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# Selective Reduction Laser Sintering: A New Strategy for NO<sub>2</sub> Gas Detection Based on In<sub>2</sub>O<sub>3</sub> Nanoparticles

Shaogang Wang, Chunjian Tan, Qihang Zong, Shizhen Li, Chenshan Gao, Huiru Yang, Qianming Huang, Paddy French,\* and Huaiyu Ye\*

This study introduces a novel strategy for fabricating flexible nitrogen dioxide (NO<sub>2</sub>) gas sensors based on Indium Oxide (In<sub>2</sub>O<sub>3</sub>) nanoparticles (NPs) employing selective reduction laser sintering (SRLS) technology. The SRLS technology utilizes ultraviolet (UV) laser selective reduction sintering to precisely and rapidly create oxygen vacancy (OV) defects in In<sub>2</sub>O<sub>3</sub> NPs. These oxygen vacancies (OVs) enhance the active adsorption sites and contribute additional free electrons, significantly improving sensor performance at room temperature. The sensors demonstrate excellent response ( $S = 460.9$  at 10 ppm), rapid response/recovery times ( $\tau_{\text{resp}}/\tau_{\text{reco}} = 27/570$  s), and superior selectivity (response ratio > 400), in addition to robust resistance to light and humidity (under ppm-level NO<sub>2</sub> gas). The sensors also exhibit a low detection limit (200 ppb), a high signal-to-noise ratio (94.8 dB), and good long-term stability (25 days). Moreover, under photo-assisted conditions, the recovery speed of the sensors is further improved. This technology not only provides an innovative strategy for the development of high-performance flexible NO<sub>2</sub> gas sensors but also broadens the application potential of laser direct writing (LDW) technology in advanced materials and sensor fabrications.

increasingly emphasized for the precise and continuous detection of gas signals.<sup>[2]</sup> As environmental detection and health monitoring require increasingly higher accuracy and adaptability, flexible gas sensors have emerged as a focal point in sensor innovation.<sup>[3]</sup> Considering power consumption and operational safety, the development of room-temperature (RT) flexible gas sensors has become a significant trend, addressing both energy efficiency and operational reliability in complex environments.<sup>[4]</sup> Among the various gases, the detection of nitrogen dioxide (NO<sub>2</sub>) has become especially critical, given its key role in environmental health monitoring (EHM). As a major by-product of fossil fuel combustion, NO<sub>2</sub> causes acid rain, photochemical smog, and ozone layer depletion, posing severe environmental risks.<sup>[5]</sup> Additionally, exposure to NO<sub>2</sub> at levels above the 3 ppm threshold is associated with severe health issues, including lung cancer, stroke, and asthma.<sup>[6]</sup> Therefore, the development of advanced RT flexible NO<sub>2</sub> sensors with excellent response, rapid response/recovery, and superior selectivity is an urgent priority.<sup>[7]</sup>

To enhance the performance of NO<sub>2</sub> gas sensors, researchers have explored various advanced materials such as metal oxide, conductive polymers, and carbon nanomaterials.<sup>[8]</sup> However, the synthesis of these materials typically involves energy-intensive, costly, and complex processes such as chemical vapor deposition, chemical polymerization, and arc discharge.<sup>[9]</sup> In addition, the fabrication of sensors based on these materials typically requires precisely engineered interdigitated electrodes made of precious metals such as platinum (Pt), gold (Au), and silver (Ag).<sup>[10]</sup> Indium Oxide (In<sub>2</sub>O<sub>3</sub>) stands out in applications such as solar cells, photocatalysis, and gas sensing due to its exceptional physical and chemical properties.<sup>[11]</sup> Notably, as an N-type semiconductor metal oxide, In<sub>2</sub>O<sub>3</sub> exhibits high sensitivity and selectivity for detecting NO<sub>2</sub> gas.<sup>[12]</sup> To further enhance the performance of In<sub>2</sub>O<sub>3</sub>-based NO<sub>2</sub> sensors, nanomorphology controls such as nanofibers, nanosheets, and nanoparticles have been utilized to increase the surface activity of In<sub>2</sub>O<sub>3</sub>.<sup>[13]</sup> Additionally, functional modifications such as constructing heterostructures, nanocomposite, and defect engineering have been applied to enhance the electronic structures of In<sub>2</sub>O<sub>3</sub>.<sup>[14]</sup> Despite these advancements, In<sub>2</sub>O<sub>3</sub>-based gas sensors still face challenges such as limited gas selectivity, high operating temperature requirements, and

## 1. Introduction

The rapid advancement of flexible sensors has surpassed the constraints of traditional sensors, becoming increasingly vital in both industrial production and daily life.<sup>[1]</sup> In addition to their applications in mechanical, thermoelectric, chemical, neuroelectric, and electrochemical signal processing, flexible sensors are

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performance degradation under humid conditions, which restrict their broader application.<sup>[15]</sup>

In response to these challenges, laser direct writing (LDW) technology has revolutionized the fabrication of flexible gas sensors with its excellent processing accuracy and control capability.<sup>[16]</sup> This technology utilizes a laser beam to precisely remove, add, or modify both the surface and interior of target materials, achieving high-resolution heat treatments at the micron or submicron level.<sup>[17]</sup> Selective laser sintering (SLS), a subset of LDW technology, is widely used for the sintering and modifying of metal, ceramic, and metal oxide nanoparticles, attributed to its low heat input and high thermal gradient.<sup>[18]</sup> Meanwhile, this technology allows maskless and customized rapid sintering processes on various substrates controlled by computer software.<sup>[19]</sup> Defect engineering, an effective material modification method, plays a crucial role in optimizing the properties of sensor materials.<sup>[20]</sup> Specifically, laser-induced defect engineering has made significant breakthroughs in enhancing gas sensor performance. This technique introduces beneficial oxygen vacancies, opening new pathways to improve the detection capability of the sensor significantly. For In<sub>2</sub>O<sub>3</sub> nanoparticles, the introduction of oxygen vacancy (OV) defects not only increases the number of adsorption sites but also modulates the electronic structure, which significantly improves the sensitivity and selectivity of the sensor.<sup>[21]</sup> However, the efficient fabrication of In<sub>2</sub>O<sub>3</sub> NPs with OV defects for flexible NO<sub>2</sub> gas sensing using SLS technology continues to pose a significant challenge.

In this study, we report the development of the flexible NO<sub>2</sub> gas sensor using selective reduction laser sintering (SRLS) technology. This technology selectively reduces polyvinyl pyrrolidone (PVP) coated In<sub>2</sub>O<sub>3</sub> nanoparticles (NPs) by controlling the key parameters of a UV pulse laser, thereby enabling the formation of OV defects in In<sub>2</sub>O<sub>3</sub> NPs. Owing to the introduction of oxygen vacancies (OVs), the sensors demonstrate excellent response ( $S = 460.9$  at 10 ppm), rapid response/recovery ( $\tau_{\text{resp}}/\tau_{\text{reco}} = 27/570$  s), and superior selectivity (response ratio > 400) at RT (25 °C). Furthermore, the sensors exhibit robust resistance to light and humidity and an even faster recovery speed under photo-assisted conditions. The sensors also demonstrate a low detection limit (200 ppb), a high signal-to-noise ratio (94.8 dB), and good long-term stability, maintaining reliable performance for up to 25 days. Through experimental verification and material characterization, the impact of varying laser scanning intervals on the OV defects and sensing performance was further explored. Additionally, the adsorption mechanism of the NO<sub>2</sub> molecule on In<sub>2</sub>O<sub>3</sub> with OV was investigated through theoretical calculations. This technology not only provides a new strategy for the fabrication of flexible NO<sub>2</sub> sensors based on In<sub>2</sub>O<sub>3</sub> with OVs but also further expands the application prospects of LDW technology in material science and device fabrication.

## 2. Results and Discussion

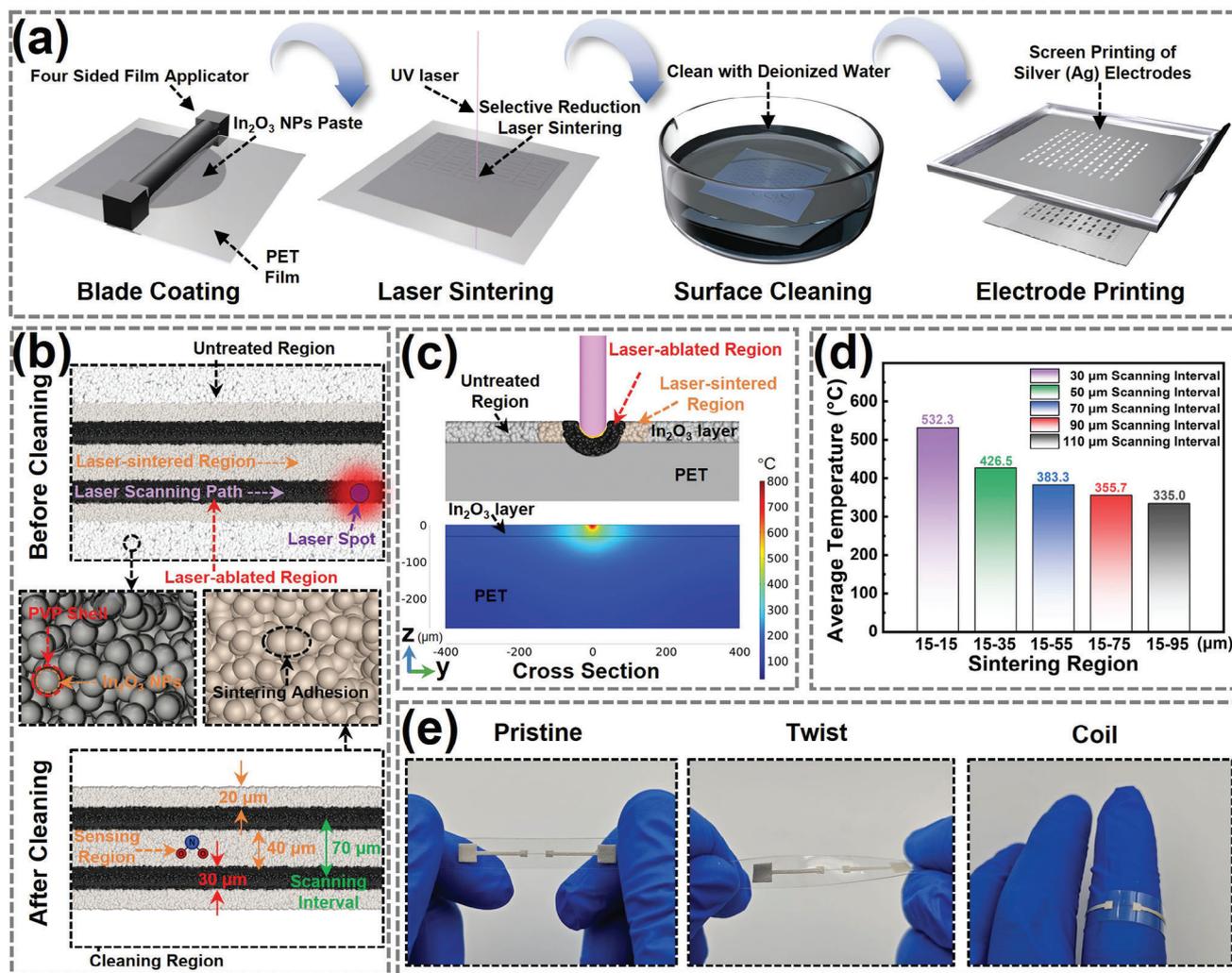
### 2.1. Investigation of the SRLS Process

Unlike traditional selective laser sintering (SLS), where the laser is directly applied to the material surface to achieve high-temperature solid-phase transformation, selective reduc-

tion laser sintering (SRLS) achieves nanoparticle sintering by finely adjusting the temperature distribution at the edges of the laser scanning path. The fabrication of the flexible gas sensors using this technology consists of four main steps: blade coating, laser sintering, surface cleaning, and electron printing (Figure 1a). The detailed methodology of this fabrication process is described in the Supporting Information (Experimental Section). In the most critical laser sintering process, In<sub>2</sub>O<sub>3</sub> NPs serve as both a crucial material for flexible gas sensors and as an essential coating for triggering the photothermal effect. It is well known that polyethylene terephthalate (PET) has a relatively low absorption coefficient for UV lasers. Therefore, when the laser is vertically irradiated onto PET films, most of the laser energy passes through without causing any noticeable physical or chemical reaction.<sup>[22]</sup> However, when the PET surface is coated with In<sub>2</sub>O<sub>3</sub> NPs, the In<sub>2</sub>O<sub>3</sub> layer absorbs UV laser energy and rapidly converts it into thermal energy. This conversion triggers a significant pyrolysis reaction on the shallow surface of PET through the photothermal effect. Under UV irradiation, the high energy density of the laser leads to the ablation of the In<sub>2</sub>O<sub>3</sub> layer and the underlying PET substrate, forming a laser-ablated region. At the same time, the high temperature generated by the laser-ablated region causes the unirradiated In<sub>2</sub>O<sub>3</sub> NPs to undergo rapid thermal sintering at the edge of the laser scanning path, forming a distinct laser-sintered region. In contrast, regions that have not been ablated and sintered can be easily removed by deionized water cleaning (Figure 1b).

The composition of In<sub>2</sub>O<sub>3</sub> nanoparticle (NP) paste, primarily consisting of active and carrier materials, is crucial for the formation of OV defects during the SRLS process. Detailed explanations of the active material and the carrier material are provided in the (Section S1, Supporting Information). Building on this, the thermal properties of In<sub>2</sub>O<sub>3</sub> NP paste and its carrier were analyzed using thermogravimetric/derivative thermogravimetric (TG/DTG) and differential scanning calorimetry (DSC) to investigate the formation mechanism of OV defects. After comparative analysis, the thermal weight loss of In<sub>2</sub>O<sub>3</sub> NP paste at a low heating rate (10 °C min<sup>-1</sup>) was summarized into three main stages (Figure S4, Supporting Information). The process initiates with the evaporation of organic solvents within the temperature range of 30–170 °C. This is followed by the decomposition of polyvinylpyrrolidone (PVP) side chains, occurring between 170–300 °C. The final stage involves the critical breakdown of the PVP backbone, which occurs from 300–550 °C. In the final stage, reduced macromolecules generated by the decomposition of the PVP main chain partially reduce In<sub>2</sub>O<sub>3</sub> to metallic Indium (In) while forming OV defects.<sup>[23]</sup> This provides a specific reference for further understanding the mechanism of the SRLS with a high-temperature gradient. Detailed analyses of the TG/DTG and DSC are presented in the (Section S2, Supporting Information).

To explore the effects of various laser parameters on the SRLS process, a series of experimental optimizations were performed using a UV laser system (Figure S7, Supporting Information). The experiments focused on finely tuning key parameters such as laser scanning speed ( $V_{\text{ss}}$ ), average laser power ( $P_{\text{avg}}$ ), pulse repetition frequency ( $F_{\text{pr}}$ ), and defocus distance ( $D_{\text{def}}$ ), all of which are closely related to the sensor performance and fabrication efficiency. Given the importance of both magnitude and stability

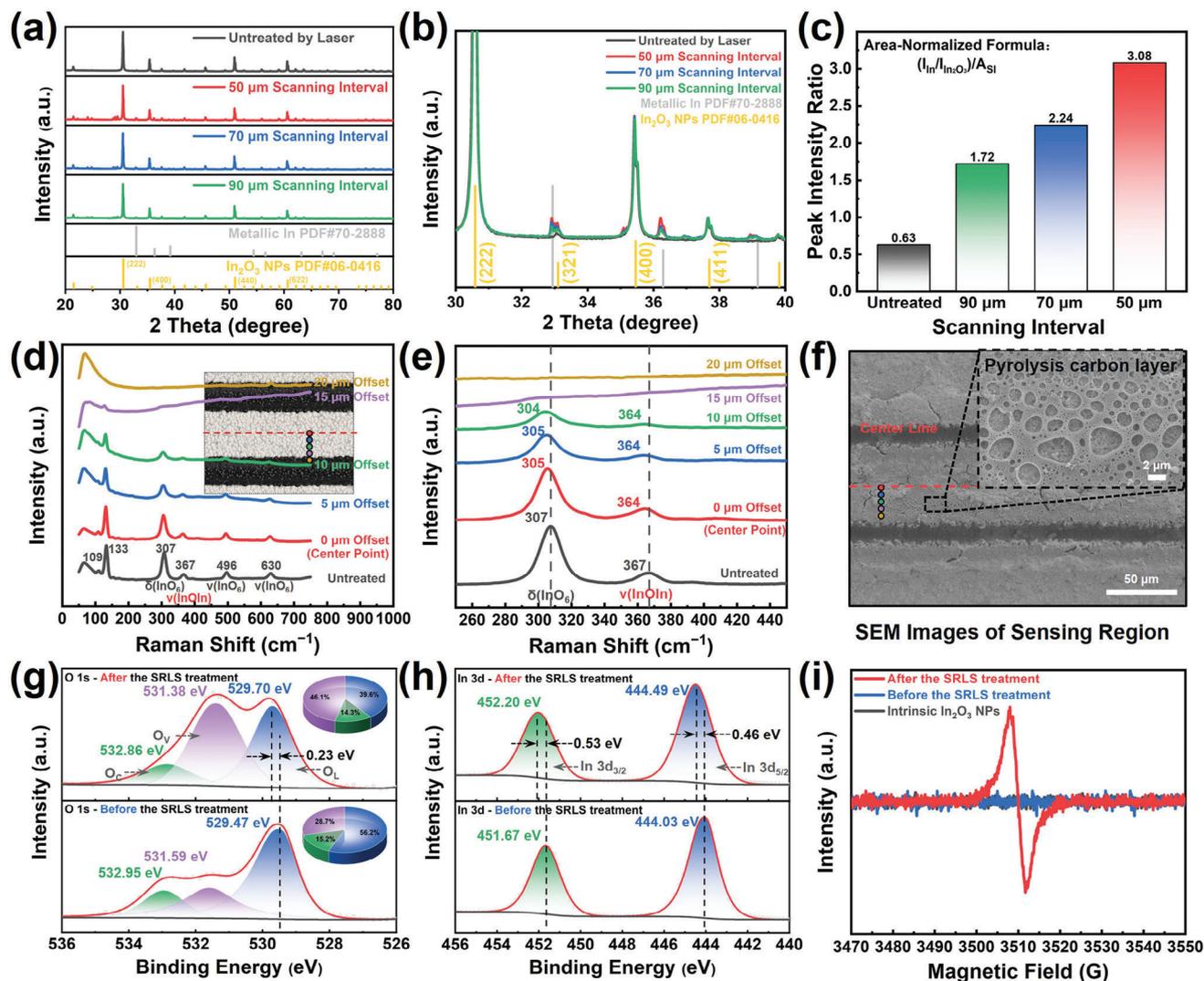


**Figure 1.** The fabrication process for flexible  $\text{NO}_2$  gas sensors is based on the SRLS technology. a) Schematic diagram of the sensor fabrication process. b) Schematic illustration of the structural changes on the surface of  $\text{In}_2\text{O}_3$  NPs due to laser sintering. c) Schematic structure and temperature distribution of the sensor cross-section during laser sintering. d) Histogram of equivalent average sintering temperatures for laser-sintered regions with different scanning intervals. e) Demonstration of the sensor in different deformation states.

in the initial resistance of the sensing region, the optimal laser parameters were set to  $10 \text{ mm s}^{-1}$  for  $V_{ss}$ ,  $0.27 \text{ W}$  for  $P_{avg}$ ,  $200 \text{ kHz}$  for  $F_{pr}$ , and  $0 \text{ mm}$  for  $D_{def}$  (Figure S10, Supporting Information). Detailed parameter optimization and implementation of the SRLS process are provided in (Section S3 and Video S1, Supporting Information).

To achieve OV defect control, the critical sintering temperature in the SRLS process is precisely controlled by the laser scanning interval. However, the high energy density and rapid scanning speed of UV lasers present significant challenges in monitoring the real-time temperature during the SRLS process. To further calibrate the influence of the laser scanning interval on the sintering temperature, finite element analysis (FEA) was used to simulate the temperature distribution and evolution within the  $\text{In}_2\text{O}_3$  layer and PET substrate during the single laser scanning process. The cross-sectional temperature distribution at the mid-

point of the linear laser scanning reveals that the photothermal effect of the laser generates a high-temperature region exceeding  $800 \text{ }^\circ\text{C}$  at the top center of the model, with a sharp decrease in temperature along the  $y$ - and  $z$ -axes (Figure 1c). This temperature distribution radiates outward from the center of the heat source, forming a high-temperature region and temperature diffusion regions on either side of it, corresponding to the laser ablation and laser-sintered regions ( $70 \text{ } \mu\text{m}$  scanning interval). The equivalent average temperatures of the laser-sintered region on one side of the laser scanning are  $523.3$ ,  $426.5$ ,  $383.3$ ,  $355.7$ , and  $335.0 \text{ }^\circ\text{C}$  at various scanning intervals, with corresponding effective sintering close intervals of  $15\text{--}15 \text{ } \mu\text{m}$ ,  $15\text{--}35 \text{ } \mu\text{m}$ ,  $15\text{--}55 \text{ } \mu\text{m}$ ,  $15\text{--}75 \text{ } \mu\text{m}$ , and  $15\text{--}95 \text{ } \mu\text{m}$  (Figure 1d). Detailed simulation model construction and discussion of the temperature distribution and evolution during linear laser scanning are provided in (Section S4, Supporting Information).



**Figure 2.** Characterization of OV defects in  $\text{In}_2\text{O}_3$  NPs. a) Overall and b) local XRD patterns of  $\text{In}_2\text{O}_3$  before and after the SRLS treatment. c) Ratio of area-normalized peak intensities in  $\text{In}_2\text{O}_3$  XRD patterns at different laser scanning intervals. d) Overall and e) local Raman spectra of  $\text{In}_2\text{O}_3$  at different points within the laser-sintered region. f) SEM images of the laser-sintered region. g) O 1s and h) In 3d XPS spectra of  $\text{In}_2\text{O}_3$  before and after the SRLS treatment. i) EPR spectra of  $\text{In}_2\text{O}_3$  before and after the SRLS treatment.

Benefiting from the high energy density and rapid scanning speed of the laser, the SRLS technology offers more flexible customization while significantly reducing the temperature requirements of the substrate material. This technology enables the rapid fabrication of flexible gas sensors on 250  $\mu\text{m}$  thick PET films, ensuring excellent sensing performance while maintaining stable mechanical properties (Figure 1e).

## 2.2. Characterization of OV Defects

To investigate the effect of different laser scanning intervals on the crystal structure and phase transition of  $\text{In}_2\text{O}_3$  NPs in the SRLS treatment, X-ray diffraction (XRD) patterns were employed to characterize the samples with untreated, 50, 70, and 90  $\mu\text{m}$  scanning intervals (Figure 2a). The XRD pattern of untreated

$\text{In}_2\text{O}_3$  NPs indicates characteristic peaks at  $30.6^\circ$ ,  $35.5^\circ$ ,  $51.0^\circ$ , and  $60.7^\circ$ , corresponding to the (222), (400), (440), and (622) crystal planes (PDF#06-0416). However, the SRLS-treated  $\text{In}_2\text{O}_3$  NPs (including both the laser-ablated and laser-sintered regions) exhibit both peaks for  $\text{In}_2\text{O}_3$  as well as new peaks for metallic In at  $32.9^\circ$ ,  $36.3^\circ$ ,  $39.2^\circ$ , and  $54.4^\circ$  (PDF#70-2888). The transition from  $\text{In}_2\text{O}_3$  to metallic In is clearly evident from the comparison of the overall peak intensities in the XRD spectra. It is noteworthy that the intensities of the metallic In peaks near the (321) and (400) crystal planes increase significantly with decreasing laser scanning intervals in the diffraction angle range from  $30^\circ$  to  $40^\circ$  (Figure 2b). In addition, normalization of the effective area of the laser scanning region shows that the intensity ratio of diffraction peaks of metal In to  $\text{In}_2\text{O}_3$  near the (321) crystal plane increases significantly with decreasing scanning intervals (Figure 2c). These results indicate that the transformation

of  $\text{In}_2\text{O}_3$  to metallic In during the SRLS process is further promoted by the increase in sintering temperature with the decrease in laser scanning interval. Furthermore, local XRD patterns reveal that the diffraction peaks near the (321) crystal plane of  $\text{In}_2\text{O}_3$  shift to a lower  $2\theta$  angle as the sintering temperature increases due to a decrease in the scanning interval (Figure S17, Supporting Information).<sup>[24]</sup> This shift indicates an expansion of the interplanar spacing in the  $\text{In}_2\text{O}_3$  crystal, leading to a relaxation of the lattice structure.<sup>[25]</sup> Notably, this also indicates that Indium ions in  $\text{In}_2\text{O}_3$  have been reduced to lower valence or even metallic states, implying the generation of OV defects.<sup>[26]</sup> Detailed discussions and localized XRD spectra of the  $\text{In}_2\text{O}_3$  NP paste before and after SRLS treatment are provided in (Section S5.1, Supporting Information).

To analyze the structure and composition of  $\text{In}_2\text{O}_3$  NPs after the SRLS treatment (70  $\mu\text{m}$  scanning interval), Raman spectroscopy was employed to characterize different points within the sensing region on the side perpendicular to the scanning direction (Figure 2d). Raman spectra were collected at five points spaced 5  $\mu\text{m}$  apart from the center of the sensing region within the wavelength range of 50–750  $\text{cm}^{-1}$  (Figure S21, Supporting Information). For comparison, the Raman spectra of pure  $\text{In}_2\text{O}_3$ , PVP, and PET are presented in (Figures S22, Supporting Information). Besides the ultra-low frequency peak at 66  $\text{cm}^{-1}$  from PET substrates, untreated  $\text{In}_2\text{O}_3$  NPs exhibit six prominent peaks at 109, 133, 307, 367, 496, and 630  $\text{cm}^{-1}$ , providing insights into the vibrational modes and properties of  $\text{In}_2\text{O}_3$ .<sup>[27]</sup> In the lower frequency range, the lattice vibrational peaks at 109 and 133  $\text{cm}^{-1}$  indicate large-scale motions involving the In atoms or the entire lattice structure.<sup>[28]</sup> The peak at 307  $\text{cm}^{-1}$  correlates with the symmetric bending vibrations of  $\delta(\text{InO}_6)$  octahedra.<sup>[29]</sup> Similarly, the peaks at 496 and 630  $\text{cm}^{-1}$  are associated with asymmetric stretching vibrations of  $\nu(\text{InO}_6)$  octahedra.<sup>[26]</sup>

Notably, the 367  $\text{cm}^{-1}$  scattering feature, identified as  $\nu(\text{InOIn})$  stretching vibrations, indicates the presence of OV defects in the  $\text{In}_2\text{O}_3$  lattice.<sup>[24,30]</sup> After the SRLS treatment, the Raman spectra of  $\text{In}_2\text{O}_3$  show a slight redshift in characteristic peaks, indicating the formation of OV defects. These defects lead to the expansion and local relaxation of the  $\text{In}_2\text{O}_3$  lattice structure and the weakening of the In–O bond. Consequently, the reduced bonding strength alters the vibrational mode of the In–O–In bridge, resulting in a shift of the Raman peak to a lower wavelength (Figure 2e).<sup>[31]</sup> Furthermore, Raman spectra collected at 0, 5, and 10  $\mu\text{m}$  offset points show a gradual decrease in overall relative peak intensity closer to the laser scanning region. Even more, the Raman spectra of the 15 and 20  $\mu\text{m}$  offset points show significant anomaly. Scanning electron microscopy (SEM) characterization reveals that the PET substrate is slightly melted in the laser scanning region due to the photothermal effect (Figure 2f). The sputtering of molten PET onto  $\text{In}_2\text{O}_3$  NPs near the laser-ablated region formed a porous pyrolytic carbon layer, which interferes with Raman spectra analysis.<sup>[32]</sup> Detailed analyses of Raman spectra, SEM, and energy dispersive X-ray (EDX) of the laser-sintered region are provided in (Section S5.2, Supporting Information). This provides a certain reference for further understanding the mechanism of the SRLS.

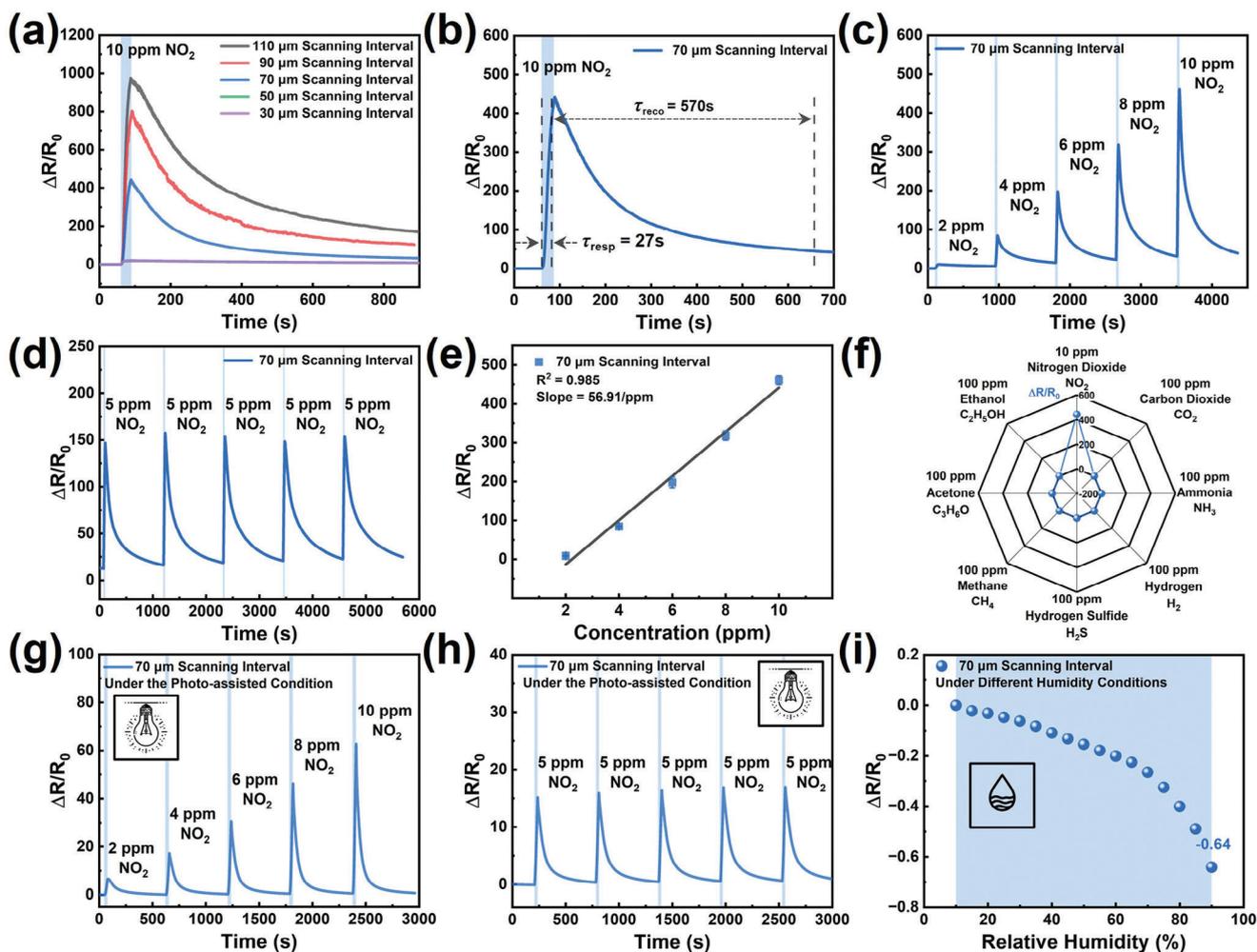
To further determine the chemical composition and defect state of the  $\text{In}_2\text{O}_3$  NPs before and after the SRLS process (70  $\mu\text{m}$  scanning interval), the sensing region was analyzed by X-ray

photoelectron spectroscopy (XPS). The full XPS survey reveals significant changes in the intensity of the binding energy peaks of In, O, and C elements before and after the SRLS treatment (Figure S25, Supporting Information). After the SRLS treatment, the intensities of the In 3d and O 1s peaks decreased significantly. In comparison, the intensity of the C 1s peak increased, demonstrating the formation of pyrolytic carbon on the surface of the laser-sintered region. Furthermore, before the SRLS treatment, the O1s peaks at 529.47, 531.59, and 532.95 eV correspond to different oxygen species in  $\text{In}_2\text{O}_3$  NPs: lattice oxygen ( $\text{O}_L$ ), oxygen vacancy ( $\text{O}_V$ ), and chemisorbed oxygen ( $\text{O}_C$ ), respectively (Figure 2g).<sup>[24,33]</sup> After the SRLS treatment, the  $\text{O}_L$  peak shifts to 529.70 eV, a positive shift of 0.23 eV. This shift indicates electronic interactions between polyvinylpyrrolidone (PVP) and  $\text{In}_2\text{O}_3$ , suggesting that the pyrolysis products of PVP contribute to the reduction and removal of lattice oxygen from  $\text{In}_2\text{O}_3$ , thereby reducing the average oxidation state in the O 1s peak.<sup>[34]</sup> Specifically, the relative peak area ratio of  $\text{O}_L$  decreases from 56.2% to 39.6%, reflecting a decrease of 16.6%. Conversely, the  $\text{O}_V$  peak area ratio increases from 28.7% to 46.1%, representing a significant increase of 17.4% (pie chart in Figure 2g). This directly demonstrates a significant increase in the density of OV defects after the SRLS treatment.<sup>[26]</sup> Furthermore, compared to the sensing region before the SRLS treatment, the In 3d<sub>5/2</sub> and 3d<sub>3/2</sub> XPS peaks of the  $\text{In}_2\text{O}_3$  exhibit positive shifts of 0.46 and 0.53 eV, respectively (Figure 2h). This suggests electron transfer from  $\text{In}_2\text{O}_3$  to pyrolytic carbon in the PVP pyrolysis product, thus dispersing electron density around In atoms.<sup>[31]</sup>

Additionally, the electron spin resonance (EPR) results reveal that the  $\text{In}_2\text{O}_3$  NPs after the SRLS treatment exhibit a signal at a g-value of 2.03, which suggests that the electrons are trapped in the OV defects generated by the reduction of  $\text{In}_2\text{O}_3$  by pyrolysis products during the SRLS process (Figure 2i). This result further confirms the presence of OV defects in  $\text{In}_2\text{O}_3$  after the SRLS treatment.<sup>[35]</sup> The methodology and process for calculating the g-value are introduced in (Section S5.4, Supporting Information).

### 2.3. Testing of Sensor Performance

Variations in sintering temperature due to different laser scanning intervals (30, 50, 70, 90, and 110  $\mu\text{m}$ ) significantly affect the performance of N-type chemoresistive gas sensors based on  $\text{In}_2\text{O}_3$  NPs during the SRLS process. To evaluate this effect, the sensor was exposed to a specific  $\text{NO}_2$  gas concentration for 30 s at RT (Figure S29, Supporting Information). The relative response of the gas sensor is quantified as  $S = \Delta R/R_0 = (R - R_0)/R_0$ , where  $R$  and  $R_0$  represent the stabilized resistance in the target gas and air environments, respectively. The response ( $\tau_{\text{resp}}$ ) and recovery ( $\tau_{\text{reco}}$ ) times are defined as the times required to achieve a 90% change in resistance when exposed to  $\text{NO}_2$  and air.<sup>[36]</sup> Detailed descriptions of the sensing test platform and test procedure are provided in (Section S6.1, Supporting Information). Test results show that sensor resistance spikes sharply when exposed to 10 ppm  $\text{NO}_2$  and then gradually recovers in the air. Interestingly, as the sintering temperature increases with decreasing laser scanning interval, the sensor response to  $\text{NO}_2$  decreases significantly with values of 967.62, 802.16, 442.24, 19.69, and 18.27,



**Figure 3.** Performance testing of sensors based on SRLS technology. a) Response curves of the sensor to 10 ppm NO<sub>2</sub> with different scanning intervals. b) Typical response curve of the sensor. c) Dynamic response curve of the sensor to NO<sub>2</sub> from 2 to 10 ppm. d) Repeatability response curve of the sensor to 5 ppm NO<sub>2</sub> over five consecutive cycles. e) Linear fit curve of the sensor response to NO<sub>2</sub> from 2 to 10 ppm with error bars representing three samples. f) Radar chart of the sensor selectivity for NO<sub>2</sub> compared to other interfering gases. g) Dynamic response curve of the sensor to NO<sub>2</sub> from 2 to 10 ppm under the photo-assisted condition. h) Repeatability response curve of the sensor to 5 ppm NO<sub>2</sub> over five consecutive cycles under the photo-assisted condition. i) Sensor response curve for relative humidity ranging from 10% to 90%.

respectively (Figure 3a). Higher sintering temperatures lead to an increase in OV defects, which theoretically should enhance the ability of NO<sub>2</sub> to capture electrons within the sensing region, thereby promoting a significant increase in sensor resistance change ( $\Delta R$ ).<sup>[37]</sup> However, narrower scanning intervals increase the baseline resistance ( $R_0$ ) of the sensor (Figures S31 and S32), Supporting Information. Consequently, the sensing gain from the increase in OV defects is counteracted by the increase in baseline resistance, which significantly reduces the sensor response to NO<sub>2</sub>. On the other hand, a larger scanning interval enlarges the effective adsorption area of the sensor, offering more sites for adsorption but also extending the desorption time, which slows down the recovery ability of the sensor.<sup>[38]</sup> Additionally, the lower sintering temperature associated with an increased scanning interval reduces the adhesion between the In<sub>2</sub>O<sub>3</sub> NP layer and the PET substrate, challenging the stability and reliability of the sensor.<sup>[39]</sup> To balance performance and stability, the

sensor with a 70  $\mu\text{m}$  scanning interval was selected for further evaluation.

The sensor exhibits rapid response and recovery times of 27 and 570 s for 10 ppm NO<sub>2</sub> at RT (Figure 3b). Additionally, the sensor also consistently detects 5 ppm NO<sub>2</sub> over five cycles, demonstrating high repeatability and reversibility (Figure 3c). Furthermore, as NO<sub>2</sub> concentrations increase from 2 to 10 ppm, the sensor response gradually increases from 9.8 to 460.9, indicating excellent dynamic response capabilities (Figure 3d). Correspondingly, the linear response of the sensor for NO<sub>2</sub> concentrations ranging from 2 to 10 ppm exhibits a slope of 56.91 ppm<sup>-1</sup> and an R<sup>2</sup> of 0.985, demonstrating stable linear response characteristics (Figure 3e). Notably, the response of the sensor to 10 ppm NO<sub>2</sub> (response ratio > 400) is significantly stronger than its response to 100 ppm of the interfering gases (C<sub>2</sub>H<sub>5</sub>OH, CO<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, and H<sub>2</sub>S), proving its superior selectivity (Figure 3f). Moreover, the signal-to-noise ratio (SNR) for the response curve to

10 ppm NO<sub>2</sub> is 94.8 dB (Figure S33, Supporting Information). The corresponding SNR calculation and analysis are shown in (Section S6.2, Supporting Information). The detection limit (LOD) of the sensor is as low as 200 ppb, with a response rate of 0.426 (Figure S34, Supporting Information). The sensor demonstrates long-term stability, with a response deviation of less than 10% over 25 days (Figure S35, Supporting Information). Correspondingly, the mechanical reliability test and analysis of the sensor are further introduced in (Section S6.3, Supporting Information).

Considering the practical application of the sensor, the impact of environmental factors such as light and humidity on the sensor performance was further evaluated. Unsurprisingly, flexible gas sensors based on In<sub>2</sub>O<sub>3</sub> NPs with OV defects demonstrate excellent NO<sub>2</sub> gas detection performance along with inherent optoelectronic properties.<sup>[37]</sup> Under the photo-assisted condition (xenon lamp irradiation), the resistance of the sensor decreases due to light-induced electronic excitation. This excitation promotes the transition of electrons from the valence band to the conduction band, leading to the formation of additional electron–hole pairs and enhancing the electrical conductivity of the sensor.<sup>[40]</sup> Additionally, OV defects in In<sub>2</sub>O<sub>3</sub> serve as trapping centers for electrons or holes, stabilizing and extending the lifetimes of photogenerated carriers. This trapping effect reduces the electron–hole recombination rate, further reducing the resistance of the sensor.<sup>[41]</sup> Under the photon-assisted condition, the sensor demonstrates excellent consistency and reversibility in response to five consecutive 5 ppm NO<sub>2</sub> at RT (Figure 3g). Meanwhile, the photon-assisted response of the sensor gradually increased from 6.6 to 62.7 as the concentration of NO<sub>2</sub> increased from 2 to 10 ppm, demonstrating its robust dynamic response and recovery under bright light (Figure 3h). Importantly, although photon assistance significantly reduces the response of the sensor to NO<sub>2</sub>, the photon-assisted sensing mechanism enhanced the half-recovery speed by 91.7% in low NO<sub>2</sub> concentration detection (Figure S38, Supporting Information). These properties not only demonstrate the light resistance of the sensor but also further expand its application potential in continuous NO<sub>2</sub> sensing applications. Considering the inherent sensitivity of semiconductor materials to humidity, the response of the sensor to different relative humidity (RH) conditions was further evaluated (Figure 3i).<sup>[42]</sup> The results indicate that as relative humidity increases, the relative resistance of the sensor decreases. At high humidity levels (90% RH), the response to humidity measures only −0.64. Although the impact of humidity on the sensor can generally be neglected when detecting high concentrations of NO<sub>2</sub> (under ppm levels), significant limitations appear when detecting low concentrations of NO<sub>2</sub> (under ppb levels). Correspondingly, in (Section S6.4, Supporting Information), the testing and analysis of the sensor under lighting and humidity conditions are further discussed, illustrating its potential applicability and challenges in practical applications.

Compared with gas based on In<sub>2</sub>O<sub>3</sub> and other advanced materials, the sensors fabricated using SRLS technology offer enhanced flexibility, efficiency, and high customizability, along with superior compatibility and adaptability. In terms of performance, these sensors demonstrate excellent sensitivity to NO<sub>2</sub>, rapid response and recovery times, and superior selectivity. In addition, these sensors exhibit a low detection limit, high signal-to-noise

ratio, and good long-term stability (Table S1, Supporting Information). A detailed comparison of the sensor performance is discussed in (Section S6.5, Supporting Information).

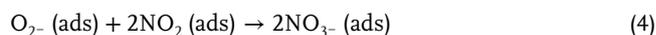
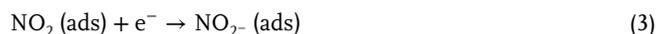
## 2.4. Analysis of Sensing Mechanism

The primary sensing mechanism of NO<sub>2</sub> gas sensors based on In<sub>2</sub>O<sub>3</sub> NPs fabricated by SRLS technology is driven by conductivity changes resulting from the adsorption and desorption of gas molecules on the sensor surface. Specifically, the OVs on the surface of In<sub>2</sub>O<sub>3</sub> NPs play a crucial role in facilitating this mechanism. These defects enable electrons to transition from the valence band to the conduction band, thereby increasing the concentration of free electrons and enhancing the conductivity of the sensing region.<sup>[43]</sup> Concurrently, these defects offer active adsorption sites in the sensing region, thereby increasing the adsorption of oxygen species.<sup>[44]</sup>

When the sensor is exposed to an air atmosphere, the oxygen (O<sub>2</sub>) molecules adsorb onto the surface of In<sub>2</sub>O<sub>3</sub> NPs and capture free electrons from the conduction band to form O<sub>2</sub><sup>−</sup>(ads) ions with higher chemical activity, as detailed in reaction Equations (1) and (2).<sup>[45]</sup>

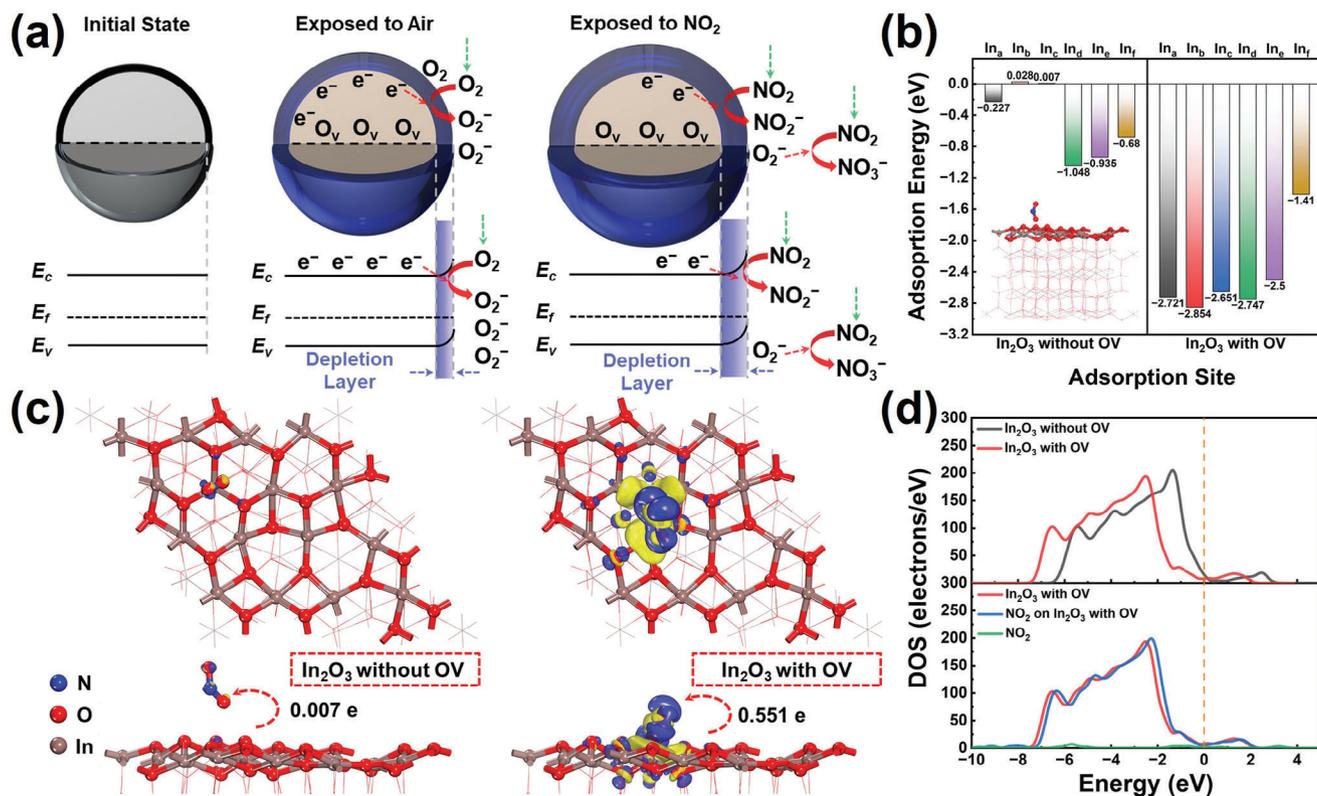


This reaction process depletes the carrier concentration on the surface of In<sub>2</sub>O<sub>3</sub>, causing the energy bands to bend upward and forming a surface electron depletion layer (Figure 4a). When the sensor is exposed to a NO<sub>2</sub> gas atmosphere, the NO<sub>2</sub> molecules interact directly with the electrons in the conduction band of In<sub>2</sub>O<sub>3</sub> to form NO<sub>2</sub><sup>−</sup>(ads) ions, driven by their high electron affinity.<sup>[46]</sup> Additionally, these NO<sub>2</sub> molecules can also react with pre-existing O<sub>2</sub><sup>−</sup>(ads) ions to form NO<sub>3</sub><sup>−</sup> ions, as described in the reaction Equations (3) and (4).<sup>[45]</sup>



This reaction process further deepens the electron depletion layer on the In<sub>2</sub>O<sub>3</sub> surface, which enhances the upward bending of the energy bands and significantly increases the resistance of the In<sub>2</sub>O<sub>3</sub> NPs. Furthermore, both of these processes deplete the conduction band electrons in In<sub>2</sub>O<sub>3</sub> NPs, resulting in an increased thickness of the electron depletion layer and an elevated potential barrier energy. However, due to its strong oxidizing properties, NO<sub>2</sub> tends to play a dominant role in the reactions at RT, which significantly increases the resistance of the sensor and enables the detection of NO<sub>2</sub> gas.<sup>[47]</sup>

To further investigate the adsorption mechanism of NO<sub>2</sub> molecules on In<sub>2</sub>O<sub>3</sub> and the role of OVs in enhancing this process, we performed a detailed computational analysis using density functional theory (DFT). Specifically, based on the number of O atoms bonded to In atoms in the In<sub>2</sub>O<sub>3</sub> unit cell and the coordination numbers of these O atoms, 16 different adsorption sites (Figures S41 and S42, Supporting Information) are



**Figure 4.** Sensing mechanisms of  $\text{NO}_2$  on  $\text{In}_2\text{O}_3$  sensors with OV defects. a) Schematic diagram of the sensing mechanism. b) Histograms of adsorption energy in different adsorption systems and different adsorption modes. c) CDD distributions of  $\text{In}_2\text{O}_3$  with and with OV after  $\text{NO}_2$  adsorption (The isosurface is set as  $0.01 \text{ e} \text{ \AA}^{-3}$ . The blue region indicates electron accumulation and the yellow region represents electron depletion). d) DOS curves of  $\text{In}_2\text{O}_3$  with and without OV, and DOS curves of  $\text{In}_2\text{O}_3$  with OV before and after  $\text{NO}_2$  adsorption.

classified into 6 distinct adsorption modes (Table S2, Supporting Information). Compared to  $\text{In}_2\text{O}_3$  without OV,  $\text{In}_2\text{O}_3$  with OV shows a stronger adsorption reaction to  $\text{NO}_2$  molecules at various adsorption modes (Figure 4b). In particular, the presence of OV at the  $\text{In}_{22}$  site in the  $\text{In}_b$  adsorption mode significantly enhances its adsorption capacity. This enhancement is thoroughly compared and analyzed using charge density difference (CDD) and density of states (DOS) calculations. The CDD results show that the interaction of the  $\text{NO}_2$  molecule in the  $\text{In}_2\text{O}_3$  adsorption system without OV not only causes a slight electron accumulation of O atoms on the  $\text{In}_2\text{O}_3$  surface but also leads to a subtle charge rearrangement inside the  $\text{NO}_2$  molecule (Figure 4c). In this process,  $\text{NO}_2$  acts as an electron acceptor, receiving 0.07 e from the  $\text{In}_2\text{O}_3$  as determined by Mulliken charge analysis.<sup>[48]</sup> The corresponding adsorption energy of 0.028 eV indicates that the reaction in this adsorption mode ( $\text{In}_b$ ) is not spontaneous (Table S3, Supporting Information). This positive adsorption energy further demonstrates the limitations of intrinsic  $\text{In}_2\text{O}_3$  in adsorbing  $\text{NO}_2$  molecules.<sup>[49]</sup> Conversely, in the  $\text{In}_2\text{O}_3$  adsorption system with OV, the CDD results reveal a more intense electronic interaction induced by the adsorption of the  $\text{NO}_2$  molecule on the  $\text{In}_2\text{O}_3$  surface. Specifically, the adsorption of the  $\text{NO}_2$  molecule leads to the formation of large-volume electron depletion regions between it and three neighboring In atoms of  $\text{In}_2\text{O}_3$ . Additionally, the N and O atoms of  $\text{NO}_2$  exhibit distinct electron accumulation regions, while an overall electron depletion region is

demonstrated around the N–O bonds. In this process, the  $\text{NO}_2$  serves as an electron acceptor, receiving 0.551 e from the  $\text{In}_2\text{O}_3$ , which indicates the formation of chemical solid adsorption between the  $\text{NO}_2$  and the  $\text{In}_2\text{O}_3$  with OV.<sup>[50]</sup> Moreover, the corresponding adsorption energy of  $-2.854 \text{ eV}$  confirms that the adsorption process is exothermic, indicating its spontaneous nature and highlighting a clear contrast with intrinsic  $\text{In}_2\text{O}_3$  (Table S4, Supporting Information).

By comparing the DOS curves of  $\text{In}_2\text{O}_3$  with and without OV, it is clear that the introduction of OV shifts the DOS curve toward lower energy levels and flattens the curves near the Fermi level (Figure 4d). This shift indicates that the introduction of the defect state creates localized states within the band gap of  $\text{In}_2\text{O}_3$ , which increases the density of electronic states and introduces intermediate energy levels.<sup>[51]</sup> This enhancement not only reduces the energy required for electron excitation from the valence to the conduction band but also provides additional electrons and transition pathways.<sup>[52]</sup> Furthermore, when the  $\text{NO}_2$  molecule is adsorbed on the surface of  $\text{In}_2\text{O}_3$  with OV, the DOS curve for the corresponding system shifts slightly to higher energy, and the density of electronic states near the Fermi level decreases. This change confirms that  $\text{NO}_2$  adsorption promotes electron transfer from the  $\text{In}_2\text{O}_3$  surface to the  $\text{NO}_2$  molecule, resulting in charge redistribution and rearrangement of energy levels.<sup>[53]</sup> Overall, these results clearly demonstrate the substantial potential of OV in improving the sensitivity of  $\text{NO}_2$  gas sensors

based on In<sub>2</sub>O<sub>3</sub> NPs fabricated by SRLS technology and provide a solid theoretical basis for understanding the sensing mechanism. The classification of different adsorption modes, the corresponding adsorption sites, adsorption energies, adsorption distances, and charge transfer are discussed in (Section S7, Supporting Information).

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### 3. Conclusion

In summary, we have successfully developed a selective reduction laser sintering (SRLS) technology based on In<sub>2</sub>O<sub>3</sub> NPs to fabricate flexible NO<sub>2</sub> sensors efficiently. This technology employs a UV laser to selectively reduce PVP-coated In<sub>2</sub>O<sub>3</sub> NPs spin-coated on PET substrates to prepare In<sub>2</sub>O<sub>3</sub> sensing regions with oxygen vacancy (OV) defects. OV defects significantly increase the active adsorption sites, thereby enhancing the capture rate of NO<sub>2</sub>. This also introduces additional free electrons, subsequently improving the conductivity of the sensor. Due to the advantages offered by these properties, In<sub>2</sub>O<sub>3</sub> NPs with OV defects exhibit outstanding NO<sub>2</sub> sensor performance at room temperature. The sensors not only exhibit exceptional response values ( $S = 460.9$  at 10 ppm), rapid response/recovery ( $\tau_{\text{resp}}/\tau_{\text{reco}} = 27/570$  s), and superior selectivity (response ratio > 400) but also demonstrate robust resistance to light and humidity under ppm-level NO<sub>2</sub> conditions. The sensors further feature a low detection limit (200 ppb), a high signal-to-noise ratio (94.8 dB), and good long-term stability (25 days). Additionally, the recovery speed of the sensors can be further enhanced under the photo-assisted condition. This work proposes a new strategy for developing high-performance flexible NO<sub>2</sub> sensors. It provides key insights into the mechanism of NO<sub>2</sub> adsorption by In<sub>2</sub>O<sub>3</sub> NPs with OVs, paving the way for the development of flexible gas sensors for environmental health monitoring.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

flexible gas sensor, indium oxide nanoparticles, nitrogen dioxide, oxygen vacancy defect, selective reduction laser sintering

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