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Effects of UV light irradiation on fluctuation enhanced gas sensing by carbon nanotube networks

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ABSTRACT

The exceptionally large active surface-to-volume ratio of carbon nanotubes makes it an appealing candidate for gas sensing applications. Here, we studied the DC and low-frequency noise characteristics of a randomly oriented network of carbon nanotubes under NO₂ gas atmosphere at two different wavelengths of the UV light-emitting diodes. The UV irradiation allowed to sense lower concentrations of NO₂ (at least 1 ppm) compared to dark conditions. Our experimental studies confirmed that the flicker noise of resistance fluctuations under UV irradiation significantly enhanced the sensing characteristics of nanotube networks at low concentrations. We observed a dominating 1/f-like noise component below 1 kHz. The sensitivity of nanotube networks was higher for shorter wavelength, whereas drift in the resistance was smaller for longer wavelength. The measurements under the NO₂ gas atmosphere revealed a remarkable reduction in DC resistance drift of the nanotube network between consecutive cycles of gas sensing. This phenomenon was explained via absorption-desorption of NO₂ gas molecules on nanotubes surface. Since small concentrations of NO₂ pose a threat to the ecosystem, these results might play a significant role in the development of sensitive nanotubes-based photo-activated gas sensors.

1. Introduction

For more than a decade, low-dimensional materials have been widely investigated for resistive gas sensing due to their exceptional properties resulting from a high active surface-to-volume ratio [1]. In general, there are several requirements, which should be fulfilled by the gas sensing layers, including selectivity, high sensitivity, long-term durability and bounded time-drift, fast response, and recovery [2]. Moreover, such devices with active surfaces should be easily fabricated and miniaturized. A combination of all the aspects mentioned above is in the scope of current research. The newest scientific outcomes in this field have been updated and reviewed by a significant number of authors [3]. Among the vast array of nanomaterials, carbon structures including two-dimensional (2D) graphene, one-dimensional (1D) nanotubes, or their composites with inorganic structures attract great attention [4].

Carbon nanotubes (CNTs) possess unique electronic and optical properties due to their high aspect ratio, with diameters of 1 nm or even less and much greater length in the order of micrometers. Depending on

the chirality, single-walled nanotubes may be metallic, semi-metallic, or semiconducting, whereas multi-walled structures exhibit semiconducting properties with *p*-type conductivity [4]. Their structure gives rise to their high sensitivity to the surrounding atmosphere due to the large surface area with a significant number of binding sites. Additionally, CNNs are sensitive to UV light irradiation similar to another commonly used gas sensing materials [6]. It is known that illumination of sensing devices with ultraviolet (UV) light leads to faster response towards gas molecules and recovery [10,11]. A thorough review of UV light-activated gas sensing metal oxide nanostructures:gas sensors can be found elsewhere [12]. Such photo-activation promotes adsorption and desorption processes on the surface of the active layer. It often refers to as the surface cleaning phenomenon, which contributes to more efficient detection and desired room-temperature sensing [13,14].

To further enhance the sensor's behavior, the fluctuation-enhanced sensing method may be introduced. It utilizes information about the power spectral density of resistance fluctuations at low frequencies where 1/f noise (flicker noise) dominates [7–9].

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In this paper we studied the CNNs as room temperature sensors of nitrogen compounds such as NO₂, NO, or NH₃, which still represent one of the most dangerous pollutants. We demonstrate that the enhancement of the sensor's properties can be achieved by the UV LEDs of different wavelengths (365 nm and 275 nm) illumination and by fluctuation-enhanced sensing. The explanation of mechanisms of resistance fluctuations for illuminated and non-illuminated CNN sensor was proposed.

2. Materials and methods

2.1. Samples fabrication and characterization

The randomly oriented carbon nanotube network was synthesized via aerosol chemical vapor deposition method and transferred on ~500 μm thick double-sided polished glass wafer (from Thor labs) using dry transfer technique (Fig. A.1) [15]. Gold electrodes were deposited on a glass substrate before the transfer of nanotubes. The scanning electron microscope (SEM), UV-Vis-NIR, and Raman spectrometer were used to characterize the nanotube network's structural and optical representation (Fig. A.2). The optical transmission spectra were measured via UV-vis-NIR Perkin Elmer Lambda 900 spectrometer. The Renishaw inVia Raman microscope was employed for the Raman measurements of the nanotube network [16]. The signal was acquired in the spectral range of 50 – 3000 cm⁻¹ using a laser wavelength of 532 nm. The excitation power of the laser was at 2 mW to avoid sample damage. The laser beam was directed to the sample through a 100 × (N.A. = 0.85) objective lens. SEM images were collected with high-resolution Zeiss Auriga 60.

2.2. Measurement set-up

A fabricated CNN sensor was placed in a glass gas chamber and attached as a component with variable resistance to the electrical circuit. The measurements were run at room temperature, during the winter season (21 °C). The sensor's voltage was set with the potentiometer to keep the current flow through the device of approximately 1 mA. The sensor was driven by a voltage source with voltage U_0 in series with a driving resistance R_L in the applied circuit. The terminals of the biased CNN sensor were connected with the low-noise voltage amplifier (Stanford Research Systems, model SR560). Voltage measurements were conducted using a data acquisition board (National Instruments, model NI USB-6216). The detailed procedure of electrical and low-frequency noise measurements at selected ambient (NO₂ diluted in synthetic air) was presented in Appendix A. All circuit components were kept in a metal box, which served as a shield against external electromagnetic radiation. The effect of UV-irradiation was investigated via two UV LEDs of different wavelengths $\lambda_1 = 365$ nm (Seoul Optodevice, type T5F) and $\lambda_2 = 275$ nm (ProLight Opto, type PB²D-1CLA-TC) at which their maximum optical power was emitted. The LEDs were positioned within approximately (0.5 – 1.0) cm from the sensor's surface. The optical power density was calculated as (0.42 – 0.55) mW/cm² and (8 – 10) mW/cm² for UV 365 nm and UV 275 nm, respectively. We considered their nominal optical power and the size of the light spot to estimate it. The bias current equals 15 mA for UV 365 nm and 50 mA for UV 275 nm and assured reaching the maximum response of a sensor for both UV LEDs (Fig. A.3).

The gas mixtures were prepared by mixing synthetic air (S.A. – 79% of N₂ and 21% of O₂) with calibration gas NO₂ (30 ppm of NO₂ diluted in N₂ as carrying gas). Mass flow controllers (Analyt-MTC, model GFC17) were used to establish the selected concentration of target gas. We introduced humidity into the gas mixture by its flow through a glass bubbler filled with deionized water. The sensor BME280 (Bosch Sensortec, Reutlingen Germany) was used to monitor a level of relative humidity. More detailed information about the gas preparation set-up is available in the [Supplementary Information](#).

3. Results

We investigated a mesh of a randomly distributed network of CNTs (Fig. A.1). The detailed fabrication process of the studied device was presented elsewhere [17]. The absorbance and transmittance of nanotube networks on glass substrate over the wide spectral range are shown in Fig. A.2A and B, respectively. The peaks at wavelength ~ 270, 970, 1400, and 2240 nm are referred to as π -plasmons, S₁₁, M₁₁, and S₂₂ peaks, respectively, and are typical for nanotubes network [18]. The average diameter of nanotubes obtained via Weisman and Kataura plots is estimated as ~1.8 – 1.9 nm [19,20] (Fig. A.2D).

CNN characterized above served as an active layer in the proposed sensing system. Fig. 1 depicts the response of a CNN sensor in S.A. and the atmosphere of NO₂ diluted in S.A. for three cycles of UV illumination with different wavelengths. The gas conditions were stabilized for at least 30 min before starting data recording. Each irradiation cycle (starting point designated as UV on) lasted 15 min, and it was sufficient to observe the sensor's response at the conditions selected during our experimental studies. Fig. 1A shows the photoresponse of CNNs in terms of relative change in DC resistance at two different wavelengths of UV illumination (275 and 365 nm) as a function of time. It is seen that in agreement with previous publications [6,17] resistance increases under illumination, demonstrating the negative photoresistance; the response for a shorter wavelength is almost two times higher than that for a longer wavelength. The measurements under the NO₂ gas atmosphere reveal a significant reduction in resistance drift over three consecutive cycles of UV illumination (Fig. 1B). It is seen that in the S.A. atmosphere, 15 min is not enough to restore the initial resistance after UV light is off. As a result, in the S.A. atmosphere, the resistance slowly increases from cycle to cycle. There is almost no drift between the cycles of UV light at the ambient of 20 ppm of NO₂ diluted in S.A., i.e., resistance is completely restored during the 15 min of illumination absence. Interestingly, resistance can go even below its initial value. We suppose that the adsorption-desorption processes of NO₂ molecules under UV illumination are much faster than of S.A. After a few months, the measurements (Fig. 1A, B) were repeated during the summer season at room temperature (25 °C) at an ambient atmosphere of dry S.A. or S.A. with 40% RH (Fig. 1C, D). We observed at the beginning of these measurements higher DC resistances (up to about three times). We suppose that this is an effect of the long-time drift process reducing the number of adsorbed water molecules. The sensor was kept in dry air for a few months between the measurements and some adsorbed water molecules were removed during this period from the CNN. UV light accelerates this process and results in an observed increase of DC resistance after switching on UV light for both wavelengths. This process was slightly different at the applied UV LEDs. The longer wavelength (365 nm) increased DC resistance at dry air. At the presence of 40% RH, we observed a slow drift decreasing DC resistance between the UV light cycles (Fig. 1D). A slow process of water molecules diffusion into the CNN structure can be responsible for the observed drift. A shorter and more energetic UV wavelength (275 nm) penetrates the thinner CNN layer much faster and results in a fast change of DC resistance (Fig. 1C). We observed later a slow decrease of DC resistance for a shorter wavelength that can be attributed to a slow process of water molecules diffusion from the inner part of the CNN. Independently of the applied UV wavelengths, we observed an increase of DC resistance resulting from the desorbed water molecules. Thus, an application of UV light results in the reduced impact of humidity on gas sensing because of its accelerated desorption. We underline that this effect is important for practical applications when various RH reduces gas detection accuracy.

We further explored the sensing strength of the device by measurements at various concentrations of NO₂ gas and studied the enhancement in sensing characteristics of CNNs under UV illumination. Under non-illumination conditions (Fig. 2A), the device only responded to high concentrations of NO₂ gas (over 4 ppm) by decreasing its resistance. However, the sensitivity of the sensor was enhanced by

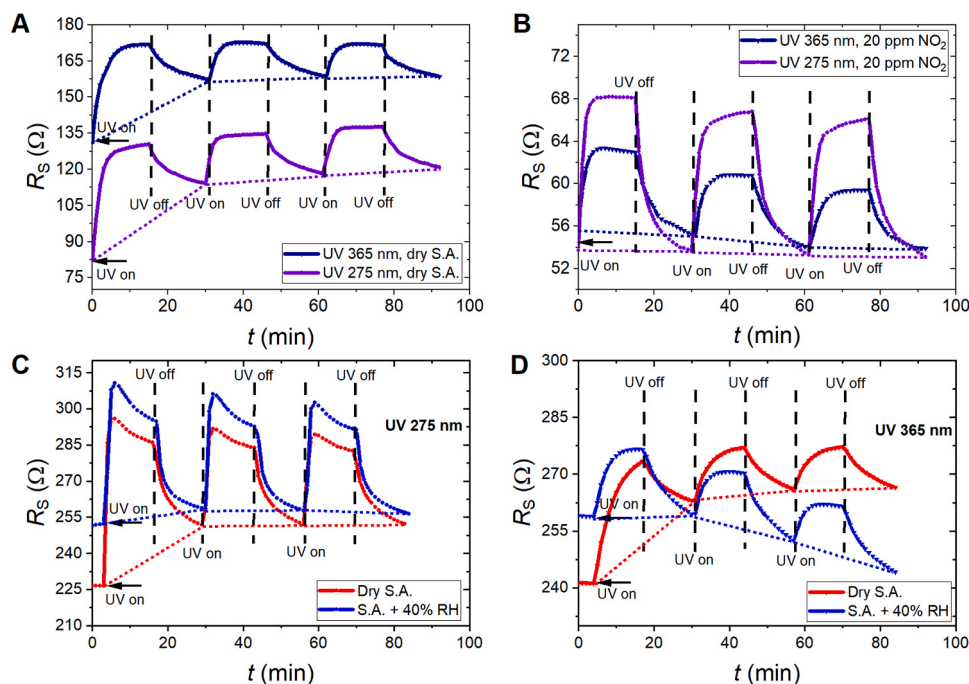


Fig. 1. Reproducibility of CNN sensor. Response (DC resistance R_S) of a device for three cycles of UV light illumination in the ambient atmosphere of (A) synthetic air (S.A.) and (B) 20 ppm of NO_2 diluted in S.A. when the sensor operated at room temperature during the winter season (21 °C). The measurements were repeated during the summer season (25 °C) at the ambient atmosphere of dry S.A. and S.A. with 40% RH during the applied cycles of the UV light (C) 275 nm or (D) 365 nm.

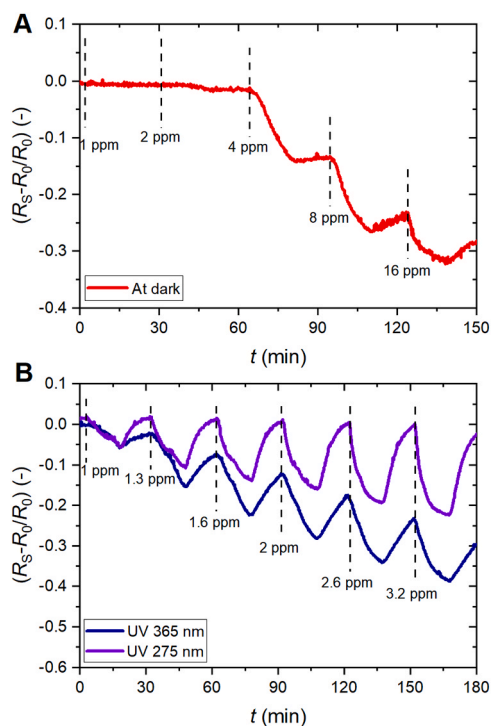


Fig. 2. CNN sensor's behavior under different measurement conditions. Response of a sensor towards various concentrations of NO_2 (A) at dark and (B) under continuous irradiation with UV LEDs of maximum emitted optical power at 365 nm and 275 nm.

employing UV LEDs. The responsivity of the sensors to NO_2 gas at two different wavelengths of UV illumination is shown in Fig. 2B. UV illumination enhanced the sensing characteristics of CNNs and allowed to sense at least 1 ppm of NO_2 .

Fig. 3 presents a summary of the sensor's resistance R_S measurements under various conditions. At lower concentrations of NO_2 (1 – 4 ppm), resistance sharply decreases as a function of NO_2 concentration for the illuminated device and tends to saturate at higher concentrations. The sharper changes of R_S were observed for 365 nm LED than for 275 nm one. Without UV assistance, resistance is constant at low NO_2 concentrations. At high NO_2 concentration, devices behave similarly with and without UV illumination. Therefore, it is clearly seen that UV illumination improves sensitivity.

Low-frequency noise measurements were further performed to confirm the enhanced NO_2 sensing characteristics of nanotube networks under UV illumination. Fig. 4A depicts the normalized power spectral density of resistance fluctuations, $S_R(f)/R_S^2$ at a few concentrations of NO_2 without UV assistance. The noise level decreases as the concentration of NO_2 gas increases. Fig. 4B summarizes the dependence of $S_R(f)/R_S^2$ at 60 Hz as a function of NO_2 gas concentrations with and without UV illumination. The noise spectra were collected simultaneously with resistance measurements to ensure reliable data comparison under

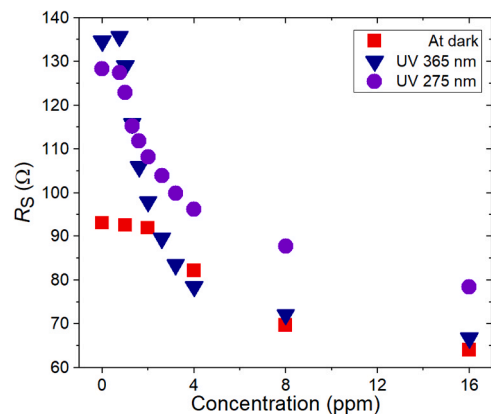


Fig. 3. Sensor's resistance R_S towards different concentrations of NO_2 for non-illuminated device and with the assistance of both UV LEDs.

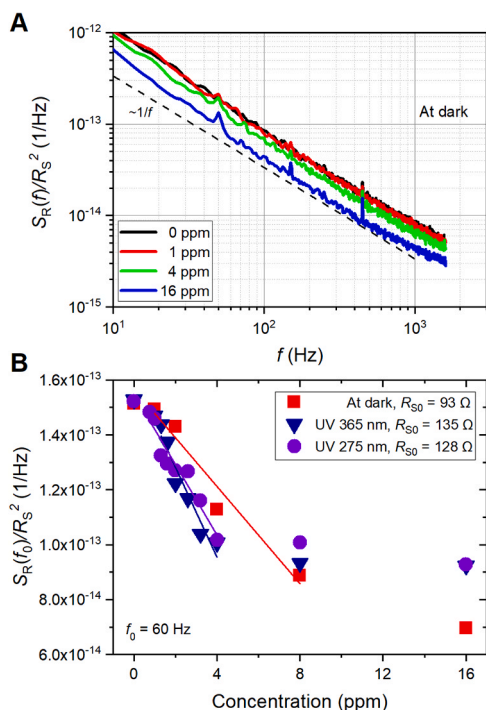


Fig. 4. Results of low-frequency noise measurements of CNN sensor in different concentrations of NO_2 . Power spectral density $S_R(f)$ of a sensor having DC resistance R_S (A) as a function of frequency f without additional UV illumination and (B) $S_R(f_0)$ values at a frequency $f_0 = 60$ Hz collected for the sensor without UV illumination and UV 365 nm and UV 275 nm LED assistance. R_{S0} corresponds to the resistance of a sensor at the beginning of the measurements in S.A. only. Solid lines represent linear dependencies between $S_R(f)$ and NO_2 concentrations at their low range.

similar operating conditions. At low concentrations, noise decreases fast with the NO_2 concentration increase (emphasized with solid lines). For concentrations exceeding a few ppm, the noise changes slower as a function of NO_2 concentration. Interestingly, at low NO_2 concentration (Fig. 4B), the noise level with and without UV illumination is the same, despite $\sim 30\%$ difference in device resistance, indicating that low-frequency noise is selectively sensitive to NO_2 molecules and not to the resistance change in general.

4. Discussion

Numerous research groups extensively studied low-frequency noise in CNT or CNNs devices [5,17,21]. Various researchers concluded that $1/f$ noise in CNNs devices is generated by the fluctuations in charge carriers number, determined by the adsorbed molecules on nanotube surface. Moreover, it is well known that $1/f$ noise is very intensive in CNTs devices compared with other devices of similar size or volume [21]. This suggests that low-frequency noise can be used as an effective tool to study the gas sensing characteristics of material.

Fig. 5 presents the dependence of power spectral density $S_R(f_0)$ at frequency $f_0 = 60$ Hz on sensor's DC resistance R_S in the presence of NO_2 in the dark and under illumination with LEDs of two different wavelengths. A linear fit to experimental data points reveals different functions for all three measurement conditions. For non-illuminated condition, the relationship between noise and resistance is nearly quadratic, whereas, under UV-illumination, the dependencies are weaker. An explanation for observed results may be based on the existing model of $1/f$ noise induced by fluctuations in charge concentrations. McWhorter's model used initially in conventional semiconductors, is the most straightforward and commonly used model for the description of $1/f$ noise [8]. Noise originates predominantly from

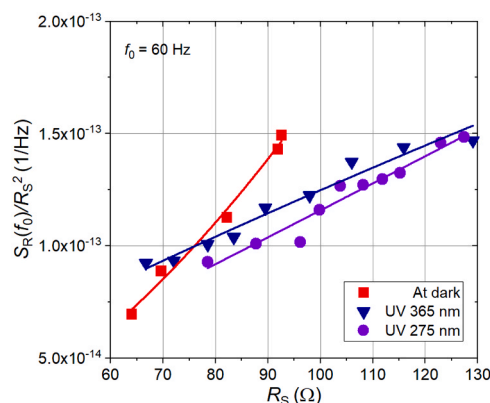


Fig. 5. Representation of noise mechanisms for CNN sensor. Linear dependence between power spectral density $S_R(f_0)$ and sensor's DC resistance R_S at frequency $f_0 = 60$ Hz for all three measurement conditions. Solid lines, which correspond to the linear fit of experimental data points, present the estimated proportionality to R_S .

fluctuations of charge carrier concentrations and is altered by trapping and de-trapping processes, mainly at the interface between the semiconductor and the insulating layer. Each trap is characterized by a specific time constant, which results in fluctuations in the number of carriers. Hence, $1/f$ noise spectrum consists of multiple G-R Lorentzian functions. Since G-R noise is inversely proportional to the square of carrier concentration or directly proportional to resistance squared (R_S^2), $1/f$ noise follow the same dependence. The dependence of the power spectral density in Fig. 5 for non-illumination condition (red squares) can be visualized as adsorption-desorption events of chemical species resemble to G-R noise induced by trapping and de-trapping of charges. However, the device illuminated with UV 365 nm or UV 275 nm exhibits different R_S dependences, suggesting a more complex detection mechanism. To provide a thorough explanation of the observed sensing process, one has to take into account phenomena triggered by UV-illumination, the presence of NO_2 in the ambient atmosphere and both variables simultaneously.

The mechanism of UV and NO_2 sensing via p -type randomly distributed carbon nanotubes is schematically shown in Fig. 6. Exposure of devices to NO_2 gas results in the attachment of negatively charged ions on the surface of nanotubes with an addition of two extra holes (Fig. 6B). The illumination with UV light cleans the surface of nanotubes. The photon of UV illumination carries sufficient energy $h\theta_{(UV)}$ to generate electron-hole pairs in carbon nanotubes:



Photo-induced holes react with the negatively charged ions from the surface, leading to desorption of gaseous oxygen:



Consequently, hole concentration decreases, leading to lower conductivity and greater resistivity of a sensor with a p -type active layer (Fig. 6C). When the UV light is turned off, oxygen molecules from the environment tend to adsorb on the surface again and thus decrease nanotubes' resistivity [17]. This mechanism can be used to explain the results from Fig. 1A. The results of Fig. 1B can be explained similarly as well. Nitrogen dioxide is a strong oxidizing agent, which makes it an electron acceptor. The adsorbed oxidizing ions extract electrons from the nanotubes' conduction band, which in turn leave extra holes. Under UV illumination, the generation of free holes and electrons takes place. Photo-induced holes may recombine with electrons from negatively charged ions, resulting in partly desorption of NO_2 and increased layer's resistance.

The presence of various concentrations of NO_2 leads to a negative

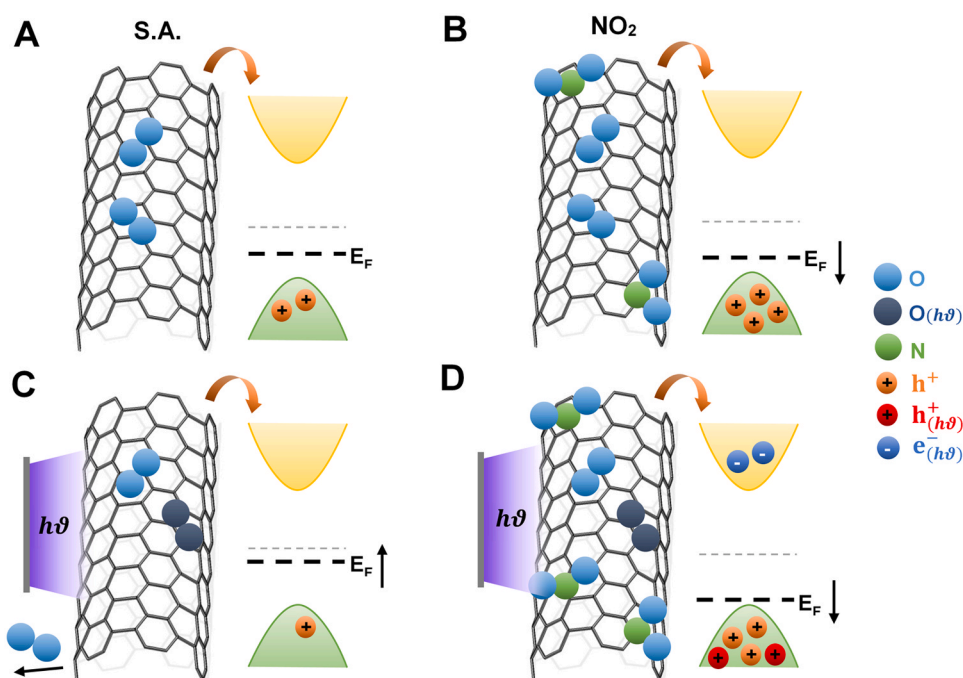
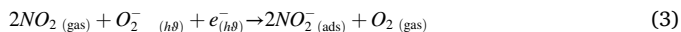


Fig. 6. Schematic representation of gas sensing mechanism for CNT surface. (A) The active layer exhibits *p*-type conductivity in S.A. due to the adsorption of oxygen ions (blue beads) from the ambient atmosphere. (B) In the atmosphere of NO_2 , a more significant amount of holes concentration and drop of Fermi level (E_F) increase the conductivity. (C) During UV-irradiation, free carriers generation results in the formation of additional weakly bonded oxygen ions (gray beads) as well as partly desorption process of primarily adsorbed oxygen (blue beads), leading to the shift of E_F and conductivity decrease. (D) With additional UV illumination, a partly cleaned surface with more binding sites and generated electron-hole pairs lead to more efficient detection of NO_2 . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

response of a sensor. The DC resistance response to NO_2 in Fig. 2 is strictly connected with the adsorption of strongly oxidizing NO_2 ions, which improves the sensor's *p*-type conductivity. UV assistance promotes the sensor's sensitivity, leading to more binding sites for NO_2 molecules. Additionally, faster recovery for the shorter wavelength of UV indicates more effective nanotubes surface cleaning owing to highly energetic UV photons. Absorbance spectrum (Fig. A.2A) reveals that CNTs exhibit strong optical absorption corresponding to ~ 5 eV (equal to ~ 270 nm) due to π -plasmons excitation. Previously, it was suggested that this phenomenon might be responsible for quick molecular photo-desorption [22]. One may expect more effective desorption of attached gas molecules from the surface since the energy provided by UV 275 nm LED correlates well with the energy required for plasmon excitation. Thereby, less energetic UV 365 nm LED cannot assure full recovery (Fig. 2B).

The mechanism of gas molecules detection may be based on one more phenomenon [14]. The excitation of free charge carriers in material occurs if the energy of UV light used in the experiment is sufficient to generate electron-hole pairs. Such photo-induced electrons may react with atmospheric oxygen and create additional photo-induced oxygen ions adsorbed on the material (Fig. 6C and D). These oxygen ions are weakly bonded to the surface and may contribute to gas adsorption as well:



While the resistance changes may be easier to interpret, changes observed in noise spectra and their mechanisms are not straightforward. Under the non-illuminated condition, the quadratic dependence of $1/f$ noise vs. DC resistance R_S may imply dominant fluctuations of carrier concentrations. It suggests that active sites on the material's surface or at the interface with the substrate may act as adsorption-desorption centers causing constant fluctuations of the number of charge carriers. Nevertheless, fluctuations of mobility contribute to overall low-frequency noise, as suggested before for graphene devices [8,23]. Since a non-quadratic relationship between resistance fluctuations and R_S were observed for UV-illuminated samples, one can conclude that local changes in carriers mobility may become more emphasized during irradiation. Nevertheless, our experimental studies do not give any conclusive remarks on the dominant mechanism generating the

observed noise. We have not identified any G-R noise of characteristic frequency, suggesting that mobility fluctuations can also impact the recorded low-frequency noise.

The applied UV light, emitted by commonly available UV LEDs, had a maximum of the radiated optical powers at the chosen wavelengths (275 nm and 365 nm). The reason for distinctively different wavelengths was various transparency for the layer of CNNs. The shorter wavelengths (~ 275 nm) penetrated the CNN at a shallower depth, and therefore the effect of UV irradiation was limited to its external thin sensing layer. Then, the major gas sensing area is related to the volume of the CNN sensor and the observed dependence between noise power spectral density and DC resistance $S_R(f_0)/R_S^2 \sim R_S^{1.85}$ was close to the dependence observed at dark condition ($\sim R_S^{1.99}$). The longer wavelengths (~ 365 nm) penetrated more deeply the CNN volume, and therefore the more significant part of the sensor was modulated by UV light. As a result, we observed less intense dependence between low-frequency noise and DC resistance ($S_R(f_0)/R_S^2 \sim R_S^{1.79}$). It suggests that the thinner layer of the CNN should be more sensitive to NO_2 when irradiated by UV light penetrating its entire volume.

Another essential difference induced by the applied UV illumination was observed at the ambient atmosphere of NO_2 . By repeatedly switching on and off the UV LEDs, the pulsed UV light generated a more intense gas sensor response when induced by the photons of shorter wavelengths (~ 275 nm). We underline that working at the pulsed UV illumination gives different sensor responses (Fig. 1) compared with continuous UV light and increased stepwise NO_2 concentration (Fig. 3). In principle, light intensity should not influence the photo-activation mechanism until photons energy is sufficient to generate charge carriers. However, the intensity of the photons stream determines the profile (the number and its dynamic changes) of the photo-generated charge carriers. As a result, it affects the sensing properties of NO_2 as reported for the nanowires of semiconducting oxides [24].

Additionally, the periodically recorded response at an ambient atmosphere of 20 ppm of NO_2 displayed lower drift between the cycles when illuminated by shorter wavelengths (~ 275 nm). It means that the photons of higher energy are keener to accelerate the process of replacing oxygen ions with NO_2 molecules even if the UV light penetration is limited to the thin external gas sensing layer.

Fig. 3 presents the sensor's DC resistance changes towards various

concentrations of analytic gas and under different measurement conditions. These dependencies may be utilized for detection limit (DL) estimation (Fig. A.4). The procedure for DL calculations is summarized in Appendix A. The results confirmed that UV irradiation enhanced gas sensitivity to NO₂ at its low concentrations and improved its DL. The best results were observed under UV irradiation of 275 nm, that is, DL = 766 ppb for the FES method (Fig. A.5) and DL = 696 ppb for the DC resistance measurements. At dark, for DC resistance measurements, the estimated DL reached 1135 ppb.

The improvement in DL values under UV light was much less impressive than the reported elsewhere for reducing gas NH₃ by at least three orders for the applied UV LED of 253.7 nm [6]. In the same work, authors present DL for oxidizing gases NO₂ and NO, which is a few orders of magnitude lower for inert carrier gas than S.A. Another work introduces DL at the level of ppb for NO₂ in laboratory conditions [1]. We underline that the mentioned results considered lower gas concentrations than noted by our experiments. The CNN sensor's response is more linear at lower gas concentrations, and the estimated DL is, therefore, more exquisite. Additionally, the lowest DL values were reported for Ar or N₂ as carrier gases, whereas we used NO₂ diluted in S.A. Moreover, the applied UV LEDs of 275 nm or 365 nm are commonly used and more popular than UV LEDs of lower wavelengths (e.g., 253.7 nm). Therefore, the reported results can be efficiently utilized in practical applications.

5. Conclusions

We have experimentally studied flicker noise and DC resistance in CNN gas sensor under UV illumination with two selected wavelengths. It was found that UV light accelerates adsorption-desorption processes and enhances the sensitivity and speed of the sensors.

The specifics of the sensor's operation depend on the CNN sensor morphology and the UV wavelengths. These factors can be optimized to further enhance its gas sensing capability by integrating with UV LEDs for applications in portable set-ups of limited energy consumptions and maintenance costs.

We discussed in detail the mechanisms of gas sensing induced by UV illumination and affecting DC resistance and flicker noise independently. A few realistic assumptions can explain our experimental results, but more detailed studies are necessary for decisive conclusions. Our studies endorsed the idea of applying UV irradiation for enhanced sensing by the CNN sensor, and the obtained results can be used for more efficient gas detection by the CNNs sensors.

CRedit authorship contribution statement

J.S. and S.R. conceived the study. K.D. established and ran the experimental electrical and optical studies, evaluated DL analysis. A.R. and A.K. fabricated the samples. A.K. characterized the CNT network by Raman spectroscopy measurements. K.P. performed SEM measurements. A.R. participated in data analysis and interpretation of optical and structural features of CNTs samples. K.D., J.S., S.R., and G.C. wrote the manuscript.

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.2021.131069.

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