO\(_2\) after doping with Pd shows particles with perfect spherical geometric shape, moreover, particles are seen isolated without aggregation. It is interesting to see that such nanospherical particles remain distinctly separated even after calcination at 500°C. The diameter of the spheres varies from 10 – 20 nm with majority of the spheres showing less than 15nm while a minor portion of larger particles. It indicates that Pd addition helps in the formation of perfect isolated nanosphers. The size matches well to that calculated by the Scherrer equation from the XRD peaks.
Figure 3.4 Transmission Electron Micrograph (TEM) of pristine (a) SnO$_2$ and (b, c) SnO$_2$ doped with 3.5 mole% Pd.
3.2.3 Gas Sensing Properties.

It is well known that gas sensing is a surface phenomenon and is mainly controlled by the adsorbed oxygen species. Doping with Pt, Pd and Ru [193, 194, 328] give rise to various oxygen species and surface states causing enhancement in the gas sensing. To check the selectivity towards gases, initially, sensing properties of pristine and Pd:SnO$_2$ with various concentrations of Pd was studied with 200ppm concentration of different reducing gases such as LPG, CO, ethanol and H$_2$ using air as a carrier gas. Figure 3.5 represents the influence of temperature on the response of the pristine SnO$_2$ and Pd:SnO$_2$.

![Figure 3.5 – a. Sensing towards different gases at various temperatures ranging from 50°C to 300°C for pristine SnO$_2$.](image)

In Figure 3.5(a) response of pristine SnO$_2$ towards various gases at temperature between 50-300°C is presented; wherein, response towards every gas is seen increasing with temperature. However, LPG shows distinctly highest sensitivity at 300°C.
Figure 3.5 – b. Sensing towards different gases at various temperatures ranging from 50°C to 300°C for 1.5%Pd:SnO$_2$.

Figure 3.5 - b, shows response of 1.5%Pd:SnO$_2$, it indicates highest response at 100°C for most of the gases. Interestingly, in comparison with all other gases the response towards LPG is highest throughout the operating temperature range. The sample exhibits high response (75%) towards LPG even at lower (50°C) as well as higher (300°C) temperature.
Figure 3.5 – c. Sensing towards different gases at various temperatures ranging from 50°C to 300°C for 2.5%Pd:SnO$_2$.

Figure 3.5 - c also shows high response towards LPG as well as ethanol in the temperature range 100-250°C, however simultaneously ethanol is detected. Similar trend is observed for all other gases; however their response is lower than that of LPG/ethanol.
Figure 3.5 - d. Sensing towards different gases at various temperatures ranging from 50°C to 300°C for 3.5%Pd:SnO₂.

Figure 3.5 - d clearly shows shift in the response temperature, it exhibits highest response towards every gas at 200°C.

As compared with Figure 3.5-a, wherein the highest response for all the gases is at around 100°C. Our results indicate that Pd has distinct role in the detection and optimum response temperature towards different gases. Out of all the compositions 1.5% Pd distinctly shows highest sensitivity at lower operating temperature. Significantly, this sample has lowest particle size and indicates nanospherical morphology. The enhanced response can also be attributed to the reduction in the crystallite size of tin oxide from ~26nm (pristine SnO₂) to ~11nm after incorporation of 1.5%Pd. The decrease in the crystallite size causing an increase in surface to volume ratio leads to enhancement in the response due to availability of more active sites for the surface reaction.

We obtained the highest response of 95% towards LPG at 100°C for 1.5%Pd:SnO₂ and hence to study the behavior of the same for different concentrations of LPG (1000-20ppm) 100°C is chosen as the optimum temperature. Figure 3.6 (a) and (b) depicts systematic study of response towards 1000-20ppm of LPG at 100°C.
The response and the recovery time vary with the concentration, for higher concentrations the recovery time is higher (21 min for 1000 ppm) and goes on decreasing regularly with decreasing concentrations (3 min for 20 ppm). The response is fast and is in the range of 25 s to 45 s for all the concentrations. As the sensor material is continuously exposed to different concentrations of LPG after a recovery
of approximately 90%, hence it does not get enough time to rejuvenate the surface and thus apparently indicates lower response than that observed when the sample is given enough time to recover the surface states (Fig.3.3.1). It can be clearly seen from Fig.3.3.2 (a) and (b) that recovery of the sample is in two stages and shows different behavior for lower and higher concentrations. For higher concentrations of LPG the recovery rate is initially slow and at final stage the recovery is faster. Whereas for lower concentrations of LPG the recovery is faster at the initial stages and then slows down at the later stage. As expected, with decreasing concentration of LPG the recovery time also decreases, it can sense as low as 20ppm LPG in 40s and recovers in just 180s at comparatively lower operational temperature of 100°C, moreover it has shown sensitivity even at 50°C (75%). Most of the SnO₂ sensors operate at a temperature between 300 and 400°C. [329, 330] This increases the power consumption, which in turn affects the cost of the sensor. Thus surface modification by Pd-doping in the present study has proved to be very effective method in achieving lower operating temperature and higher response values for LPG. Compared with the LPG gas sensing properties of SnO₂/Pd composite films [331] synthesized by sophisticated techniques like magnetron sputtering exhibits only 65% of sensitivity at a higher temperature of 350°C for 3000 ppm of LPG. In the present study we obtained a sensitivity of 75 and 95% for 1.5%Pd:SnO₂ at 50 and 100°C respectively (Figure 3.5 - b). In 2.5 and 3.5%Pd:SnO₂ samples the sensitivity values show a similar trend with higher sensitivity at lower temperatures as shown in Figure 3.5 - c, d. The improved sensitivity values towards LPG are due to enhanced catalytic dissociation of the molecular oxygen on the tin oxide surface due to Pd-catalyst.

The present method has several advantages due to formation of nanospheres to yield a high sensitivity towards LPG for a relatively low palladium concentrations compared with 72% response for 7at% Pd at 300°C [332]. The response is lower as compared to that in the present study (95% at 100°C with 1.5 mole% Pd), besides it needs higher temperature for detection. Yamazoe et al. [333] have suggested two mechanisms operational for the sensitization of gases viz. chemical and electronic. Srivastava et al. [334] have reported that Pd responses towards gas through the electronic sensitization mechanism by forming Pd(II)O which reduces by the reducing gas, making in to the Pd⁰ form. In the process, initially the resistance increases due to additional surface states provided by PdO and then decreases due to availability of free electrons by the reduction of PdO. The importance of the surface states in
enhancing the response of surface ruthenated tin oxide has been discussed earlier by us [193] wherein we reported the sensing mechanism through dissociation of LPG into various organic species, which gives free electrons for the conduction. In the present work we have incorporated Pd and expect the presence of Pd in the bulk as well as on the surface. The Pd atoms on the surface of the SnO$_2$ nanospheres follow a chemical mechanism wherein Pd being a better oxygen dissociation catalyst than SnO$_2$, enhances the rate of dissociation and diffusion of oxygen species on the surface of SnO$_2$. The resulting dissociative adsorption of oxygen on the surface results in a greater degree of electron withdrawal from the SnO$_2$ bulk at a lower temperature than pristine SnO$_2$. This mechanism is known as the “spill-over” effect. [335]. The “spill-over” mechanism is as shown in Figure 3.8.

![Figure 3.7 “Spill-Over” of oxygen from the catalyst onto SnO$_2$.](image)

We had reported that LPG adsorbs on the surface by formation of surface acetate. The electron transfer to the surface states, caused by dopant near the conduction band edge of tin oxide, gives rise to its higher oxidation state. The energy released during decomposition of gas causes electrons to jump into the conduction band of oxide giving rise to increase in the conductivity. With desorption of such species from the surface, oxygen is again adsorbed on the oxide surface forming O$^2-$ /O$^-$ species by abstraction of electrons from the conduction band causing a decrease in the conductance. We propose a similar mechanism for the detection of LPG as shown in Figure 3.8.
Where the surface of Pd:SnO$_2$ is exposed to LPG, which contains butane as one of the major component, undergoes complete oxidation forming water and carbon dioxide with surface acetate as the intermediate species. We propose that in the present study on Pd:SnO$_2$ the surface palladium plays the similar role as that of ruthenium in tin oxide.

**Figure 3.8** Mechanism for LPG detection on the Pd:SnO$_2$ surface.
3.2.4 Conclusions

Nanosherical Pd:SnO$_2$ has been successfully synthesized using a simple modified Pechini citrate route. The nanosized particles of tin oxide remain isolated even after calcination at 500°C due to incorporation of palladium. Besides, it gives good response towards LPG at the lower operating temperature of 50°C. The ‘spill-over’ mechanism is proposed for such low temperature LPG response caused by palladium, the nanospheres although is more sensitive towards LPG however, simultaneously detect ethanol. Thus Pd in the SnO$_2$ nanocrystals strongly influences the electronic properties of the final material. In particular, the resulting sensor material is very sensitive to LPG at low temperature (50°C), with a detection limit of ~20ppm.