ZnO nanoparticles and nanowires decorated with platinum nanoparticles in different loading concentrations were prepared to detect low concentrations of NO₂ under 365-nm ultraviolet-light emitting diode (UV-LED) irradiation at room temperature. Solution precipitation, self-assembly crystallization, and photo-deposition techniques were used to synthesize the sensing material. The synthesized sensors at different stages of development were characterized by XRD, HRTEM and FE-SEM analyses. Although the sensing response of the pristine ZnO nanoparticles was 0.41 for NO₂ detection, the response improved significantly to 1.5 using ZnO nanowires in the identical photo-activation settings of 365 nm UV wavelength and 25 mW/cm² irradiance. The decoration of the surface of the ZnO nanowires with Pt nanoparticles further enhanced the sensing performance, whereas the 0.1 wt% Pt-decorated ZnO nanowire sensor exhibited a response of 4.33 with a 140-s response time, which is more than one order of magnitude higher and 50× faster than the response generated by the ZnO nanoparticles. This improved performance is attributed to the role of Pt active sites in promoting NO₂ adsorption on the ZnO nanowires’ surface as well as enhancing the layer electron utilization.

There has been an increasing demand for inexpensive, reliable, and high-performance gas sensors for monitoring indoor/outdoor air quality. A drawback of conventional chemical-resistive gas sensors is the high operating temperature (200 °C to 500 °C) that is required for sensor layer activation to react with target gas components. Elevated temperatures induce high cost and drift problems, and, most importantly, limit the technical applicability of the sensors in the detection of flammable gases. A new concept is to utilize recently emerged ultraviolet (UV) sources, such as UV-LEDs (light emitting diodes), to activate the sensors and allow detection of chemicals. UV-LEDs can provide adequate energy for promoting charge carriers within the optically adapted semiconductor layer to develop highly effective sensors that operate at ambient temperature. Furthermore, poisoning and deterioration of the sensing layer, such as exposure to SO₂ or NOₓ, in harsh environments is a challenge for high temperature-resistive gas sensors. In this regard, UV radiation has shown promise in desorbing surface contaminants and thus can reduce poisoning and elongate the useful lifetime of the sensor.

Developing high-performance gas sensors requires highly engineered sensing materials that effectively interact with the target gas components. Recently, ZnO nanoparticles (NPs) and nanowires (NWs) have been widely studied for photo-activated gas sensing application, especially for trace NO₂ detection, due to their unique optical and electrical properties. Fabbri et al. studied the ZnO NPs under LEDs at a wide range of wavelengths (365–525 nm) against several gases, including NO₂, alcohols, and hydrocarbons. A higher response and faster recovery time were observed at shorter wavelengths, while long wavelengths resulted in irreversible responses. Fan et al. compared the sensing performance of different patterns of polycrystalline ZnO against NO₂ under 365-nm UV-LED with 25 mW/cm² irradiance. No response was observed for ZnO NWs, while the response of ZnO NPs toward 20 ppm NO₂ and 100 ppm H₂ was 0.83 and 1.6, respectively. The improved performance of ZnO NWs was attributed to the large surface-to-volume ratio and the Joule heating effect imposed by applying continuous bias. Accordingly, Catto et al. showed that one-dimensional ZnO NWs are more sensitive to ozone under 351-nm UV-LEDs compared to ZnO NPs.

It has been shown that the photo-activity of ZnO NWs can be further improved by the incorporation of noble metals such as Platinum (Pt) nanoparticles, which have unique optical and catalytic properties. These modifications can lower the required activation energy and reduce the recombination rate of photo-generated charge carriers within the sensing material. Recently, several metal loading techniques, including conventional impregnation, photo-deposition, sputtering, and wet-chemical reduction methods, have been proposed to incorporate noble metals into semiconductor layers. However, the gas-phase approaches require expensive equipment and extreme preparation conditions for the metal precursor delivery. Although the impregnation and reduction methods are relatively simple, they suffer from large particle size distribution and lack of control of particle dispersion. In contrast, photo-deposition selectively locates the metal nanoparticles at the reaction sites, and normally no post-activation step is needed. This is due to the direct reduction of a metal salt to its metallic state as the result of the interaction with photo-induced electrons of the sensing layer. Because the photons evenly strike the sample surface, the excited electrons will cover the entire area. As a result, the particles are well-dispersed over the irradiated sample using the photo-deposition technique. The effectiveness of photo-deposition for surface modification has been reported previously in the literature.

Figure 1 represents a schematic illustration of the photo-deposition process on the surface of a semiconductor layer. In this study, the photo-responded gas sensing behavior of ZnO nanostructures is examined. The gas sensing behavior of ZnO NPs is initially characterized under different irradiances in an NO₂ environment. Then, the response of the one-dimensional ZnO structure was studied in the optimum irradiance, and the highest response, shortest response time, and complete sensor recovery was observed. Further, to rule over the energy structure of the ZnO sensing layer, Pt nanoparticles in 0.01, 0.1, and 1 wt% concentrations are loaded on the structure through a photo-deposition technique. The ZnO NPs, NWs, and Pt-loaded NWs samples are prepared by precipitation, hydrothermal, and photo-deposition methods, respectively. The results indicated that the sensor response to 5 ppm NO₂ could be significantly enhanced by using ZnO NWs and Pt-loaded ZnO NWs, compared to ZnO NPs.

Experimental

Material synthesis.—All chemicals were purchased from the Sigma-Aldrich Canada Corporation, were of analytical grade, and were used without further purification.

ZnO nanoparticles (NPs).—Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and a 2.0M ammonia (NH₃) solution in
ethanol (CH₃CH₂OH) were used as source materials. 0.89 g of zinc nitrate powder was dissolved in 100 mL of the ethanol solution. The solution was vigorously stirred for 30 min at 50°C in a water bath under a fume hood. Drops of the ammonia solution were then added to the solution at a rate of 1 drop/s while the pH value was measured continuously to reach a pH of ≥ 9. The solution was then stirred for 4 h and slowly cooled to room temperature. The resulting precipitates were centrifuged, washed, and calcined at 550°C for 2 h.

**ZnO nanowires (NWs).—Seeding.**—A substrate (pre-deposited with interdigitated gold electrodes) was cleaned with a 50–50 V% isopropanol-ethanol solution and was seeded with ZnO NPs by triple spin coating of the zinc acetate solution in absolute ethanol. The substrate was thermally treated for 2 min between each coating at 180°C to ensure adequate adhesion of NPs. The coated substrate was annealed in a laboratory muffle furnace at 250°C for 20 min.

**Growth.**—Single crystal ZnO NWs were fabricated through the technique described in the literature. The seeded substrate was placed upside-down in an aqueous stoichiometry solution of Zn(NO₃)₂.xH₂O and Hexamethylenetetramine in a glass vial. The vial was placed in a laboratory oven at 93°C for 6 h. The obtained NWs were washed with pure water and ethanol and subsequently annealed in a furnace at 350°C for 30 min.

**Platinum loading.**—In a typical procedure, the as-fabricated ZnO NWs-coated substrate was placed in a top-irradiated photo-reactor filled with an appropriate amount of hexachloroplatinic acid (H₂PtCl₆.6H₂O) in distilled water. The reaction chamber was deoxygenated with ultra-pure nitrogen for 20 minutes before irradiation. The coated substrate was then irradiated with a high-pressure mercury lamp for 30 min. After this period, the irradiation was terminated, and the Pt-loaded ZnO thin film was taken out, washed with pure water, dried at room temperature, and subsequently treated at 350°C for 20 min.

**Sensor fabrication and performance measurement.**—The sensor response measurement was performed by a laboratory-made experimental setup. Figure 2a shows a schematic illustration of the platform. Prior to the deposition of sensing layer, interdigitated gold electrodes were deposited onto the ceramic substrate using an E-beam evaporation method via an interdigitated shadow mask. The width, spacing, and length of the interdigitated electrodes are shown in Figure 2b. The UV-LED was connected to a dual adjustable power supply to control the operating intensity and was mounted outside a quartz window. The actual incident irradiance on the surface of the sensor was measured by an Ocean Optics USB2000+ spectrometer equipped with a Sony ILX511B CCD detector. The gas was introduced to the sensing chamber in certain concentrations through a set of remotely controlled mass flow controllers. Prior to each test, the sensors were blown with dry purified air for 1 h at a constant flow rate of 50 mL/min to stabilize the response and to remove moisture or any adsorbed molecules from the surface.

![Figure 1. Schematic illustration of the photo-deposition technique for metal loading.](image1)

![Figure 2. (a) Schematic illustration of the experimental platform for gas sensing measurements (b) The prepared evaporated, interdigitated gold E-beam electrodes with the sensing layer.](image2)
surface. Then, the target gas was diluted in air and was introduced into the sensing chamber with a total volumetric flow rate of 50 mL/min. Sensor resistance variations were monitored by a volt-amperometric technique in which the sensors were constantly biased by 5.0 V, and the film resistance was measured over time by a picoumeter, which was controlled using LabView software. The sensor response was defined as the change in the thin film resistance when the sensor was exposed to the target gas and pure air, and the difference in resistance was normalized by the initial resistance in air. The response time ($\tau_{\text{res}}$) and recovery time ($\tau_{\text{rec}}$) are defined as the time that it takes for the sensor resistance to change from 10% to 90% of its total variation, either in response or recovery operation, respectively.

Characterization

The morphologies and structure of the prepared sensors were characterized by the field emission scanning electron microscopes, FE-SEM (Helios NanoLab 650 dual-beam scanning microscope) and high-resolution transmission electron microscopy (HRTEM) analyses. The crystal phase and structure of the materials were also analyzed by X-ray diffraction (XRD) analysis (Bruker APEX DUO equipped with Mo and Cu sources). The photo-induced behavior of the sensor was also monitored using the Keithley 6487 Picoammeter/Voltage Source before gas exposure.

Results and Discussion

Microstructure and morphology.—Figure 3 illustrates the X-ray diffraction of prepared ZnO NPs and NWs, which exhibits the prominent pattern of hexagonal ZnO, which is indexed by JCPDS file No. 36-1451. The XRD data in Figure 3a suggest a crystalline structure of the synthesized ZnO NPs, with an average crystallite size of 53.1 nm, as estimated through the Scherrer equation ($d_{\text{crystallites}} = k\lambda/\beta\cos(\theta)$). The highly crystalline hexagonal structure of the prepared ZnO NWs can be identified from the X-ray diffraction pattern in Figure 3a. Treating the acetate precursor at 250°C results in exposed crystallographic facets of ZnO seeds to wurtzite the c-plane, thus promoting the crystallization of nanowires toward the (002) direction. The high intensity of the (002) peak at $2\theta = 34.5^\circ$ in the XRD pattern of the fabricated NWs, in contrast to its bulk (presented in supporting information) and nanoparticle counterparts, indicates that the one-dimensional growth occurred through the hexagonal c-axis crystallization. The presence of the (101) diffraction peak at $2\theta = 36.3^\circ$ is likely attributed to the secondary growth direction, particularly in structures in which the nanowire arrays are not fully-aligned, while the (100) peak at $2\theta = 31.8^\circ$ refers to the six symmetrical crystallographic planes parallel to the [002] axis with various polarities. As expected, the Pt or PtO diffraction patterns were not observed in any of the samples’ diffraction data, which confirmed the formation of heterojunction active sites on the surface of NWs, rather than homogenous doping within the crystalline structure. This is important because metal doping, the so-called homogeneous incorporation into a crystallographic structure, creates mid-band energy levels within the host materials’ bandgap, and subsequently changes the electrochemical characteristics of the host material and alters its charge transfer mechanism.

On the other hand, the surface deposition of the active metal, as a co-catalyst, promotes the rate of redox reaction while maintaining the electrochemical properties of the structure that are identical to those of the intrinsic semiconductor.

Figure 4 shows the high-magnification FE-SEM images of bare and Pt-loaded ZnO samples. The ZnO NPs in Figure 4a consist of 50–100-nm semi-spherical shape particles that have agglomerated, due to high-temperature sintering, to bundles with sizes of up to 200 nm. Comparing the crystallite size estimated from the XRD data and particles’ diameter in SEM data suggest the fairly high crystallinity of the synthesized nanoparticles, with a low density of defects and grain boundaries. Figure 4b shows the as-prepared ZnO NWs with an estimated density of $0.7 \times 10^9 – 1.4 \times 10^9$ NW/cm², a diameter between 140–300 nm, and an average length of 4.0 μm. The hexagonal tip of the prepared NWs indicates their single crystal structure with a favored growth direction toward the wurtzite c-axis, in agreement with XRD data. The high-resolution micrograph of the Pt-decorated samples revealed that the morphology of thin film is affected by the metallic precursor content during UV-induced photo-deposition. As illustrated in Figure 4c, the morphology of NW arrays remained unchanged after 0.01 wt% Pt loading, compared to the pristine ZnO NWs. However, as demonstrated in Figure 4d, increasing the Pt content in the photo-deposition solution to 0.1 wt% formed agglomerated regions within the ZnO NWs structure. The density of these regions was further increased for the 1 wt% Pt-ZnO NWs sample, as illustrated in Figure 4e. The formation of these agglomerates is likely related to the presence of photo-deposited Pt with comparable volumetric-content to NW arrays and mostly to the residues of chloroplatinic acid precursor.

To obtain a certain visual evidence of Pt NPs on the surface of ZnO NWs, High-resolution transmission electron microscopy (HRTEM) and STEM imaging were employed. The HRTEM image in Figure 5 shows the deposited Pt nanoparticles as dark spots for 1 wt% Pt-decorated samples, which are indicated by red circles that are dispersed semi-uniformly along the NW. The presence of Pt nanoparticles is dispersed semi-uniformly along the NW.
Figure 4. FE-SEM images of the prepared sensing material: (a) ZnO NPs, (b) bare ZnO NWs, (c) 0.01 wt% Pt-ZnO, (d) 0.1 wt% Pt-ZnO, and (e) 1 wt% Pt-ZnO.

nanoparticles was further confirmed through high-angle annular dark-field (HAADF) STEM analysis illustrated in the inset of Figure 5, where Pt NPs are indicated with distinct bright spots, which have an estimated size distribution of around 1.0–5.0 nm. The advantages of the photo-deposition method for the decoration of nanostructured semiconductors and conductive electrodes, compared to conventional methods such as impregnation, are well documented in the literature.31,32 For photon-mediated applications, the deposition of active sites at structural defects, where high electron density is anticipated, is highly desirable.33 Such effective decoration can be realized through in-situ photo-deposition, which results in selective deposition of Pt nanoparticles on the surface of ZnO NWs.

**Electrical properties and UV response.**—Several studies confirm that the gas sensing response can be affected by ohmic contact and contacting junctions.34,35 To understand the contribution of heterostructural resistivity of nanomaterials in the sensing response, the resistances of the sensors were measured at room temperature before and after UV-LED irradiation in the presence of pure air (Figure 6a). The observed initial dark resistance of ZnO NWs was higher than that of the ZnO NPs sensor, thus suggesting the high resistance of NWs compared to NPs. It should be noted that a significantly large dark resistance is expected from a well-defined nanowire array. However, controlling the exposed crystallographic facets of ZnO seeds in this study results in the formation of disoriented NWs, as illustrated in Figure 4b, which create ohmic contact through the NWs’ tips and eventually reduce the dark resistance. The higher dark resistance of ZnO NWs, compared to their NPs counterparts, is likely attributed to the less electrical contacts among the network of ZnO NWs that are selectively grown on seeded NPs with a self-assembly technique, compared to the agglomerated regions that exist in the ZnO NPs’ structure.

The initial dark resistance of the pristine ZnO NWs was 9 × 10⁸ Ω. As the Pt concentration on the surface of ZnO NWs increases to 1 wt%, the layer becomes more conductive and the film’s dark resistance reduces to 4 × 10⁷ Ω. The lower resistance is attributed to the higher mobility of valance electrons throughout the material, as the result of Pt nanoparticles.

Upon UV exposure, a significant resistance change was observed for ZnO NWs’ sensors (ΔR~−9 MΩ), compared to those of ZnO NPs (ΔR~9 GΩ). This observed resistance change was greater for
the samples with higher Pt contents. It has been shown that surface defects, such as oxygen vacancies, dominate the electronic properties and adsorption reactions of a metal oxide surface. Therefore, the larger change in $R_a$ before and after UV illumination can be explained based on the number of defects in the layer, which provides suitable nucleation sites for the diffusion of photo-excited electrons. Thus, Pt deposition increases the oxygen ions’ surface occupancy and results in the rapid injection of photo-excited charges to surface active sites with larger working functions and the subsequent reduction of favorable catalytic facets.

The I-V characteristics of gas sensors are known to be a promising representative of electron density and oxygen vacant defects of nanostructures. As illustrated in Figure 6b, the electrical current proportionally increases with Pt concentration in the samples, thus confirming the higher number of oxygen vacant sites. Given that the number of adsorbed oxygen ions is an indication of layer capability in adsorbing NO$_2$ molecules due to a higher number of active sites, we expect to observe enhanced sensing performance in ZnO NWs, especially for the ones that are loaded with Pt.

The photo-induced electrical behavior of ZnO NPs and pristine ZnO NWs (Figure 7a) was very stable before and after UV illumination. The resistance decreased by three and four orders of magnitudes for ZnO NPs and ZnO NWs, respectively, and reached a plateau value after some time. However, in the 1 wt% Pt-loaded sample, a slight increase was observed upon UV irradiation (Figure 7b); this increase was likely related to the electron/hole recombination and the presence of precursor residues. Indeed, irradiation mobilizes the surface electrons and results in a rapid increase in the density of charge carriers on the surface. These excited electrons are very unstable, and some of them react with the available holes, which results in a slight reduction of the layer resistivity. This phenomenon was observed repeatedly in several experiments. The resistance then reached a stable value within an hour.

Photo-induced gas sensing response.—The sensing performance of the developed sensors was tested against 5ppm NO$_2$ in the absence and presence of UV radiation at 365 nm wavelength. This wavelength was chosen based on the fact that the maximum response in UV-activated sensors can be achieved when striking photons have energy close to the bandgap of the sensing material. The bandgap of the ZnO semiconductor is about 3.3 eV at room temperature. Therefore, the appropriate UV wavelength for gas sensing calculated by Planck’s law, $\lambda = \frac{1.24}{E}$ (where $\lambda$ is the wavelength in mm and E is the bandgap energy), is around 370 nm.

In terms of gas sensing performance, no major resistance change was observed when the sensors were exposed to 5 ppm NO$_2$ in the absence of UV radiation. This poor response in dark conditions can be ascribed to the low carrier concentration, which results in the low density of adsorption sites. However, the photo-generated charge carriers under UV-LED illumination lead to a significant resistance change upon exposure to NO$_2$.

For a proper sensing performance in UV-based gas sensors, UV-LEDs must operate at the right irradiance. Irradiance is defined as the rate of light striking the surface per unit area. It depends upon the intensity and distance of the light source and mostly affects the gas adsorption/desorption processes in sensing applications. In this study, to obtain the most appropriate UV irradiance for ZnO, the sensor response to 5ppm NO$_2$ was measured under several irradiances within

---

**Figure 6.** (a) Resistances of prepared sensors in the air before and after UV illumination, (b) I-V characteristics of the prepared sensors in dark conditions.

**Figure 7.** The photo-induced behavior upon UV irradiation: (a) pristine ZnO NWs, (b) 1 wt% Pt-ZnO NWs. UV-LED was turned on at a time near zero.
the range of 8–145 mW/cm². The irradiance of the UV-LED must be adjusted to provide the highest response and stability of developed sensors with the shortest response time and complete recovery. Figure 8a shows the effect of irradiance on the response of the ZnO NPs sample. The ZnO NPs showed almost similar responses in 8 and 25 mW/cm². However, the response and recovery time constants under 25 mW/cm² irradiance were faster and more stable than that of 8 mW/cm². Furthermore, operating the sensor with higher irradiances (i.e. 65 mW/cm² and 145 mW/cm²) resulted in lower response values. This could be due to the progressive desorption of reactants at higher irradiances, which leads to a saturated surface of generated electrons with fewer numbers of active sensing sites. In other words, increasing UV irradiance shifts the following equilibrium reaction to the right direction, which leads to the desorption of NO₂ molecules and a decrease in the response.

\[
NO_2 + h\nu \rightleftharpoons NO + \frac{1}{2} O_2
\]  

Another possible explanation for the lower response values at higher irradiances could be the higher recombination rate when the density of electrons increases in the vicinity of surface. This may disrupt the electrical double layer at the interface and eventually re-inject the electrons to the bulk.

Therefore, we calculate the appropriate UV irradiance for ZnO to be 25 mW/cm², which gives a reasonable response time while demonstrating a fast sensor recovery. This is consistent with those optimal irradiances reported in the literature.\textsuperscript{12,13,38}

The gas sensing results under 25 mW/cm² against 5ppm NO₂ indicated that the response of ZnO NWs is almost three times greater than that of the ZnO NPs samples. This is mainly due to the higher surface area, the higher defect quantity, and the higher bulk density of charge carriers, which enable the sensor to adsorb more gas molecules. Although the observed response of the pristine ZnO NWs against 5 ppm NO₂ was 1.6 (Figure 8b), the response time was around 300s, which is almost twice as long as that of ZnO NPs. The long response time of ZnO NWs can be attributed to the longer migration path of gas molecules to reach the active areas within the NWs’ structure.\textsuperscript{39}

We investigated the response of the ZnO NWs’ sensors loaded with different amounts of Pt to 5 ppm NO₂ under 25 mW/cm². As shown in Figure 8c, the response time decreased significantly to about 150s upon the addition of Pt nanoparticles. However, it was revealed that the response values were highly dependent on the Pt concentration. The response of the 1 wt% Pt-ZnO sample to 5 ppm NO₂ was 0.675, which is lower than that of the sample of pristine ZnO NWs. The low response can be attributed to the excessive deposition of Pt nano-particles, which block incident photons with opaque Pt nanoparticles.\textsuperscript{40} Furthermore, the response of the sample of 0.01 wt% Pt-ZnO NWs was very similar to that of the pristine ZnO NWs, which indicates that the low concentrations of Pt would not affect the sensing response. The sensing performance of 0.1 wt% Pt-ZnO NWs to 5ppm NO₂ increased remarkably to 4.33, with a fast response time of about 150s. This improved response is attributed to the role of Pt in producing additional NO₂ adsorption sites on the ZnO surface, which function as active reduction sites for reactions that are responsible for sensing. Therefore, the enhanced response to NO₂ can be achieved only at an optimum concentration of platinum on the surface. More experiments are required to conclude the optimum concentration with more accuracy.

A summary of the sensor responses to 5ppm NO₂ and 25 mW/cm² UV irradiation is shown in Figure 8d. The obtained results indicate that forming NWs structures along with the addition of appropriate platinum concentration could result in a significant improvement of more than one order of magnitude in the sensor response compared to that of ZnO NPs. There are several research reports on photo-activated NO₂ gas sensing in the literature. Table I summarizes the highlight of the results reported in the literature and compares the responses with the 0.1 wt% Pt-loaded ZnO NWs’ sensor response of this study.
Table I. Comparison of the NO2 response of the 0.1 wt% Pt-ZnO NWs’ sensor prepared in this study under UV-LED irradiation with those reported in the literature.

| Sensing Material                | Detection Concentration (ppm) | UV wavelength (nm) | Irradiance (mW/cm²) | Response (ΔR/R₀) | Reference |
|---------------------------------|-----------------------------|------------------|--------------------|-----------------|-----------|
| Pt-ZnO NWs                      | 5                           | 365              | 25                 | 4.33            | This Study|
| 100 nm wide line ZnO            | 20                          | 365              | 25                 | 0.83            | 13        |
| Au-ZnO                          | 5                           | 365              | 1.2                | 3.55            | 45        |
| MoS2                            | 5                           | 400              | -                  | 4               | 46        |
| MoS2-ZnO NWs                    | 0.1                         | 365              | -                  | 0.5             | 47        |
| MoS2                            | 100                         | 365              | 2                  | 0.08            | 48        |
| Thin film ZnO                   | 5                           | 365              | -                  | 0.8             | 49        |
| SnO2 NWs                        | 10                          | 338              | -                  | 1.9             | 50        |
| Mesoporous In₂O₃                | 5                           | 400              | -                  | 0.11            | 51        |
| Al/TiO₂/Al₂O₃/P-Si              | 20                          | 365              | -                  | -               |           |

To evaluate the sensors’ stability, the sensing performance of the sensors to 5 ppm NO2 was measured repeatedly under the same operating conditions. The results confirmed that the responses are quite stable and reproducible. As illustrated in Figure 9, the selectivity of the prepared 0.1 wt% Pt-ZnO NWs’ and ZnO NPs’ sensors were also evaluated against interfering gases such as Ammonia (NH3) and Carbon Monoxide (CO). The experiments were performed under the same irradiation condition (365 nm wavelength and 25 mW/cm² irradiance). Although the concentrations of NH3 (50 ppm) and CO (50 ppm) were significantly greater than that of NO2 (5 ppm), the UV activated sensors showed high selectivity to NO2, while no response was observed against CO for the sensors. Decorating sensing material with Pt nano-particles could enhance the response to NH3 (0.71), compared to ZnO NPs’ sensors (0.18), but the response was still lower than that for NO2 (4.33).

**Gas sensing principle.**—The NO2 sensing mechanism of the photo-activated ZnO NPs and NWs under UV irradiation can be described as follows:

Oxygen adsorbates such as O²⁻, O²⁻, and O²⁻ that exist on the surface of ZnO in an air environment can form a space charge layer near the surface.41 In the absence of UV irradiation, only O²⁻ can react at low temperatures (i.e. 25°C). As illustrated in Figure 10, upon UV irradiation, electron-hole pairs are generated and oxygen adsorbates are accelerated. A decrease in the sensor resistance is observed upon UV radiation, which is due to the increase in the number of charge carriers or desorption of oxygen adsorbates from the surface as the result of interaction with photo-induced holes on the surface. When the sensor is exposed to NO2, gas molecules interact with more electrons and react with the adsorbed oxygen ions according to the following reactions,42,43 and thereby the resistance of the sensing material increases:

\[ NO_2(e^{-}) + h\nu \rightarrow NO_2{^-} \]  \[ NO_2 + O_2{^-}(ads) + 2e^- \rightarrow NO_2{^-}(ads) + 2O_2{^-}(ads) \]

When NO2 evacuates the sensor environment, its molecules desorb from the surface, and the sensor signal returns to its initial value. This explanation confirms that the effective participation of a larger amount of photo-generated electrons in Pt-loaded samples could improve the gas-surface interaction. Also, using the density functional theory, it has been reported that the adsorption energy of NO2 gas molecules on the oxygen-vacant sites of ZnO surface is around E_{ad} = −0.98 eV. This energy is three times greater than that of the vacant-free ZnO layer (E_{ad} = −0.30 eV). Therefore, the charge transfer from the oxygen-vacant sites to the NO2 adsorbate is much larger than that of the vacant-free sample.36,44 This means that oxygen vacancies provide effective bindings with NO2 molecules by attracting more charge from the ZnO surface, compared to the oxygen-vacant-free ZnO surface. Based on this concept, the substantial improvement in the sensor response of the Pt-loaded sensor may be attributed to the greater oxygen vacancies, which act as preferential adsorption sites for NO2 molecules.

**Conclusions**

In this research, the effects of Pt loading in different concentrations on the photo-activated gas sensing performance of ZnO NWs for the detection of 5 ppm NO2 was investigated. Single-crystal ar-

---

Figure 9. The response of the 0.1 wt% Pt-ZnO NWs sensor to 5 ppm NO2, 50 ppm CO, and 50 ppm NH3.

Figure 10. A schematic illustration of the detection mechanism of UV-LED-activated ZnO NWs’ sensors. Nanowires provide a higher surface area and enhance the adsorption capability of the sensing layer.
SEM imaging is acknowledged.

The assistance of the Centre for High-Throughput Phenogenomics at UBC for high-resolution SEM imaging is acknowledged.

Acknowledgments

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). The assistance of the Centre for High-Throughput Phenogenomics at UBC for high-resolution SEM imaging is acknowledged.

ORCID

Fariborz Taghipour  https://orcid.org/0000-0002-9001-6967

References

1. N. Faal Hamedani, A. R. Mahjoub, A. A. Khodadadi, and Y. Mortazavi, Sensors Actuators B Chem., 156, 737 (2011).
2. E. Espid and F. Taghipour, Sensors Actuators B Chem., 241, 828 (2017).
3. V. Palmisano, E. Weidner, L. Boon-brett, C. Bonato, and F. Harskamp, Int. J. Hydrogen Energy, 40, 11740 (2015).
4. C. Guo, Z. Lin, W. Song, X. Wang, Y. Huang, and K. Wang, J. Nanoparticle Res., 15 (2013).
5. T. Wu, Z. Wang, M. Tian, J. Miao, H. Zhang, and J. Sun, Sensors Actuators B Chem., 259, 526 (2018).
6. R. Chen, J. Wang, Y. Xia, and L. Xiang, Sensors Actuators B Chem., 255, 2538 (2018).
7. Y. Zhou, C. Gao, and Y. Guo, J. Mater. Chem. A, 6, 10286 (2018).
8. L. Qi, L. Yu, Z. Liu, F. Guo, Y. qiang Gu, and X. Fan, J. Alloys Compd., 749, 244 (2018).
9. H. Tian, H. Fan, J. Ma, Z. Liu, L. Ma, S. Lei, J. Fang, and C. Long, J. Hazard. Mater., 341, 102 (2018).
10. X. Su, G. Duan, Z. Xu, F. Zhou, and W. Cai, J. Colloid Interface Sci., 503, 150 (2017).
11. B. Fabbri, A. Giairdito, A. Giberi, V. Guidi, C. Malagii, A. Martucci, M. Sturaro, G. Zonta, S. Gherardi, and P. Bernardoni, Sensors Actuators B Chem., 222, 1251 (2015).
12. S. W. Fan, A. K. Srivastava, and V. P. Dravid, Appl. Phys. Lett., 95, 2007 (2009).
13. S. W. Fan, A. K. Srivastava, and V. P. Dravid, Sensors Actuators B Chem., 144, 159 (2010).
14. A. C. Catto, L. F. da Silva, C. Ribeiro, S. Bernardini, K. Aguir, E. Longo, and V. R. Mastelaro, RSC Adv., 5, 19528 (2015).
15. J. Yuan, E. S. G. Choo, X. Tang, Y. Sheng, J. Ding, and J. Xue, Nanotechnology, 21, 185506 (2010).
16. Y. Ding, B. Yang, H. Liu, Z. Liu, X. Zhang, X. Zheng, and Q. Liu, Sensors Actuators B Chem., 259, 775 (2018).
17. M. Chen, B. Yang, J. Zhu, H. Liu, X. Zhang, X. Zheng, and Q. Liu, Mater. Sci. Eng., C, 90, 610 (2018).
18. E. Espid and F. Taghipour, ECS J. Solid State Sci. Technol., 7, 3089 (2018).
19. T. Hsieh, S. Chang, C. Hsu, Y. Lin, I. Chen, T. Hsieh, and S. Chang, Appl. Phys. Lett., 53111 (2007).
20. P. Albers and K. Seibold, Phys. Inorg. Chem., 20, 1510 (1989).
21. J. He, I. Ichinose, T. Kunitake, and A. Nakao, Langmuir, 25, 10005 (2002).
22. Y. Zhang, J. Xu, P. Xu, and Y. Zhu, Nanotechnology, 21 (2010).
23. K. Wu, X. Zhao, M. Chen, H. Zhang, Z. Liu, X. Zhang, X. Zhu, and Q. Liu, New J. Chem., 42, 9578 (2018).
24. H. Liu, Y. Ding, B. Yang, Z. Liu, Q. Liu, and X. Zhang, Sensors Actuators B Chem., 271, 336 (2018).
25. N. Sakamoto, H. Ohtsuka, T. Ikeda, K. Maeda, D. Lu, M. Kanehara, T. Teranishi, and K. Domen, Nanoscale, 1, 106 (2009).
26. B. Adeli and F. Taghipour, Appl. Catal. A Gen., 521, 250 (2016).
27. B. A. Koudeshi, thesis, University of British Columbia (2017).
28. L. Zhang, M. Qin, W. Yu, Q. Zhang, H. Xie, Z. Sun, Q. Shao, H. Lao, H. Zhao, Y. Zheng, and Z. Guo, J. Electrochem. Soc., 164, H1086 (2017).
29. L. Zhang, W. Yu, C. Han, J. Guo, Q. Zhang, H. Xie, Q. Shao, Z. Sun, and Z. Guo, J. Electrochem. Soc., 164, H651 (2017).
30. B. Adeli and F. Taghipour, ECS J. Solid State Sci. Technol., 2, Q118 (2013).
31. K. Maeda, A. Xiong, T. Yoshinaga, T. Ikeda, N. Sakamoto, T. Hisatomi, M. Takashima, D. Lu, M. Kanehara, T. Setoyama, T. Teranishi, and K. Domen, Angew. Chemie - Int. Ed., 49, 8096 (2010).
32. K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue, and K. Domen, J. Phys. Chem. B, 110, 13753 (2006).
33. B. Adeli and F. Taghipour, Chem. Eng. Technol., 39, 142 (2016).
34. H. Tian, H. Fan, G. Dong, L. Ma, and J. Ma, RSC Adv., 6, 109091 (2016).
35. X. Wang, F. Sun, Y. Duan, Z. Yin, W. Liao, Y. A. Huang, and J. Chen, J. Mater. Chem. C, 3, 11397 (2015).
36. M. Ahn, K. Park, J. Heo, J. Park, D. Kim, K. J. Choi, J. Lee, and S. Hong, Appl. Phys. Lett., 93, 263103 (2008).
37. B. Adeli and F. Taghipour, Visible-Light Photocatal. Carbon-Based Mater. Based Mater., 8 (2017).
38. E. Espid and F. Taghipour, Crit. Rev. Solid State Mater. Sci., 1, 1 (2017).
39. F. H. Saboor, T. Ureda, K. Kamada, T. Hyodo, Y. Mortazavi, A. A. Khodadadi, and Y. Shimizu, Sensors Actuators B Chem., 223, 429 (2016).
40. A. Cabot, J. Arbiol, J. R. Morante, U. Weimar, N. Bársan, and W. Göpel, Sensors Actuators B Chem., 70, 87 (2000).
41. N. Yamazoe, G. Sakai, and K. Shimano, Catal. Surv. from Asia, 7, 63 (2003).
42. H. Chen, Y. Liu, C. Xie, J. Wu, D. Zeng, and Y. Liao, Ceram. Int., 38, 503 (2012).
43. J. D. Prades, R. Jimenez-Diaz, M. Manzannes, F. Hernandez-Ramirez, A. Cirera, A. Romano-Rodriguez, S. Mathur, and J. R. Morante, Phys. Chem. Chem. Phys., 11, 10881 (2009).
44. W. An, X. Wu, and X. C. Zeng, J. Phys. Chem. C, 112, 5747 (2008).
45. Y. Mun, S. Park, S. An, C. Lee, and H. W. Kim, Ceram. Int., 39, 8615 (2013).
46. Y. Kang, S. Pyo, D.-H. Back, and J. Kim, in 2017 19th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSUCERS), p. 1429, IEEE (2017).
47. Y. Zhou, C. Gao, and Y. Guo, J. Mater. Chem. A, 6, 10286 (2018).
48. R. Kumar, N. Goel, and M. Kumar, ACS Sensors, 2, 1744 (2017).
49. J. D. Prades, R. Jimenez-Diaz, F. Hernandez-Ramirez, S. Barth, A. Cirera, A. Romano-Rodriguez, S. Mathur, and J. R. Morante, Sensors Actuators B Chem., 140, 337 (2009).
50. T. Wagner, C. D. Kohl, C. Malagui, N. Donato, M. Latino, G. Neri, and M. Tiemann, Sensors Actuators B Chem., 187, 488 (2013).
51. I. Karaduman, D. E. Yildiz, M. M. Sincar, and S. Acar, Mater. Sci. Semicond. Process, 28, 43 (2014).