High Sensitivity of NO Gas Sensors Based on Novel Ag-Doped ZnO Nanoflowers Enhanced with a UV Light-Emitting Diode

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ABSTRACT: An ultraviolet-enhanced (UV-enhanced) nitric oxide (NO) sensor based on silver-doped zinc oxide (ZnO) nanoflowers is developed using a low-cost hydrothermal method. The results indicate that silver (Ag) ions were doped into the ZnO nanostructure successfully, thus changing the morphology. In the high-resolution transmission electron microscopy images, we also found that some Ag ions were separated out onto the surface of the ZnO nanoflowers and that the Ag-doped and Ag nanoparticles improved the sensing property. The NO sensing property increased from 73.91 to 89.04% through the use of a UV light-emitting diode (UV-LED). The response time was approximately 120 s without the UV-LED, and the UV-enhanced Ag-doped ZnO nanoflower sensor exhibited a reduced response time (60 s). The best working temperature could be reduced from 200 to 150 °C using UV light illumination, and it was found that the NO response increased by 15.13% at 150 °C. The UV photoresponse of the Ag-doped ZnO nanoflowers and the mechanisms by which the improvement of NO sensing property occurred through the use of UV light illumination are discussed. The property of the gas sensor can be calibrated using a self-photoelectric effect under UV light illumination. These interesting UV-enhanced Ag-doped ZnO nanoflowers are viable candidates for practical applications.

1. INTRODUCTION

Currently, many researchers have studied the detection of nitric oxide (NO) because of environmental problems, such as the greenhouse effect and health-related problems, such as itching, breathing, and asthma. NO gas is a forerunner of acid rain and ozone-depleting substances. The concentration of NO can influence the chemical reaction time in the environment. The Occupational Safety and Health Administration (OSHA) indicated that the prevalence of pulmonary edema and fatality rates will increase when people are frequently exposed to NO gas. The permissible exposure limit of NO is 25 ppm, as indicated by OSHA. Furthermore, airway inflammation, such as bronchiectasis and asthma, can be detected by the concentration of exhaled NO as a biomarker. Previous studies have reported that transcriptional regulation and ion channel functions are influenced by NO, and thus neuron death caused by neurodegenerative diseases can be implied by the level of NO. Overall, asthma patients breathe out high concentrations of NO of approximately 35–50 ppb, which is 3–4 times higher than that breathed out by healthy people.

Semiconductor metal oxides have been widely applied in gas sensors for over several decades because of their unique advantages, including low cost, high gas sensitivity, and excellent integration with silicon microfabrication. Zinc oxide (ZnO) has a hexagonal structure, lattice constants of $a = 0.324–0.326$ nm and $c = 0.513–0.543$ nm, a high band gap energy ($\sim 3.4$ eV), and a high exciton binding energy ($60$ meV) at room temperature, which makes it one of the most popular and most widely used gas-sensing metal oxides for the detection of environmentally harmful and toxic gases such as nitric oxide (NO), ethanol, ozone (O$_3$), carbon monoxide (CO), and sulfur dioxide (SO$_2$). Recently, ZnO nanostructures, such as nanorods, nanowires (NWs), nanoflowers (NFs), nanotubes, and nanosheets have been fabricated with optimized gas-sensing properties, which have been achieved by their high surface-to-volume ratio and their
unequal physical and chemical properties originating from their microscopic sizes. Generally, low operating temperature fabrication is necessary for low-cost sensors, which is compatible with glass and even plastic substrates. Previously, a novel acetone gas sensor was reported with a low working temperature of 270 °C based on ZnO nanoneedles, which was fabricated with Ag-doped ZnO by Raffah et al.\textsuperscript{17} Lee et al. reported that urchin-like Mg-doped ZnO NWs can detect ethanol in high humidity situations.\textsuperscript{1} Thus, ZnO nanostructures can enhance the sensing properties of gas sensors.

Despite these advantages, the working temperature of ZnO gas sensors is defined as approximately 300 °C.\textsuperscript{18} Several methods have been published to reduce the working temperature of ZnO sensors, such as ultraviolet (UV) illumination,\textsuperscript{19} microheater chips,\textsuperscript{20} and metal doping.\textsuperscript{21} In a previous report, ZnO microwave gas sensors optimized by surface etching and UV illumination were introduced by Wang et al.\textsuperscript{22} Gas-sensing measurements provide a novel application to optimize the property of gas sensors working at low temperatures by using a photoinduced effect. Choopun et al. reported an ethanol response enhancement of ZnO nanostructure sensors exposed to UV illumination.\textsuperscript{23} A UV-enhanced ozone gas-sensing response of ZnO–SnO\textsubscript{2} heterojunctions at room temperature was reported by Aguir et al.\textsuperscript{24} Recently, a wide variety of ZnO nanostructures doped with noble metal Ag have become popular research area because of their unique properties. Pan et al. reported that the ZnO optical properties are enhanced by silver doping. Zhang et al. reported that Ag-doped ZnO nanostructures have enhanced gas-sensing response properties.\textsuperscript{25} To our knowledge, works on gas sensors with ZnO/Ag NFs grown using the hydrothermal method are rare. The advantages of sensors with NF structures are low working temperature and high sensitivity.

In this work, the approach mentioned above was applied for the optimization of NO gas-sensing response and working temperature by using Ag-doped ZnO NFs as a new sensing material and it was expected that the fabricated UV-enhanced Ag-doped ZnO NFs would improve NO sensing performance. Last, the potential sensing mechanism of NO derived from the UV-enhanced Ag-doped ZnO NFs was also discussed with regard to the properties of NO response with and without UV enhancement.

2. EXPERIMENTS

2.1. Preparation of Ag-Doped ZnO NFs and Gas-Sensing Devices. The Ag-doped ZnO NFs were grown with a low-temperature hydrothermal process using zinc nitrate hydrate [Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O], hexamethylenetetramine (C\textsubscript{6}H\textsubscript{12}N\textsubscript{6}, HMTA), and silver nitrate (AgNO\textsubscript{3}). To synthesize the Ag-doped ZnO NFs, aqueous solutions of 0.06 M zinc nitrate and 0.06 M HMTA were mixed under regular stirring for 20 min at 90 °C and then mixed with 1, 2, and 3 mM AgNO\textsubscript{3} solutions. The final solution was stirred for 40 min, and the temperature was maintained at 95 °C as illustrated in the following equation\textsuperscript{26}

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{N}_6 + 6\text{H}_2\text{O} &\xrightarrow{\text{heat}} 6\text{HCHO} + 4\text{NH}_3 \\
\text{NH}_3 + \text{H}_2\text{O} &\rightarrow \text{NH}_4^+ + \text{OH}^- 
\end{align*}
\] (1)

Deposition of the ZnO nanostructure occurred according to the following equation

\[
\begin{align*}
\text{Zn}^{2+} + 2\text{OH}^- &\rightarrow \text{ZnO(OH)}_2 \\
\text{Zn(OH)}_2 &\xrightarrow{\text{heat}} \text{ZnO} + \text{H}_2\text{O} 
\end{align*}
\] (2)

After stirring, the solution was immediately transferred to a Teflon-lined autoclave, which was sealed and heated up to 120 °C for 6 h. After the completion of the reaction, the autoclave was cooled to room temperature and the samples were cleaned with deionized (DI) water and dried in air. Before the hydrothermal process, a 100 nm thick ZnO film was fabricated on the substrate as a seed layer using radio frequency sputtering and annealing at a temperature of 550 °C in air for 5 min.

The as-fabricated Ag-doped ZnO NFs with 4 mol ratios of Ag and ZnO were prepared using the hydrothermal process described in the above paragraph. The gas-sensing devices were labeled AG0Z, AG1Z, AG2Z, and AG3Z, respectively, corresponding to the pure ZnO NWs, 1 mM Ag-doped ZnO NFs, 2 mM Ag-doped ZnO NFs, and 3 mM Ag-doped ZnO NFs (Table 1). Figure 1 shows a schematic of the Ag-doped ZnO NF gas-sensing device fabricated by using a 450 nm platinum (Pt) micropatterned interdigital transducer (IDT) electrode with electron beam evaporation. A specific location and region of the synthesized Ag-doped ZnO NFs were defined by photoresist. Then, the devices were placed in the hydrothermal process solution and heated up to 120 °C for 6 h. Last, the photoresist was slightly lifted off in acetone, isopropanol, and DI water and then annealed at 550 °C in air for 5 min.

2.2. Characteristics and Sensing Tests. The morphology of the Ag-doped ZnO NFs was characterized with an ultrahigh-resolution scanning electron microscope (HR-SEM;
Hitachi SU8000, Japan) and a high-resolution transmission electron microscope (HR-TEM; JEOL JEM-2100F CS-STEM, Japan). The Ag-doped ZnO NFs were analyzed using X-ray diffraction (XRD; 18 kW rotating anode X-ray generator, Rigaku) and photoluminescence (PL) emission spectroscopy (KIMMON, IK3552R-G, Japan).

A UV light-emitting diode (UV-LED) was chosen as the light source to enhance the gas-sensing device (LED, wavelength = 325 nm), and the spacing between the UV-LED and the gas sensors was 1.5 cm. A source meter (Keithley 2400) connected each gas-sensing device to a personal computer for data processing. The property of the gas sensor was tested based on the resistance of the sensing device in various gases with an accurate concentration in a test chamber (20 L). The sensing devices were operated under UV irradiation and in the dark.

The response, $S$, is defined by the following equation

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}}$$

where $R_{\text{air}}$ and $R_{\text{gas}}$ are the resistance of the sample in air and in a test gas, respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterizations of the Materials.

Figure 2 shows the ZnO nanostructures doped with different Ag concentrations measured using HR-SEM. Figure 2a–c displays SEM top-view images of the sample that are evidence of the NF structure morphology of the Ag-doped ZnO nanostructures. Figure 2a shows an SEM image of AG1Z, which demonstrates that the synthesized ZnO nanomaterials doped with a low Ag concentration exhibit low-density flower-shaped morphologies. Figure 2b exhibits the SEM top-view image of sample AG2Z, which clearly shows that the density of the as-synthesized NFs has increased. The as-fabricated Ag-doped ZnO NFs consist of several triangular-shaped petals and curved bases. These curved bases are associated with the petals in an appropriate, unique way, where nanostructures with beautiful flower-like morphologies are created. The most common diameters of the Ag-doped ZnO NF petals are ~300 nm. The lengths of the petals range from 4 to 5.5 μm, and the size of a single flower is measured to be approximately 7 μm. The SEM top view of sample AG3Z is shown in Figure 2c. It is evident that the dimension of Ag-doped ZnO NFs corresponds to the Ag concentration. The dimension of a single NF structure increased to almost 10 μm. The insets of Figure 2a–c show the HR-SEM top-view images for AG1Z, AG2Z, and AG3Z, respectively. It can be seen that the morphologies are all similar, but the dimension and the density increase with the amount of Ag-doping. The SEM cross-sectional images of AG1Z, AG2Z, and AG3Z samples are shown in Figure 2d–f, respectively. From Figure 2d–f, it can be seen that the average lengths of AG1Z, AG2Z, and AG3Z are 3.89, 4.29, and 5.87 μm, respectively. It is obvious that a higher concentration of Ag doping influences the dimension, density, and length of the Ag-doped ZnO NFs. This trend is similar to that previously reported by Rajasekaran et al.27

The crystal phase of the pure ZnO NWs and the Ag-doped ZnO NFs with different Ag concentrations was determined using XRD. As shown in Figure 3, the sharp diffraction peaks in the XRD patterns are generally identified as the characteristics of the ZnO hexagonal wurtzite (JCPDS no. 36-1451). The XRD patterns demonstrated that pure ZnO NWs and Ag-doped ZnO NFs have related peak intensities and shapes similar to those of the ZnO hexagonal wurtzite structure. In the AG3Z sample, diffraction peaks observed at angles of 2θ degree of 31.88°, 34.52°, 36.46°, 47.76°, 56.84°, and 63.12° correspond to (100), (002), (101), (102), (110), and (103) reflections of the crystal planes of the hexagonal wurtzite zinc oxide, respectively. Additionally, there are no diffraction peaks related to the Ag element, which is perhaps because of the low doping concentration of Ag. High intensities of the ZnO(002) peak were obviously observed in the pure ZnO NWs (AG0Z) and Ag-doped NFs (AG1Z, AG2Z, and AG3Z), which were located at 34.66°, 34.61°, 34.57°, and 34.52°, respectively. Figure 3b shows a comparison of all of the samples. The Ag-doped samples (AG1Z, AG2Z, and AG3Z) were demonstrated to slightly shift toward a smaller angle. This slight shift in the diffraction peaks was due to an increase in their lattice constants by the substitution of Zn2+ ions (ionic radius 0.74 Å) with larger Ag+ ions (ionic radius 1.15 Å). This trend for the Ag-doped ZnO nanostructures has already been observed in a previous report.28

PL emission spectroscopy is a reliable measurement, especially for measuring structural defects and energy bands in materials. The PL emission of ZnO has been previously reported by Voigt et al.29 It was reported that the PL emission of ZnO is strongly affected by oxygen vacancies for ZnO, and Lam et al.30 presented a correlation between PL spectra and ZnO nanostructures related to the gas-sensing property. In previous studies, the silver doping effect on the PL properties of zinc oxide has also been reported. Figure 4a shows the PL emission spectra of pure ZnO NWs (AG0Z) and Ag-doped ZnO NFs (AG1Z,
AG2Z, and AG3Z). The PL peaks of AG0Z, AG1Z, AG2Z, and AG3Z can be found at 378, 385, 389, and 392 nm, respectively. This UV emission is commonly attributed to the near band edge emission and originates from the recombination of the free excitons through an exciton collision process. The obvious red shift in the PL emission in Ag-doped ZnO NFs indicated the existence of an anisotropic energy band of the flower-like ZnO nanostructures. The broad band with a visible green emission near 625 nm is normally believed to be a result of structural defects and the radiative recombination of electrons and photogenerated holes in the crystal, such as oxygen vacancies and zinc interstitials. In the present work, the broad peak at approximately 625 nm may be attributed to the fabrication process in a poor oxygen environment because of the hydrothermal reaction in the sealed Teflon-lined autoclave. Therefore, some O\(^{2-}\) vacancies might appear in the samples. The induced hybridization leads to the replacement of Zn\(^{2+}\) ions by Ag\(^{+}\) ions in the crystals and a donor-derived impurity band because of the charge transfer to unoccupied 3d states at the ZnO Fermi level. Figure 4b exhibits the absorbance spectrum of AG2Z. A wide optical absorption range below 375 nm can be found due to the band−band transition of the ZnO wurtzite hexagonal structure. The absorbance measurement using UV−vis spectroscopy for Ag-doped ZnO NFs did not show any significant change in the absorption spectrum when Ag was doped into the ZnO lattices. The results of this study are similar to those of a previous report by Zhu et al. HR-TEM was performed to prove the doping of Ag into the ZnO structure, as shown in Figure 5. Figure 5a demonstrates the fragments of Ag-doped ZnO NFs scraped from the sample. It was found that the average size of the Ag atoms ranged from 9 to 15 nm, and some of Ag ions were separated out onto the ZnO NF surface. The high-resolution images in Figure 5b showed that the spherical Ag atom was attached to the ZnO NFs very well, and the diameter of the distributed Ag atom was around 12 nm. Figure 5c,b presents the lattice fringes with the Zn and Ag d-spacings, which were 0.264 and 0.241 nm, corresponding to the crystallographic (002) plane of ZnO and the (111) plane of the face-centered cubic Ag atoms, respectively. Figure 5e,f shows the selected-area electron diffraction (SAED) patterns confirming the existence of ZnO and Ag. Figure 5e shows the SAED patterns of the ZnO NFs, indexed as (11̅00), (011̅0), (101̅0), (1̅010), and (112̅0) planes, which illustrates the good hexagonal single-crystalline ZnO structure. Figure 5f presents an SAED image of the Ag doping atoms, where circular rings can be found that correspond to the polycrystalline crystallographic (111), (200), and (220) planes. Figure 5g shows the elemental mapping for a selected area of the Ag-doped ZnO NF sample as a pink rectangular frame, which indicates a uniform distribution of the Ag element (green) in the sample. Moreover, the other elements are also presented, such as Zn (red) and O (yellow). Thus, the measurements of energy-dispersive X-ray spectroscopy spectra and mapping are consistent with the HR-TEM results (for more details see Figure S2).

3.2. NO Sensing Performance. The nitric oxide (NO) sensing properties of the Ag-doped ZnO NFs are shown in Figure 6, where it can be seen that they have good sensitivity and response time in air under dark conditions. Figure 6a shows that the NO response of 2 mM Ag-doped ZnO NFs (AG2Z) is higher than that of the pure ZnO NFs (AG0Z) at 200 °C and that the responses of AG2Z and AG0Z were 78.95 and 68.75%, respectively. This result indicates that silver doping and precipitated silver ions can improve the response, similar to the findings of a previous report. HR-TEM was performed to prove the doping of Ag into the ZnO structure, as shown in Figure 5. Figure 5a demonstrates the fragments of Ag-doped ZnO NFs scraped from the sample. It was found that the average size of the Ag atoms ranged from 9 to 15 nm, and some of Ag ions were separated out onto the ZnO NF surface. The high-resolution images in Figure 5b showed that the spherical Ag atom was attached to the ZnO NFs very well, and the diameter of the distributed Ag atom was around 12 nm. Figure 5c,b presents the lattice fringes with the Zn and Ag d-spacings, which were 0.264 and 0.241 nm, corresponding to the crystallographic (002) plane of ZnO and the (111) plane of the face-centered cubic Ag atoms, respectively. Figure 5e,f shows the selected-area electron diffraction (SAED) patterns confirming the existence of ZnO and Ag. Figure 5e shows the SAED patterns of the ZnO NFs, indexed as (11̅00), (011̅0), (101̅0), (1̅010), and (112̅0) planes, which illustrates the good hexagonal single-crystalline ZnO structure. Figure 5f presents an SAED image of the Ag doping atoms, where circular rings can be found that correspond to the polycrystalline crystallographic (111), (200), and (220) planes. Figure 5g shows the elemental mapping for a selected area of the Ag-doped ZnO NF sample as a pink rectangular frame, which indicates a uniform distribution of the Ag element (green) in the sample. Moreover, the other elements are also presented, such as Zn (red) and O (yellow). Thus, the measurements of energy-dispersive X-ray spectroscopy spectra and mapping are consistent with the HR-TEM results (for more details see Figure S2).

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Figure 3. XRD patterns of (a) pure ZnO NWs and Ag-doped ZnO NFs. (b) Enlarged XRD patterns of the (002) peak.

Figure 4. (a) PL spectra of pure ZnO NWs and Ag-doped ZnO NFs. (b) UV−vis spectrum of as-synthesized Ag-doped ZnO NFs.

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ranging from 100 to 300 °C, where the responses of 21.6 ppb NO are 53.28, 73.91, 78.95, 75.00, and 67.25% at 100, 150, 200, 250, and 300 °C, respectively. The response of NO increased to a maximum with the temperature raised to 200 °C, and the response of NO decreased at 250 °C. Figure 6c provides a comparison of the NO responses of all sensors (AG0Z, AG1Z, AG2Z, and AG3Z) at different working temperatures. It can be seen that Ag doping improved the NO sensing properties of ZnO nanostructures and that the best sensitivity was achieved with sample AG2Z.

Figure 7a presents the measurement of sample AG2Z toward different concentrations of NO at 200 °C. The resistance of AG2Z monotonically increased when the NO concentration increased from 7.2 to 36 ppb. The AG2Z responses of AG2Z to 7.2, 14.4, 21.6, 28.8, and 36 ppb NO were 63.28, 71.06, 78.95, 86.52, and 90.14%, respectively. The slope of the sensing response to different NO concentrations was 0.960, which is a very linear rise, as shown in the inset of Figure 7a. Figure 7b shows the repeatability of sample AG2Z. The variation in the sensor response was less than 4% for a 21.6 ppb NO injection with five switching on/off cycles, indicating the reliability and stability of the Ag-doped ZnO NFs. The responses of the Ag-doped ZnO NF sensor toward 21.6 ppb testing gases including NO, SO2, formaldehyde (HCHO), ethanol, and CO were further measured, to check the selectivity of the sensor. As shown in Figure 7c, the responses of the sensor to NO, SO2, HCHO, ethanol, and CO are 78.95, 15.91, 10.63, 8.05, and 5.97%, respectively. It was also found that the Ag-doped ZnO NF sensor had a higher selectivity toward NO gas compared with the Ag-doped sensor. Figure 7d shows the relative humidity (R.H.) effect on the response of 2 mM Ag-doped ZnO NFs toward 21.6 ppb NO at 200 °C. The sensing response decreased when the relative humidity increases. The sensing response is 66.46, 59.67, 49.02, and 39.01% in 25, 45, 65, and 85% R.H., respectively, as the result is similar to the previous report of Lu et al. Overall, it was found that the NO sensing property of the ZnO nanostructure can be optimized with Ag doping. Chen and Tsang reported a similar observation of Ag-doped WO3-based sensors for the detection of NO.

In this study, we improve the gas-sensing properties of Ag-doped ZnO NFs using UV illumination. Above all, Figure 8a shows the resistance response to UV-LE at different working temperatures for sample AG2Z. The UV photoresponses of AG2Z were approximately 45.3, 31.2, 15.1, 7.2, 4.9, and 1.8% at 50, 100, 150, 200, 250, and 300 °C, respectively. It is obvious that the photoelectron activation leads to a drastic decrease in resistance when the sensor is exposed to UV light. The UV-LED obviously impacts the response of the sample at lower temperatures. Conversely, the effect of UV-LED at high temperatures is quite limited because the thermal activation of electrons is more significant than the UV effect. The ZnO band gap of ZnO partially overlaps with the broad bandwidth of the UV-LED. The response and recovery times are 120 and 122 s, respectively, without UV-LED, whereas they can be reduced to 60 and 120 s, respectively, when UV is on for optimization of the sensor (for more details see Figure S1). Thus, UV light can still stimulate the generation of carriers and accordingly raise the density of the free electron−hole pairs in ZnO even though the intensity of radiation is not at a maximum value near the ZnO energy band gap. The inset in Figure 8a presents the response of sample AG2Z when exposed to UV light at 150 °C. Figure 8b shows the response of sample AG2Z toward 21.6 ppb NO gas injection under UV-on and UV-off conditions. At the same working temperature, the measured responses of the sample AG2Z were 89.04 and 73.91% under the UV-on and UV-off conditions, respectively. It is obvious that the response of sample AG2Z to the 21.6 ppb NO gas injection increased by approximately 16% when the UV light was on as compared to the UV-off condition. In addition, the response and recovery times were also optimized when the sample was exposed to the UV-LED. The results suggest that the Ag-doped ZnO NF
sensing device exhibits an increased response and optimized recovery time for NO gas under a UV-LED.

Figure 9a shows the response of all samples to NO gas injection under UV illumination at 150 °C. Figure 9b shows the responses of the AG0Z and AG2Z sensing devices to NO gas injection under UV-on and UV-off conditions at different working temperatures ranging from 50 to 300 °C. Overall, the AG2Z UV-on responses were higher than the UV-off responses, especially at 150 °C. The response still exhibited a slight increase when the temperature was over 250 °C. It was also found that the original optimal working temperature for AG2Z is 200 °C without the UV-LED, but the best working temperature can be reduced to 150 °C under UV light illumination, where the response of the AG2Z to NO gas also increases. Conversely, the response of the pure ZnO NWs (AG0Z) toward NO gas decreased with UV-LED illumination. The responses of all sensing devices toward NO gas injection were compared under UV-on and UV-off situations at 150 °C, as shown in Figure 9c. It was found that the sensing action capability with the UV-LED can be affected by Ag doping. On
the other hand, UV illumination had almost no influence on the pure ZnO NWs. Table 2 shows a comparison of the NO responses for both the pure ZnO NWs and the Ag-doped ZnO NFs with UV illumination. All of the sensing device responses toward NO gas injection based on the Ag-doped ZnO NFs were improved when the UV light was on. The optimal response to NO gas was achieved with the 2 mM Ag-doped (AG2Z) sample under both UV-on and UV-off conditions, and more Ag doping did not improve the NO response property. Additionally, it is also the importance of sensors operating at room temperature. Unfortunately, the response time was too long in our study. We will consider using metal nanoparticles to optimize the sensing properties of metal oxide sensor materials such as gold and palladium in a future work by Pinna et al.44

### 3.3. UV-Enhanced NO Sensing Mechanism

O₂ can be easily adsorbed onto the surface of Ag-doped ZnO NFs because of the extensive surface-to-volume ratio, which produces lower conductivity in the depletion layer (O₂(gas) + e⁻ → O₂⁻(adsorption)).45 The electron–hole pairs of ZnO are produced under UV-LED illumination. The light-generated holes migrate to the surface under the potential gradient, and then oxygen is desorbed from the ZnO surface because of band bending (O₂⁻(adsorption) + h⁺ → O₂(gas)).46 Thus, the concentration of free carriers increases, which reduces the thickness of the depletion layer when the NO gas is injected under the UV-on condition. The generated photoelectrons

### Table 2. Comparison of Nitric Oxide Sensors Based on Pure ZnO NW and Ag-Doped ZnO NFs with a UV-LED

| sensor | response at 100 °C (%) | response at 150 °C (%) | response at 200 °C (%) |
|--------|-----------------------|-----------------------|-----------------------|
| AG0Z   | 43.49                 | 56.09                 | 68.75                 |
| UV-off |                       |                       |                       |
| AG0Z   | 38.02                 | 51.21                 | 67.38                 |
| UV-on  |                       |                       |                       |
| AG2Z   | 53.28                 | 73.91                 | 78.95                 |
| UV-off |                       |                       |                       |
| AG3Z   | 60.12                 | 89.04                 | 82.02                 |
| UV-on  |                       |                       |                       |

**Figure 8.** (a) Resistance measurement of the UV-LED influence on the 2 mM Ag-doped ZnO NFs at different working temperatures (inset: the UV response of the 2 mM Ag-doped ZnO NFs). (b) Responses of the sample 2 mM Ag-doped ZnO NFs to 21.6 ppb NO under UV-on and UV-off conditions at 150 °C.

**Figure 9.** (a) Responses of all samples to 21.6 ppb NO under the UV-on condition at 150 °C. (b) Comparison of the responses of pure ZnO NWs and 2 mM Ag-doped ZnO to NO with and without UV-LED illumination at 150 °C. (c) Comparison of the responses of all samples toward 21.6 ppb NO in UV-on and UV-off situations at 150 °C.
easily react with the NO molecules because of the electron affinity of ZnO according to the following equation\(^{(4)}\)

\[
2\text{NO} + e^- = N_2(g) + O_2^-
\]

Figure 10 shows the UV-LED-enhanced sensing mechanism and the energy band bending of the pure ZnO NWs and Ag-doped ZnO NFs. \(^{(52)}\)

\[
\lambda_D = \left( \frac{e k T}{2 \pi q^2 N_D} \right)
\]

\[
V_s = \frac{2 \pi Q_s^2}{\epsilon N_D}
\]

where \(\epsilon\) is the dielectric constant, \(k\) is the Boltzmann constant, \(T\) is the absolute temperature in kelvin, \(q\) is the unit electron-charge, and \(Q_s\) is the charge density of the surface.

Because of the high formation energies, the incorporation of Ag at the interstitial (\(Ag_i\)) sites and the oxygen sites (\(AgO_i\)) is more difficult than the incorporation of Ag at the Zn sites (\(Ag_{Zn}\)). \(^{(50)}\) The net donor density (\(N_D\)) decreases because the substitution reaction of silver ions generally replaces the Zn\(^{2+}\) ions as acceptors in ZnO, as shown in previous studies. \(^{(52)}\) Thus, the increase in \(N_D\) leads to an increase in \(\lambda_D\), following eq 5. \(Q_s\) increases due to the reduced defect-surface ratio and causes \(V_s\) to increase (eq 6). Therefore, through eq 5, it can be found that the thickness of the electron-depleted layer, \(\lambda_{AGZ}\), increases more than that of \(\lambda_{ZnO}\), which results in the conduction channel of the Ag-doped ZnO NF (\(D_{AGZ}\)) being narrower than that of the pure ZnO NWs (\(D_{ZnO}\)). Additionally, the value of \(L\) has to be small because the electron-depleted layer thickness can be effective with regard to avoiding the flat-band condition. \(^{(50)}\) According to a previous report, \(qV_{S(1)}\) and \(N_D(ZnO)\) were \(\sim 1.45\) eV and \(\sim 10^{18} \text{ cm}^{-3}\), respectively, and the thickness of the electron-depleted layer was predicted to be \(\sim 35\) nm (\(L_{ZnO}\)) at room temperature for pure ZnO NWs. \(^{(50)}\) On the other hand, the \(L_{AGZ}\), \(qV_{S(1)}\) and \(N_D(AGZ)\) of Ag-doped ZnO NFs were \(\sim 115\) nm, 1.55 eV, and \(\sim 10^{17} \text{ cm}^{-3}\), respectively. \(^{(52)}\) It can be seen that Ag doping can have an effective impact on the morphology and the property of a ZnO nanostructure. Figure 10a,b shows the electron–hole pairs of pure ZnO NWs without and with UV-LED enhancement. Figure 10c,d shows the electron–hole pairs of Ag-doped ZnO NFs under the UV-on and UV-off conditions. The thicknesses of the electron-depleted layer, \(L_{ZnO(UV)}\) and \(L_{AGZ(UV)}\), decreased because the photogenerated holes migrated to the surface, and the surface electron–hole recombination could be discharged by adsorbed oxygen ions (\(h^+ + O_2(g) \rightarrow O_2(g)^{-}\)). \(^{(47)}\)

According to the nanostructure characterization presented above, it can be inferred that the properties of the Ag-doped ZnO NF sensor were improved more than those of the pure ZnO NW sensors under UV-LED illumination. This is similar to the previous study by Lupan et al., \(^{(52)}\) which reported that a narrower conduction channel of the silver-doped zinc oxide single NW leads to photocurrent enhancement. Interestingly, the same interaction can be observed for the UV-LED-enhanced Ag-doped ZnO NF sensor in this study. These results suggest that Ag doping enhances the sensing property for light-induced gas-sensing applications at low temperatures.

4. CONCLUSIONS

In this study, we demonstrated an NO sensor based on Ag-doped ZnO NFs using a hydrothermal method and UV-LED illumination was successfully applied to improve the properties of the NO sensor. The results indicate that the working temperature of the Ag-doped ZnO NFs enhanced by UV-LED illumination can be reduced to 150 °C. The NO response time was reduced by half (60 s) with a UV-LED, whereas the response time was 120 s without the UV-LED. The response of NO increased from 73.91 to 89.04% under UV light illumination and in the dark. As a result, the control of the Debye length (\(L \approx \lambda_D\)) by acceptor doping with silver ions may be the possible mechanism by which to explain the UV-LED-influenced response of the Ag-doped ZnO NFs in this study. The thickness of the Debye length for the surface layer and the interfacial potential are as follows. \(^{(47)}\)
illumination at 150 °C. This enhancement can be explained by a narrower conduction channel in the Ag-doped ZnO NFs with UV-LED enhancement. The selectivity of NO gas was significant, and the response of NO was also highly sensitive, ranging from 7.2 to 36 ppb and was repeatable (variation was less than 4%). The results of this study indicated the noteworthy potential of nitric oxide gas sensors for applications in disease detection in the human body and as environmental monitors in the future.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01882.

Effect of response time of Ag-doped ZnO NFs with UV-LED and energy-dispersive X-ray spectrometer with Ag-doped ZnO NFs (PDF)

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**Notes**
The authors declare no competing financial interest.

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