

Green Synthesis of Pd-Bi₂O₃ Nanostructures by Azadirachta indica leaves extract for Selective and Stable Gas Sensing Performance

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Abstract

Nanostructured palladium-decorated bismuth oxide (Pd-Bi₂O₃) synthesized via a green and energy-efficient hydrothermal approach and systematically investigated as a multifunctional resistive gas sensing material. While electron microscopy demonstrated a porous nanostructured morphology with uniformly distributed Pd species, X-ray diffraction and Raman spectroscopy verified the formation of phase-pure monoclinic Bi₂O₃ with effective Pd incorporation and defect-induced lattice distortion. Gas sensing properties assessed in the concentration range of 25–200 ppm for NO₂, H₂, CO, and LPG. The Pd-Bi₂O₃ sensor exhibited outstanding selectivity toward NO₂, delivering a sensitivity of ~ 73% at 100 ppm with a low operating temperature of 120°C. Sensitivities of approximately 65%, 55%, and 50% were observed for reducing gases at the optimal working temperatures of 140°C (H₂), 160°C (CO), and 170°C (LPG), respectively. With reaction periods of 240 s for NO₂ and 141–429 s for reducing gases, the sensor showed reliable and reversible response behaviour. The 95.06% of the NO₂ response sustained after 30 days, according to long-term stability testing. Pd-induced catalytic activation, oxygen spillover, and effective regulation of charge transport at the Pd-Bi₂O₃ interface are responsible for the improved sensing performance.

1. Introduction

Metal-oxide semiconductors (MOS) have long been recognised as one of the most important classes of materials for resistive gas-sensing applications. N-type oxide materials have been extensively explored as resistive gas sensors owing to their simple device configuration, robustness, and compatibility with large-scale fabrication. Traditional metal oxides (TMOs) such as SnO₂, ZnO, and In₂O₃ have been the most widely employed in commercial gas sensor technology for decades. TMOs can identify flammable and poisonous gases at concentrations as low as parts per million (ppm) and typically operate at temperatures between 100 and 400°C [1–4]. However, the development of sensing materials capable of detecting gaseous species at extremely low concentrations, down to parts per billion (ppb), is imperative. This is due to the growing demand for high-performance gas sensors in healthcare diagnostics, automotive exhaust control, industrial safety, environmental monitoring, and novel hydrogen-based energy systems [5–7]. The primary sensing mechanism of MOS gas sensors relies on surface-controlled processes, including gas adsorption, surface redox reactions, charge transfer between adsorbed species and the semiconductor, and subsequent regulation of electrical conductance. Therefore, improving gas-sensing performance crucially depends on modifying surface features such as surface area, defect density, catalytic activity, and electronic structure [8–11]. In this context, nanostructured metal oxides have gained considerable attention because of their unusually high surface-to-volume ratio, reduced diffusion routes for charge carriers, and enhanced population of active surface sites [12–15]. Recently, Bi₂O₃ has emerged as a promising alternative TMOs sensing material. Numerous polymorphic phases, a low band gap, high oxygen-ion mobility, and an abundance of oxygen vacancies are among the unique physicochemical properties of Bi₂O₃ that are beneficial for gas

adsorption and charge transfer [16–18]. Bi_2O_3 -based nanostructures (NSs) are well-suited for multifunctional gas-sensing platforms because they are more sensitive to oxidising and reducing gases than other traditional oxides. [19–22]. One viable solution to these limitations is noble-metal modification, which has been widely used to enhance gas-sensing performance through chemical catalysis and electrical sensitisation. Because of its strong catalytic activity, exceptional hydrogen dissociation capability, and ability to promote spillover effects, palladium (Pd) is one of the most desirable noble metals [23–25]. By promoting the adsorption and dissociation of gas molecules such as NO_2 , H_2 , CO , and hydrocarbons, Pd nanoparticles (NPs) enhance charge transfer and surface reaction rates at the metal-oxide interface [26–27]. Additionally, Pd ornamentation introduces Schottky barriers at the Pd/ Bi_2O_3 junction, increasing resistance modulation upon gas exposure. Despite these advantages, Pd-modified Bi_2O_3 systems remain widely studied, particularly for multi-gas sensing applications [28–29].

From a structural perspective, nanocrystalline TMOs can be classified according to the number of confined dimensions into layer-like (1-D confinement), wire- or rod-like (2-D confinement), and particle-like (3-D confinement) NSs. Among these, low-dimensional NSs with dominant exposed facets offer superior gas-sensing performance due to their well-defined surface planes, higher density of unsaturated surface atoms, and simplified charge-depletion behaviour [28–33]. For NPs-based systems such as Pd- Bi_2O_3 , reducing particle size to the nanoscale ensures that the Debye length becomes comparable to the crystallite size, allowing the entire particle to participate in the sensing process. The gas sensing process in MOS consists of three consecutive steps: (i) adsorption and surface reactions of gas molecules; (ii) charge transfer between adsorbates and surface states leading to the accumulation or depletion of charge carriers; and (iii) variation in electrical resistance, which serves as the measurable sensor response. The removal of electrons from the conduction band by oxidising gases such as NO_2 increases the resistance of n-type Bi_2O_3 . Conversely, reducing gases such as H_2 , CO , and LPG react with deposited O_2 species, releasing electrons back into the semiconductor and decreasing resistance. The size of the reaction is greatly influenced by surface temperature, gas concentration, surface defect type, and catalytic activity. Although several theoretical models have been proposed to explain this power-law behaviour by combining surface reaction kinetics with semiconductor depletion theory, many of these models rely on simplified assumptions regarding charge transfer and surface homogeneity. Charge transfer occurs in fractional electron units and strongly depends on the local atomic environment, crystallographic facets, and defect states such as O_2 vacancies [1, 16, 34–41]. Another critical aspect in gas sensor research is identifying the dominant active surface sites responsible for sensing. There is an ongoing debate over whether gas-sensing reactions occur primarily on defect-free surface sites, at oxygen vacancies, or at both. Since oxygen vacancies play a vital role in the adsorption and activation of gas molecules, especially in Bi_2O_3 -based materials, controlling their concentration is essential for optimizing sensor performance. In parallel with performance enhancement, environmentally benign synthesis routes have gained increasing importance. Green synthesis methods that use plant extracts as stabilising and reducing agents provide sustainable alternatives to conventional chemical procedures.

Neem (*Azadirachta indica*) leaf extract controlled the nucleation and growth of NPs while reducing toxic effects. When paired with the hydrothermal approach, neem-assisted synthesis yields excellent crystallinity, a homogeneous particle size, and an improved surface defect density, all of which are highly beneficial for gas sensing applications.

In this study, the green hydrothermal synthesis of Pd-Bi₂O₃ NSs is investigated, and their gas-sensing capabilities towards NO₂, H₂, CO, and LPG are evaluated using neem leaf extract as a catalytic support. The link between surface structure, Pd sensitisation, and gas-induced conductance modulation is systematically investigated to elucidate the major sensing processes. The results demonstrate that eco-friendly Pd-Bi₂O₃ NSs provide a potential platform for high-sensitivity, multi-gas detection.

2. Experimental details

2.1. Synthesis of Pd-Bi₂O₃ nanomaterials:

Fresh neem leaves (100 g) were thoroughly cleaned, heated to 100°C, and continuously stirred at 500 rpm for two hours before being extracted in 500 mL of distilled water. To remove any solid residue, the extract was filtered twice through Whatman filter paper after cooling to room temperature. The resulting leaf extract was subsequently employed as a green catalytic and stabilising agent in the synthesis of Pd-Bi₂O₃ nanomaterials. Neem leaf extract and distilled water were combined in a volume ratio of 60 mL (leaf extract) to 40 mL (water) for the synthesis. Solution A was obtained by dissolving 0.2 mol of bismuth nitrate pentahydrate [Bi (NO₃)₃·5H₂O] in a small amount of concentrated nitric acid. 0.2 mol of citric acid [C₆H₈O₇] was dissolved in distilled water to create Solution B, and 0.05 mol (approximately 10.3 wt% of Pd relative to Bi₂O₃) of palladium nitrate pentahydrate [Pd (NO₃)₂·5H₂O] was dissolved in distilled water to create Solution C. All chemicals were of analytical reagent (AR) grade and procured from Sigma-Aldrich and were used without further purification. All three solutions (A, B, and C) were combined with the neem extract-water mixture under continuous stirring to obtain a homogeneous precursor solution. The resulting mixture was transferred into a Teflon-lined stainless-steel hydrothermal autoclave and heated at 120°C for 6 h. After completion of the reaction, the autoclave was allowed to cool naturally to room temperature. The final product was collected by filtration using double filter paper, thoroughly washed, and dried to obtain Pd-Bi₂O₃ NSs.

2.2. Preparation of electrodes:

Pd-Bi₂O₃ nanomaterials were synthesized using a hydrothermal method. The sensing layer was fabricated by dispersing the Pd-Bi₂O₃ NSs in a polyvinyl alcohol (PVA) binder and depositing it onto a non-conducting glass substrate using the doctor-blade technique, yielding a film with an average thickness of 1.5 µm. The coated substrates were subsequently transferred to a muffle furnace and heated at 150°C for 1 h to remove residual organic components deposited on the sensing layer. Metal electrodes with an average thickness of ~ 1.5 µm were patterned onto the glass substrate to serve as

electrical contacts. After coating, the films were dried at room temperature and further annealed to improve film adhesion and electrical connectivity. To ensure good ohmic contact between the sensing layer and the electrodes, silver paste was applied at the electrode-film interfaces.

2.3. Analysis of sensing property

The gas-sensing characteristics of the Pd-Bi₂O₃ nanomaterials were evaluated using a computer-controlled gas-sensing characterisation system. Gas sensing performances were carried out using certified standard gas cylinders supplied by Space Cryogases Pvt. Ltd. The source gases NO₂ (100% pure), H₂ (100% pure), CO (1000 ppm balanced with N₂), and LPG (1000 ppm balanced with N₂) were provided as target gases in standard cylinders. The experimental setup consisted of a sealed test chamber, a computer interface, a regulated heating power supply, manual gas-injection ports, and a digital nanoammeter (Model DNM-121) for accurate resistance measurements. The sensor device was mounted on a temperature-controlled hot chuck positioned inside the test chamber. The sensor's operating temperature was precisely regulated via the hot chuck controller. The electrical resistance of the Pd-Bi₂O₃-based gas sensor was evaluated as a function of the target gas type, operating temperature, and gas concentration. The sensor response was measured in ambient air containing 100 ppm of the target gas, with temperatures varied from 30 to 250°C to determine the optimum operating temperature. Further, response and recovery times, gas concentration effects, and the effect of gas concentration were determined. The gas concentration is controlled by injecting a gas volume, and the chamber is purged with air to restore the sensor resistance. The sensor response was calculated as the following relation [15];

$$\text{Gas Response (\%)} = (|R_a - R_g| / R_a) \times 100 \quad (1)$$

Where R_a is the sensor resistance in air, and R_g is the sensor resistance in the presence of gas.

To assess sensitivity, selectivity, and dynamic response behaviour, gas-sensing measurements were conducted for a variety of target gases, including NO₂, H₂, CO, and LPG, over a range of concentrations. To evaluate the sensor's long-term performance and dependability under the same operating conditions, stability and repeatability tests were also conducted.

3. Results and discussion

3.1 Structural elucidation and vibrational spectroscopy studies

The well-crystallized nature and phase composition of the Pd-Bi₂O₃ NSs are shown by the XRD pattern shown in Fig. 1(a). The (120) plane, a distinctive reflection of monoclinic α -Bi₂O₃ and a sign of the dominant phase development, is indicated by the sharp diffraction peak at about $2\theta = 33.9^\circ$. Additional diffraction peaks appearing at $2\theta \approx 27.3^\circ$, 40.1° , 42.3° , 46.5° , 55.1° , 61.2° , and 72.3° can be indexed to

(002), (111), (110), (200), (-121)/ (122), (130), and (041) crystallographic planes, respectively, in good agreement with the standard ICCD data 27-0050 and 41-1107. The retention of the Bi_2O_3 crystal structure following Pd inclusion is confirmed by the distinct indexing of these (hkl) planes. The absence of any further diffraction peaks associated with Pd metal or PdO phases indicates that either is successfully integrated into the Bi_2O_3 lattice. Furthermore, slight variations in peak positions suggest lattice deformation due to the ionic radius mismatch between Bi^{3+} and $\text{Pd}^{2+}/\text{Pd}^{3+}$ ions. Overall, phase-pure $\alpha\text{-Bi}_2\text{O}_3$ with altered crystallographic properties is formed, as shown by the XRD data. The Raman spectra, which provide information about the local bonding environment and lattice vibrations, are displayed in Fig. 1(b). Bi-O-Bi bending modes are responsible for the significant Raman band about $\sim 150\text{--}180\text{ cm}^{-1}$, confirming the basic structure of the Bi_2O_3 lattice. Strong coupling between Pd and the host lattice is shown by the peak around $\sim 280\text{--}300\text{ cm}^{-1}$, which is due to Bi-O stretching combined with Pd-O contact. The structural integrity of Bi_2O_3 is further supported by another unique band about $\sim 420\text{--}450\text{ cm}^{-1}$, which corresponds to Bi-O stretching vibrations. The slight shifts and intensity variations in Raman modes in Pd-incorporated Bi_2O_3 indicate lattice distortion and defect generation. The XRD and Raman analyses consistently confirm the successful formation of Pd- Bi_2O_3 , with modified structural and vibrational characteristics beneficial for functional applications such as gas sensing.

3.2 Morphological evolution studies

The FE-SEM micrographs of the synthesised Pd- Bi_2O_3 sample, taken at various magnifications, are shown in Fig. 2(a-d), revealing distinct morphological features. At lower magnification (Fig. 2(a), $2.0\text{ }\mu\text{m}$ scale), the surface appears highly agglomerated, consisting of irregularly shaped clusters formed due to the high surface energy of fine particles. Figure 2(b) at a $1.0\text{ }\mu\text{m}$ scale further confirms the porous, loosely packed morphology, with interconnected grains that facilitate gas diffusion and surface reactions. As magnification increases, compact regions and loosely connected granular structures coexist within a diverse texture (Fig. 2(c), 500 nm). This non-uniform distribution suggests the effect of Pd incorporation on the growth

kinetics of Bi_2O_3 grains. The high-magnification image (Fig. 2d, 200-nm scale) clearly shows nanoscale granules with distinct borders and rough surfaces. Such surface roughness and reduced particle size significantly improve the effective surface area. The porous network and numerous grain boundaries observed in all micrographs are highly beneficial for applications such as gas sensing, as they enhance charge transfer processes and increase the number of active sites for gas adsorption.

3.3 TEM analysis

The morphology, microstructure, elemental distribution, and crystallinity of the Pd- Bi_2O_3 NSs were clarified using TEM. The sample consists of agglomerates of nanocrystallites with an irregular, porous morphology, as shown in the TEM image in Fig. 3(a). As is frequently observed in TMOs produced by wet-chemical processes, they are densely packed and form interconnected clusters. Because it offers a

large specific surface area and numerous active sites for gas adsorption and surface reactions, such porous NSs are highly beneficial for gas-sensing applications. The (120) plane of monoclinic can be indexed to the measured interplanar spacing (d-spacing), which is roughly 0.32 nm, which can be indexed to the (120) plane of monoclinic α - Bi_2O_3 . This observation is in excellent agreement with the XRD results, where the dominant diffraction peak corresponding to the (120) plane was identified, confirming phase purity and crystallographic consistency between bulk and local structural analyses. Lattice distortion induced by Pd inclusion accounts for the small change in lattice spacing relative to pure Bi_2O_3 , further supporting successful Pd doping. The particle distribution and elemental composition of the component elements were examined by EDS elemental mapping, as shown in **Fig. 3(b-d)**. The formation of a stable Bi_2O_3 framework is evidenced by the Bi elemental map (**Fig. 3(b)**), which reveals a uniform, continuous distribution of bismuth throughout the NSs. Pd species are uniformly distributed throughout the Bi_2O_3 matrix, with no discernible aggregation and phase separation, according to the Pd elemental map (**Fig. 3(c)**). This consistent dispersion indicates that Pd is either integrated into the Bi_2O_3 lattice/substitutional sites within Bi_2O_3 or is finely dispersed on the surface. It is well known that these widely distributed Pd species serve as efficient catalytic centres, enhancing gas adsorption, dissociation, and charge transfer. The homogeneous presence of oxygen is further confirmed by the elemental oxygen map (**Fig. 3(d)**), which validates the oxide stoichiometry and structural integrity of the Pd- Bi_2O_3 NSs. It is anticipated that the nanoscale Pd- Bi_2O_3 morphology, high crystallinity, homogeneous Pd dispersion, and polycrystalline nature would greatly improve surface reaction kinetics, catalytic activation, and electron transport. By promoting effective charge transfer and surface depletion layer modification, these structural benefits are essential for enhancing gas sensing performance, especially concerning oxidizing gases like NO_2 .

3.4 Chemical composition and surface elemental analysis

The elemental composition of the produced material is confirmed by the EDS spectra shown in Fig. 4(a). The effective inclusion of Pd in the Bi_2O_3 matrix is evidenced by distinct characteristic peaks corresponding to Pd (L-series), Bi (L-series), and O (K-series). The sample's high purity is confirmed by the lack of any other impurity-related peaks. According to the quantitative elemental analysis shown in the inset (a-1), Pd, Bi, and O are present in the right amounts to promote the synthesis of Pd- Bi_2O_3 . The oxygen peak verifies the material's oxide composition and appropriate stoichiometry. Overall, the chemical composition and homogeneity of the Pd- Bi_2O_3 are confirmed by the EDS. The wide-scan XPS survey spectrum, which provides detailed information on the elemental states and surface

chemical composition, is shown in Fig. 4(b). The presence of Bi, Pd, and O is evident in the spectrum through their distinctive core-level peaks, including Bi 4f, Bi 4d, Pd 3p, Pd 3d, and O 1s. Successful Pd integration at the surface level is further confirmed by the existence of Pd-related peaks. The usual electrical environment of Bi^{3+} in Bi_2O_3 is shown by the Bi 4f and Bi 5s characteristics. The O 1s and O 2s peaks confirm lattice oxygen as well as possible surface-adsorbed oxygen species. This survey

spectrum establishes a strong basis for detailed core-level analysis. The high-resolution XPS spectrum, which focuses on the Bi 4d, Pd 3p, and O 1s regions, is shown in Fig. 4(c) and provides information on the elemental chemical states. The oxidation state of bismuth in the BiO₃ lattice is confirmed by the appearance of the Bi 4d_{1/2} and Bi 4d_{3/2} peaks at binding energies typical of Bi³⁺. The existence of Pd in an oxidized state is shown by the Pd 3d_{1/2} and Pd 3d_{3/2} peaks, indicating a significant interaction between Pd and the oxide matrix. Although its modest asymmetry may suggest oxygen vacancies or surface-adsorbed oxygen species, the significant O 1s peak is linked to lattice oxygen. Surface reactivity can be improved by these oxygen-related flaws. Good chemical stability and consistent bonding conditions are indicated by the distinct peak separation and sharp features. Strong Pd-O-Bi interactions, effective Pd doping, and defect-rich surface chemistry, confirmed by the high-resolution XPS data.

3.5 Textural properties and thermal stability analysis

As shown in Fig. 5(a), the nitrogen (N₂) adsorption-desorption isotherm of the Pd-Bi₂O₃ NSs provides insight into its surface textural characteristics. From BET, it is observed that Pd-Bi₂O₃ NSs exhibit a surface area of 14.1 m² g⁻¹. Mesoporous materials are characterized by the isotherm's typical type-IV behaviour and a distinct hysteresis loop. Monolayer adsorption on the surface is indicated by a slow rise in adsorbed volume at low relative pressure ($P/P_0 < 0.1$). Multilayer adsorption and capillary condensation within mesopores are suggested by the significant absorption in the intermediate pressure range. The filling of larger mesopores and macropores is associated with a rapid increase in adsorption at high relative pressure ($P/P_0 > 0.8$). Pore connection and non-uniform pore shape are confirmed by the existence of a hysteresis loop between the adsorption and desorption branches. The accessible surface area is increased, and mass transport is facilitated by this permeable design. These characteristics are especially helpful for applications such as gas detection and catalysis that require strong surface reactivity. The pore size distribution obtained from the adsorption branch using the BJH approach is shown in Fig. 5(b). From BJH, it is observed that Pd-Bi₂O₃ NSs exhibit an average pore diameter of 23.4 nm. The structural consistency shown in the BET isotherm is supported by a significant contribution in the mesoporous region. Instead of isolated pores, linked pore networks are suggested by the slow

rise in pore volume with pore size. The kinetics of gas diffusion and adsorption are enhanced by such hierarchical porosity. Additionally, during adsorption-desorption processes, the presence of bigger pores lowers diffusion resistance. Overall, the wide range of pore sizes indicates a highly porous structure with improved access to active sites. Catalytic efficiency and sensory responsiveness are enhanced by this hierarchical pore design. The temperature-dependent electrical resistance behaviour of the prepared sample was studied by measuring resistance in the temperature range of 30–250°C, as shown in Fig. 5(c). The log₁₀(R) value decreases continuously with increasing temperature, indicating a negative temperature coefficient of resistance (NTCR) characteristic of semiconducting materials. The decrease in resistance with temperature is attributed to the thermally activated increase in charge-carrier concentration and enhanced mobility at elevated temperatures. The Pd-Bi₂O₃ NSs combined TGA and DTA are shown in Fig. 5(d). The removal of physically adsorbed moisture and residual solvents accounts

for the initial small decrease in weight in the TGA curve below about 150°C. The breakdown of residual organic species and weakly bonded surface groups is associated with a slow weight loss in the intermediate temperature range (200–500°C). A structural rearrangement or partial oxygen loss from the lattice is indicated by the more noticeable weight loss seen at around 600°C. Accordingly, endothermic and exothermic characteristics associated with these thermal events are displayed on the DTA curve. The phase stability or crystallization of the oxide matrix is suggested by the wide exothermic peak at 400–500°C. Good thermal stability up to moderate temperatures is confirmed by the high-temperature thermal behaviour. The sample has sufficient thermal resilience for high-temperature sensing applications, according to the TGA-DTA data.

3.6 Gas sensing properties

In a semiconductor gas sensor, target gases react with oxygen species absorbed on the surface of the oxide semiconductor, resulting in the change in the electric resistance of the gas sensing film. Therefore, the dependence of the electric resistance on the oxygen partial pressure is an important factor for the operation of a semiconductor gas sensor. At a gas concentration of 100 ppm, Fig. 6(a) illustrates how sensor sensitivity varies with operating temperature for NO₂, H₂, CO, and LPG. The sensitivity initially increases with temperature for all target gases, primarily due to improved charge-transfer mechanisms at the sensor interface, higher surface reaction rates, and enhanced gas-molecule adsorption. Chemisorbed oxygen species become more reactive at higher temperatures, which makes it easier for gas molecules to interact with the Pd-Bi₂O₃ sensing layer. At a comparatively low operating temperature of 120°C, the Pd-Bi₂O₃ sensor exhibits the highest sensitivity to NO₂ among all investigated gases. This

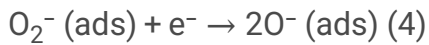
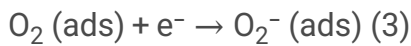
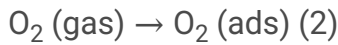
phenomenon can be linked to the high electron affinity of NO₂ and its strong oxidising properties, which enable effective electron removal from the sensing material and a noticeable change in resistance. Compared with reducing gases, the lower ideal temperature for NO₂ also suggests significant surface contact and favourable adsorption kinetics. On the other hand, to achieve maximum sensitivity, reducing gases such as H₂, CO, and LPG requires somewhat higher working temperatures of 140°C, 160°C, and 170°C, respectively. The increased activation energy required for the oxidation processes of reducing gases on the sensor surface is the cause of this discrepancy. The increasing molecular complexity and bond strength of these gases, which need greater thermal energy for efficient surface reactions, are reflected in the progressive rise in optimum temperature from H₂ to LPG. All gases exhibit a drop in sensitivity beyond their individual optimal temperatures, which may be explained by rapid desorption of gas molecules and a decrease in surface residence time, thereby limiting the number of effective gas-surface interactions. The Pd-Bi₂O₃ sensor's greater selectivity toward oxidising gases is demonstrated by its lower working temperature and higher sensitivity for NO₂. The dynamic response and recovery behaviour of the sensor toward several gases at their respective optimal operating temperatures (120°C for NO₂, 140°C for H₂, 160°C for CO, and 170°C for LPG) and at a concentration of 100 ppm are shown in Fig. 6(b). The recovery time is the time required to restore to 90% of the baseline resistance after gas removal, whereas the response time is the time required to attain 90% of the maximum sensitivity upon

gas introduction. Because of its high adsorption and rapid charge transfer to the sensor surface, NO_2 exhibits the fastest response (240 s) and recovery (410 s) among the gases. A rapid shift in resistance arises from the adsorption of NO_2 , which produces a sharp electron-depletion layer. Because of its small molecular size and high diffusivity, which enable it to react rapidly with surface oxygen species, hydrogen has the fastest reaction time (141 s) among reducing gases. However, because of the desorption of water molecules from the surface, its recovery

time (214 s) is somewhat longer. Because of its higher binding energy to surface oxygen, CO exhibits modest response (351 s) and recovery (541 s) times. Because of its large hydrocarbon structure and several oxidation processes, LPG has the slowest response (429 s) and recovery (618 s). Pd's catalytic function improves overall response kinetics by enhancing oxygen dissociation and spillover effects. In contrast, reducing gases exhibit a slower but steady response-recovery pattern, whereas oxidising gases react more quickly. The sensitivity changes with increasing gas concentration (25–200 ppm) for each gas's corresponding optimal operating temperature (120°C for NO_2 , 140°C for H_2 , 160°C for CO, and 170°C for LPG) are displayed in Fig. 6(c). Sensitivity rises monotonically with concentration for all gases, demonstrating the sensor's strong linearity and repeatability. A greater number of gas molecules interacting with chemisorbed oxygen species leads to more pronounced charge transfer, thereby increasing sensitivity. NO_2 's robust electron-withdrawing capacity and dominant surface contact are confirmed by its maximum sensitivity at all concentrations. Because of effective oxidation on Pd catalytic sites, H_2 rapidly increases at lower concentrations. Due to their slower surface reaction rates and diffusion constraints, CO and LPG show very modest sensitivity improvement. Sensitivity tends to saturate at higher concentrations, indicating depletion of active sites on the sensor surface. Selectivity toward oxidizing gases is shown in the comparison pattern $\text{NO}_2 > \text{H}_2 > \text{CO} > \text{LPG}$. The sensor's appropriateness for low-ppm detection is confirmed by the linear response at low concentrations. The long-term stability of the Pd- Bi_2O_3 sensor, which was continuously tested for 30 days at a gas concentration of 100 ppm and the corresponding optimal operating temperatures (120°C for NO_2 , 140°C for H_2 , 160°C for CO, and 170°C for LPG), is shown in Fig. 6(d). The sensor's structural and chemical durability is confirmed by its outstanding stability and low sensitivity degradation. 95.06% for NO_2 , 91.21% for H_2 , 86.77% for CO, and 81.33% for LPG are the remaining sensitivities after 30 days. Reversible adsorption-desorption behavior and low surface poisoning are responsible for the better stability toward NO_2 . Because of partial oxidation and the generation of carbonaceous residue, reducing gases exhibit somewhat greater deterioration. Long-term exposure to hydrocarbon cracking and surface pollution is associated with a progressive decrease in LPG responsiveness. By limiting irreversible adsorption and promoting surface renewal, Pd considerably increases stability. The little baseline drift attests to the sensor's dependability. In contrast, the sensor performs exceptionally well over the long term, especially in detecting NO_2 and H_2 . The Pd- Bi_2O_3 sensor performs best against NO_2 , followed by H_2 , CO, and LPG. It also exhibits low working temperature, rapid response, high sensitivity, and great stability. Pd-assisted catalytic activity, oxygen vacancy production, and effective surface charge transfer processes control the improved sensing behavior.

3.7 Gas sensing mechanism

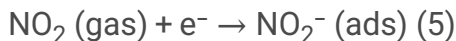
Based on surface adsorption-desorption processes, electron depletion layer modulation, catalytic activation by Pd NPs, and Schottky junction effects, the gas sensing behavior of the Pd-Bi₂O₃ sensor can be fully comprehended. Figure 7 shows a schematic representation of the suggested sensing mechanism, which is in good agreement with the previously stated experimental data of temperature optimization, response-recovery characteristics, concentration dependency, and long-term stability. Pd-Bi₂O₃ exhibits n-type semiconducting metal oxide behavior, with electrons serving as the primary charge carriers. Oxygen molecules are initially physically adsorbed on the sensor's surface when the sensor is exposed to ambient air at high operating temperatures. They are then chemisorbed by taking electrons from the Bi₂O₃ conduction band. Depending on the operating temperature, these oxygen molecules are ionized into several oxygen species, including O₂⁻, O⁻, and O²⁻ [1, 5–6]. The adsorption and ionization processes can be expressed as:



The extraction of electrons from the conduction band forms an electron depletion layer near the sensing material's surface, thereby increasing the sensor's resistance in air. The thickness of this depletion layer plays a crucial role in determining the baseline resistance and the magnitude of resistance modulation upon exposure to target gases. The presence of Pd NPs on the Bi₂O₃ surface significantly enhances the sensing performance, as clearly depicted in Fig. 7. Due to the difference in work function between Pd (higher work function) and n-type Bi₂O₃, a Schottky junction is formed at the Pd-Bi₂O₃ interface. This junction acts as an additional electron barrier, further widening the depletion region and increasing the baseline resistance in air. Consequently, even small changes in surface charge density caused by gas adsorption result in a pronounced change in resistance. Moreover, Pd acts as an efficient catalytic activator, facilitating gas dissociation and spillover effects. Gas molecules adsorbed on Pd NPs are dissociated into more reactive species and subsequently migrate ("spill over") onto the Bi₂O₃ surface, where they participate in surface reactions with ionized oxygen species. This dual role of Pd-electronic sensitisation via Schottky barrier formation and chemical sensitisation via catalytic activity explains the enhanced sensitivity and faster kinetics observed experimentally. Response transients of the Pd-Bi₂O₃ by using measured sensor resistance in the presence of 100 ppm of NO₂ (120°C), H₂ (140°C), CO (160°C), and LPG (170°C) were measured at their respective optimum operating temperatures, as shown in Fig. S1.

3.8. Sensing mechanism toward oxidizing gas (NO₂):

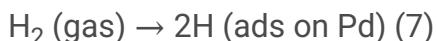
When the sensor is exposed to NO₂, an oxidizing gas, the resistance increases sharply, as NO₂ has a strong electron-withdrawing capability. NO₂ molecules directly interact with the sensor surface and capture electrons from the conduction band or from ionized oxygen species. The adsorption of NO₂ leads to the formation of NO₂⁻ and NO₃⁻ species, further deepening the depletion layer [1–2, 4]:



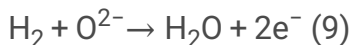
This additional electron withdrawal significantly increases the sensor resistance. The strong oxidizing nature of NO₂ and its high electron affinity explain the high sensitivity and low optimal operating temperature (120°C) observed for NO₂. The rapid interaction between NO₂ molecules and the Pd-activated surface also accounts for the relatively fast response and recovery behavior. The mechanism clearly shows the expansion of the depletion layer and upward band bending upon NO₂ exposure, resulting in a strong electrical signal.

3.9. Sensing mechanism toward reducing gases (H₂, CO, and LPG):

In contrast, reducing gases such as H₂, CO, and LPG exhibit an opposite sensing response, characterized by a decrease in resistance. These gases react with the chemisorbed oxygen species on the sensor surface, releasing electrons back into the conduction band and thereby narrowing the depletion layer. Hydrogen sensing is significantly enhanced by Pd due to its well-known ability to dissociate hydrogen. H₂ molecules are first adsorbed on Pd **NPs** and dissociate into atomic hydrogen [8, 34, 37]



The dissociated hydrogen atoms then react with ionized oxygen species on the Bi₂O₃ surface:



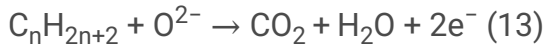
The released electrons reduce the depletion layer width, thereby decreasing the sensor resistance. The catalytic role of Pd lowers the activation energy for hydrogen dissociation, explaining the relatively low optimal operating temperature (140°C) and fast response time for H₂ sensing observed experimentally. For CO sensing, the reaction kinetics are comparatively slower due to stronger molecular adsorption and higher activation energy requirements. CO molecules react with chemisorbed oxygen species as follows [22, 35]:





The electrons released during this reaction return to the conduction band, thereby reducing resistance. The interaction of CO with the Pd-Bi₂O₃ surface results in a moderate modulation of the depletion layer, which explains the intermediate sensitivity and the higher optimal operating temperature (160°C) compared to H₂.

LPG is a mixture of hydrocarbons (C_nH_{2n+2}) and requires higher thermal energy for complete oxidation. LPG molecules react with surface oxygen species according to [4, 8]:



The release of multiple electrons leads to a measurable decrease in resistance; however, due to the complex molecular structure and slower diffusion kinetics, LPG exhibits the highest optimal operating temperature (170°C) and comparatively longer response and recovery times. The schematic highlights the gradual contraction of the depletion layer during LPG exposure, consistent with the experimental observations. The mechanism effectively explains the comparative sensing behavior observed in Fig. 6 **(a-d)**. The superior NO₂ response arises from strong electron withdrawal and efficient surface adsorption at lower temperatures, while the reducing gases require higher temperatures to activate oxidation reactions. The presence of Pd NPs enhances charge transfer, accelerates surface reactions, and stabilises the sensing interface, contributing to excellent repeatability and long-term stability. The minimal degradation in sensitivity over 30 days further confirms the robustness of the Pd-Bi₂O₃ sensor and the stability of the Pd-induced Schottky junction. As a summary, the gas sensing mechanism of Pd-doped Bi₂O₃ is governed by (i) oxygen adsorption and ionisation in air, (ii) formation and modulation of an electron depletion layer, (iii) catalytic activation and spillover effects of Pd NPs, and (iv) Schottky barrier modulation at the Pd-Bi₂O₃ interface. The synergistic combination of these effects results in high sensitivity, selectivity, and stability toward both oxidizing and reducing gases, making Pd-Bi₂O₃ a promising material for advanced gas sensing applications.

4. Conclusion

Utilizing thorough structural, morphological, and surface investigations, Pd-Bi₂O₃ Nanomaterials were effectively synthesized utilizing an ecologically safe (green) synthesis method and thoroughly examined as multifunctional resistive gas sensing materials. Raman spectroscopy revealed lattice deformation and defect formation induced by Pd doping, whereas XRD confirmed the formation of phase-pure crystalline Bi₂O₃ without secondary phases, indicating effective Pd incorporation below the detection limit. EDS elemental mapping verified the uniform distribution of Bi, Pd, and O throughout the matrix, whereas TEM investigation revealed a porous, agglomerated nanostructure made of nanoscale particles. The meso-macroporous design with linked pores, which offers abundant active sites and efficient gas

diffusion pathways, was evidenced by the BET data. The presence of Bi³⁺, surface oxygen species, and catalytically active Pd states was confirmed by XPS, underscoring Pd's role in enhancing surface reactions and modulating the electronic structure. The ability of the Pd-Bi₂O₃ sensor to detect NO₂, H₂, CO, and LPG gases was quantitatively assessed. At a low working temperature of 120 °C (100 ppm), the sensor showed a maximum sensitivity of ~73% for NO₂, indicating great selectivity toward oxidizing gases. The ideal working temperatures for reducing gases were found to be 140 °C (H₂), 160 °C (CO), and 170 °C (LPG), yielding sensitivities of approximately 65%, 55%, and 50%, respectively, at 100 ppm. Reliable and reversible sensing behavior was confirmed by the response times of 240 s (NO₂), 141 s (H₂), 351 s (CO), and 429 s (LPG), with matching recovery durations of 410 s, 214 s, 541 s, and 618 s. Over the 25-200 ppm range, the sensor showed a monotonic concentration-dependent response and exceptional long-term stability, maintaining 95.06% (NO₂), 91.21% (H₂), 86.77% (CO), and 81.33% (LPG) of its original response after 30 days. As supported by the suggested sensing mechanism, the improved sensing performance is ascribed to the combined effects of Pd-induced catalytic activation, Schottky barrier formation at the Pd-Bi₂O₃ interface, increased oxygen vacancy concentration, and effective modulation of the surface electron depletion layer. All things considered, Pd-Bi₂O₃ shows promise as a reliable material for multi-gas, low-temperature, and selective sensing applications.

Declarations

Credit authorship contribution statement

Pramod S. Borule: Writing-original draft, Conceptualisation, Investigation. Conceptualisation, Investigation. **Suprimkumar D. Dhas:** Review & Editing, Conceptualisation, Investigation, **Pranita M. Jondhale:** Software, Methodology. **Vijay D. Chavan:** Visualisation, **Deok-kee Kim:** Formal analysis, **Shankar P. Phulwale:** Formal analysis, Data curation, **Sadaf J. Gilani:** Project administration, Resources, Funding acquisition, **Maqsood Waikar:** Review & Editing, Data curation, **Shoyebmohamad F. Shaikh:** Validation, Data Curation, **Shivaji D. Waghmare:** Review & Editing, Funding acquisition, Supervision, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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Figures

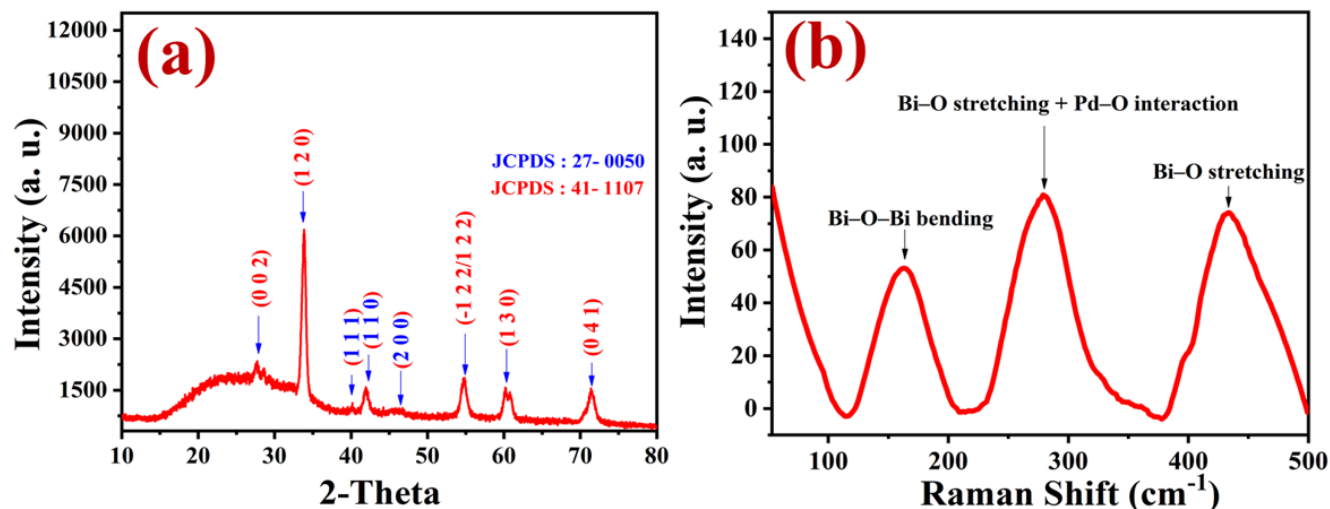


Figure 1

(a) XRD pattern confirming the crystalline phase and phase purity of Pd-Bi₂O₃ NSs. (b) Raman spectrum showing characteristic Bi-O-Bi bending, Bi-O stretching, and Pd-O interaction modes.

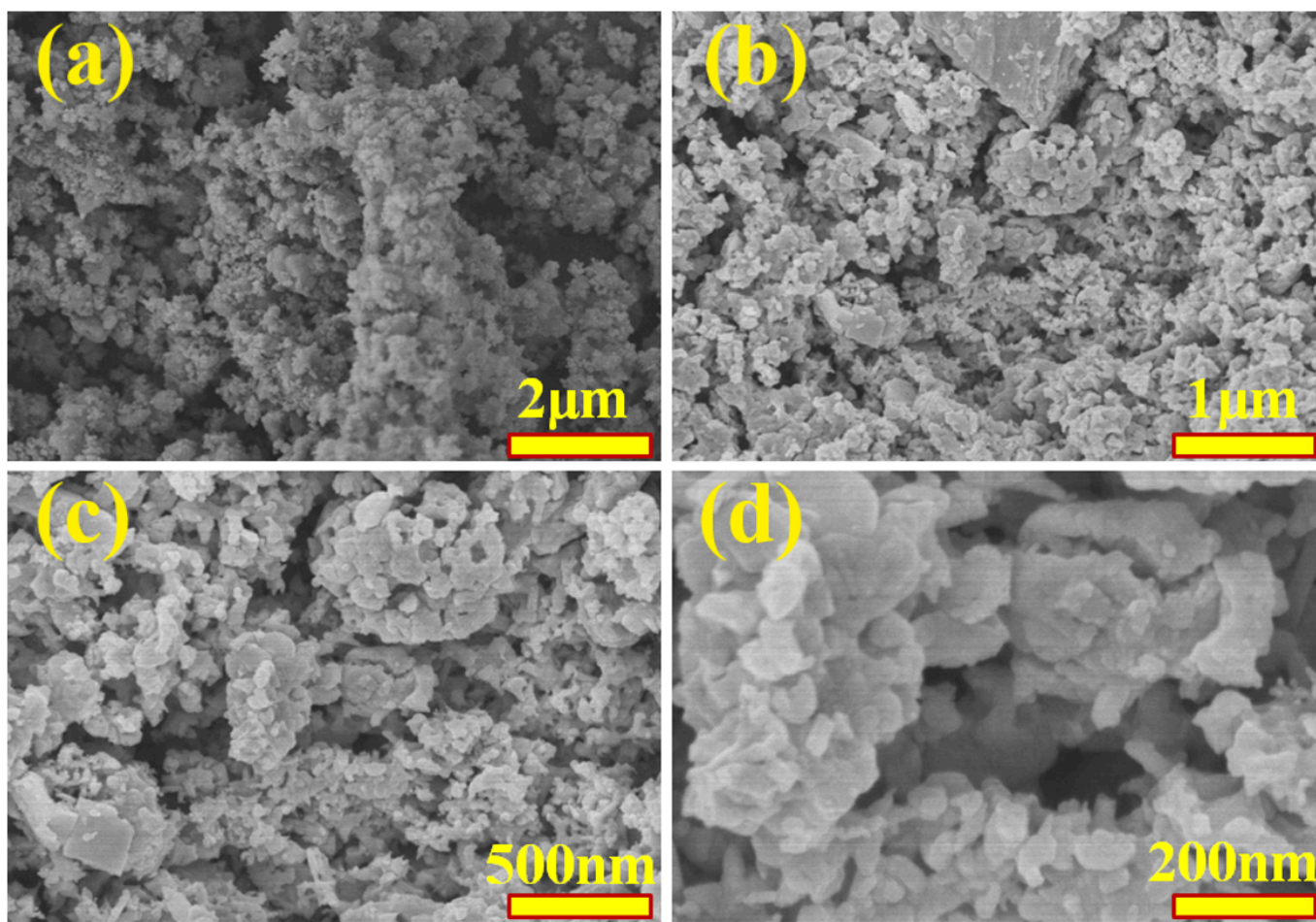


Figure 2

FE-SEM images of Pd-decorated Bi_2O_3 nanostructures at different magnifications.

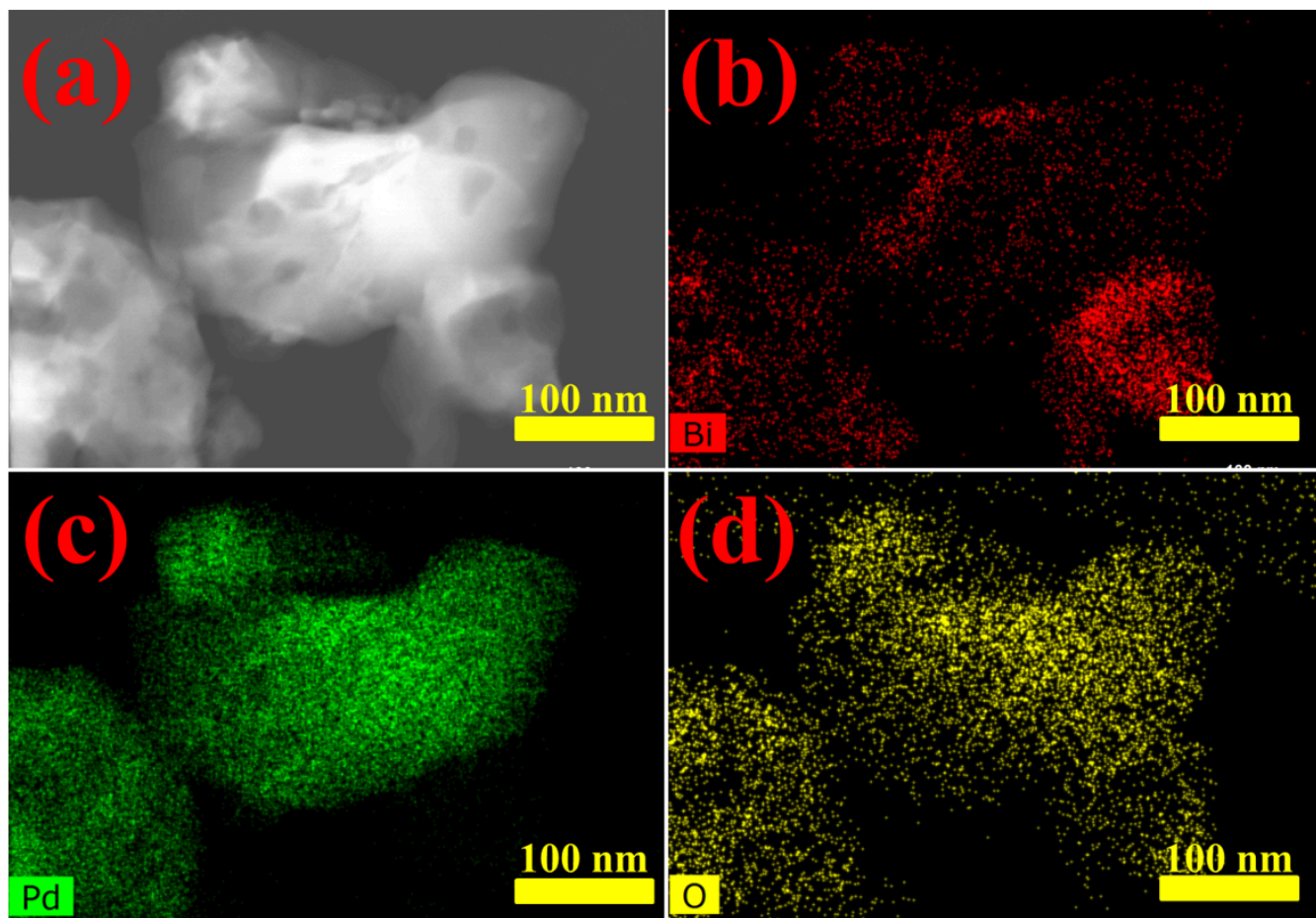


Figure 3

(a) TEM image and corresponding EDS elemental mapping of (b) Bi, (c) Pd, and (d) O.

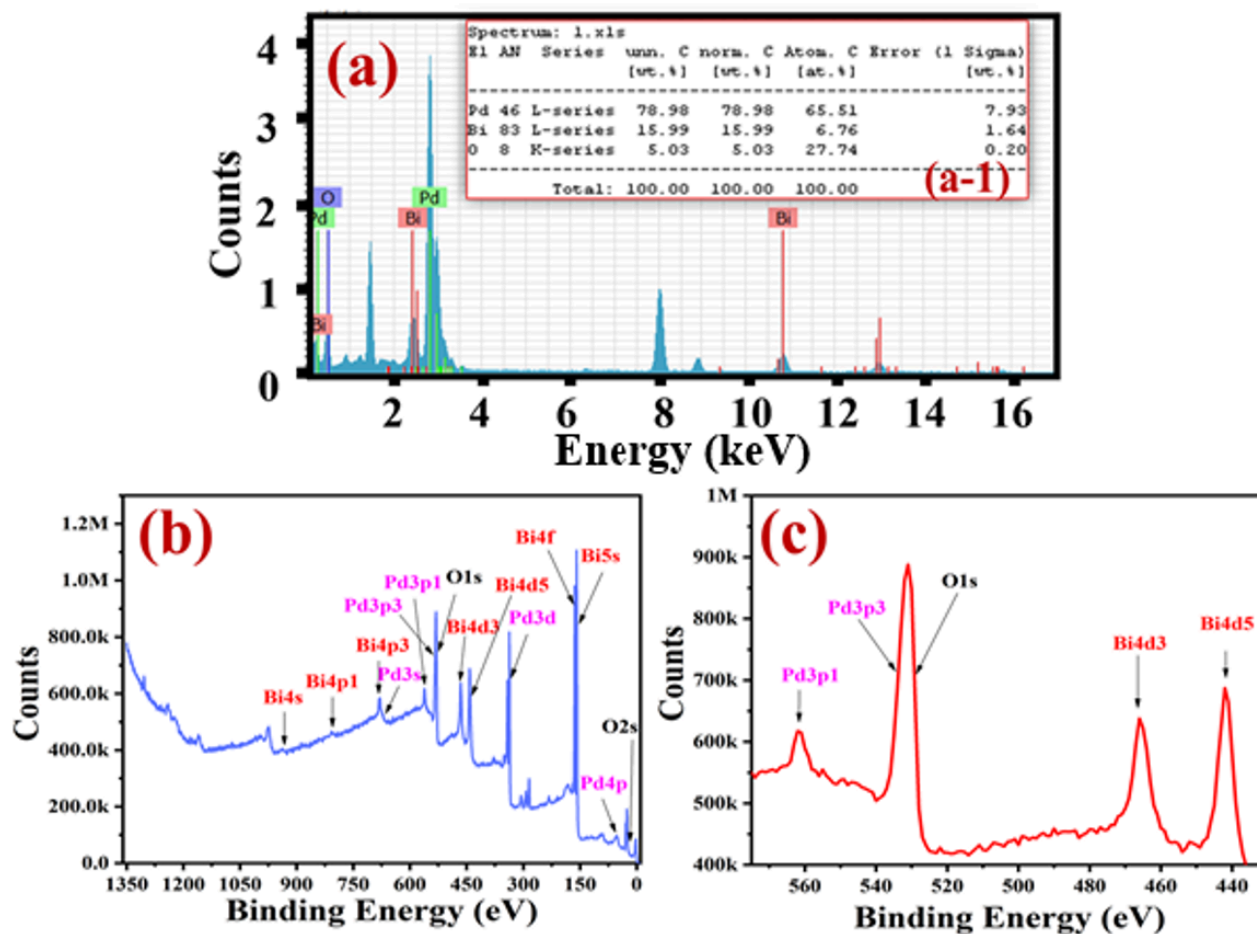


Figure 4

(a) EDS spectrum with elemental composition and (b-c) XPS survey and high-resolution spectra.

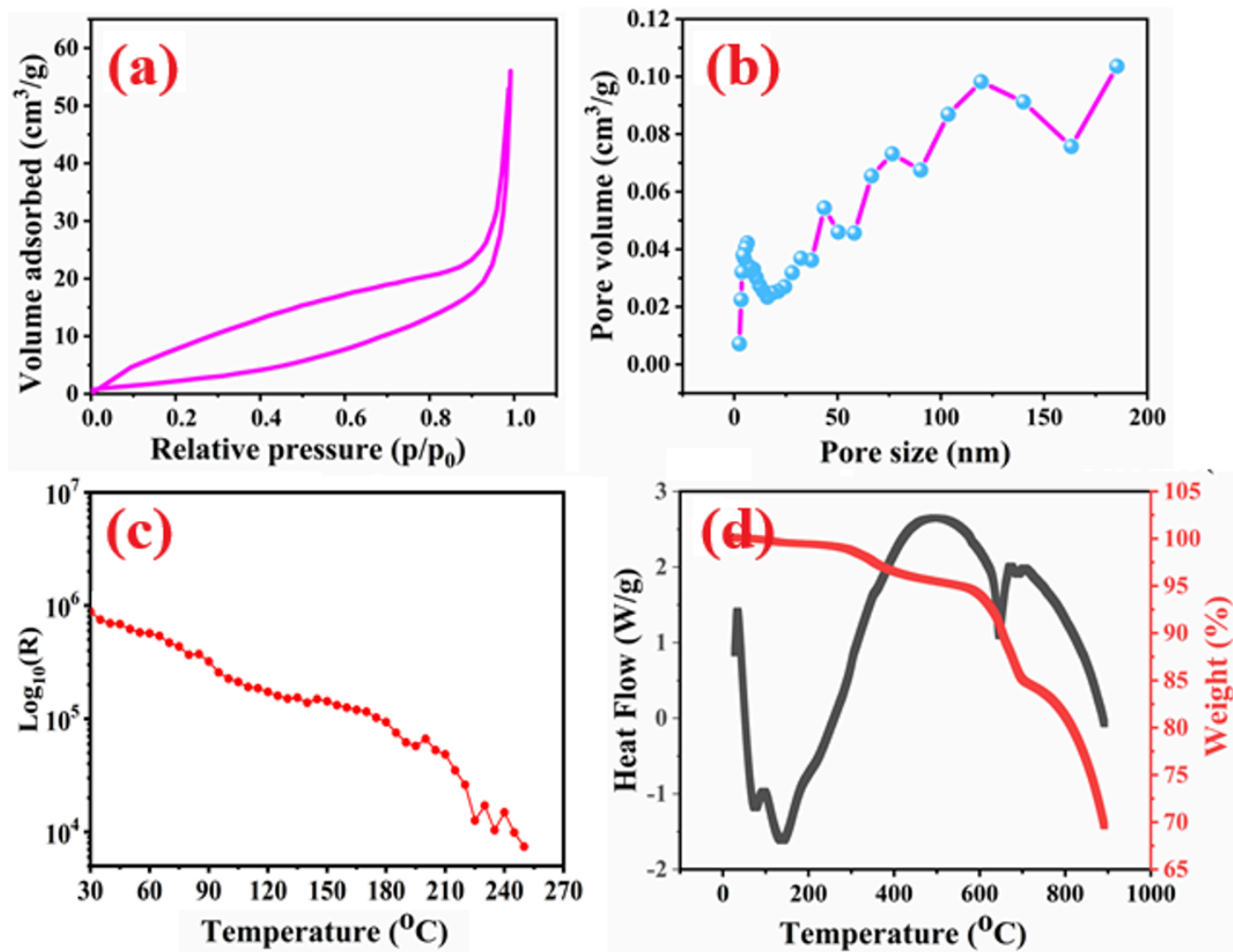


Figure 5

(a) N₂ adsorption-desorption isotherm, (b) pore size distribution, (c) Variation of log₁₀(R) as a function of temperature, (d) TG-DSC curves of Pd-Bi₂O₃.

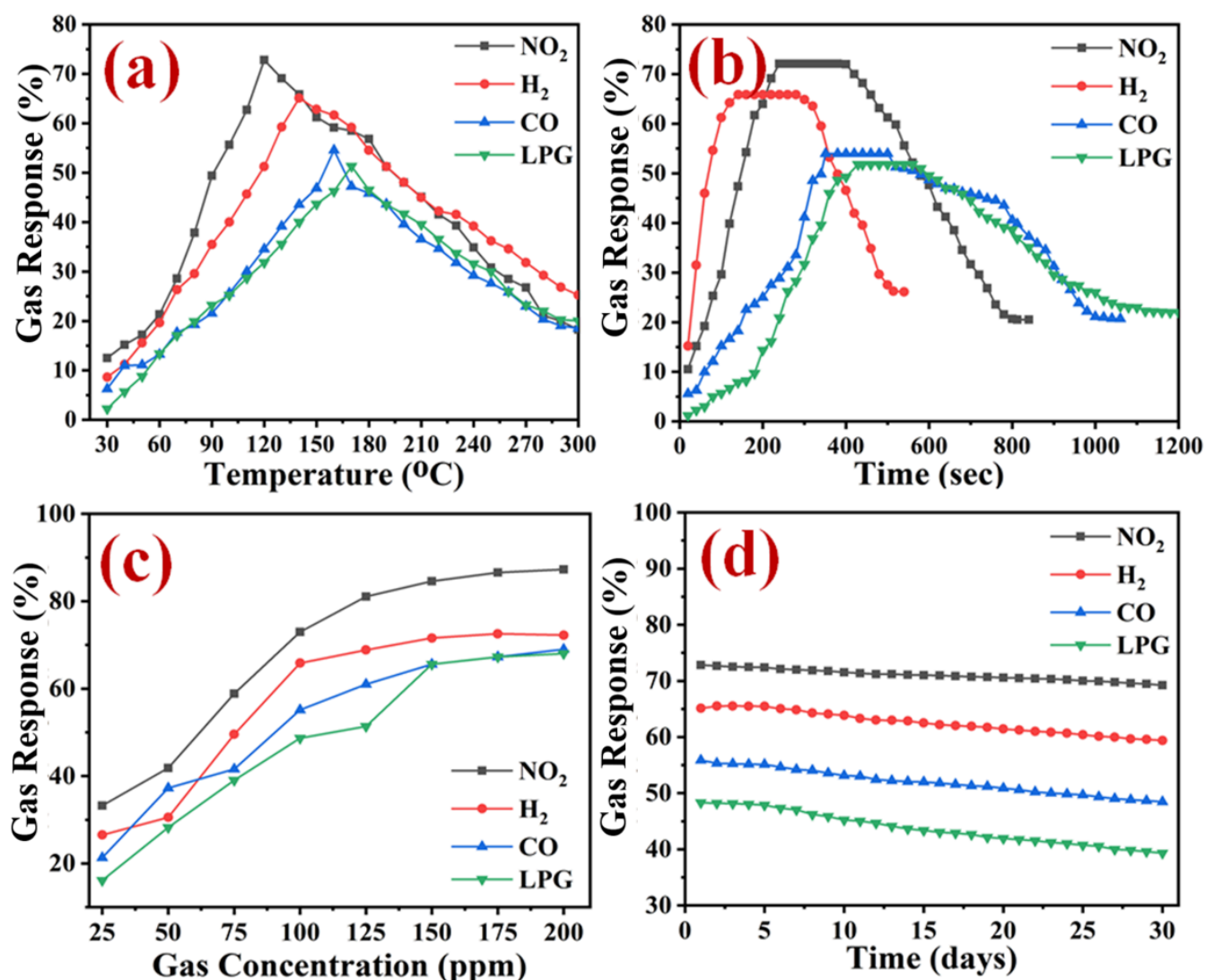


Figure 6

(a) Gas response (%) of the Pd-Bi₂O₃ sensor at 100 ppm as a function of operating temperature. (b) Dynamic response-recovery transients of the sensor toward 100 ppm of NO₂ (120 °C), H₂ (140 °C), CO (160 °C), and LPG (170 °C) were measured at their respective optimum operating temperatures. (c) Gas response (%) as a function of gas concentration (25-200 ppm) for NO₂ (120 °C), H₂ (140 °C), CO (160 °C), and LPG (170 °C) recorded at their respective optimum operating temperatures. (d) Long-term stability of the Pd-Bi₂O₃ sensor toward 100 ppm of NO₂ (120 °C), H₂ (140 °C), CO (160 °C), and LPG (170 °C) was evaluated at their respective operating temperatures.

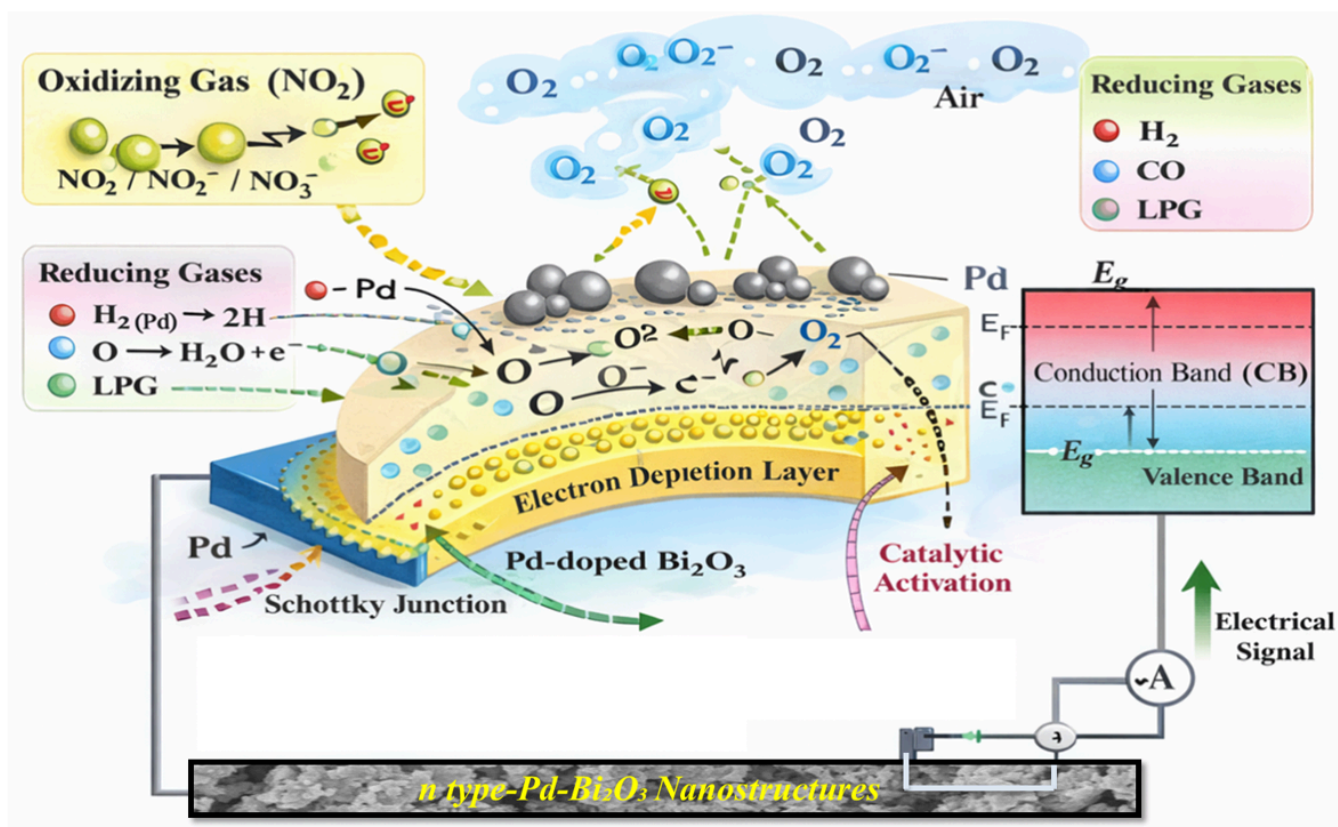


Figure 7

Schematic illustration of the NO_2 and reducing gas (H_2 , CO and LPG) sensing mechanism of $\text{Pd-doped Bi}_2\text{O}_3$.

Supplementary Files

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