Enhancing visible light-activated NO$_2$ sensing properties of Au NPs decorated ZnO nanorods by localized surface plasmon resonance and oxygen vacancies

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Abstract

Increasing light absorption is of crucial importance for optimizing light-activated gas detection. However, the relevant research is still far from sufficient. Herein, a high performance visible light-activated NO$_2$ gas sensor is developed relied on the localized surface plasmon resonance (LSPR) and increased surface oxygen vacancies. Au NPs decorated ZnO nanorod array as sensitive materials was synthesized via a two-step low temperature hydrothermal process. The influences of Au decoration and light wavelength on the sensing behaviors were systematically investigated. It is found that the Au NPs decoration can largely promote the visible light-activated gas sensing properties in comparison with pure ZnO film. In addition, the as-prepared sensors demonstrate excellent repeatability and selectivity as well as moisture stability. Moreover, the sensing mechanism based on LSPR was discussed in detail. This work not only sheds some lights on the fundamental understanding for the LSPR enhanced gas sensing mechanism, but also offers an approach in constructing high-performance light-activated gas sensor.

1. Introduction

Nitrogen dioxide (NO$_2$), as one of the main ambient pollution gases, not only renders acid rain and photochemical smog but also causes respiratory diseases in human [1–4]. Over the years, massive endeavors have been carried out to develop various monitoring technologies with excellent performances to detect nitrogen dioxide. Among them, the chemoresistive gas sensors hold tremendous superiority due to its fast-response, sensitive, high-efficiency and portability [3, 5–7]. So far, semiconducting metal oxides, such as ZnO, TiO$_2$, CuO, WO$_3$, and In$_2$O$_3$, have been widely employed as sensitive materials for NO$_2$ detection on account of their attributes such as easy-fabrication, low-cost, high sensitivity and long-term robustness. Recently, some nanoheterostructures with noble metal and another semiconductor have been built to improve their gas sensing properties [8–10]. However, high operating temperature is still required to achieve brilliant sensing behavior by promoting the gas diffusion and dissociation kinetics. Elevated temperature incurs high power consumption and poor long-term stability as well as safety hazards, limiting its applicability and feasibility in practical utilization. To solve this issue, light activation was utilized to enhance the mobile carrier density in sensitive materials and ensure the high performance gas sensing at room temperature [11, 12]. Nevertheless, the large band gap energy of ZnO ($E_g = 3.37$ eV) hamper its absorption in visible and infrared light region and hence the efficiency of solar-activated chemoresistive NO$_2$ detection.

Localized surface plasmon resonance (LSPR) is known as a phenomenon arising from the confinement of a surface plasmon around the nanoparticle with a size much smaller than the incident wavelength, which remarkably improves the optical absorption of nanoparticles at the plasmon resonant frequency as well as the electric fields near the nanoparticles. Since noble metal nanoparticles possess resonance at visible wavelengths,
the decoration of plasmonic metal NPs (mainly Ag and Au) into metal oxide nanostructures prominently extends the absorption spectrum profile and boosts the adsorptance in the visible region [13, 14]. Meanwhile, the enhanced electric field near the nanoparticles accelerates the separation of photo-excited electron-hole pairs, which further increase the efficiency of as-fabricated photodevices. LSPR of metallic nanostructures have extensively been employed in designing sensors requiring optical detection of gas. Liu et al [15] demonstrated antenna-enhanced hydrogen sensing at the single-particle level. They placed a single palladium nanoparticle near the tip region of a gold nanoantenna and detected the changing optical properties of the system on hydrogen exposure by dark-field microscopy. Ahmadivand et al [16] proposed a molecular nanostructure composed of Al3/Al2O3 NPs that can be employed to design precise sensors that are highly sensitive to the extremely minor environmental perturbations. In contrast, limited works has been done in the filed of LSPR enhanced gas sensors requiring electrical measurements, thereby, it is highly desired to develop visible light-activated room temperature NO2 sensor based on LSPR effect.

In this work, we demonstrate a high-performance visible light-activated room temperature NO2 sensor based on localized surface plasmon resonance (LSPR) effect. The Au NPs decorated ZnO nanorod array was synthesized as the sensitive material via a two-step low temperature hydrothermal process. XRD, SEM, TEM, XPS and UV–vis absorption spectra were employed to characterize the componential and structural properties of Au NPs decorated ZnO nanorod array film. In addition, the influences of Au decoration amount and illumination wavelength on NO2 sensing characteristics were studied. The moisture stability, repeatability and selectivity was investigated to verify the practicability of the sensors. Moreover, the physical rationale behind the phenomenon was discussed in detail to unravel the sensing mechanism for the LSPR enhanced light-activated gas sensing.

2. Experimental

2.1. Synthesis of ZnO nanorod array films
Zinc acetate dihydrate (Zn(CH3COO)2 ⋅ 2H2O), zinc nitrate hexahydrate (Zn(NO3)2 ⋅ 6H2O), and hexamethylenetetramine (C6H12N4) were purchased from Chengdu Kelon Chemical Reagent Factory (Chengdu, China), and were of analytic grade and used as received without further purification. A hydrothermal growth process consisting of two steps was utilized to synthesize ZnO nanorod array films. In this procedure, ZnO precursor solutions were prepared firstly by dissolving 10 mM Zn(CH3COO)2 ⋅ 2H2O in ethanol and stirred magnetically at room temperature for 2 h. The ZnO seed layer was formed onto the Au/Ti interdigital electrodes (IDEs, the electrode structure was described in our previous publication [17]) by spin coating (500 rpm for 5 s followed by 2000 rpm for 15 s) of the above precursor solution and heat treatment at 350 °C in air for 20 min (this process was repeated thrice). Secondly, ZnO nanorods were grown by placing the seed layer-coated IDEs vertically in a Teflon-lined stainless steel autoclave filled with a homogeneously mixed aqueous solution (20 mM) of Zn(NO3)2 ⋅ 6H2O and C6H12N4 (the molar ratio of 1:1) followed by heated to 93 °C for 4.5 h. After cooling to room temperature naturally, the obtained samples were rinsed repeatedly with deionized water and absolute ethanol, and then dried at 80 °C for the subsequent Au NPs decoration.

2.2. Synthesis of Au NPs decorated ZnO nanorod array films
Au NPs decorated ZnO nanorod array films were synthesized through another hydrothermal process [18]. Typically, a given amount (1–6 ml) of HAuCl4 ⋅ xH2O (J&K Chemicals Ltd, Beijing, China) aqueous solution (2 mg ml−1) and 1 ml methanol were added into deionized water. The pH of the solution was adjusted to 7–8 with 10 mM NaOH solution, and finally form 40 ml reaction solution under slow stirring. Then the IDEs with ZnO nanorods were immersed in it after the above solution was transferred to a hydrothermal reactor. The hydrothermal reactions proceed at 120 °C for 1 h, and when the reactor cooled down the subsequent procedures including washing and drying were carried out according to those shown in the section 2.2. The resultant Au decorated ZnO film samples were labeled ZA-1, ZA-2, ZA-3, ZA-4, corresponding to the amount of HAuCl4 aqueous solution—1, 2, 4, 6 ml, respectively. In this hydrothermal process, methanol serves as an agent reducing Au3+ ions from HAuCl4 in the solution [18]. During the second hydrothermal process, Au3+ ions are easily attracted on the surface defects of the ZnO nanorods and gradually assemble together. Followed by Au nanoparticles form along with occurrence of the reducing reaction. The corresponding mechanism is shown in figure S1 is available online at stacks.iop.org/MRX/7/015924/mmedia.

2.3. Films characterization
The crystalline structures and phase compositions of the film samples were characterized by grazing incidence x-ray diffraction (GIXRD) mode with a PANalytical X’Pert Pro MPD diffractometer (Eindhoven, Holland) equipped using Cu Kα radiation (λ = 1.5418 Å and 2θ = 20–80°) at room temperature. The morphologies of the films and the microstructures of the nanorods were observed by field emission scanning electron microscope
(FESEM, FEI Inspect F, 20 kV) and transmission electron microscope (TEM, FEI Tecnai G2 F20 S-TWIN, 200 kV). X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALAB 210 photoelectron spectrometer (VG Scientific, UK) equipped with a Mg Kα1,2 exciting source (300 W), using adventitious carbon (C 1s = 285.0 eV) as the calibration reference to analyze the surface elements. Ultraviolet-visible (UV–vis) absorption spectra were measured by a UV–vis spectrophotometer (Shimadzu UV1700, Japan) and the bandgap energies of the samples were determined by the Tauc equation.

2.4. Gas sensing measurements

The NO₂ sensing properties of the as-fabricated sensors were performed on a home-made light-activated gas sensing measurement system, and the detailed processes were described in our previous work [19]. During the measurements, UV (λ = 365 nm), blue (λ = 455 nm), blue-green (λ = 495 nm), orange (λ = 595 nm) and red (λ = 620 nm) LED light sources (3 W, Taiwan light macro chip) were applied for illuminating the sensors. The illumination intensities were determined to be 40, 70, 50, 20 and 60 mW cm⁻², respectively, using UV-A and FZ-A light irradiation meters (Photoelectric Instrument Factory of Beijing Normal University, China).

To study the influences of ambient humidity, the light-activated NO₂ sensing responses of the sensor were measured at various relative humidity (RH) levels at room temperature (∼25 °C) through injecting 5 ppm NO₂.
gas into saturated solutions of LiCl (11.3% RH), MgCl₂ (33.0% RH), NaBr (57.6% RH), NaCl (75.0% RH) and K₂SO₄ (97.3% RH), respectively.

The sensing response and sensitivity are respectively defined as \( \frac{R_g - R_0}{R_0} \) and \( S = \frac{\Delta (R_g - R_0)}{\Delta C_g} \), where \( R_g, R_0 \) and \( C_g \) are the real-time resistance of the sensing film upon exposure to NO₂ gas, the baseline resistance in dry \( N_2 \) or air and the NO₂ concentration. The response and recovery times are defined as the time required for reaching 90% variations of the sensor resistance upon exposure to NO₂ gas and air.

3. Results and discussion

Figure 1 (a) presents the Grazing Incidence x-ray Diffraction (GIXRD) patterns of pure ZnO and Au decorated ZnO nanorod array films. The characteristic diffraction peaks marked with *** correspond to the (111) and (220) crystal planes of face-centered-cubic (fcc) metallic Au (JCPDS # 89-3697). These peaks for (111) are observed only in Au decorated ZnO films, indicative of the introduction of Au ions during the secondary hydrothermal reaction process. It can be clearly seen that the intensity of peaks goes up with increasing Au content. The peaks belonging to (220) is ascribed to Au in interdigital electrodes (IDEs). The unmarked characteristic diffraction peaks can be well indexed to the hexagonal wurtzite ZnO (JCPDS # 36-1415). In addition, the dominant (002) diffraction peak confirms the preferential anisotropic growth of ZnO nanorods along [001] direction, and is gradually decreased with increasing chloroauric acid (HAuCl₄·xH₂O) concentration, indicating Cl- erosion on the ZnO nanorods. The FESEM images further validate the XRD results. As displayed in figure 1 (b), pure ZnO nanorods exhibit a hexagonal prismatic structure with a diameter of ~50 nm and a length of ~1.5 μm. These grass-like ZnO nanorods align densely and intercross with each other. Figures 1 (c)–(f) show the morphologies of the Au decorated ZnO films prepared at diverse concentrations of HAuCl₄. The configuration of the as-synthesized films varies remarkably with varying HAuCl₄ concentration. Once the concentration exceeds 0.2 mg ml⁻¹ (figures 1(e) and (f)), the ZnO nanorod array film was etched into a porous sponge structure with thickness of 500 nm. This is because with increasing HAuCl₄ concentration gradually destroys the crystal structure of ZnO nanorods owing to the strong corrosivity of Cl⁻ ions in reaction solution.

Figure 2 reveals a high resolution transmission electron microscopy (HRTEM) images of the Au NPs decorated nanorods in ZA-2 sample. It is obvious that Au NPs (the small darker points in TEM images) homogeneously attach onto the surfaces of the ZnO nanorods (figures 2(a) and (b)). The particle size of Au NPs is less than 10 nm, and a heterojunction was formed between ZnO nanorods and Au NPs (figures 2(c) and (d)). The interplanar spacings of 0.520 nm and 0.280 nm respectively correspond to the (002) and (100) lattice planes.
of hexagonal ZnO, which signifies the dominantly exposed non-polar (100) planes in ZA-2 sample. The interplanar spacings of 0.235 nm is related to the (111) lattice planes of Au with fcc structure.

The core level XPS spectra was employed to investigate the surface chemical state of pure ZnO and Au NPs decorated ZnO films, as presented in figure 3. The strong signal peaks associated with Zn, O and Au elements (figure 3(a)) demonstrate the high purity of ZnO and Au decorated ZnO film. The detected C element can be attributed to the hydrocarbon from XPS instrument itself [20]. In high resolution Zn 2p XPS spectra (figure 3(b)), the binding energies of Zn 2p_{3/2} and Zn 2p_{1/2} peaks are located at 1021.7 ± 0.4 eV and 1044.8 ± 0.4 eV, respectively. A spin–orbit splitting of 23.1 eV is consistent with that of photoelectrons excited from Zn^{2+} atoms in the ZnO crystal lattice [21, 22]. The weakening Zn 2p XPS peak and its slight chemical shift toward high binding energy with increasing Au content (i.e., an increase in HAuCl₄ concentration) indicate the deficiency of O atoms [23]. In high resolution Au 4f XPS spectra (figure 3(c)), the Au 4f peaks of Au NPs

| Samples | O_L (eV) | O_C (eV) | Percentage of O_L to total O (%) | Percentage of O_C to total O (%) |
|---------|---------|---------|---------------------------------|---------------------------------|
| ZnO     | 530.30  | 531.84  | 26.68                           | 73.32                           |
| ZA-1    | 530.72  | 532.14  | 9.90                            | 90.10                           |
| ZA-2    | 530.49  | 532.09  | 8.24                            | 91.76                           |
| ZA-3    | 530.70  | 532.43  | 15.11                           | 84.89                           |
| ZA-4    | 530.68  | 532.78  | 6.52                            | 93.48                           |

Figure 3. (a) XPS survey spectra, (b) Zn 2p, (c) Au 4f and (d) O 1s XPS spectra of pure ZnO and Au NPs decorated ZnO nanorod array films.
decorated ZnO films obviously overlap with the Zn 3p peaks, which can be resolved into several peaks corresponding to Au 4f$_{7/2}$ (83.3–84.0 eV), Au 4f$_{5/2}$ (86.5–87.7 eV), Zn 3p$_{3/2}$ (87.7–88.7 eV) and Zn 3p$_{1/2}$ (90.2–91.5 eV), respectively, via a Gaussian fitting method. Such a strong Au XPS signal demonstrates the metallic nature of Au NPs attached on the ZnO surfaces [21]. For ZA-2 and ZA-3 samples, the relatively weaker Au 4 f peaks is attributed to the uniform distribution of Au NPs. However, the erosion of ZnO nanorod array structure under high concentration of HAuCl$_4$ aqueous solution gives rise to the aggregation of Au NPs (figure 1(f)), consequently, Au 4 f peak enhances and the corresponding binding energy values approximate those of bulk Au (4f$_{7/2}$ ~ 84.0 eV and 4f$_{5/2}$ ~ 87.7 eV) [24, 25]. It is noted that the binding energy shifts (toward low binding energy direction) of ZA-1 and ZA-2 samples can be attributed to the strong interactions between Au NPs and ZnO nanorods [21, 24, 26]. In general, the donor level of ZnO is nearly equal to the Fermi level of Au (5.4 eV), and correspondingly electrons easily transfer from ZnO to Au, causing an increment in the charge density on Au NP surfaces [22, 25]. These interactions has been proved to enhance photocatalytic activity [27, 28].

As shown in figure 3(d), the asymmetric peaks of O 1 s can be deconvoluted into two components located at 530.5 ± 0.3 eV and 532.3 ± 0.5 eV, denoted as O$_1$ and O$_2$, respectively. The O$_1$ peaks are associated with the lattice oxygen of ZnO [22, 24] while the O$_2$ peaks are arisen from the chemisorbed oxygen species (such as adsorbed OH, H$_2$O or O$_2$) on the surfaces of ZnO nanorods [29]. The calculated percentages from the quantitative analysis of XPS spectra were summarized in table 1. The Au decoration onto ZnO nanorods rises the ratio between O$_2$ component and O$_1$ component, validating the introduction of surface oxygen vacancies.

The UV–vis absorption spectra of pure ZnO and Au decorated ZnO films are shown in figure 4(a). Two absorption band in the UV region (300–370 nm) and visible region (around 534 nm) are respectively originated from the band edge absorption of ZnO and the localized surface plasmon resonance (LSPR) absorption of Au NPs [25, 30, 31]. The light absorption (300–800 nm) is proportional to the Au content. This is due to the fact that...
the enhanced surfac-to-volume ratio coming from the Au NPs decoration favours the absorption of incident light, as reveal in figures 1(b)–(f). According to the plot of \((\alpha \nu)^2\) versus photon energy \((\nu)\) in figure 4(b), the increasing Au content lowers bandgap energy of Au NPs decorated ZnO films. This might be ascribed to that the induced surface oxygen vacancies during the preparation introduce impurity energy levels into bandgap.

Figure 5 demonstrates the NO\(_2\) sensing performance of pure ZnO and Au NPs decorated ZnO films under 365 nm light illumination \((40 \text{ mW cm}^{-2})\) at room temperature. It can be clearly seen that Au NPs decorated ZnO film sensors exhibit much higher response and sensitivity than those of pure ZnO nanorod array film sensor, where the maximum response and sensitivity were observed in ZA-2 sensor (figure 5(b)). The high baseline resistance and poor recovery behaviour of the ZA-4 sensor are ascribed to the fact that the strong corrosivity of HAuCl\(_4\) in reaction solution devastates the conductive paths of photogenerated charge carriers in ZnO nanorod array. Therefore, the conductivity relative variation toward NO\(_2\) was suppressed as revealed in figure 5(b) and inset.

To investigate the effects of illumination wavelength on the light-activated gas sensing properties, the NO\(_2\) sensing performance of the ZA-2 sensor were measured under various light wavelengths from 365 nm to 620 nm, as shown in figure 6. The baseline resistance of the sensor rises with the wavelength (figure 6(a)) as fewer photogenerated charge carriers were excited under long-wavelength illumination because of low photon energy. A better response and sensitivity \((1.093 \text{ ppm}^{-1})\) was achieved under 495 nm light illumination in comparison

Figure 6. NO\(_2\) sensing characteristics of ZA-2 sensor under light illumination at various wavelengths at room temperature \((-25^\circ\text{C}, 0\% \text{RH})\); (a) Electrical resistance changes, (b) response changes and (c) response-concentration plots of the ZA-2 sensor toward NO\(_2\) with concentrations ranging from 1 ppm to 5 ppm. (d) Comparison of dynamic response profile under various wavelength light illumination. (e) Effect of light wavelength on the response time and recovery time of the ZA-2 sensor when exposed to 5 ppm NO\(_2\). (f) Repeatability of the sensor under 1 ppm NO\(_2\).
Table 2. Sensing properties comparison of sensors towards NO\textsubscript{2} gas.

| Materials                              | NO\textsubscript{2} concentration (ppm) | Operating conditions | Response \((\frac{R_g-R_0}{R_0}) \times \text{sensitivity (ppm}^{-1}\) | Reference |
|----------------------------------------|----------------------------------------|----------------------|------------------------------------|-----------|
| Au-functionalized porous ZnO nanosheets| 1–5                                    | RT\textsuperscript{(385 nm/1.2 mW cm\textsuperscript{−2})}      | 1.05 (1 ppm 0.623)                 | [32]      |
| Au-functionalized ZnGa\textsubscript{2}O\textsubscript{4} nanowires | 1–5                                    | RT\textsuperscript{(385 nm/1.2 mW cm\textsuperscript{−2})}      | 0.22 (1 ppm 0.930)                 | [33]      |
| Au-ZnS nanowires                       | 1–5                                    | 300 °C\textsuperscript{(254 nm/1.2 mW cm\textsuperscript{−2})} | 7.84 (5 ppm 1.535)                 | [34]      |
| Au-decorated ZnO microspheres         | 10                                     | 120 °C\textsuperscript{(a)}                          | 1.41                               | [35]      |
| MoS\textsubscript{2}-Au thin films     | 2.5                                    | RT (25 °C)\textsuperscript{(365 nm)}                 | 0.30                               | [36]      |
| Au-ZnO nanorod array films            | 1–5                                    | RT (25 °C)\textsuperscript{(495 nm, 50 mW cm\textsuperscript{−2})} | 1.25 (1 ppm 1.093)                 | This work |

\textsuperscript{a} Under continuous light illumination.

\textsuperscript{b} Where \(R_g\) and \(R_0\) are the resistance of the sensing film upon exposure to target gas and baseline resistance in background gas.

\textsuperscript{c} Slope of response-concentration plots.
with the other visible wavelength (figures 6(b) and (c), S2). This discrepancy can be interpret in terms of the coupling between photoelectric effect and chemoresistive effect. Considering the number of effective adsorption sites is fixed on the surface of sensitive film, under short-wavelength illumination, the numerous photogenerated charges make the charge transfer amount during gas adsorption quite negligible in comparison with total charge amount ($\Delta R/R$), leading to a limited response. While, under long-wavelength irradiation, fewer photogenerated charges is responsible for the little variation of the resistance and hence a low response. Therefore, the amount of surface-accumulated electrons plays an dominant role in the light-activated NO$_2$ gas detection\cite{19}, and an appropriate carrier amount gives rise to a optimal sensing properties. A comprehensive performance comparison of recently reported semiconductor NO$_2$ sensors is listed in table 2, where the as-prepared Au NPs decorated ZnO film sensors in this work deliver superior NO$_2$ sensing properties at room temperature than the previously reported NO$_2$ gas sensors (table 2).

The influence of incident wavelength on the real-time response and recovery behavior of the ZA-2 sensor was measured toward 5 ppm NO$_2$ (figure 6(d)), in which the reduced photon energy (at longer wavelength) dramatically prolongs the response and recovery times by orders of magnitude (figure 6(e)). Reproducibility is one of the key parameters for practical gas sensor. Little fluctuation in resistance was observed in five sensing cycles of 1 ppm NO$_2$ injection as displayed in figure 6(f), indicating a good repeatability.

To explore the influence of ambient moisture on the sensing properties, the real-time electrical resistance and the response of the ZA-2 sensor was respectively recorded at various relative humidity (RH) levels, as displayed in figures 7(a) and (b) (figure S3, supporting information). The response of the ZA-2 sensor falls down with increasing ambient humidity (figure 7(b)). This is because that the water molecules occupy the adsorption sites of on the surface of ZnO and inhibits the adsorption of O$_2$ and NO$_2$\cite{35,36}, shrinking the response of the sensor. Conversely, the adsorption of NO$_2$ molecules on the sensor surface reaches a saturation state faster when the adsorbed water molecules increase. Therefore, it is found that the increased moisture level shortens the response time but has insignificant influence on the recovery time (figure 7(c)). In addition, the ambient moisture has insignificant influence on the recovery time. To explore the ability of the fabricated sensor in distinguishing NO$_2$ from mixed gas atmosphere, the response to NO$_2$ (5 ppm) was compared with other

![Figure 7. Practicability of the ZA-2 sensor exposed to NO$_2$ gas under 495 nm light illumination (50 mW cm$^{-2}$) at room temperature ($\sim25$ °C): (a) Electrical resistance changes and (b) response changes of the sensor under various moisture when exposed to 5 ppm NO$_2$. (c) Plots for response time and recovery time versus RH of the ZA-2 sensor. (d) Selectivity of the sensor with presence of interference gases (0% RH).]
interfering gases under 495 nm light illumination at room temperature, including HCHO (50 ppm), CH₄ (100 ppm), NH₃ (10 ppm), H₂S (30 ppm) and CO₂ (10k ppm), as shown in figure 7(d). The response to NO₂ is at least 50-fold higher than other interfering gases, implying an excellent selectivity.

Figure 8 illustrates the mechanism of the visible light activated gas sensing enabled by LSPR absorption and surface oxygen vacancies. At the metal–semiconductor interface, the Fermi level of ZnO shifts to a more positive potential with the electron transferring from ZnO nanorods to Au NPs, resulting in an upward band bending at the interface and the Schottky barrier. The light–excited electrons produced in Au NPs can overcome Schottky barrier and inject into the CB of ZnO due to the LSPR absorption upon exposure to visible light [37–39]. Meanwhile, oxygen vacancies introduce defect levels between the valence band and conduction band of ZnO, which is conducive to the transition of trapped electrons at oxygen vacancies to conduction band induced by the visible light illumination [33]. As a result, more free electrons are capable of participating in chemical specific reaction with surface-adsorbed O₂ and NO₂ molecules, leading to a larger responsivity.

4. Conclusion

In summary, a LSPR enhanced visible light-activated NO₂ sensor was developed. A two-step low temperature hydrothermal process was applied to synthesize Au NPs decorated ZnO nanorod array as sensitive materials. The experimental results show that the film morphology is substantially affected by the concentration of HAuCl₄ aqueous solution and the sensor fabricated at 0.1 mg ml⁻¹ exhibits the optimal sensing performance. The LSPR effect together with the increased surface oxygen vacancies promotes the light activated gas sensing properties. Furthermore, the influence of wavelength and moisture on the sensing performance were investigated. This work demonstrates a strategy in optimizing visible light activated gas sensing and looks into the working principle of LSPR enhanced light assisted activity.

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