Chapter 3: Results and Discussion
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3.1 Biosynthesis mechanism for pure and doped SnO₂

The natural biomolecule present in the extract which is responsible for biosynthesis of SnO₂ nanoparticles was found to be pectin. Pectin is a complex polysaccharide that is present in most primary cell walls. It is a natural part of the human diet but does not contribute significantly to nutrition¹. Pectin is commonly used in the food industry as a gelling and stabilizing agent, as the pectin molecules can bind some organic and inorganic materials via molecular interactions, thus finding its use for targeted drug delivery².

![Figure 3.1 Schematic representation of biosynthesis mechanism using Gram bean extract.](image)

The synthesis mechanism is schematically represented in Figure 3.1 and can be explained using FTIR spectra shown in Figure 3.2. Room temperature FTIR spectra of drop cast gram bean extract, the as prepared SnO₂ and SnO₂ calcined at 600 °C are shown in Figure 3.2. The FTIR spectra of the extract resemble the IR spectra for pectin present in the extract, thus an obvious absorption peak at about 514 cm⁻¹ can be found for the pectin–SnO₂ composite sample; this is a typical IR absorption peak originating from stretching mode of the Sn–OH bond. The remaining peaks in pectin–SnO₂ composite is induced by pectin, which is confirmed by comparing of the IR spectrum of the composite with that of the pectin³. The peak at 1030 cm⁻¹ is assigned to C=O or C=C double bond of pectin. The absorption peaks at 1386 and 1579 cm⁻¹ are related to stretching bands of COO⁻ groups of pectin. It is found that the intensities of a peak around 2925 cm⁻¹ (induced by carboxyl and CH₂ groups of pectin) can be attributed to pectin–SnO₂ composite is obviously weaker than that for pectin. This may originate from the participation of COO⁻ and
CH$_2$ groups in a hydrogen bond system, which stabilizes the pectin conformation in the solid state.

![Figure 3.2 FTIR spectra of (a) gram bean extract (b) as prepared SnO$_2$ nanoparticles and (c) SnO$_2$ nanoparticles calcined at 600 °C.](image)

The above results indicate that the final product is a true composite of pectin and SnO$_2$. The pectin peaks were not removed even after washing the sample repeatedly, suggest that the interactions between pectin and SnO$_2$ are strong. The peak at around 614-930 cm$^{-1}$, which refers to Sn-O stretching modes of Sn-O-Sn, appeared even after calcination at 600 °C.

From the synthesis mechanism summarized in Figure 3.1, we can conclude that, when gram beans are soaked in de-ionised water, autolysis of the cell wall occurs, which results in the release of pectin molecules in the extract$^{4,5}$. These molecules have a tendency to bind metal ions$^6$. Thus, when tin chloride is added to the extract, the tin ions get bound to the pectin molecules as shown in Figure 3.1. As the pH of the solution is increased, this tin-hydroxide-pectin gel shrinks$^2$ and inhibits the further growth of the
nanoparticles. Subsequently, when it is calcined, we get very small-sized nanoparticles with narrow size distribution.

### 3.2 Biosynthesized pure SnO$_2$ nanoparticles

#### 3.2.1 X-ray Diffraction

![XRD spectra](image)

**Figure 3.3(a)** XRD spectra of SnO$_2$ nanoparticles biosynthesized (gram bean extract mediated) calcined at 600 °C **(b)** WH-plot of pure SnO$_2$

Crystal structure, phase and particle size of the product were determined using XRD patterns obtained from the samples. XRD spectra of the biosynthesized SnO$_2$ nanoparticles calcined at 600°C and from standard JCPDS card # 71-0652 are shown in **Figure 3.3(a)**. The diffraction peaks in **Figure 3.3(a)** were indexed to represent the rutile phase of the SnO$_2$ with calculated lattice parameters $a = 4.741$ Å, $c = 3.189$ Å, which are consistent with the literature reported values ($a = 4.738$ Å, $c = 3.186$ Å, JCPDS No. 71-0652), and can be attributed to the space group $P4_2/mnm$. The high purity of the final product was confirmed by the absence of any peaks due to the metallic tin or any other Sn-based oxide or hydroxide. In order to understand the effect of strain on the crystallite size, it is calculated by both Scherrer formula and Williamson-Hall (W-H) plot (**Figure 3.3(b)**). The Scherrer’s formula does not consider the strain while the Williamson-Hall (W-H) plot considers the strain while calculating the crystallite size. The average crystallite size of the product was determined from XRD peaks using Scherrer’s formula $D = \frac{K\lambda}{\beta\cos\theta}$, where $K$ is the Scherrer’s constant ($K = 0.9$), $\lambda$ is the wavelength of the incident X- rays, $\beta$ is the full width at half
maximum of the XRD peaks expressed in radian. The lattice parameters for tetragonal structure were calculated by
\[ d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}} \]

Where h, k, l are all integers, (hkl) is the lattice plane index, a and c are lattice constants. The crystallite size \( d \) and lattice strain \( \eta \) are calculated from W-H plot by plotting the variation of \( \beta \text{Cos} \theta \) with \( 4 \text{Sin} \theta \). We can see a difference between the sizes calculated by both the methods which is due to the lattice strain in the system. The negative strain implies contraction in the system.

![Graph](image)

**Figure 3.4** Rietveld refinement of 600 °C calcined pure SnO\(_2\) nanoparticles.

To further confirm the crystal structure and lattice parameters of the pristine SnO\(_2\), Rietveld refinement was performed (**Figure 3.4**). The results obtained are tabulated in **Table 3.1**.
Table 3.1 Structural parameters of pure SnO₂.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure SnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Bruker D8 Advance</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα₁(1.5406Å)</td>
</tr>
<tr>
<td>2θ range</td>
<td>20-80</td>
</tr>
<tr>
<td>Scan Step</td>
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</tr>
<tr>
<td>Peak Shape</td>
<td>Pseudo-Voigt</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>SnO₂</td>
</tr>
<tr>
<td>Space group</td>
<td>P 42/m n m</td>
</tr>
<tr>
<td>a(Å)=b(Å)</td>
<td>4.74133</td>
</tr>
<tr>
<td>c(Å)</td>
<td>3.18923</td>
</tr>
<tr>
<td>c/a</td>
<td>0.672645</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>71.69456</td>
</tr>
<tr>
<td>Rp(%)</td>
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<tr>
<td>Rexp(%)</td>
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</tr>
<tr>
<td>χ²</td>
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</tr>
<tr>
<td>R_Bragg (%)</td>
<td>2.41</td>
</tr>
<tr>
<td>R_F (%)</td>
<td>1.59</td>
</tr>
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<td>Crystallite size (Scherrer’s)</td>
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<tr>
<td>Crystallite size (WH-plot)</td>
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</tr>
<tr>
<td>Strain</td>
<td>-0.00145</td>
</tr>
</tbody>
</table>

3.2.2 Transmission Electron Microscopy

The TEM image of SnO₂ and corresponding size distribution plot are shown in Figure 3.5(a) and 3.5(b), respectively. These TEM images confirm that the prepared pristine SnO₂ is in nano regime. No agglomeration of nanoparticles is seen, which is very much expected as the biomolecules present in the extract act as surfactants. The TEM image of pristine SnO₂ shows that the particles are of a random shape having size around 12 nm.
3.2.3 Scanning Electron Microscopy

The surface morphology of the biosynthesized pure SnO$_2$ nanoparticles was examined by SEM. Figure 3.6 shows the micrograph of pure SnO$_2$ nanoparticles calcined at 600 °C demonstrating spherical shaped nanoparticles with narrow size distribution.

Figure 3.5(a) The TEM image of biosynthesized pure SnO$_2$ and (b) size distribution plot.

Figure 3.6 SEM image of drop cast biosynthesized pure SnO$_2$ nanoparticles.
3.2.4 Raman spectroscopy

Investigation of the vibrational mode within the system can be effectively analyzed using Raman spectroscopy. A normal mode can be described by the $3n$ coordinates, where $n$ is the number of atoms in the primitive cell. This gives the displacements of the atoms from their equilibrium positions. Rutile SnO$_2$ having 6 atoms unit cell gives out 18 possible vibrations. The normal lattice vibrations at the $\Gamma$ point of the Brillouin zone on the basis of group theory are as follows.

$$\Gamma = \Gamma_1^{+}(A_{1g}) + \Gamma_2^{+}(A_{2g}) + \Gamma_3^{+}(B_{1g}) + \Gamma_4^{+}(B_{2g}) + \Gamma_5^{-}(E_g) + 2\Gamma_1^{-}(A_{2u}) + 2\Gamma_4^{-}(B_{1u}) + 4\Gamma_5^{+}(E_u).$$

Two modes $A_{2u}$ and $E_u$ are infrared (IR) active while four modes, i.e., $A_{1g}$, $B_{1g}$, $B_{2g}$ and $E_g$ are found to be Raman active. The $A_{2g}$, $B_{1u}$ modes are silent.

![Raman spectrum of biosynthesized pure SnO$_2$](image)

**Figure 3.7** Raman spectrum of biosynthesized pure SnO$_2$
A$_{1g}$ mode results from the vibration of Sn–O bond, wherein the oxygen atoms vibrate while Sn atoms are at rest.

The Raman spectra of the pure SnO$_2$ (Figure 3.7) shows peaks at 635 cm$^{-1}$ (A$_{1g}$) and 780 cm$^{-1}$ (B$_{2g}$)$^9$, whereas a hump appears at 474 cm$^{-1}$ (E$_g$) and 685 cm$^{-1}$. The hump at 685 cm$^{-1}$ can be attributed to the presences of oxygen vacancies leading to lattice disorder$^8$.

3.2.5 UV-Vis spectroscopy

![Absorbance spectrum and $(\alpha h\nu)^2$ vs $h\nu$ plot of pure biosynthesized SnO$_2$ nanoparticles.](image)

Figure 3.8(a) Absorbance spectrum and (b) $(\alpha h\nu)^2$ vs $h\nu$ plot of pure biosynthesized SnO$_2$ nanoparticles.

Absorption spectroscopy is a powerful non-destructive technique to have a better understanding of the optical properties of semiconducting nanoparticles. The absorption spectrum of pure SnO$_2$ nanoparticles is shown in Figure 3.8(a). The absorbance is expected to depend on several factors, such as band gap, oxygen deficiency, surface roughness and impurity centers. An ultraviolet cut-off around 250-290 nm can be attributed to the photoexcitation of electrons from valence band to conduction band. The bandgap of the pure SnO$_2$ nanoparticle thin films was calculated by extrapolating the plot of $(\alpha h\nu)^2$ vs $h\nu$ using the Tauc’s relation. The prepared pristine SnO$_2$ has a band gap of 3.54 eV. Urbach type absorption is the absorption below band gap (inset in Figure 3.8(b)). The Urbach energy was found to be $E_a=0.54695$eV.
3.2.6 Electronic structure investigation

The DFT calculations have been performed to correlate the structural and optical properties of SnO₂.

Figure 3.9 Supercell (2x2x2) of pure SnO₂ (Sn is shown by gray balls, O by red balls)

Figure 3.9 shows the 2x2x2 supercell of pure SnO₂. The pure SnO₂ forms a 48 atom SnO₂ supercell (Sn\textsubscript{16}O\textsubscript{32}). The bond lengths for minimized supercell are listed in Table 3.2.

Table 3.2 Bond lengths in Sn\textsubscript{16}O\textsubscript{32} supercell

<table>
<thead>
<tr>
<th>System</th>
<th>Bond lengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn\textsubscript{16}O\textsubscript{32}</td>
<td>Sn-Sn 3.36</td>
</tr>
</tbody>
</table>
Figure 3.10(a) Bandstructure and (b) Density of States calculated from 2x2x2 supercell of pure Sn$_{16}$O$_{32}$.

Sn$_{16}$O$_{32}$ supercell was tested with both spin-polarized and spin-unpolarized calculation. The ground state energy for Sn$_{16}$O$_{32}$ is found to be same for both types of calculations. We considered the spin-polarized structure to calculate its band structure and density of state (DOS). The upper part of the valence band is mainly made of O2p states while the lower part of the conduction band is dominated by Sn5s states. Figure 3.10 shows the band structure of the pure SnO$_2$ supercell. Though the band gap value obtained from DFT calculation is not reliable, the relative positions of different levels and the pattern of bands can be seen from the bandstructure. The band diagram shows that the system has a direct band gap. The total DOS is shown in Figure 3.11(a) and Figure 3.11 (b) shows the PDOS for central Sn atom. This central Sn atom will be replaced by the dopant atom when the doped system is under investigation.
3.2.7 Gas sensing

NH₃ sensing mechanism

When tin oxide nanoparticle thin films are exposed to ammonia gas, the pre-adsorbed oxygen over SnO₂ surface and NH₃ molecules interact with each other and release electrons to SnO₂.

Figure 3.12(a) Gas sensing mechanism of SnO₂ nanoparticle thin film on exposure to ammonia gas. (b) Schematic showing electron transfer and change in electrical signal (resistance) upon exposure to the ammonia gas.
The interaction of pre-adsorbed oxygen and NH$_3$ molecules on the surface of SnO$_2$ is indicated in Eqs:

\[
\begin{align*}
O_2^{\text{gas}} & \xrightarrow{\text{SnO}_2 + \text{air}} O_2^{\text{(ads)}} \\
O_2^{\text{(ads)}} + e^{-} & \xrightarrow{\text{SnO}_2 + \text{air}} O_2^{-}(\text{ads}) \\
O_2^{-}(\text{ads}) + e^{-} & \xrightarrow{\text{SnO}_2 + \text{air}} 2O^{-}(\text{ads}) \\
\text{NH}_3^{\text{(gas)}} & \leftrightarrow \text{NH}_3^{\text{(ads)}} \\
2\text{NH}_3^{\text{(ads)}} + 3O^{-}(\text{ads}) & \leftrightarrow N_2 + 3H_2O + 3e^{-}
\end{align*}
\]

The release of electrons to SnO$_2$ results in an increase of carries, thus leading to increase in surface conductivity of SnO$_2$ thin film and decrease in the barrier height at the grain boundaries between the nanocrystallites.

**Figure 3.12(a)** shows the schematic of the sensing mechanism involving adsorption of oxygen species on the surface of tin oxide nanoparticles, which abstract electrons, and thus, cause an increase in the potential barrier at the grain boundaries. The gas molecules interact with the oxygen species and produce a notable change in an electronic property of the material. Thus, the density of oxygen species on the surface defines the rate of reaction and catalytic property. “In the case of a catalytic reaction, the ammonia gas is first adsorbed on a catalyst, gets split up into ions and then spills over on the surface and reacts with surface oxygen ions of the functional material, thereby decreasing the resistance of the sensor and enhancing the response”\textsuperscript{10-11}.

**Figure 3.12(b)** shows the schematic demonstrating change of the sensor resistance upon exposure to the target gas. Under ambient conditions, the electrons in the conduction band of the tin oxide nanoparticles are removed by the adsorbed oxygen ions. This causes a decrease in the carrier concentration, thereby increasing resistance at the operating temperature. When the sensor is exposed to the NH$_3$ gas, the electrons gained from the chemical reaction are given back to the conduction band leading to the decrease in sensor resistance\textsuperscript{10}.

**Ammonia sensing properties**

**Figure 3.13(a)** shows the I-V curve obtained from biosynthesized SnO$_2$ nanoparticles thin film maintained at room temperature, before and after insertion of NH$_3$ gas and on exposure for various time intervals recorded with
the bias voltage (+3V, -3V). Significant change in current is noted with variation in exposure time, justifies its sensitivity.

Figure 3.13(a) I-V curve for the bio-synthesized SnO$_2$ nanoparticles thin film (maintained at room temperature), before and after insertion of NH$_3$ gas at various time intervals. (b) Change in current as a function of time with SnO$_2$ thin-film being exposed to varying ammonia concentration. (c) Response curve as a function of varying ammonia concentration.
Figure 3.13(b) shows the change in current as a function of time obtained from SnO$_2$ thin-film on exposure to ammonia atmosphere with a varying ammonia concentration (200, 300, 400 ppm). “The response and recovery time of a sensor can be defined as the time required for a film resistance to reach 90% of its saturation value from the starting value, from the time of gas exposure and on the removal of the gas, respectively”\textsuperscript{12}. Here, the response and recovery time for SnO$_2$ thin-film were found to be ~6 and 8 s, respectively. “Response is defined as the ratio of the current in the gas atmosphere versus the current in an air atmosphere”\textsuperscript{13}.

\[ \frac{I_g}{I_a} = \text{Response} \]

Figure 3.13(c) shows the gas response curve as a function of gas concentration (200–600 ppm). Increasing trend and good linearity in the gas response curve is noted with the increase in the ammonia concentration (200-600 ppm). This is probably attributable to the very fact that the amount of NH$_3$ molecules reacting with the O\textsuperscript{−} species increase with an increase in gas concentration. The ammonia gas with varying concentrations (200 ppm and 600 ppm) was inserted consecutively into the test chamber. With 200 ppm of ammonia, the response was found to be nearly 5 (Figure 3.13(c)), followed by very good recovery on the withdrawal of gas from the test chamber. Similarly, with 600 ppm of ammonia, the sample exhibited the stable and reproducible response of 34 (Figure 3.13(c)). A linear response was noted from 200 ppm of ammonia extending up to 600 ppm. Interestingly, the gas sensing studies were explored at room temperature and the results were promising considering the fact that the SnO$_2$ particles were small with minimum to no aggregation, which increased the surface area and improved the sensing efficiency.
3.3 Biosynthesized Ni-doping SnO₂ nanoparticles

3.3.1 X-ray Diffraction

![Image](image.jpg)

**Figure 3.14** Representative XRD spectra of pure and Ni-doped biosynthesized SnO₂ nanoparticles calcined at 600 °C.

The representative powder X-ray diffraction patterns of pure and Ni-doped SnO₂ (5 wt%) samples are shown in **Figure 3.14**. The diffraction peaks in the spectra were indexed to the rutile phase of the SnO₂ and the lattice parameters were calculated to be $a=4.78$ Å and $c=3.21$ Å, which is consistent with the literature values ($a=4.738$ Å, $c=3.186$ Å, JCPDS No. 71-0652), belonging to the space group of $P42_{1}/nm$. No peak due to the metallic tin, NiO, Ni or any other Sn-based oxide or hydroxide were observed, indicating the high purity of the final product. There have been reports of the occurrence of traces of NiO in the Ni-doped SnO₂ for the excessive dopant concentration of 50 wt% Ni\(^{14}\). In the present study, we have used only 5 wt% Ni as a dopant. Thus, the Ni-doped SnO₂ can be expected to be phase pure. The average crystallite size of the pure and Ni-doped SnO₂ nanoparticles was determined from XRD peaks by using Scherrer’s formula $D=K\lambda/\beta\cos\theta$ and noted to be ~11 nm and ~6 nm.
respectively, where $K$ is the Scherrer’s constant ($K = 0.9$), $\lambda$ is the wavelength of the incident X-rays, $\beta$ is the full width at half maximum of the XRD peaks expressed in radian. It is known that for tetragonal structure, the lattice parameters can be calculated by

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$

Where $h$, $k$, $l$ are all integers, $(hkl)$ is the lattice plane index, $a$ and $c$ are lattice constants.

There is no significant change in the lattice parameters and cell volume, possibly due to the nearly equal size of dopant Ni ion (0.69 Å) with that of host ion Sn (0.71 Å). However, upon doping of Ni, a pronounced broadening of diffraction peaks is observed. This can be attributed to the decrease of particle size on doping of SnO$_2$ with Ni through the formation of a Ni–Sn solid solution and/or to the induced microstrain.$^{15}$

### 3.3.2 Transmission Electron Microscopy

TEM studies indicated that both the pristine and Ni-doped SnO$_2$ (calcined at 600 °C) formed spherical nanoparticles and that the particle sizes decreases due to Ni doping. Figure 3.15(a) shows the representative TEM image of pristine SnO$_2$ nanoparticles, while Figure 3.15(b) shows representative TEM image of Ni-doped SnO$_2$ nanoparticles calcined at 600 °C. The particles were observed to be monodispersed and the size was noted to be ~11 nm for pure and ~6nm for Ni-doped nanoparticles showing narrow size distribution. Interestingly, no aggregation of SnO$_2$ nanoparticles was observed and the connected crystallites of ~6 nm formed a random network. The selected area electron diffraction (SAED) pattern (insets in Figure 3.15(a) and 3.15(b)) were obtained to investigate the crystallinity.

It is observed that the SAED pattern obtained from the nanoparticles showed a ring-like pattern, which confirms the polycrystalline nature of the biosynthesized nanoparticles. It clearly indicates the growth of nanoparticles along 110, 200, 211 planes (inset in Figure 3.15 b), which is in agreement with the XRD data. The particle size distribution histograms of pure and Ni-doped biosynthesized SnO$_2$ nanoparticles calcined at 600 °C are shown in
**Figure 3.15 c** and **Figure 3.15 d**, respectively, demonstrating the average size of the particles.

![Figure 3.15 Representative TEM images of (a) biosynthesized pure SnO$_2$ nanoparticles (b) biosynthesized Ni-doped SnO$_2$ nanoparticles calcined at 600 °C. The insets show corresponding SAED patterns. Particle size distribution histogram plots of (c) biosynthesized pure SnO$_2$ nanoparticles and (d) biosynthesized Ni-doped SnO$_2$ nanoparticles.](image1)

**3.3.3 Scanning Electron Microscopy**

**Figure 3.16** Representative FE-SEM image of (a) biosynthesized pure SnO$_2$ nanoparticles and (b) biosynthesized Ni-doped SnO$_2$ nanoparticles calcined at 600 °C.

![Figure 3.16 Representative FE-SEM image of (a) biosynthesized pure SnO$_2$ nanoparticles and (b) biosynthesized Ni-doped SnO$_2$ nanoparticles calcined at 600 °C.](image2)
The surface morphology of the biosynthesized SnO$_2$ and Ni-doped SnO$_2$ nanoparticles were examined by SEM. Figure 3.16 shows the micrograph of pure and Ni-doped SnO$_2$ nanoparticles calcined at 600 °C demonstrating spherical shaped nanoparticles with narrow size distribution.

### 3.3.4 Fourier Transform Infrared spectroscopy

![FTIR spectra](image)

**Figure 3.17** FTIR spectra of (a) gram bean extract (b) as prepared Ni-doped SnO$_2$ nanoparticles and (c) Ni-doped SnO$_2$ nanoparticles calcined at 600 °C.

Room temperature FTIR spectra of drop cast gram bean extract, the as prepared Ni-doped SnO$_2$ and Ni-doped SnO$_2$ calcined at 600 °C are shown in **Figure 3.17**. The FTIR spectra of the extract resemble the IR spectra for pectin present in the extract, thus an obvious absorption peak at about 514 cm$^{-1}$ can be found for the pectin–SnO$_2$ composite sample; this is a typical IR absorption peak originating from stretching mode of the Sn–OH bond. The remaining peaks in pectin–SnO$_2$ composite is induced by pectin, which is confirmed by comparing of the IR spectrum of the composite with that of the pectin$^3$. The peak at 1030 cm$^{-1}$ is assigned to C=O or C=C double bond of
pectin. The absorption peaks at 1386 and 1579 cm$^{-1}$ are related to stretching bands of COO- groups of pectin.

It is found that the intensities of a peak around 2925 cm$^{-1}$ (induced by carboxyl and CH$_2$ groups of pectin) can be attributed to pectin–SnO$_2$ composite is obviously weaker than that for pectin. This may originate from the participation of COO- and CH$_2$ groups in a hydrogen bond system, which stabilizes the pectin conformation in the solid state. The above results indicate that the final product is a true composite of pectin and SnO$_2$. The pectin peaks were not removed even after washing the sample repeatedly, suggest that the interactions between pectin and SnO$_2$ are strong. The peak at around 614 cm$^{-1}$ and 930 cm$^{-1}$, refers to Sn-O stretching modes of Sn-O-Sn, which appeared even after calcination at 600 °C.

### 3.3.5 UV-Vis spectroscopy

Absorption spectroscopy is a powerful non-destructive technique to explore the optical properties of semiconducting nanoparticles. The absorption spectra of pure and Ni-doped SnO$_2$ nanoparticles are shown in Figure 3.18. The absorbance is expected to depend on several factors, such as band gap, oxygen deficiency, surface roughness and impurity centers. Absorbance spectra show an ultraviolet cut-off around 250-290 nm, which can be attributed to the photoexcitation of electrons from valence band to conduction band.
Tauc’s relation is used to calculate the band gap, $\alpha h\nu = A (h\nu - E_g)^n$ where $\alpha$ is the absorption coefficient, $A$ is a constant and $n=1/2$ for direct band gap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ vs $h\nu$ gives the value of the optical band gap $E_g$. The measured band gap was found to be 3.6 eV for undoped SnO$_2$ nanoparticles and 3.3 eV for Ni-doped SnO$_2$. The bandgap of the pure SnO$_2$ nanoparticles is in agreement with the reported value. However, on doping with nickel, the band gap energy decreases even though the particle size decreases. This is in contrast to the normal phenomenon of quantum confinement. A similar phenomenon was observed by Ahmed et.al.\textsuperscript{16} for samples containing 5% Ni concentration, the SnO$_2$–SnO$_{2-x}$ alloying effect was considered responsible for the band gap narrowing effect.

### 3.3.6 Gas sensing

Gas-sensing behaviors of the Ni-doped SnO$_2$ sensor was explored after NO$_2$ gas injection. The response–recovery properties of semiconducting oxide gas sensors depend on the operating temperature and gas concentrations. From
the literature survey, we observe that for a higher response at a lower concentration, sophisticated synthesis methods are to be used. While in the present work, simple, economic and eco-friendly biosynthesis method is used. For better comparison of the gas sensing properties of the biosynthesized Ni-doped SnO$_2$, gas sensing properties of biosynthesized both pure and nickel doped SnO$_2$ and chemically synthesized (sol-gel method) both pure and nickel doped SnO$_2$ were studied and their respective response curves for 100 ppm NO$_2$ gas at 200 °C are shown in Figure 3.19.

![Figure 3.19](image)

**Figure 3.19** Gas sensitivity for chemically and biosynthesized pure and Ni-doped SnO$_2$ nanoparticles thin film. The inset shows variation in response and recovery time of Ni-doped SnO$_2$ sensor with varying NO$_2$ gas concentration.

The resulting gas responses along with response and recovery time are summarized in Table 3.3. The sensor resistance increased when exposed to the NO$_2$ gas and consequently recovered to its original value on the removal of the NO$_2$ gas. From Figure 3.19 we can clearly see that the response was relatively higher for biosynthesized Ni-doped SnO$_2$ compared to chemically synthesized Ni-doped SnO$_2$. The sensor response for chemically synthesized SnO$_2$ was similar to the reported value$^{[17]}$. Furthermore, we observe that the sensor response increased with Ni doping for both the samples. This may be
due to the reduction of particle size with Ni doping\textsuperscript{15}, which resulted in increased surface area for adsorption of NO\textsubscript{2} gas. The inset in Figure 3.19 shows a decrease in response time and increase in recovery time with an increase in gas concentration for biosynthesized Ni-SnO\textsubscript{2}. The decrease in response time may be due to the large availability of vacant sites on the film for gas adsorption and increase in the recovery time may be due to the heavier nature of NO\textsubscript{2} and the reaction products which are not leaving the interface immediately after the reaction, resulting in a decrease in desorption rate\textsuperscript{17}.

**Table 3.3 Summarised responses, response time and recovery time of pure and Ni-doped SnO\textsubscript{2} sensors for varying NO\textsubscript{2} gas concentration.**

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Sensing Material</th>
<th>NO\textsubscript{2} conc. (ppm)</th>
<th>Response Time(s)</th>
<th>Recovery Time(s)</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20 ppm</td>
<td>60 ppm</td>
<td>100 ppm</td>
<td>20 ppm</td>
</tr>
<tr>
<td>1</td>
<td>Chem-SnO\textsubscript{2}</td>
<td>26</td>
<td>20</td>
<td>14</td>
<td>145</td>
</tr>
<tr>
<td>2</td>
<td>Chem-Ni-SnO\textsubscript{2}</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>145</td>
</tr>
<tr>
<td>3</td>
<td>Bio-SnO\textsubscript{2}</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Bio-Ni-SnO\textsubscript{2}</td>
<td>10</td>
<td>10</td>
<td>8</td>
<td>66</td>
</tr>
</tbody>
</table>

It is well known that the NO\textsubscript{2} sensing mechanism of SnO\textsubscript{2} depends on the surface oxygen adsorbed on the SnO\textsubscript{2} nanoparticles surface. The sensing mechanism involving adsorption of oxygen species on the surface of tin oxide nanoparticles abstract electrons, and thus, cause an increase in the potential barrier at the grain boundaries. The gas molecules interact with the oxygen species and produce a notable change in an electronic property of the material. Thus, the density of oxygen species on the surface defines the rate of reaction and catalytic property. NO\textsubscript{2} is an oxidizing gas with electron affinity much higher than oxygen (0.48 eV); NO\textsubscript{2} can interact with SnO\textsubscript{2} by trapping electrons directly through the surface oxygen ions thereby forming new surface electron acceptor levels\textsuperscript{18-19}. 
To explore further the picture of NO\textsubscript{2} sensing mechanism, we plotted the response at different NO\textsubscript{2} gas concentrations in **Figure 3.20**. The inset shows a power-law relationship of response (S) and NO\textsubscript{2} gas concentration.

The power exponent value (m) was fitted as m = 0.48566. These exponent values depend on the final adsorbed species at the surface, when the adsorbed species are NO\textsubscript{2} or O\textsuperscript{−}, the exponent values for both are 1. In the case of 2O\textsuperscript{−}, the exponent value is 0.5\textsuperscript{20}. Thus, our results indicate that electrons in SnO\textsubscript{2} will transfer to the new surface adsorbed species due to NO\textsubscript{2} adsorption, increasing the surface potential barrier of SnO\textsubscript{2} and thus making its resistance to increase.
Figure 3.21 Gas selectivity for a Ni-doped SnO$_2$ sensor for different gasses (H$_2$S, LPG, NH$_3$, and NO$_2$) of 100 ppm concentration.

Selectivity was studied as another sensor parameter. The responses of Ni-doped SnO$_2$ sensors towards a variety of flammable, toxic and corrosive gasses including H$_2$S, LPG, NH$_3$, and NO$_2$ of 100 ppm at the optimal operating temperature of NO$_2$ (200 °C) were explored to evaluate their selectivity. Figure 3.21 shows that the gas sensor of ‘Ni-doped SnO$_2$’ exhibited excellent selectivity to NO$_2$ gas when compared to other gasses. The results suggest that the Ni-doped SnO$_2$ thin film sensor can be fabricated to monitor highly toxic NO$_2$ in polluted air.
3.4. Biosynthesized Co-doped SnO$_2$ nanoparticle thin films

3.4.1 X-ray Diffraction

Figure 3.22 represents the XRD pattern of the (a) pristine and (b) Co-doped SnO$_2$ nanoparticles, while the inset shows WH- plots of pristine and doped SnO$_2$. The diffraction peaks of both the patterns in the spectra were indexed to the rutile phase of the SnO$_2$ and the lattice parameters were calculated to be $a = 4.74$ Å, $c = 3.19$ Å for pure SnO$_2$ and $a = 4.74$ Å, $c = 3.180$ Å for Co-doped SnO$_2$ which are consistent with the literature values ($a = 4.738$ Å, $c = 3.186$ Å, JCPDS No. 71-0652), belonging to the space group of P42/mnm. To understand the effect of strain on the crystallite size, it was calculated by Scherrer’s formula and Williamson-Hall (W-H) plot. The
differences of two sizes yield the required information. The crystallite size from Scherrer’s formula is calculated by using the equation, \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( d \) is the crystallite size, \( \lambda \) is the wavelength of X-ray used, and \( \theta \) is the Bragg angle of diffraction peaks. The crystallite size \( D \) and lattice strain \( \eta \) are calculated from W-H plot by plotting the variation of \( \beta \cos \theta \) with \( 4 \sin \theta \)^2.

Comparing the crystallite size from both the methods show that cobalt doping results in an increase in the crystallite size. The ionic radius of Sn\(^{4+}\) and Co\(^{2+}\) in octahedral coordination is 0.69 Å and 0.745 Å, respectively, and thus, the Co\(^{2+}\) ion prefers to occupy the Sn\(^{4+}\) site. Due to Co doping in the SnO\(_2\) system, the lattice planes gets distorted and the lattice strain is induced in the system. The ionic size of Co\(^{2+}\) being larger results in expansion of the system, which ultimately induces the positive strain listed in Table 3.4. Thus, the doped system has higher W-H calculated crystallite size values compared to the crystallite sizes calculated by Scherrer’s equation. No characteristic peaks of Co or oxides of Co were seen which confirm that no new phase of Co is formed. The interplanar spacing in pristine and 5% Co-doped SnO\(_2\) nano-system for 110 plane calculated from XRD is found to be 0.34 and 0.33 nm, respectively.

To further confirm the crystal structure and lattice parameters of the pristine and Co-doped SnO\(_2\) Rietveld refinement are performed (Figure 3.22(b)). The results obtained are tabulated in Table 3.4. These results confirm the decrease in lattice constants due to Co doping, which results in increased crystallite size and lattice strain.
Table 3.4 Structural parameters of pure and Co-doped SnO$_2$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure SnO$_2$</th>
<th>Co-doped SnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Bruker D8 Advance</td>
<td>Bruker D8 Advance</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK$\alpha_1$(1.5406Å)</td>
<td>CuK$\alpha_1$(1.5406Å)</td>
</tr>
<tr>
<td>2(\theta) range</td>
<td>20-80</td>
<td>20-80</td>
</tr>
<tr>
<td>Scan Step</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Peak Shape</td>
<td>Pseudo-Voigt</td>
<td>Pseudo-Voigt</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>SnO$_2$</td>
<td>Sn$<em>{0.95}$Co$</em>{0.05}$O$_2$</td>
</tr>
<tr>
<td>Space group</td>
<td>P 42/m n m</td>
<td>P 42/m n m</td>
</tr>
<tr>
<td>(a(\text{Å})=b(\text{Å}))</td>
<td>4.74133</td>
<td>4.74025</td>
</tr>
<tr>
<td>(c(\text{Å}))</td>
<td>3.18923</td>
<td>3.18721</td>
</tr>
<tr>
<td>(c/a)</td>
<td>0.672645</td>
<td>0.672372</td>
</tr>
<tr>
<td>(V(\text{Å}^3))</td>
<td>71.69456</td>
<td>71.61651</td>
</tr>
<tr>
<td>(R_p(%)</td>
<td>17.9</td>
<td>15.3</td>
</tr>
<tr>
<td>(R_{wp}(%)</td>
<td>15.3</td>
<td>13.7</td>
</tr>
<tr>
<td>(R_{exp}(%)</td>
<td>12.40</td>
<td>10.52</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>1.53</td>
<td>1.71</td>
</tr>
<tr>
<td>(R_{Bragg}(%)</td>
<td>2.41</td>
<td>1.99</td>
</tr>
<tr>
<td>(R_f(%)</td>
<td>1.59</td>
<td>1.51</td>
</tr>
<tr>
<td><strong>Crystallite size</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Scherrer’s)</td>
<td>~12</td>
<td>~18.4</td>
</tr>
<tr>
<td><strong>Crystallite size</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(WH-plot)</td>
<td>~12.4</td>
<td>19.1</td>
</tr>
<tr>
<td><strong>Strain</strong></td>
<td>-0.00145</td>
<td>2.52E-04</td>
</tr>
</tbody>
</table>
Figure 3.23(a) The TEM image (inset) size distribution histogram of Co-doped SnO$_2$. (b) SEM image (c) FTIR spectra of (i) gram bean extract (ii) as-prepared Co-SnO$_2$, (iii) Co-SnO$_2$ calcined at 600 °C (d) Raman spectra of pure and Co-doped SnO$_2$ nanoparticles.

3.4.2 Transmission Electron Microscopy

The TEM image of 5% Co-doped SnO$_2$ and corresponding size distribution plot is shown in Figure 3.23(a). This TEM image confirms that the prepared Co-doped SnO$_2$ is in nano regime. No agglomeration of nanoparticles is seen, which is very much expected as the biomolecules present in the extract act as surfactants. The average crystallite size from TEM image of pristine SnO$_2$ reported in our previous work$^{23}$ was ~12 nm, while the TEM image of Co-doped SnO$_2$ shows the clear formation of nanoparticles of ~19 nm. This confirms that the doping of Co in SnO$_2$ results in increased particle size compared to pristine SnO$_2$.

3.4.3 Scanning Electron Microscopy

The surface morphology of the biosynthesized Co-doped SnO$_2$ nanoparticles is also examined by SEM. Figure 3.23(b) shows the micrograph of Co-doped SnO$_2$ nanoparticles calcined at 600 °C which demonstrate the
spherical shaped nanoparticles with narrow size distribution. No major change in morphology of the Co-doped SnO\textsubscript{2} nanoparticles is observed when compared to pure SnO\textsubscript{2}.\textsuperscript{23}

### 3.4.4 Fourier Transform Infrared spectroscopy

Figure 3.23(c). shows the room temperature FTIR spectra of [i] gram bean extract [ii] as prepared Co- SnO\textsubscript{2}, [iii] Co-SnO\textsubscript{2} calcined at 600 °C. The results are similar to our previous reports. The biomolecule pectin present in the gram bean extract can be confirmed by the FTIR spectra. Pectin is a complex polysaccharide that is present in most primary cell walls. It is a natural part of the human diet\textsuperscript{1} and due to its ability to bind some organic and inorganic materials via molecular interactions, it has also found its use for targeted drug delivery\textsuperscript{2}. A typical IR absorption peak originating from stretching mode of the Sn–OH bond is found for the pectin–Co-SnO\textsubscript{2} composite sample at about 504 cm\textsuperscript{-1}; the remaining peaks in pectin–SnO\textsubscript{2} composite were induced by pectin, which was confirmed by comparing the IR spectrum of the composite with that of the pectin\textsuperscript{3}. The peaks obtained and their corresponding modes are tabulated in Table 3.5.

#### Table 3.5 Peaks and their corresponding modes in FTIR spectra of pectin–Co-SnO\textsubscript{2} composite

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Peak Position</th>
<th>Mode of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>514 cm\textsuperscript{-1}</td>
<td>Sn-OH (stretching)</td>
</tr>
<tr>
<td>2</td>
<td>1030 cm\textsuperscript{-1}</td>
<td>C=O or C=C double bond of pectin</td>
</tr>
<tr>
<td>3</td>
<td>1386 and 1579 cm\textsuperscript{-1}</td>
<td>stretching bands of COO- groups of pectin</td>
</tr>
<tr>
<td>4</td>
<td>2925 cm\textsuperscript{-1}</td>
<td>carboxyl and CH\textsubscript{2} groups of pectin</td>
</tr>
</tbody>
</table>

Thus, from the FTIR results, we can confirm that the final product is a true composite of pectin and SnO\textsubscript{2}. The retention of pectin peaks even after repeated washing of the samples suggests that the interactions between pectin and SnO\textsubscript{2} are strong. The peak at around 601-920 cm\textsuperscript{-1} refers to Sn-O stretching modes of Sn-O-Sn and it appeared even after calcination at 600 °C.
3.4.5 Raman spectroscopy

The Co-doped SnO$_2$ samples were investigated using Raman spectroscopy to confirm the substitution of Co$^{2+}$ ions and to understand its effect on vibrational properties. The Raman spectra for pure and Co-doped SnO$_2$ samples are shown in Figure 3.23(d). Raman spectroscopy can be used to effectively analyze the vibrational modes within the system. The normal lattice vibrations at the $\Gamma$ point of the Brillouin zone on the basis of group theory are as follows:

$$\Gamma = \Gamma_1^+ (A_{1g}) + \Gamma_2^+ (A_{2g}) + \Gamma_3^+ (B_{1g}) + \Gamma_4^+ (B_{2g}) + \Gamma_5^- (E_g) + 2\Gamma_1^- (A_{2u}) + 2\Gamma_4^- (B_{1u}) + 4\Gamma_5^+ (E_u).$$

Two modes $A_{2u}$ and $E_u$ are infrared (IR) active while four modes, i.e., $A_{1g}$, $B_{1g}$, $B_{2g}$ and $E_g$ are found to be Raman active. The $A_{2g}$, $B_{1u}$ modes are silent. The $A_{1g}$ mode results from the vibration of Sn–O bond, wherein the oxygen atoms vibrate while Sn atoms are at rest.

The Raman spectra of the pure SnO$_2$ shows peaks at 635 cm$^{-1}$($A_{1g}$) and 780 cm$^{-1}$($B_{2g}$) whereas hump appears at 474 cm$^{-1}$ ($E_g$) and 685 cm$^{-1}$. The hump at 685 cm$^{-1}$ can be attributed to the presences of oxygen vacancies leading to lattice disorder.

The Raman peaks for Co-doped SnO$_2$ are obtained at 474 cm$^{-1}$, 575 cm$^{-1}$ (hump), 643 cm$^{-1}$, 685 cm$^{-1}$ and 780 cm$^{-1}$. The $A_{1g}$ mode shifted to higher wavenumber 643 cm$^{-1}$ may be due to lattice distortion because of cobalt doping and due to the increase in crystallite size. Also, the hump observed at 575 cm$^{-1}$ can be attributed to the oxygen vacancies in the SnO$_2$ lattice due to Co doping.

3.4.6 UV-Vis spectroscopy

The absorption spectra of pure and Co-doped SnO$_2$ nanoparticles are shown in Figure 3.24(a). The absorbance is expected to depend on several factors, such as band gap, oxygen deficiency, surface roughness and impurity centers. Absorbance spectra show an ultraviolet cut-off around 250-290 nm, which can be attributed to the photoexcitation of electrons from valence band to conduction band. The bandgap of the pure and Co-doped nanoparticle thin films was calculated by extrapolating the plot of $(\alpha h\nu)^2$ vs $h\nu$ (Figure 3.24(b)).
using the Tauc’s relation. The prepared pristine SnO$_2$ has a band gap of 3.54 eV while its band gap decreases with the Co doping to 3.44 eV. The doping of Co increases the crystallite size, thus decrease in band gap with the Co doping is very obvious (quantum confinement effect). Urbach type absorption is the absorption below band gap (inset Figure 3.24(b)). When defects in the system increase then the below band absorption occurs. With Co doping, the Urbach energy increases which mean that the distortion increases$^{27}$. The increase in distortion can be due to two reasons either Co is creating levels nearby conduction band or incorporation of Co in the system producing oxygen vacancies which are making levels nearby conduction band.

![Figure 3.24(a)](image)

**Figure 3.24(a)** Absorbance spectra and (b) $(\alpha h\nu)^2$ vs $h\nu$ plot of pure and Co-doped SnO$_2$ nanoparticles.

The inset in Figure 3.24(a) shows the higher absorption in near infra-red region. This peak is due to the d-d transition of an electron in Co$^{2+}$. The ground state of Co$^{2+}$ in octahedral coordination is $t_{2g}$ and its excited state is $e_g$, so in exact words, the transition is from $t_{2g}$ to $e_g$. This peak further confirms the presence of cobalt in 2+ state$^{28}$.

In order to rationalize the relation between structural disorder and optical changes, we have made a detailed theoretical study of electronic structure of Co-doped and undoped SnO$_2$ system.

### 3.4.7 Electronic structure investigation

The DFT calculations have been performed on pure and Co-doped systems and the results are correlated with the experimental results for the structural and optical properties of pure and doped SnO$_2$. The substitution of one Sn by a Co atom in a 48 atom SnO$_2$ supercell (inset Figure 3.25 (c)) affects all the bond length within the system. The bond lengths are listed in Table 3.6. When
tested for both spin-polarized and non-magnetic calculation the ground state energy for the pure system was found to be the same, but the spin-polarized system was found to be 159 meV more stable for the Co-doped system. Thus, the spin-polarized structure was used to calculate its band structure and density of state (DOS) in both the cases. The band structure pure and Co-doped systems are shown in Figure 3.25(a) and (b) respectively. From the band structure, the upper part of the valence band was found to be mainly made of O2p states, while the lower part of the conduction band is dominated by Sn5s states. Also, it shows that both the systems have a direct band gap. The band gap value obtained from DFT calculation is not reliable but it can be seen that two levels within the band gap region are generated with the inclusion of Co in the system. Along with this, there are many reports on the generation of oxygen vacancies with Co-doping in the SnO2 system29-30. Which can be explained as, in Co-doped SnO2 system the Co ions must have an ionic valance of Co4+ for charge balance. But 4+ oxidation state being unavailable for Co and to reach a more stable oxidation state, an adjacent oxygen vacancy is created in the Co-doped SnO2 system. Furthermore, these vacancies are reported to be close to Co atoms31-32, with densities to be highest for the concentration of Co below the in SnO2 system33.

Table 3.6 Bond lengths in Sn16O32 and CoSn15O32 supercell

<table>
<thead>
<tr>
<th>System</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn16O32</td>
<td></td>
</tr>
<tr>
<td>Sn-O</td>
<td>2.0627, 2.0784</td>
</tr>
<tr>
<td>CoSn15O32</td>
<td></td>
</tr>
<tr>
<td>Sn-O</td>
<td>2.0923, 2.066, 2.0995, 2.062, 2.077, 2.0621, 2.0441, 2.0529, 2.0783, 2.0792, 2.0773, 2.084, 2.0541, 2.1198, 2.0757, 2.0693, 2.0684, 2.0336, 2.1086,</td>
</tr>
</tbody>
</table>

The DOS for Co-doped SnO2 is shown in Figure 3.25(e). The sharp crossing of the Fermi level through the minority spin impurity states shows that the system is half-metallic. Further, it can be seen from Figure 3.25(d) that the Co 3d state splits up into e_g and t_{2g} states and strongly hybridize with the O-2p states at the top of the valence band and thus valence band of the impurity supercell is partly spin-polarized30. The results are in good agreement
with previous studies on 5% Co-doped SnO$_2$ systems reported showing room temperature ferromagnetism (RFM)$^{29-32, 34}$.

**Correlation between experimental and theoretical results**

The differences in the bond lengths of the Co-doped SnO$_2$ system compared to the undoped SnO$_2$ are also observed in XRD and Raman spectroscopy results for both the systems.

The UV- spectra and DOS results obtained for Co-doped SnO$_2$ system confirms the Co to be in octahedral coordination with 2+ valence state.

The structural and optical properties are found to be in good agreement with literature reports for Co-doped SnO$_2$ showing RFM. Thus the synthesized Co-doped SnO$_2$ nanoparticle thin films are supposed to show RFM.

![Figure 3.25](image-url) Bandstructure calculated from 2x2x2 supercell of (a) pure Sn$_{16}$O$_{32}$ (b) CoSn$_{15}$O$_{32}$ and (c) Total DOS calculated from 2x2x2 supercell of pure SnO$_2$ and Co-doped SnO$_2$ (d) PDOS from Sn-d and Co-d

**3.4.8 Gas Sensing**

Gas-sensing behaviors of the biosynthesized Co-doped SnO$_2$ sensor were explored after gas injection. For better comparison of the properties, the NH$_3$
gas sensing properties of biosynthesized Co-doped SnO$_2$ and those reported in the literature are shown in Table 3.7.

The important gas sensing properties include response, recovery time, operating temperature and gas concentration. From the Table 3.7, we can clearly see that higher response with lower operating temperature has been obtained by sophisticated synthesis methods requiring expensive instrumentation, while we report promising results with simple economic and eco-friendly biosynthesis method. Along with this, we report increased response with cobalt doping for NH$_3$ sensing at room temperature.

Table 3.7 Comparative table of gas-sensing characteristics of biosynthesized Co-doped SnO$_2$ and those reported in the literature.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(rGO--SnO$_2$)</td>
<td>Hydrothermal</td>
<td>NH$_3$</td>
<td>25 ppm</td>
<td>RT</td>
<td>1.4 times</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>SnO$_2$–SnS$_2$</td>
<td>Hydrothermal</td>
<td>NH$_3$</td>
<td>100 ppm</td>
<td>RT</td>
<td>~2</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>Pd/SnO$_2$/RGO</td>
<td>one-pot route</td>
<td>NH$_3$</td>
<td>100 ppm</td>
<td>RT</td>
<td>~20</td>
<td>37</td>
</tr>
<tr>
<td>4</td>
<td>MWCNTs/SnO$_2$</td>
<td>Mixing process</td>
<td>NH$_3$</td>
<td>60 ppm</td>
<td>RT</td>
<td>~8</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>Graphene/SnO$_2$</td>
<td>Hydrothermal</td>
<td>NH$_3$</td>
<td>50 ppm</td>
<td>RT</td>
<td>~15.9</td>
<td>39</td>
</tr>
<tr>
<td>6</td>
<td>SnO$_2$ nanoparticles</td>
<td>Gram bean extract mediated</td>
<td>NH$_3$</td>
<td>600 ppm</td>
<td>RT</td>
<td>~34</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>Co-SnO$_2$ nanoparticles</td>
<td>Gram bean extract mediated</td>
<td>NH$_3$</td>
<td>100 ppm</td>
<td>RT</td>
<td>~43</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 3.26(a) shows the response curves for different gas concentrations at room temperature (~30 °C). The response curves show a linear increase in response to an increase in gas concentration. Figure 3.26(b) shows response recovery time vs gas concentration; wherein the response time is seen to decrease with increasing gas concentration while the recovery time increases. This is due to the fact that with the increasing gas concentration large numbers of surface sites are occupied by the gas within lesser time and the decomposition of NH$_3$ to N$_2$ and H$_2$O on the surface leads to slow recovery of the sensor. Figure 3.26(c) shows the gas response vs gas concentration plot which also shows a linear increase in response to an increase in NH$_3$ gas concentration. The NH$_3$ gas sensing mechanism consists of surface reactions between the pre-adsorbed oxygen over SnO$_2$ surface and NH$_3$ molecules, they
interact with each other and release electrons to SnO$_2$. The interaction of pre-adsorbed oxygen and NH$_3$ molecules on the surface of SnO$_2$ is indicated in Eqs:

\[
\begin{align*}
O_2^{\text{gas}} & \xrightarrow{\text{SnO}_2+\text{air}} O_2^{\text{ads}} \\
O_2^{\text{ads}} + e^- & \xrightarrow{\text{SnO}_2+\text{air}} O_2^-^{\text{ads}} \\
O_2^-^{\text{ads}} + e^- & \xrightarrow{\text{SnO}_2+\text{air}} 2O^-^{\text{ads}} \\
NH_3^{\text{gas}} & \leftrightarrow NH_3^{\text{ads}} \\
2NH_3^{\text{ads}} + 3O^-^{\text{ads}} & \leftrightarrow N_2 + 3H_2O + 3e^-
\end{align*}
\]

The release of electrons to SnO$_2$ results in an increase of carries thus leading to increase in surface conductivity of SnO$_2$ thin film and decrease in the barrier height at the grain boundaries between the nanocrystallites. The structural modifications in the SnO$_2$ nanoparticle, the generated oxygen vacancies and the chemisorbed oxygen on the sensor surface due to the incorporation of Co in SnO$_2$ lattice, plays an important role in enhancing the response to NH$_3$ gas$^{41}$. With 5 wt% Co doping in the SnO$_2$ lattice, the lattice expands and significant structural strain is induced. From the band structure of Co-doped SnO$_2$ obtained using DFT calculations, we can see the acceptor states generated near the lower conduction band edge. These states are responsible for the generation of oxygen vacancies$^{33, 42}$.

The optimum defect generation is expected with 5 wt% Co doping$^{33, 43}$, which exerts stronger positive influence on gas sensing properties. NH$_3$ is a reducing gas and the chemisorbed oxygen is reported to be strongly controlling the detection of reducing gases$^{41}$ also the oxygen chemisorption at the SnO$_2$ surface requires the participation of tin atom (Sn) and oxygen vacancy$^{44}$. Thus with a larger number of oxygen vacancies present, higher oxygen chemisorptions at SnO$_2$ surface is expected which results in higher gas response.
Figure 3.26(a) Response curves for different NH$_3$ gas concentrations, (b) Sensor response and recovery time vs NH$_3$ gas concentration, (c) Sensor response vs NH$_3$ gas concentration and (d) Gas selectivity of Co-doped SnO$_2$ sensor

Selectivity is another important sensor parameter. The responses of Co-doped SnO$_2$ sensors towards a variety of gasses including NO$_2$, H$_2$S, LPG, and NH$_3$ of 100 ppm at room temperature (30 °C) were explored to evaluate their selectivity. Figure 3.26(d) shows that the gas sensor of ‘Co-doped SnO$_2$’ exhibited excellent selectivity to NH$_3$ gas when compared to other gasses. The results suggest that the Co-doped SnO$_2$ thin film sensor can be fabricated to monitor NH$_3$ polluted air.
3.5 Biosynthesized Cu-doped SnO\textsubscript{2} nanoparticle thin films

3.5.1 X-ray Diffraction

Figure 3.27 shows the XRD patterns of (a) the pristine and (b) Cu doped SnO\textsubscript{2} nanoparticles (Rietveld refined) and the inset shows WH- plots of pristine and doped SnO\textsubscript{2}. The diffraction peaks of both the patterns in the spectra were indexed to the rutile phase of the SnO\textsubscript{2} and the lattice parameters were calculated to be $a=4.741$ Å, $c=3.189$ Å for pure SnO\textsubscript{2} and $a=4.744$ Å, $c=3.187$ Å for Cu doped SnO\textsubscript{2}, which is consistent with the literature values ($a=4.738$ Å, $c=3.186$ Å, JCPDS No. 71-0652), belonging to the space group of P42/mmm.

In order to consider the effect of strain on the nanoparticles, the crystallite size is calculated by Williamson-Hall (W-H) plot and Scherrer’s formula. The crystallite size from Scherrer’s formula is calculated by using the equation,
D=0.9λ/β Cos θ, Where D is the crystallite size, λ is the wavelength of X-ray used, and θ is the Bragg angle of diffraction peaks. The variation of β Cos θ with 4Sin θ gives the W-H plot wherein the crystallite size D and lattice strain η can be calculated\(^{21}\). The calculated crystallite size from W-H plot is found to be lower compared to size calculated using Scherrer’s formula. Also, the calculated sizes using both the methods show that the crystallite size of Cu-doped nanoparticles is smaller than pure SnO\(_2\) nanoparticles. This decrease in size is due to lattice distortion and induced strain\(^{25}\). The strain in the system is induced due to the difference in the ionic radius of Sn\(^{4+}\) and Cu\(^{2+}\) ions in octahedral coordination\(^{22}\). No characteristic peak of Cu or oxides of Cu were seen, which indicates that no new phase of Cu is created.

To further confirm the crystal structure and lattice parameters of the pristine and Cu-doped SnO\(_2\), Rietveld refinement was performed. The results obtained are tabulated in Table 3.8. These results confirm the changes in lattice constants due to Cu doping, which resulted in lattice strain and decreased crystallite size.
Table 3.8 Structural parameters of pure and Cu-doped SnO$_2$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure SnO$_2$</th>
<th>Cu-doped SnO$_2$</th>
</tr>
</thead>
<tbody>
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<td>Diffractometer</td>
<td>Bruker D8 Advance</td>
<td>Bruker D8 Advance</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK(\alpha_1)(1.5406 Å)</td>
<td>CuK(\alpha_1)(1.5406 Å)</td>
</tr>
<tr>
<td>2(\theta) range</td>
<td>20-80</td>
<td>20-80</td>
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<tr>
<td>Scan Step</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Peak Shape</td>
<td>Pseudo-Voigt</td>
<td>Pseudo-Voigt</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>SnO$_2$</td>
<td>Sn$<em>{0.95}$Cu$</em>{0.05}$O$_2$</td>
</tr>
<tr>
<td>Space group</td>
<td>P 42/m n m</td>
<td>P 42/m n m</td>
</tr>
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<td>a(Å)=b(Å)</td>
<td>4.74133</td>
<td>4.74385</td>
</tr>
<tr>
<td>c(Å)</td>
<td>3.18923</td>
<td>3.18715</td>
</tr>
<tr>
<td>c/a</td>
<td>0.672645</td>
<td>0.671849</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
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<td>71.72398</td>
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<td>Rp(%)</td>
<td>17.9</td>
<td>17</td>
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<tr>
<td>Rwp(%)</td>
<td>15.3</td>
<td>16.7</td>
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<tr>
<td>Rexp(%)</td>
<td>12.40</td>
<td>11.10</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>1.53</td>
<td>2.26</td>
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<tr>
<td>R$_{\text{Bragg}}$ (%)</td>
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<tr>
<td>R$_{\text{F}}$ (%)</td>
<td>1.59</td>
<td>1.34</td>
</tr>
<tr>
<td><strong>Crystallite size (Scherrer’s)</strong></td>
<td>~12</td>
<td>~9.9</td>
</tr>
<tr>
<td><strong>Crystallite size (WH-plot)</strong></td>
<td>~12.4</td>
<td>~9.1</td>
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<tr>
<td><strong>Strain</strong></td>
<td>-0.00145</td>
<td>-4.82E-04</td>
</tr>
</tbody>
</table>

3.5.2 Transmission Electron Microscopy

The TEM image of 5% Cu doped SnO$_2$ and corresponding size distribution plot are shown in Figure 3.28(a) and the inset, respectively. This TEM image confirms that the prepared pristine and Cu doped SnO$_2$ is in nano regime. No agglomeration of nanoparticles is seen, which is very much expected as the biomolecules present in the extract act as capping agents. The average crystallite size from TEM image of pristine SnO$_2$ reported in our previous
work\textsuperscript{23} was \(~12\) nm, while TEM image of Cu doped SnO\textsubscript{2} shows the clear formation of nanoparticles of \(~9\) nm. This confirms that doping of Cu in SnO\textsubscript{2} has decreased the particle size compared to pristine SnO\textsubscript{2}.

![Figure 3.28(a)](image)

Figure 3.28(a) The TEM image of 5% Cu doped SnO\textsubscript{2} and (inset) size distribution plot (b) SEM image of Cu-doped SnO\textsubscript{2} nanoparticles (c) FTIR spectra of [i] gram bean extract, [ii] as prepared Cu-doped SnO\textsubscript{2} and [iii] Cu-doped SnO\textsubscript{2} calcined at 600 °C (d) Raman spectra of pure and Cu-doped SnO\textsubscript{2} nanoparticles.

3.5.3 Scanning Electron Microscopy

The surface morphology of the biosynthesized Cu-doped SnO\textsubscript{2} nanoparticles was examined by SEM as shown in Figure 3.28(b). The micrograph shows Cu-doped SnO\textsubscript{2} nanoparticles calcined at 600 °C demonstrating spherical shaped nanoparticles with narrow size distribution. No major change in morphology of the Cu-doped SnO\textsubscript{2} nanoparticles was observed when compared to pure SnO\textsubscript{2}\textsuperscript{23}. 
3.5.4 Fourier Transform Infrared spectroscopy

Figure 3.28(c) Shows the room temperature FTIR spectra of (a) drop cast gram bean extract, (b) as prepared Cu-doped SnO₂ and (c) Cu-doped SnO₂ calcined at 600 °C. The results are similar to our previous reports²³ and they further, confirm the synthesis mechanism of the nanoparticles. The pectin biomolecule present in the gram bean extract is confirmed by the FTIR spectra. A typical IR absorption peak originating from the stretching mode of the Sn–OH bond is found for the pectin–Cu-SnO₂ composite sample at about 504 cm⁻¹; the remaining peaks in pectin–SnO₂ composite were induced by pectin, which is confirmed by comparing with the IR spectrum of the composite with that of the pectin³. The peaks obtained and their corresponding modes are tabulated in Table 3.9.

Table 3.9 Peaks and their corresponding modes in FTIR spectra of pectin–Cu-SnO₂ composite

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Peak Position</th>
<th>Mode of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>514 cm⁻¹</td>
<td>Sn-OH (stretching)</td>
</tr>
<tr>
<td>2</td>
<td>1030 cm⁻¹</td>
<td>C=O or C=C double bond of pectin</td>
</tr>
<tr>
<td>3</td>
<td>1386 and 1579 cm⁻¹</td>
<td>stretching bands of COO- groups of pectin</td>
</tr>
<tr>
<td>4</td>
<td>2925 cm⁻¹</td>
<td>carboxyl and CH₂ groups of pectin</td>
</tr>
</tbody>
</table>

The interactions between pectin and SnO₂ are strong, which could be confirmed from the retention of pectin peaks even after repeated washing of the samples. The peak at around 601 cm⁻¹ and 920 cm⁻¹ refers to Sn-O stretching modes of Sn-O-Sn, appearing even after the calcination at 600 °C.

3.5.5 Raman spectroscopy

Raman spectroscopy can be used to effectively analyze the vibrational modes within the system, thus it is an important tool to confirm doping and to understand its effect. The Raman spectra for pure and Cu doped SnO₂ samples is shown in Figure 3.28(d). A normal mode can be described by the 3n coordinates, where n is the number of atoms in the primitive cell. This gives the displacements of the atoms from their equilibrium positions⁷. Rutile SnO₂ having 6 atoms unit cell gives out 18 possible vibrations. The normal lattice
vibrations at the Γ point of the Brillouin zone on the basis of group theory are as follows\(^8\):

$$\Gamma = \Gamma_1^{+}(A_{1g}) + \Gamma_2^{+}(A_{2g}) + \Gamma_3^{+}(B_{1g}) + \Gamma_4^{+}(B_{2g}) + \Gamma_5^{-}(E_g) + 2\Gamma_1^{-}(A_{2u}) + 2\Gamma_4^{-}(B_{1u}) + 4\Gamma_5^{+}(E_u).$$

From the Raman spectra, we can clearly see that the pure SnO\(_2\) exhibits the obvious A\(_{1g}\) mode at 634 cm\(^{-1}\) and Eg mode at 476 cm\(^{-1}\), but the intensity of A\(_{1g}\) mode reduces with the 5 wt% Cu doping and also the Eg mode shifts to lower wavenumber. Similar observation of a reduction in the intensity and the shift of peaks to lower wavenumber on doping of Cu in SnO\(_2\) has been reported earlier\(^{25}\) wherein, both the phenomena are attributed to a reduction in size caused by copper doping. Apart from these obvious vibration modes, a broad peak observed at 572 cm\(^{-1}\) is attributed to the in-plane oxygen vacancies which are energetically favorable and easily appear on the surface of small NCs demonstrating a large surface-to-volume ratio\(^{45}\). Thus, this confirms the generation of a large number of oxygen vacancies in the Cu-doped SnO\(_2\) system. These generated oxygen vacancies are responsible for larger chemisorptions of oxygen species resulting in higher gas sensing response\(^{44}\)

### 3.5.6 UV-Vis spectroscopy

![Figure 3.29(a)](image)

**Figure 3.29(a)** Absorbance spectra and (b) \((\alpha h\nu)^2\) vs \(h\nu\) plot of pure and Cu-doped SnO\(_2\) nanoparticles

The effect of doping on optical properties of semiconducting nanoparticles can be effectively studied using absorption spectroscopy. As the optical absorbance is governed by several factors, such as band gap, oxygen deficiency, surface roughness and impurity centres\(^{16}\). **Figure 3.29(a)** shows
the absorption spectra of pure and Cu doped SnO$_2$ nanoparticles. Absorbance spectra show an ultraviolet cut-off around 250-290 nm, which could be attributed to the photoexcitation of electrons from valence band to conduction band. The Tauc’s relation is used to calculate the bandgap of the pure and Cu-doped nanoparticle thin films by extrapolating the plot of $(\alpha h\nu)^2$ vs $h\nu$ (Figure 3.29(b)). The band gap of pristine SnO$_2$ and Cu-doped SnO$_2$ were found to be 3.54 eV and 3.08 eV, respectively. The doping of Cu decreases the crystallite size, thus increase in band gap with the Cu doping is expected (quantum confinement effect). However, in this case, the bandgap is found to decrease with a decrease in particle size. A similar phenomenon was observed by Ahmed et al.$^{16}$ for samples containing 5% Ni concentration, where the SnO$_2$–SnO$_{2-x}$ alloying effect was considered responsible for the band gap narrowing. Urbach type absorption is the absorption below band gap (inset in Figure 3.29(b)). Such type of absorption occurs when defects in the system increase. With Cu doping, the Urbach energy increases, which means that the distortion increases.$^{27}$ The increase in distortion can be due to two reasons, either Cu is creating levels nearby conduction band and or incorporation of Cu in the system is producing oxygen vacancies which are making levels nearby the conduction band.

The inset in Figure 3.29(a) shows the higher absorption in near infra-red region. This absorption is due to the d-d transition of an electron in Cu$^{2+}$. The transition takes place from ground state $^2E_g$ to excited state $^2T_{2g}$ of Cu$^{2+}$ in octahedral coordination.$^{28}$

The relation between structural disorder and optical changes has been further rationalized by the detailed theoretical study of electronic structure of Cu-doped and undoped SnO$_2$ system.

### 3.5.7 Electronic structure investigation

To study the effect of Cu doping on SnO$_2$ DFT calculations have been performed using 2x2x2 supercells of pure and doped SnO$_2$ system. The substitution of one Sn atom by Cu in a 48 atom SnO$_2$ supercell (as shown in inset Figure 3.30(c)) affects all the bond length within the system. All the bond lengths, i.e., Sn-O and Cu-O in the Sn$_{16}$O$_{32}$ and CuSn$_{15}$O$_{32}$ supercell,
respectively, are listed in Table 3.10. We have found changes in the bond lengths of Cu doped SnO$_2$ system compared to the undoped SnO$_2$.

**Table 3.10 Bond lengths in Sn$_{16}$O$_{32}$ and CuSn$_{15}$O$_{32}$ supercell**

<table>
<thead>
<tr>
<th>System</th>
<th>Bond lengths (Å)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{16}$O$</em>{32}$</td>
<td>Sn-O 2.0627, 2.0784</td>
<td></td>
</tr>
<tr>
<td>CuSn$<em>{15}$O$</em>{32}$</td>
<td>Sn-O 2.0743, 2.0919, 2.0769, 2.0643, 2.0516, 2.0691, 2.0605, 2.0779, 2.0799, 2.0792, 2.0599, 2.0793, 2.079, 2.066, 2.0806, 2.069, 2.0722, 2.086, 2.0467</td>
<td>Cu-O 2.0044, 1.9982</td>
</tr>
</tbody>
</table>

When tested for both spin-polarized and non-magnetic calculation, the ground state energy for the pure system was found to be the same, but the spin-polarized system was found to be 61 meV more stable for the Cu-doped system. Thus, the spin-polarized structure was used to calculate its band structure and density of state (DOS) in both the cases. The band structure pure and Cu-doped systems are shown in Figure 3.30(a) and (b) respectively. From the band structure, the upper part of the valence band was found to be mainly made of O2p states, while the lower part of the conduction band is dominated by Sn5s states. Also, it shows that both the systems have a direct bandgap. The band gap value obtained from DFT calculation is not reliable, but it can be seen that two levels within the band gap region are generated with the inclusion of Cu in the system. Along with this, there are many reports on the generation of oxygen vacancies with Cu-doping in the SnO$_2$ system$^{46-48}$. The inclusion of Cu in the system produces two levels within the band gap region. The Cu is in octahedral coordination, so according to crystal field theory, in the ground state, its d states split up into $e_g$ and $t_{2g}$ states. Similar splitting of the d level into $e_g$ and $t_{2g}$ states as in Figure 3.30(d) is reported earlier$^{25}$ Along with this splitting, the oxygen vacancy states are also formed in the band gap region$^{49}$. These states in the band gap region are likely responsible for the reduction of bandgap with Cu doping$^{49}$. 


Figure 3.30 Bandstructure calculated from 2x2x2 supercell of (a) pure Sn$_{16}$O$_{32}$ (b) CuSn$_{15}$O$_{32}$ and Total DOS calculated from 2x2x2 supercell of (c) pure SnO$_2$ and Cu-doped SnO$_2$ (d) DOS from Sn-d and Cu-d

3.5.8 Gas sensing

Gas sensing behaviors of the biosynthesized Cu-doped SnO$_2$ sensor were explored after gas injection. Table 3.11 shows the H$_2$S gas sensing properties of biosynthesized Cu-doped SnO$_2$ and those reported in the literature for better comparison of the properties.

The gas sensing properties include response, recovery time, operating temperature and gas concentration. Figure 3.31(a) shows the response curves for H$_2$S gas with varying gas concentrations at an operating temperature of 200 °C. The response curve shows a linear increase in response to increasing gas concentration. Figure 3.31(b) shows response recovery time vs the gas concentration; wherein, the response time is observed to decrease with increasing gas concentration, while the recovery time increases. This is due to the fact that, with the increasing gas concentration, large numbers of surface sites are occupied by the gas within less time and the decomposition of H$_2$S to SO$_2$ and H$_2$O on the surface leads to slow recovery of the sensor. Figure 3.31(c) shows the gas response vs gas concentration plot, which also shows a
linear increase in response to an increase in H$_2$S gas concentration. A response of 38.33% is obtained at 100 ppm. The H$_2$S gas sensing mechanism consists of surface reactions between the pre-adsorbed oxygen over SnO$_2$ surface and H$_2$S molecules, which interact with each other releasing electrons to SnO$_2$. The interaction of pre-adsorbed oxygen and H$_2$S molecules on the surface of SnO$_2$ is indicated in Eqs:

$$H_2S + 3O_2 \rightarrow SO_2(gas) + 2H_2O + 6e^-$$

**Table 3.11 Comparison of gas-sensing characteristics of biosynthesized Cu-SnO$_2$ in present work and those reported in the literature.**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnO$_2$ multi-tube array</td>
<td>Papilio maackii butterfly wings</td>
<td>H$_2$S</td>
<td>5 ppm</td>
<td>RT</td>
<td>~1.45</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Fe$_2$O$_3$</td>
<td>Papilio paris butterfly wings</td>
<td>H$_2$S</td>
<td>50 ppm</td>
<td>180 °C</td>
<td>~19.2</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>ZnO</td>
<td>Fir-Wood</td>
<td>H$_2$S</td>
<td>50 ppm</td>
<td>332 °C</td>
<td>~200</td>
<td>52</td>
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<tr>
<td>4</td>
<td>A gold-binding M13 bacteriophage</td>
<td>M13 bacteriophage</td>
<td>H$_2$S</td>
<td>0.5 ppm</td>
<td>RT</td>
<td>~35</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>Au-SnO$_2$ NTs</td>
<td>protein (apoferitin)</td>
<td>H$_2$S</td>
<td>5ppm</td>
<td>300 °C</td>
<td>34</td>
<td>54</td>
</tr>
<tr>
<td>6</td>
<td>SnO$_2$</td>
<td>eggshell membrane</td>
<td>H$_2$S</td>
<td>50ppm</td>
<td>300 °C</td>
<td>~7</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>CuO fiber</td>
<td>cotton fiber</td>
<td>H$_2$S</td>
<td>100ppm</td>
<td>200°C</td>
<td>~3</td>
<td>56</td>
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<tr>
<td>8</td>
<td>Cu-SnO$_2$</td>
<td>Gram bean extract mediated synthesis</td>
<td>H$_2$S</td>
<td>100 ppm</td>
<td>200 °C</td>
<td>~38</td>
<td>This work</td>
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</table>

The release of electrons to SnO$_2$ results in an increase of carries, thus leading to increase in surface conductivity of SnO$_2$ thin film and decrease in the barrier height at the grain boundaries between the nanocrystallites.
Discussion

Though there are many reports on enhanced H$_2$S sensing response for Cu-doped SnO$_2$ nanostructures, the bio green synthesized Cu-doped SnO$_2$ has further contributed to the enhancement of the response. As explained above, the bio-green synthesis consists of a coating of organic molecules on the nanoparticle surface, which on annealing oxidizes to form carbon-free oxide nanoparticles. As per our previous report$^{57}$, the biomolecules coated over the nanoparticle surface completely oxidize above 430 °C to form carbon-free pure oxide nanoparticles. The biomolecules capped onto the surface help prevent aggregation, thereby restricting the growth of the particle size. Apart from this, the biomolecules while decomposing on the SnO$_2$ surface, abstracts the surface oxygen for self-oxidation thereby contributing to the generation of a large number of oxygen vacancies. This phenomenon is further supported by Cu ions present in the lattice, which are reported to weaken the metal oxygen bond in the SnO$_2$ lattice. Choudhary et. al.$^{58}$ reported that the doping of
transition metal in zirconia-modified catalysts strongly enhances the reactivity of the lattice oxygen, which is due to the creation of crystal defects and also increases the mobility of the lattice oxygen\textsuperscript{59}. Thus, Cu-doped SnO\textsubscript{2} nanoparticles synthesized using bio-green approach consists of a large number of oxygen vacancies, which is also confirmed by the Raman analysis. With 5 wt\% Cu doping in the SnO\textsubscript{2} lattice, the lattice contracts, and significant negative structural strain is induced. The structural changes found in the XRD and Raman results are also confirmed by the changes in the bond lengths obtained from DFT calculation found in Cu doped SnO\textsubscript{2} system compared to the undoped SnO\textsubscript{2}. From the band structure of Cu doped SnO\textsubscript{2} obtained using DFT calculations, we can see the acceptor states generated near the lower conduction band edge. These states are responsible for the generation of oxygen vacancies\textsuperscript{33, 60}. The observed splitting of d state as shown in Figure 3.30(d) is due to Cu substitution on octahedral Sn site. This substitution is further confirmed from the peak in the near-IR region in UV-Vis spectra, the peak appears due to the transition of an electron from \textsuperscript{2}E\textsubscript{g} to \textsuperscript{2}T\textsubscript{2g}. The optimum defect generation is expected with 5 wt\% Cu doping\textsuperscript{33, 43}, which exerts stronger positive influence on the gas sensing properties.

H\textsubscript{2}S is a reducing gas and the chemisorbed oxygen is reported to be strongly controlling the detection of reducing gases\textsuperscript{41} and also the oxygen chemisorption at the SnO\textsubscript{2} surface requires the participation of tin atom (Sn) and oxygen vacancy\textsuperscript{41, 44}. Hence, a large number of oxygen vacancies indicates higher chemisorption of oxygen on the SnO\textsubscript{2} surface resulting in the observed enhanced gas response.

Selectivity is another important sensor parameter. The responses of Cu-doped SnO\textsubscript{2} sensors towards a variety of gasses including NO\textsubscript{2}, H\textsubscript{2}S, LPG, and NH\textsubscript{3} of 100 ppm at 200 °C temperature were explored to evaluate their selectivity. Figure 3.31(d) shows that the Cu-doped SnO\textsubscript{2} gas sensor exhibits excellent selectivity to H\textsubscript{2}S gas when compared to other gasses (NH\textsubscript{3}, LPG, and NO\textsubscript{2}). The results suggest that the Cu-doped SnO\textsubscript{2} thin film sensor can be fabricated to monitor H\textsubscript{2}S gas in the polluted air.
3.6 Biosynthesized Au-doped SnO$_2$ nanoparticle thin films

3.6.1 X-ray Diffraction

Figure 3.32 represents the XRD pattern of (a) pristine and (b) Au-doped SnO$_2$ nanoparticles (Rietveld refined) while the Inset shows W-H plots for pristine and Au-doped SnO$_2$. The diffraction peaks of both the patterns in the spectra were indexed to the rutile phase of SnO$_2$ and the lattice parameters were calculated to $a = 4.741 \, \text{Å}$, $c = 3.189 \, \text{Å}$ for pure SnO$_2$ and $a = 4.742 \, \text{Å}$, $c = 3.189 \, \text{Å}$ for Au-doped SnO$_2$, which is consistent with the literature values ($a = 4.738 \, \text{Å}$, $c = 3.186 \, \text{Å}$, JCPDS No. 71-0652), belonging to the space group of P4$_2$/mm.

![XRD pattern of the (a) pristine and (b) (Rietveld refined) Au-doped SnO$_2$ nanoparticles.](image)

In order to check the effect of strain on crystallite size, the crystallite size was calculated by Scherrer’s formula and Williamson-Hall (W-H) plot as well. The differences of two sizes yield the required information. The crystallite size from Scherrer’s formula, $D = 0.91\lambda / \beta \cos \theta$, where $D$ is the crystallite size, $\lambda$ is the wavelength of X-ray used, and $\theta$ is the Bragg angle of diffraction peaks.
The variation of $\beta \cos \theta$ with $4 \sin \theta$ gives the W-H plot from which the crystallite size $D$ and lattice strain $\eta$ can be calculated\textsuperscript{21}. The results from both the methods show that the crystallite size increases with doping of Au. Due to Au doping, the system and lattice planes get distorted, and thus the crystallite size increases. We can see a clear difference between sizes calculated by both the method and which is due to the lattice strain in the system. The positive strain implies an expansion in the system and hence doped system has higher W-H calculated crystallite size values compared to the crystallite sizes calculated by Scherer equation. No characteristic peak of Au was seen which indicates that no new phase of Au is created.

### Table 3.12 Structural parameters of pure and Au-doped SnO$_2$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pure SnO$_2$</th>
<th>Au-doped SnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffractometer</td>
<td>Bruker D8 Advance</td>
<td>Bruker D8 Advance</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuK$_{\alpha 1}$ (1.5406Å)</td>
<td>CuK$_{\alpha 1}$ (1.5406Å)</td>
</tr>
<tr>
<td>2$\theta$ range</td>
<td>20-80</td>
<td>20-80</td>
</tr>
<tr>
<td>Scan Step</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Peak Shape</td>
<td>Pseudo-Voigt</td>
<td>Pseudo-Voigt</td>
</tr>
<tr>
<td>Chemical Formula</td>
<td>SnO$_2$</td>
<td>Sn$<em>{0.95}$Au$</em>{0.05}$O$_2$</td>
</tr>
<tr>
<td>Space group</td>
<td>P 42/m n m</td>
<td>P 42/m n m</td>
</tr>
<tr>
<td>$a$(Å)=$b$(Å)</td>
<td>4.74133</td>
<td>4.74255</td>
</tr>
<tr>
<td>$c$(Å)</td>
<td>3.18923</td>
<td>3.18926</td>
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<tr>
<td>$c/a$</td>
<td>0.672645</td>
<td>0.67248</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
<td>71.69456</td>
<td>71.73236</td>
</tr>
<tr>
<td>Rp(%)</td>
<td>17.9</td>
<td>11.1</td>
</tr>
<tr>
<td>Rwp(%)</td>
<td>15.3</td>
<td>10.8</td>
</tr>
<tr>
<td>Rexp(%)</td>
<td>12.40</td>
<td>9.45</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.53</td>
<td>1.32</td>
</tr>
<tr>
<td>$R_{\text{Bragg}}$ (%)</td>
<td>2.41</td>
<td>1.90</td>
</tr>
<tr>
<td>$R_e$ (%)</td>
<td>1.59</td>
<td>4.33</td>
</tr>
<tr>
<td><strong>Crystallite size (Scherrer’s)</strong></td>
<td>~12 nm</td>
<td>~25nm</td>
</tr>
<tr>
<td><strong>Crystallite size (WH-plot)</strong></td>
<td>~12.4 nm</td>
<td>~29nm</td>
</tr>
<tr>
<td><strong>Strain</strong></td>
<td>-0.00145</td>
<td>5.58E-04</td>
</tr>
</tbody>
</table>
Also with Au doping, the peak positions slightly shift to the lower angles indicating a slight increase of the lattice parameter due to the strain on the lattice derived from the incorporation Au ions\textsuperscript{61}. The ionic radius of Sn and Au in octahedral coordination is 0.69 Å and 0.85 Å, respectively\textsuperscript{22}, thus the Au ion prefers to occupy the Sn site. The ionic size of Au\textsuperscript{2+} being larger results in expansion of the system, which ultimately increases the positive strain listed as shown in Table 3.12. The interplanar spacing in pristine and Au 5 wt% doped SnO\textsubscript{2} nanosystem for 110 plane calculated from XRD is found to be 0.34 and 0.35 nm, respectively. To further confirm the crystal structure and lattice parameters of the pristine and Au-doped SnO\textsubscript{2}, Rietveld refinement was performed. The results obtained are tabulated in Table 3.12. These results confirm the slight increase in lattice constants due to Au doping, which resulted in increased crystallite size and lattice strain.

![Figure 3.33](image)

**Figure 3.33(a)** The TEM image (inset) size distribution histogram. (b) SEM image (c) FTIR spectra of [i] gram bean extract [ii] as-prepared Au- SnO\textsubscript{2}, [iii] Au-SnO\textsubscript{2} calcined at 600 °C (d) Raman spectra of pure and Au-doped SnO\textsubscript{2} nanoparticles.
3.6.2 Transmission Electron Microscopy

Figure 3.33(a) shows the TEM image of 5% Au-doped SnO\textsubscript{2} and the inset shows the corresponding size distribution plot. TEM image confirms the prepared Au-doped SnO\textsubscript{2} nanoparticles to be in nano regime. No agglomeration of nanoparticles can be seen, which is very much as expected as the biomolecules present in the extract act as surfactants. The average crystallite size from TEM image of pristine SnO\textsubscript{2} reported in our previous work\textsuperscript{23} was \(\sim 12\) nm, while TEM image of Au-doped SnO\textsubscript{2} shows the clear formation of nanoparticles of \(\sim 25\) nm. This confirms that doping of Au in SnO\textsubscript{2} has increased the particle size compared to pristine SnO\textsubscript{2}.

3.6.3 Scanning Electron Microscopy

The surface morphology of the biosynthesized Au-doped SnO\textsubscript{2} nanoparticles was examined by SEM. Figure 3.33(b) shows the micrograph of Au-doped SnO\textsubscript{2} nanoparticles calcined at 600 °C demonstrating spherical shaped nanoparticles with narrow size distribution. No major change in morphology of the Au-doped SnO\textsubscript{2} nanoparticles was observed when compared to pure SnO\textsubscript{2}\textsuperscript{23}.

3.6.4 Fourier Transform Infrared spectroscopy

Figure 3.33(c) shows the room temperature FTIR spectra of drop cast (i) gram bean extract, (ii) as prepared Au-doped SnO\textsubscript{2} and (iii) Au-doped SnO\textsubscript{2} calcined at 600 °C. The results are similar to our previous reports\textsuperscript{23}. The biomolecule pectin present in the gram bean extract can be confirmed by the FTIR spectra. A typical IR absorption peak originating from stretching mode of the Sn–OH bond is found for the pectin–Au-SnO\textsubscript{2} composite sample at about 508 cm\textsuperscript{-1}; the remaining peaks in pectin–SnO\textsubscript{2} composite are induced by pectin, which is confirmed by comparing the IR spectrum of the composite with that of the pectin\textsuperscript{3}. The peaks obtained and their corresponding modes are tabulated in Table 3.13.

The strong interactions between pectin and SnO\textsubscript{2} can be confirmed from the retention of pectin peaks even after repeated washing of the samples. The peaks at around 601 cm\textsuperscript{-1} and 920 cm\textsuperscript{-1} refer to Sn-O stretching modes of Sn-
O-Sn, which appear even after calcination at 600 °C. From the synthesis mechanism summarized in Figure 3.1, we conclude that the pectin molecules are released in the extract due to autolysis of the cell walls when gram beans are soaked in de-ionised water\(^4\). Pectin molecules have a tendency to bind metal ions\(^6\), thus when tin chloride is added to the extract, the tin ions get bound to the pectin molecules as shown in Figure 3.1. Tin-hydroxide-pectin gel shrinks\(^2\) as the pH of the solution is increased and this inhibits the further growth of the nanoparticles. Subsequently, after calcination of the sample, we get very small-sized nanoparticles with narrow size distribution.

**Table 3.13** Peaks and their corresponding modes in FTIR spectra pectin–Au-SnO\(_2\) composite

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Peak Position</th>
<th>Mode of vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>514 cm(^{-1})</td>
<td>Sn-OH (stretching)</td>
</tr>
<tr>
<td>2</td>
<td>1030 cm(^{-1})</td>
<td>C=O or C=C double bond of pectin</td>
</tr>
<tr>
<td>3</td>
<td>1386 and 1579 cm(^{-1})</td>
<td>stretching bands of COO- groups of pectin</td>
</tr>
<tr>
<td>4</td>
<td>2925 cm(^{-1})</td>
<td>carboxyl and CH(_2) groups of pectin</td>
</tr>
</tbody>
</table>

**3.6.5 Raman spectroscopy**

Raman spectroscopy is an effective tool to study the structural and vibrational properties of a material. The Au-doped SnO\(_2\) samples were investigated using Raman spectroscopy to confirm the substitution of Au ions in SnO\(_2\) lattice and to understand its effect on vibrational properties. The Raman spectra for pure and Au-doped SnO\(_2\) sample is shown in Figure 3.33(d). A normal mode can be described by the 3\(n\) coordinates, where \(n\) is the number of atoms in the primitive cell. This gives the displacements of the atoms from their equilibrium positions\(^7\). Rutile SnO\(_2\) having 6 atoms unit cell gives out 18 possible vibrations. The normal lattice vibrations at the \(\Gamma\) point of the Brillouin zone on the basis of group theory are as follows\(^8\):

\[
\Gamma = \Gamma_1^+ (A_{1g}) + \Gamma_2^+ (A_{2g}) + \Gamma_3^+ (B_{1g}) + \Gamma_4^+ (B_{2g}) + \Gamma_5^- (E_g) + 2\Gamma_1^- (A_{2u}) + 2\Gamma_4^- (B_{1u}) + 4\Gamma_5^+ (E_u).
\]

From the Raman spectra, we can clearly see that the pure SnO\(_2\) exhibits the obvious \(A_{1g}\) mode at 634 cm\(^{-1}\) and \(E_g\) mode at 476 cm\(^{-1}\) but the intensity of \(A_{1g}\) mode gets reduced with the 5 wt\% Au doping. The reduction in the intensity of \(A_{1g}\) mode can be attributed to the lattice distortion due to the
substitution of Au at the Sn site\textsuperscript{25}. Along with the distortion, generation of oxygen vacancies is another possible reason for the reduction of the peak intensity\textsuperscript{62}. The substitution of the metal ions in the lattice is reported to weaken the metal oxygen bond in the SnO\textsubscript{2} lattice. Choudhary et al.\textsuperscript{58} reported increased reactivity of the lattice oxygen due to the doping of metals. This increase in the reactivity of the lattice oxygen was surmised to be due to the creation of crystal defects and an increase in the mobility of lattice oxygen\textsuperscript{59}.

### 3.6.6 UV-Vis spectroscopy

![Absorbance spectra and (αhν)\textsuperscript{2} vs. hν plot of pure and Au-doped SnO\textsubscript{2} nanoparticles.](image)

**Figure 3.34(a)** Absorbance spectra and **(b)** (αhν)\textsuperscript{2} vs. hν plot of pure and Au-doped SnO\textsubscript{2} nanoparticles.

Absorption spectroscopy is a powerful non-destructive technique to have a better understanding of the effect of Au doping on optical properties of semiconducting nanoparticles. The absorption spectra of pure and Au-doped SnO\textsubscript{2} nanoparticles are shown in **Figure 3.34(a)**. The absorbance is expected to depend on several factors such as band gap, oxygen deficiency, surface roughness and impurity centers. Absorbance spectra show an ultraviolet cut-off around 250-290 nm, which can be attributed to the photoexcitation of electrons from valence band to conduction band. The bandgap of the pure and Au-doped nanoparticle thin films was calculated by extrapolating the plot of (αhν)\textsuperscript{2} vs hν using the Tauc’s relation. The prepared pristine SnO\textsubscript{2} has a band gap of 3.54 eV, while its band gap slightly increases to 3.56 eV with the Au doping. Similar results were also observed for Au-doped SnO\textsubscript{2} synthesized by magnetron reactive sputtering\textsuperscript{63}. Urbach type absorption is the absorption below band gap (inset **Figure 3.34(b)**). When defects in the system increase
then the below band absorption occurs. With Au doping the Urbach energy increases, which mean that the distortion increases\textsuperscript{27}.

The inset in Figure 3.34(a) shows the higher absorption in near infra-red region. This peak is due to the d-d transition of electrons in Au ion. The transition takes place from ground state \( ^2\text{Eg} \) to excited state \( ^2\text{T}_{2g} \) of Au in octahedral coordination\textsuperscript{28}.

### 3.6.7 Gas Sensing

![Figure 3.35(a)](image)

**Figure 3.35(a)** Response curves for varying gas concentrations, (b) sensor response and recovery time vs NO\(_2\) gas concentration, (c) sensor response vs NO\(_2\) gas concentration and (d) gas selectivity of the Au-doped SnO\(_2\) sensor.

Gas-sensing behaviors of the biosynthesized Au-doped SnO\(_2\) sensor were explored after gas injection. **Figure 3.35(a)** shows the response curves for different gas concentrations of NO\(_2\) at 200 \(^\circ\)C temperature. The response curve shows a linear increase in response with an increase in gas concentration. **Figure 3.35(b)** shows the response and recovery time as a function of gas concentration. The response time is observed to decrease with increasing gas concentration while the recovery time increases. This may be due to the
heavier nature of NO₂ and the reaction products which delay the desorption of the gas and species from the interface after the interaction, resulting in a decrease in desorption rate\textsuperscript{17}. Figure 3.35(c) shows gas response vs gas concentration plot which also shows a linear increase in response to increasing NO₂ gas concentration. A response of 30.21% is obtained at 100 ppm. Table 3.14 shows the comparison of gas-sensing characteristics of Au-doped SnO₂ sensing material in the present work and those reported in the literature. The biomaterials used for synthesis are used either as templates or as binders. The use of biomaterials such as butterfly wings restricts their large scale industrial use, whereas the bio-green synthesis method reported in this work gives promising results with suitability for large-scale industrial production.

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Sensing Material</th>
<th>Biomaterial</th>
<th>Analyte gas</th>
<th>Gas conc.</th>
<th>Response</th>
<th>Ref. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>quasi-honeycomb like Fe₂O₃</td>
<td>Papilio Paris butterfly wings</td>
<td>NO₂</td>
<td>50 ppm</td>
<td>~5</td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>A gold-binding M13 bacteriophage</td>
<td>M13 bacteriophage</td>
<td>NO₂</td>
<td>0.5 ppm</td>
<td>~5</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>Co₂O₃-carbon hybrids</td>
<td>Trogonoptera Brookiana butterfly wings</td>
<td>NO₂</td>
<td>100 ppm</td>
<td>14.7</td>
<td>64</td>
</tr>
<tr>
<td>4</td>
<td>Ni-CoOOH</td>
<td>Morpho butterfly wings</td>
<td>NO₂</td>
<td>100 ppm</td>
<td>~1</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>Au-SnO₂ nanoparticles</td>
<td>Gram bean extract mediated synthesis</td>
<td>NO₂</td>
<td>100 ppm</td>
<td>~30</td>
<td>This work</td>
</tr>
</tbody>
</table>

It is well known that the NO₂ sensing mechanism of SnO₂ depends on the surface oxygen adsorbed on the SnO₂ nanoparticles surface. The sensing mechanism involving adsorption of oxygen species on the surface of tin oxide nanoparticles abstract electrons, and thus, cause an increase in the potential barrier at the grain boundaries. The gas molecules interact with the oxygen species and produce a notable change in the electronic property of the material. Thus, the density of oxygen species on the surface defines the rate of reaction and catalytic property. NO₂ is an oxidizing gas with electron affinity much higher than oxygen (0.48 eV). Thus, NO₂ can interact with SnO₂ by trapping electrons directly through the surface oxygen ions thereby forming new surface electron acceptor levels\textsuperscript{18-19}.  

[This work]
The interaction of pre-adsorbed oxygen and NO\textsubscript{2} molecules on the surface of SnO\textsubscript{2} is indicated in Eqs:

\[ O\textsubscript{2}\text{gas} \overset{Au-SnO\textsubscript{2}+ air}{\longrightarrow} O\textsubscript{2}(ads) \]
\[ O\textsubscript{2}(ads) + e^{-} \overset{Au-SnO\textsubscript{2}+ air}{\longrightarrow} O\textsubscript{2}^{-}(ads) \]
\[ O\textsubscript{2}^{-}(ads) + e^{-} \overset{Au-SnO\textsubscript{2}+ air}{\longrightarrow} 2O^{-}(ads) \]
\[ NO\textsubscript{2}(gas) \leftrightarrow NO\textsubscript{2}(ads) \]
\[ NO\textsubscript{2}(ads) + O\textsubscript{2}^{-}(ads) + 2e^{-} \leftrightarrow NO\textsubscript{2}^{-}(ads) + 2O^{-}(ads) \]

These series of reactions result in the further decrease in concentration of electrons on the surface of SnO\textsubscript{2}, which lead to the increase in resistivity of the material. This change in resistivity can be used for the detection of NO\textsubscript{2}. There are many reports\textsuperscript{66-71} for enhanced gas sensing behaviors of SnO\textsubscript{2} nanoparticles decorated with Au nanoparticles and the mechanism is explained by “spill-over effect”, meaning that the Au particles enhance the surface of the active metal oxide with oxygen species. However, the Au-doped SnO\textsubscript{2} nanoparticles in this work showed no evidence of forming metallic particles either at the surface or in the interior of SnO\textsubscript{2} nanoparticles. This is confirmed by the TEM results. On the basis of the TEM observations and the previous report\textsuperscript{72}, the first principle calculations for the formation energies of Au dopants in SnO\textsubscript{2} reveals that Au prefers the substitutional site. Thus, in the present case, the enhancement in response is supposed to be explained by the structural defects generated due to the incorporation of the Au ions in the SnO\textsubscript{2} lattice. Along with this, acceptor-compensated charge transport mechanism is supposed to be responsible for the enhanced gas sensing behavior\textsuperscript{72}. Selectivity is another important sensor parameter. The responses of Au-doped SnO\textsubscript{2} sensors towards a variety of gasses including NO\textsubscript{2}, H\textsubscript{2}S, LPG, and NH\textsubscript{3} of 100 ppm at 200 °C temperature were explored to evaluate their selectivity. Figure 3.35(d) shows that the gas sensor of ‘Au-doped SnO\textsubscript{2}’ exhibits excellent selectivity to NO\textsubscript{2} gas when compared to other gasses. The results suggest that the Au-doped SnO\textsubscript{2} thin film sensor can be fabricated to monitor NO\textsubscript{2} gas from the polluted air. In summary, the NO\textsubscript{2} sensing performances of SnO\textsubscript{2} nanoparticle thin film were improved greatly by Au doping. This study provides novel insights as well as aids the development of next-generation green chemical sensors.
3.7 References


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54. Jang, J. S.; Kim, S. J.; Choi, S. J.; Kim, N. H.; Hakim, M.; Rothschild, A.; Kim, I. D. Thin-walled SnO$_2$ nanotubes functionalized with Pt and Au catalysts via the protein templating route and their selective detection of


