

Cotton-Templated, Defect-Engineered LaFeO₃ Ceramics Coupled with MXene for Low-Temperature, Selective NO₂ Sensing

Yikun Wang, Wei Zhao*, Yang Chen

Division of Environment Metrology, Jiangsu Institute of Metrology, Nanjing, China
received October 7, 2025; received in revised form October 31, 2025; accepted November 6, 2025

Abstract

This study reports on the rational design of a high-performance, low-temperature nitrogen dioxide (NO₂) gas sensor with a multi-scale material engineering strategy that integrates cotton-templated morphology control, oxygen vacancy defect engineering, and MXene heterostructuring. Porous LaFeO₃ ceramics synthesized via cotton biotemplating exhibited a fourfold increase in surface area (65.8 m²/g) compared with pristine LaFeO₃ (15.2 m²/g), while controlled reducing-atmosphere calcination induced a high oxygen vacancy fraction of 25.3 %, as confirmed by XPS analysis. Coupling defect-engineered LaFeO₃ (DE-LFO) with Ti₃C₂T_x MXene nanosheets is expected to form a p-p contact that amplifies sensing. The optimized DE-LFO/MX-4 composite demonstrated an ultrahigh response of 14.2 ($S = R_a/R_g$) toward 5 ppm NO₂ at 25 °C, more than 11 times higher than pristine LaFeO₃, with exceptionally fast response and recovery times of 8 s and 25 s, respectively. The sensor showed reliable detection down to 12 ppb, linear response in the 0.1–2 ppm range ($R^2 = 0.995$), and outstanding selectivity with a coefficient > 10 against common interferents (NH₃, CO, CH₄, H₂S, ethanol). Long-term testing confirmed stable performance over 30 days with < ± 4 % variation, while humidity tolerance experiments revealed retention of > 75 % response even at 80 % RH. Comparative benchmarking against reported MXene-based systems highlights the unique synergy of hierarchical porosity, defect-rich LaFeO₃, and MXene interfacial amplification in enabling ultra-sensitive, rapid, and stable room-temperature NO₂ sensing. This work not only demonstrates a promising candidate for real-world environmental monitoring and wearable applications but also establishes a versatile paradigm combining biotemplating, defect engineering, and 2D coupling for next-generation gas sensor development

Keywords: Biotemplating strategy, oxygen vacancy engineering, heterojunction amplification, porous perovskite oxide, environmental monitoring

I. Introduction

The escalating emission of nitrogen dioxide (NO₂), a byproduct primarily of fossil fuel combustion from industrial processes and vehicular exhaust, presents a significant and growing threat to both public health and environmental stability¹. Chronic exposure to NO₂, even at concentrations in the parts-per-billion (ppb) range, is linked to severe respiratory ailments and can exacerbate existing conditions². Environmentally, NO₂ is a key precursor to the formation of acid rain and photochemical smog, contributing to widespread ecological damage. Consequently, the development of reliable, sensitive, and cost-effective sensors for the real-time monitoring of ambient NO₂ levels is of paramount importance. While traditional analytical techniques such as mass spectroscopy and gas chromatography offer high precision, their high cost, large footprint, and complex operation render them unsuitable for widespread, distributed deployment.

Chemiresistive gas sensors based on metal oxide semiconductors (MOS), such as tin oxide (SnO₂) and

zinc oxide (ZnO), have been extensively investigated as a viable alternative due to their low manufacturing cost, simple fabrication, and high sensitivity³. However, the practical application of these conventional MOS sensors is severely hampered by a fundamental limitation: their reliance on high operating temperatures, often exceeding 200 °C, to achieve sufficient sensing kinetics and response magnitude⁴. This high-temperature operation leads to substantial power consumption, which is incompatible with the requirements for portable, battery-powered devices, and can also cause long-term material degradation and sensor drift, compromising reliability⁵. Therefore, a central challenge in the field of gas sensing is the design of novel materials that exhibit superior performance at or near room temperature⁶.

Among the diverse classes of sensing materials, perovskite oxides with the general formula ABO₃ have emerged as highly promising candidates owing to their exceptional structural stability, tunable electronic properties, and inherent catalytic activity⁷. Lanthanum ferrite (LaFeO₃), a canonical p-type semiconductor, is particularly attractive for detecting oxidizing gases like NO₂⁸. Its crystal structure is thermally stable, and its

* Corresponding author: zw136668@163.com

electronic properties, including a moderate band gap of approximately 2.1–2.4 eV, are conducive to gas-sensing applications⁹. The p-type conductivity, governed by hole carriers, provides a direct mechanism for interaction with electron-accepting NO₂ molecules, leading to a measurable change in resistance¹⁰.

To unlock the full potential of LaFeO₃ for low-temperature sensing, advanced material engineering strategies are required. Morphology engineering, which aims to maximize the surface-to-volume ratio, is a critical approach for enhancing gas-surface interactions¹¹. In this work, we employ an eco-friendly and scalable biotemplating method using natural cotton fibers to synthesize a three-dimensional, porous fibrous network of LaFeO₃ ceramics³. This hierarchical structure is expected to facilitate gas diffusion and provide a significantly higher density of active sites compared to conventional nanoparticulate materials. Concurrently, defect engineering, specifically the intentional introduction of oxygen vacancies (V_O), represents another powerful strategy to boost sensing performance⁷. Oxygen vacancies can act as preferential adsorption sites for electronegative gas molecules, lower the energy barrier for surface reactions, and modulate the local electronic structure of the material, thereby amplifying the sensor response¹².

To further enhance charge transport and signal transduction, we couple the engineered perovskite with a two-dimensional (2D) material possessing metallic-like conductivity. Ti₃C₂T_x MXene, a prominent member of the 2D transition metal carbide family, is an ideal candidate for this purpose¹³. It uniquely combines high electrical conductivity, which minimizes intrinsic sensor noise, with a large surface area and abundant surface functional groups (e.g., -O, -OH, -F) that serve as additional active sites for gas adsorption¹⁴. The potential of Ti₃C₂T_x and its composites for room-temperature NO₂ detection has been increasingly recognized, making it a compelling synergistic component¹⁵.

Herein, we hypothesize that a novel composite material, comprising cotton-templated, defect-engineered LaFeO₃ (DE-LFO) ceramics intimately coupled with Ti₃C₂T_x MXene nanosheets, will form a p-p heterojunction that exhibits a profound synergistic effect for low-temperature NO₂ sensing. The highly porous DE-LFO matrix, rich in oxygen vacancies, is designed to maximize NO₂ adsorption, while the highly conductive MXene network provides an efficient pathway for charge transport. The modulation of the potential barrier at the p-p interface upon gas exposure is anticipated to yield an ultra-sensitive, highly selective, and rapid sensing response. This study details the synthesis of this multi-scale engineered composite, provides an exhaustive characterization of its structural and chemical properties, and presents a systematic evaluation of its gas-sensing performance, culminating in the elucidation of the underlying synergistic mechanism.

II. Materials and Methods

(1) Materials

Lanthanum(III) nitrate hexahydrate, iron(III) nitrate nonahydrate, citric acid monohydrate, and potassium hydroxide were purchased from Sigma-Aldrich. Ti₃AlC₂ MAX phase powder (200 mesh, 98 %) was obtained from Forsman Scientific. Lithium fluoride and hydrochloric acid were acquired from Merck. Medical-grade absorbent cotton was sourced from a local supplier. All chemicals were used as received without further purification. Deionized (DI) water (18.2 MΩ·cm) was used throughout all experiments.

(2) Synthesis of Porous LaFeO₃ Ceramics (C-LFO and DE-LFO)

A precursor solution was prepared by dissolving 4.33 g (10 mmol) of La(NO₃)₃·6H₂O and 4.04 g (10 mmol) of Fe(NO₃)₃·9H₂O in 100 mL of DI water under magnetic stirring. Subsequently, 4.20 g (20 mmol) of citric acid was added as a chelating agent, and the solution was stirred for 1 hour to ensure homogeneity⁸. Medical-grade cotton (1.0 g) was thoroughly cleaned by washing with ethanol and DI water, dried, and then immersed in the prepared precursor solution for 2 hours to ensure complete infiltration. The saturated cotton was then transferred into a 200 mL Teflon-lined stainless-steel autoclave, which was sealed and heated to 180 °C for 12 hours in an electric oven⁸. After cooling to room temperature, the resulting solid product was collected, washed several times with DI water and ethanol to remove any residual ions, and dried at 80 °C for 12 hours.

The dried precursor was subjected to a two-stage calcination process. To obtain cotton-templated LaFeO₃ (C-LFO), the precursor was calcined in a muffle furnace under an ambient air atmosphere at 600 °C for 4 hours with a heating rate of 5 K/min. This process ensures the complete combustion of the cotton template and the crystallization of the perovskite phase¹⁶. For the synthesis of defect-engineered LaFeO₃ (DE-LFO), the precursor first underwent an initial calcination in air at 450 °C for 2 hours to remove the bulk of the organic template. This was followed by a subsequent annealing step at 600 °C for 2 hours in a tube furnace under a controlled reducing atmosphere (5 % H₂ in Ar) to intentionally generate a high concentration of oxygen vacancies¹⁷. For comparison, a pristine LaFeO₃ (LFO) sample was synthesized using the same hydrothermal and air-calcination procedure but without the cotton template.

(3) Synthesis of Ti₃C₂T_x MXene nanosheets

Ti₃C₂T_x MXene nanosheets were synthesized with the minimally intensive layer delamination (MILD) method¹⁸. In a typical synthesis, 3.2 g of LiF was dissolved in 40 mL of 9 M HCl in a Teflon beaker under magnetic stirring for 10 minutes. Then, 2 g of Ti₃AlC₂ MAX phase powder was slowly added to the solution over 5 minutes to control the initial exothermic reaction. The mixture was then stirred continuously at 40 °C for 24 hours to selectively etch the aluminum layers from the MAX phase. The resulting dark slurry was repeatedly washed

with DI water by means of centrifugation (8 000 rpm for 5 min per cycle) until the pH of the supernatant reached approximately 6. For delamination, the sediment was re-dispersed in 100 mL of DI water and sonicated for 1 hour in an ice bath under a continuous Ar gas purge to prevent oxidation. The resulting dispersion was centrifuged at 3 500 rpm for 1 hour, and the stable, dark green supernatant containing delaminated, few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets was carefully collected and stored at 4 °C for further use.

(4) Synthesis of DE-LFO/MXene composites

The DE-LFO/MXene composites were prepared with a simple hydrothermal assembly method. First, a 1 mg/mL dispersion of DE-LFO powder was prepared in DI water by sonication. The concentration of the as-prepared $\text{Ti}_3\text{C}_2\text{T}_x$ MXene dispersion was determined by drying a known volume and measuring its mass. Specific volumes of the MXene dispersion were then added to the DE-LFO dispersion to achieve final MXene weight percentages of 2 wt%, 4 wt%, and 6 wt%. The mixtures were ultrasonicated for 30 minutes to ensure uniform mixing. Each mixture was then transferred to a 50-mL Teflon-lined autoclave and heated at 120 °C for 2 hours to promote the formation of an intimate interface between the DE-LFO fibers and MXene nanosheets³. The resulting composite powders were collected by means of centrifugation, washed with DI water, and dried at 60 °C in a vacuum oven. The final samples were designated as DE-LFO/MX-2, DE-LFO/MX-4, and DE-LFO/MX-6, respectively.

(5) Sensor fabrication and gas sensing measurements

The gas sensors were fabricated by preparing a homogeneous paste of the sensing material (5 mg) in ethanol (0.5 mL). This paste was then carefully drop-cast onto a commercial alumina substrate (10 mm × 5 mm) fitted with interdigitated gold electrodes (IDE, 100 μm gap). The sensors were subsequently dried at 80 °C for 6 hours to evaporate the solvent. Gas sensing measurements were conducted using a static gas testing system (CGS-8, Elite Tech, China) with a sealed 1 L chamber at ~25 °C and 1 atm. Target concentrations generated by means of microsyringe dosing were calculated based on ideal-gas volumetric dilution as: $C_{\text{ch}}(\text{ppmv}) \approx C_{\text{stock}} \times V_{\text{inj}} / V_{\text{ch}}$, where C_{stock} is the stock-gas concentration (ppmv), V_{inj} is the injected gas volume, and $V_{\text{ch}} = 1.000 \text{ L}$. Immediately after dosing, the resistance was logged continuously and responses were extracted only after the signal reached a stable plateau to mitigate transient inhomogeneity. All measurements were performed at room temperature (25 °C) and a relative humidity (RH) of approximately 40 %, unless stated otherwise. For humidity tests, RH = 20/40/60/80 % was randomized; $\text{NO}_2 = 1 \text{ ppm}$; sensors stabilized 10 min at each RH; responses averaged over three repeats. For selectivity tests, each interferent (NH_3 , CO, CH_4 , H_2S , ethanol) was challenged at 5 ppm for 180 s, with 600 s purge in clean air; exposure order was randomized ($n = 3$). The sensor response (S) is defined as $S = R_a / R_g$ (R_a : resistance in air; R_g : resistance in target gas). All responses in

the manuscript are reported as this unitless ratio. When conversion is desired, the relative change (%) equals $(S - 1) \times 100 \%$. The response time (t_{res}) and recovery time (t_{rec}) were defined as the time taken for the sensor to reach 90 % of its total resistance change upon gas exposure and removal, respectively. For calibration, responses at $\text{NO}_2 = [0.10, 0.20, 0.50, 1.0, 2.0, 5.0] \text{ ppm}$ were recorded with $[N_{\text{device}}]$ independently fabricated sensors, each concentration repeated $[n_{\text{repeat}}]$ times. Linear fitting used 0.10–2.0 ppm. The limit of detection (LOD) was calculated as $\text{LOD} = 3\sigma/b$, where b is the slope of the linear fit and σ is the standard deviation of the baseline signal recorded in air (25 °C, ~40 % RH) over a 5-min window immediately prior to dosing.

III. Results and Discussion

The synthesis strategy was designed to achieve a multi-scale architecture, leveraging a biotemplate for macro-scale morphology, controlled calcination for nano-scale defect engineering, and heterostructuring for electronic-scale functionality. The successful execution of each step was verified by means of comprehensive material characterization. The thermal decomposition behavior of the cotton template was first investigated using thermogravimetric analysis (TGA), as shown in Fig. 1. The raw cotton fiber exhibits a sharp weight loss between 300 °C and 400 °C, corresponding to the pyrolysis of cellulose. The $\text{LaFeO}_3/\text{cotton}$ precursor shows a similar primary decomposition stage, followed by further gradual weight loss associated with the decomposition of metal nitrates and citric acid complexes. The residue remains stable above 550 °C, confirming that a calcination temperature of 600 °C is sufficient for the complete removal of the organic template and the formation of the crystalline oxide phase.

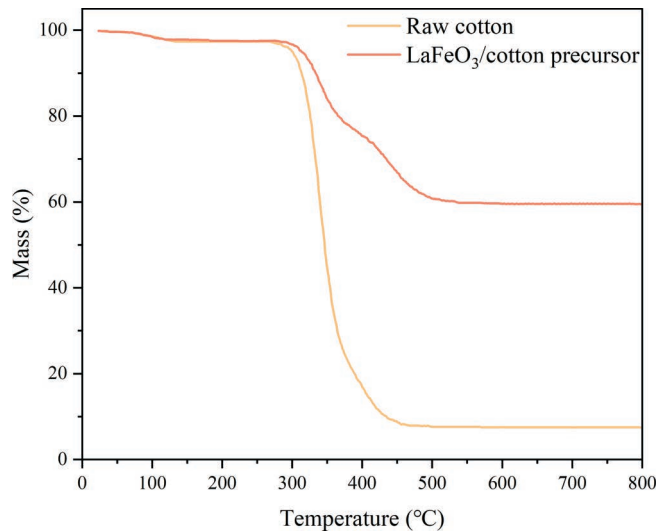


Fig. 1: Thermogravimetric analysis of raw cotton and $\text{LaFeO}_3/\text{cotton}$ precursor.

The crystal structure and phase purity of the synthesized materials were analyzed by means of X-ray diffraction (XRD), with the patterns presented in Fig. 2. The patterns for LFO, C-LFO, and DE-LFO all exhibit sharp diffraction peaks that can be indexed to the orthorhombic perovskite structure of LaFeO_3 (JCPDS card No. 37-

1493), with no observable impurity phases such as LaO_2 or Fe_2O_3 ¹⁹. This confirms the successful formation of the pure perovskite phase. The XRD pattern of the synthesized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene shows a significant shift of the characteristic (002) peak from approximately 9.5° in the parent Ti_3AlC_2 MAX phase (pattern not shown) to a lower angle of 6.5° . This shift indicates an expansion of the c-lattice parameter, a hallmark of the successful removal of the Al atomic layers and the formation of the 2D MXene structure¹⁸. The XRD pattern of the final DE-LFO/MX-4 composite clearly displays the characteristic peaks of both the orthorhombic LaFeO_3 and the (002) peak of $\text{Ti}_3\text{C}_2\text{T}_x$, confirming the successful formation of the composite material without altering the crystal structures of the individual components²⁰.

Fourier-transform infrared (FTIR) spectroscopy was employed to investigate the chemical bonding within the materials, as shown in Fig. 3. All samples containing LaFeO_3 (LFO, DE-LFO, and DE-LFO/MX-4) display a strong absorption band centered around 558 cm^{-1} , which is attributed to the Fe-O stretching vibration of the corner-sharing FeO_6 octahedra, a characteristic feature of the perovskite structure¹⁹. The spectrum for the DE-LFO/MX-4 composite exhibits this Fe-O band along with broad absorption features in the regions of $1\,000\text{--}1\,400\text{ cm}^{-1}$ and $\sim 3\,400\text{ cm}^{-1}$, which correspond to C-F/C-O and -OH surface functional groups present on the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets, respectively. This provides further evidence for the successful integration of both components in the composite material.

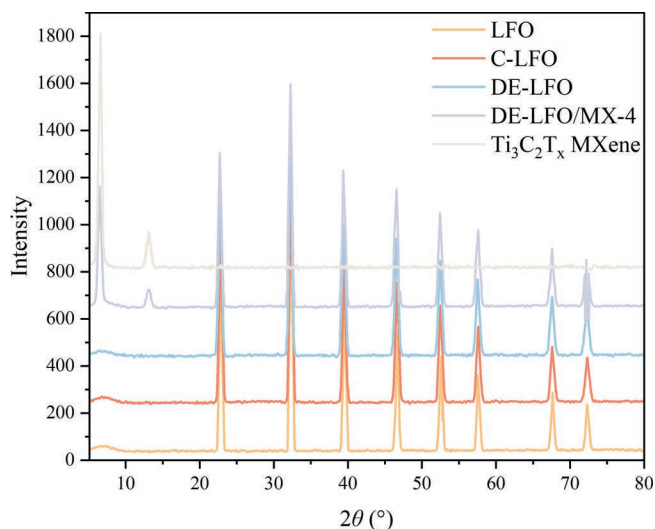


Fig. 2: XRD patterns of LFO, C-LFO, DE-LFO, $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, and the DE-LFO/MX-4 composite.

The morphology of the synthesized powders was examined using scanning electron microscopy (SEM). Fig. 4 compares the morphologies of the non-templated LFO (Fig. 4a) and the cotton-templated DE-LFO (Fig. 4b). The LFO sample consists of randomly agglomerated nanoparticles with no defined macroscopic structure. In stark contrast, the DE-LFO sample exhibits

a highly porous, three-dimensional network of interconnected microfibers, with fiber diameters ranging from $5\text{--}15\text{ }\mu\text{m}$. This fibrous morphology is a clear replication of the original cotton template, demonstrating the efficacy of the biotemplating approach in creating a hierarchical porous architecture¹⁶. Fig. 5 presents SEM images of the optimal DE-LFO/MX-4 composite. At lower magnification (Fig. 5a), the interconnected fibrous network is clearly visible. At higher magnification, it is evident that the flexible, sheet-like $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets are conformally coated onto the surface of the LaFeO_3 fibers (Fig. 5b), creating an intimate physical contact between the two components²⁰.

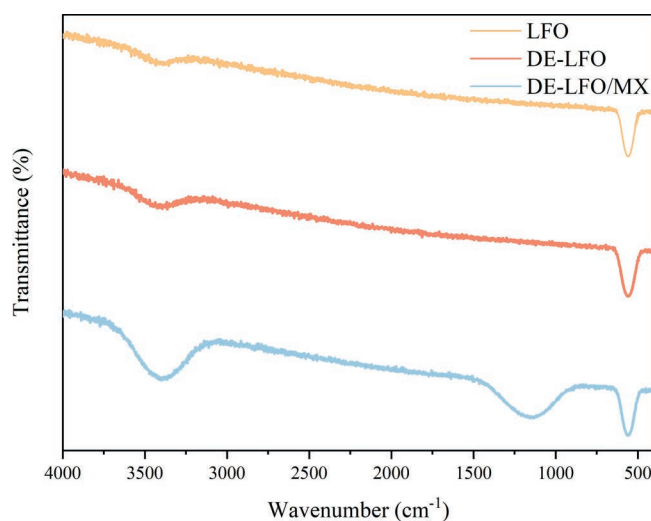


Fig. 3: FTIR spectra of LFO, DE-LFO, and DE-LFO/MX-4.

The specific surface area (SSA) and porosity of the materials, which are critical for gas sensing applications, were quantified using N_2 adsorption-desorption analysis. Fig. 6 displays the isotherms (Fig. 6a) and corresponding pore size distribution (Fig. 6b) plots for the LFO, C-LFO, and DE-LFO samples. The LFO sample exhibits a Type II isotherm with a low SSA of $15.2\text{ m}^2/\text{g}$, characteristic of non-porous or macroporous materials. In contrast, both C-LFO and DE-LFO samples display Type IV isotherms with distinct H3-type hysteresis loops, which are indicative of mesoporous structures formed by the aggregation of plate-like particles²¹. The pore size distribution plots confirm the presence of a significant volume of mesopores centered around $10\text{--}30\text{ nm}$. The key physicochemical properties are summarized in Table 1. The SSA of C-LFO ($61.5\text{ m}^2/\text{g}$) and DE-LFO ($65.8\text{ m}^2/\text{g}$) are more than four times greater than that of the non-templated LFO. This dramatic increase in surface area is a direct result of the cotton-templating strategy, which creates a hierarchical porous network that provides a vastly increased number of accessible active sites for gas interaction²². The slightly higher surface area of DE-LFO compared to C-LFO may be attributed to the reducing atmosphere during annealing, which can induce minor structural rearrangements.

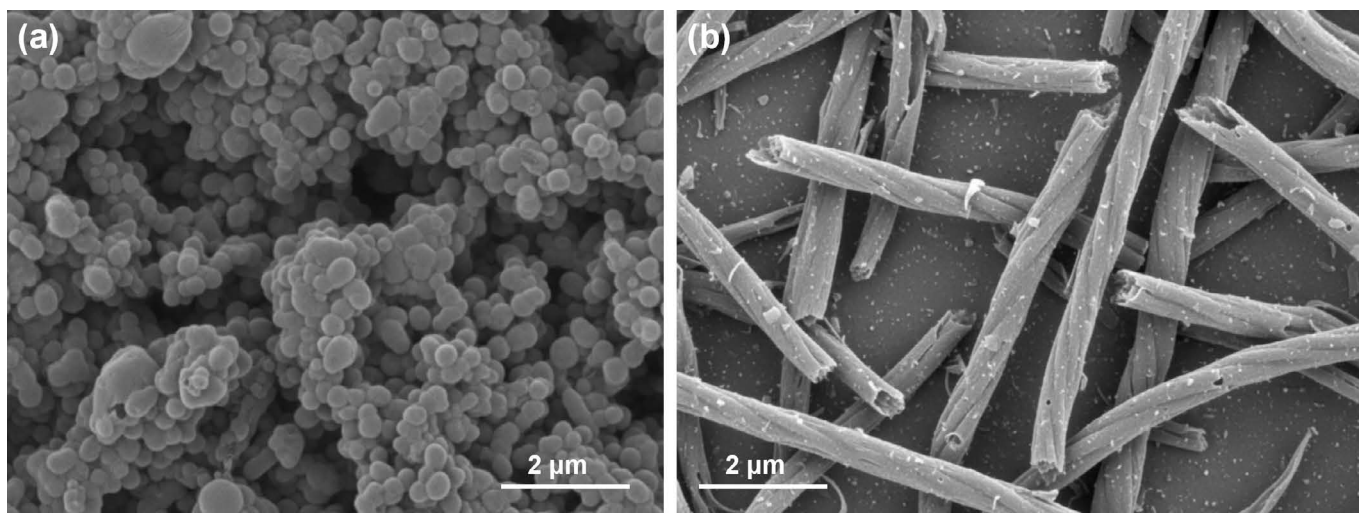


Fig. 4: SEM images of (a) LFO nanoparticles and (b) cotton-templated DE-LFO.

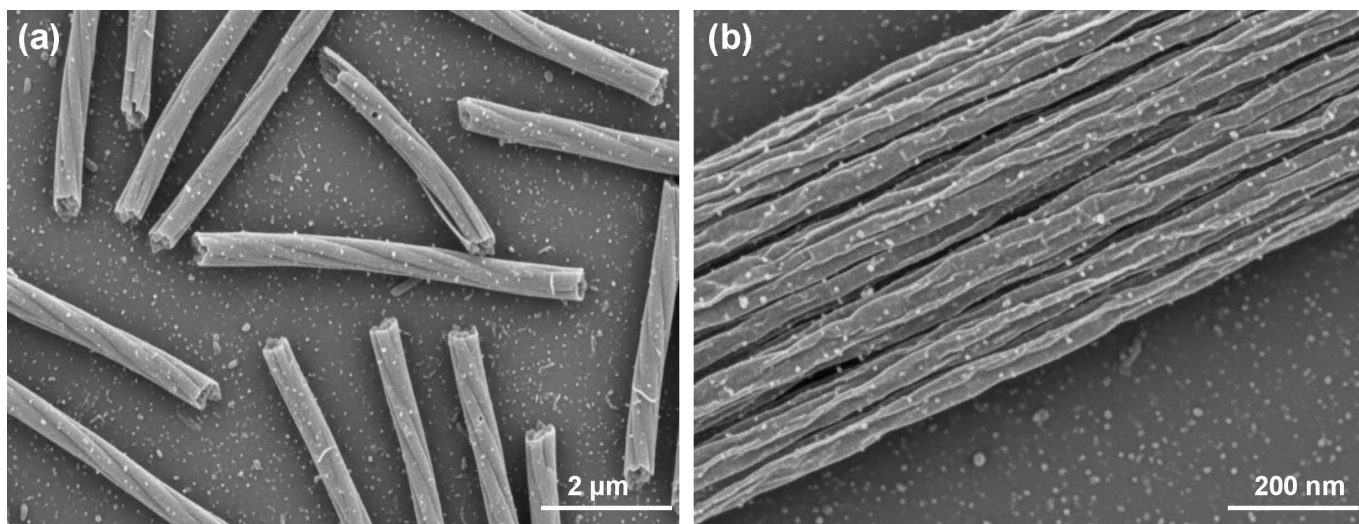


Fig. 5: SEM of DE-LFO/MX-4 at (a) low magnification and (b) high magnification.

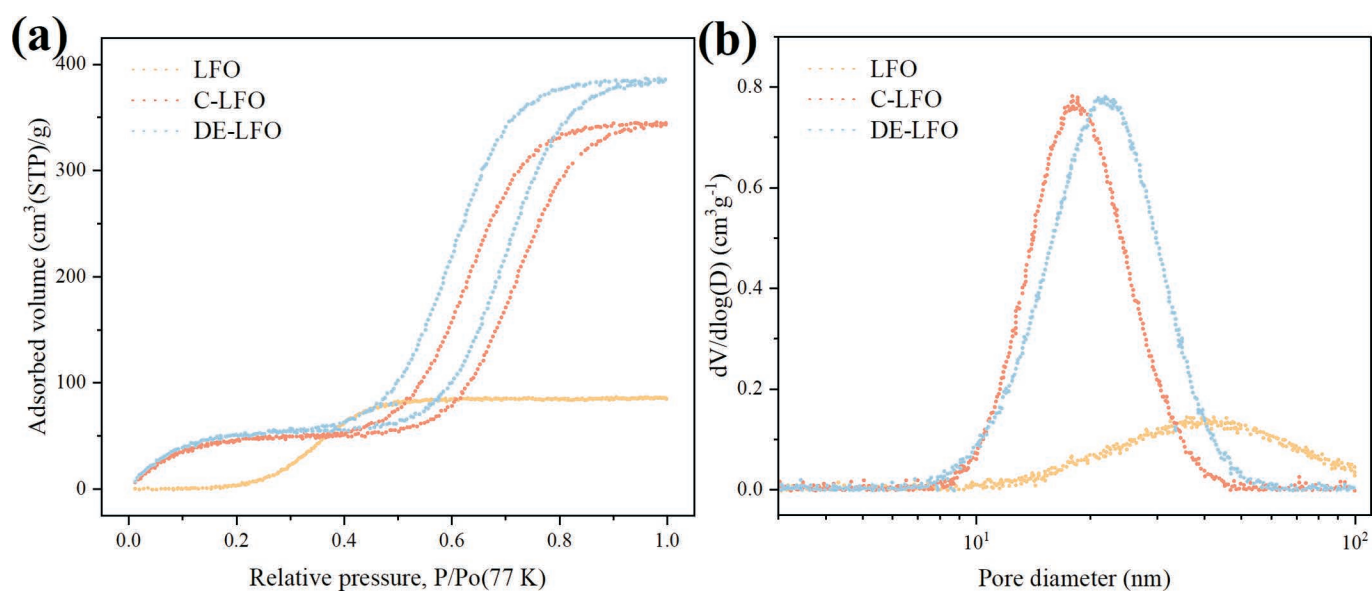
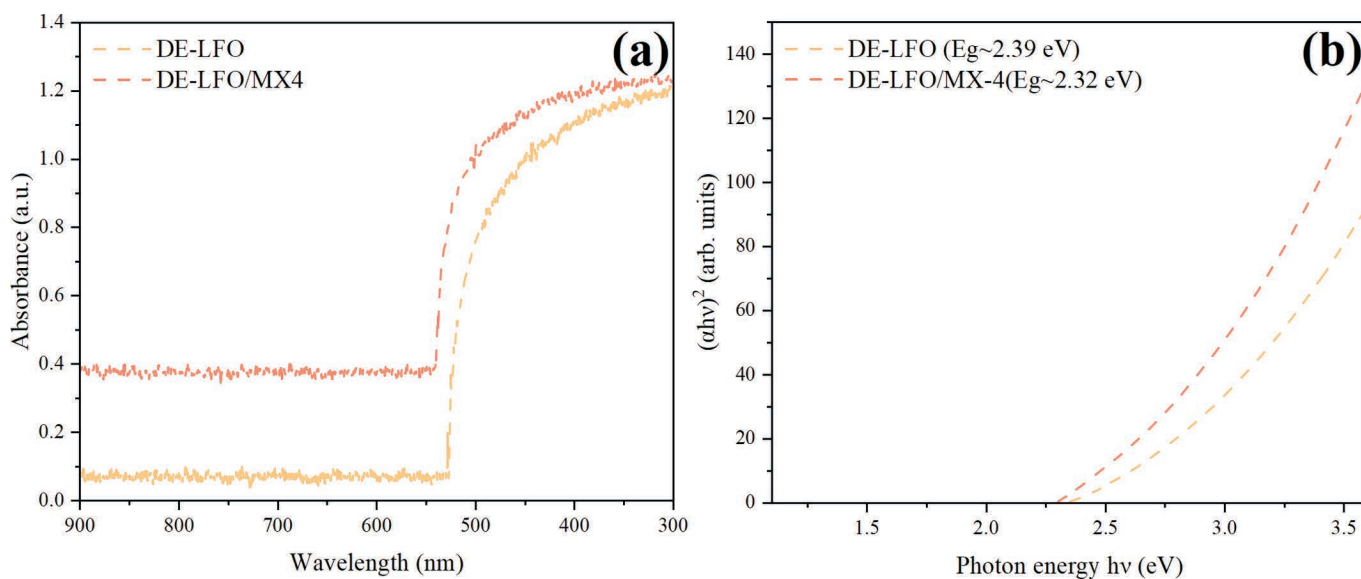


Fig. 6: (a) N_2 adsorption-desorption isotherms and (b) pore-size distributions of LFO, C-LFO, and DE-LFO.

Table 1: Textural, defect, and optical parameters of LFO, C-LFO, DE-LFO, and DE-LFO/MX-4 (BET surface area, pore volume, oxygen-vacancy fraction, band gap).

Sample	Crystallite Size (nm)	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	O _v /(O _{lat} + O _v) Ratio (%)	Band Gap (eV) [from UV-vis]
LFO	45.3	15.2	0.08	8.1	2.41
C-LFO	38.6	61.5	0.25	12.5	2.38
DE-LFO	37.1	65.8	0.29	25.3	2.35
DE-LFO/MX-4	36.9	78.3	0.34	-	-

**Fig. 7:** (a) UV-vis DRS spectra and (b) Tauc plots of DE-LFO and DE-LFO/MX-4.

The optical properties of the materials were investigated using UV-visible diffuse reflectance spectroscopy (DRS). **Fig. 7a-b** shows the absorption spectra and the corresponding Tauc plots for DE-LFO and the DE-LFO/MX-4 composite. The DE-LFO sample exhibits a strong absorption edge in the visible region. Based on extrapolation of the linear portion of the Tauc plot, the direct band gap (E_g) of the DE-LFO is calculated to be 2.35 eV, which is consistent with reported values for LaFeO_3 . Upon forming the composite with MXene, the DE-LFO/MX-4 sample shows significantly enhanced light absorption across the entire visible and near-infrared spectrum. This broadband absorption is characteristic of the metallic-like nature of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene²³. The apparent band gap of the composite shows a slight redshift, suggesting a strong electronic interaction at the hetero-junction interface that modifies the overall electronic band structure. To quantitatively validate the defect-engineering strategy, the chemical states and surface oxygen vacancy concentrations were investigated by means of XPS, with the high-resolution O 1s spectra. The asymmetric O 1s peaks were deconvoluted into two main components: lattice oxygen at a lower binding energy (~ 529.6 eV) and oxygen species associated with defects or vacancies at a higher binding energy (~ 531.5 eV). The relative concentration of oxygen vacancies was calculated using the area ratio. As summarized in Table 1, the DE-LFO sample, which underwent secondary annealing in a

reducing atmosphere, exhibited the highest O_v ratio of 25.3 %. This was significantly higher than that of the air-calcined C-LFO (12.5 %) and pristine LFO (8.1 %). This direct evidence confirms the successful generation of a high density of oxygen vacancies, which are expected to serve as preferential adsorption sites for NO_2 molecules.

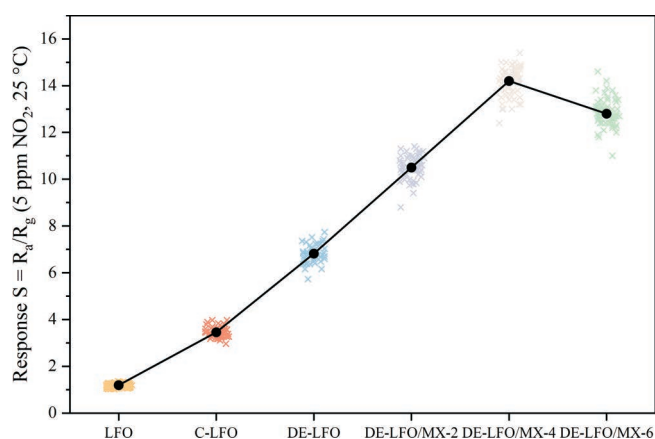
The gas sensing properties of the synthesized materials were systematically evaluated towards NO_2 at room temperature (25 °C). To contextualize our results within LaFeO_3 -based sensing, **Table 2** compiles representative reports alongside this work. Typical LaFeO_3 sensors require elevated temperatures (≥ 120 -250 °C) to reach double-digit responses and often exhibit slower kinetics. A cotton-modified LaFeO_3 at ~ 28 °C reached only a modest response ($S \approx 3.8$ at 5 ppm NO_2). By contrast, our DE-LFO/MX-4 delivers $S = 14.2$ at 5 ppm with 8 s/25 s response/recovery at 25 °C, underscoring the combined impact of hierarchical porosity, engineered oxygen vacancies, and the MXene-mediated interfacial amplification. This places the present sensor at the high end of room-temperature performance among LaFeO_3 derivatives, without external activation (heaters or UV/LED).

Fig. 8 presents a comparative summary of the response of all prepared samples to 5 ppm NO_2 . A clear and systematic enhancement in sensing performance is observed with each step of the material engineering process. The pristine LFO sensor shows a negligible response ($S \approx 1.2$). The

Table 2: Performance comparison of representative LaFeO_3 -based gas sensors reported in the literature versus this work (DE-LFO/MX-4) at low/room temperature.

Sensing Material	Target Gas	Operating Temp. ($^{\circ}\text{C}$)	Concentration	Response	Response/Recovery Time (s)	Ref.
LaFeO_3 microspheres	NO_2	250	3 ppm	12.5%	120/180	41
rGO- LaFeO_3 microspheres	NO_2	250	3 ppm	183.4%	65/90	41
Pd- LaFeO_3	H_2S	120	1 ppm	36.29	19.6/15.2	55
Ni-doped LaFeO_3	Triethylamine	190	100 ppm	102	-/-	2
Cotton-modified LaFeO_3 (CLFO)	NO_2	28	5 ppm	~ 3.8	-/-	3
DE-LFO/MX-4 (This Work)	NO_2	25	5 ppm	1320%	8/25	-

introduction of a porous structure via cotton templating (C-LFO) increases the response to 3.5, highlighting the importance of a high surface area. The creation of oxygen vacancies (DE-LFO) further boosts the response to 6.8, demonstrating the critical role of surface defects as active sites. Upon coupling with MXene, the response is dramatically amplified. The response increases with MXene content, reaching a maximum for the DE-LFO/MX-4 sample with a response value of 14.2, which is over 11 times higher than that of pristine LFO. However, further increasing the MXene content to 6 wt% (DE-LFO/MX-6) leads to a slight decrease in response, likely due to the excessive coverage of LaFeO_3 active sites by the MXene sheets or the short-circuiting effect of the highly conductive MXene network. These results identify DE-LFO/MX-4 as the optimal sensing material.

**Fig. 8:** Room-temperature response (S) to 5 ppm NO_2 for all samples, identifying DE-LFO/MX-4 as the optimum composition.

The dynamic sensing performance of the champion DE-LFO/MX-4 sensor was further investigated. **Fig. 9** shows the real-time response curve of the sensor to successive exposures of NO_2 at concentrations ranging from 100 ppb to 5 ppm. The sensor exhibits clear, stable, and highly reversible step-like responses, with the response magnitude increasing systematically with the gas concentration. The sensor is capable of reliably detecting NO_2 even at the ppb level. The response and recovery kinetics of the sensor are exceptionally fast, as highlighted

in **Fig. 10**. Upon exposure to 1 ppm NO_2 , the sensor reaches 90 % of its final response in just 8 seconds (t_{res}), and upon removal of the gas, it recovers 90 % of its baseline resistance in 25 seconds (t_{rec}). These rapid kinetics are significantly faster than most reported MOS-based sensors, especially at room temperature, and are crucial for real-time monitoring applications³.

The relationship between sensor response and NO_2 concentration is plotted in **Fig. 11**. The response shows a good linear correlation ($R^2 = 0.995$) in the low concentration range of 100 ppb to 2 ppm, which is highly desirable for quantitative analysis. The LOD was computed as $\text{LOD} = 3\sigma/b$ with b from the linear regression and σ obtained from the baseline noise (air, 5 min window) acquired for each replicate prior to dosing. Using this convention, the LOD for DE-LFO/MX-4 is 12 ppb¹.

Selectivity is a critical parameter for any practical gas sensor. **Fig. 12** shows the response of the DE-LFO/MX-4 sensor to 5 ppm of NO_2 and various potential interfering gases, including ammonia, carbon monoxide, methane, hydrogen sulfide and ethanol. The sensor exhibits a remarkably high response to NO_2 ($S = 14.2$), while its response to all other gases is minimal ($S < 1.5$). The selectivity coefficient for NO_2 over these interfering gases is greater than 10, indicating outstanding selectivity and reliability for NO_2 detection in complex gas mixtures⁶.

The long-term stability and humidity tolerance of the sensor were also evaluated. As shown in **Fig. 13**, the response of the DE-LFO/MX-4 sensor to 1 ppm NO_2 was monitored over a period of 30 days. The response value remained highly stable, with a variation of less than $\pm 4\%$ from its initial value, demonstrating excellent long-term durability²⁴. The effect of RH on the sensor's performance is presented in **Fig. 14**. As the RH increases from 20 % to 80 %, the sensor's response to 1 ppm NO_2 shows a gradual decrease. This is a common phenomenon in MOS sensors, as water molecules can compete with target gas molecules for adsorption sites. However, even at a high RH of 80 %, the sensor retains over 75 % of its response in dry air, indicating a good tolerance to humidity, which is a significant advantage for real-world applications²⁵. Mechanistically, H_2O displaces chemisorbed O^-/O_2^- and generates surface $-\text{OH}$ on LaFeO_3 , diminishing

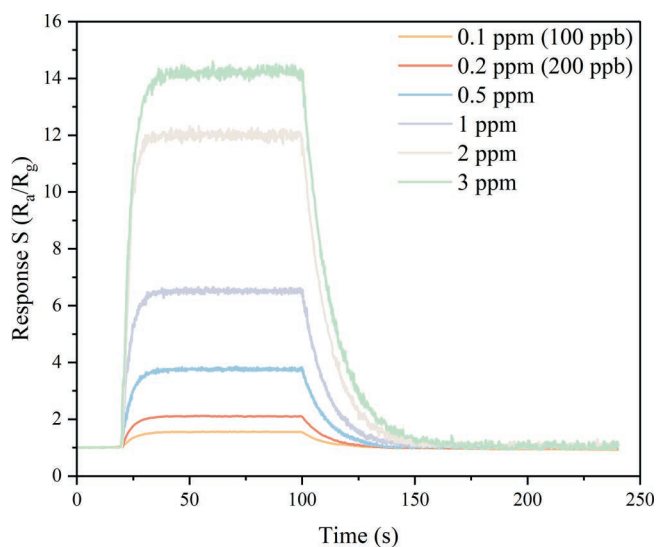


Fig. 9: Dynamic, step-like response-recovery curves of DE-LFO/MX-4 to successive NO_2 exposures from 100 ppb to 5 ppm.

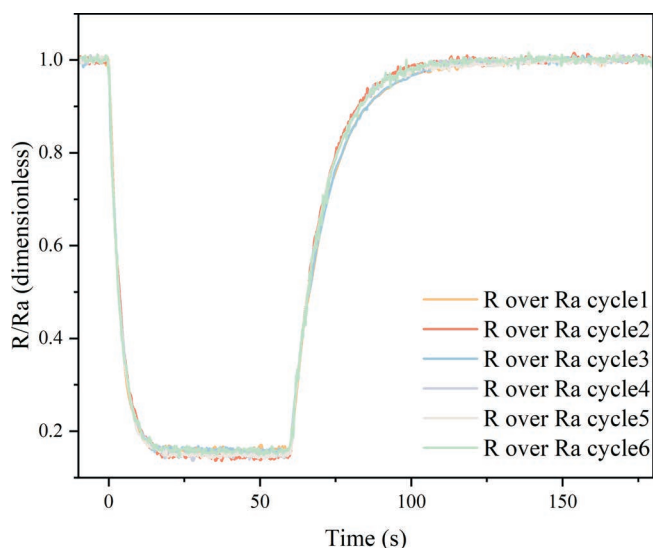


Fig. 10: Transient kinetics of DE-LFO/MX-4 at 1 ppm NO_2 .

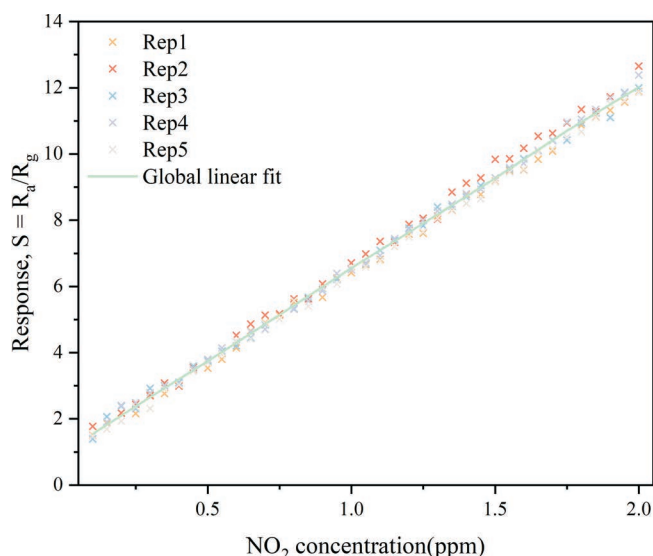


Fig. 11: Calibration plot of response versus NO_2 concentration with linearity from 0.1 to 2 ppm.

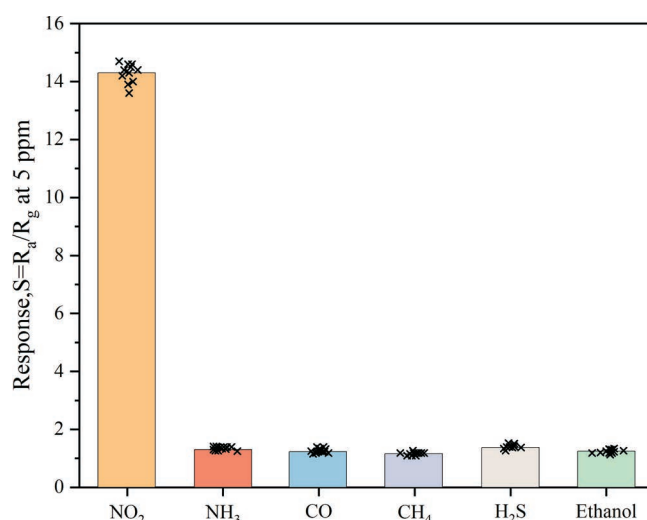


Fig. 12: Selectivity comparison at 5 ppm for NO_2 versus common interferents (NH_3 , CO , CH_4 , H_2S , ethanol).

electron-withdrawing NO_2 adsorption; hydrophilic -O/-OH on $\text{Ti}_3\text{C}_2\text{T}_x$ also promotes H_2O layers that screen NO_2 . To mitigate RH effects, thin hydrophobic/molecular-sieving overlayers (e.g., ZIF-8/ZIF-71 or PDMS/silane), brief blue/UV pulses for accelerated H_2O desorption, and RH-based software compensation can be implemented in future devices. **Table 3** benchmarks the present sensor against MXene-based NO_2 devices. Systems such as $\text{Ti}_3\text{C}_2\text{T}_x/\text{WS}_2$ on paper attain low LODs (~ 11 ppb) but respond more slowly ($\approx 150/300$ s), while hybrids like $\text{SnO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ achieve very large responses at elevated temperature (80°C). DE-LFO/MX-4 uniquely combines an ultra-low LOD (12 ppb) with fast 8/25 s kinetics at 25°C and strong selectivity, indicating that the p-p heterojunction here acts as an electronic amplifier: NO_2 -induced hole accumulation in DE-LFO collapses the interfacial barrier within the conductive MXene network, producing large signal gain without thermal or optical assistance.”

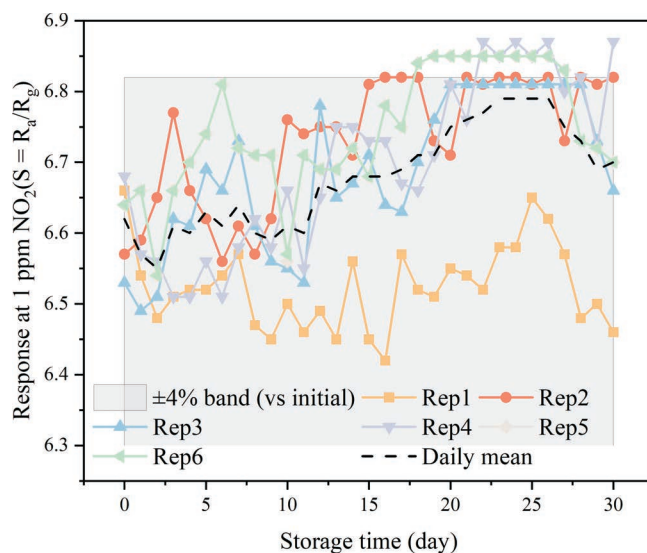


Fig. 13: Long-term stability of DE-LFO/MX-4 response to 1 ppm NO_2 over 30 days.

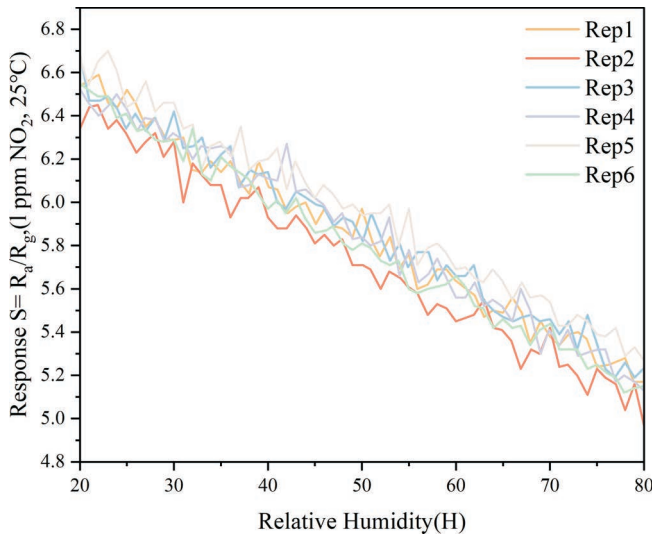
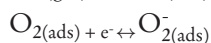
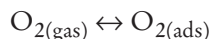


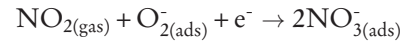
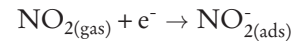
Fig. 14: Humidity tolerance of DE-LFO/MX-4: response to 1 ppm NO_2 under RH 20–80 %, retaining >75 % of dry-air response at 80 % RH.

The superior sensing performance of the DE-LFO/MX-4 composite can be attributed to a multi-faceted synergistic mechanism that leverages the unique properties of each component and their interaction at the heterojunction interface. The fundamental sensing process is based on the modulation of charge carriers in the p-type LaFeO_3 semiconductor. In an air atmosphere, oxygen molecules adsorb onto the LaFeO_3 surface and capture electrons from its valence band, forming chemisorbed oxygen ions. This process increases the concentration of majority charge carriers, forming a hole accumulation layer (HAL) near the surface and thereby reducing the material's baseline resistance²⁶. The reactions are as follows:



When the sensor is exposed to NO_2 , a strong oxidizing gas with high electron affinity, NO_2 molecules directly adsorb onto the surface and trap additional electrons from the LaFeO_3 , leading to a further, more significant increase

in the hole concentration and a sharp decrease in resistance. The relevant surface reactions can be described as:



This fundamental mechanism is amplified by three key factors engineered into our composite material. First, the hierarchical porosity derived from the cotton template provides an extensive network of channels for rapid gas diffusion, ensuring that NO_2 molecules can efficiently access the entire sensing surface, maximizing the interaction volume and thus the overall response magnitude³. Second, the high concentration of engineered oxygen vacancies on the DE-LFO surface serves a dual purpose. These defect sites act as energetically favorable, preferential adsorption centers for NO_2 molecules, increasing the adsorption density and facilitating charge transfer²⁷. Furthermore, these vacancies modulate the local electronic structure, enhancing the catalytic activity of the surface for redox reactions involving the adsorbed gas species²⁸.

The most critical contribution to the drastically enhanced sensitivity and rapid kinetics arises from the formation of a p-p heterojunction at the DE-LFO/ $\text{Ti}_3\text{C}_2\text{T}_x$ interface. Importantly, the relative work functions are termination- and surface-state-dependent²⁹. Reported UPS/Kelvin-probe values place $\Phi(\text{Ti}_3\text{C}_2\text{T}_x)$ broadly in $\sim 3.4\text{--}5.8$ eV (lower for F/OH-rich terminations; higher for oxidized or acceptor-modified surfaces), while $\Phi(\text{LaFeO}_3)$ is reported $\sim 4.4\text{--}6.2$ eV with $E_g \approx 2.2\text{--}2.35$ eV depending on stoichiometry and film quality. Using these ranges, the expected built-in potential $V_{\text{bi}} \approx \Phi(\text{LFO}) - \Phi(\text{MXene})$ spans $\sim 0\text{--}1.3$ eV, with band bending localized mainly in the p-type LFO. At equilibrium, Fermi-level alignment yields an interfacial hole-transport barrier whose height/width is highly susceptible to surface charge transfer. Under NO_2 (strong electron acceptor), additional hole injection into LFO reduces this barrier, thereby opening a high-conductance pathway through the MXene network and producing the observed electronic amplification and fast kinetics.

Table 3: Benchmarking of MXene-based NO_2 sensors from the literature and the DE-LFO/MX-4 sensor (this work) at room temperature.

Sensing Material	Operating Temp. ($^{\circ}\text{C}$)	Concentration	Response (%)	Response/Recovery Time (s)	LOD (ppb)	Ref.
Pristine $\text{Ti}_3\text{C}_2\text{T}_x$	25	1 ppm	0.2%	–/–	–	56
$\text{Ti}_3\text{C}_2\text{T}_x/\text{WS}_2$ on paper	25	1 ppm	15.2%	150/300	11.0	56
$\text{SnO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	80	5 ppm	2680%	11/23	~ 50	57
APTES- Nb_2CT_x	25	25 ppm	31.5%	–/–	3	49
DE-LFO/MX-4 (This work)	25	1 ppm	550%	8/25	12	–

Before contact, the work function of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene is typically higher than that of p-type. Upon contact, to achieve Fermi level alignment, holes diffuse from the MXene (higher hole concentration) to the DE-LFO (lower hole concentration). This charge redistribution results in the formation of a hole accumulation layer on the DE-LFO side and a corresponding hole depletion layer on the MXene side of the interface. This depletion layer creates a potential barrier for hole transport across the heterojunction. When the sensor is exposed to NO_2 , the massive injection of holes into the DE-LFO due to electron trapping by NO_2 molecules causes a significant downward shift of its valence and conduction bands. This drastically reduces the height and width of the potential barrier at the p-p interface, effectively “opening the gate” for hole transport. Since the overall conductivity of the composite is dominated by the highly conductive MXene network, which is modulated by this interfacial barrier, even a small change in the barrier height leads to a large change in the total resistance of the sensor. This heterojunction-mediated amplification is the primary reason for the observed ultra-high sensitivity.

IV. Conclusions

In summary, this research successfully demonstrates a multi-scale material engineering strategy for the fabrication of a high-performance, low-temperature NO_2 gas sensor. A novel hierarchical composite consisting of defect-engineered, cotton-templated LaFeO_3 ceramic fibers coupled with $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets was synthesized via a combination of biotemplating, controlled-atmosphere calcination, and hydrothermal assembly. Comprehensive characterization confirmed the formation of a porous, fibrous LaFeO_3 network with a high specific surface area, a significant concentration of surface oxygen vacancies, and an intimate interfacial contact with the conductive MXene sheets. The optimized DE-LFO/MX-4 sensor exhibited outstanding LaFeO_3 sensing capabilities at room temperature (25°C). It demonstrated a high response ($S = 14.2$ to 5 ppm NO_2), an exceptionally low theoretical detection limit of 12 ppb , and ultra-fast response/recovery kinetics of 8 s and 25 s , respectively. Furthermore, the sensor showed excellent selectivity against common interfering gases and robust long-term stability over 30 days, highlighting its potential for practical applications. The remarkable enhancement in sensing performance was attributed to a powerful synergistic effect. The porous, defect-rich NO_2 architecture provides abundant active sites for efficient LaFeO_3 adsorption, while the formation of a p-p heterojunction with the highly conductive MXene serves as an electronic amplifier. The adsorption of LaFeO_3 molecules on the NO_2 surface modulates the potential barrier at the heterojunction interface, leading to a large and rapid change in the overall resistance of the composite. This work not only presents a promising new material for low-power environmental monitoring and wearable sensing devices but also provides a versatile design paradigm – combining biotemplating, defect engineering, and heterostructuring – with

quantified defect metrics and interface optimization beyond prior cotton-modified LFO/MXene RT sensors.

Acknowledgements

The study was supported by Jiangsu Provincial Administration for Market Regulation Science and Technology Program (Grant No. KJ2024011).

References

- Cruz Lozada, J.A., Rosario, R.A., Flores, S.Y., Kisslinger, K., Fonseca, L.F., Piñero Cruz, D.M.: High-sensitivity NO_2 gas sensor: exploiting UV-enhanced recovery in a hexadecafluorinated iron phthalocyanine-reduced graphene oxide, *ACS Omega*, **10**, 2809–2818, (2025). doi: <https://doi.org/10.1021/acsomega.4c08662>
- Guo, J., Li, W., Zhao, X., Hu, H., Wang, M., Luo, Y., Xie, D., Zhang, Y., Zhu, H.: Highly sensitive, selective, flexible and scalable room-temperature NO_2 gas sensor based on hollow SnO_2/ZnO nanofibers, *Molecules*, **26**, 6475, (2021). doi: <https://doi.org/10.3390/molecules26216475>
- Dhariwal, N., Yadav, P., Kumari, M., Akanksha, Sanger, A., Kang, S.B., Kumar, V., Thakur, O.P.: Engineering an ultrafast ambient NO_2 gas sensor using cotton-modified $\text{LaFeO}_3/\text{MXene}$ composites, *ACS Sens.*, **9**, 6800–6814, (2024). doi: <https://doi.org/10.1021/acssensors.4c02597>
- Shafiei, M., Bradford, J., Khan, H., Piloto, C., Wlodarski, W., Li, Y., Motta, N.: Low-operating temperature NO_2 gas sensors based on hybrid two-dimensional SnS_2 -reduced graphene oxide, *Appl. Surf. Sci.*, **462**, 330–336, (2018). doi: <https://doi.org/10.1016/j.apsusc.2018.08.115>
- Pan, X., Zhao, X., Bermak, A., Fan, Z.: A humidity-insensitive NO_2 gas sensor with high selectivity, *IEEE Electron Device Lett.*, **37**, 92–95, (2016). doi: <https://doi.org/10.1109/LED.2015.2504260>
- Flores, S.Y., Pacheco, E., Malca, C., Peng, X., Chen, Y., Zhou, B., Pinero, D.M., Diaz-Vazquez, L.M., Zhou, A.F., Feng, P.X.: Highly selective room-temperature blue LED-enhanced NO_2 gas sensors based on $\text{ZnO-MoS}_2\text{-TiO}_2$ heterostructures, *Sensors*, **25**, 1781, (2025). doi: <https://doi.org/10.3390/s25061781>
- Souri, M., Salar Amoli, H.: Gas sensing mechanisms in ABO₃ perovskite materials at room temperature: A review, *Mater. Sci. Semicond. Process*, **156**, 107271, (2023). doi: <https://doi.org/10.1016/j.mssp.2022.107271>
- Meng, F., Yu, Z., Zhang, R., Gao, H., Yuan, Z.: Study of the gas sensing performance of Ni-doped perovskite-structured LaFeO_3 nanospheres, *Chemosensors*, **12**, 65, (2024). doi: <https://doi.org/10.3390/chemosensors12040065>
- Toan, N.N., Saukko, S., Lantto, V.: Gas sensing with semiconducting perovskite oxide LaFeO_3 , *Phys. B Condens. Matter*, **327**, 279–282, (2003). doi: [https://doi.org/10.1016/S0921-4526\(02\)01764-7](https://doi.org/10.1016/S0921-4526(02)01764-7)
- Whitten, A., Guo, D., Tezel, E., Denecke, R., Nikolla, E., McEwen, J.-S.: Deconvoluting XPS spectra of La-containing perovskites from first-principles, *JACS Au*, **4**, 3104–3117, (2024). doi: <https://doi.org/10.1021/jacsau.4c00440>
- Choi, M.S., Kim, M.Y., Mirzaei, A., Kim, H.-S., Kim, S., Baek, S.-H., Chun, D.W., Jin, C., Lee, K.H.: Selective, sensitive, and stable NO_2 gas sensor based on porous ZnO nanosheets, *Appl. Surf. Sci.*, **568**, 150910, (2021). doi: <https://doi.org/10.1016/j.apsusc.2021.150910>
- Yu, J., Li, H., Lin, N., Gong, Y., Jiang, H., Chen, J., Wang, Y., Zhang, X.: Oxygen-deficient engineering for perovskite

- oxides in the application of AOPs: regulation, detection, and reduction mechanism, *Catalysts*, **13**, 148, (2023). doi: <https://doi.org/10.3390/catal13010148>
- 13 Kim, S.J., Koh, H.-J., Ren, C.E., Kwon, O., Maleski, K., Cho, S.-Y., Anasori, B., Kim, C.-K., Choi, Y.-K., Kim, J., Gogotsi, Y., Jung, H.-T.: Metallic Ti₃C₂T_x MXene gas sensors with ultrahigh signal-to-noise ratio, *ACS Nano*, **12**, 986–993, (2018). doi: <https://doi.org/10.1021/acsnano.7b07460>
 - 14 Hosseini-Shokouh, S.H., Zhou, J., Berger, E., Lv, Z.-P., Hong, X., Virtanen, V., Kordas, K., Komsa, H.-P.: Highly selective H₂S gas sensor based on Ti₃C₂T_x MXene-organic composites, *ACS Appl. Mater. Interfaces*, **15**, 7063–7073, (2023). doi: <https://doi.org/10.1021/acsnano.7b07460>
 - 15 Zhang, H., Xu, H., Zeng, W., Wang, Z., Zhou, Q.: Gas sensing performance of Ti₃C₂T_x MXene heterojunction structures in greenhouse environments: A mini review, *Front. Chem.*, **12**, 1509732, (2024). doi: <https://doi.org/10.3389/fchem.2024.1509732>
 - 16 Deng, H., Mao, Z., Xu, H., Zhang, L., Zhong, Y., Sui, X.: Synthesis of fibrous LaFeO₃ perovskite oxide for adsorption of rhodamine B, *Ecotoxicol. Environ. Saf.*, **168**, 35–44, (2019). doi: <https://doi.org/10.1016/j.ecoenv.2018.09.056>
 - 17 Yu, J., Li, H., Lin, N., Gong, Y., Jiang, H., Chen, J., Wang, Y., Zhang, X.: Oxygen-deficient engineering for perovskite oxides in the application of AOPs: regulation, detection, and reduction mechanism, *Catalysts*, **13**, 148, (2023). doi: <https://doi.org/10.3390/catal13010148>
 - 18 Jothiramalingama, R., Radhikab, T., Kavithac, N., Al-Lohedana, H., Aldhayan, D., Karnand, M.: Synthesis, morphology and electrical property characteristics of MXene based titanium carbide (Ti₃C₂T_x) coating on non-woven cotton paper, *Dig. J. Nanomater. Biostruct.*, **19**, 15–24, (2024).
 - 19 Theingi, M., Tun, K.T., Aung, N.N.: Preparation, characterization and optical property of LaFeO₃ nanoparticles via sol-gel combustion method, *SciMedicine J.*, **1**, 151–157 (2019). doi: <https://doi.org/10.28991/SciMedJ-2019-0103-5>
 - 20 Zhou, L., Niu, C., Hu, Y., Zhang, H., Shao, X., Ding, Z., Zhang, D.: High-performance SO₂ gas sensor based on MXene/LaFeO₃ nanotubes by electrospinning technology, *J. Mater. Sci. Mater. Electron.*, **35**, 1309, (2024). doi: <https://doi.org/10.1007/s10854-024-13030-4>
 - 21 Han, S., Tao, Y., Liu, Y., Lu, Y., Pan, Z.: Preparation of monolithic LaFeO₃ and catalytic oxidation of toluene, *Materials*, **16**, 3948, (2023). doi: <https://doi.org/10.3390/ma16113948>
 - 22 Shen, C., Liang, H., Zhao, Z., Guo, S., Chen, Y., Tan, Z., Song, X.-Z., Wang, X.: Mo-doped LaFeO₃ gas sensors with enhanced sensing performance for triethylamine gas, *Sensors*, **24**, 4851, (2024). doi: <https://doi.org/10.3390/s24154851>
 - 23 Abdel-Aal, S.K., Abdel-Rahman, A.S.: Graphene influence on the structure, magnetic, and optical properties of rare-earth perovskite, *J. Nanoparticle Res.*, **22**, 267, (2020). doi: <https://doi.org/10.1007/s11051-020-05001-7>
 - 24 John, R.A.B., Vijayan, K., Septiani, N.L.W., Hardiansyah, A., Kumar, A.R., Yulianto, B., Hermawan, A.: Gas-sensing mechanisms and performances of MXenes and MXene-based heterostructures, *Sensors*, **23**, 8674, (2023). doi: <https://doi.org/10.3390/s23218674>
 - 25 Kumar, A.N., Pal, K.: Amine-functionalized stable Nb₂C_{tx} MXene toward room temperature ultrasensitive NO₂ gas sensor, *Mater. Adv.*, **3**, 5151–5162, (2022). doi: <https://doi.org/10.1039/D2MA00301E>
 - 26 Zhang, Y., Jiang, B., Yuan, M., Li, P., Li, W., Zheng, X.: Formaldehyde-sensing properties of LaFeO₃ particles synthesized by citrate sol-gel method, *J. Sol-Gel Sci. Technol.*, **79**, 167–175, (2016). doi: <https://doi.org/10.1007/s10971-016-4025-0>
 - 27 Wei, Z., Zhao, M., Yang, Z., Duan, X., Jiang, G., Li, G., Zhang, F., Hao, Z.: Oxygen vacancy-engineered titanium-based perovskite for boosting H₂O activation and lower-temperature hydrolysis of organic sulfur, *Proc. Natl. Acad. Sci.*, **120**, e2217148120, (2023). doi: <https://doi.org/10.1073/pnas.2217148120>
 - 28 Zhu, L., Zhang, J., Wang, J., Liu, J., Zhao, W., Yan, W.: Efficient formaldehyde gas sensing performance via promotion of oxygen vacancy on In-doped LaFeO₃ nanofibers, *Nanomaterials*, **14**, 1595, (2024). doi: <https://doi.org/10.3390/nano14191595>
 - 29 Xiao, C., Tang, Z., Ma, Z., Gao, X., Wang, H., Jia, L.: High-performance porous LaFeO₃ gas sensor with embedded p-n junctions enabling ppb-level formaldehyde detection, *Sens. Actuators B Chem.*, **397**, 134670, (2023). doi: <https://doi.org/10.1016/j.snb.2023.134670>

