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MEMS-Compatible, Gold NANOisland Anchored 1D Aligned ZnO Heterojunction Nanofibers: Unveiling NO\textsubscript{2} Sensing Mechanism with Operando Photoluminescence Studies

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Production and alignment of heterojunction metal oxide semiconductor nanomaterials-based sensing elements for microsensor devices has always posed fabrication challenges since it involves multi-step synthesis process. Herein, we demonstrate a coaxial electrosprning with in-situ photoreduction process for the fabrication of MEMS-compatible, 1D aligned gold nanoislands (GNI) anchored ZnO based Heterojunction Nanofibers (HNFs) and their complex plasmon-mediated NO\textsubscript{2} gas sensing mechanism has been investigated using operando photoluminescence studies. Evaluation of the gas sensing properties of aligned ZnO-GNI HNFs has exhibited excellent sensor response (196%) with rapid response time towards 500 ppb NO\textsubscript{2} gas at reduced operating temperature (200°C). Operando studies using photoluminescence and electrical measurements ascertained the existence of supplementary active sites in the multicrystalline nanofibers owing to the existence of Au nanograins over aligned ZnO nanofibers (NFs), thereby induces spill-over zone aiding the charge transfer phenomenon. The operando PL studies also revealed that the plasmonic effect of metallic Au and role of Zinc interstitial (Zn) defects and oxygen vacancies (V\textsubscript{O}) which influence the charge transfer between ZnO and surface anchored Au nanoislands. This study revealed atomistic insights into the structural defects and charge transport properties and the coaxial integration method of aligned ZnO-GNI HNFs paves way for unique strategy and development of suitable MEMS based gas sensors for real-time applications.

Among various MOS materials, quantum confined ZnO based one dimensional (1D) nanostructures, such as nanorods, nanowire, nanofibers, etc. have received huge attention in recent years towards development of advanced devices owing to their directed electron transport properties.\textsuperscript{8} 1D heterojunction nanomaterials based on ZnO could be an appropriate strategy for development of NO\textsubscript{2} gas sensors. While the catalytic behaviour promoting spill-over effect and localized surface plasmon resonance (LSPR) originated from noble metal nanoislands created on ZnO nanofibers can effectively enhance the NO\textsubscript{2} sensing properties, it can also further trigger its performance owing to its 1D structure. Although number of literature reports have endeavoured to explore the complex sensing mechanism in such heterojunction materials, more detailed analysis is not yet reported. Further to explore the detection mechanism of pure MOS towards various gas analytes, Raman spectroscopy,\textsuperscript{9,10} Diffuse Reflection Infrared Fourier Transform,\textsuperscript{11} X-ray Photoelectron Spectroscopy,\textsuperscript{12,13} UV-Visible Diffuse Reflectance spectroscopy,\textsuperscript{14} Electron Paramagnetic Resonance,\textsuperscript{15,16} etc. have been employed as an effective operando and in-situ methods. Among various operando techniques, Photoluminescence (PL) spectroscopy is found to be a unique approach which can simultaneously deliver information about recombination dynamics of charge transfer phenomenon and defect emission ascribing to the recombination in various defect states involved in enhancing the gas adsorption.\textsuperscript{17–19} However, real time studies based on PL...
spectral analysis to explore the sensing mechanism are limited to pure MOS materials towards various gas analytes.\textsuperscript{20-23} Recently, Li et al., described an \textit{ex-situ} photoluminescence studies to reveal the sensing mechanism of spinel type ZnFe\textsubscript{2}O\textsubscript{4} based NO\textsubscript{2} sensor and attempted to understand the oxygen vacancy-mediated charge transfer process.\textsuperscript{17} Cho \textit{et al.}, performed \textit{in-situ} PL analysis for 2D MoS\textsubscript{2} to elucidate the electron transfer mechanism during NO\textsubscript{2} gas adsorption. The electron depletion of MoS\textsubscript{2} by NO\textsubscript{2} adsorption was found to be leading to an enhanced intensity of the A\textsuperscript{1} peak and a quenching of A\textsuperscript{0} peak pointing towards the nature of electron transfer among MoS\textsubscript{2} and NO\textsubscript{2} molecules.\textsuperscript{19} Similarly, Ou \textit{et al.}, observed strongly quenched PL of SnS\textsubscript{2} upon exposure towards NO\textsubscript{2} thereby predicted the electron transfer mechanism.\textsuperscript{23} It is noteworthy that there are no reports exiting on operando PL studies for unveiling the complex gas sensing mechanism of heterojunction MOS materials under operational conditions. On the other hand, while considering MOS based heterojunction nanostructures as suitable materials for current sensor industries, the multi-step synthetic processes impede their wider use.\textsuperscript{24} Although wet-chemically synthesized heterojunction MOS based 1D nanorods or nanowires offer high charge transport properties, integration of such wet-chemically synthesized materials often found issues during fabrication like, device-to-device inconsistency and integration issues during device fabrication.\textsuperscript{25} Many researchers have attempted to develop on-chip fabrication of sensor devices and such methods are either based on pristine MOS materials or composites which involve multi stage processes hindering their device integration.\textsuperscript{26-29} Such issues can be addressed by adopting single-step production methods for the on-chip fabrication of MOS heterojunction nanofibers with controlled surface doping of catalytic metals/metal oxides. Among various synthetic methods, electrospinning is a versatile technique used for fabrication of MOS nanofibers. Especially, on-chip fabrication of MOS HNFs can be easily accomplished using coaxial electrospinning with effective control over orientation of 1D nanofibers and eliminates solvent and impurity effects during wet-chemical synthesis of MOS heterojunction materials. This study focus on a facile single-step fabrication process of 1D aligned coaxial heterojunction metal oxide semiconductor nanofibers (with ZnO/Au as a model nanosystem) based microsensor devices, which always have posed fabrication challenges, since existing methodologies involves multi-step synthetic processes. Coaxial electrospinning of nanofiber can also allow suitable functionalization of metal/metal oxide nanofibers and permit proper alignment of nanofibers on the active area of the sensor device. Until now, direct on-chip fabrication of aligned MOS based heterojunction nanofibers using coaxial electrospinning for NO\textsubscript{2} sensor applications is not yet reported. In this investigation, we have developed one dimensionally aligned ZnO-GNI nanofibers as a model heterojunction nanosystem, where the effect of catalytic sensitization and structural orientation can be easily achieved to understand their complex sensing mechanism that affects the sensor device performance. A novel synthetic approach based on coaxial electrospinning coupled with \textit{in-situ} photoreduction has been developed for the direct on-chip fabrication of 1D aligned core-shell heterojunction MOS nanofibers, which is otherwise a tedious multistep process. Investigation of the surface catalysis associated with the noble metal cluster (Au) anchored on ZnO nanofibers by analyzing gas/material interactions occurring at the heterojunction interfaces can also lead to a holistic understanding of the sensing mechanism which was further verified by \textit{in-situ} spectroscopic and crystallographic investigations. NO\textsubscript{2} gas sensing calibration of aligned ZnO-GNI nanofibers revealed an excellent sensitivity, high selectivity and fast response/recovery time towards the trace level concentration of NO\textsubscript{2}. Moreover, in order to reveal the charge transport, role of surface defects and oxygen vacancies associated with heterojunction nanostructures, operando PL analysis coupled with electrical measurements were performed. The NBE emission with deep level defects observed under operational condition explored the surface band bending phenomenon associated with the heterojunctions that can aid in understanding the complex detection mechanism of aligned ZnO-GNI HNFs based sensor at reduced working temperature. To the best of our knowledge, this is the first report on on-chip, single step fabrication of aligned ZnO-GNI HNFs for NO\textsubscript{2} gas sensor application and \textit{operando} PL spectral analysis during electrical characteristics acquisition. This investigation can contribute greatly towards the choice of better sensing materials and process conditions for sensor device fabrication and can pave way for development of low-cost aligned single nanowire devices with improved selectivity.

2. Experimental Section:

\textbf{Materials:} Zinc acetate (Zn(CH\textsubscript{3}COO)\textsubscript{2}.2H\textsubscript{2}O, 98%, Merck), Gold chloride (HAuCl\textsubscript{4}, 99.99%), polyvinyl alcohol (PVA-1,40,0000), polyvinyl pyrrolidone (PVP-2,00,000) were purchased from Sigma Aldrich chemicals. Ultrapure water (Millipore, Resistivity \textasciitilde 18.2 MO.cm) was used for all the experiments.

2.1 Co-axial electrospinning of 1D aligned ZnO-GNI nanofibers:

Aligned ZnO-GNI HNFs were fabricated using coaxial electrospinning technique. Experimental set-up used for coaxial electrospinning consisted of a high voltage DC power supply, dual syringe pump, coaxial spinneret and copper collector. The inner feed solution, Zinc acetate/PVA mixture was prepared as a homogeneous solution (A). While preparing the outer feed solution, 2.5 mM HAuCl\textsubscript{4}.nH\textsubscript{2}O was added to 10 mL of ultrapure water and subjected to stirring for 1 h. 8 wt. \% of polyvinyl pyrrolidone (PVP) was added to this solution to prepare the outer feed solution (B). The precursor solutions A and B were loaded in two 10 mL syringes, connected to a teflon coaxial spinneret. Both feed solutions were subjected to simultaneous electrospraying at a voltage, 20 kV with needle-collector distance of 22 cm using an independently controlled dual syringe pump. The flow rates were set as 0.5 mL/h and 0.8 mL/h for outer and inner fluids respectively. During the
electrospinning process, the spinning space was exposed to UV radiation (λ=254 nm) to facilitate in-situ photoreduction of Au3+ present in outer shell layer to form Au (0) nanoclusters to form heterojunctions on the inner core ZnO nanofibers. The electrospun Zn(CH3)2COO2/PVA@ Au(0)/PVP nanofibers were annealed at 550°C for 4 h in a tubular furnace at the rate of 4°C/min to remove the organic matter and to form crystalline ZnO-GNI HNFs on IDA transducers. For production of aligned ZnO-GNI HNFs, the electrospinning process was attempted using gold sputtered interdigitated array (IDA) electrodes with interfinger gap of 80 μm and overall sensing area of 18 mm2 as the collector plate. The parallel collector geometries associated with the IDA fingers assisted in alignment of the nanofibers across the finger electrodes.

2.2 Fabrication of coaxial spinneret assembly and Coaxial Electrospinning with in-situ UV-irradiation:

An in-house electrospinning unit with in-situ Ultraviolet (UV) irradiation facility was designed and developed for coaxial electrospinning process as shown in Figure S1(a). For the production of core-shell HNFs, noble-metal nanoclusters constituted the shell layer, which was produced using in-situ photo reduction by UV-irradiation of the electrospun fibers. The high voltage power supply of 30 kV was used for electrospinning unit with Glassman system. In order to synthesis core-shell nanofibers, coaxial spinneret components was designed using AutoCAD (Figure S1b) and fabricated using teflon as depicted in Figure S1(c-d).

2.3 Operando PL Studies:

Operando Photoluminescence emission studies were performed to explore the defect-mediated NO2 sensing mechanism of ZnO-GNI heterojunction nanosystems through their unique near band edge (NBE) emission characteristics and defect level emission behaviour during gas/material interactions. PL spectra were acquired using excitation monochromatic laser source at 355 nm with 1800 g/mm gratings in the backscattering arrangement. The spectra were acquired in the wavelength range of 350 to 750 nm. Emission spectra were collected in the backscattering geometry through a 20X objective lens during the gas/material interactions at the sensor operating conditions. LINKAM probe station (HF5600E-PB4) equipped with a Temperature-dependent heating stage capable of varying temperature up to 600°C was used to examine the operando emission properties under working conditions. The NO2 gas flow rate was maintained constant as 100 sccm under dynamic conditions with N2 as carrier gas.

3. Results and Discussions:

1D aligned ZnO-GNI HNFs were developed using a direct, on-chip fabrication method using coaxial electrospinning with in-situ photo reduction followed by thermal treatment at 550°C as shown in the Figure 2(a). The unidirectional alignment of nanofibers between the IDA electrode fingers were initially simulated using finite element method (FEM), which was used to analyse the 3D distribution of electric field lines during the
needle and collector and induced reduction of Au\(^{3+}\) to Au\(^0\) and eliminated the agglomeration of Au nanoclusters during thermal decomposition of polymeric contaminants. The alignment of nanofibers was carried out using Au sputtered IDA electrode and the overall coaxial electrosprinning process was performed inside dark enclosure. The nanofibers were aligned across the IDA fingers following the electric field lines as predicted by simulations. Thus, the Au nanoparticles decorated ZnO-GNI nanofibers could be directly aligned on the IDA sensor device.

Figure 2(b-c) depict the SEM images of the fabricated aligned ZnO-GNI nanofibers onto IDA electrode before thermal treatment. The as spun nanofibers were found to be highly aligned and with several micro-meter length and high aspect ratio applicable for electronics-sensing applications. As observed from the TEM image shown in Figure 2(d), the ZnO-GNI nanofibers possessed nanograined morphology after thermal treatment process and the relative grain size was estimated as 22±5 nm with typical fibre diameter of 90±8 nm. This unique method can offer many advantages over the existing technologies for sensor fabrication, such as (i) direct on-chip fabrication method of sensing materials on sensor devices using a cost-effective coaxial electrosprinning process (ii) offers single-step method for fabrication of aligned HNFs with effective control over orientation of 1D nanofibers (iii) eliminates solvent and impurity effects during wet-chemical synthesis of sensing materials (iv) allows suitable functionalization of metal oxide nanofibers by coaxial nanofiber assembly (v) reduced operating temperature with improved selectivity with the HNFs (vi) provides a model platform for a holistic understanding of the gas/material interactions for unravelling the complex sensing mechanism and (vii) can pave way to low-cost method for single nanowire devices with improved selectivity.

3.1 Structural analysis of 1D ZnO-GNI nanofibers:
XRD spectral analysis of pure ZnO and ZnO-GNI HNFs were performed to confirm the space lattice structure as depicted in Figure 3(a).

The intense diffraction peaks detected at 2θ resembles to the respective lattice planes further correlated to the hexagonal wurtzite phase of pure ZnO as revealed in our previous report. In the case of ZnO-GNI HNFs, along with the characteristic peaks of ZnO, the 2θ peaks detected at 38.33 and 44.12 were...
recognized to be fcc structure of Au with existing lattice plane of (111) and (200) (JCPDS # 01–1174). Diffraction peaks corresponding to gold nanoislands and absence of peak shifts for hexagonal ZnO suggest the decoration of gold nanoislands which further confirmed the existence of heterojunctions in ZnO-GNI HNFs.\textsuperscript{35}

Raman spectra of bare ZnO nanofibers and ZnO-GNI HNFs were performed using 532 nm laser in backscattering approach as compared in Figure 3(b). Raman spectra of 1D pristine ZnO nanofibers acquired at RT exhibited an intense peak observed at 437 cm\(^{-1}\) due to \(E_{2\text{high}}\) mode of wurtzite phase of ZnO nanostructure. The strong peak observed at \(E_2\) mode confirms the crystallinity of ZnO. Moreover, additional peaks arise near minor frequency at 331 cm\(^{-1}\) and 377 cm\(^{-1}\) corresponds to the phonons vibrations at the zone boundary, \(E_{2\text{high}}\) - \(E_{2\text{low}}\) and \(A_1\) (TO) modes respectively. Likewise, the peaks detected at 329 and 437 cm\(^{-1}\) could be attributed to the zone-boundary interactions of phonons in ZnO. Comparable Raman peaks of ZnO were detected for ZnO-GNI HNFs with considerable shift as depicted in Figure 3(b), owing to the existence of gold nanoislands anchored over the ZnO surface.\textsuperscript{36–38} A broad peak detected near 578 cm\(^{-1}\) related with the \(E_1(LO)\) mode reflecting the prevalence of high oxygen vacancies (\(V_o\)) and zinc interstitials (\(Z_{ni}\)) in the materials. Pristine ZnO and ZnO-GNI HNFs showed a prominent \(E_1(LO)\) band, which confirmed the existence of \(V_o\) and \(Z_{ni}\) defects. The formation of heterojunctions leads to interfacial charge transfer which was confirmed from the quenched \(E_{2\text{high}}\) and \(E_{1(LO)}\) bands with significant shift in peak as observed for ZnO-GNI HNFs which may enhance the NO\(_2\) sensing characteristics.\textsuperscript{39}

### 3.2 Morphological characterization of ZnO-GNI nanofibers:

TEM image analysis of porous ZnO-GNI HNFs is depicted in Figure 4. ZnO-GNI nanofibers displayed characteristic nanograined multicrystalline structure with one dimensional morphology as depicted in Figure 4(a). Further, it is evident from the high resolution TEM images of ZnO-GNI HNFs and histogram (inset) in Figure 4(b) that the average grain size of ZnO in ZnO-GNI HNFs are estimated as 22±6 nm and length extending to some micrometers through high aspect ratio as appropriate to electronics and sensing applications. The average particle size of Au nanoparticles achored on ZnO were calculated as 15±2 nm (Figure 4a-b). The SAED pattern of heterojunction nanofibers displayed concentric ring patterns of ZnO-GNI as depicted in Figure 4(c) further confirmed the multicrystalline nature of the nanoparticles corresponding to hexagonal ZnO and cubic Au owing to the formation nanograined morphology. The SAED pattern was further indexed and the planes (101), (203), (110) and (112) represents the wurzite ZnO crystal lattice and the planes (111) and (311) correspond to cubic Au crystal plane as inferred from the JCPDS card no. 36-1451 for ZnO and JCPDS card no. 04-0748 for Au respectively. HRTEM image of ZnO-GNI nanofiber depicted in Figure 4(d) evidently display the presence of discrete lattice fringes for individual ZnO nanograin and Au nanoislands. Further, in order to estimate the \(d\)-spacing values of ZnO-GNI, inverse FFT image processing was carried out using digital
micropore spacing of ZnO was measured as 2.81 Å, which corresponds to [100] lattice and 2.41 Å of Au nanoisland is related to [111] lattice as revealed in Figure S11(c-d). The results further confirmed the formation of ZnO-GNI heterojunctions at the interfaces.40 Moreover, the ZnO-GNI HNFs exhibited nanograin morphology with intrinsic porosity formed while calcination process coupled with abundant surface area could emboss ZnO-GNI HNFs as an efficient sensing material at reduced operating temperature. Furthermore, BET analysis was carried out to quantify the specific surface area and analyze the porous structure of ZnO-GNI HNFs. Detailed BET surface area analysis of ZnO nanofibers and porous ZnO-GNI nanofibers are depicted in Figure S12 and the calculated BET surface area, pore volume and pore size were summarized in Table S6. The increase in specific surface area of 26.688 m²/g and pore volume of 0.092 cm³/g for ZnO-GNI HNFs compare to pristine ZnO nanofibers can provide abundant surface-active sites and facilitate the easy charge-carrier transport leading to enhanced NO₂ sensing properties.

3.3 XPS analysis of ZnO-GNI nanofibers:

The XPS analysis was conducted to examine the oxidation states of the chemical elements present in ZnO-GNI HNFs. Figure 5(a) displays the survey scan spectra of pristine ZnO and ZnO-GNI nanofibers which revealed the existence of peaks consistent to Zinc, gold and oxygen confirming the material purity. Figure 5(b) depicts the fine-scan Zn 2p peaks of pure ZnO and ZnO-GNI ZnO-GNI HNFs. Fine scan Zn 2p peaks exhibited major binary peaks detected at binding energy value of 1044.5 eV and 1021.5 eV consistent with Zn 2p₁/₂ and Zn 2p₃/₂ respectively which indicated the divalent oxidation state of ZnO. Further, energy separation between these two peaks is 23.0 eV which confirms the existence of Zn²⁺ state in the ZnO crystal plane in nanofibers.41 Whereas, ZnO-GNI HNFs exhibited chemical shift to lower binding energy of 1020.4 and 1043.4 eV, associated to pure ZnO nanofibers due to accommodation of Au nanofibers over the surface of ZnO and existence of Zn defects in the nanograin structure. The fine scan analysis of O1s spectrum of ZnO-GNI nano fibers is depicted in Figure 5(c). The O1s bands in pristine ZnO and ZnO-GNI nanofibers were deconvoluted into two peaks corresponding to O₁, and O₆; peak at 528.8 eV assigned to lattice oxygen species existing in Zn–O bonding and the peak at 530.4 eV is related to oxygen-deficient region (O⁻ and O²⁻ ions) in the fibre network.42

As inferred from Figure 5(c), the binding energy peak is attributed to O₆ i.e., chemisorbed oxygen species which was found to be dominant in ZnO-GNI nanofibers owing to the existence of more nanograins, that can be further correlated with the sensing phenomenon. The O1s peak in the ZnO-GNI HNFs was found to shift to lower binding energy compared to pristine ZnO nanofibers owing to the existence of gold nanofibers that accept electrons from the surface of ZnO at the heterojunctions and thereby create oxygen vacancies.42-44 Hence, oxygen vacancies induce a lower energy shift of O 1s peak. Consequently, the occurrence of surface-active sites and enhanced catalytic behaviour of Au nanofibers at the heterojunctions can make it as an active sensing material. Figure 5(d) shows the fine scan spectra of Au 4f and Zn 3p peaks in ZnO-GNI nanofibers.

Figure 5. (a) Survey scan XPS spectrum and high-resolution peaks of (b) Zn 2p (c) O 1s, (d) Au 4f corresponding to pristine ZnO and ZnO-GNI HNFs, (e) Valence band onset region of UPS spectra of pure ZnO NFs and ZnO-GNI HNFs and (f) Secondary edge region.

The high-resolution Au 4f peak of ZnO-GNI nanofibers was found to be overlayed with Zn 3p of ZnO, which was further deconvoluted to corresponding peaks related to Au 4f₁/₂ (81.7eV), Au 4f₃/₂ (85.3eV), Zn 3p₁/₂ (86.9eV) and Zn 3p₃/₂ (89.6eV), respectively as depicted in Figure 5d. Moreover, absence of Au 4f signal in the pure ZnO nanofibers was clearly evident in the high-resolution Zn 3p spectra. This indicates the distribution of Au nanofibers formed on ZnO nanofibers during coaxial spinning followed by thermal treatment.43 However, ZnO-GNI nanofibers showed characteristic nanograin morphology and randomly oriented Au nanofibers, the conduction band of ZnO is nearly equivalent to the Fermi level of Au, so that the electron can transfer from ZnO to Au producing higher electron density on at the surface anchored Au nanofibers. These findings can be further affirmed with the operating PL spectral studies performed under the sensor operational conditions. Such intricate analysis can also unveil the electron transfer phenomenon and intrinsic defects present in the ZnO-GNI HNFs which can significantly enhance the NO₂ gas sensing characteristics. Furthermore, the valence band
onset ($E_{\text{ onset}}$) and secondary electron cut-off ($E_{\text{ off}}$) of pure ZnO NFs and ZnO-GNI HNFs are shown in the Figure 5(e–f). As observed from the UPS spectra, $E_{\text{ onset}}$ and $E_{\text{ off}}$ was calculated to be 2.39 and 2.22 eV and 15.6 and 16.8 eV, respectively. Using the incident energy, $h\nu = 21.2$ eV (HeI laser source), the work functions of pristine ZnO NFs and ZnO-GNI HNFs have been estimated as 5.2 eV and 4.5 eV respectively. The gold nanoislands anchored ZnO nanofibers show reduction in the work function owing to the formation of Schottky contact which further leads to easy electron transfer from ZnO to Au.

### 3.4 Aligned ZnO-GNI nanofibers based NO$_2$ Gas sensor calibration:

The NO$_2$ sensing characteristics of aligned ZnO-GNI HNFs fabricated onto IDA transducer electrode were evaluated using the gas sensor calibration unit existing in our laboratory. The NO$_2$ sensing properties of ZnO-Au nanosystems were assessed using a custom-built gas sensor test station. The details of the gas sensor calibration unit have been given in the supporting information (section S4). The working temperature of gas sensors is one of the important parameters that have considerable impact on sensitivity and selectivity. Figure 6(a) shows the sensor response of bare and 10 aligned ZnO-GNI HNFs towards exposure to 1 ppm of NO$_2$ gas at varied temperature (50–350°C). The highest sensitivity (S) was observed at 300°C and 200°C for ZnO nanofibers (193%) and aligned ZnO-GNI HNFs (462%) respectively, toward NO$_2$ gas, which were further selected as the operating temperature. It was revealed that the operating temperature was decreased for aligned ZnO-GNI HNFs compared to pure ZnO nanofibers. The current study reveals that aligned ZnO-GNI nanofibers exhibited reduced sensor working temperature and boost the response to NO$_2$ compared to pristine ZnO owing to the presence of catalytic Au nanoislands upon physisorption of analyte gas. For pristine ZnO nanofibers, higher operating temperature induces greater number of O$^+$ ions on the ZnO surface and thereby rate of NO$_2$ adsorption was found to be increased. In the case of aligned ZnO-GNI nanofibers, owing to the difference in workfunction of ZnO and Au, electrons transfer from ZnO to Au site and therefore the catalytic Au nanoislands become electron rich active centers. Therefore, during NO$_2$ exposure, excess electrons present in the Au nanoislands can be easily captured by the oxidizing NO$_2$ molecules at reduced temperature and spill-over effect leading to further surface reactions with surrounding ionsorbed oxide ions on ZnO. This could further promote the formation of depletion region near the heterojunctions on the surface of ZnO-GNI nanofibers. Hence, the energy needed to achieve maximum sensor response is significantly less for ZnO-GNI nanofibers than pristine ZnO nanofibers.

The electronic sensitization takes place when NO$_2$ species adsorb on the core ZnO nanograined fibre and spill-over from catalytic Au nanocluster to ZnO. The change in resistance occurs during surface reaction of NO$_2$ with the chemisorbed negative ions exist over ZnO surface. Figure 6(b–c) depicts the dynamic sensor response/recovery plots for pristine ZnO and aligned ZnO-GNI nanofibers at different NO$_2$ concentrations under ideal operating temperature. With increase in NO$_2$ gas concentration, variation of resistance was found to be correspondingly increased. Figure 6(d) depict the comparative sensor response ($\Delta R/R_o$) as a function of NO$_2$ concentration ranging from 500 ppb to 3 ppm which was tailed to be in linear trend. The NO$_2$ concentration.
sensor parameters are tabulated in Table S3. The NO$_2$ sensing properties depicted in Table S3 shows that the sensitivity increased from ~32% to ~196% towards exposure to 500 ppb of NO$_2$ gas for pristine ZnO and aligned ZnO-GNI nanofibers respectively with fast response time ($t_{res}$) of 4-5s than that of pristine ZnO nanofibers with response time ($t_{res}$) of 7-10s. However, 1D aligned ZnO-GNI HNFs based sensor possesses lower detection limit (LOD) of 500 ppb which is an important index of gas sensor performance as depicted in Figure S13. The enhanced sensitivity of heterojunction nanofibers can be ascribed to the directed electron transfer via radial conduction process through 1D ZnO nanofiber and the charge transfer at the Au-ZnO interfaces. Also, highly aligned nanofibers oriented across the IDA fingers and co-existence of intrinsic defects in the nanograined heterojunction fibers lead to higher NO$_2$ adsorption compared to pristine nanofibers.

While exposing the heterojunction nanofibers towards NO$_2$ atmosphere, the NO$_2$ gas species primarily interact with chemisorbed O$^-$ and minor O$_2^-$ species, and further trap additional carriers from the higher state instead of interacting directly on the ZnO surface. Therefore, the resistance increases by reducing the electron accumulation region ($L_D$) of the heterointerface. In order to ascertain the nature of the adsorbed oxygen species on ZnO-GNI HNFs, the slope of log ($S_{GNI}-1$) against log ($P_{NO2}$) was estimated from Figure 5(e). Typically, the exponent $\beta$ expressed in the relation ($S_{GNI} = \alpha P_{NO2}^{\beta}$) is the stoichiometry of the elementary reaction on the surface. It is well known that, the value of $\beta$ near to 0.5 and 1 can be attributed to O$^2-$ and O$^-$ ions adsorbed on the sensing material surface. As estimated from the gradient of tailored line in Figure 5(e), the value of $\beta$ was estimate to be 0.68 for 1D aligned ZnO-GNI nanofibers at its operating temperature indicate that the major adsorbed oxide species might be O$^-$ instead of O$_2^-$ ions for ZnO-GNI nanofibers. Aligned ZnO-GNI nanofibers possess enhanced sensitivity owing to the adsorbed O$^-$ ions which is considerably more dynamic and chemically energetic than O$_2^-$ and produces more favourable space for active catalytic reactions. The band bending values were further estimated from the transient sensor response. The $q\Delta V$ was assessed from the NO$_2$ sensor response of aligned ZnO-GNI HNFs with various NO$_2$ gas concentration. The surface band bending state of aligned ZnO-GNI nanofibers possessed higher energy when compared to pure ZnO nanofibers, further confirms the creation of wider depletion region during exposure to NO$_2$ as depicted in Figure 6(f). The construction of aligned ZnO-GNI heterojunctions at the nanograined ZnO heterointerfaces could be consequently responsible for the preferred carrier transfer and higher rate of NO$_2$ adsorption.

Moreover, selectivity towards NO$_2$ for the ZnO-GNI HNFs was examined towards possible intrusive gases like, NH$_3$, H$_2$S, SO$_2$, C$_2$H$_5$OH and C$_3$H$_6$O. 1D aligned ZnO-GNI HNFs exhibited good selectivity at its operating conditions owing to the existence of Au nanocluster and its intrinsic surface defects mediated sensing performance as shown in Figure S8. These ZnO-GNI heterojunctions on the surface of nanofibers favored effective electron mobility, inter-band transitions, development of Schottky contacts at the heterointerfaces and spill-over sensitization of NO$_2$ compared to other gases. Additionally, ZnO-GNI has also shown promising efficiency due to their unique SPR properties and interfacial charge transfer. Apart from this, while forming the ZnO-GNI heterojunctions, the electrons could move from ZnO to Au due to work function difference making the Au centers as electron rich active sites, creating more oxygen vacancies at the ZnO interfaces. Therefore, metallic gold nanoslands could act as suitable sites for adsorption of oxidizing gas molecules (NO$_2$) and hence that can promote greater ionsorption via spill-over sensitization aiding to achieve selectivity towards NO$_2$.

The intervention of moisture on NO$_2$ sensing characteristics of ZnO-GNI HNFs in the RH range of 10–85% is depicted in Figure S9(a-b). As RH % increased the sensitivity tends to decreased for ZnO-GNI nanofibers due to intervention of moisture which persisted on the material decreasing the electron transfer process. Aligned, ZnO-GNI HNFs exhibited a minimal reduction in the sensor response as shown in the Figure S9 (b) and comparatively stable response in the RH range of 10% to 25%, which is due to the lower operating temperature (200°C) of the sensor. When the RH% increases above 25%, the interference of humidity persists over the sensor material that can further reduce the flow of electrons, and thereby decrease the rate of NO$_2$ adsorption. Furthermore, the transient response studies of aligned ZnO-GNI HNFs were acquired towards 1 ppm of NO$_2$ under its operating temperature of 200°C before and after 10 months is shown in Figure S10(a-b). The aligned ZnO-GNI nanofibers showed acceptable constancy even after 10 months for repeated cycles of NO$_2$ exposure. Over a period of time, it was observed a minimal reduction (15%) in the sensor response, but similar base resistance value was maintained during the sensor operating temperature. This result illustrates the long term stability of aligned ZnO-GNI nanofibers sensor along with repeatability.

3.5 Operando Electrical and PL Studies:

Operando PL emission spectral analysis was performed for 1D aligned ZnO-GNI nanofibers while acquiring the temperature-dependent electrical characteristics (I-V) using LINKAM probe station under operating conditions of the sensor. The I-V characteristics measurement was performed under different environments, such as ambient condition (air, room temperature) at operating temperature and during NO$_2$ exposure as showed in Figure S6(a-d). The ZnO-GNI nanofibers showed improved conductivity as compared to pristine ZnO nanofibers owing to evolution of heterointerfaces which introduces more surface defects and free charge carriers.

In order to understand the influence of one-dimensional structure, operando studies were performed for ZnO-GNI nanorods and compared with that of ZnO-GNI nanofibers. The increase in electrical conductivity for ZnO-GNI nanorods at its operating temperature is mainly due to the existence of available free charge carriers and the formation of ZnO-GNI heterojunctions and also crystalline nature of ZnO nanorods. However, the conductivity of ZnO-GNI nanofibers was observed to be decreased under the working temperature compared to heterojunction nanorods. This indicates that the free electrons
existing in ZnO-GNI nanofibers have been significantly trapped by enormous ionosorbed oxygen species due to nanograined structure which possess higher active sites for the oxygen ionosorption and therefore, enhanced sensitivity towards NO2 gas can be expected. The conductivity of all the materials were further reduced, when exposed to NO2 gas as evident in Figure S6 (a-d).

For better understanding about the enhanced NO2 gas sensitivity, electrical conductivity (I-V characteristics) measurements were used to estimate the barrier height ($\phi_b$) under various conditions using the relation,\(^5,49\)

$$\phi_b = \frac{KT}{q} \ln \left( \frac{A^*T^2}{I_b} \right)$$  (1)

Where, $\phi_b$ is the barrier height, $k$ is the Boltzmann constant, $T$ is the temperature, $A$ is the effective area, $A^*$ is the effective Richardson constant, $q$ is the electronic charge and $I_b$ is the reverse saturation current. The barrier height was estimated at various environments by evaluating the in-situ electron transport properties to correlate the emission properties during gas adsorption. Figure 7(g) shows the bar chart comparing the barrier height and relative sensor response for the investigated materials. The barrier height ($\phi_b$) was noticed to be increased for ZnO-GNI nanofibers than the ZnO-GNI nanorods at the operating temperature, whereas the barrier height was further increased upon exposure to NO2 (Figure 7g). The difference in the barrier height before and during NO2 exposure under operational conditions was estimated for ZnO-GNI nanorods and ZnO-GNI nanofibers as 0.083 eV and 0.104 eV respectively. This increment in barrier height can be correlated with the enhanced deep levels (DLs) emission peaks, due to abundant free charge carriers and complex oxygen vacancies, which are also primarily responsible for superior gas sensitivity for aligned ZnO-GNI nanofibers towards NO2 exposure. Furthermore, the depletion layer width, (Debye length, $L_D$) of pristine ZnO and ZnO-GNI HNFs was estimated using the relation,\(^50\)

$$L_D = \left[ \frac{2\varepsilon ZnOq}{\varepsilon ZnO_0 q_0} \right]^{1/2}$$  (2)

Where, $\phi$ is the barrier height established by oxygen adsorption, $\varepsilon ZnO$ is the permittivity of ZnO, $N_{ZnO}$ is the electron concentration in ZnO, and $q$ is the electron charge (= 1.6 × 10\(^{-19}\) C). The values of $N_{ZnO}$ ≈ 10\(^{16}\) cm\(^{-3}\) at room temperature, $\varepsilon ZnO$ ≈ 8.5, and $\varepsilon ZnO_0$ ≈ 1.15 and 1.34 eV for ZnO NFs and ZnO-GNI HNFs respectively were calculated from the I-V curves shown in Figure S6 and the barrier height bar chart depicted in Figure 7g. The Debye length ($L_D$) was estimated to be ~8.7 nm and ~9.4 nm for ZnO NFs and ZnO-GNI HNFs respectively.

Operando photoluminescence emission spectral studies were performed during electrical measurements to explore the defect-mediated NO2 sensing mechanism of ZnO-GNI heterojunction nanosystems through their unique features such as near band edge (NBE) emission and defect level emission behaviour during gas/material interactions. Scheme 1 shows the schematic illustration of experimental setup used for operando Photoluminescence studies of porous ZnO-GNI nanosystems. Figure 7 displays the emission spectra of pristine ZnO and ZnO-GNI nanofibers under different operating conditions. Similarly, the emission bands for ZnO nanorods and ZnO-GNI heterojunction nanorods are depicted in Figure S7. The PL spectra were collected at room temperature and at operating temperature conditions in order to understand the influence of temperature on their structural and defect-mediated changes of the sensors in the absence of NO2 gas. Further, PL spectra were acquired during NO2 exposure to study the role of defects while NO2 adsorption. The room temperature PL spectra of 1D pristine ZnO and ZnO-GNI...
nanorods and nanofibers in air was analysed by the presence of two major emission bands including a highly intense UV peak corresponding to the exciton luminescence and visible luminescence originated from the intrinsic defects existing in ZnO. The corresponding emission peaks of the observed complex band revealed that the intensity of edge luminescence is stronger than the intensity of visible luminescence, indicating the excellent crystalline quality of ZnO-GNI systems as depicted in Figure 7 and Figure S7.

The room temperature PL emission spectra of all the investigated 1D materials are represented in black line as shown in Figure 7 and Figure S7. Each material exhibited two major peaks, a near-band-edge (NBE) emission at ~390 nm and deep levels (DLs) emission at visible region ~490 – 750 nm. The dominant peak at UV region is the NBE emission, which is due to direct recombination of free-exciton including bound state excitons and shallow states. The DLs comprise of the major bands related to oxygen vacancies ($V_{0}^+$), oxygen interstitials ($O_i$), and zinc vacancies ($V_{zn}$). The band at ~500–540 nm originates from the non-radiative electron capture from the conduction band (CB) of ZnO by singly charged oxygen vacancy ($V_{0}^+$), leading to an unstable state that recombines with a photo- excited hole in the valance band (VB) of ZnO. Whereas, the band between ~550-610 nm corresponds to the grain boundary-induced depletion region which undergoes radiative recombination with the CB electrons. The peak within 610–750 nm is typically attributed to oxygen interstitials ($O_i$). Similar trend was observed in the emission spectra obtained under operational conditions (red line) and under NO$_2$ exposure (blue line). It is clearly observed from the PL spectra depicted in Figure 7(a-b) and Figure S7(a-b) that, with increasing operating temperature, the NBE emission shows a red shift from 401 to 412 nm for ZnO nanorods, 400 to 404 nm for ZnO-GNI nanorods, 406 – 412 nm for ZnO nanofibers and 401 – 408 nm for ZnO-GNI nanofibers respectively. The band shifting of NBE emission is due to the increase in carrier density introduced by oxygen vacancies which indicates the narrowing of energy band gap observed in the case of NO$_2$ gas sensing properties, the PL spectra were deconvoluted into Gaussian peaks and fitted with the experimental data. The deconvoluted NBE and DLs peaks of pristine 1D ZnO and ZnO-GNI nanosystems with corresponding energy level diagrams are shown in the Figure 7(c-d) and Figure S7(c-d). Initially, the relative area under the deconvoluted curves of NBE emission and DLs emissions were estimated as shown in bar chart in Figure 7(e-f). The NBE emission clearly indicated thermal quenching effect in the case...
of both ZnO-GNI nanorods and ZnO-GNI nanofibers under sensor operational conditions (red line). The results revealed that, due to the existence of Au nanoislands on the surface of core ZnO fibre, back spill-over phenomenon occurs i.e., excited electrons from ZnO can transfer back to Au producing more electron density at the Au centres of the ZnO-GNI heterojunctions. In the case of heterojunctions, electron transfer occurs due to the workfunction difference of the constituent materials, where, the metal (Au) work function ($\phi_m$) is higher than that of the semiconductor ($\phi_s$), i.e., $\phi_m > \phi_s$ and hence the electrons flow from the CB of ZnO to Au. The electron transfer continues until the Fermi levels of Au and ZnO attain equilibration. Under the sensor operational conditions, Au nanoislands present on the surface of ZnO can extract more electrons from the conduction band of ZnO which further restrict the direct and trap related charge carrier excitons since the Fermi level ($E_f$) of Au nanoislands occurs beside the $E_{CB}$ of ZnO. Therefore, the thermal quenching of NBE emission was observed in the PL spectra of ZnO-GNI systems under the sensor operating temperature. The accumulation of charge density on Au induces more catalytic activity to make more ionosorbed oxygen species surrounding near to the Au/ZnO interfaces which leads to enhanced NO$_2$ adsorption compared to pristine ZnO.

Further, it is interesting to note that during NO$_2$ exposure, the intensity of NBE emission peak (blue line) of ZnO-GNI HNFs was increased compared to the NBE peak at working temperature, which means, the self-trapped electrons; free electrons present in the CB of ZnO and electron rich Au centres have major roles in increasing the rate of NO$_2$ adsorption on the surface of ZnO-GNI nanofibers and ZnO-GNI nanorods as inferred from Figure 7(b and e). Whereas, the intensity of NBE emission of pristine ZnO nanofibers was found to be drastically reduced under NO$_2$ exposure owing to the recombination dynamics as depicted in Figure 7(a and e). Consequently, the enhanced sensitivity of ZnO-GNI nanofibers can be due to the 1D nanograin morphology having enormous active sites to adsorb more NO$_2$ molecules than that of ZnO-GNI nanorods. Hence, the NO$_2$ adsorption takes places mostly through spill-over by Au nanoislands significantly influenced by the charge recombination process during the gas/material interactions.

On the other hand, the DLs emissions consist of intrinsic defects such as oxygen vacancies ($V_{O}^{\cdot\cdot\cdot}$, $V_{O}^{\cdot\cdot}$), deep interstitials of oxygen (O$_{i}$), Zinc (Zn$_{i}$) and anti-site oxygen (O$_{Zn}$) that may be formed on the surface of the pristine ZnO and ZnO-GNI nanostructures during the synthesis process may also have equal responsibility towards enhanced NO$_2$ sensitivity. The broad DLs emission spectra were deconvoluted to evaluate the relative concentrations of structural defects present in pristine ZnO and ZnO-GNI nanosystems revealed in Figures 7(c-d) and 5(c-d). Being under ambient conditions, the ZnO-GNI heterojunction nanosystems possessed more defect states compared to the pristine ZnO nanostructures as depicted in Figure 7(e-f). During operational conditions, the intensity of DLs emission peaks decreases for pristine ZnO nanorods and nanofibers compared to that of ambient conditions, which could limit the rate of NO$_2$ adsorption. Whereas, under operational conditions, the free excitons and self-trapped electrons were trapped by the Au nanoislands further becoming more negative and ZnO become more positively depleted, and shows enhanced DLs emission. Hence, the singly charged oxygen vacancies ($V_{O}^{\cdot}$) and anti-site oxygen (O$_{Zn}$) play major roles in enhancing the NO$_2$ sensitivity of ZnO-GNI nanofibers as evident from Figure 7(c-d). During NO$_2$ exposure, the DLs emission was found to be suppressed due to the adsorption of NO$_2$ molecules on the surface of the materials. The relative concentration of $V_{O}^{\cdot}$ and O$_{Zn}$ were quenched drastically as depicted in Table S5 compared to DLs emission observed under operational conditions owing to charge recombination process occurring when NO$_2$ molecules react with the dangling bonds present on the surface of the ZnO nanostructures as evident from Figure 7(a-d). The oxygen vacancies ($V_{O}^{\cdot}$) can bind more firmly with NO$_2$ molecules drawing more electrons from ZnO surfaces compared to defect-free ZnO surface and can also act as preferential adsorption sites for NO$_2$ molecules. It is noteworthy that the enhanced sensitivity of ZnO-GNI nanofibers can be attributed to the nanograin structured having enormous active heterojunction interfaces to adsorb more NO$_2$ molecules compared to the crystalline 1D ZnO-GNI nanorods. Based on the intricate analysis, we have understood that 1D aligned ZnO-GNI hetero-junction nanofibers possess enhanced sensing behavior due to the directed electron transport properties, hetero-junctions and formation of surface adsorbed oxide species, band-bending and spill-over sensitization, which have been justified by performing operando PL and electrical measurements. The NBE emission with deep level defects observed under operational condition was found to be favoring the band bending process in the heterojunctions, which further aided in understanding the complex sensing mechanism in 1D aligned MOS heterojunction MOS nanofibers at reduced operating temperature.

Typically, ZnO-GNI nanofibers when exposed to ambient environment under working temperature, surface adsorption of oxygen takes place resulting in seize of free electrons and produces charge carrier separation on the surface of heterojunction nanofibers. Based on the value of $\theta$ estimated from the transient NO$_2$ sensor response plot, the ionosorbed oxide species on aligned ZnO-GNI HNFs are predominantly O$^{-}$ rather than O$_{2}^{2-}$ ions as illustrated in the graphic representation Scheme 2(a-b). The energy band structure of pure ZnO and 1D aligned ZnO-GNI nanofibers were theoretically simulated using AFORS-HET v.2.5 as depicted in Scheme 2. The constructed band diagram evidently depicted the upward bending state of ZnO interface, while forming the ZnO-GNI heterojunctions as a result of their electron transfer due to the changes in position state of Fermi level energy. The Fermi level of the ZnO was found to align with that of Au when the electron transfer reaches equilibrium while forming the heterojunctions. The difference in CB and VB of ZnO and ZnO-GNI nanostructures were estimated from UV-DRS analysis as shown in Figure S4 which was used as the input parameter for the simulation studies. Upon NO$_2$ exposure, Au nanoislands anchored over the ZnO nanofibers dissociate the adsorb NO$_2$ molecule into NO$_2^{-}$ which
further interact with the oxide ions existing near the interface possesses formation of NO$_2$ as denoted in the relations below,

$$\text{NO}_2(\text{ads}) + e^- \rightarrow \text{NO}_2(\text{ads-Au})$$

(3)

$$\text{NO}_2(\text{ads-Au}) \rightarrow 2\text{O}^- + \text{NO}_2$$

(4)

Due to the presence of surface ionosorbed oxide ions, the surface potential barrier drastically increased and thereby the resistance of the sensor increases which further leads to band bending at the ZnO interface. As evident from operando PL studies of ZnO-GNI nanostructures, the variation in the estimated percentage of area under the dominant band such as NBE emission and deep level defects (DLs) emission greatly influence the electrical properties and sensing performances. The inherent surface defects, (V$_{\text{O}}$, Zn$_{\text{vac}}$, and O$_{\text{O}}$) vigorously overwhelm the barrier height of schotky ZnO-GNI which can turn into conducting channel for free electrons in the aligned 1D heterojunction nanofibers. Moreover, as evident from the emission spectra, the unique SPR behaviour of Au nanoislands further confirmed the high-density $e^-$ carriers exist in the higher energy states that occurs during $e^-$ transfer between ZnO to Au as depicted in Scheme 2. The effective back spillover phenomenon aids in adsorption of more oxide species over the surface of ZnO-GNI HNFs. The operando studies based on PL and electrical measurements confirmed the development of barrier potential at the ZnO-GNI heterojunctions, which reduces the $e^-$ mobility and thereby broaden the trap depth ($L_o$) compared to pristine ZnO leading to the band bending, one of the most pertinent phenomena that should be considered during gas sensor development. From the aforementioned experimental evidences, it can be understood that the influence of spillover and back-spill effects on mechanism, plasmonic properties of Au nanoclusters, DLs defects and ideal band bending phenomenon enhance the rate of electronic sensitization process, apart from the directed electron transport due to the 1D structure of aligned ZnO-GNI HNFs. Table S7 compares the performance of ZnO-GNI nanofibers based NO$_2$ sensors reported in literature. It can be seen that the direct on-chip fabrication of 1D aligned ZnO-GNI nanofibers displays higher potential in detecting trace level concentration of NO$_2$ gas compared to existing reports apart from the manufacturing feasibilities. The insights derived from the present investigation points towards excellent potential of 1D aligned ZnO-GNI HNFs in detecting trace level NO$_2$ gas at lower operating temperatures.

Overall, an effective strategy developed with this investigation for the single-step fabrication of 1D aligned ZnO-GNI HNFs directly onto the sensor device can be considered as a unique method for sensor development owing to its multiple benefits both in terms of ease of fabrication as well as superior sensor performance. The directed electron transport properties of the aligned multicrostalline ZnO-GNI HNFs not only acquired through an on-chip direct coaxial electrospinning with in-situ photoreduction method, but also significantly promotes its NO$_2$ sensing properties. Such aligned heterojunction nanofibers show superior sensing properties compared to its randomly oriented 1D nanorods structures. The outcome of this work suggests that on-chip fabrication of 1D aligned ZnO-GNI nanofibers could be a single-step and cost-effective fabrication process which opens up a new paradigm for the design and development of low-cost, aligned single nanofiber devices with improved selectivity for real time NO$_2$ sensor applications and also bridge the gap between gas sensor research and industries for making better products.
4. Conclusions

To summarize, we have demonstrated an efficient direct on-chip fabrication of aligned ZnO-GNI HNFs based NO$_2$ sensor using coaxial electrosprinning with in-situ photoengraving method. The sensor fabrication method provides effective surface functionalization of nanofibers without any tedious and time-consuming steps. Aligned ZnO-GNI heterojunctions nanofibers exhibited higher sensor response (196%) with rapid response time towards 500 ppb trace level concentration of NO$_2$. The superior sensor response was due to abundant active sites through nanograined morphology and presence of Au nanocatalyst sites that can seize more O$^-$ ions by spill-over effect on the ZnO surface leading to the development of larger potential barrier with more electron donors, along with the directed electron transport due to its 1D aligned structure. More insights towards the electronic sensitization mechanism of the ZnO-GNI HNFs were unveiled from operando PL and electrical studies, which endowed the role of Zinc interstitial defects and oxygen vacancy on the spill over process and charge transfer between ZnO and Au nanofibers. The study also unravelled the complex sensing mechanism associated with localised surface plasmon resonance while forming heterojunctions, which is responsible for the enhancement of NO$_2$ sensing properties. The single-step production of aligned ZnO-GNI HNFs directly onto the sensor device can be considered as a promising strategy for developing high performance NO$_2$ gas sensor devices for real-time applications.

Conflicts of interest

“There are no conflicts to declare”.

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