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Sensors and Actuators: B. Chemical





# UV light-activated gas mixture sensing by ink-printed  $WS_2$  layer

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#### **1. Introduction**

Gas sensors are continuously highly interesting due to numerous practical needs (safety, industry, medical diagnosis [\[1,2\]](#page-8-0)). Two-dimensional materials (2DMs) have become an essential platform for gas sensors. Starting from graphene, 2DMs have been extensively studied recently because of their unique properties – repeatable structures of low dimensions with interesting physical properties and a high ratio of active surface to volume [3–[5\]](#page-8-0). Transition metal dichalcogenides (TMDCs) belong to the group of 2DMs with the general formula MX2, where M is the transition metal (*e.g.*, Mo, W, Nb, Ta, Zr) and X is the chalcogen atom (S, Se, Te). Those that exhibit semiconducting properties possess band gaps dependent on the number of stacked monolayers [\[6\]](#page-8-0). Thus, their physical and optoelectronic properties can be tuned on the fabrication level and adjusted to the desired applications, which is impossible in graphene. Apart from the numerous advantages of 2D materials, sensors based on graphene or TMDCs reported up-to-date exhibit some serious shortcomings. These include complex and expensive fabrication procedures, the need to functionalize the main material to increase its selectivity, slow responsivity, limited recovery at ambient conditions and the problem with cross-sensitivity and distinguishing between different gases when they produce similar magnitude of sensing responses.

Among TMDCs,  $MoS<sub>2</sub>$  is the leading representative observed to have attractive properties for gas detection, including light-assisted sensing [7–[9\]](#page-8-0). Both visible light (corresponding to the optical band gap) and ultraviolet (UV) light were reported to enhance the gas-sensing prop-erties of MoS<sub>2</sub> [\[10,11\]](#page-8-0). Since investigations on MoS<sub>2</sub> were promising for the fabrication of sensors, studies on other semiconducting TMDCs have recently started to develop. Tungsten disulfide  $(WS_2)$  is another two-dimensional (2D) semiconductor potentially used as a gas-sensitive part of the conductometric sensors. Its bandgap is higher than the  $MoS<sub>2</sub>$ mentioned above, and, therefore, it can be even more promising for some gas sensing because of the possibility of more intense energy barrier modulations (*e.g.*, by light irradiation [\[12\]](#page-8-0)). This material is still less investigated for gas sensing applications than other 2DMs. Therefore, the experimental studies are attractive for a better understanding gas sensing mechanisms and can result in enhanced sensing properties

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and potentially new applications. Similarly to  $MoS<sub>2</sub>$ , the band gap of  $WS_2$  increases with the decreasing number of layers, going from  $\sim$ 1 eV in the bulk to  $\sim$  2 eV in the monolayered form while also changing from indirect to direct gap  $[13,14]$ . 2D WS<sub>2</sub> usually exhibits *p*-type conductivity; however, it was recently presented that its  $n/p$  property can be tuned using different fabrication methods. For instance, a drop-coated film comprising  $WS_2$  flakes exhibited *p*-type conductivity, whereas inkjet-printed layers showed *n*-type behavior due to the interaction of the ink with an inert carrier gas  $(N_2)$  during printing  $[15]$ . In general, solution processing followed by various coating and printing techniques, employed initially mainly for depositing organic materials, has become increasingly common for producing gas-sensitive layers from different 2D structures [16–[18\].](#page-9-0) Ink printing from solution with 2D flakes dispersed in the selected solvent requires less complex apparatus than chemical vapor deposition and less labor-demanding than mechanical exfoliation while preserving high production yield at low cost [\[19\]](#page-9-0). Ink-printed layers consisting of overlapping 2D flakes can provide multiple adsorption sites, particularly edges and connection spots between nanoflakes. Incident light can additionally create binding sites during the photoactivation of the sensing surface. S. Noyce *et al.*  investigated a single atomic layer of  $MoS<sub>2</sub>$  incorporated in a field-effect transistor *via* atomic force microscopy with a customized tip polarized with a selected voltage bias  $[20]$ . The authors mapped the electrical activity of the channel with MoS<sub>2</sub> monolayer and discovered specific hot spots whose activity increased with increasing voltage between the FET channel and the mapping tip. The intriguing but not yet explored issue is how light activation affects the hot spots in the 2D structure and how it can be related to gas adsorption. Mapping the sensitivity of printed  $WS_2$ layers utilized in light-assisted gas sensors can be crucial to understanding light-driven detection by ink-printed devices.

Ink-printed layers consist of multiple structures, so their specific morphology can result in lower sensitivity and selectivity than individual single-atomic layers because electron hopping between the flakes reduces the semiconducting character of the  $WS_2$  single-atom layer. Monitoring changes in DC resistance is the primary way to measure responses to gases induced in resistive sensors. However, low-frequency resistance fluctuations (fluctuation-enhanced sensing – FES) can also provide valuable information for gas detection [\[21\]](#page-9-0). The FES manifested its utility in discriminating between some organic vapors by graphene-FET  $[13]$  or identifying NO<sub>2</sub> concentrations by carbon nanotube networks [\[22\]](#page-9-0). Processes of charge trapping and scattering occurring during molecular adsorption/desorption induce fluctuations in the resistance of the gas-sensitive material [\[23\]](#page-9-0). The limited research on employing the FES method for light-enhanced gas sensors by 2D materials leaves room for original discoveries, especially for detecting mixtures of different gases by a single sensor and studying the effect of their cross-sensitivity – the practical problem that needs fixing. These issues are addressed in our studies, trying to explain the existing research gap when a low-cost gas sensor operating at RT is proposed.

This work demonstrates a resistive sensor with the ink-printed layer comprising  $WS_2$  flakes studied in the atmosphere of two gases of opposite redox properties. The measurement methodology includes collecting DC resistance responses in time and resistance fluctuations spectra in the low-frequency range (1–800 Hz) under selected ambient conditions. Electrical AFM investigated the effect of UV light activation of the WS2 layer, which confirmed that UV irradiation locally enhanced conductivity in the structure of overlapping  $WS_2$  flakes. The UV-assisted sensor was studied in different ambient gases, including the mixtures of nitrogen dioxide (NO2) and ammonia (NH3), which unraveled the specificity and complexity of detecting two crossing gases with distinct resistance and noise features. This way, we demonstrate the utility of the FES method toward mixed concentrations of gases detected by UVenhanced ink-printed sensors. Additionally, mapping of the sensing surface activity employing AFM supports understanding the effect induced by UV light. Irradiation creates (or amplifies) hot spots of enhanced carrier transport properties, which locally increases the

number of binding sites exploitable during molecular adsorption. Our work emphasizes the methodology of utilizing DC resistance monitoring with FES for UV-enhanced printed gas sensors based on  $WS_2$  flakes. By simplifying the fabrication of the WS<sub>2</sub>-based sensors and introducing the FES method and machine learning for differentiating between target species, we point toward low-cost devices for  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  detection (including mixtures of these gases).

## **2. Experimental section**

#### *2.1. Ink-printed sensors fabrication*

WS2 flakes dispersed in ethanol-water solution (concentration of flakes = 26 mg/L) were purchased from Graphene Supermarket and used as ink to print gas sensing layers. The lateral size of flakes is 50–150 nm, and their thickness is 1–4 monolayers. The structural and optical characteristics of pristine  $WS_2$  flakes, including SEM image, UV–vis absorption spectrum, Raman spectrum, and depiction of the crystal structure, can be found on the producer's website [\(www.graph](http://www.graphene-supermarket.com)  [ene-supermarket.com\)](http://www.graphene-supermarket.com). Ceramic  $(AI<sub>2</sub>O<sub>3</sub>)$  platforms from Tesla (type KBI2) were used as substrates for  $WS_2$  flakes deposition. Each sensing substrate has a platinum interdigitated electrodes structure (IDES) of line/gap width of 15/15 µm. More details on the used ceramic substrates can be found on the producer's website ([www.tesla-blatna.cz](http://www.tesla-blatna.cz)).

Prior to ink printing of  $WS_2$  layers, ceramic substrates were ultrasonically cleaned in isopropanol and acetone and cleansed with deionized water. The solution with  $WS_2$  nanoflakes was subjected to sonication for 30 minutes to ensure no aggregates. Printing of the sensing layer was realized using Nordson Precision Fluid Dispenser (type Ultimus Plus II). Droplets covering the whole IDES were formed using the needle tip of the inner diameter of 610 µm. The time of releasing a single droplet was 0.05 s, and the carrier gas  $(N_2)$  pressure was 0.04 bar. Printing repetitions were performed ten times to ensure the continuity of the printed layer between the electrodes. After the deposition of each droplet, the material was dried in airflow ( $\sim$ 50 °C) to evaporate the residuals of the solvent. The same printing procedure was performed to obtain  $WS_2$  layers on  $Si/SiO_2$  for optical imaging and on glass substrates with deposited Au layer for electrical AFM imaging. The photographs of the printing station and  $WS_2$  sensor with the scheme of the printing process are demonstrated in Fig. A1.

#### *2.2. Optical, electrical, and flicker noise measurements*

Optical imaging of the printed  $WS_2$  flakes was performed using a Delta Optical MET-1000-TRF microscope with up to 1000x magnification. AFM imaging (topographic and current) was realized using the Ntegra Prima atomic force microscope manufactured by NT-MDT (Russia). For contact mode scanning (by-sample mode), a CSG10Pt probe manufactured by NT-MDT was utilized. The probe was characterized by the following geometric parameters: cantilever length 225  $\pm 5$  µm, width 30 $\pm 5$  µm, thickness 0.5 $\pm 1.5$  µm, tip curvature radius 15–20 nm, the thickness of Pt conductive tip coating was 20–30 nm. The value of the spring constant  $(k = 0.1 \text{ N/m})$  was determined by the Sader method and corresponded to the contact force of 12 nN. The current flow was caused by applying a voltage of 5 V transversely to the applied layer. Scanning was performed at a speed of 1.01  $\mu$ m/s, corresponding to spatial resolution of 3.92 nm. UV irradiation was realized using the same LED, type PB2D-1CLA-TC (wavelength of 275 nm and optical power density of 1.59 mW/cm<sup>2</sup>) as for other measurements. The TS-150 active anti-vibration table was also part of the vibration-damping system.

For electrical and low-frequency noise measurements, IDES terminals of the sensor were connected with the measuring and biasing units *via* the Teflon board to reduce eventual leakage currents. The sensor was connected in series with the loading resistor of  $R = 478$  kΩ (having a similar magnitude to the sensor resistance). Keysight E3648A DC power supplier was used to polarize the sensor and the resistor. Time-resolved <span id="page-2-0"></span>measurements were conducted at 20 V bias, resulting in 6–10 V across the sensor. Low-frequency noise measurements were performed using the same circuit with two accumulators. Noise spectra were collected with a signal analyzer (Stanford Research Systems, model SR785), and the signal was amplified using a low-noise voltage amplifier (Stanford Research Systems, model SR560). The sensing chamber, batteries, and voltage amplifier were put inside a grounded metal shielding box covered with an amorphous cobalt foil, type MCF5 YSHIELD® (yshield. com), to reduce external noise interferences at low frequencies, the effect of ambient light, laboratory airflow, and ambient temperature changes. The sensing responses were monitored in the dark and under UV light (275 nm, 1.59 mW/cm<sup>2</sup>). UV LED was positioned close to the sensing surface (less than 0.5 cm).

The circuit used for DC and noise measurements utilized the voltage divider (sensor  $R_S$  in series with resistor  $R$ ), so  $R_S$  was calculated as  $(V_S \cdot R)/(V_0 \cdot V_S)$ , where  $V_S$  is the measured voltage across the sensor, and *R* and  $V_0$  are 478 kΩ and 20 V, respectively. Similarly, the measured voltage fluctuations (power spectral density of voltage fluctuations,  $S_V$ ) were converted into power spectral density of resistance fluctuations  $S_R$ by following dependence:  $S_R/R_S^2 = S_V/V_0^2 \cdot [(R+R_S)^2/(R\cdot R_S)^2]$ , as presented elsewhere [\[24\].](#page-9-0) The detection limit (DL) was calculated based on changes in the sensor resistance in time or the average noise spectrum in the selected frequency range (2–20 Hz). The procedure for DL estimation is described in detail in Supplementary Material.

## *2.3. Gas-sensing experiments*

We selected nitrogen dioxide  $(NO<sub>2</sub>)$  and ammonia  $(NH<sub>3</sub>)$  as target

gases due to their opposite redox properties. Both gases are harmful to the environment and humans at concentrations of single ppm and below and are relevant for studying the effect of cross-sensitivity. Dry synthetic air (S.A.) was used as a carrier gas and a reference atmosphere. To obtain selected concentrations of target gases, we mixed S.A. with calibrating gases (20 ppm of  $NO<sub>2</sub>$  diluted in S.A. or 30 ppm of  $NH<sub>3</sub>$  diluted in  $N<sub>2</sub>$ ) at specific proportions. We maintained a constant overall gas flow of 50 mL/min regulated by mass flow controllers (Analyt-MTC, model GFC17). Sensing experiments were conducted at room temperature (RT ~25 °C) and ambient pressure (~1 bar). For experiments with a humid atmosphere, relative humidity (RH) of 40 % was produced by transferring 50 mL/min of S.A. through the container with deionized water before mixing with target gases and reaching the sensing surface.

## **3. Results and discussion**

An optical image of the ink-printed layer (Fig. 1a) indicates that  $WS_2$ flakes formed a continuous film on the micrometer level after ten printing repetitions. Printing sensing layers from inks with low-viscosity solvents (*e.g.*, ethanol) usually leads to the coffee-ring effect at the edges of the released droplet, formed due to the faster evaporation of the solvent at the droplet edge than in its center [\[16\].](#page-9-0) Comparing optical images in the center and at the edge of the deposited WS<sub>2</sub> layer (Fig. A2), the discontinuity starts to be visible in some parts of the film, around 50–60 µm from the outer edge of the droplet. To avoid the inhomogeneity of the sensing layer printed on Pt electrodes (inset in Fig. 1a), the printing parameters were adjusted to form a droplet covering a larger area than only the IDES part of the ceramic substrate.



**Fig. 1.** (a) Optical image of the WS<sub>2</sub> layer under 500x magnification (the scale bar is 20 µm) printed on a ceramic substrate with IDES of line/gap of 15/15 µm (the picture of the substrate under 50x magnification in the inset). **(b)** An AFM image of the WS<sub>2</sub> layer obtained after ten printing repetitions. An AFM image in the electrical mode for **(c)** non-irradiated sample and **(d)** for the same area irradiated with UV light. The yellow ovals indicate UV-activated areas.

<span id="page-3-0"></span>The percolation path was provided by flakes overlapping each other after multiple printing repetitions. AFM image of the  $WS_2$  layer shows that the thin film consists of aggregated sub-µm flakes, and the structure height varies at around tens of nanometers [\(Fig. 1b](#page-2-0)). The thickness of the ink-printed WS<sub>2</sub> layer measured locally with a profilometer was 50 nm on average, which agrees with the AFM imaging results.  $WS_2$  thin film printed on the glass substrate with an Au conducting layer was used to map the electrical activity of the sensing surface by a polarized AFM probe. The current flowing from the conducting substrate to the probing tip through the  $WS_2$  layer was measured locally, revealing some electrically active spots corresponding primarily to the edges of the agglomerated nanoflakes [\(Fig. 1](#page-2-0)c). These hot spots provide charge transfer through the printed layer and can be correlated with the localized surface activity of the resistive gas sensor. After irradiation with UV light, the activity of spots visible in the dark was magnified, and a few appeared in new locations. Yellow ovals in [Fig. 1d](#page-2-0) highlight the hot spots visible only after irradiating the structure with UV light. Notably, photoactivation of the  $WS_2$  layer occurs non-homogeneously; however, UV light activates the surface and increases charge transfer through the printed structure by photoinduced charge carriers. Such surface activation can be beneficial for enhanced gas detection based on surface adsorption and charge transfer between molecules and the sensing surface.

We started gas sensing experiments by comparing the repeatability of DC resistance responses to  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  in the dark and under UV light. Fig. 2 shows that sensor resistance  $R_S$  varies between about 0.1 and 0.4 MΩ depending on the ambient gas and irradiation conditions when

the voltage across the sensor was set between 6–10 V. The voltage divider was supplied with a voltage  $V_0 = 20$  V. We opted for  $> 6$  V across the sensor to obtain the stable baseline; however, we observed that the relative change in the sensor resistance induced by UV light or target gas was the same regardless of the voltage supply (reduced to even 1 V), despite the semiconducting character of the WS<sub>2</sub> layer. Thus, we believe the voltage supply could be reduced at least a few times, which offers low power consumption while maintaining the sensor responsivity. Sensor baseline resistance in S.A. decreased almost twice, which can be explained by the effect of UV irradiation that cleans the surface from the adsorbed oxygen and humidity. The anti-humidity effect was observed before for UV-assisted  $WS_2/PbS$  heterostructure  $[25]$  and is a well-established effect for UV-irradiated sensors composed of low-dimensional materials [\[26,27\]](#page-9-0). Five consecutive cycles of introducing 5 ppm of NO<sub>2</sub> or NH<sub>3</sub> resulted in repeatable responses with the absolute changes in  $R<sub>S</sub>$  higher for the irradiated sensor (almost two times for  $NO<sub>2</sub>$  and more than three times for  $NH<sub>3</sub>$ ).  $R<sub>S</sub>$  increases in the presence of NO2 and decreases for NH3, as these gases exhibit opposite oxidizing/reducing properties.  $NO<sub>2</sub>$  is an electron-accepting molecule that captures electrons from the conduction band of  $WS_2$ . NO<sub>2</sub> adsorption increasing sensor resistance indicates that the  $WS<sub>2</sub>$  layer behaves as an *n*-type semiconductor. This is confirmed by the decreasing resistance after the adsorption of  $NH<sub>3</sub>$ , an electron-donating compound. Such semiconducting behavior is less common for  $WS_2$  flakes of nanoscale dimensions as this material usually exhibits *p*-type conductivity in the low-dimensional form. Nevertheless, *n*-type conductivity has been reported recently for printed  $WS_2$  layers, indicating that the fabrication



**Fig. 2.** Time-resolved measurements (sensor resistance  $R_S$ ) of the ink-printed WS<sub>2</sub> sensor in the dark and under UV light (275 nm) for five consecutive cycles of (a) 5 ppm NO2 and **(b)** 5 ppm NH3 introduction. The voltage bias *V*0 = 20 V. The effect of RH 40 % **(c)** on the sensor resistance baseline and **(d)** on responses to 5 ppm of NO2 and NH3 under UV irradiation. The value for dry S.A. conditions was derived as an average response from five cycles presented in **(a)** and **(b)**.

<span id="page-4-0"></span>process can be adjusted to tune the *n*/*p* semiconducting properties of this material [\[15\]](#page-9-0). We estimated the response and recovery times based on cycles from [Fig. 2](#page-3-0)a ( $NO<sub>2</sub>$ ) and [Fig. 2b](#page-3-0) ( $NH<sub>3</sub>$ ) as an average value from five consecutive detection cycles. We define the response and recovery time as the time required for the sensor to reach 90 % of the saturated response/recovery. In the case of  $NO<sub>2</sub>$ , the average response time was 1218 s in the dark and almost two times shorter – 656 s under UV light, whereas the recovery time was 1122 s in the dark and only 450 s under irradiation. For  $NH_3$ , the response/recovery time was  $874/908$  s in the dark and 630/646 s under UV light, showing an enhancement in the speed of operation for both investigated gases when the sensing surface is irradiated.

We also tested the effect of relative humidity (RH) on sensing responses. We utilized humid air of  $RH = 40$  % and measured how the sensing baseline stabilized in time. In [Fig. 2c](#page-3-0), we notice that a humid atmosphere increases the sensor resistance by  $\sim$  20 % in the first 30 minutes, and then the baseline stabilizes. Moreover, we tested whether such humid air changes the sensor responsivity to  $NO<sub>2</sub>$  and NH3. [Fig. 2d](#page-3-0) compares the relative changes in sensor resistance obtained in dry and humid S.A., which are close in values. Notably, in our measurements, we reduce the effect of humidity by utilizing irradiation with UV light. Water molecules occupy some adsorption/desorption centers, but UV irradiation assures sufficient binding sites for investigated gases. Thus, the responses to  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  are similar, at least for RH ~40 % (the typical value for indoor ambiance). Therefore, we focused on studying sensing responses in dry S.A. for further experiments with varied and mixed concentrations of  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ . We also want to notice that the sensor baseline resistance was stable and remained at similar levels after irradiation with UV light ( $\sim$ 300 kΩ) for more than nine months. The sensor also maintained its responsivity to two investigated gases ( $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ ) and their mixtures over a few months of exploitation. We observed that the sensor DC resistance stabilizes under UV light after polarizing the sample, and the irradiation time can be modulated and extended if necessary when the sensor remained in the ambient conditions for longer or aged.

Next, we tested the sensor responsivity to selected concentrations of target gases under UV light. Fig. 3 depicts the results of the quantitative detection of  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  (1-10 ppm) established as the relative changes in the sensor resistance, where the reference condition was baseline resistance  $R_0$  at the beginning of each measurement (Time  $=$ 0 from the corresponding graphs). The results demonstrate that  $NO<sub>2</sub>$ induces more significant changes in  $R<sub>S</sub>$  than  $NH<sub>3</sub>$ , presumably ascribed to the higher adsorption energy of NO<sub>2</sub>. Thus, 10 ppm of NO<sub>2</sub> changes  $R_S$ to 20 %, whereas the same ammonia concentration induces a resistance decrease of less than 10 %. We also tested if the sensor responds to other

gases, *e.g.,* organic ethanol. DC resistance measurements with 110 ppm of ethanol revealed a response of  $~68$ %. It signals that the WS<sub>2</sub> sensor has limited selectivity and can be highly sensitive to various gases; therefore, an extended methodology of measurements and data analysis are required to utilize the unmodified ink-printed  $WS_2$  layers as gas sensors in practical applications.

Apart from the sensor DC resistance in selected atmospheres, the random resistance component can provide information about the detected gases and their concentrations. [Fig. 4](#page-5-0) summarizes the noise spectra collected for selected concentrations of  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  $(1-10$  ppm) in the dark and under UV light. WS<sub>2</sub> sensor exhibits  $1/f$ -like noise in the investigated frequency range, and the noise intensity gradually increases with the increasing concentration of both gases. The lack of distinct Lorenztian components in the spectrum indicates that the observed noise is most likely generated by multiple trapping states over a wide range of relaxation times. Then, the ultimate low-frequency noise spectrum is the summation of numerous events of different lifetimes observed in semiconductors [\[28\].](#page-9-0)

[Fig. 5](#page-5-0) shows the product of normalized power spectral density of resistance fluctuations and the frequency  $S_R(f)/R^2\times f$ . A concentration of 1 ppm induced a minor effect close to the S.A. case for both species. Producing the concentration of 1 ppm was burdened with a significant error due to limitations of the utilized gas calibration system, so this point was omitted in the subsequent analysis of noise responses. The data points in [Fig. 5](#page-5-0) correspond to the average value from the 2–20 Hz frequency range, selected as the most informative noise bandwidth preserving linear dependence with gas concentration increase, and show the differences between the noise amplitude in the dark and under UV light. The change in  $S_R(f)/R_S^2 \times f$  due to increasing gas concentrations follows a linear dependence. In the case of all concentrations of  $NH<sub>3</sub>$ , the variation between dark and light-enhanced conditions is minor. For NO2, the differences start to be more apparent for higher concentrations, over 2 ppm. In this case, the change in the noise amplitude is steeper for the UV-irradiated sensor. Even though  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  produce opposite changes in sensor DC resistance, the adsorption of both gases causes increased resistance fluctuations. The adsorbed molecules act as scattering centers for charge carriers, like additional surface defects, increasing flicker noise intensity with the number of adsorbed/desorbed molecules (increased gas concentration).

The dependence between the relative change in DC resistance or noise amplitude and concentration of target gases informs about the sensitivity of the investigated WS<sub>2</sub> gas sensor. [Fig. 6](#page-6-0) presents the relative changes in sensor DC resistance or normalized power spectral density of resistance fluctuations multiplied by *f* in reference to the case of S.A. Detection limits (DLs) for  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  were calculated separately for



**Fig. 3.** Time-resolved measurements (relative change of sensor resistance Δ*R*<sub>S</sub> in reference to *R*<sub>0</sub> in S.A.) of the ink-printed WS<sub>2</sub> sensor under UV light (275 nm) for **(a)**  $1-10$  ppm  $NO_2$  and **(b)**  $1-10$  ppm  $NH_3$ . The voltage bias  $V_0 = 20$  V.

<span id="page-5-0"></span>

**Fig. 4.** Power spectral density of resistance fluctuations  $S_R$  normalized to the square of sensor resistance  $R_S^2$  measured between 1–800 Hz for selected concentrations of NO2: **(a)** – in the dark and **(c)** – under UV light (275 nm); and NH3: **(b)** – in the dark and **(d)** – under UV light (275 nm). Dashed lines marked on the graphs follow the 1/*f*-like dependence. The voltage bias  $V_0 = 20$  V.



**Fig. 5.** The product of normalized power spectral density of resistance fluctuations  $S_R(f)/R_S^2$  and frequency  $f$  as an averaged value in the range 2–20 Hz for NO2 and NH3 in the dark and under UV light (275 nm).

DC resistance and noise data. For NO<sub>2</sub>, DL was estimated as 103 ppb from DC resistance responses and 220 ppb from noise responses. Additional DC resistance measurements with  $NO<sub>2</sub>$  of lower concentrations (50–500 ppb) showed that the  $WS_2$  sensor is responsive to concentrations at ppb level for this gas (see Fig. A3). Theoretical DL estimated for

data points obtained in the low-concentration range was only 6 ppb, showing a potential of the printed sensor working with high-sensitivity when the high-accuracy measuring equipment is used. Even though lower DL was obtained from DC measurements, the noise responses were approximately two times higher for all concentrations. For instance, adsorption of 10 ppm of  $NO<sub>2</sub>$  resulted in the growth in sensor resistance by 22 %, but the average noise intensity increased by 52 %. The difference between resistance and noise responses is even more apparent for NH<sub>3</sub>. For 10 ppm of ammonia, resistance change was only 7 %, whereas the noise intensity increased by 41 %, which is almost six times higher. Moreover, DL estimated using noise measurements was reduced to 168 ppb for  $NH_3$ . The results of DL estimation are biased by lower accuracy of noise measurements due to random error of the estimated power spectral density (averaging within 400 spectra, each at observation time  $= 1$  s, supports the reduction of the random error to 5 %). Moreover, the method of DL estimation has additional limitations in the case of nonlinear sensor response. The corresponding DL values can be much better when we only apply more accurate noise measurement results and the range of DC resistance changes versus gas concentration to its linear dependence. These factors will reduce the RMS value estimated for the noise data and result in lower DL values.

The effect of cross-sensitivity to various gases of different sensing materials is a challenge for producing highly efficient devices – sensors able to detect gas mixture components. Although the selectivity to particular analytes can be improved through surface functionalization or fabricating hybrid structures and, therefore, can limit the effect of background species, the cross-reactivity of sensors based on 2D materials requires broader studies. Two target gases investigated in this work

<span id="page-6-0"></span>

**Fig. 6.** Dependence between the concentration of the target gases and the relative change of (a) sensor resistance  $\Delta R_S$  in reference to  $R_0$  in S.A. or (b) normalized power spectral density of resistance fluctuations multiplied by *f* as the average value in the 2–20 Hz range Δ*S*<sub>R</sub> in reference to *S*<sub>R0</sub> in S.A. Solid curves refer to the polynomial functions fitted to the experimental data points, and dashed lines are linear fits used to estimate detection limits.

are common toxic species occurring in the ambient air at varied concentrations due to automotive and industrial processes  $(NO<sub>2</sub>)$  or agricultural sector ( $NH<sub>3</sub>$ ). Thus, the sensor operating in the real-life scenario is highly likely to be affected by both gases simultaneously. Therefore, we studied the effect of their mixed concentrations on the ink-printed WS2 sensor and compared noise and resistive responses to selected mixtures. Fig. 7 presents three-dimensional graphs summarizing the relative changes induced in sensor DC resistance and its random fluctuations by concentrations of pure and mixed gases. Data points for relative changes in noise were derived from the low-frequency noise spectra demonstrated in Fig. A4. Measurements of selected concentrations of pure  $NO<sub>2</sub>$  or  $NH<sub>3</sub>$  gases confirm that both gases produce changes in DC resistance in opposite directions. Still, the direction of changes in noise spectra with increasing gas concentration is the same for the considered gases of opposite redox properties (see Fig. A5).

Moreover, NO<sub>2</sub> generates a few times higher DC resistance responses than NH3, but both gases affect the low-frequency noise spectra in the same magnitude for their considered concentrations. Interestingly, the relative changes in resistance fluctuations are not a direct summation of the noise amplitude of both gases in the case of the mixtures. Instead, all data points obtained for mixed concentrations are between or below those obtained for pure  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ . Another intriguing observation is that most of the DC resistance responses are negative for mixed concentrations, even though the electron-accepting  $NO<sub>2</sub>$  was observed to



**Fig. 7.** (a) Relative change in the average value of  $S_R(f)/R_S^2 \times f$  (in the range 2–20 Hz) at specific target gases ( $\Delta S_R$ ) in reference to the corresponding value in S.A.  $(S_{R0})$  and (b) relative change in the sensor resistance  $(\Delta R_S)$  in reference to the corresponding value in S.A.  $(R_0)$ . The measurements were performed under UV light (275 nm) and at a voltage bias  $V_0 = 20$  V. Green and blue points refer to pure NO<sub>2</sub> or NH<sub>3</sub> concentrations, whereas red points depict their mixtures and S.A. case. Black points are the X-Y projection of the 3D points for guidance and easier analysis of the results.

produce higher relative changes in sensor resistance when it remained the only target gas and was expected to dominate the sensor responsivity. In this case, it looks like  $NH<sub>3</sub>$  has the dominant effect on DC resistance when both gases are mixed. The partial suppression of lowfrequency noise and DC responses not being exact resultant quantities in the case of mixtures suggest more complex sensing mechanisms and processes occurring at or close to the sensing surface of  $WS_2$  flakes. These effects can be explained by interactions between the molecules of the considered gases, creating distinct responses and affecting charge transfer at the sensing interface in a particular way. We also performed dynamic sensing studies to see the direction of changes in the DC resistance when  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  of selected concentrations are introduced simultaneously. Fig. A6 shows how the sensor resistance changes in the 30-minute cycles of mixture introduction. It confirms that for small concentration of  $NH<sub>3</sub>$  (2 ppm),  $NO<sub>2</sub>$  dominates the response, especially in the first minutes. On the other hand, when 5 or 10 ppm of  $NH<sub>3</sub>$  is admitted to the sensing surface, the reducing gas starts to decrease sensor resistance. It signifies that after longer exposure to both gases,  $NH<sub>3</sub>$  can dominate the DC resistance, whereas  $NO<sub>2</sub>$  provides an immediate and dominant effect in the first minutes of the detection cycle. The detailed explanation of the observed gas-crossing effects requires more in-depth studies. Additionally, we suppose these mechanisms can only be characteristic of the considered gases and can be modified at different concentrations. Some reactions should occur at the gas sensing layer but in the ambient gas mixture, depending on gas concentrations and the probability of occurrence.

The presented detection data confirm that a single ink-printed  $WS_2$ sensor can detect two toxic gases, namely  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ , when only one is present in the ambient atmosphere. The change of DC resistance ([Fig. 3\)](#page-4-0) compared with the recorded one at the ambient atmosphere of S. A. determines which gas was introduced. Then, the intensity of flicker noise can be used to determine gas concentrations by considering the linear dependence presented in [Fig. 5.](#page-5-0) This situation is similar to that presented elsewhere [\[29\]](#page-9-0) but with much better gas sensitivity observed for the proposed ink-printed  $WS_2$  sensor.

When we consider the data recorded for the investigated gas mixture of NO2 and NH3, the detection results by the studied single sensor of two gas components are less vivid. The data ([Fig. 7](#page-6-0)) report an ambiguous behavior of the sensor at selected gas mixture compositions. The observed flicker noise changes [\(Fig. 7](#page-6-0)a) were determined mainly by  $NO<sub>2</sub>$ concentrations. The presence of  $NH<sub>3</sub>$  had some impact on the noise intensity, but only at the lowest considered concentrations of  $NO<sub>2</sub>$ . However, considering the changes in DC resistance, the situation is less clear ([Fig. 7b](#page-6-0)).  $NO<sub>2</sub>$  gas dominates the sensor DC resistance only at low concentrations of NH<sub>3</sub>. When a concentration of NH<sub>3</sub> exceeds 5 ppm, we observe an opposite direction of DC resistance changes induced by NO2 increase. This means that the contrary effects of these two gases on the DC resistance of the sensor reduce the possibility of gas mixture identification to some limits of concentrations. Better results of gas mixture components identification can be expected when the sensor is additionally modulated (*e.g.*, by UV irradiation of various optical powers or wavelengths) to secure more data for the considered detection algorithms. Such an approach was successfully applied to gas sensors elsewhere using support vector machine (SVM) or other machine learning algorithms [29–[31\].](#page-9-0) As an example, the SVM algorithm classifies data by finding the most optimum hyperplane to maximize the distance between different classes of data; it can also be used for regression models. SVM can be very efficient for high dimensional spaces (as in the case of the FES method) and when there is a nonlinear dependence between the variables (*e.g.*, noise intensity and gas concentration).

We applied detection algorithms to determine gas mixture components by the considered gas sensor, using the data of DC resistances (9 values for the considered  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  concentrations but excluding the cases for zero concentrations of  $NO<sub>2</sub>$  or  $NH<sub>3</sub>$  – see [Fig. 7](#page-6-0)) and noise power spectral densities (9 functions  $S_R(f)/R_S^2 \times f$  in the selected subband 2–20 Hz). We excluded seven measurement points in [Fig. 7](#page-6-0) (no presence

of  $NO<sub>2</sub>$ ,  $NH<sub>3</sub>$ , or both gases) because these data were biased by a drift visible in measurement time. We suppose that there is a slow diffusion process that is better visible at low concentrations of the considered gases. However, it should be reduced when the sensor thickness is optimized, and the sensor is effectively refreshed between consecutive measurements. More details on the used detection algorithms, are described in Supplementary Material.

Exemplary results for detecting gas mixture components are pre-sented in [Fig. 8.](#page-8-0) As we mentioned above,  $NO<sub>2</sub>$  is determined mainly by noise power spectral density, and NH<sub>3</sub> is determined mainly by DC resistance in the considered range of gas concentrations 2–10 ppm. Therefore, we investigated  $NO<sub>2</sub>$  detection at the random error of noise power spectra estimation increased by 10 % (*k* = 100, random error equals 100 %/sqrt(*k*) [\[32\],](#page-9-0) [Fig. 8a](#page-8-0)), and NH3 detection at DC resistance error increased by 1 % [\(Fig. 8](#page-8-0)b). The results suggest that  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ can be detected in a gas mixture by a single  $WS_2$  sensor utilizing DC resistance and its fluctuations (power spectral density of resistance fluctuations) but at their limited concentration range. The worked-out detection model is robust against measurement errors but only to some extent. We conclude that a single  $WS_2$  gas sensor can determine gas components ( $NO<sub>2</sub>$  and  $NH<sub>3</sub>$ ) of the considered gas mixture at selected concentrations. Still, these conclusions cannot be transferred to other mixtures.

## **4. Conclusions**

We demonstrated an ink-printed  $WS_2$  sensor for UV-assisted detection of two gases of opposite redox properties (oxidizing  $NO<sub>2</sub>$  and reducing NH3). We presented the prospect of utilizing measurements of both DC and random components of resistance toward gas detection. The effect of UV light on the surface of the  $WS_2$  structure was depicted on electrical-AFM images, which showed that irradiation was responsible for amplified charge transfer and activation of the sensing surface. This had implications on sensor responses toward target gases, especially in the DC resistance response. Low-frequency noise spectra revealed that the fluctuations in the  $WS_2$  sensor follow  $1/f$ -like dependence, with the noise intensity increasing proportionally to the concentration of gases. Detection limits estimated from relative changes in sensor DC resistance or noise amplitude (averaged between 2–20 Hz) were 103 ppb or 220 ppb for  $NO<sub>2</sub>$  and 553 ppb or 168 ppb for  $NH<sub>3</sub>$ . Although the overall noise responses were higher than DC resistance responses, the estimation of theoretical DLs is biased by the lower accuracy of noise measurements. Still, this result can be improved by lowering the random error of the estimated noise power spectral densities using more extended measurements and longer averaging of noise data. Compared to other reports, such low limits of detection for NO<sub>2</sub> (hundreds or tens of ppb) were obtained before for  $WS_2$ -based sensors but either in high temperature (180  $°C$ ) [\[13\]](#page-9-0) or for a hybrid structure that does not facilitate a simplified fabrication [\[25\]](#page-9-0). Comparing our sensors with those reported in recent years, we propose to use pure  $WS_2$ material without complex fabrication procedures or structure modifications and UV light assistance at RT instead of heating. Supplementary Table A.1 summarizes and compares gas sensing devices based on WS<sub>2</sub> reported in recent years with the one proposed in our work.

Detecting mixtures of gases and the effect of the sensor crosssensitivity remains an open issue. The primary observation is that the ultimate DC resistance or low-frequency noise response toward a mixture of selected concentrations is not a direct summation of the data obtained for pure gases. Therefore, the interaction between  $NO<sub>2</sub>$  and NH3 during the transfer to the sensing surface or at the interface of the material must be included and requires more in-depth investigation, *e.g.*, based on computational methods. The proposed ink-printed WS<sub>2</sub> sensor can determine concentrations of the mixed  $NO<sub>2</sub>$  and  $NH<sub>3</sub>$  gases for a considered but limited range of their concentrations when the selected SVM algorithm is applied. The detection model is robust against measurement error to some extent. Our work presents the potential of using

<span id="page-8-0"></span>

Fig. 8. Results of gas concentrations detection in gas mixture (NO<sub>2</sub> mixed with NH<sub>3</sub> in the concentrations range 2–10 ppm) for a set of 9 data records: **(a)** NO<sub>2</sub> when random error of the measured product  $S_R(f)/R_S^2 \times f$  (in the considered range 2–20 Hz) was increased by 10 % (green dots), measurement numbers 1, 4, 7 respond to 2 ppm of NH3, measurement numbers 2, 5, 8 respond to 5 ppm of NH3, measurement numbers 3, 6, 9 respond to 10 ppm of NH3; **(b)** NH3 when random error of DC resistance  $R_S$  was increased by 1 % (blue dots), measurement numbers 1, 4, 7 respond to 2 ppm of NO<sub>2</sub>, measurement numbers 2, 5, 8 respond to 5 ppm of NO<sub>2</sub>, measurement numbers 3, 6, 9 respond to 10 ppm of NO<sub>2</sub>. The algorithm *Optimizable SVM* was selected to prepare the most appropriate regression model.

ink-printed  $WS_2$ -based resistors to quantitatively detect toxic species by combining DC resistance and low-frequency noise measurements with UV light that activates detection sites (hot spots) in the  $WS_2$  structure. Additionally, our results shed light on the possibilities of detecting mixed concentrations of target gases of opposite redox properties based on DC resistance and noise responses of the printed WS<sub>2</sub>. We also want to highlight that although we focused on studying sensing responses to mixtures of two target gases, the effect of humidity on the DC and noise sensor response can also add an informative contribution to machine learning models. In our studies, we purposely limited the effect of RH by utilizing UV irradiation of a short wavelength (275 nm) that helps to clean the sensing surface from the preadsorbed molecules and prevents humidity from re-adsorption during gas detection. We believe the presented results are valuable for gas sensing with UV-light assistance for mixed target gases; however, the issue requires broader investigation because of additional phenomena that may occur between target gases and water molecules, specifically when the RH level changes during detection time.

#### **CRediT authorship contribution statement**

**Janusz Smulko:** Writing – review & editing, Writing – original draft, Supervision, Formal analysis, Conceptualization. **Katarzyna Drozdowska:** Writing – review & editing, Writing – original draft, Visualization, Resources, Investigation, Formal analysis, Data curation. **Andrzej Kwiatkowski:** Writing – review & editing, Visualization, Software, Formal analysis, Data curation. Artur Zieliński: Writing – review & editing, Investigation, Data curation.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **Appendix A. Supporting information**

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2024.136923.](https://doi.org/10.1016/j.snb.2024.136923)

# **Data Availability**

Data will be made available on request.

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