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Ultra-exclusive Selectivity for the Detection of Formaldehyde in Laser-induced ZnO Mesh Sensor with Few-nanometer Pores

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ABSTRACT

Formaldehyde is classified as a Group 1 biological agent that is "carcinogenic to humans." A gas sensor can be developed as a chemiresistive device with rapid response, outstanding sensitivity, reproducibility, and excellent selectivity for the detection of formaldehyde, providing a crucial pathway to protect human health in formaldehyde-rich environments. To this end, we designed a formaldehyde gas sensor that demonstrates ultra-exclusive selectivity, including a superior sensing response of 6682.8 at 10 ppm formaldehyde and 1687.6 for the optimized sensor with reasonable response (2.96 s) and recovery (46.2 s) times, based on a ZnO mesh structure. The sensor was fabricated using a rapid 1-minute CO₂ laser process, forming a ZnO precursor into a mesh structure with few nanometer-sized pores between ZnO crystal domains. The small kinetic size (2.43 Å) and large dipole moment (2.30 D) of formaldehyde allow for effective adsorption and good permeability within these pores, providing exceptional selectivity. Other gases such as acetone, styrene, and CO₂ showed significantly lower responses, confirming the sensor's selectivity for formaldehyde. Oxygen vacancies, which increased with laser power (up to 38% at 4 W), played a crucial role in enhancing the interaction between formaldehyde and the ZnO surface, contributing to the sensor's high sensitivity and efficiency. Additionally, the sensor exhibited excellent long-term stability, with only a 15% reduction in response over 7 weeks of continuous operation at 400°C. The sensor also showed a linear correlation ($R^2 = 0.999$) across a range of formaldehyde concentrations (0.01 ppm to 10 ppm), with a low detection limit (LOD) of ~0.1 ppm, making it suitable for detecting even trace amounts of formaldehyde. This ultra-exclusive formaldehyde gas sensor design offers a promising strategy for air quality monitoring in both indoor and outdoor environments, with significant potential for public health protection.

KEYWORDS

ZnO gas sensor, formaldehyde gas sensor, laser-induced ZnO, ZnO mesh structure, formaldehyde selectivity

Journal Pre-proof

1. INTRODUCTION

Formaldehyde, a simple aldehyde, has been widely used in the synthesis of bakelite as a plastic material, disinfectant, and building material. In particular, as a toxic gas, it causes sick building syndrome and is a main issue to occur atopic dermatitis. It becomes a destroyer that causes ecological environmental problems and biological disturbance, it is thereby classified as a Group 1 human carcinogen [1-3]. Chemically understanding this pollutant and its selective detection is seriously important to defend human health in life-threatening environments.

The highly selective detection of formaldehyde, especially in air pollutants, is still a longstanding challenge. However, it is feasible in several strategies. In terms of molecular formation, it is one of the smallest molecules with a kinetic diameter of 2.43 Å in size [4].

Formaldehyde molecules have competitiveness of gas adsorption in the finite area of the sensing materials, bringing an idea that an increase in the surface area of the materials allows high adsorption response of the molecules [5-9]. In this case, a few nanometer-sized structures [5-7], the formation of the porous or hollow shape [10-11], generation of nano-gap or -crack [12], or introduction of embossing structure [13], etc., can be suggested. In the chemical structure perspective, the molecule has the effectiveness of chemisorption with adsorbed oxygen ion species on the surface of air-exposed sensing materials. It means that semiconducting metal oxide, in particular n-type semiconductor, is a great candidate to generate the ion species in the oxygen-deficient crystal structure by trapping electrons released from the conduction band of the metal oxide [14]. Therefore, a zinc oxide (ZnO)-based chemiresistor device with few nanometer-sized pores in the ZnO structure would be a superior gas sensor with high selectivity toward formaldehyde.

Many studies regarding formaldehyde gas sensors with ZnO semiconductors have mainly focused on metal-incorporated ZnO (metal: Au, Ag, Ni, or Al) [15-18], the materialization of ZnO nanocomposites with other oxide materials [19-20], or a polymer hybrid structure [21].

Applications for pure ZnO structure in the sensors have been rarely reported, two research show a 5-10 μm -sized agglomeration consisting of ZnO nanorods [22] and porous ZnO nanoplates with a pore diameter of ca. 100 nm [23], respectively.

In this work, we developed a formaldehyde chemiresistor sensor that has a ZnO mesh structure with few nanometer-sized pores. Laser irradiation enables a ZnO precursor to design the mesh structure that has few nanometer-sized pores between ZnO crystal domains. The structure allows effective gas adsorption and the generation of sufficient oxygen ion species on the surface, facilitating efficient chemical interaction with the formaldehyde target gas. It thereby leads to the detection toward formaldehyde in an excellent sensing response (over 6,682 value to 10 ppm formaldehyde), corresponding to ultra-exclusive selectivity manner.

Through the development of the ZnO mesh structure with few nanometer-sized pores, we finally realized an ideal ZnO sensor device toward formaldehyde in indoor and outdoor air monitoring.

2. EXPERIMENTAL SECTION

2.1. Preparation of a ZnO metallo-hydrogel precursor solution

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade 98 %) and gelatin (type A from porcine, gel strength 300) were purchased from Sigma-Aldrich. The chemicals were received and used directly without further purification. A $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution (2 mol/kg) was prepared by dissolving in deionized water (di-water) at 80 °C. Gelatin of 20 wt% was added to the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution, and then the mixture was blended for 10 min at 800 rpm using a high-torque overhead stirrer (WiseStir® HT-50T). During blending the mixture, high-density bubbles were generated. To remove the bubbles, it was sealed to prevent air interaction and heated at 80 °C for 36 h. The bubbles in the solution disappeared, and a transparent ZnO precursor solution was obtained.

2.2. Fabrication of the laser-induced ZnO mesh sensor devices

Interdigitated electrodes (IDEs) that were composed of Cr and Pt with a 50 nm and 100 nm thickness, respectively, were patterned on a SiO₂/Si substrate (8.5 mm × 8.5 mm) by the liftoff method [24]. The SiO₂/Si substrate was cleaned by ultrasonication in acetone and isopropyl alcohol for each 15 min. To pattern the electrodes by the lift-off method, the LOR 5A resist (purchased from AllforLab, Inc.) was spin-coated onto the cleaned substrate at 3000 rpm for 45 s. After the LOR 5A layer was solidified at 190 °C for 5 min, AZ GXR-601 (photoresist / viscosity 14 CP, purchased from NM Tech.) was spin-coated onto the LOR 5A layer at 3000 rpm for 30 s. A soft bake was sequentially performed at 110 °C for 1 min. The resist layer was treated from a UV exposure (15 s) with a patterned mask, and then the substrate was soaked into a developer solution (AZ 300 MIF, purchased from Sigma-Aldrich) for 11 s without a post-exposure bake (PEB) process. The Cr/Pt electrode was thermally deposited, and the substrate was soaked in acetone to remove the resist layer. The IDEs with a 10 μm gap can be an active site for the deposition of ZnO precursor, whereas the non-active area was covered by polyimide (PI) tape as passivation. On the active site, the ZnO precursor solution was spincoated for 30 s at 1000 rpm, and the ZnO precursor film was exposed to CO₂ laser irradiation (a scan speed of 126 mm s⁻¹) with different laser power (0, 1, 2, 3, and 4 W in this work) for ~ 1 min. Finally, the PI passivation tape was removed, and the laser-induced ZnO mesh sensor was fabricated.

2.3. Gas sensing measurement of the laser-induced ZnO mesh sensor devices

The sensing abilities of the laser-induced ZnO mesh sensors were evaluated using a customized sensing measurement system with four-channel test equipment. It has a tube furnace (quartz tube with a 25Ø) chamber equipped with a gas flow system (the gas line has a 6Ø), which is connected to mass flow controllers (MFCs) and gas cylinders. For the selective sensing test,

all gases (formaldehyde (HCHO – dry gas, concentration of 10.8 $\mu\text{mol/mol}$ with N_2 balance gas), acetone (concentration of 10 $\mu\text{mol/mol}$ with N_2 balance gas), styrene (concentration of 10 $\mu\text{mol/mol}$ with N_2 balance gas), carbon dioxide (CO_2 – dry gas, concentration of 197.8 $\mu\text{mol/mol}$ with dry air balance gas), ammonia (NH_3 – dry gas, concentration of 10 $\mu\text{mol/mol}$ with dry air balance gas), nitrogen dioxide (NO_2 – dry gas, concentration of 49.2 $\mu\text{mol/mol}$ with dry air balance gas), and nitric oxide (NO – dry gas, concentration of 103.7 $\mu\text{mol/mol}$ with N_2 balance gas), acetaldehyde (dry gas, concentration of 10.1 $\mu\text{mol/mol}$ with N_2 balance gas), and ethanol (dry gas, concentration of 10.1 $\mu\text{mol/mol}$ with N_2 balance gas)) were used with a concentration of 10 ppm that was diluted to the standard gas (80 % nitrogen and 20 % oxygen) with dry air. In the gas sensitivity test, the concentration of the formaldehyde ranged from 0.01 ppm to 10 ppm. The specific concentrations of the target gas were also diluted to the standard gas with dry air. For both gas testing cases, specific concentrations of the target gas and the standard gas with dry air as the balance gas were injected into the chamber at a constant flow rate of 1000 sccm. The operating temperature (300 $^\circ\text{C}$ – 500 $^\circ\text{C}$) of the chemiresistive sensor was provided and adjusted using a temperature controller embedded in the tube furnace. The temperature controller utilized a typical algorithm that incorporated feedback from the temperature sensor with an error range of ± 0.5 $^\circ\text{C}$. The electrical sensing resistance was measured using a nanovoltmeter (Keithley 2182) at a constant current of 1 μA (a DC current source - Keithley 6220) with a time interval of 1 s under an LabView environment, which controlled all the accessories.

2.4. General characterization

Feld-emission scanning electron microscopy (FE-SEM) images including cross-sectional results of the laser power-dependent ZnO mesh films were measured using a JEOL-6701F

instrument. The internal crystal morphologies of the ZnO mesh structures were confirmed by transmission electron microscopy (TEM) which was operated at an acceleration voltage of 200 kV (JEM -ARM 200F, JEOL Ltd). The crystal lattice phases of the mesh structure were evaluated by X-ray diffraction (XRD) (Cu K α radiation, $\lambda = 1.541 \text{ \AA}$) (Ultima IV/ME 200DX, Rigaku). Ex-situ temperature-dependent XRD results were measured by thermal-annealing for each sample at 45 min with the same Rigaku XRD instrument. X-ray photoelectron spectroscopy (XPS) measurement was performed with a K-alpha system (Thermo Fisher Scientific) using a monochromatic Al K α irradiation (1486.6 eV) to investigate the surface composition and chemical states of the laser-induced ZnO mesh samples. The electronic spin states and surface structures were examined using an electron paramagnetic resonance (EPR) spectrometer (EMXplus-9.5/12/P/L, Bruker) operating at an X-band frequency ($f \approx 9.774 \text{ GHz}$). The distribution of pore diameters was measured using a porosimeter (Quantachrome PM33GT). The surface area including pore volume was investigated by Brunauer-Emmett-Teller (BET) method from the desorption branch data of nitrogen adsorption isotherm at 77.4 K with an Autosorb IQ (Quantachrome).

RESULTS AND DISCUSSION

A speedy-fabricated ZnO mesh sensor can be designed by CO₂ laser irradiation. Fig. 1a shows the overall design of the chemiresistive device that designates an extremely selective formaldehyde sensor (details are described in the Experimental section). A ZnO solution is exposed to CO₂ laser irradiation for ~ 1 min. The strong power of the laser enables to spark instantaneous high temperature ($\sim 2000 \text{ K}$ can be reached in a few seconds), which allows the generation of ZnO crystals in a mesh structure from the precursor.

We expected that the ZnO mesh structure has a laser power-dependent effect. Indeed, depending on the laser power, the morphological ZnO structures were varied; Fig. 1b-f exhibits

FE-SEM images. Each orange box in the Figure below shows an enlarged view. A pure structure without morphological feature was shown in the as-cast ZnO film (0 W, Fig. 1b).

Upon laser irradiation, however, a thin foil sheet with over 1 μm -sized holes was observed in the ZnO film processed with a 1 W power (Fig. 1c). As an increase of the laser power to 2 W (Fig. 1d), the ZnO foil sheet was changed to a mesh structure that has aggregated particles on the surface with hundreds of nanometers in size (Fig. 1d). For stronger power conditions at 3 W (Fig. 1e) and 4 W (Fig. 1f), the ZnO films keep the mesh structure, however, hundred nanometer-sized particles that were shown in the 2 W laser condition mostly disappeared. It suggests that ZnO crystals might be formed in the mesh structure without non-reactive particle aggregation. In comparison between 3 W and 4 W conditions, the 4 W laser-induced ZnO film showed a closer mesh structure with ca. 200 nm-sized holes (the 3 W laser-induced ZnO film has over 650 nm-sized holes). The cross-sectional SEM images show the growth of the ZnO crystals in the mesh film in detail (Fig. 1g-k). Beyond the foil sheet that is shown at the 1 W laser condition (Fig. 1h), we found that the ZnO crystals were randomly grown with a spark shape in the mesh structure (Fig. 1i). However, the spark formation gradually decreased as a function of laser power (Fig. 1j-k), indicating that the aggregated formation in Fig. 1d might be from the ZnO spark crystals, and thus higher laser power allows the formation of ZnO crystal domains in the mesh structure without aggregated ZnO spark feature.

To understand the internal structure of the ZnO crystals in the mesh film, we measured TEM images. Fig. 2 exhibits laser power-dependent ZnO structures, and higher magnified TEM results were highlighted as an orange box. As consistent with the surface morphology of Fig. 1c, the aggregated ZnO formation was observed in the 1 W laser-induced ZnO mesh structure (Fig. 2b). It indicates that non-reactive particle aggregation in the synthesis of ZnO crystal is shown in the internal mesh structure. As an increase of the laser power to more than 2 W, a specified structure, i.e., the aggregated particle formation, was rarely revealed, whereas a

nanosheet morphology was observed (Fig. 2c for 2 W, Fig. 2d for 3 W, and Fig. 2e for 4 W laser power condition). When a sectional point in the sheet is focused, we understand that the sheet has a hexagonal wurtzite structure from the ZnO crystal (yellow marks) [25]: (100) lattice plane with a spacing of 0.28 nm, (002) lattice plane with a spacing of 0.26 nm, and (110) lattice plane with a spacing of 0.25 nm. It demonstrates that ZnO crystals are randomly synthesized without specific features in the mesh film and they are uniformly dispersed in the mesh structure in the laser power condition over 2 W.

From the surface and internal morphologies, we understand that 1) higher laser power, in particular over 2 W condition, allows the generation of ZnO crystals in the mesh film with a more compact formation and 2) the crystals are more evenly dispersed in the mesh structure as the nanosheet formation. All laser-induced ZnO mesh structures present ZnO crystal phases including ZnO aggregation in the morphologies, however, the degree of the ZnO crystallinity has a laser power dependency; XRD data of Fig. 2f proves this comment (a highlighted figure that has an X-axis range of $25^\circ - 45^\circ$ was displayed from a blue dash box in Fig. 2f). In the ZnO precursor state without laser irradiation (0 W laser power), two-theta peaks at 23.0° , 30.5° , and 53.3° were observed, corresponding to α -Zn(OH)₂ (JCPDS No. 041-1359) and λ -Zn(OH)₂ (JCPDS No. 038-0356). At 1 W laser power, similar diffraction peaks appeared, indicating that neither the 0 W nor 1 W conditions provide enough energy for ZnO crystallization. However, at 2 W, the diffraction profile (green line) revealed the hexagonal wurtzite ZnO crystal (JCPDS No. 36-1451), as shown by the sharper peaks and increased intensity. For 3 W and 4 W, higher diffraction intensities at the same Bragg positions indicated a trend of increased crystallinity. The sharpening of peaks and reduction in broadening suggest larger crystallite sizes and less internal strain at higher powers. Using the Scherrer equation, it would be possible to calculate crystallite sizes, which would likely show increasing size with higher laser power. Furthermore, no secondary phases were observed at higher laser powers, demonstrating the removal of

hydroxide impurities and the formation of phase-pure ZnO. Thus, the XRD results clearly show that higher laser power enhances both crystallinity and phase purity, resulting in well-formed ZnO crystals.

As a strategy in the design of the formaldehyde gas sensor, we argued that few nanometer sized pores in the sensing material lead to a superior selective sensor in the detection of formaldehyde. Thus, we investigated the distribution of pore diameters in the ZnO mesh structures. Fig. 2g describes the laser power dependent-distribution of pores in size, which was measured by a porosimeter. Stronger laser power provides smaller pores in the ZnO mesh structure; no pore at 0 W, 20 nm-sized pores in diameter at 1 W (majority, 40 nm-sized pores are minor), 15 nm-sized pores in diameter at 2 W, 9 nm-sized pores in diameter at 3 W, and 7 nm-sized pores in diameter at 4 W. This trend is similar results with previously reported papers using the CO₂ laser system [26-27] and demonstrates that the ZnO crystals are synthesized in the mesh structure with smaller pores between the crystal domains as an increase of the laser power. The 3 W or 4 W laser powers provide few nanometer-sized pores in the ZnO mesh structure, which might allow exclusive permeability for formaldehyde gas. The BET results support the distribution of pore diameters that the surface area including pore volume showed an increased trend as a function of laser power (Fig. S1). With the information on pore size in the morphological studies, therefore, we expect that the laser-induced ZnO mesh structure processed with higher laser power, in particular at 3 W or 4 W would provide excellent sensing performance, in particular for the formaldehyde selectivity. We suggest this ideal ZnO mesh structure as shown in Fig. 2h.

We investigated the surface composition and chemical states of elements on the laserinduced ZnO mesh films. From the XPS analysis, we understand that higher contents of oxygen vacancies are formed in the ZnO mesh structure that has a well-structured ZnO crystal framework. Fig. 3 displays the XPS spectra of the O 1s state for the laser power-dependent

ZnO mesh films (the full-scan spectra of Fig. S2 provide an involvement of Zn, O, N, and C elements). The O 1s peaks are deconvoluted into three individual quasi-Gaussian peaks and they were centered at ~ 530.1 , ~ 531.4 , and ~ 532.4 eV (the 0 W laser power condition was excluded due to the non-synthesized ZnO crystal). The three peaks were determined to be O Lattice, O vacancy, and O chemisorbed, and the meaning of each peak corresponds to the following [28-30]: The O Lattice refers to O^{2-} ions of Zn-O bonds in the ZnO crystal, which is shown as a low-energy curve (blue line). The O vacancy is attributed to the oxygen ions of O^- or O^{2-} in the oxygen-deficient regions in the ZnO framework (intermediate-energy curve, pink line). The O chemisorbed means the chemisorbed oxygen species e.g., O^- , O^{2-} or OH groups, on the ZnO surface (high-energy curve, green line). Among the oxygen states, it is important to understand the O vacancy level because oxygen vacancies in the crystal donate electrons that are obtained from the conduction band of the ZnO semiconductor to adsorbed oxygen molecules, allowing chemical interactions of the molecules with a target gas [14,31]. In the curve of the O vacancy state, therefore, the number of oxygen vacancies was estimated as a relative percentage of the area fraction (pink diagonal lines); $\sim 9\%$ for 1 W (Fig. 3b), $\sim 22\%$ for 2 W (Fig. 3c), 36% for 3 W (Fig. 3d), and 38% for 4 W (Fig. 3e). We find a gradually emerging trend as a function of laser power, which is shown in Fig. 3f. The trend indicates that higher laser power allows the formation of ZnO crystals with higher crystallinity in the mesh structure, more oxygen vacancies were generated in the crystals.

We investigated the electronic properties of the laser-induced ZnO mesh films using EPR spectroscopy. The EPR analysis provided insights into the oxygen vacancy sites in the ZnO structure by monitoring the behavior of unpaired electrons trapped within these vacancies. Fig. S3 displays the EPR spectra for the ZnO mesh films synthesized under varying laser powers. As shown in Fig. S3, the g-factor values exhibited a clear increasing trend with higher laser power, indicating the generation of a greater number of oxygen vacancies[32-34]. The g-factor,

a parameter that reflects the interaction of unpaired electrons with the magnetic field, is directly related to the presence of oxygen vacancy sites. Higher g-factor values correspond to an increased density of unpaired electrons trapped in oxygen-deficient regions of the ZnO framework. This observation suggests that as the laser power used during ZnO synthesis increases, the rapid heating and cooling cycles promote the formation of oxygen vacancies, which serve as trapping sites for unpaired electrons. The data align with previous findings that demonstrated enhanced crystallinity and structural modifications with increased laser power. The higher density of oxygen vacancies at elevated laser powers further confirms the trend observed in XPS analysis, providing complementary evidence that laser power significantly influences the structural and electronic properties of ZnO mesh films. These vacancies are crucial for enhancing gas sensing performance by facilitating stronger adsorption and reaction dynamics with target gas molecules.

To investigate the effect of the ZnO mesh structure on a gas sensor, the gas-sensing characteristics were tested. The laser-induced ZnO mesh sensors were operated for the detection of 10 ppm formaldehyde at various temperatures ranging from 300 °C to 500 °C. All sensor devices showed an n-type oxide semiconductor behavior [35] and temperature dependent sensing resistance (Fig. 4a-e). All sensors exhibited a variation of initial resistance level in air (R_a) as a function of temperature. It is because of the change in the intrinsic properties of ZnO according to the oxygen molecules adsorbed on the surface when the ZnO is exposed to air [33]. In general, the chemisorbed oxygen species can be ionized to different chemical forms depending on the operating temperature [36-37];



Based on the 400 °C, the predominant adsorbed oxygen species are different, which causes one of the reasons for the change in the electrical resistance of n-type ZnO. In the selective resistance result at the operating temperature of 400 °C (Fig. 4f), we find that the R_a level increases as an increase of the laser power in the ZnO mesh sensor with a basis of R_a signal at the 0 W laser power. It means that a thicker electron depletion layer that generates more electrons is formed on the surface of ZnO with higher laser power [38], which has a larger possibility to interact with more chemisorbed oxygen molecules from the air, i.e., O^- and O^{2-} on the surface.

With the resistance concept, in the air environment, we thereby understand that the electrons are transferred from the conduction band of ZnO to the chemisorbed oxygen species, leading to an increase in both the energy potential barrier (E_p) and thickness of the electron depletion layer as the electron concentration decreases (Fig. 5a and 5c). In the formaldehyde condition, formaldehyde target molecules chemically interact with the chemisorbed oxygen molecules with the following chemical reactions [39-40].



Therefore, the trapped electrons by the O^- and O^{2-} ions were released back into the conduction band of ZnO, which decreased the electron depletion layer, resulting in a low resistance state (Fig. 5b and 5d).

The sensing property was obtained from the resistance result, thus the gas response is defined as $\Delta R/R_g$, where R_a and R_g are the resistances in air and gas, respectively, and $\Delta R = |R_a - R_g|$ [1,41]. In the sensing response plots converted from Fig. 4 (Fig. S4a-e), we found two main results; dramatically different response has a laser power dependency and all sensor devices show the highest response result at an operating temperature of 400 °C. We understand the optimum temperature of 400 °C is the formaldehyde sensing operation for all sensors. This

result is the same data with other types of ZnO-based formaldehyde sensors at the operating temperature of 400 °C [42]. In the representative plot of the chemiresistive variation at 400 °C in the laser power dependence (Fig. 6a), the 3 W laser-induced ZnO mesh sensor exhibited the highest sensing response with a ca. 6,682.8 value, the sensor with the 4 W laser power condition represented a quite similar level to that of the 3 W system (response = 6,234.6, and other responses are 386.4 for 0 W, 901.8 for 1 W, and 1687.6 for 2 W). Indeed, the higher laser power leads to a superior sensing response. In particular, at the 3 W or 4 W laser power condition, the response is extremely high value. It is because not only a more ideal ZnO crystal in the mesh structure that allows effective physical adsorption of formaldehyde including superior permeability via the few nanometer-sized pores but also a higher O-deficient level that generates more oxygen ion species interacting with formaldehyde. Most of all, at the high operating temperature, it is important to maintain the integrity of the structure to claim a relationship between the sensing response and morphological effect. We thereby investigated the variation of crystal phases of the laser power-dependent ZnO mesh structures at the temperature range of 300 – 500 °C (Fig. S5). We found that the ZnO crystal structure was kept, in particular at the laser power conditions over 2 W, and a trend of its crystallinity followed the crystal result at room temperature of Fig. 2f. From the results, we tentatively argue that the laser-induced ZnO mesh sensor showed an excellent sensing performance in the mesh structure formed as a precise ZnO crystal framework.

With the gas detection level, the transient response is another key parameter to determine the sensing ability of gas sensors. We focused on the sensing curves in the response results to understand the sensing transients for the response and recovery as a function of laser power. The response (τ_{res}) and recovery (τ_{rec}) time can be estimated as the time required to reach a 90 % resistance level when the device is exposed to formaldehyde and air, respectively [43]. The higher laser power even enables the ZnO mesh sensor to respond to faster adsorption of

the formaldehyde, as follows in a sequence; τ_{res} is 0.98 s, 1.06 s, 2.96 s, 3.92 s, and 2.92 s for 4 W, 3 W, 2 W, 1 W, and 0 W condition, respectively (Fig. 6b). In particular, at the 4 W laser power condition, the sensor device exhibited ultra-fast response reactivity within 1 s. It is a considerably worthy result because the current state of formaldehyde sensors shows around 4 s in the τ_{res} time [44]. A considerably high surface area according to the mesh structure including few nanometer-sized pores allows tremendous formaldehyde molecules in the structure in a short time, leading the ultra-fast response time. For the τ_{rec} times, however, they show a different transient trend compared with the τ_{res} . As shown in Fig. S4f, up to 2 W laser power condition, the recovery response revealed a similar τ_{rec} of ca. 46 s. In the sensor devices with higher laser power conditions of 3 W and 4 W (inset figure in Fig. S4f), slow gas desorption was observed.

Based on the τ_{rec} result including the τ_{res} , we targeted the 2 W laser-induced ZnO mesh sensor that revealed sufficiently fast recovery performance. We thereby investigated the effect of formaldehyde sensitivity on the 2 W laser-induced ZnO mesh sensor. Fig. 6c displays the sensing responses depending on the formaldehyde concentration from 0.01 ppm to 10 ppm at 400 °C. At the low concentration, i.e., under 0.1 ppm, the chemiresistive device sensitively detected formaldehyde gas, demonstrating that the 2 W laser-induced ZnO mesh sensor achieved a low detection limit (LOD) of ~ 0.1 ppm formaldehyde. This LOD is a quite similar level to the required value which is the World Health Organization (WHO), and thus the LOD is a significantly meaningful value in formaldehyde-based sensors. Furthermore, the sensor showed precisely concentration-dependent sensing performance. This result exhibited a linear relationship with a high linear correlation coefficient of $R^2 = 0.999$ as a function of formaldehyde concentration, resulting in an ultra-high sensitivity value of ca. 172.2 (a slope of the linear plot) (Fig. 6d). It means that depending on the formaldehyde concentration,

formaldehyde molecules that are provided with a certain amount at each concentration totally reacted with adsorbed oxygen ions on/in the ZnO mesh structure.

Ultimately, the effect of the ZnO mesh structure that has few nanometer-sized pores is remarkable on the formaldehyde selectivity. We tested the sensing response for other target gases in the 2 W laser-induced ZnO mesh sensor at 400 °C (Fig. 7a). As investigated in Fig. 6, in the formaldehyde detection to 10 ppm, the 2 W laser sensor device showed a high response of 1687.6. In terms of the sensing response of the 3 W laser-induced ZnO mesh sensor, the response result is 6682.8. The response values in the detection of 10 ppm acetone and styrene showed 28.5 and 12.8, respectively, whereas responses to other gases such as CO₂, NH₃, NO₂, NO, acetaldehyde, and ethanol at the same concentration of 10 ppm were negligibly low (all gases are almost 0). This selectivity trend was also observed in the comparison result between 0 W and 2 W laser-induced ZnO mesh sensors (Fig. S6) and the operating temperature-dependent selectivity results (Fig. S7). The exclusive detection of formaldehyde (inset figure of Fig. 7a) is due to the design of the ZnO structure, specifically the mesh structure with few nanometer-sized pores. The sensing response is significantly influenced by the molecular size and dipole moment of the gas molecules. The molecular size of formaldehyde is 2.43 Å in kinetic diameter, while other target molecules show larger sizes: 4.69 Å for acetone, 3.34 Å for styrene, 3.26 Å for NH₃, 3.40 Å for NO₂, 5.10 Å for acetaldehyde, and 4.50 Å for ethanol. For the dipole moment (D), formaldehyde has a relatively high value of 2.30 D (acetone of 2.88 D, styrene of 0.13 D, CO₂ of 0 D, NH₃ of 1.46 D, NO₂ of 0.63 D, acetaldehyde of 2.69 D, and ethanol of 1.69 D) [45]. The tiny size and large D value of formaldehyde enable effective chemical adsorption on the mesh structure and good permeability through the few nanometer-sized pores. This exclusive selectivity for formaldehyde can be attributed to several factors. Chemical interaction plays a crucial role, as the unique molecular structure of formaldehyde allows for stronger interactions with the ZnO surface compared to larger molecules, enhancing

both adsorption capacity and sensitivity. Additionally, formaldehyde may require lower activation energy for effective adsorption on the ZnO mesh structure, facilitating detection even at low concentrations and contributing to the observed high response levels. Furthermore, the presence of oxygen vacancies on the ZnO surface is critical for enhancing selectivity. These vacancies can interact favorably with formaldehyde, enabling a more efficient detection mechanism. The ultra-exclusive selectivity of formaldehyde in the laser-induced ZnO mesh sensor stands out when compared to previously reported results (Fig. 7b) [46-65]. Most formaldehyde gas sensors have shown sensing responses between 0 and 20 as a function of formaldehyde concentration, from 0.05 ppm to 10 ppm. The maximum response of approximately 52.5 was observed in reference [58] for formaldehyde detection at 10 ppm concentration. In a more specific category, our laser-induced ZnO mesh sensor showed an extremely high sensing response, even at low concentrations of formaldehyde [54, 57, 64, 67-70].

In terms of stability in the sensing performance, the 2 W laser-induced ZnO mesh sensor showed an excellent stable chemiresistive device. We tested the sensor device for the detection of 10 ppm formaldehyde with 40 cycles at 400 °C. Fig. 7c exhibited a considerably constant resistance result in the gas-in and out system, which is confirmed in the magnified plot of the real-time resistance curves with a highlight of 5 cycles (dash blue box) in detail. Fig. 7d represents the long-term stability of the sensor device when exposed to 10 ppm formaldehyde at 400 °C for 7 weeks. During the sensing period under the high operating temperature, the sensing response value was only changed with a ~ 15 % reduction level.

CONCLUSIONS

In this work, we designed a formaldehyde gas sensor that exhibits ultra-exclusive selectivity based on a ZnO mesh structure. CO₂ laser irradiation enabled the rapid fabrication of the ZnO

mesh structure within 1 minute, forming few nanometer-sized pores between ZnO crystal domains. With increasing laser power, particularly at 3 W and 4 W, the ZnO crystals were precisely synthesized, and smaller pores under 9 nm were formed, which enhanced gas permeability and adsorption. Furthermore, more oxygen vacancies were generated in the ZnO crystal framework, reaching up to 38% at 4 W, significantly contributing to the sensor's selectivity and sensitivity. This unique structure allowed for efficient chemical interaction between formaldehyde and the oxygen ion species on the surface of ZnO crystals. As a result, the 3 W laser-induced ZnO mesh sensor achieved an exceptional sensing response of over 6,682 and an ultra-fast response time of 0.98 s, demonstrating superior performance in formaldehyde detection. In terms of recovery time, the 2 W laser-induced ZnO mesh sensor exhibited a response value of 1,687.6 with a low detection limit of < 0.1 ppm, meeting the requirements for detecting trace formaldehyde concentrations in real-world environments. Moreover, the sensor exhibited remarkable long-term stability, with only a 15% reduction in performance after 7 weeks of continuous operation at 400°C, confirming its durability. The combination of fast response, high selectivity, low detection limit, and long-term reliability makes this performance an overwhelming advancement in the field of formaldehyde gas sensors. Therefore, our ZnO mesh structure with few nanometer-sized pores offers a promising strategy for developing high-performance formaldehyde sensors, with significant potential for indoor and outdoor air monitoring.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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Journal Pre-proof

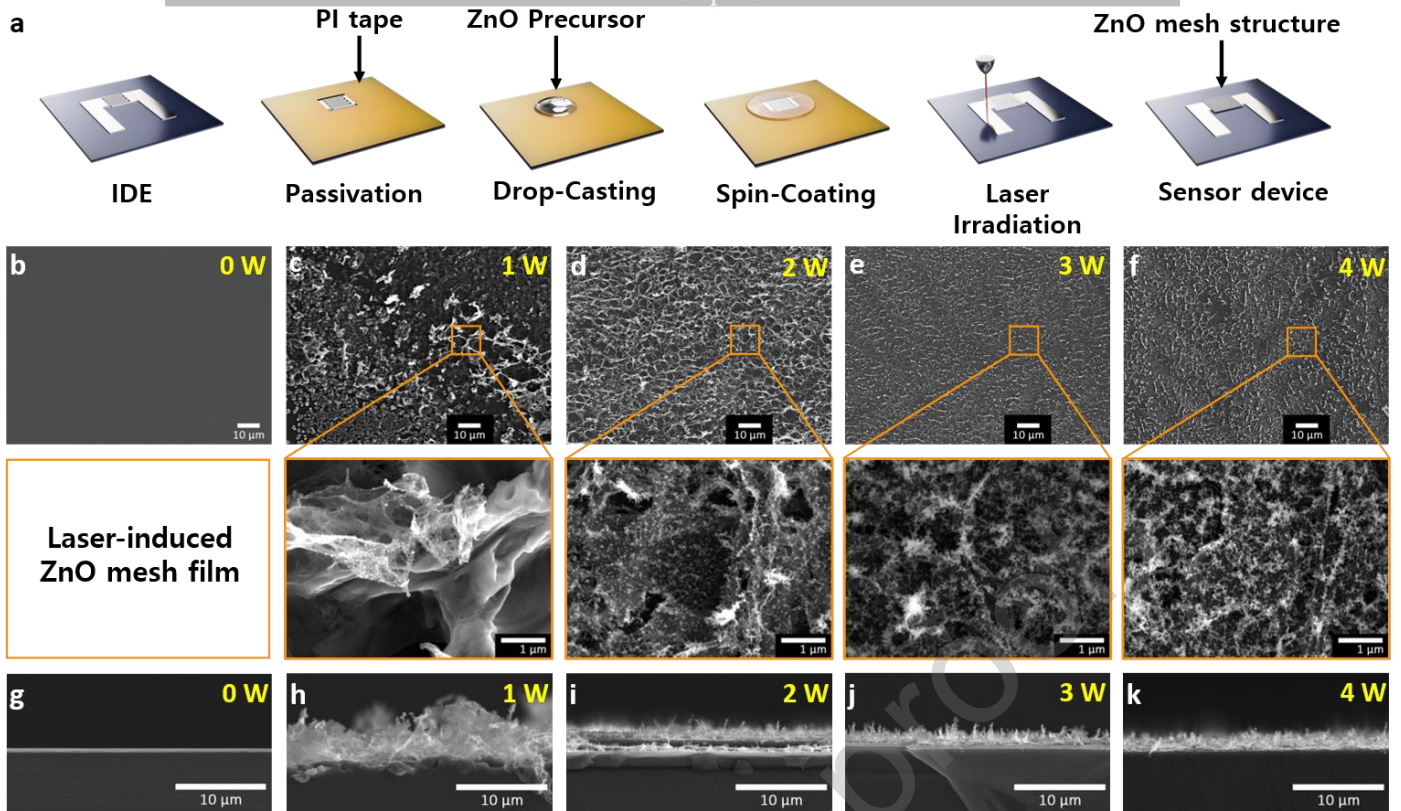


Fig. 1 (a) A step scheme of the fabrication of a laser-induced ZnO gas sensor (IDE: interdigitated electrodes). Surface morphological structures of laser-induced ZnO mesh films in laser power dependence: (b-f) SEM images, corresponding to (g-k) cross-sectional SEM results (b and g – 0 W, c and h – 1 W, d and i – 2 W, e and j – 3 W, and f and k – 4 W).

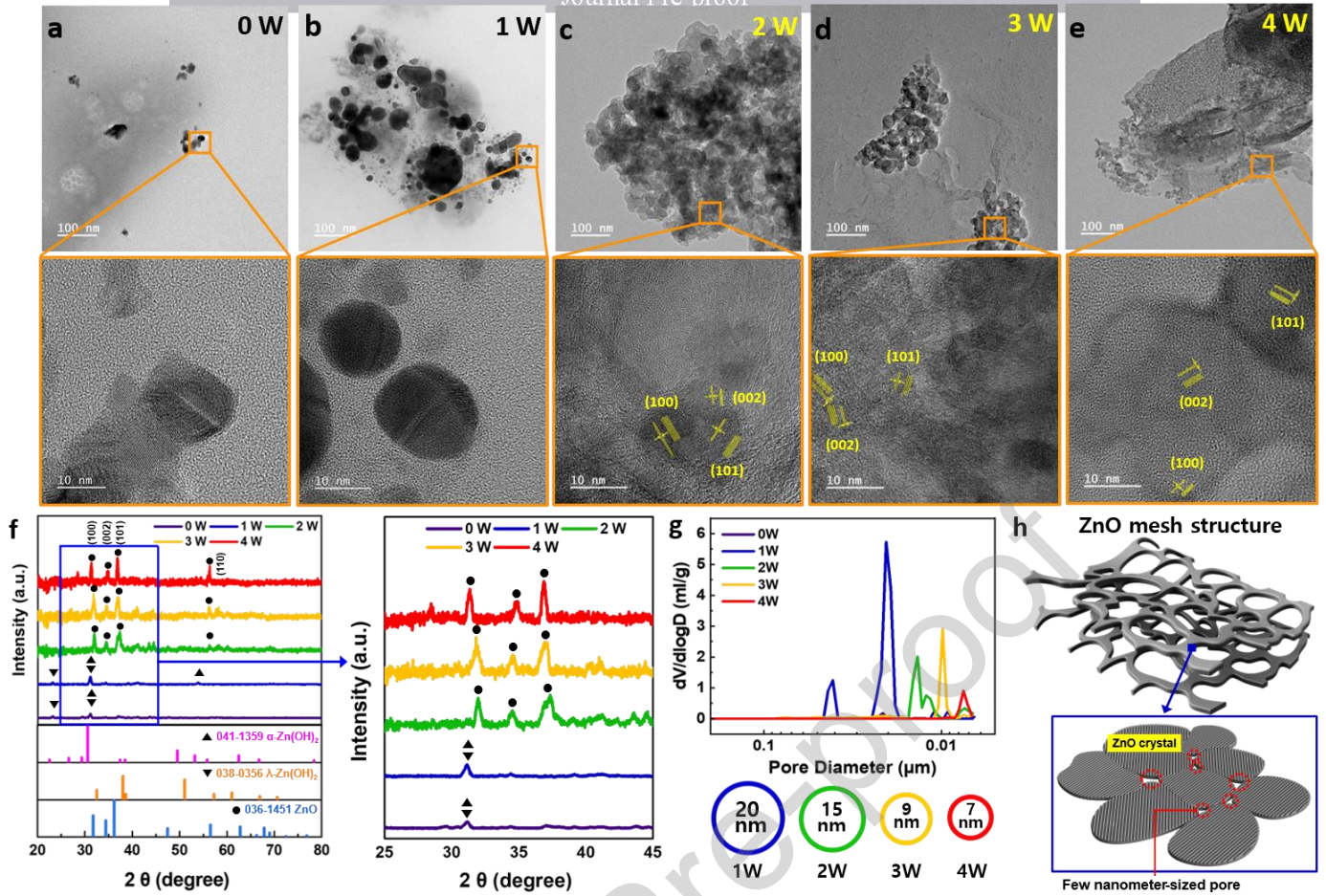


Fig. 2 Internal structures of laser-induced ZnO mesh films as a function of laser power: (a – e) TEM images, (f) XRD results, (g) pore size distributions, and (h) suggested ZnO mesh structure.

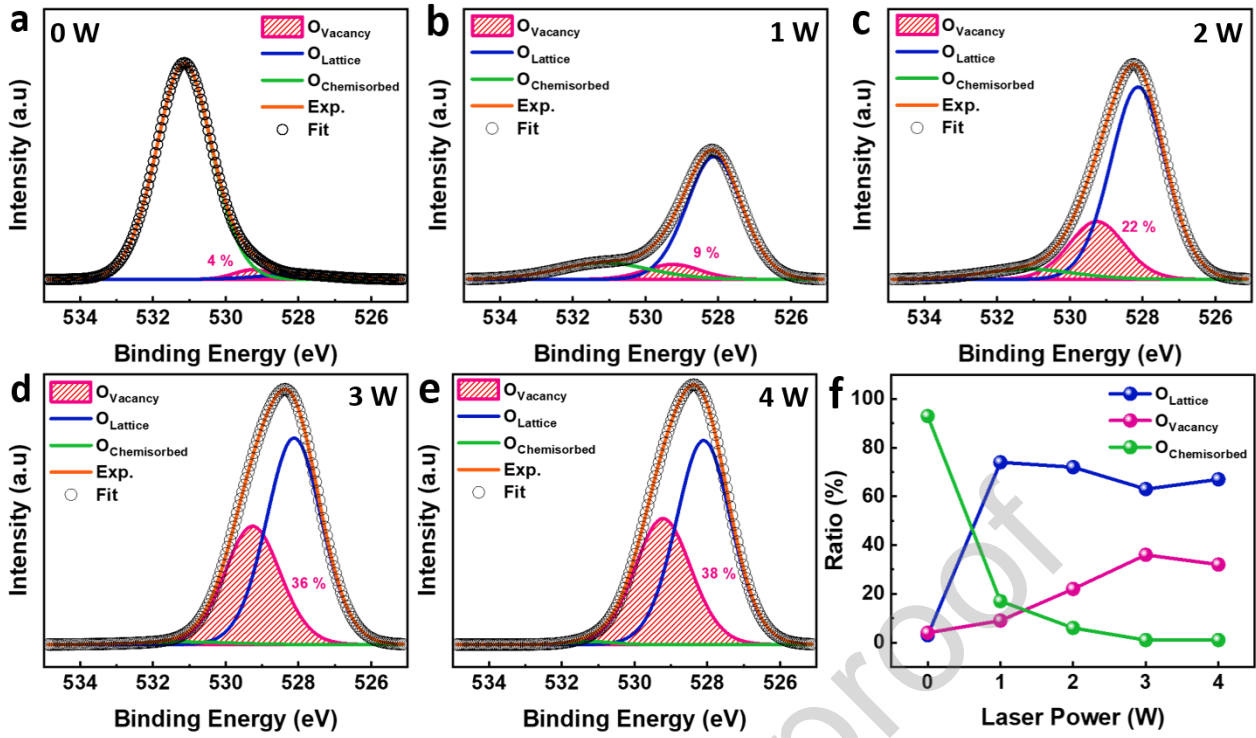


Fig. 3 XPS core-level spectra of O 1s for the chemical state analysis of the surface on the laser-induced ZnO mesh structures depending on the laser power (a-e, 0 W – 4 W). (f) Trends of lattice oxygen (O Lattice), oxygen vacancy (O vacancy), and chemisorption of oxygen (O chemisorbed) depending on the laser power.

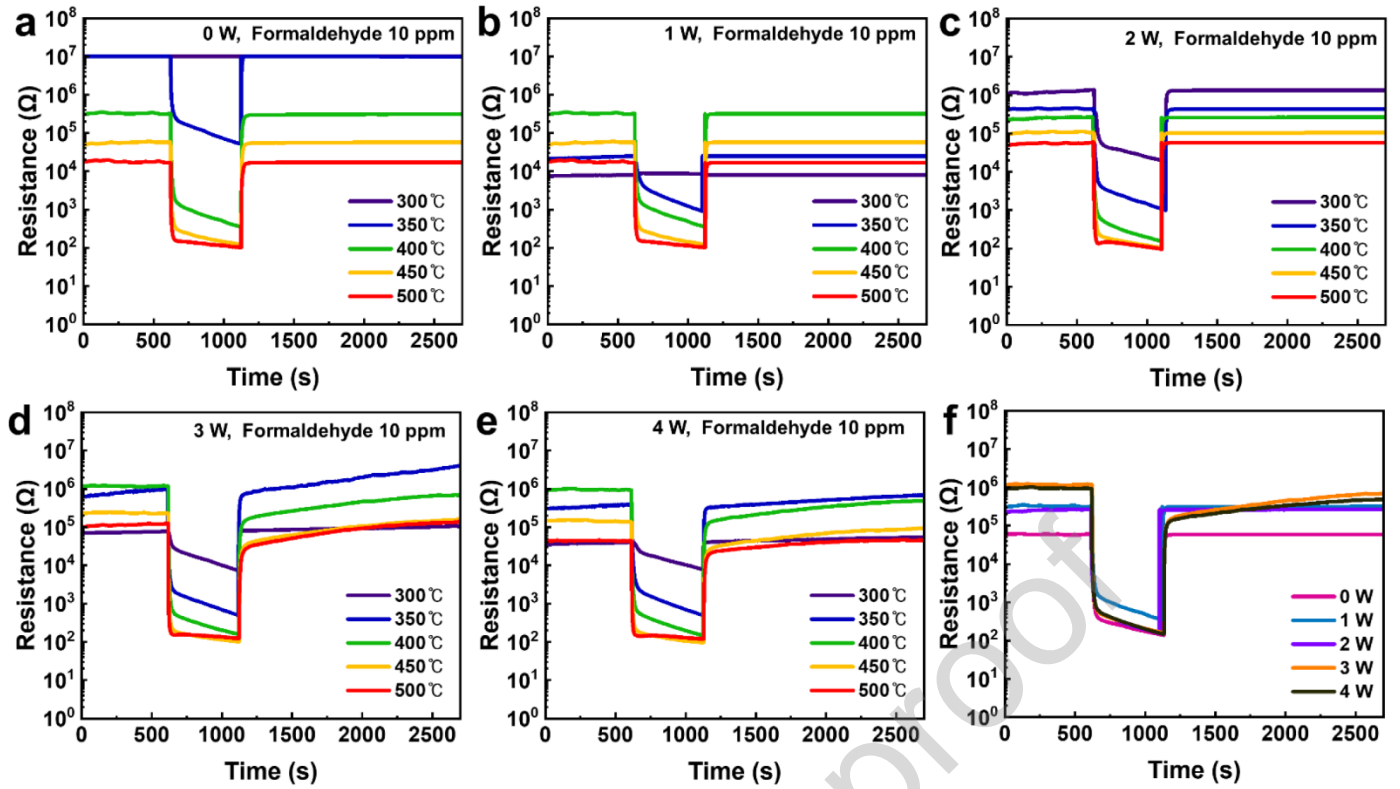


Fig. 4 Dynamic results for sensing resistance (formaldehyde 10 ppm) of the laser-induced ZnO mesh sensors prepared by laser power of (a) 0 W, (b) 1 W, (c) 2 W, (d) 3 W, and (e) 4 W. (f) Variation in the resistance at 400 °C measured by the laser-induced ZnO mesh sensors depending on the laser power.

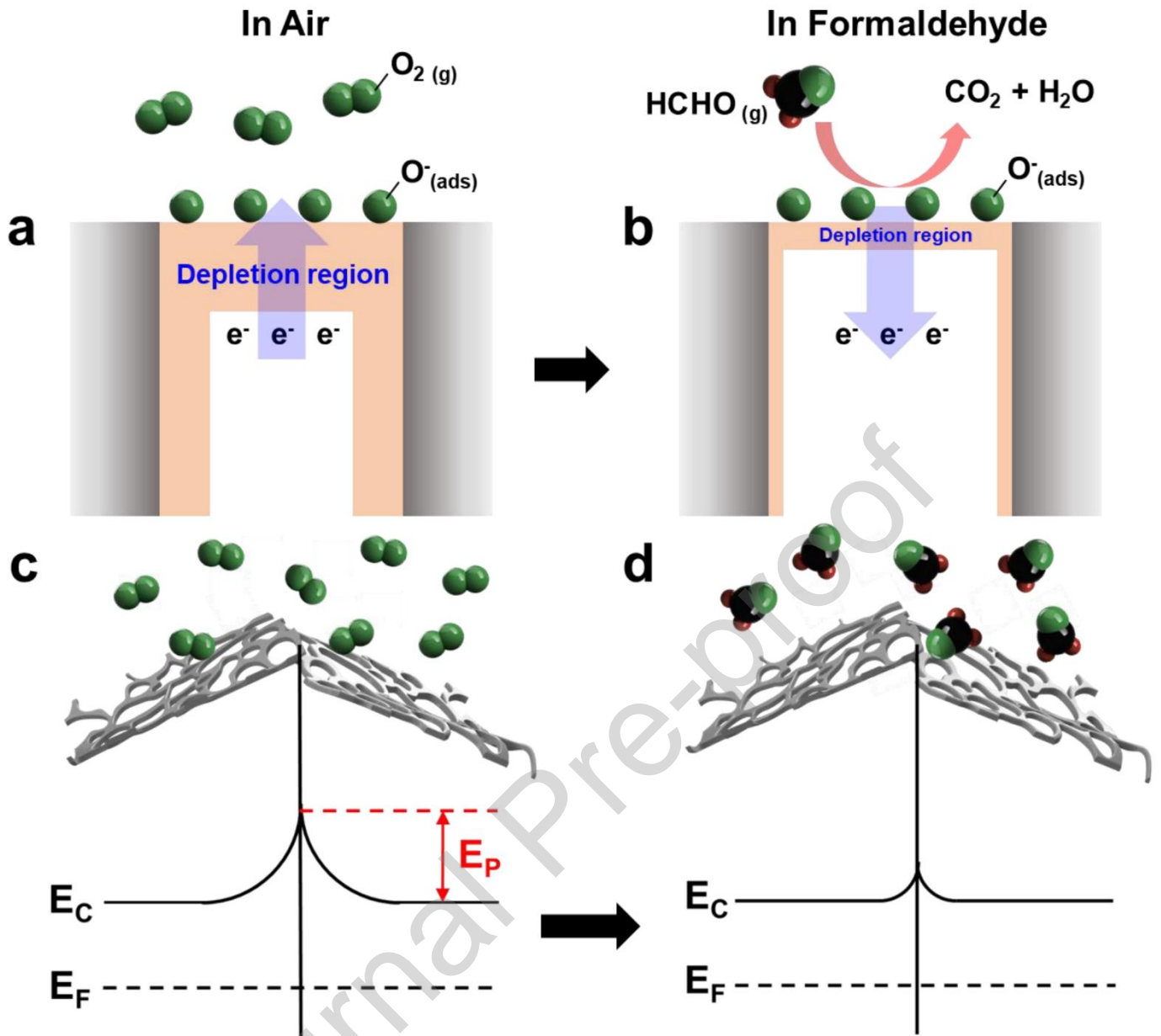


Fig. 5 Schematic illustrations of the gas sensing mechanism in air (a and c) and formaldehyde (b and d) environment. In Fig. c and d, the energy barrier potential (E_p) is expressed with the conduction band level of E_c and Fermi level of E_f .

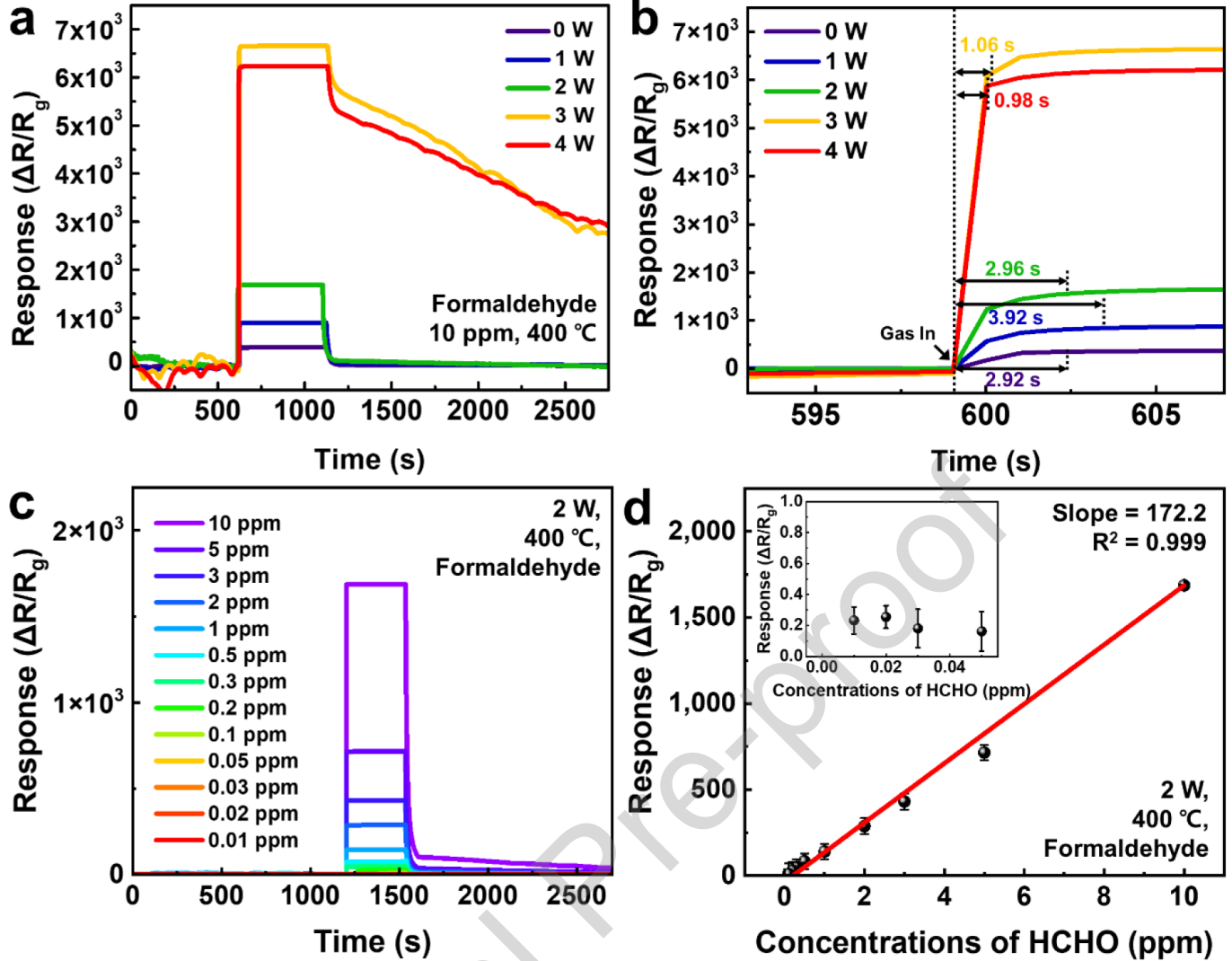


Fig. 6 (a) Representative plot of sensing responses for the laser power-dependent ZnO chemiresistive devices at an operating temperature of 400 °C. (b) Response time in sensing transients. (c) Formaldehyde concentration-dependent sensing responses in the 2 W-ZnO mesh sensor. (d) Corresponding to the sensitivity result with the slope of a linear fit.

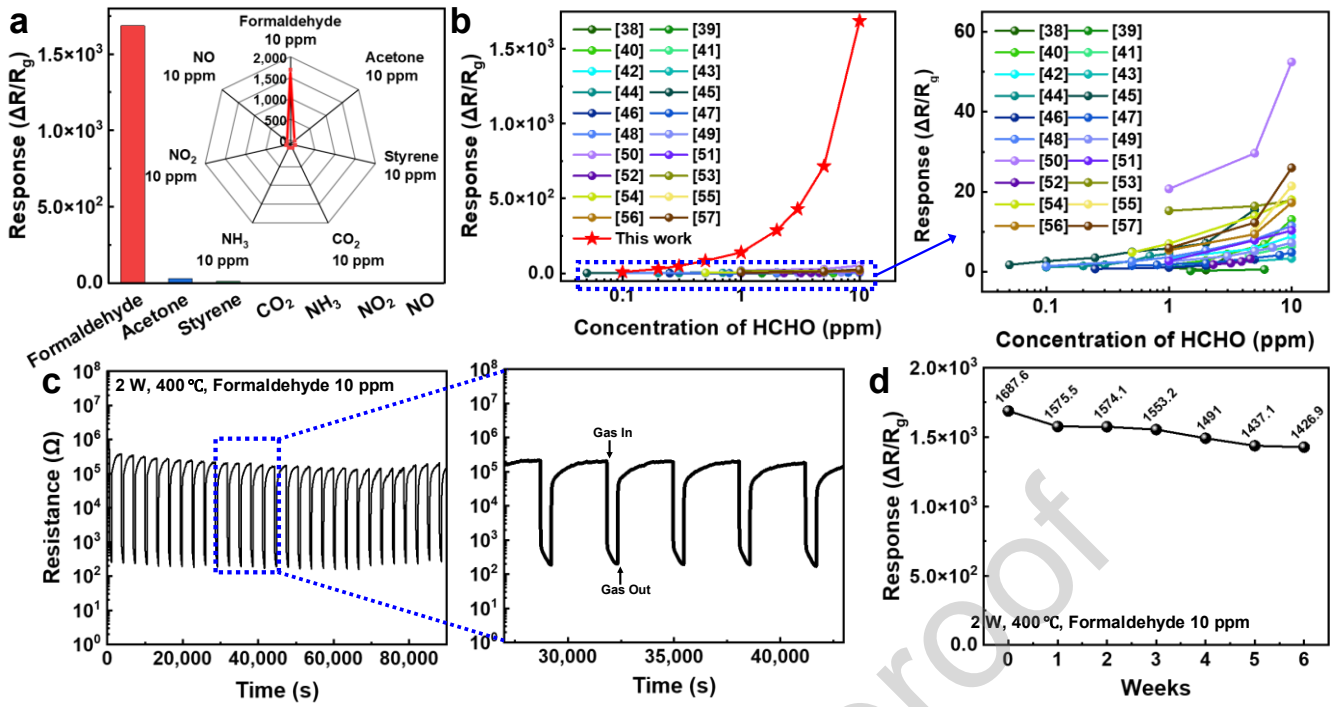
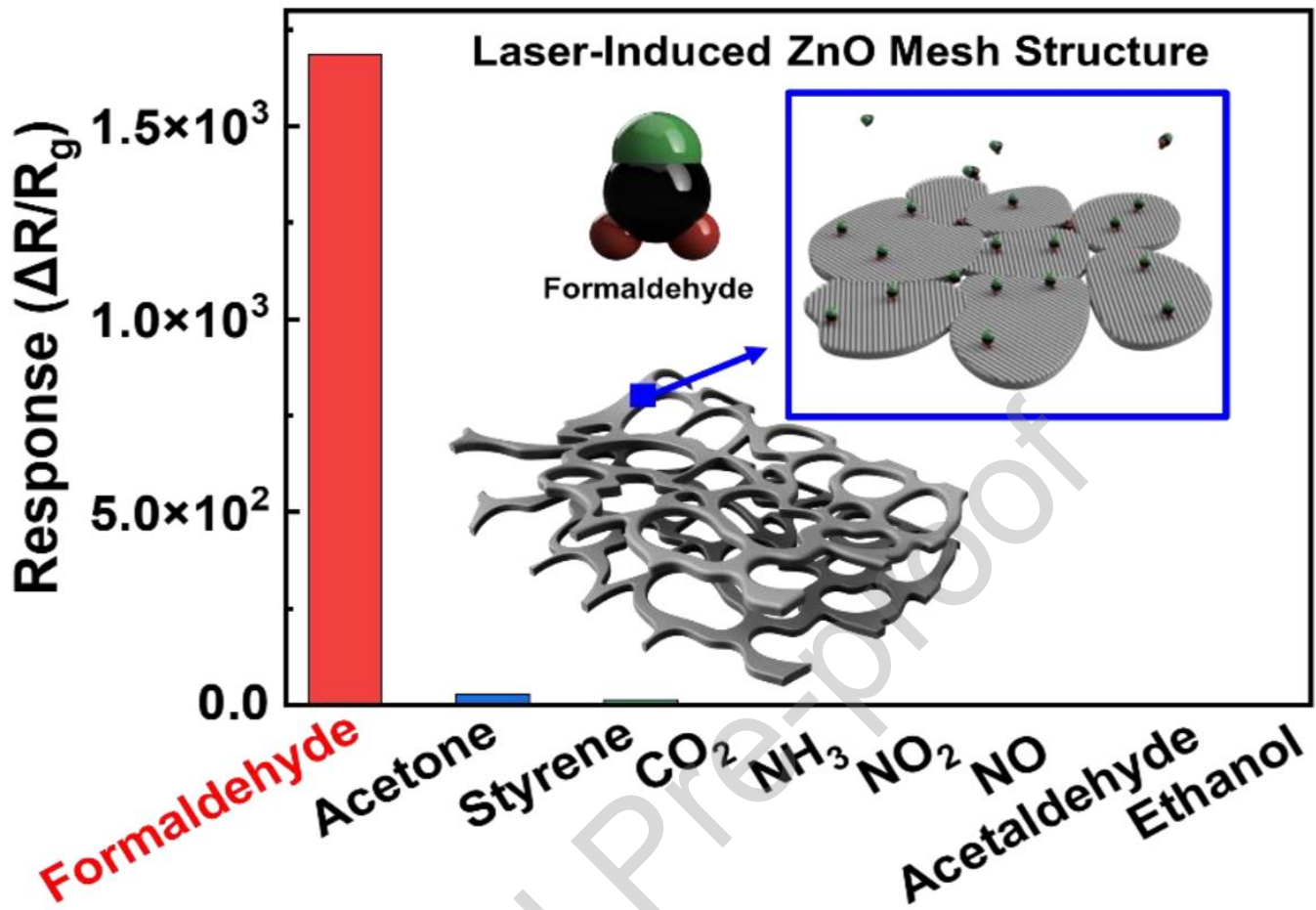


Fig. 7 (a) Gas responses toward various test gases for the 2 W laser-induced ZnO mesh sensor in a 400 °C condition. (b) Comparison of sensing response of the laser-induced ZnO mesh sensor to previously reported formaldehyde gas sensors (references were highlighted as a dashed blue box). (c) Repeated sensing transients (40 cycles), and the blue dash square shows a highlighted curve of real-time 5-cycle resistance. (d) Long-term stability in the sensing performance.



Declaration of Competing Interest

The authors declare no competing financial interest.

Highlights

- Synthesize mesh-structured ZnO by irradiating a laser to a precursor.
- Structure for gas adsorption and generation of sufficient oxygen ion species
- Excellent detection response to formaldehyde