Chapter 5: Result & Discussion of Au@SnO$_2$/Pt Core-Shell

5.1. Synthesis of Au@SnO$_2$/Pt

Au@SnO$_2$ core-shell nanoparticles were synthesized via a two-step process; the synthesis of gold colloid followed by the encapsulation of the oxide shell by a simple hydrothermal technique [1]. A 10 mL aliquot of the citrate stabilized gold colloid was taken in a conical flask and placed in a water bath at 60$^\circ$C. This solution was stirred vigorously for 5 min followed by the rapid addition of 500 IL of sodium hexahydroxostannate (40 mM) (Chemical Pure, Junsei Chemicals Co., Ltd.). A purple color colloid was obtained which indicated the formation of Au@SnO$_2$ core-shell nanoparticles [1,2].

This process was repeated to obtain large amounts of colloid. Then this colloid was concentrated by rotary-evaporator (volume was reduced to 1/10th of the original volume). The colloid was centrifuged and washed with deionized water to remove the unreacted species and impurities (mostly sodium chloride). Then nanoparticles are redispersed in the equal amount of deionized water. A calculated amount of 0.5 wt. % aqueous Platinum salt was added to the above gold-tin oxide colloid under constant stirring. This solution was used to deposit film on silica glass substrate [1, 2]. The synthesis process of Au@SnO$_2$/Pt is shown in Fig 5.1.
5.2. Optical Property of Au@SnO₂

Metal NPs are known to exhibit excellent surface Plasmon (SP) band due to the abundance of electrons on their surface. It is a well known phenomenon that the SP band is significantly sensitive to slight alteration of particle surface chemistry. This concept [5] has been employed to monitor the formation of as synthesized Au@SnO₂/Pt Nanocomposite (NC). In Fig 5.2 a clear and distinct peak of Au colloid at 519 nm has been obtained. The color of the Au colloid changed from ruby red to dark red on formation of a tin oxide shell [1] circumfering the Au NPs. The theoretical prediction of SP band using the volume fraction of the shell layer unity[1-5], for Au@SnO₂ is expected to be at 536 nm.
However, interestingly this value is relatively close [2] to the observed value at 539 nm. The dramatic shift in the SP band [4] is due to the transfer of electronic charge [3-4] from the core to the shell [3-6]. It was also found that a clear red shift has occurred in case of Au@SnO\textsubscript{2}/Pt NCs. On addition of Pt the dark red colored Au@SnO\textsubscript{2} turned into a brownish red complex. A corresponding SP peak at 549 nm is obtained. The further red shift of the SP band by 5-10nm may be correlated to the adjacent change in the surface property due to deposition of Pt as individual islands on the surface of metal oxide (SnO\textsubscript{2}). It is also evident that formation of Au@SnO\textsubscript{2}/Pt NCs is indicated not only by the formation of hyperchromic shift but also a damping in the absorbance intensity has been observed. The governing mechanism may be the generation of dipole coupling [7-14] between the closely interacting Pt particles. The particular interaction may play an important role in transforming the property of the environment, from its aqueous phase to formation of a thin film setting.

Fig. 5.2. UV-visible spectrophotometric analyses of Au@SnO\textsubscript{2}/Pt colloid
5.3. Surface Morphology

The surface morphology of the as synthesized material is investigated with Transmission Electron microscopy (TEM). TEM image is obtained for both Au@SnO$_2$ and Au@SnO$_2$/Pt. Fig. 5.3 (a) and (b) shows the formation of Au@SnO$_2$ core shell NCs. Presence of Au metal ion in the core with a concentric hallow of SnO$_2$ encircling the metal ion as a shell is observed distinctly. Comparison of the TEM image for Au@SnO$_2$/Pt given in Fig. 5.3 (c) and (d) with that of Au@SnO$_2$, an interesting and unique morphological alteration is observed. Presence of Pt particles on the surface of the shell as individual islands is clearly visible.

![TEM images showing formation of Au@SnO$_2$ and Au@SnO$_2$/Pt NCs bearing core-shell morphology](image)

![Fig. 5.3 TEM images showing (a) & (b) formation of Au@SnO$_2$; (c) & (d) formation of Au@SnO$_2$/Pt NCs bearing core-shell morphology](image)

The crystal structure and phase has been studied by X-ray. From Fig 5.4 three different peaks corresponding to gold nanoparticles[1] with face centered cubic structure (JCPDS
No. Card No. 77-0451) can be identified[1-4]. Additionally, three different peaks for Casseterite tin dioxide with tetragonal structure are observed. However, the peak for platinum is not very clear. This may suggest that the platinum may be in a poor crystalline or amorphous state. Interestingly, no peak was obtained for Au-Sn compound. Hence this result may suggest that both the materials is expected to retain their individual physical structures and therefore is supposed to form a colloid rather than an alloy [1-4].

Fig. 5.4. XRD analyses of Au@SnO$_2$/Pt NCs

5.4. Volatile Organic Gas Sensing and Shooting

The Au@SnO$_2$/Pt NCs have been explored for gas sensing and shooting application. The particular thick film semiconductive device is engineered to detect five different gases[1-4] (acetaldehyde, carbon monoxide, ethanol, propane[1-4] and pyridine) with varying specificity. It is observed from experimental data that the particular NC shows excellent response towards detection of acetaldehyde. Fig. 5.5 (a) shows the efficiency of the sensor towards detecting various concentrations of acetaldehyde ranging from 5 ppm to 500 ppm. It is observed that the optimum sensor response was obtained under a temperature range of 250$^\circ$C–350$^\circ$C. A linear correlation between sensor response and
targeted gas concentration is established in Fig. 5.5 (b). The detection range is found to be within a range of 10-500 ppm with a limit of detection (LOD) at 5 ppm. It is also evident from the experimental data that efficiency of gas sensing is proficient at 300-400 ppm. The mechanism behind the enhanced gas sensing property of the as synthesized material is expected to be the tactical formation of metal (Au) core with a metal oxide (SnO$_2$) shell, impregnated with isolated islands of Pt. the chemical property of the composite may play a crucial role in maintaining the critical diameter ($D$) of the material on being excited at high thermal energy. It is a known fact that sensing materials without a core shell, when being applied for gas sensing purpose under a constant thermal excitation have resulted in the increase of the mean crystalline diameter resulting in the grain growth which ultimately leads to agglomeration of the materials and the sensing response is compromised.

Fig. 5.5. (a) Correlation between the sensor response with respect to sensing temperature (b) Change in sensor response with respect to varying concentration of propane gas.

Uncontrolled increase in the critical diameter may also hamper the integrity of space charge layer hence this may be another cause for poor sensor response. However, in case of the as synthesized modified structure, the electron transfers from the valence band of the metal oxide to the conduction band and from the conduction band to the conduction band of the metal particle at the core [15-17]. This helps in increasing the surface recombination time of the electron and hole created during the process. Also availability
of electrons in the surface charge layer increases and hence an excellent response is expected. However the tactical impregnation of Pt on to the shell surface may create crystalline defect which may help in storing and quick shuttling of electrons [18]. The unique feature of this particular sensing device is its capability of in situ degradation of the sensed gas compound. The hole created in the valence band on excitation may be expected to play the critical role in decomposing the targeted gaseous species. The gaseous compounds which are adsorbed on to the material surface may come in contact to the hole and therefore gets oxidized to its non-reactive by-products. In Fig. 6.5 the degradation of acetaldehyde as a function of time is represented. It can be inferred that 99% degradation of the targeted gas is achieved within 85-90 min.
References


