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SnO₂ Nanoparticle- Reduced Graphene Oxide Hybrids for NO₂ Sensing

(Cited work: Verma et al., ACS Appl. Nano Mater. 2023, 5, 19053–19061)

3.1 Introduction

Various synthesis methods such as hydrothermal, solvothermal, and sol-gel are adopted in literature to synthesize SnO₂-rGO nanocomposites/ nanohybrids resulting in a p-n heterojunction between rGO and SnO₂ lattice, which broadly impact the performances of these heterostructures [Ravichandran et al., 2018; Mao et al., 2012]. The SnO₂-rGO nanocomposites performed best at room temperature but suffered from high response/ recovery time (Figure 3.1).

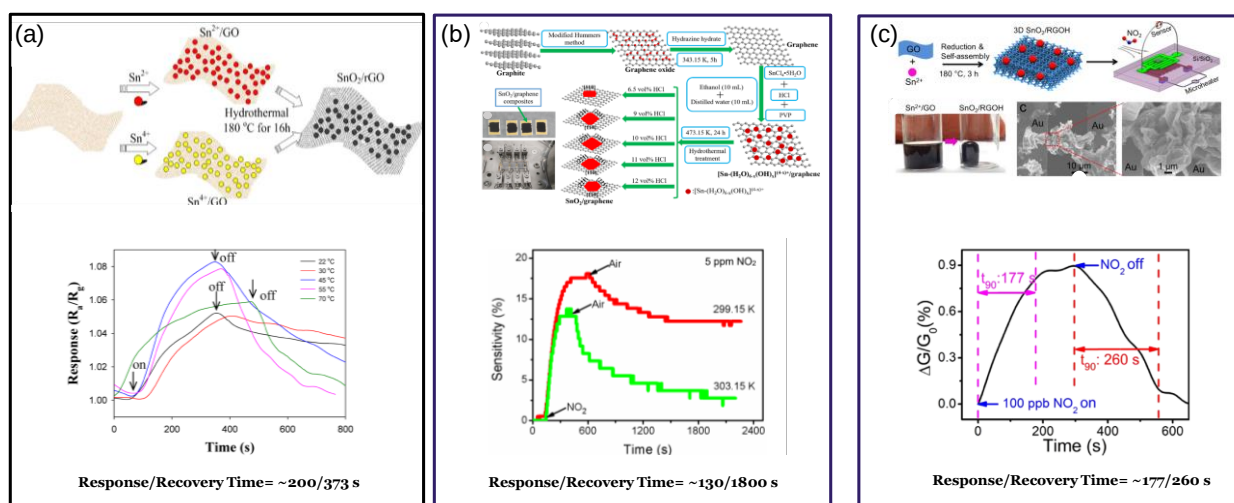


Figure 3.1: (a-c) NO₂ sensing characteristics of SnO₂-rGO synthesized using different synthesis methodologies. Figures in a-c are adapted from [Li et al., 2015], [Zhang et al., 2019a] and [Wu et al., 2020], respectively.

For example, Li *et al.*, synthesized a 3D SnO₂-rGO hybrid sensor with the response of 11.2 at 110 ppm NO₂ operable at 55 °C with a high response and recovery time of 200/ 373 s respectively [Li et al., 2015]. Zhang *et al.* explored the tin oxide nanocrystal-loaded graphene oxide showing a relatively better response time of 130 s but high recovery time limit room temperature operation of sensor [Zhang et al., 2019a]. Wu *et al.*, synthesized 3D SnO₂- rGOH nanohybrid with the good response towards NO₂ operable at 25 °C but exhibits high response/recovery time (177/260 sec) [Wu et al., 2020]. So, to tackle these issues, tuning the interaction between SnO₂ and rGO can be one possible way. SnO₂-rGO nanocomposites can form p-n heterojunction through either physisorption or chemisorption, depending on whether the interaction is chemical/physical at the interface. Non-covalent interactions through physisorption do not have a significant effect on the properties of the individual constituents of a hybrid material. However, covalent interactions between SnO₂ and graphene through Sn-O-C linkage or directly through Sn-C bonding can alter the charge distribution by changing the sp² hybridized state of graphene to sp³ and enhancing the conductivity of the SnO₂-rGO composite. These aspects can greatly influence the performance of the sensing material, which is not paid

much attention to in the literature [Bhati et al., 2021]. The SnO₂-rGO nanohybrid sensor's performance also needs to be optimized so that synergistic functional properties of r-GO and SnO₂ can be exploited [Gui et al., 2017; Jian et al., 2020; Kim et al., 2017; Liu et al., 2014; Wu et al., 2020; H. Zhang et al., 2014; Zhu et al., 2017]. Indeed, there is a requirement for an in-depth study to optimize the synthetic conditions for the best-performing SnO₂-rGO nanohybrid material.

3.1.1 Objectives of Work

The objectives of this work are as follows:

1. To perform the detailed structural, chemical, and morphological characterisation of solvothermal synthesized SnO₂-rGO nanocomposites.
2. To test the performance of fabricated chemiresistive sensor toward different gases/VOCs.
3. To identify the best chemiresistive sensor device capable of monitoring NO₂ gas at room temperature, using a combinatorial strategy.
4. To establish the structure-property relationship between the sensing material (SnO₂-rGO) and the sensing gas (NO₂).

3.2 Experimental

3.2.1 Synthesis of SnO₂-rGO

SnO₂-rGO nanohybrid was prepared by a single-step solvothermal method. 2.5 mM SnCl₂·2H₂O (Rankem, CAS No. 10025-69-1) was dissolved in 160 ml of the ethanol-water mixture (1:1) and stirred for one hour. The pH of the solution was adjusted to 11 by adding 7 mL of 1M NaOH and continued stirring for another 10 minutes. 5 mg of graphene platelet nanopowder (Sisco Research Laboratories Pvt. Ltd., average particle size of 5 μm, thickness of 6-8 nm) was dispersed in 2 mL ethanol by sonication for 10 minutes and added to the Sn precursor solution in a Teflon vessel. The solvothermal reaction was carried out at 120 °C for 10 hours, and the resulting dispersion was washed with ethanol and water several times till the pH became neutral. Differential centrifugation (DC) separates the multiple fractions of the obtained product. The mixture of SnO₂ and graphene is centrifuged numerous times at different speeds of 500, 2000, 6000, and 10000 rpm successively to separate individual layers, L1, L2, L3, and L4, respectively, collecting the supernatant. Finally, the powder was obtained by centrifuging each layer at a successively higher speed, followed by drying the solid sediment in a vacuum oven at 60 °C overnight.

3.2.2 Characterization

Bruker D8 Advance diffractometer equipped with Cu-Kα radiation (1.54 Å wavelength) was used for X-ray diffraction analysis. DLS and Zeta potential was measured using Zetasizer Nano ZSP (ZEN5600) for colloidal dispersions of L1-L4 (1 mg/mL). Raman spectra of the samples were recorded with a 532 nm laser diode from Renishaw, UK. FESEM imaging was performed on (Tescan-Mira 3 LMH) for surface morphology. TEM imaging was performed by transmission electron microscope (FEI Technai G2 T20 ST) equipped with energy-dispersive X-ray spectroscopy (Bruker X-100). For imaging, ~10 mg of sample was dispersed in ethanol and drop cast on a copper grid and allowed to dry before imaging. HRTEM images were analyzed using Image J and Gatan digital micrograph software. The surface area was obtained from N₂ adsorption-desorption isotherms (Quantachrome autosorb iQ3). X-Ray Photoelectron Spectroscopy (XPS) was performed on the Thermoscientific NEXSA surface analysis system using the He1 (21.2 eV). The XPS fitting was performed using the Fityk software. Kelvin probe force microscopy of samples was performed using MFP-3D Origin Plus AFM using ASYELEC-01-R2 probe with tip (28 ± 10 nm) and Ti/Ir tip coating at a scan rate of 1 Hz and pixel size of

256 × 256. Electrochemical Impedance spectroscopy (EIS) measurements were performed on Ivium Stat instrument in three-electrode geometry using nanohybrid coated glassy carbon electrode as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a reference electrode in 0.5M Na₂SO₄ solution.

3.2.3 Fabrication of gas/VOC sensor and sensing measurements

Cleaned glass substrates were used to fabricate Au-coated ~10 μm gap electrodes of 4 mm length by physical vapor deposition (VEC Vacuum, India) over carbon fiber as a physical mask. A 10 μL (1 mg/mL) colloidal dispersion of the sensing material was drop-cast across the Au gap. Electrical contacts were made using silver paste (SPI) and copper wire for sensor measurements. For gas sensing, dynamic experiments were conducted in a custom-designed setup that involved creating a VOC/gas of desired concentration using a calibrated syringe of 50 mL volume and flowing it on a sensor inside the chamber at a controlled rate (~100 SCCM) using a syringe pump. In the case of VOCs, desired concentration was prepared using the equation below:

$$C = \frac{22.4 \times \rho \times T \times V_1}{273 \times M \times V_2} \times 1000 \dots \dots (1)$$

Where C (ppm) is the target VOC concentration, T is the testing temperature (K), ρ (g/mL) is the density of the VOC, V_1 (μL) is the volume of VOC, and V_2 (L) is the volume of the chamber, and M (g/mol) is the molecular weight of VOC. NO₂ was produced from HNO₃ and Cu turnings in a sealed flask, and the desired volume was taken in a calibrated syringe for further experiments as detailed above. Further, the VOC/gas concentration was cross-calibrated, with the help of a commercial sensor from Honeywell (ppbRAE3000). A relative error of 9.71% was obtained in the gas concentration values created using the designed set-up.

The electrical response of the sensor was measured in the form of current at an applied fixed DC potential of 1 V. Unless specified, all gas sensing measurements were performed at a humidity of 30% RH under room temperature conditions (~25 °C). The humidity was created using a mist humidifier to calibrate VOC response under known humidity levels. For continuous monitoring of humidity and temperature commercial Testo sensor was also kept inside the gas/VOC sensing chamber.

The response of the sensor was calculated using the formula:

$$\text{Response} = \frac{I_g - I_a}{I_a} \times 100 \dots \dots (2)$$

where I_a and I_g stand for the device's current in the presence of atmospheric air and gases/VOCs, respectively. The response and recovery time are calculated from the transient response as the time taken for 90% of the total resistance change in the response/recovery profile by the sensor. The selectivity of the sensor is tested by analysing the response of the sensor upon exposure to various interfering polar and non-polar gases/ VOCs.

3.3 Result and Discussion

3.3.1 Synthesis Optimization of SnO₂-rGO Nanocomposites

Figure 3.2 shows the scheme adopted for the synthesis of SnO₂-rGO nanohybrids. The single-step solvothermal synthesis of SnO₂-rGO nanohybrid was carried out by adding 1 wt.% graphene flakes to the Sn precursor solution during the reaction (**Figure 3.2**, see experimental details). Graphene flakes are expected to improvise the conductivity of SnO₂ and increase the base current of the sensing material. The product obtained was washed repeatedly with water, and a gradient coloration of the product, dirty yellow at the top and whitish grey at the bottom, was obtained, indicating the formation of a mixture of rGO and SnO₂ hybrid (**Figure 3.3a**).

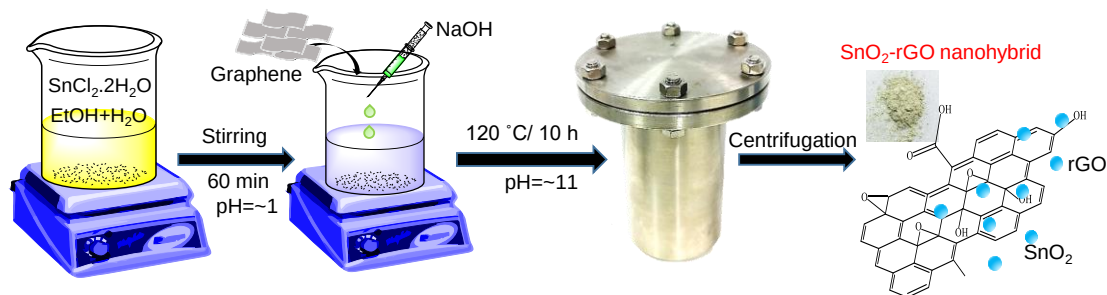


Figure 3.2: Schematic showing the synthesis of SnO₂-rGO nanohybrids.

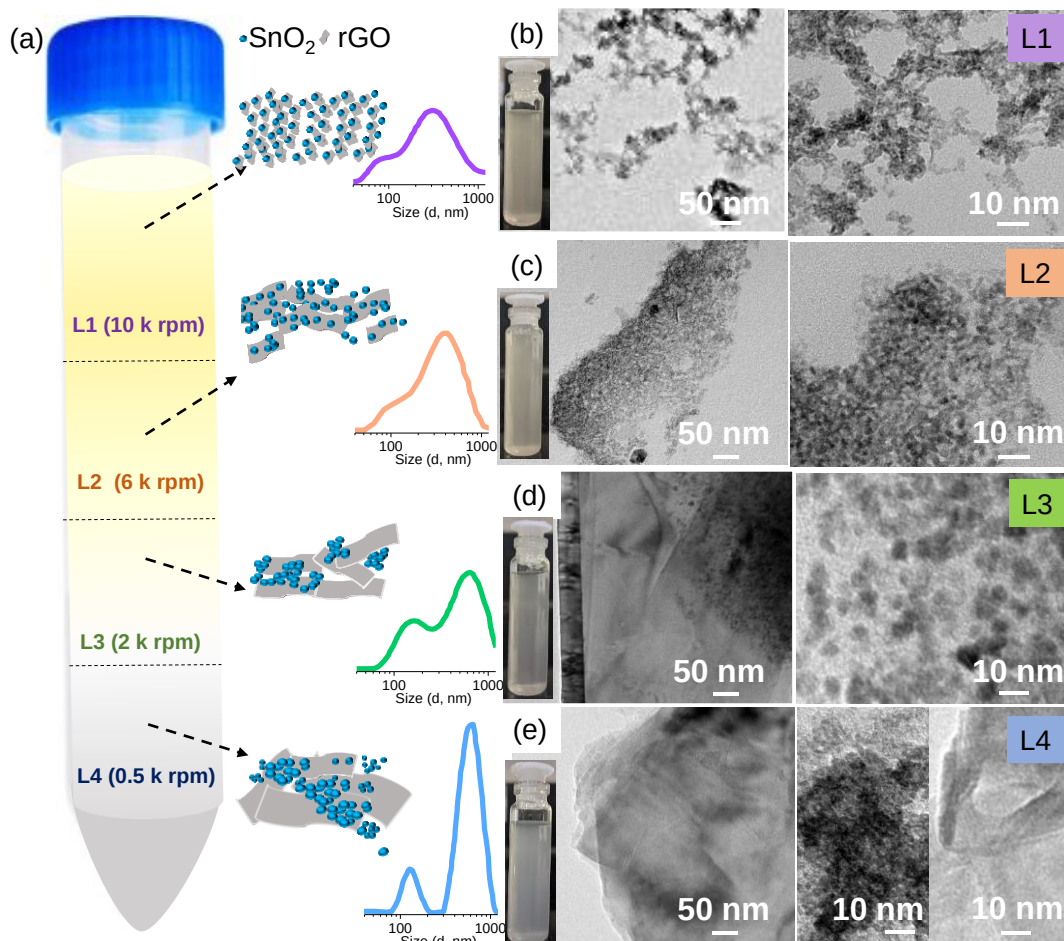


Figure 3.3: (a) Schematic demonstrating the protocol adopted for separating SnO₂-rGO nanohybrid from product mixture using the differential centrifugation technique. L1 to L4 indicates the different fractions obtained based on the difference in hydrodynamic size obtained from DLS particle size distribution. (b-e) Transmission electron microscopy (TEM) images of the L1-L4, respectively. The digital photographs of the colloidal dispersions are given in the inset (left).

As detailed in the experimental section, these different product fractions in water were separated by following the differential centrifugation method. The sedimentation of the layer was separated at low rpm, and the supernatant was centrifuged at a successively higher centrifugal force to obtain four different layers. Each of the different SnO₂-rGO layers obtained was re-dispersed in water and shown in **Figure 3.3b-e**, inset. The hydrodynamic size and zeta potential values of different layers were obtained to gain insight into the colloidal solutions (**Table 3.1**). Interestingly, all layers show two broad peaks in size distribution data (**Figure 3.3a**). From DLS peak analysis, peak-1 can be associated with SnO₂ and small-sized rGO platelets, while peak-2 is related to SnO₂ and large-sized rGO. As seen in TEM images, the top layer, L1, is enriched with small-sized SnO₂ particles (2.5 ± 0.5 nm) that are highly

monodispersed (**Figure 3.3b**). In the second layer, L2, the average size of the particles is 4.0 ± 0.9 nm, which is higher than L1, yet uniformly distributed over rGO platelets (**Figure 3.3c**). However, in mid-layer L3, a non-uniform mixture of SnO₂ nanoparticles of 6.3 ± 1.2 nm and large rGO sheets can be observed, which is evident from two separate peaks from DLS data (**Figure 3.3d**). Large rGO sheets are mainly observed in the bottom layer, L4 (**Figure 3.3e**).

Table 3.1: Structural analysis for different layers of SnO₂-rGO.

	DLS (nm)	HRTEM Size (nm)	Zeta Potential (mV)	Raman A _{ig} /G	XRD SnO ₂ (110/101)
L1	297.1 ± 6.8	2.5 ± 0.5	-39.2 ± 0.2	3.35	1.15
L2	321.5 ± 1.9	4.0 ± 0.9	-41.2 ± 1.6	2.54	1.18
L3	439.6 ± 16.3	6.3 ± 1.2	-42.0 ± 2.6	1.51	0.38
L4	588.2 ± 61.8	N.A.	-31.7 ± 0.5	1.15	0.35

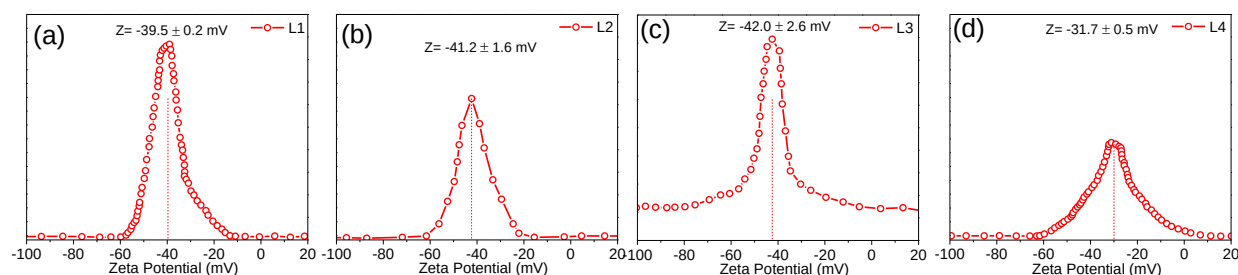


Figure 3.4: (a-d) Zeta potential of different layers of SnO₂-rGO.

Table 3.2: Statistical Study of zeta potential of all samples (L1-L4).

Data Number	Zeta Potential (mV)			Mean	Standard Deviation
	1	2	3		
L1	-39.5	-39.3	-39	-39.266	0.251
L2	-42.2	-42.1	-39.3	-41.2	1.646
L3	-44.9	-41.4	-39.7	-42	2.651
L4	-32.3	-31.3	-31.7	-31.766	0.503

Overall, the TEM particle size increases from L1-L4 in line with the average hydrodynamic size. However, the DLS determined hydrodynamic sizes are higher than the actual nanoparticle size obtained from TEM, thus providing a relative estimation. All the layers (L1- L4) formed a stable colloidal dispersion with a zeta potential > -30 mV. The mean and standard deviation is calculated over three different measurements (**Table 3.2**), and represented data is shown in **Figure 3.4**. Thus, this simple differential centrifugation allowed the SnO₂-rGO nanohybrid to be separated into homogenous size fractions.

3.3.2 Structural and Morphological Characterisation: Raman, XRD, TEM and BET Analysis

A thorough structural characterization is performed using Raman Spectroscopy, X-Ray Diffraction (XRD), and High-resolution Transmission Electron Microscopy (HRTEM) analysis techniques. Graphene flakes used during synthesis are used as a control; however,

since it converts to rGO during synthesis, later, it is referred to as rGO.

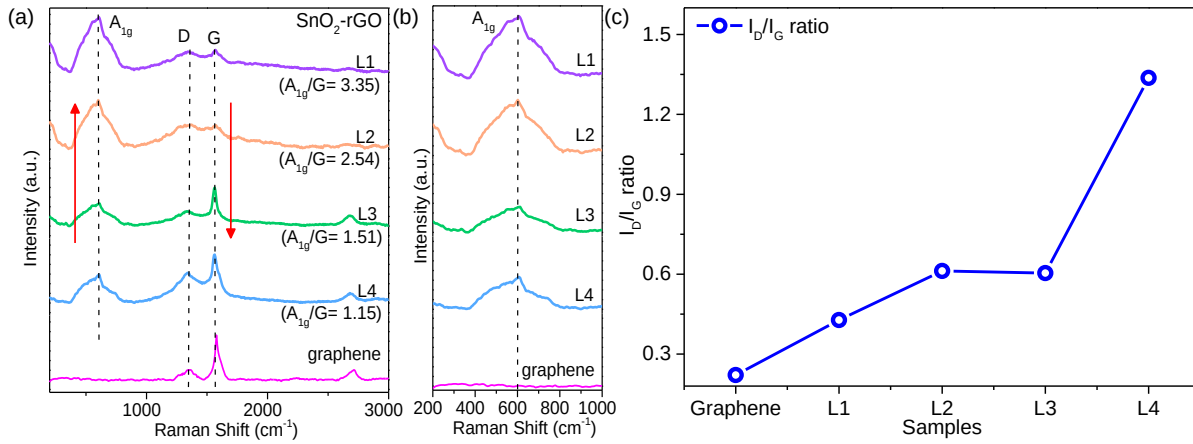


Figure 3.5: (a) Raman spectra of L1 to L4 and corresponding (b) zoom-in view of A_{1g} peaks. (c) Variation of I_D/I_G ratio concerning oxidation level of graphene from L1 to L4.

Table 3.3: XRD and Raman peak analysis for different layers of SnO₂-rGO.

No.	Raman Analysis			XRD Analysis		
	Intensity A _{1g}	Intensity G	Intensity ratio A _{1g} /G	Intensity SnO ₂ (110)	Intensity SnO ₂ (101)	Intensity ratio SnO ₂ (110/101)
L1	1818.04	542.90	3.35	2732.34	2367.12	1.15
L2	1594.93	627.43	2.54	2531.47	2139.68	1.18
L3	734.47	485.32	1.51	757.57	1980.97	0.38
L4	882.34	763.66	1.15	686.88	1968.95	0.35

As shown in **Figure 3.5a**, all layers exhibit characteristic A_{1g} peaks of rutile SnO₂ at 607 cm⁻¹ and graphitic D, G, and 2D bands at 1344 cm⁻¹, 1570 cm⁻¹, and 2705 cm⁻¹, respectively. Interestingly, distinct changes in the A_{1g} band of SnO₂ and D and G bands of graphene from L1-L4 are further analyzed to understand the nature of SnO₂-rGO in all four cases (**Table 3.3**). Importantly, the A_{1g}/G band ratio decreases systematically from L1 to L4, indicating higher SnO₂ in top layers and the reverse trend for rGO (**Figure 3.5b**). The increased I_D/I_G ratio from L1 to L4 is probably due to the introduction of oxygen functionalities in graphene flakes (**Figure 3.5c**).

XRD analysis of samples was performed to study the crystalline features of the synthesized sensing materials. The XRD patterns of pristine SnO₂ and all four SnO₂-rGO layers (L1-L4) resemble that of the SnO₂ rutile phase (**Figure 3.6a**). There is an overall decrease in intensities of SnO₂ peaks from L1 to L4, except for the 110 peaks. The increase in sharpness of 110 is a clear manifestation of overlapped 002 planes of graphene, which is further deconvoluted in **Figure 3.6b**. From the XRD analysis, the indistinguishable XRD peak of SnO₂ (110) and rGO (002) in L1 and L2 while deconvoluted peaks in L3 and L4 bring out unique features of the SnO₂-rGO nanohybrid layers. Firstly, the rGO is present as platelets with the size of the order of SnO₂ nanoparticles in L1 and L2, resulting in a peak with broad FWHM, concomitant with TEM images. In L3 and L4, the large rGO sheets and relatively higher graphitic content result in a sharp 110 peak.

The HRTEM images of L1-L4 show well-resolved lattice fringes and d-spacing of 0.345 nm (marked in **Figure 3.7a-d**) corresponding to SnO₂ nanoparticles or rGO nanoplatelets.

However, the SnO₂ nanoparticles in L3 and L4 are covered by rGO.

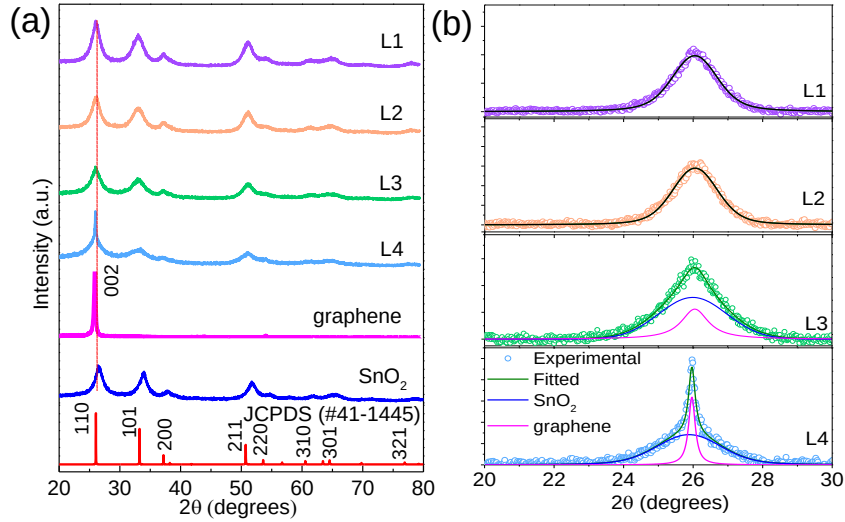


Figure 3.6: (a) X-ray diffraction (XRD) patterns of SnO₂, graphene, nanohybrids and corresponding (b) deconvoluted 110 peaks.

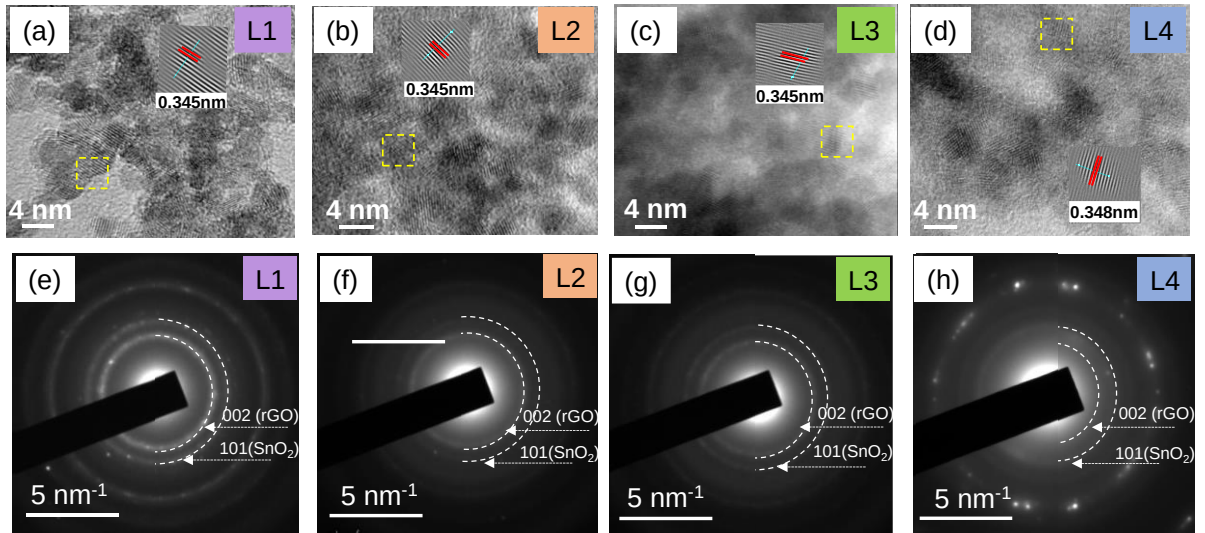


Figure 3.7: (a-d) High-resolution transmission electron microscopy (HRTEM) images. The areas marked in HRTEM images by yellow are enlarged and shown in the inset (right) after i-FFT processing by Image J. (e-f) Selected Area Electron Diffraction (SAED) patterns of layers L1 to L4.

Additionally, the SAED pattern also shows L1 to be more crystalline than other layers and the presence of r-GO content in all four layers (**Figure 3.7e-h**). The variation in the particle size, surface charge, crystallinity, and structural composition obtained from Raman and XRD analysis are presented in **Table 3.1**. The trend in the A_{1g}: G band in Raman analysis and 110/101 peak ratio from the XRD pattern indicates the differences in graphitic content and SnO₂ particle size distribution in all four layers (**Table 3.1**).

The SnO₂-rGO layers were further characterized by nitrogen adsorption-desorption isotherms (**Figure 3.8a**). N₂ adsorption-desorption isotherms exhibit a type-IV isotherm indicating a mesoporous structure with a multipoint BET (MBET) specific surface area of 107.50 m²/g, 50.70 m²/g, 37.96 m²/g, 60.09 m²/g for L1, L2, L3, and L4, respectively (**Figure 3.78b, inset**). Furthermore, the pore volume calculated using non-local density functional theory (NLDFT) decreases drastically from L1 to L2 (**Figure 3.8b**). Thus, the high specific surface area and pore volume of L1 can provide a more accessible surface area for gas diffusion and electron transport to enhance the sensor's performance.

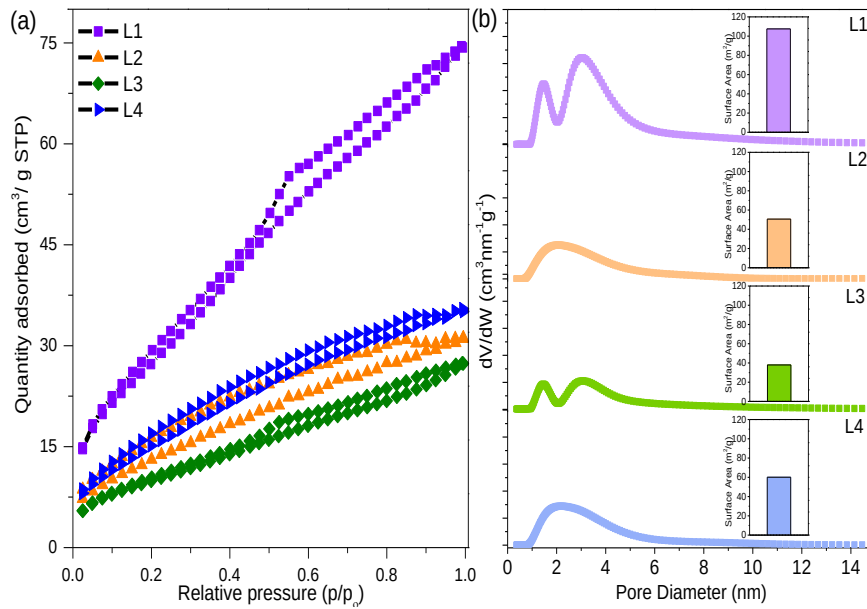


Figure 3.8: (a) Nitrogen adsorption-desorption isotherm of different layers of SnO₂-rGO. (b) NLDFT pore size distribution and specific surface area (SSA) were calculated using BET isotherms for L1-L4 layers.

3.3.3 Compositional Characterisation: XPS Analysis

The XPS analysis was performed on all four layers (L1-L4) to analyze the composition and the chemical state of SnO₂-rGO. XPS survey spectra show the presence of Sn, O, and C with comparable intensity for all layers (**Figure 3.9a**). In the high-resolution Sn 3d spectra (**Figure 3.9b**), the characteristic signals for Sn⁴⁺ 3d_{5/2} and 3d_{3/2} appear at $\sim 487.0 \pm 0.2$ eV and $\sim 495.5 \pm 0.2$ eV, respectively for all four layers [Bahuguna, Verma, and Gupta 2021; Yayi Cheng et al. 2017]. Interestingly, the shifting of Sn3d peaks towards lower binding energies in L1 and L2 indicates enhanced interaction of SnO₂ lattice with r-GO. The C1s XPS spectrum in the case of all layers consists of the dominant peak corresponding to sp² carbon at 284.6 eV and other peaks for C-C (defect) ~ 285.4 eV, Sn-O-C ~ 286.3 eV, and C=O at ~ 288.9 eV (**Figure 3.9c**) [Rani et al., 2013]. Interestingly, in L1 and L2 layers, the C1s deconvolution shows an additional peak at ~ 283.7 eV assigned to Sn-C (**Figure 3.9c**) [Cheng et al., 2017b, 2017a]. It is interesting to observe the formation of the Sn-C bond due to stronger chemical interaction between the SnO₂ and the r-GO lattice rather than just physical adherence. This can be related to the small-sized SnO₂ particles, and r-GO observed in L1 and L2, which exhibit high surface energy and lower activation energy for forming Sn-C bonds. For clarity, XPS peak positions and Sn-C ratio are tabulated in **Table 3.4**. As observed in the literature, the Sn-C bond can act as a fast electron transfer pathway instead of an indirect bond through Sn-O-C [Cheng et al., 2017b]. Further, the increase in the C-O and C=O peaks in C1s spectra from L1-L4 suggests the probable oxidation of rGO in L3 and L4, which supports the results obtained from Raman and SAED pattern analysis. **Figure 3.9d** shows the O 1s core-level high-resolution spectra of all layers, which can be deconvoluted into four peaks at ~ 530.4 eV, $\sim 531.0 \pm 0.3$ eV, $\sim 531.8 \pm 0.3$ eV, and ~ 532.7 eV. These peaks correspond to (i) lattice oxygen anions (O²⁻), (ii) oxygen bonded r-GO carbon (C-O), (iii) oxygen ions (O²⁻ and O⁻) in the oxygen-deficient regions caused by oxygen vacancies, and (iv) chemisorbed oxygen species respectively [L. Zhang et al. 2019]. However, in L3 and L4, the O1s spectra are dominated by r-GO content with high C-O making it unsuitable for gas sensing compared to L1 and L2.

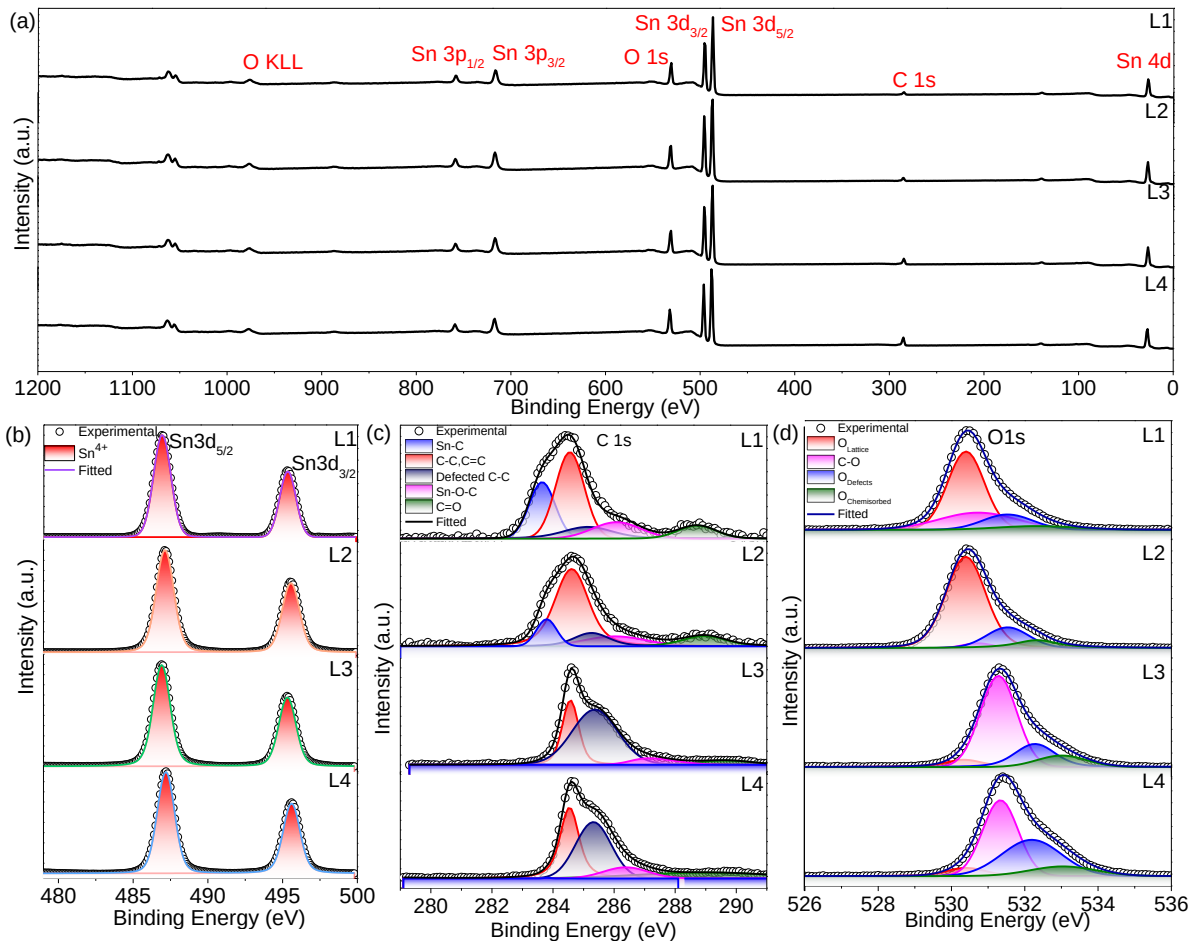


Figure 3.9: (a) XPS survey spectra of L1 to L4. Deconvoluted high-resolution XPS spectra of (b) Sn3d, (c) C 1s and (d) O 1s for L1-L4 layers.

Table 3.4: The peak position and Sn-C ratio for high-resolution C1s XPS data.

	Sn-C		C-C/ C=C		Sn-C/ C-C ratio
	Peak position (eV)	Area under the curve	Peak position (eV)	Area under the curve	
L1	283.7	7059.27	284.6	11900.5	0.59
L2	283.7	4854.05	284.6	26815.5	0.18
L3	N.A.	N.A.	284.6	24930.4	N.A.
L4	N.A.	N.A.	284.6	45121.3	N.A.

3.3.4 Electrochemical Characterisation: Electrochemical Impedance Spectroscopy Analysis

Nyquist measurements were performed to evaluate the conductivity of hybrid materials L1 to L4 and compared with pristine components (**Figure 3.10 a,b**). A smaller semicircle diameter is associated with lower charge transfer resistance and higher material conductivity. The charge transfer resistance (R_2) at the solid-liquid interface (obtained from fitting of equivalent circuit diagram, **Table 3.5**) decreased by ~25% from L1 to L4 which lies in between that of SnO_2 and graphene. Thus, L1 (SnO_2 -rGO hybrid) was identified as the best sensing material and further explored as a NO_2 sensing device.

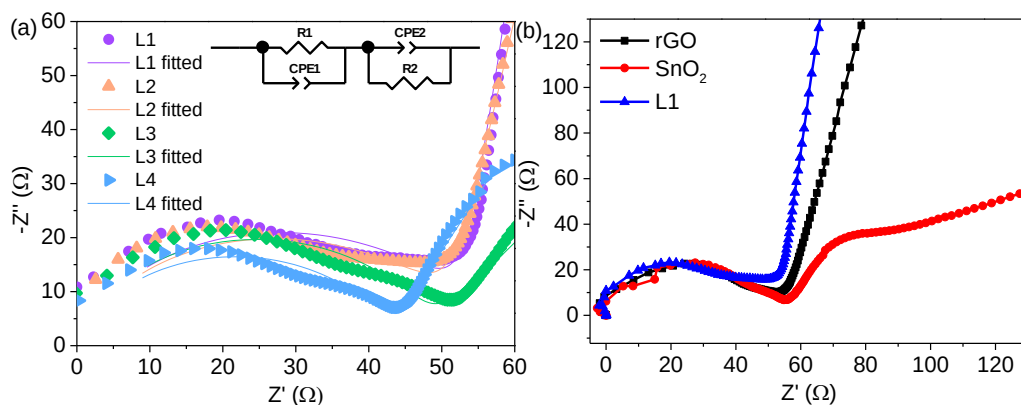


Figure 3.10: (a) Nyquist plot of L1-L4 fitted with equivalent circuit diagram and corresponding (b) comparison of L1 nanohybrid with pristine rGO and SnO_2 samples.

Table 3.5: The derived EIS parameters by Nyquist plot fitting.

Sample	Resistance, $R1(M\Omega)$	Capacitance CPE1		Resistance, $R2(\Omega)$	Capacitance CPE2	
		$p1 (\mu F)$	$n1$		$p1 (nF)$	$n1$
L1	0.49	0.52	0.93	52.84	49	0.82
L2	2.49	0.98	0.90	51.04	67	0.81
L3	9.94	75.9	0.61	46.98	25	0.86
L4	5.50	27.8	0.72	42.20	51	0.82

3.3.5 Gas Sensing Characteristics

A chemiresistive sensing array was fabricated by drop-casting SnO_2 -rGO nanohybrid dispersions in water (L1-L4) on the Au gap electrodes of $\sim 10 \mu m$ (Figure 3.11a, Section 3.2.1). The nanohybrids are randomly distributed across the gap on drying without forming a continuous film, as seen in the FESEM image, Figure 3.11b. The drop volume was optimized to be $\sim 10 \mu L$ to obtain a base current in the range of ~ 1 -10 nA for the devices fabricated under ambient conditions (RH= $\sim 30\%$, $T = 25^\circ C$) [Yingyi Wang et al. 2021]. The gas/VOC sensing experiments were carried out in dynamic mode using a custom-designed setup as discussed in the experimental section. The baseline current of sensors increases from L1 to L4 to a maximum of 49.5 %, which is due to the higher amount of rGO present in the hybrid material (Figure 3.11c). The sensors were first exposed to the NO_2 gas of 10000 ppm, and the transient response is shown in Figure 3.12a. A high concentration of 10000 ppm was intentionally chosen to mimic practical leakage situations that a sensor can withstand without failing. Interestingly, the sensor response for L1 is not saturated and appears as a pulse due to the limited volume of high concentration NO_2 gas injected into the sensing chamber. The L1 exhibited an ultrafast and high response towards NO_2 gas, while L2 recorded a moderate response. Surprisingly, L3 and L4 sensing materials did not show any appreciable response probably due to the aggregation of SnO_2 nanoparticles and the absence of the Sn-C bond (Figure 3.12a, inset). The individual components, SnO_2 , and graphene sensor had a low response and in addition, the graphene sensor possessed poor recovery to 10000 ppm NO_2 compared to L1 and L2 hybrids at room temperature conditions (Figure 3.12b, c).

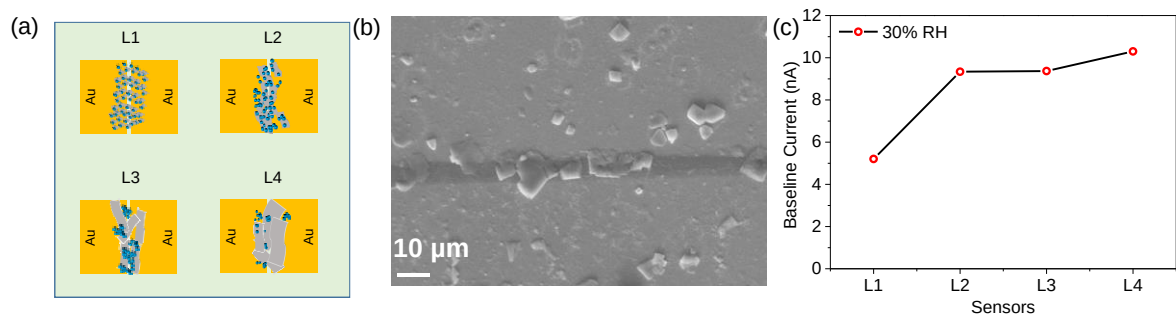


Figure 3.11: (a) Schematic showing the 2 × 2 chemiresistive sensing array of the device fabricated on the gap electrode and (b) a representative FESEM image of fabricated gas/VOC sensor. (c) Baseline current of all sensors, L1-L4 at 30% RH.

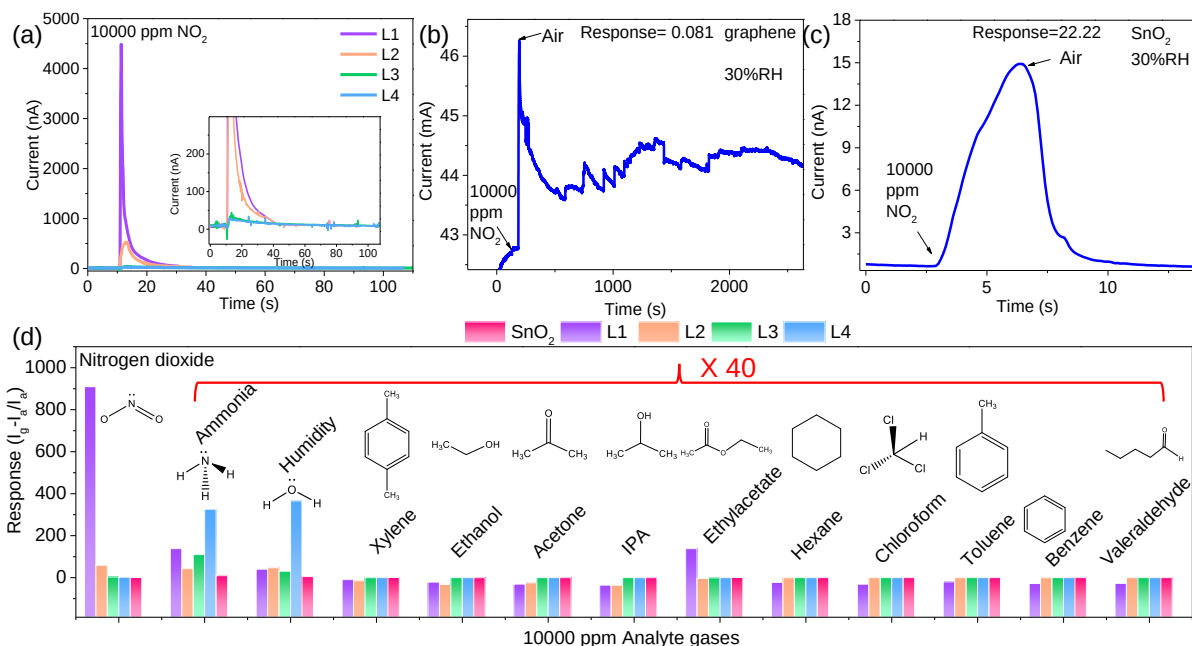


Figure 3.12: (a) Dynamic sensing transients of L1-L4 towards NO₂ for 10000 ppm NO₂ (inset shows the zoomed-in view of L3 and L4). (b-c) The NO₂ gas sensing transients of graphene and SnO₂ at room temperature and 30% RH conditions. (d) The response of different sensors towards various analyte gases. (Note: All the measurements in a-d are performed in ambient conditions, 25 °C and 30% RH).

The response in L1 can be attributed to the increase in BET surface area and direct Sn-C interaction between SnO₂ nanoparticles and rGO, providing more accessible faster electron transport pathway. The BET surface area of L1 is twice higher than L2, yet it is marginal against seven times increase in the sensing response of L1. The selectivity of a sensor to a specific analyte is one of the important parameters and interference of gases/VOCs (ammonia, humidity, xylene, ethanol, acetone, IPA, acetone, ethyl acetate, hexane, chloroform, toluene, benzene, and valeraldehyde) is studied in **Figure 3.12d**. The SnO₂-rGO (L1) device continued to exhibit exceptionally high selectivity along with sensitivity for NO₂ gas in comparison to other analytes with an $R(\text{NO}_2): R(\text{ethanol})$ and $R(\text{NO}_2): R(\text{NH}_3)$ of 1690.49 and 263.16, respectively. The formation of high conductivity Sn-C bond is considered as a dominant factor in boosting the sensitivity and selectivity.

The SnO₂-rGO nanohybrid developed in this study is further analyzed for room temperature ppm-level NO₂ sensing under calibrated gas concentrations (1-100 ppm). On exposure to 80 ppm NO₂ gas, the device responds with a rapid increase in the current, which drops down to the base value upon expelling out the NO₂ gas by air exposure (**Figure 3.13a**). NO₂ gas is diluted from 80 ppm to 1 ppm, and consequently, a linear reduction in the current response was observed. The response is significant even at one ppm of NO₂ gas

exposure (**Figure 3.13b**). The plot of logarithmic increase in NO₂ gas concentration for response ($I_g - I_a / I_a$) resulted in a linear slope ($R^2 = 0.97$) and the limit of detection (LOD) calculated was 209 ppb. LOD is a crucial parameter for practical use as even short-term exposure to a few hundred ppb concentration of NO₂ is detrimental to human health [Wang et al., 2021]. The SnO₂-rGO device exhibits a low response time (5.6 s) and recovery time (14.1 s) in the presence of 80 ppm of NO₂ gas, which is appreciable for a room temperature NO₂ sensor (**Figure 3.13c**).

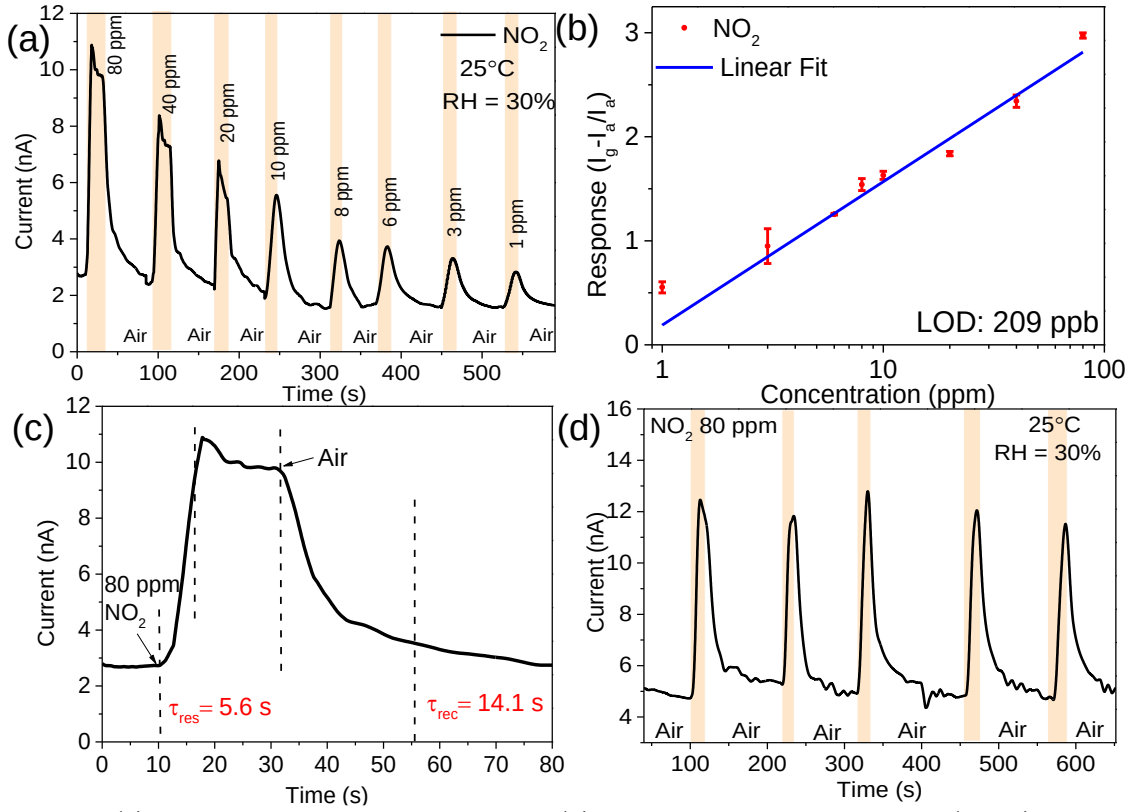


Figure 3.13: (a) SnO₂-rGO sensing transients and (b) the corresponding response ($I_g - I_a / I_a$) to varying concentrations of NO₂. (c) The typical response-recovery curve of SnO₂-rGO nanohybrid for 80 ppm NO₂. (d) Repeating transient response of the sensor to 80 ppm NO₂ exposure cycles. (Note: All the measurements in a-d are performed in ambient conditions, 25 °C and 30% RH).

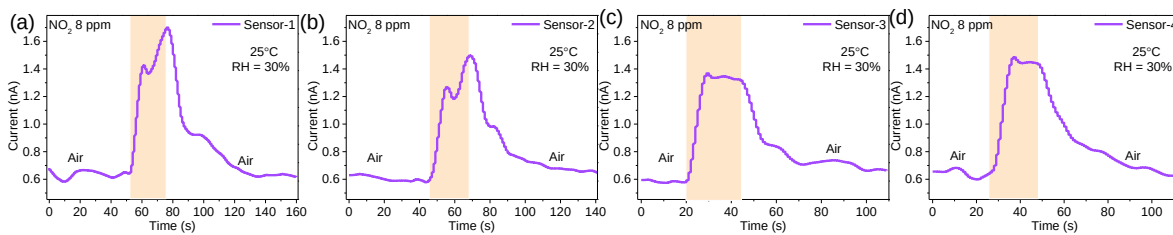


Figure 3.14: (a-d) The sensing response of four different sensors fabricated using L1 sensing material indicating reproducibility.

The device exhibits a repeatable response for 80 ppm NO₂ gas with RSD of 10.6% (**Figure 3.13d**). The value is slightly higher from a practical point of view (<5%), since the error originating from the gas calibration using the custom-designed gas sensing setup have an RSD of 9.7%. Thus, the actual RSD of sensor is 0.9% for a repeatable response.

Several sensors fabricated and tested under the same environment demonstrated an RSD of 1 % indicating the reproducibility of the device (**Figure 3.14**). The atmospheric humidity can interfere with the VOC/gas response, it is crucial to analyze the characteristics of the

VOC/gas sensor at fluctuating humidity conditions for its reliability of operation under real-life conditions. As seen in **Figure 3.15a**, the base current of the sensor drifted linearly due to humid response without any impact on the NO₂ sensing performance as observed by the mean response of 3.06 ± 0.89 (calculated over 20-50% humidity) for 80 ppm NO₂.

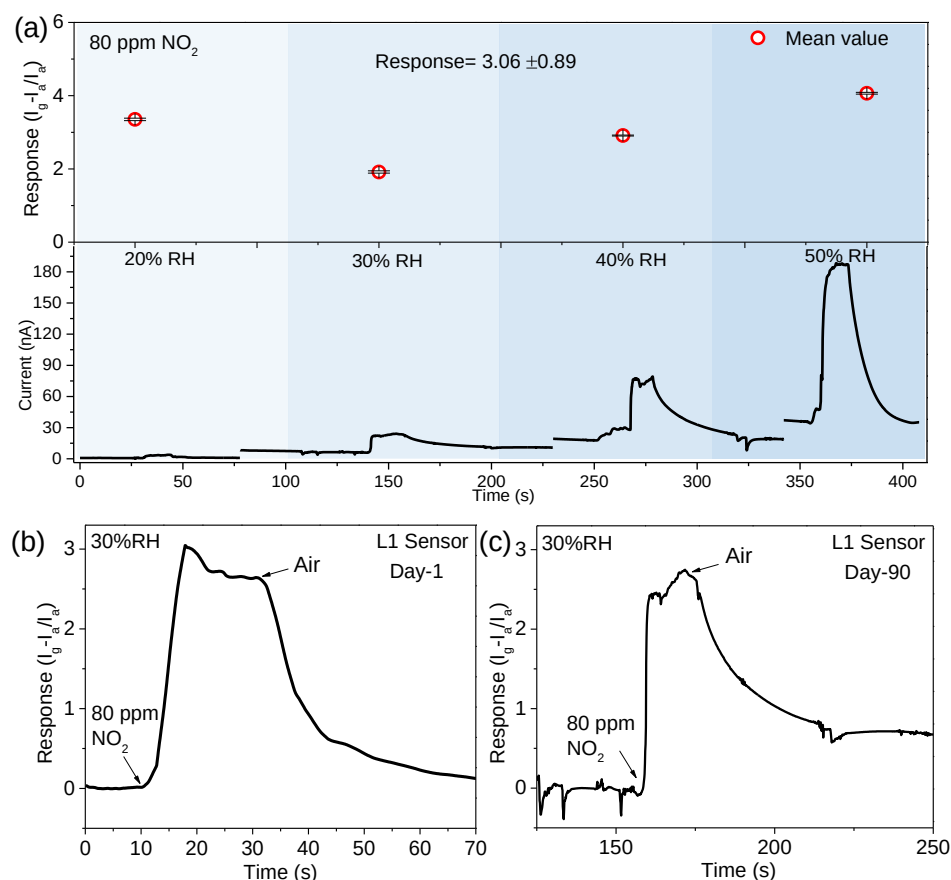


Figure 3.15: (a) The sensor's L1-L4 current and response in the presence of different relative humidity (20-50%). The transient response of L1 sensor in presence of 80 ppm NO₂ at (b) day-1 and (c) day-90 indicating stability of sensor with slight irreversibility in the signal which could be due to adsorbed gases from the ambient.

Above 50% humidity, sensor got damaged due to excessive current flow. Further, the device exhibits a stable, repeatable NO₂ gas response when tested continuously for 90 days (**Figure 3.15b, c**), proving the practical applicability of the sensor. Thus, a reliable room temperature ppm level NO₂ gas sensor was realized using SnO₂-rGO (L1) as an active sensing material which outperforms as compared with literature due to the presence of Sn-C bonds not reported earlier (**Table 1.1**).

3.3.6 Proposed Gas Sensing Mechanism

It is important to understand the gas sensing mechanism in SnO₂ nanohybrids considering the modulation in resistance of the sensor on NO₂ interaction. As SnO₂-rGO nanohybrids show an increase in conductivity on NO₂ exposure, there is a possible heterojunction formation between n-type SnO₂ and p-type rGO.[Pargoletti et al., 2020; Zhao et al., 2016] The optimized 10 μ L (1 mg/mL) dispersion of pure rGO, SnO₂, L1 and L2 nanohybrid were drop cast on silicon substrates for AFM imaging and kelvin probe force microscopy measurements (Figure S13). Topography images show that the L1 nanohybrid material exhibits a height of ~ 105 nm which is more comparable to SnO₂ height indicating the major contribution of SnO₂ particles in nanohybrid (**Figure 3.16a-d**).

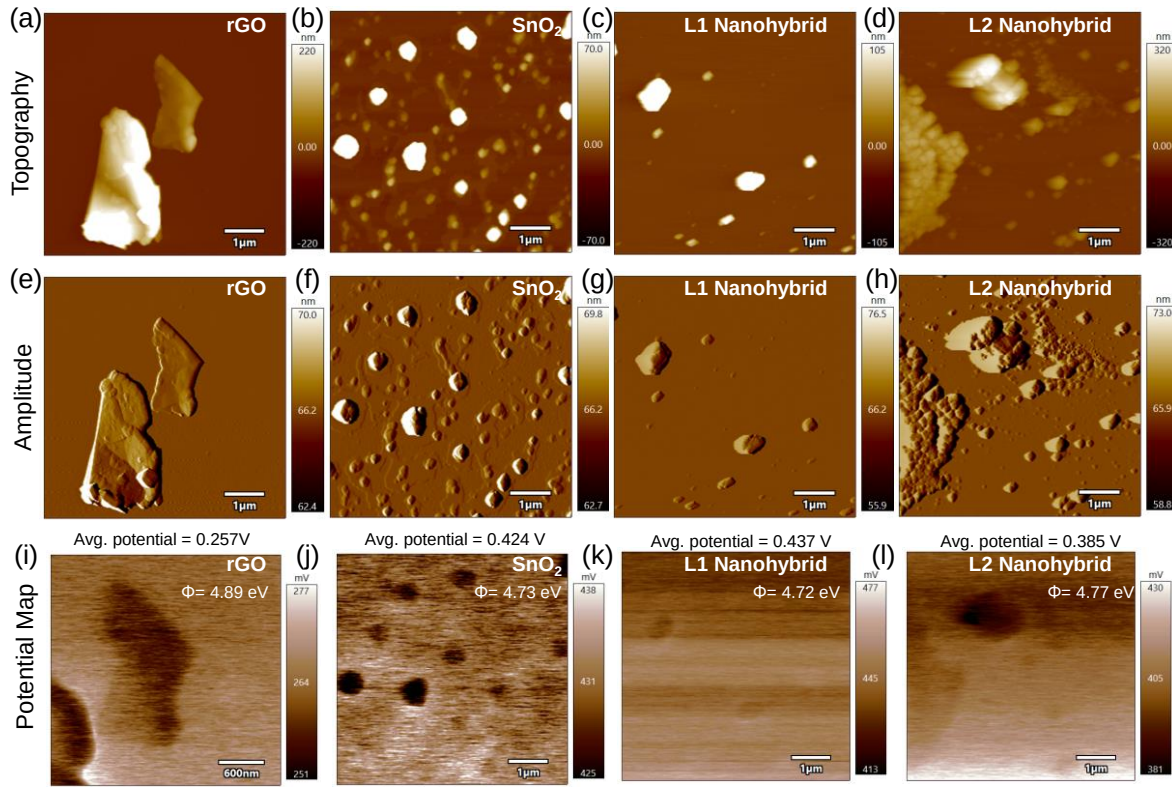


Figure 3.16: (a-d) Atomic force microscopy images showing the surface topography for height estimation, (e-h) amplitude images for more visual clarity and (i-l) Kelvin probe force microscopy images show the potential map for rGO, SnO₂, L1 and L2 nanohybrid.

Further, the amplitude images bring out the visual clarity of shape of the nanoparticles in all materials and the L1 nanohybrid depicts agglomerated particles of $\sim 1 \mu\text{m}$ (Figure 3.16e-h). Amplitude-modulated Kelvin Probe measurements are performed (Figure 3.16i-l) for deriving the work function (Φ) of rGO, SnO₂, and SnO₂-rGO nanohybrids. The L1 and L2 hybrid exhibits a Φ_{L1} value (4.719 eV) and Φ_{L2} (4.771 eV) close to that of pristine SnO₂ (4.732 eV), which is slightly lower than that of rGO (4.899 eV). The work function values for the SnO₂-rGO hybrids are close to pristine SnO₂ due to the presence of lower quantity of rGO which is also established in XRD and Raman analysis. It is to be noted that the low sensitivity of the lift mode in KPFM measurements and ambient atmosphere during imaging is one of the limitations, however, a relative picture of the band structure is obtained by these measurements.[Gupta Chatterjee et al., 2015; Wang et al., 2022; Zhou et al., 2018]

The band diagram for one of the high-performing SnO₂-rGO hybrid, L1 heterostructure demonstrating a work function difference of $\Delta\Phi_{L1}$ of $\sim 0.16 \text{ eV}$ is shown in Figure 3.17a,b.[Bhangare et al., 2019, 2020] As observed in the band diagram, the Fermi level (E_f) of p-type rGO lies above SnO₂ ($\Delta E_f \sim 0.16 \text{ eV}$), leading to the formation of a depletion layer at the SnO₂-rGO interface due to the transfer of electrons from the E_f of SnO₂ to that of rGO (Figure 3.17b and Figure 3.16i-l). The interaction of electron withdrawing NO₂ molecules with rGO shifts the Fermi level (E_f) away from the conduction band due to the extraction of electrons. This in turn leads to thinning of the depletion layer ($\Delta\Phi < 0.16 \text{ eV}$), eventually resulting in better charge transport between rGO and SnO₂ (Figure 3.17c). It is important to notice that the $\Delta\Phi$ of $\sim 0.16 \text{ eV}$ for the SnO₂-rGO interface is significantly lower in comparison to the literature reports ($\Delta\Phi \sim 0.39 \text{ eV}$) [Bhangare et al., 2019] and can further result in better charge transport by reducing the recombination losses.

Apart from the typical heterojunction effect, the sensitivity highly depends on the charge transfer efficiency across the r-GO and SnO₂. In the L1 and L2, due to the direct Sn-C bond, a

fast electron transfer at the SnO₂ and r-GO interface occurs, leading to higher NO₂ sensitivity than in L3 and L4, where the charge transfer is governed via the sluggish Sn-O-C bond pathway (Figure 3.17d and e).

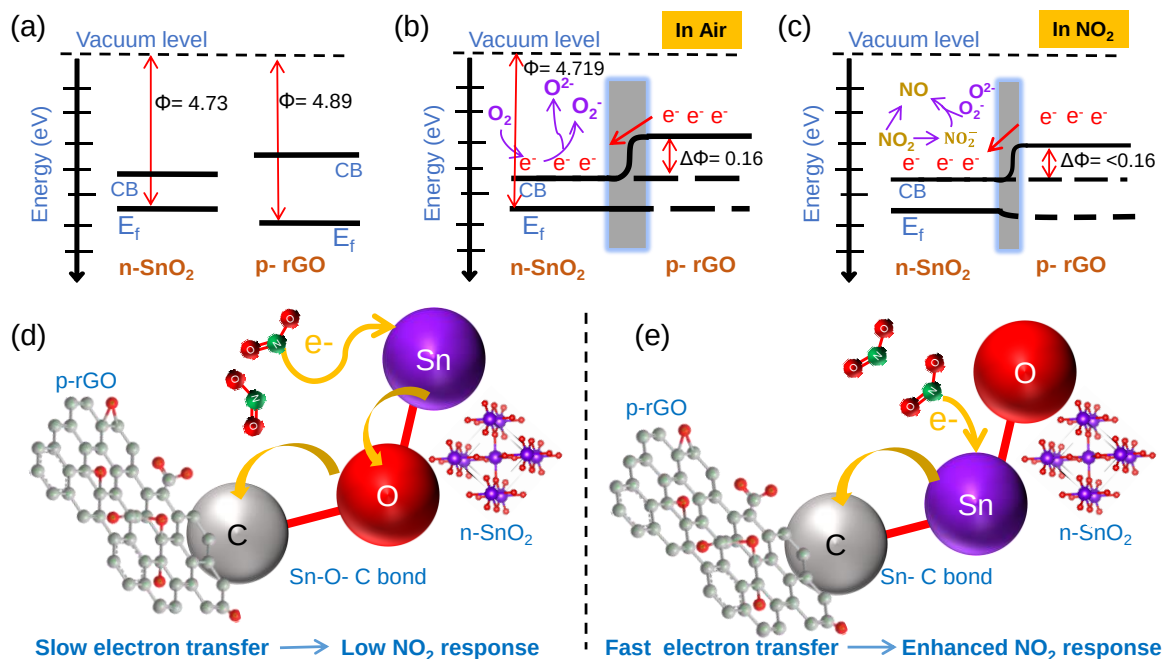


Figure 3.17: (a,b) Energy band diagram of pristine SnO₂, rGO, and L1, respectively. (c) Gas sensing mechanism in L1 is illustrated with the help of an energy band diagram on exposure to NO₂ gas. (d,e) Schematic demonstrating a physical model for SnO₂-rGO interaction, taking into account via Sn-O-C and Sn-C bonding in the NO₂ sensing mechanism.

Undoubtedly, the response in L1 is also enhanced due to a considerably higher surface area (107.5 m²/g) that allows more gas diffusion and oxygen adsorption at the surface of the sensing material and creates more reactive sites for the NO₂ interaction. Thus, when the sensor is exposed to different interfering gases/VOCs (NO₂, ammonia, humidity, xylene, ethanol, acetone, IPA, ethyl acetate, hexane, chloroform, toluene, benzene, and valeraldehyde), the most electron-deficient NO₂ gas showed the highest electrostatic attraction towards the electron-rich rGO which governs the ultra-selectivity of the sensor. Overall, the synergistic effect of the heterostructure, Sn-C bond formation, and high surface area enhances the sensitivity and selectivity in nanohybrid (L1). Thus, the fabricated SnO₂-rGO nanohybrid (L1) sensor showed a highly reliable ultrasensitive and ultrasensitive response towards NO₂ at room temperature.

3.4 Conclusion

SnO₂-rGO nanohybrid mixture was synthesized using a simple solvothermal method, and content was bifurcated into four layers based on size and density using the differential centrifugation method. A detailed structural characterization showed that SnO₂-rGO from the topmost layer (L1) with the optimum functional parameters (mesoporosity, specific surface area, pore-volume, crystallinity, smallest particle size, and Sn-C bonding) make it suitable for gas sensing application. The combinatorial approach was used for the fabrication of sensors and testing them simultaneously as a 2 × 2 array for different VOCs/gases. The L1 sensor showed the ultrahigh selectivity towards NO₂ with a response of 2.99 at 80 ppm and a limit of detection below one ppm (209 ppb) at room temperature. Interestingly, the response for NO₂ gas is highest for SnO₂-rGO nanohybrid (L1) due to the synergized contribution of optimum structural, morphological and chemical properties. The

high electronegativity difference between Sn and C facilitates faster electron transfer leading to enhanced NO₂ sensitivity. In contrast, enhanced electrostatic interaction between electron-rich r-GO and electron-deficient NO₂ enables selectivity. The approach presented in the study on synthesis and selection of SnO₂-rGO nanohybrid for sensor fabrication opens the route to more reliable gas sensors for practical applications.