

## Research Article

# UV Light-Modulated Fluctuation-Enhanced Gas Sensing by Layers of Graphene Flakes/TiO<sub>2</sub> Nanoparticles

Janusz Smulko <sup>1</sup>, Tomasz Chludziński,<sup>1</sup> Umut Çindemir,<sup>2</sup> Claes G. Granqvist,<sup>2</sup> and He Wen<sup>3</sup>

<sup>1</sup>Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, Gdańsk 80-233, Poland

<sup>2</sup>Department of Materials Sciences and Engineering, The Ångström Laboratory, Uppsala University, SE-75121 Uppsala, Sweden

<sup>3</sup>College of Electrical and Information Engineering, Hunan University, Changsha, China

Correspondence should be addressed to Janusz Smulko; [janusz.smulko@pg.edu.pl](mailto:janusz.smulko@pg.edu.pl)

Received 31 January 2020; Revised 19 May 2020; Accepted 24 June 2020; Published 8 July 2020

Academic Editor: Xinyu Liu

Copyright © 2020 Janusz Smulko et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We present experimental results of fluctuation-enhanced gas sensing by low-cost resistive sensors made of a mixture of graphene flakes and TiO<sub>2</sub> nanoparticles. Both components are photocatalytic and activated by UV light. Two UV LEDs of different wavelengths (362 and 394 nm) were applied to modulate the gas sensing of the layers. Resistance noise was recorded at low frequencies, between 8 Hz and 10 kHz. The sensors' response was observed in an ambient atmosphere of synthetic air and toxic NO<sub>2</sub> at selected concentrations (5, 10, and 15 ppm). We observed that flicker noise changed its frequency dependence at different UV light wavelengths, thereby providing additional information about the ambient atmosphere. The power spectral density changed by a few times as a result of UV light irradiation. The sensors were operated at 60 and 120°C, and the effect of UV light on gas sensing was most apparent at low operating temperature. We conclude that UV light activates the gas-sensing layer and improves gas detection at low concentrations of NO<sub>2</sub>. This result is desirable for the detection of the components of gas mixtures, and the modulated sensor can replace an array of independent resistive sensors which would consume much more energy for heating. We also suggest that a more advanced technology for preparing the gas-sensing layer, by use of spin coating, will produce corresponding layers with thickness of about a few μm, which is about ten times less than that for the tested samples. The effects induced by the applied UV light, having a penetration depth of only a few μm, would then be amplified.

## 1. Introduction

Resistive gas sensors are of much current interest because of their low-cost production and simple applications to detect a range of gases [1, 2]. A large variety of metal oxide semiconductors (MOs)—such as SnO<sub>2</sub>, WO<sub>3</sub>, ZnO, TiO<sub>2</sub>, MoO<sub>3</sub>, NiO, and Fe<sub>2</sub>O<sub>3</sub>—exhibit different gas-sensing characteristics and can be used to detect various gases. The resistance is altered upon exposure to the ambient atmosphere. The change depends on the reducing or oxidizing ability of the gas molecules and can be employed to determine gas concentration.

The sensors are activated for gas detection at elevated temperature, and the operating temperature determines the selectivity and sensitivity of the MOS sensors. Nanoparticles,

typically of noble metals such as Au and Pt, can also dope the sensors and induce catalytic effects so as to further improve selectivity and sensitivity [3]. For some applications, a complicating aspect is that the gas mixture may contain different amounts of humidity, which is the case, e.g., for exhaled breath analysis for medical check-ups, in office environments, etc. One can improve gas detection by applying an array of MOS gas sensors with selectivity optimized for chosen gases, but this solution leads to additional costs of preparing the set of gas sensors and their operation during practical use. Furthermore, an array of gas sensors requires additional energy to operate at elevated temperature. Consequently, novel gas-sensing methods are desired for enhancing gas detection by low-cost MOS sensors and need to be applied beyond measuring the sensors' DC resistance.

One method for enhancing gas sensing utilizes low-frequency (low- $f$ ) resistance noise and was proposed about two decades ago [4, 5]. Specifically, this method was found to be efficient for improving selectivity and sensitivity; it makes use of power spectral densities of recorded resistance noise as an additional source of information about the ambient atmosphere of the gas sensor [5, 6]. This method is referred to as fluctuation-enhanced sensing (FES) [5]. Moreover, recorded  $1/f$  noise can be easily modified by changing the operating temperature or by UV light irradiation onto photocatalytic materials [7].

Power spectral density is a function of frequency; its slope can change locally around a characteristic corner frequency  $f_c = 1/2\pi\tau_c$  by adsorption-desorption events, of specific time constants  $\tau_c$ , induced by the gas molecules present in the ambient atmosphere. A similar mechanism leading to  $1/f$  noise is well known for generation-recombination (G-R) events in semiconductors. Each G-R event is described by a Lorentzian having a power spectral density of  $S(f) = S_0/\{1 + (2\pi\tau f)^2\}$ , where  $S_0$  determines the noise intensity at frequencies  $f < (2\pi\tau)^{-1}$  and  $\tau$  is the time constant of the trapping state. The  $1/f$  spectrum is given by summing up the independent events having time constants  $\tau$  and distributed logarithmically between the limits  $\tau_1$  and  $\tau_2$  [8]. Any deviation from the assumed logarithmically distributed  $\tau$ —e.g., due to scattering from charged impurities with specific properties—results in a local deviation from the  $1/f$  dependence. The difference is usually observed as a plateau at a given corner frequency. Its intensity and position in the frequency domain may be characteristic for the adsorbed gas molecules and utilized for their identification by low-frequency noise measurements.

Experimental studies on a single-layer-graphene field-effect transistor (FET) have reported different corner frequencies of the plateau characteristic for a set of gases [9]. The corner frequency of the plateau was repeatable for a batch of specimens, thus demonstrating the potential of high gas selectivity for the FES method [10]. It was also observed that the graphene layer could be modulated—e.g., cleaned after gas exposure to remove adsorbed gas molecules [9]—by UV light. These results imply that one can use graphene for gas sensing and UV light irradiation to enhance its sensing properties.

In two-dimensional materials, such as graphene, the gas molecules adsorbed on the surface change the surface potential, whereas in resistive gas sensors, the gas molecules alter the potential barrier between grains. This barrier differs among the grains of various sizes which jointly form the resistive gas-sensing layer. Single-layer-graphene has stable physical properties, and therefore, one can expect high repeatability of the corner frequency for different gases. However, a back-gated FET with single-layer-graphene in its channel requires complicated and expensive technology. Therefore, we propose to study layers made of two-dimensional material and assuring more homogenous properties than the mixture of MOS grains of different sizes and various potential barriers between them.

In the present work, we explore gas sensing with layers made of graphene flakes and titanium dioxide ( $\text{TiO}_2$ ) nano-

particles. Both materials are photocatalytic and therefore can be easily modulated by UV light irradiation. The layers can be produced by low-cost technology, specifically by painting and subsequently backing the solution located between gold electrodes to form the gas-sensing layer [11]. Our experimental studies consider the effect of UV light irradiation on  $1/f$  noise. Furthermore, we discuss how this technology can be advanced in order to accomplish enhanced gas sensing.

## 2. Materials and Methods for Sensor Preparation

Our sensors were prepared by an earlier presented technology [11]. The gas-sensing layer comprises a mixture of reduced graphene oxide (rGO) and  $\text{TiO}_2$  nanoparticles. Graphene is sensitive to various gases of practical interest, and the generated  $1/f$  noise depends on the ambient atmosphere [12, 13]. Graphene oxide and reduced graphene oxide have been used as templates for preparing graphene-metal particle nanocomposite in earlier work [14], but these composite materials (graphene sheets with attached metal particles) are new in the context of gas sensors and catalysts. In our exploratory studies, reported below, we investigated this type of mixture and demonstrated its high potential for gas-sensing applications.

An rGO honeycomb network deteriorates at high temperature, but this process can be impeded by introducing  $\text{TiO}_2$  nanoparticles which are gas sensitive and exhibit a photocatalytic effect as well.  $\text{TiO}_2$  is characterized by a large bandgap, about 3.2 eV, and therefore, adding graphene will decrease the resistance of the gas-sensing layer. It was necessary to establish an appropriate weight proportion between  $\text{TiO}_2$  nanoparticles and graphene for assuring a reasonable conductivity for gas-sensing measurement (employing DC resistance and resistance fluctuations), high gas sensitivity, and time stability of the prepared material.

The gas-sensing layers were prepared by mixing the two ingredients, painting on the substrate (Figure 1), and subsequently baking at  $50^\circ\text{C}$  for 30 minutes to stabilize the structures by removing the solvents, viz., ethanol for diluting  $\text{TiO}_2$  nanoparticles (Aeroxide  $\text{TiO}_2$  P25) and n-butyl acetate for diluting graphene flakes (Graphene Supermarket UHC-NPD-100ML) [11]. Four-point gold contacts on silicon were used as electrodes; the distance between each gold strip was  $300\ \mu\text{m}$ . The gas-sensing layers were very porous and displayed a large active surface (Figure 2). The thickness of the layers was below  $75\ \mu\text{m}$  and, due to the deposition technology, varied even within a single substrate by as much as up to  $25\ \mu\text{m}$  with a concave cross-section. We prepared layers with different graphene/ $\text{TiO}_2$  weight ratios in order to find the most promising composition for gas-sensing applications [15]. The gas-sensing layers exhibited some drift in the time domain, but this effect can be disregarded in our experimental studies limited to a few months. We are conscious that the considered technology is used to present the potential of gas sensing of the investigated layers, and any commercial applications require optimized technology.



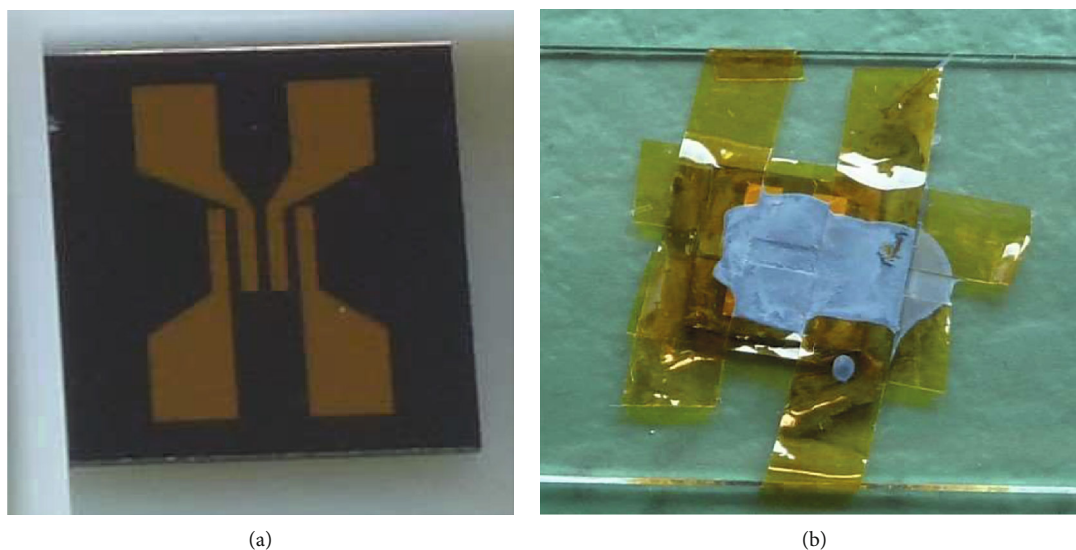


FIGURE 1: Preparation of the gas-sensing layer, showing (a) a silicon substrate with four gold electrodes and (b) the gas-sensing layer whose extent was confined by adhesive tape during painting.

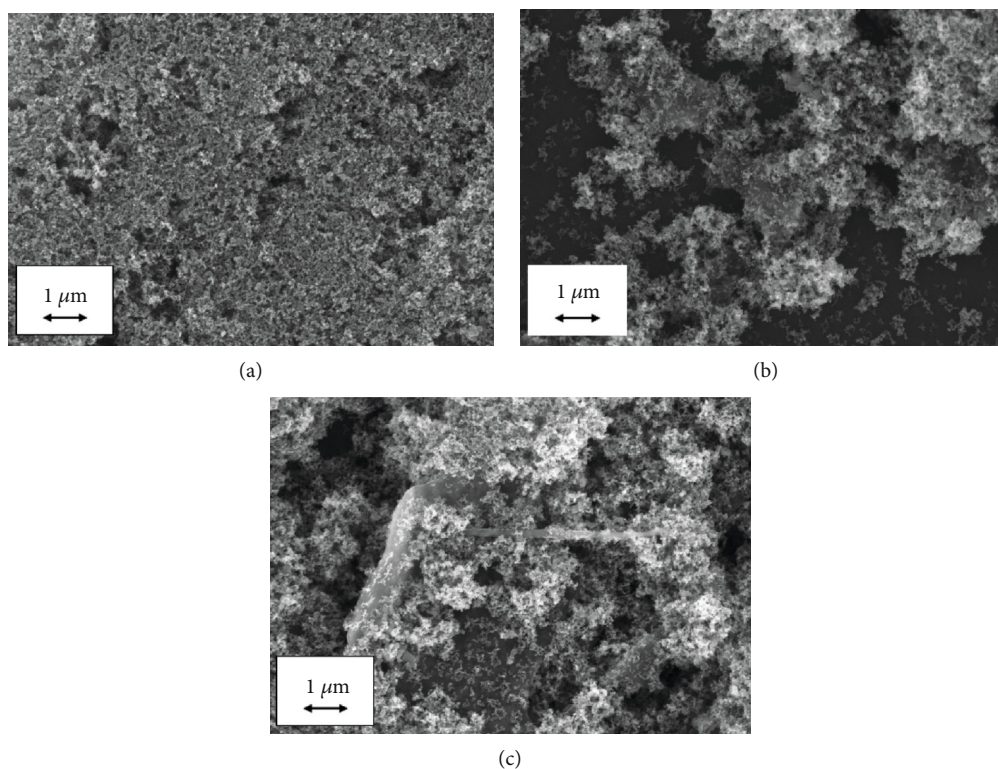


FIGURE 2: Scanning electron microscopy images of porous layers comprised of graphene flakes/TiO<sub>2</sub> nanoparticles with ratios being (a) 5, (b) 10, and (c) 20 wt%.

Noise measurements can be made on specimens whose DC resistance is no larger than hundreds of k $\Omega$ . The gas sensor is placed in a feed-back loop of a low-noise operational amplifier working as a current-voltage converter [16]. The RC filter embodying DC resistance and parasitic capacitance determines the frequency characteristic, and low-frequency noise cannot be measured appropriately when the DC resis-

tance is too high. Thus, we selected for further studies three ratios of graphene flakes and TiO<sub>2</sub> nanoparticles, namely 5, 10, and 20 wt%. The resistance of these layers did not exceed about 20 k $\Omega$  at the chosen operating temperatures of 60 and 120°C. We also prepared sensors with 1 wt% of TiO<sub>2</sub> nanoparticles, but these samples had a DC resistance of up to tens of M $\Omega$  as well as low gas sensitivity and were therefore

excluded from detailed studies. The selected layers were investigated by scanning electron microscopy and showed porous structures comprised of graphene flakes decorated with TiO<sub>2</sub> nanoparticles (Figure 2).

### 3. Measurement Set-Up

Our gas-sensing layers were studied under exposure to selected ambient atmospheres by observing changes of DC resistance and resistance fluctuations at low frequencies. The sensors were placed in a metal gas chamber with a volume of one litre. The gas-sensing layers were sensitive to various gases, and in order to explore the potential of the FES method for gas detection, we used an ambient atmosphere of toxic NO<sub>2</sub> gas, which is of a large practical interest. Mass-flow meters (Analyt-MTC, GFC17 type) were used to establish the selected concentrations of NO<sub>2</sub> diluted in synthetic air. We mixed calibration gas (100 ppm of NO<sub>2</sub> in N<sub>2</sub> as carrying gas) with synthetic air (20% O<sub>2</sub>, 80% N<sub>2</sub>), and no humidity was present there. The gas mixture was introduced into the gas chamber at a flow rate below 200 ml/min in order to avoid gas turbulence, which might provide a spurious source of fluctuations not related to resistance fluctuations induced by adsorption-desorption events. The operating temperature was set by a DC voltage to a heater at the rear side of the silicon substrate and was monitored by a thermocouple.

The sensor was placed in a feed-back loop of a low-noise operational amplifier (Maxim Integrated MAX4478) working as a current-voltage converter. The output voltage was recorded by a precise data acquisition board (National Instruments, model PCI-4474 with 24-bit resolution of the A/D converter). The output voltage was determined by DC biasing the gas-sensing layer. This voltage had two components: a DC voltage depending on the resistance  $R$  of the gas-sensing layer and a random element proportional to resistance fluctuations. We confirmed that the recorded  $1/f$  noise was dominated by noise generated within the gas-sensing structure, i.e., not by contact noise generated between the gold electrodes and the gas-sensing layer. This was verified by the square dependence between the DC voltage  $U$  across the sensor and the power spectral density of the voltage noise  $S(f)$  [16]. Thus, there was no need to use a four-point contact method to reduce eventual contact noise. Our measurement set-up ensured that the normalized power spectral density,  $S(f)/U^2$ , was equal to the normalized power spectral density of resistance fluctuations,  $S_R(f)/R^2$  [17].

The metal gas chamber was used for shielding against external electromagnetic interference. UV LEDs were placed at a distance of 1.5 cm from the gas-sensing layer. Two UV LEDs were applied, designated LED 1 (type T5F, Seoul Opto-device) and LED 2 (type OSV4YL5451B, OptoSupply). The bias currents  $I_D$  of the UV LEDs were set so as to assure the same maximum optical power emitted at different wavelengths  $\lambda$  (LED 1:  $I_D = 8.3$  mA,  $\lambda = 362$  nm; LED 2:  $I_D = 10$  mA,  $\lambda = 394$  nm). This arrangement enabled us to see how the wavelength of the UV light affected the generated low-frequency noise and the ability for gas detection.

### 4. Experimental Results and Discussion

Experimental data confirmed the usefulness of  $1/f$  noise measurements on the low-cost gas-sensing layers. An  $1/f$  noise component dominated up to a few kHz, which implies that the FES method can be utilized for these sensors by applying a low-noise measurement set-up. The voltage across the gas-sensing layer was recorded at a sampling frequency  $f_s$  of 20 kHz. We estimated the power spectral density of voltage fluctuations across the sensor by averaging over 512 spectra, and each spectrum was estimated by using 4096 voltage noise samples. The product of power spectral density and frequency was then normalized with the DC voltage, and  $S(f)/U^2$  was evaluated to expose any discrepancy from a  $1/f$  dependence (Figure 3). This product presents a  $1/f$  noise component as a flat line in the low-frequency range. Deviations from  $1/f$  noise is represented as a local maximum. We did not give spectral data at frequencies close to the maximum frequency  $f_s/2 = 10$  kHz when the antialiasing filter of the data acquisition board attenuated the signal.

Apart from the  $1/f$  noise component, dominating within a frequency range up to a few kHz, we identified a Lorentzian at a corner frequency of 70 Hz under dark conditions and at an operating temperature  $T$  of 60°C (Figure 3(a)). The maximum of the Lorentzian is about twice larger than the  $1/f$  noise recorded under UV light irradiation. The Lorentzian shifted to another frequency range upon irradiation of UV light. We observed that LED 1, with a short-wavelength emission, increased the white-noise component as compared with the effect induced by irradiation from LED 2. It appears that the higher energy at the shorter wavelengths generated shot noise. This effect is not so vivid at a higher operating temperature of 120°C (Figure 3(b)), and we can state that shot noise induced by UV light is not so intense when compared with the thermal noise of the sensing layer at  $T = 120^\circ\text{C}$ . The experimental results suggest that the second temperature is too high to be used together with UV light irradiation.

We observed a similar change of the slope of  $1/f$  noise when the sensor was in an ambient atmosphere of NO<sub>2</sub> gas (Figure 4). The presence of the gas shifted the Lorentzian (Figure 4(a)) at low concentration (5 ppm) in a similar way as UV light irradiation but did not increase the white-noise component as observed when the LED 1 was used (Figure 3(a)). Higher concentrations of NO<sub>2</sub> (10, 15 ppm) induced an increase of  $1/f$  noise and white-noise components by up to a few times. The white-noise component is related to shot noise and thermal noise and, at high concentrations of NO<sub>2</sub>, its increase is also related to a change of the DC resistance.

When we irradiated the gas-sensing layer by UV light in an ambient atmosphere with a low concentration of NO<sub>2</sub> (5 ppm), we observed amplification of  $1/f$  noise at low frequencies (below 10 Hz) for the LED 2 only (Figure 4). The LED 2 emitted light at longer wavelengths (maximum at 394 nm) and supplied smaller energy as compared with the LED 1 (maximum at 362 nm). This fact explains why the LED 2 induced intense  $1/f$  noise at frequencies below 10 Hz (Figure 4(c)) whereas the LED 1 did not (Figure 4(b)).

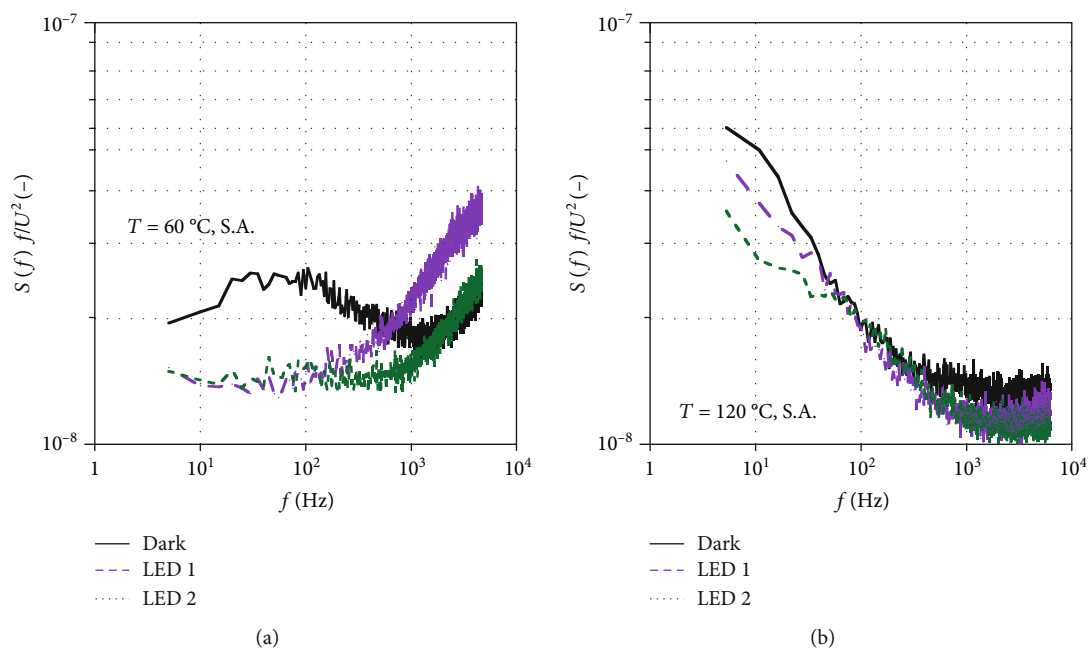


FIGURE 3: Normalized product  $S(f) f/U^2$  of frequency  $f$  and power spectral density  $S(f)$  of voltage fluctuations across a gas sensor biased by a DC voltage  $U$  when the sensor is in an ambient atmosphere of synthetic air (S.A.) and operating at (a)  $T = 60^\circ\text{C}$  and (b)  $T = 120^\circ\text{C}$ . The sensing layer (graphene flakes/ $\text{TiO}_2$  ratio 10 wt%) was working in the dark and under UV light supplied by LEDs with emission wavelengths of 362 nm (LED 1) and 394 nm (LED 2).

We should underline that the power spectral densities changed by up to a few times, and these differences are much larger than the observed changes of the DC resistance induced by UV light irradiation or by the ambient atmosphere of  $\text{NO}_2$ . Moreover, the Lorentzian is characterized by a corner frequency whose value is very informative for gas detection algorithms. This result can be explained by the activation mechanism of UV light irradiation on gas sensing. It is known that UV light generates ions  $\text{O}_2^-(\text{g})$  covering the surface of gas-sensing grains [18]. These ions have much weaker binding to the grains than the chemisorbed ions  $\text{O}_2^-$ . Therefore, any changes in fluctuation phenomena induced by the introduced gas can be more intense due to lower binding energy. Moreover, corner frequencies  $f_c = 1/2\pi\tau_c$  for G-R events can be higher due to lower energy and visible at higher frequencies, as observed in our experimental studies.

The DC resistance depended on operating temperature and graphene flakes/ $\text{TiO}_2$  ratio. When UV light, irradiating the sensor or toxic  $\text{NO}_2$  gas, was introduced, we observed a drop of the DC resistance. Relative change of DC resistance was about 60% of the initial value for the lowest investigated graphene flakes/ $\text{TiO}_2$  ratio of 5 wt%. The sensor with a graphene flakes/ $\text{TiO}_2$  ratio of 20 wt% had a DC resistance of about a few hundred  $\Omega$  only, and the observed drop did not exceed 30% at the highest concentration of 15 ppm of  $\text{NO}_2$ . The layers with the graphene flakes/ $\text{TiO}_2$  ratio of 10 wt% had a DC resistance of some tens of  $\text{k}\Omega$ . Slightly higher DC resistance was exhibited for the gas-sensing layer with a graphene flakes/ $\text{TiO}_2$  ratio of 5 wt%. The DC resistances of the gas-sensing layers varied because of different graphene fla-

kes/ $\text{TiO}_2$  ratios and because of differences in the thicknesses of the tested specimens. All recorded DC resistances and time series of voltage across the sensor, and the detailed description of the files, were saved as data sets in MATLAB workspace format (the files \*.mat) and are available for further use at <https://drive.pg.edu.pl/s/G4R5w0CMzjJpRIA>.

It should be noted that graphene is sensitive to irradiation at the wavelengths of the applied UV light, and it has been experimentally confirmed that UV light at a wavelength of 280 nm can damage and alter the characteristics of a single-layer-graphene sensing device [9]. Thus, the combination of operating temperature and UV light wavelengths determines the frequency position of the Lorentzian and its presence. We observed that at the operating temperature of  $120^\circ\text{C}$ , and in an ambient atmosphere of SA, the UV light intensified the  $1/f$  noise at low frequencies (Figure 5(a)). At the same operating temperature and under dark conditions, but at an ambient atmosphere of 15 ppm of  $\text{NO}_2$ , there was a Lorentzian at a corner frequency of 100 Hz (Figure 5(b)). The corner frequency shifted when UV light was applied.

We conclude that the presented results are very promising with regard to practical applications of the FES method implemented with low-cost gas-sensing layers. We observed for a few sets of working conditions that the Lorentzians occurred at different corner frequencies. Their presence can be easily utilized to enhance gas detection even when the ambient atmosphere is a gas mixture. The results are similar to those observed for a back-gated field-effect transistor with single-layer-graphene in its channel [9], and the identified corner frequencies, characteristic for different investigated gases, were in a range similar to the frequencies observed in

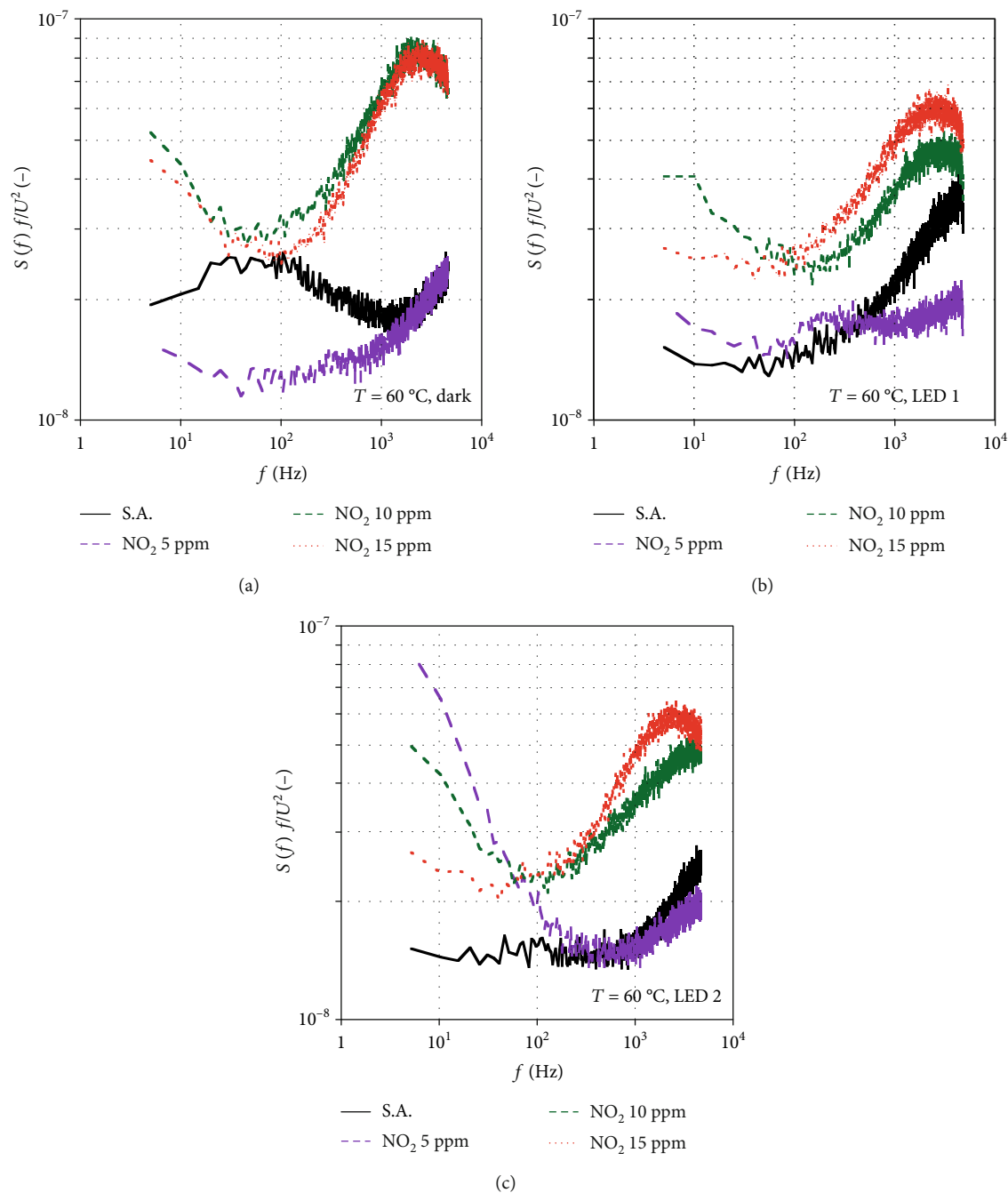


FIGURE 4: Normalized product  $S(f)f/U^2$  of frequency  $f$  and power spectral density  $S(f)$  of voltage fluctuations across a gas sensor biased by a DC voltage  $U$  when the sensor, operating at  $T = 60\text{ }^{\circ}\text{C}$ , was in an ambient atmosphere of synthetic air (S.A.) and in the shown concentrations of NO<sub>2</sub>. The sensing layer (graphene flakes/TiO<sub>2</sub> ratio 10 wt%) was working in the dark and under UV light supplied by LEDs with emission wavelengths of 362 nm (LED 1) and 394 nm (LED 2).

the present work. We suppose that the addition of TiO<sub>2</sub> nanoparticles, which decreases the bandgap, makes the graphene flakes more sensitive to gas detection. Unfortunately, the introduced nanoparticles change the  $1/f$  noise and alter its intensity between the various samples of gas-sensing layers as a result of unavoidable imperfections induced on the graphene surface. The results suggest that the considered low-cost technology utilizing a two-dimensional material (graphene flakes) can give acceptable gas-sensing properties.

Our results are close to those for very selective, and certainly more sensitive, sensors utilizing single-layer-graphene, which offer highly repeatable sensing parameters but are very fragile and expensive.

There are still problems associated with our technology, which require further in-depth studies, and we do not know how repeatable and durable the technology is with the investigated gas-sensing layers. The layers were rather thick and as a consequence of the simple, and very cheap, technology,



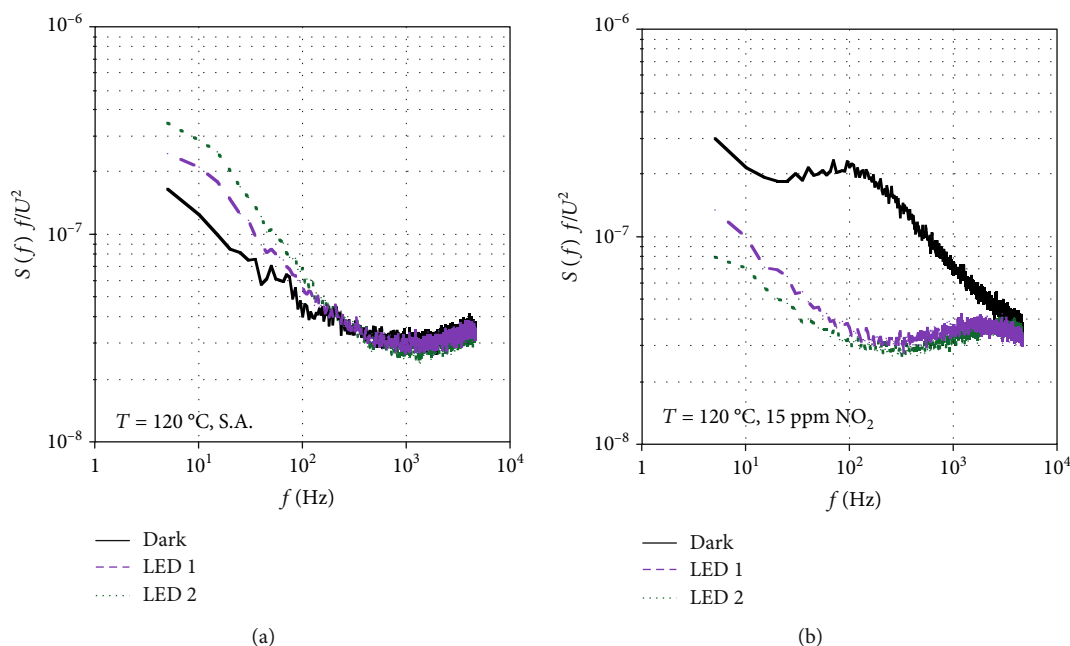


FIGURE 5: Normalized product  $S(f)f/U^2$  of frequency  $f$  and power spectral density  $S(f)$  of voltage fluctuations across a gas sensor biased by a DC voltage  $U$  when the sensor was in an ambient atmosphere of (a) synthetic air (S.A.) and (b) 15 ppm of  $\text{NO}_2$  diluted in S.A. The operating temperature was  $T = 120^\circ\text{C}$ . The sensing layer (graphene flakes/ $\text{TiO}_2$  ratio 10 wt%) was working in the dark and under UV light supplied by LEDs with emission wavelengths of 362 nm (LED 1) and 394 nm (LED 2).

their thicknesses vary significantly. We are confident that much better results could be reached by spin coating technology. Sensing parameters would then be more reproducible, and the sensing layers could be as thin as a few  $\mu\text{m}$  only. Then, we expect an even more significant impact of UV light irradiation on the sensing properties. In fact, the penetration depth of UV light in the graphene flake/ $\text{TiO}_2$  layer does not exceed a few  $\mu\text{m}$ ; its value depends on the morphology of the layer and is determined by the specific graphene flakes/ $\text{TiO}_2$  ratio. This issue has to be studied experimentally in order to ascertain optimal technical parameters. Moreover, a very thin layer would decrease the response time and make gas detection more facile and measurement time much shorter than for the experiments reported above. A decrease of the response time would require advanced signal processing to account for differential values for gas detection in order to remove unavoidable drifts in practical measurements. It would also be possible to apply some drift removal algorithms [19] in order to reduce this detrimental effect, and the same solution could be used to reduce effects of sensor ageing. In future work, the selected detection algorithm should be applied to detect gases in the ambient atmosphere [20]. Some of these algorithms were designed specifically for the FES method and utilize changes of the estimated power spectral densities [21].

## 5. Conclusions

We presented experimental results of  $\text{NO}_2$  sensing by low-cost gas-sensing layers made from graphene flakes/ $\text{TiO}_2$  nanoparticles mixtures. The layers were modulated by UV light irradiation using two LEDs with different emitted wave-

lengths. The FES method was applied to detect an ambient gas, and the recorded  $1/f$  noise exhibited Lorentzians at different corner frequencies. The Lorentzians were modulated by UV light and can be used to detect the ambient gas. Preliminary work indicated that optimum properties were obtained when the graphene flakes/ $\text{TiO}_2$  nanoparticles ratio was 5 wt%. The DC resistance of the sensing layer was about tens of  $\text{k}\Omega$  and allowed accessible low-frequency noise measurements by applying low-cost technology embodying a low-noise operational amplifier and A/D converter.

In addition, we proposed to advance the technology by applying spin coating to reduce the thickness of the gas-sensing layer, which would enhance the modulation by UV light. Our preliminary results suggest that low-cost gas detection can be sensitive to selected gases in a manner similar to that with much more expensive sensors based on a single-layer-graphene FET transistor. This result is promising for the detection of the components of gas mixtures when the modulated sensor replaces an array of independent resistive sensors, which consume much more energy for heating and require significant maintenance costs. The proposed sensors can be potentially applied in wearable applications as a consequence of their low cost and their low operating temperature which requires little energy for heating. In principle, temperature-activated adsorption-desorption of gas molecules was replaced by UV light modulation to produce similar effects. However, more thorough studies are needed to determine the repeatability of the sensitivity and gas selectivity for the sensors discussed in the present work.

The same remark is valid for determining the gas sensors' response at various humidity levels and optimal selection of operating temperature for detected gases. The reported

results for relatively low temperatures (60°C, 120°C) are important for practical applications since the energy consumed by the sensors is small.

It is worth mentioning that various two-dimensional materials (composite of rGO and TiO<sub>2</sub> [22], a few layers of MoS<sub>2</sub> [23]), decorated with nanoparticles of Au, exhibit photocatalytic effect and enhance their gas sensing under UV light irradiation. The observed changes of DC resistances are more profound when UV light activates adsorption-desorption processes. We can expect even better results for the FES method when applied for these materials. It means that our presented results open a new perspective on enhanced gas sensing for emerging gas-sensing materials.

We should underline that there are new proposals of physical phenomena that can be utilized to enhance gas sensing, including triboelectric effect [24] or even triboelectric-photoelectric coupling effect [25]. These proposals improve gas sensing and suggest self-powered sensors for wearable applications. We hope that such sensors applied for monitoring human activities can also utilize the FES method and introduce new sensing operations.

## Data Availability

The data used to support the findings of this study using MATLAB workspace format (\*.mat) have been deposited in the local repository (<https://drive.pg.edu.pl/s/G4R5w0CMzjJpRIA>) and are available for further use.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

## Acknowledgments

We thank Dr. Maciej Trawka for his help with noise time series recording. Financial support for work at Uppsala University was received from the European Research Council under the European Community's Seventh Framework Program (FP7/2007–2013)/ERC Grant Agreement 267234 ("GRINDOOR").

## References

- [1] G. Korotcenkov, "Gas response control through structural and chemical modification of metal oxide films: state of the art and approaches," *Sensors and Actuators B: Chemical*, vol. 107, no. 1, pp. 209–232, 2005.
- [2] P. Heszler, R. Ionescu, E. Llobet et al., "On the selectivity of nanostructured semiconductor gas sensors," *Physica Status Solidi (b)*, vol. 244, no. 11, pp. 4331–4335, 2007.
- [3] S. Vallejos, P. Umek, T. Stoycheva et al., "Single-Step deposition of Au- and Pt-nanoparticle-functionalized tungsten oxide nanoneedles synthesized via aerosol-assisted CVD, and used for fabrication of selective gas microsensor arrays," *Advanced Functional Materials*, vol. 23, no. 10, pp. 1313–1322, 2013.
- [4] A. Dziedzic, B. Licznarski, and A. Kolek, "Noise and nonlinearity of gas sensors: preliminary results," in *Proc. 22nd International Spring Seminar on Electronics Technology*, pp. 99–104, Dresden-Freital, Germany, May 1999.
- [5] L. B. Kish, R. Vajtai, and C. G. Granqvist, "Extracting information from noise spectra of chemical sensors: single sensor electronic noses and tongues," *Sensors and Actuators B: Chemical*, vol. 71, no. 1–2, pp. 55–59, 2000.
- [6] Ł. Lentka, J. M. Smulko, R. Ionescu, C. G. Granqvist, and L. B. Kish, "Determination of gas mixture components using fluctuation enhanced sensing and the LS-SVM regression algorithm," *Metrology and Measurement Systems*, vol. 22, no. 3, pp. 341–350, 2015.
- [7] M. Trawka, J. Smulko, L. Hasse, C. G. Granqvist, F. E. Annanouch, and R. Ionescu, "Fluctuation enhanced gas sensing with WO<sub>3</sub>-based nanoparticle gas sensors modulated by UV light at selected wavelengths," *Sensors and Actuators B: Chemical*, vol. 234, pp. 453–461, 2016.
- [8] J. Smulko, "Advanced operating methods," in *Advanced Nanomaterials for Inexpensive Gas Microsensors*, E. Llobet, Ed., pp. 189–208, Elsevier, 2020.
- [9] S. Rumyantsev, G. Liu, R. A. Potyraiolo, A. A. Balandin, and M. S. Shur, "Selective sensing of individual gases using graphene devices," *IEEE Sensors Journal*, vol. 13, no. 8, pp. 2818–2822, 2013.
- [10] S. Rumyantsev, G. Liu, M. S. Shur, R. A. Potyraiolo, and A. A. Balandin, "Selective gas sensing with a single pristine graphene transistor," *Nano Letters*, vol. 12, no. 5, pp. 2294–2298, 2012.
- [11] Z. Ye, H. Tai, C. Liu et al., "The investigation of reduced graphene oxide/titanium dioxide-based sensor for formaldehyde detection at room temperature," in *2015 IEEE SENSORS*, pp. 731–734, Busan, South Korea, November 2015.
- [12] M. Donarelli and L. Ottaviano, "2D materials for gas sensing applications: a review on graphene oxide, MoS<sub>2</sub>, WS<sub>2</sub> and phosphorene," *Sensors*, vol. 18, no. 11, p. 3638, 2018.
- [13] A. A. Balandin, "Low-frequency 1/f noise in graphene devices," *Nature Nanotechnology*, vol. 8, no. 8, pp. 549–555, 2013.
- [14] C. Xu, X. Wang, and J. Zhu, "Graphene-metal particle nanocomposites," *Journal of Physical Chemistry C*, vol. 112, no. 50, pp. 19841–19845, 2008.
- [15] J. Smulko, M. Trawka, U. Cindemir, C. G. Granqvist, and C. Duran, "Resistive gas sensors: perspectives on selectivity and sensitivity improvement," in *Presented at the Conf. NANOJIM 2016*, Chemnitz, Germany, 8–9 September 2016, URN: urn:nbn:se:uu:diva-302554.
- [16] M. Kotarski and J. Smulko, "Noise measurement set-ups for fluctuations-enhanced gas sensing," *Metrology and Measurement Systems*, vol. 16, no. 3, pp. 457–464, 2009.
- [17] B. Ayhan, C. Kwan, J. Zhou et al., "Fluctuation enhanced sensing (FES) with a nanostructured, semiconducting metal oxide film for gas detection and classification," *Sensors and Actuators B: Chemical*, vol. 188, pp. 651–660, 2013.
- [18] S. Zhang, T. Lei, D. Li, G. Zhang, and C. Xie, "UV light activation of TiO<sub>2</sub> for sensing formaldehyde: how to be sensitive, recovering fast, and humidity less sensitive," *Sensors and Actuators B: Chemical*, vol. 202, pp. 964–970, 2014.
- [19] Ł. Lentka and J. Smulko, "Methods of trend removal in electrochemical noise data - Overview," *Measurement*, vol. 131, pp. 569–581, 2019.
- [20] R. Gutierrez-Osuna, "Pattern analysis for machine olfaction: a review," *IEEE Sensors Journal*, vol. 2, no. 3, pp. 189–202, 2002.



- [21] H.-C. Chang, L. Kish, M. King, and C. Kwan, "Binary fingerprints at fluctuation-enhanced sensing," *Sensors*, vol. 10, no. 1, pp. 361–373, 2010.
- [22] Y. Zhou, X. Li, Y. Wang, H. Tai, and Y. Guo, "UV illumination-enhanced molecular ammonia detection based on a ternary-reduced graphene oxide–titanium dioxide–Au composite film at room temperature," *Analytical Chemistry*, vol. 91, no. 5, pp. 3311–3318, 2018.
- [23] Y. Zhou, C. Zou, X. Lin, and Y. Guo, "UV light activated NO<sub>2</sub> gas sensing based on Au nanoparticles decorated few-layer MoS<sub>2</sub> thin film at room temperature," *Applied Physics Letters*, vol. 113, no. 8, article 082103, 2018.
- [24] S. Wang, Y. Jiang, H. Tai et al., "An integrated flexible self-powered wearable respiration sensor," *Nano Energy*, vol. 63, p. 103829, 2019.
- [25] Y. Su, M. Yao, G. Xie et al., "Improving sensitivity of self-powered room temperature NO<sub>2</sub> sensor by triboelectric-photoelectric coupling effect," *Applied Physics Letters*, vol. 115, no. 7, article 073504, 2019.