



Selective light-activation of sensing regions in hybrid Au-graphene-TiO₂ chemiresistive gas sensor

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ABSTRACT

Controlling the sensing activity of novel gas sensors is a desirable and simultaneously challenging issue. In this work, ink-printed graphene-based hybrid sensors are demonstrated, and the possibility of selective activation of gas-sensitive components with light is presented. Graphene flakes were mixed with TiO₂ nanoparticles and decorated with Au nanoparticles to produce sensors of photocatalytic and plasmonic properties (Au-G-TiO₂). The sensors decorated with Au exhibited enhanced selectivity to NO₂ and a detection limit of 10 ppb under UV light (275 nm) by DC resistance measurements. Activating the plasmon resonance with green light (515 nm) in Au improved sensor sensitivity to NO₂ compared to dark conditions but did not enhance response and recovery time constants as UV light. Low-frequency resistance noise measurements confirmed that the Au-G-TiO₂ sensor exhibits $\sim 1/f$ spectrum shape with a characteristic Lorentzian at 100–200 Hz, ascribed to Au decorating the defect sites in graphene. Noise spectra revealed that different parts of the sensing surface are activated by irradiation. Green light induces charges in the vicinity of Au, whereas UV light excites parts with TiO₂. These phenomena generate Lorentzians in noise power spectra of intensity and position dependent on NO₂ concentration, making the noise features a sensitive and selective sensing platform. The sensors exhibited long-term stability of their performance with reproducible DC and noise features for more than four months (resistance baseline shift of 5 %), showing the perspectives of their practical applications.

1. Introduction

Since the discovery of a single atomic layer of carbon atoms in 2004, graphene has become a leading representative of the two-dimensional (2D) materials family. Very soon, graphene was found to exhibit highly attractive properties for practical applications such as mechanical durability, high optical transparency (transmission of $\sim 2\%$ of the incident light), high carrier mobility, and increased electrical and thermal conductivity [1]. Thanks to these intrinsic properties, graphene has attracted significant attention in electronics, optoelectronics, and materials science. To this day, researchers have proposed numerous devices with elements composed of graphene, including field-effect transistors (FETs), photovoltaic devices, and different types of sensing platforms [2]. Graphene is a naturally highly sensitive platform for molecular detection due to its exceptional surface-to-volume ratio and all surface atoms exposed to the surrounding environment. Thus, it can successfully detect even a single molecule [3]. Unfortunately, pristine graphene exhibits serious shortcomings when used outside controlled

laboratory conditions. The surface of graphene is highly susceptible to surrounding humidity and oxygenic species from the ambient air, which limits its sensitivity. The capability of detection by high-quality graphene is also limited due to strong sp^2 C-C bonds and the lack of dangling bonds [4]. Moreover, the pristine structure lacks selectivity and requires functionalization with more complicated fabrication routes or specific measurements and data analysis methodology to limit the effect of cross-sensitivity [4,5]. Therefore, novel solutions for overcoming these problems are needed to propose graphene-based gas sensors for the market requirements.

The option to secure the ease of fabrication and operation of the graphene gas sensors is to utilize solution-based ink printing or coating to produce resistive gas sensing devices [6,7]. Printing techniques require the ink with the sensing material dispersed in the solvent. Some additives or binders can be added to obtain the dispersion of specific physical properties like density and viscosity [8]. Optimization of the printing process provides the automation of fabrication, guiding mass production of miniaturized gas sensors. On the other hand, the high

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sensitivity and other crucial sensing parameters must be considered for such devices. Since single-atomic graphene layers with a few types of defects exhibit severe sensitivity and selectivity limitations, hybrid materials and structures (binary or ternary) can be proposed to modulate adsorption/desorption centers for a wider variety of gas molecules [9]. One option is incorporating metal oxides (MOx), e.g., SnO₂, ZnO, WO₃, TiO₂, NiO, Co₃O₄, and others as catalytic and sensing components [10]. Although nanostructured MOx usually requires high operating temperatures to be gas-sensitive, its combination with graphene can provide enhanced sensitivity and selectivity at lower temperatures [11]. This way, a hybrid sensing material combining the advantages of both components can be produced. Semiconducting MOx with specific band gaps can also be used as photocatalysts for light-assisted gas sensing; e.g., TiO₂ has an optical band gap in the UV light range of ~400 nm and below [12]. Another option is to introduce metallic nanostructures to graphene that can act as electronic and chemical sensitizers, which increase the specific sensing area [13] and initiate the spillover effect when the nanoparticle acts as a catalyst for gaseous dissociation and subsequent spreading of charged gaseous ions on the material beneath it [14]. Such accumulation of charges at the sensing surface can lead to increased electrical responses to ambient gases. Additionally, noble metals such as Au, Ag, Pt, or Pd exhibit localized surface plasmon resonance (LSPR) – collective charge oscillations within metallic nanoparticles when the wavelength of incoming light satisfies the resonance condition. The incoming electromagnetic wave interferes with the electric field generated by electrons moving around the nucleus, resulting in resonance movement and an instantaneous dipole within the nanoparticle [15]. Moreover, the induced resonating electron cloud is not limited to the particle volume. Consequently, effective absorption occurs in a volume greater than the structural size, which enhances the light-activated processes (e.g., adsorption of gas molecules), and plasmonic resonance highly depends on the surrounding medium. Thus, a light-enhanced gas sensor can be proposed by applying the hybrid structure of graphene and photoactive additives that utilize different light-induced phenomena (photocatalytic MOx and plasmonic metal nanoparticles). Additionally, the considered hybrid sensor components – graphene flakes, MOx nanostructures, and metallic nanoparticles can be used in the printing process when prepared as dispersions, and the discussed phenomena in the ink-printed layer can be observed between the sensor terminals. We suppose that even using this simple printing technology, the selected hybrid components (e.g., TiO₂, Au nanoparticles) are associated with different graphene imperfections, which results in better gas selectivity. Such an effect was observed for MoS₂ flakes decorated with noble metal nanoparticles [16].

This work discusses the effects of light on the activation of selected gas-sensitive regions in the hybrid Au-graphene-TiO₂ (Au-G-TiO₂) devices. The sensing performance of hybrid sensors fabricated with a straightforward ink printing method is demonstrated, and the superiority of Au-decorated devices is presented. The hybrid structure is composed of individual graphene flakes, TiO₂, and Au nanoparticles and junctions between these components that are susceptible to irradiation of different wavelengths connected with the intrinsic properties of each component. The sensor is investigated with classic (resistance measurements) and fluctuation-enhanced sensing (FES) methods, which were not applied before for hybrid ink-printed graphene-based sensors. The results of FES specifically show how different types of irradiation (UV or visible light) activate parts of the hybrid sensing structure and increase the sensitivity and selectivity of the investigated device. In particular, the proposed sensors most attractive properties are detection limits for NO₂ under UV irradiation and the printed sensing layers long-term stability. Along with the ease and low cost of fabrication, these are crucial features for developing sensing devices for the market requirements. The results demonstrate a selective sensing platform of selected sensing features activated with light with a high potential for practical application as a miniaturized gas sensor based on printed graphene.

2. Experimental section

2.1. Materials and sensors fabrication

Conductive graphene dispersion in n-butyl acetate (Graphene Supermarket), titanium (IV) dioxide (TiO₂) powder (Aeroxide® P25, Acros Organics), ethanol (purity >99.8 %, Carl Roth), and gold nanoparticles (AuNPs) suspension in citrate buffer (10 nm diameter, stabilized, Sigma Aldrich) were purchased for sensors fabrication and used without further purification. Graphene dispersion comprises graphene nanoplatelets of ~7 nm thickness (23 % total graphene content). According to the data provided by the producer (Graphene Supermarket), graphene flakes have a low quantity of defects and sizes up to a single µm. Low defectiveness is confirmed on the Raman spectrum by the high ratio of G to D band intensity characteristic for graphene sheets. Raman spectra and SEM images confirming the material properties of the pristine graphene flakes available from the corresponding datasheet can be found in Figure A.1. Ceramic substrates from Tesla were used as platforms for printing the sensing layers. Each substrate consists of interdigitated platinum electrodes (IDES) of line/gap width of 15/15 µm, a heater, and a Pt 1000 temperature sensor. All substrates were ultrasonically cleaned in acetone and isopropanol and rinsed with deionized water before deposition of the ink. More details on the used substrates can be found on the producer's website (<https://tesla-blatna.eu/>).

To produce the ink, 30 mg of TiO₂ powder was dispersed in 2 mL of ethanol and subjected to ultrasonication for 30 minutes. Next, TiO₂ dispersion was mixed with graphene dispersion (13 mg of dispersion of flakes in n-butyl acetate means 3 mg of pure graphene) and ultrasonicated for another 30 minutes. The mass ratio of graphene to TiO₂ in the ink was 1:10 (10 wt%). The prepared dispersion was dark gray, as depicted in supplementary Figure A.2. As reported, the mass ratio between 5 wt% and 15 wt% of graphene ensured the sensitivity to selected gases for devices based on graphene flakes and TiO₂ nanoparticles [17].

Printing of the sensing layers was realized using Nordson Precision Fluid Dispenser (type Ultimix Plus II) with the needle tip of the inner diameter of 610 µm. The time of releasing a single ink droplet was 0.05 s, and the carrier gas (N₂) pressure was 0.04 bar. Printing repetitions were performed two times to ensure the continuity of the printed layer and complete coverage of the IDES. After the deposition of each droplet, the material was dried in airflow (50–60 °C) to evaporate the residuals of the solvent. Details on printing parameters and a photograph of the printed sensors can be found in Table A.1 and Figure A.2. AuNPs dispersion was used to decorate the sensing surface with plasmonic nanoparticles (LSPR at 515–519 nm, according to the producer). Parameters for AuNPs layer deposition are summarized in Table A.1. After decoration with Au, the sensors were left overnight for complete drying.

2.2. Optical characterization, electrical, and noise measurements

Optical imaging of the printed sensing layers was performed using a Delta Optical MET-1000-TRF microscope. The sensors IDES terminals were connected to the measuring and biasing units via the PCB for DC measurements. Each measured sensor was connected to a circuit with the voltage divider (sensor resistance R_S in series with resistor $R = 1$ kΩ). Keysight E3648A DC power supplier was used to polarize the sensor and the resistor. When the input voltage was fixed at 1 V, the voltage across the sensor was tens of mV depending on the ambient conditions. The voltage across the sensor was measured to calculate changes in sensor DC resistance R_S in time according to the formula $R_S = (V_S R) / (V_0 - V_S)$, where V_S is the measured voltage across the sensor, and $V_0 = 1$ V, respectively. For low-frequency noise measurements, the sensors were directly connected to a circuit with a low-noise operational amplifier and biased by a current source set to 370 µA. Voltage amplification was 784 V/V. The power spectral density of voltage fluctuations generated by resistance fluctuations and exposed by the stable input current flow was measured using a spectrum analyzer (Stanford Research Systems,

model SR785). The noise spectra were measured from 4 to 3200 Hz with a step of 4 Hz, and 400 averages were collected to reduce the sampling error to 5 %. The sensing chamber 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 DC and noise sensing responses were monitored in the dark, under green light (Roithner Lasertechnik, type LED515–10–30, $\lambda = 515$ nm), and under UV light (Prolight Opto, type PB2D-1CLA-TC, $\lambda = 275$ nm). The LEDs were positioned at 0.5–1 cm from the sensing surface to obtain relatively high and similar optical power densities (~ 2 mW/cm²). The optical power density was determined using a Si photodiode (Hamamatsu S1227–1010BQ). The current flowing through the photodiode under UV and green light was measured, and optical power densities were determined based on the dependence between photosensitivity (A/W) and wavelength available in the Si photodiode datasheet. DC measurements were conducted at room temperature (RT of ~ 25 °C) or 80 °C. Noise spectra were collected at RT (~ 25 °C).

2.3. Detection limit (DL) estimation

The detection limit (DL) was calculated based on sensor responses to selected target gas concentrations. The sensor responses were presented as relative changes in the sensor resistance R_S in reference to the sensor resistance in the carrier gas (synthetic air – S.A.) R_0 via the relation $(R_S - R_0)/R_0$ or noise amplitude $S_V(f_c)/V^2 \times f$ where $S_V(f_c)$ is the power spectral density of voltage fluctuations with the observed Lorentzian at the corner frequencies f_c between 100 and 200 Hz and multiplied by the frequency f . The detection limit (DL) was estimated according to the procedure described elsewhere [18]. Briefly, a third-order polynomial function was used to fit the experimental data points (sensor response vs. gas concentration). Then, the root mean square (RMS) was calculated from the deviation between experimental and fitted values of the sensor resistive or noise response. DL was determined using the formula: $DL = (S/N) \cdot \text{RMS}/\text{slope}$, where $S/N = 3$ (signal-to-noise ratio). The slope was derived by fitting the quasi-linear region of each set of data points.

2.4. Gas-sensing experiments

Gas-sensing experiments were conducted using nitrogen dioxide (NO₂), ammonia (NH₃), and acetone (C₃H₆O) as target gases. The selected target gases are representatives of analytes of different

properties (strongly oxidizing NO₂, reducing inorganic NH₃, and reducing organic C₃H₆O). Detecting these gases is essential for environmental, safety, and health monitoring. Dry synthetic air (S.A.) was used as a carrier gas and a reference atmosphere. To obtain selected concentrations of target gases, S.A. was mixed with calibrating gases (20 ppm of NO₂ diluted in S.A., 30 ppm of NH₃ diluted in N₂, or 40 ppm of C₃H₆O diluted in N₂) at specific proportions. A constant overall gas flow of 50 mL/min was regulated by mass flow controllers (Analyt-MTC, model GFC17). Sensing experiments were conducted at room temperature (RT ~ 25 °C) or 80 °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

3.1. Characterization of the sensing layers

The printing procedure described in the Experimental section assured the production of continuous films comprising graphene flakes of μm size and sub- μm TiO₂ nanoparticles forming the additives between the flakes, as depicted in the photograph in Fig. 1a. The porosity of the Al₂O₃ substrates provided good adhesion of the thin film to the ceramic platform and enabled the production of mechanically stable sensing layers of the given physical properties. The main difference between traditional coating methods (drop casting, spin-coating, blade coating, etc.) and printing is the possibility of automation of the process and better control of the volume of the droplets and the distance between the substrate and the needle. After completely drying the ink-printed graphene-TiO₂ (G-TiO₂) layers, their resistance was between 60 and 70 Ω . Such high conductivity is the result of using graphene conductive paste for which the resistance of the dried film was only ~ 23 Ω . The low resistance of mixed G-TiO₂ layers suggests that micrometer-sized graphene flakes create the conduction path between adjacent electrodes, whereas TiO₂ nanoparticles form the matrix surrounding the graphene flakes, which is also consistent with the microscopic image. The size of the used TiO₂ particles was evaluated using dynamic light scattering (DLS). The characterization of TiO₂ dispersed in ethanol revealed that particles are mostly 500–600 nm in size (see Figure A.3 for more details). Images of graphene flakes embedded in the TiO₂ matrix are consistent with SEM images of similar structures presented in other

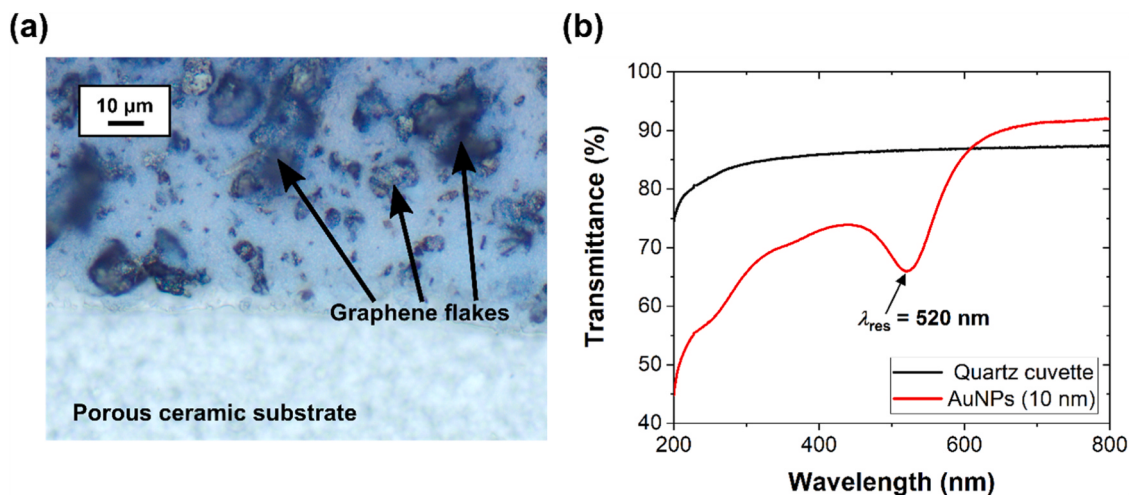


Fig. 1. (a) Optical image of the G-TiO₂ sensing layer under 500x magnification (the scale bar is 10 μm) printed on a ceramic substrate showing the edge of the printed G-TiO₂ layer with dark graphene flakes of μm size and the surrounding matrix formed with sub- μm TiO₂ nanoparticles (light additives in between graphene flakes). The porosity of the ceramic substrate ensures good adhesion of the printed layer. (b) UV–vis spectrum of the AuNPs dispersion and quartz cuvette used for the measurement. The minimum transmittance corresponding to the plasmon resonance is at 520 nm for Au particles of an average size of 10 nm.

works [17,19]. The AuNPs of 10-nm size dispersed in citrate buffer used to decorate the surface of the G-TiO₂ sensors exhibited LSPR at ~520 nm, as confirmed by UV-vis spectroscopy (Fig. 1b).

3.2. DC resistance measurements

Initial experiments with G-TiO₂ sensors studied resistive responses to selected gases under various conditions, including higher operating temperatures and light assistance. Fig. 2a shows the repeatability of the resistance responses of the exemplary G-TiO₂ sensor to 5 ppm of NO₂. Since metal oxides, including TiO₂, require elevated temperatures to operate effectively, we investigated sensor responsivity at $T = 80^\circ\text{C}$, a compromise between accelerated adsorption-desorption of ambient gas molecules and avoiding burning graphene flakes. On the other hand, UV light was previously used to improve gas detection and provide the energy necessary to enhance the surface processes of adsorption/desorption as an alternative to higher temperatures [20]. It was confirmed that the sensitivity of graphene increased after irradiating its surface with UV light [21]. Additionally, TiO₂ nanoparticles have high absorbance in the UV light range due to their optical energy band gap, so they can act as UV light absorbers for the whole sensing layer. The maximum absorbance of the TiO₂ used in this work is at 277 nm, as confirmed by UV-vis spectroscopic studies (see Figure A.4, which shows UV-vis absorbance spectra for TiO₂ dispersion). Thus, G-TiO₂ sensitivity at RT with UV light assistance (275 nm) and at 80°C in the dark was compared. The elevated temperature was adjusted so that the power supply required for obtaining high temperature and polarizing the diode to its maximal emitted optical power was the same in both experiments (~500 mW). This way, it is apparent which working condition is more effective for gas sensing when both enhancement types absorb the same power, which is relevant for practical applications. Notably, increased temperature reduced sensor resistance (by less than 10 %), which is a common observation for semiconducting films. The relative changes in sensor resistance were lower in consecutive cycles at $T = 80^\circ\text{C}$, and the recovery was poorer than under UV light. Continuous UV irradiation resulted in higher responsivity and faster recovery than elevated temperature. Moreover, the sensitivity to NO₂ and the pace of recovery were lower when the sensor was in the dark and remained at RT (see Figure A.5). Next, UV light assistance was applied for NH₃ (10 ppm) and C₃H₆O (20 ppm) sensing, as seen in Fig. 2b. Unlike NO₂, resistive responses to two reducing gases were minor (less than 1 %), even though higher concentrations of 10 ppm or 20 ppm were admitted to the sensing surface. The response to NO₂ was 15 and 14 times higher than to NH₃ and C₃H₆O, respectively, signaling the selectivity of the G-TiO₂ toward oxidizing NO₂.

The following experiments aimed to compare the pure G-TiO₂ sensor

and the same sensor decorated with AuNPs (labeled as Au-G-TiO₂). The nanoparticles of 10-nm size deposited onto the G-TiO₂ surface were expected to act as electronic and chemical sensitizers to the investigated structure. The Au-G-TiO₂ sensor has moderately higher resistance, presumably due to some Schottky contacts formed between AuNPs and TiO₂ nanoparticles. At the same time, Au has a higher work function than graphene, and ohmic contact is formed between these two materials [14]. Such an interface is susceptible to electron-accepting and donating gases. Thus, AuNPs are mainly chemical sensitizers for graphene but can be both chemical and electronic sensitizers for TiO₂ nanoparticles. Fig. 3a compares resistive responses to NO₂ (5 ppm), NH₃ (10 ppm), and C₃H₆O (20 ppm) for the non-decorated (dotted curves) and Au-decorated sensor (solid curves) under UV light. In the case of both sensors, there is good repeatability in responses to NO₂, but the magnitude of changes in resistance is higher after decoration with AuNPs. The average response to 5 ppm of NO₂ is 6.9 % for G-TiO₂ and 16.7 % for Au-G-TiO₂, which is a 2.4 times increase. Additionally, AuNPs decoration diminished the response to reducing gases, which was already low before decoration. Therefore, the sensor selectivity increased, and the Au-G-TiO₂ device demonstrated superior sensitivity to NO₂ compared to NH₃ or C₃H₆O. Charge transfer is established as the main mechanism driving gas detection by graphene. The direction of charge transfer is related to electron-accepting (NO₂) or -donating (NH₃, C₃H₆O) properties of target gases. NO₂ decreases the resistance of the sensing layer, suggesting *p*-type semiconducting properties of the G-TiO₂ and Au-G-TiO₂ hybrid layers. Junctions formed between AuNPs and graphene or TiO₂ of specific energy barriers can be responsible for limited sensitivity to reducing gases and enhanced selectivity to NO₂. Sensing responses to varied concentrations of NO₂ are depicted in Fig. 3b, confirming that Au-G-TiO₂ is also better at sensing low concentrations of this gas.

The relative changes in sensor resistance were derived from time-resolved measurements and demonstrated as a function of NO₂ concentration to estimate detection limits (DLs) in Fig. 4. DL was calculated based on the quasi-linear region of the sensor response (first three points in Fig. 4 – between 1 and 3 ppm of NO₂ concentration). Both sensors exhibit DL at the ppb level; however, the value is 10 times lower for Au-G-TiO₂. Au-G-TiO₂ sensor with DL reaching 10 ppb can be successfully applied to detect traces of NO₂. However, the DL = 100 ppb obtained for the non-decorated sample is still sufficient for sensing industrial levels of NO₂.

UV light activates the photocatalytic effect in the sensing structure since semiconducting TiO₂ nanoparticles are a good absorbing medium in the UV part of the spectrum. Additionally, UV wavelengths activate graphene by generating electron-hole pairs that can participate in the surface processes of gas detection. On the other hand, when the sensing

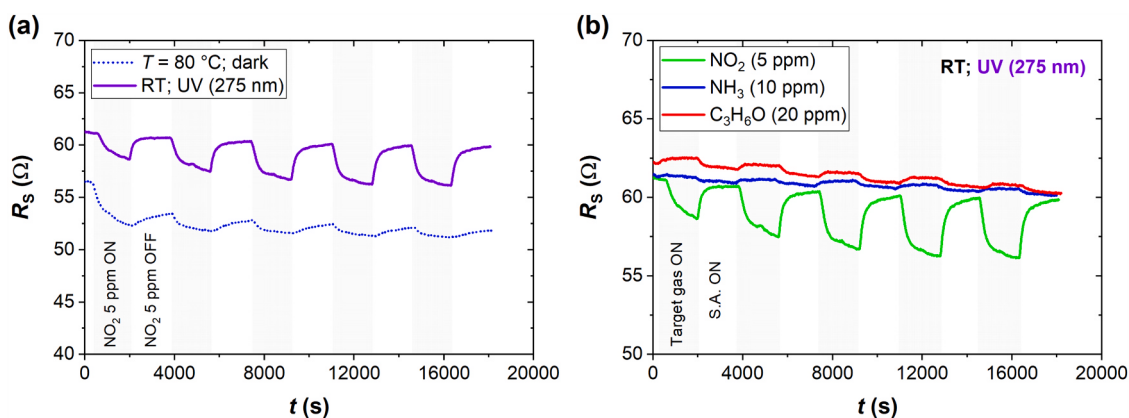


Fig. 2. Time-resolved measurements (sensor resistance R_s) of the ink-printed G-TiO₂ sensor: (a) five consecutive cycles of NO₂ (5 ppm) introduction in the dark at $T = 80^\circ\text{C}$ and under UV light (275 nm) at RT; and (b) comparison of sensor sensitivity and repeatability to NO₂ (5 ppm), NH₃ (10 ppm), and C₃H₆O (20 ppm) under UV light (275 nm) at RT.

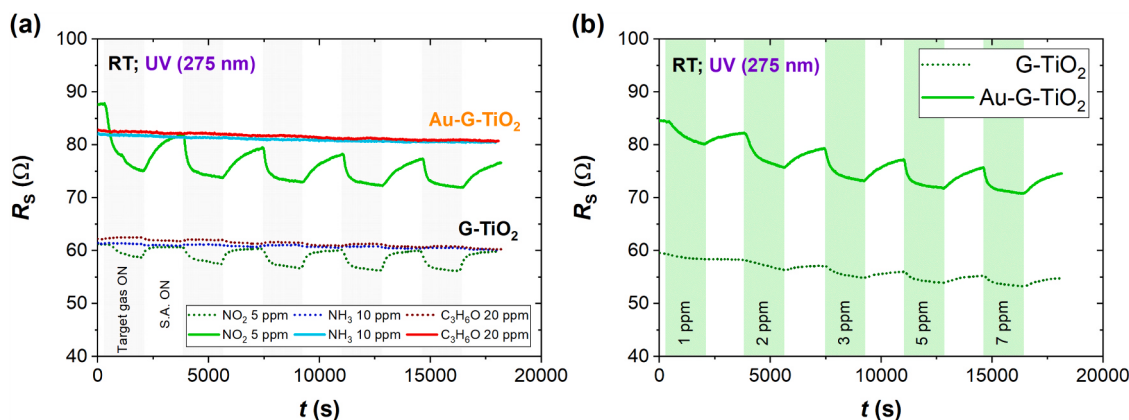


Fig. 3. Time-resolved measurements (sensor resistance R_s) of the ink-printed G-TiO₂ sensor before and after decorating with AuNPs: (a) comparison of sensor responsivity to NO₂ (5 ppm), NH₃ (10 ppm), and C₃H₆O (20 ppm) under UV light (275 nm) at RT; and (b) G-TiO₂ and Au-G-TiO₂ sensors response to selected concentrations of NO₂ (1–7 ppm) under UV light (275 nm) at RT.

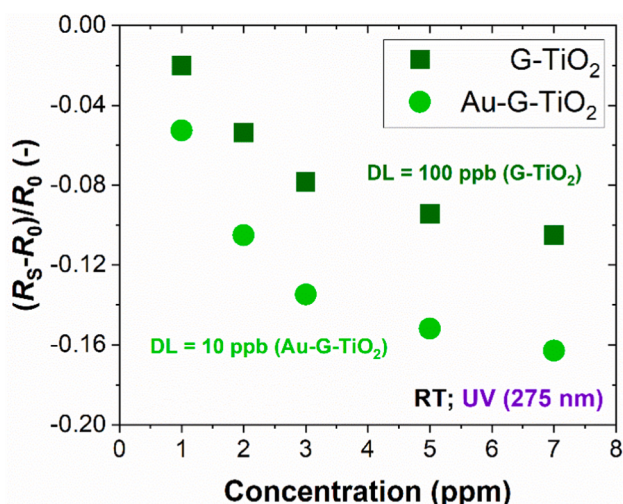


Fig. 4. Dependence between the NO₂ concentration and the relative change of sensor resistance in reference to resistance in S.A for G-TiO₂ before and after decoration with AuNPs. Estimated detection limits (DL) are highlighted on the graph. The points are derived from the time responses of each sensor collected under UV light (275 nm) at RT.

surface is covered with AuNPs, incident wavelength correlating with the LSPR of the plasmonic nanostructures can activate the sensing layer differently. For AuNPs of size ~ 10 nm, wavelengths close to the resonance peak (~ 520 nm) activate the collective movement of charges within the nanoparticles, which can affect the charge transfer into graphene flakes during gas sensing. Thus, in the subsequent measurements, the effect of green light on gas sensing by the Au-G-TiO₂ sensor was studied and compared to sensor performance without any light and with irradiation of shorter wavelengths than green light of the same optical power. The green LED had the maximum optical power at 515 nm (~ 2 mW/cm²), sufficient to excite LSPR in AuNPs. Fig. 5a compares time responses to 5 ppm of NO₂ in selected lighting conditions. At the starting point ($t = 0$), it can be noticed that UV light increased the baseline resistance more significantly than green light. The resistive responses to NO₂ are higher under UV light in each detection cycle, and the recovery is faster than under green light or in the dark. Such results were expected since although green light excites LSPR, it has a wavelength that is too long to affect TiO₂ nanoparticles and graphene flakes significantly. UV light generates electron-hole pairs in graphene and TiO₂, whereas visible light is not energetic enough to efficiently excite these two materials, so the effect is milder. Notably, the photocatalytic

activity is crucial to enhance the sensitivity and speed of operation of the Au-G-TiO₂ sensor. Response and recovery time constants were derived from the time-resolved measurements by fitting the exponential functions to the NO₂ detection cycle, as depicted in Fig. 5b. The response time τ_{resp} is lower under UV light (269 s), whereas it has similar values in the dark (503 s) and under green light (502 s). The recovery time τ_{rec} is also the lowest under UV light (1320 s), then for green light (1651 s), and it reaches the highest value in the dark (1782 s). It is clear that only UV light significantly reduces the time constants; however, due to the hybrid sensing structure comprised of overlapping flakes and nanoparticles, achieving the ultimate sensing response requires minutes. The prospective solution to improve the response and recovery rates of the sensor is its thickness and area reduction combined with short thermal or light pulses to stabilize the sensors parameters, increase sensitivity and potentially reduce response and recovery times. Thermal modulation was previously reported for sensors based on metal oxides to obtain microwatt sensing power consumption and increase the detection limits to selected gases [22,23]. On the other hand, short UV light pulses were reported for metal oxides and graphene-based sensors, showing the prospect of sensor performance modulation [24,25]. Thus, there is a possibility of reducing time constants with pulsed irradiation or heat, which is worth considering for future studies.

Fig. 6 shows resistive responses in time obtained for Au-G-TiO₂ sensor in the dark or irradiated with UV or green light for selected concentrations of NO₂ (1–7 ppm). The relative changes in R_s obtained in each cycle were used to estimate DLs (see Figure A.6 for the scatter plot). DL obtained in the dark and under green light was 70 ppb, so only UV light reduces DL significantly (to 10 ppb). Light modulation enhances charge transfer between adsorbing molecules and the sensing layer by generating photocarriers and oxygen photoions that participate in adsorption/desorption processes. A shorter wavelength (275 nm) carries more energy and impacts DC resistance more than green light (515 nm) and the induced plasmonic resonance. Comparing the results obtained in this work with other recently reported similar sensing structures, the more complex fabrication procedures allow us to obtain sensors of even lower DL. However, as demonstrated elsewhere [26], it comes with the cost and laborious techniques. On the other hand, reports showing the hybrid sensors based on TiO₂ and graphene or Au and graphene fabricated *via* coating methods (e.g., drop casting) exhibit DLs of hundreds or tens of ppb and sensing responses up to tens % but for high concentrations of NO₂ [27–29]. This situates the sensors proposed in this work close to or above the exemplary hybrid sensors, as the lowest DL obtained for the Au-G-TiO₂ device was only 10 ppb, and the fabrication technique is beneficial for eventual mass production. See Table A.2 for a comparison of characteristics of the sensors proposed in this work with others reported for similar sensing materials comprising

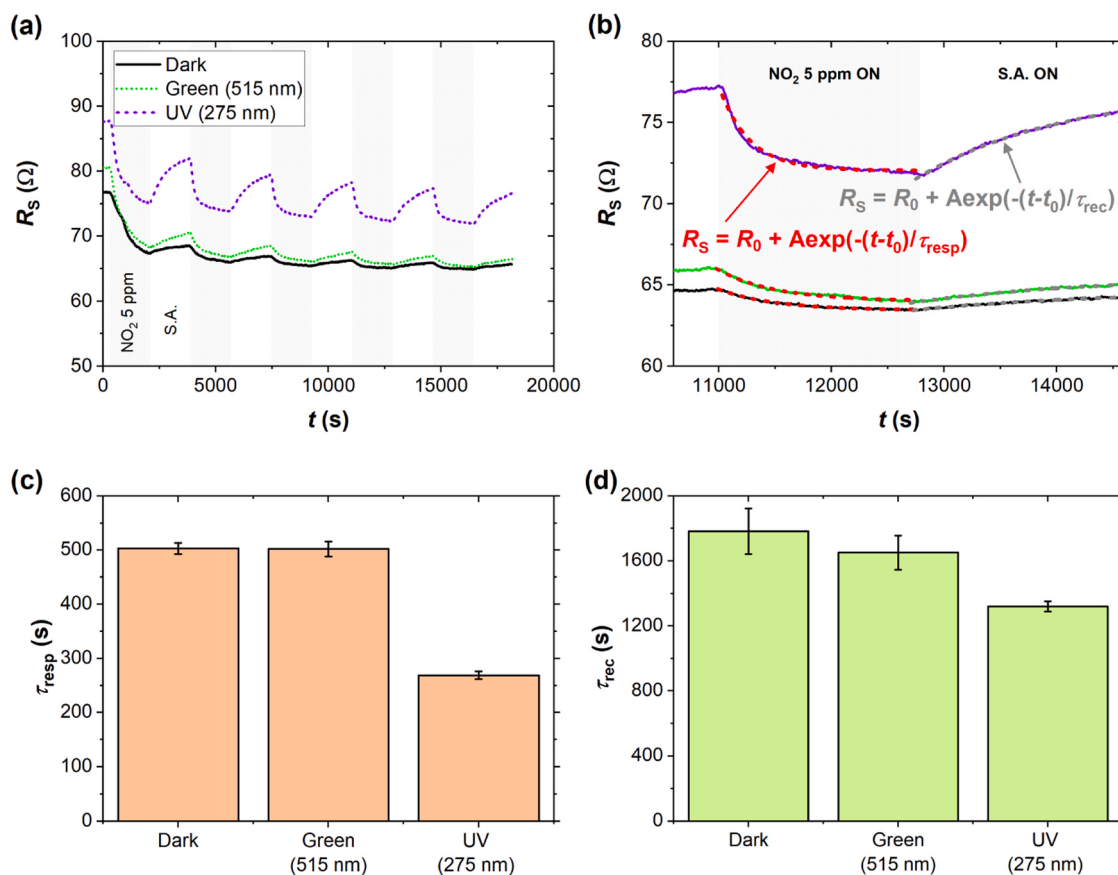


Fig. 5. (a) Time-resolved measurements (sensor resistance R_s) of the Au-G-TiO₂ sensor for five cycles of NO₂ (5 ppm) introduction; (b) magnification of one response/recovery cycle for different lighting conditions with the exponential curves fitted to derive response and recovery time constants; and comparison of (c) response and (d) recovery times for sensor operating in the dark, under green light (515 nm) and UV light (275 nm).

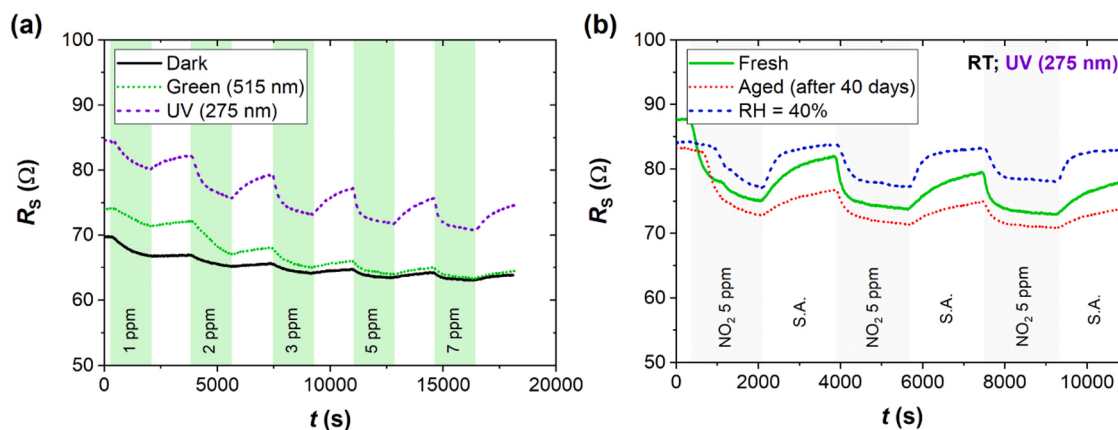


Fig. 6. Time-resolved measurements (sensor resistance R_s) of the ink-printed Au-G-TiO₂ sensor: (a) comparison of sensor responsivity to NO₂ (1–7 ppm) in the dark (black solid), under green light (515 nm; green dotted) and UV light (275 nm; violet dashed) at RT; and (b) Au-G-TiO₂ sensor response to NO₂ (5 ppm) for the sample as prepared (green solid), aged for 40 days (red dotted) and in the humid atmosphere of RH = 40% at RT (blue dashed).

graphene or its derivatives and TiO₂ or Au.

Long-term stability measurements confirmed that after 40 days of keeping the sensor in laboratory air, its baseline resistance shifted by only 5 %, and sensitivity to NO₂ remained similar (15 % for fresh and 14 % for aged sensor), as demonstrated in Fig. 6b. Overall, the sensors were repeatedly measured and analyzed for over 120 days, showing stability in baseline resistance (with deviations up to 3 % only between 40 and 120 days) and sensing responses. The measurements repeated in a humid atmosphere of RH = 40 % show a lower response (~8 %),

which is expected when the water molecules occupy some of the binding sites on graphene and TiO₂. At the same time, covering the sensing surface with AuNPs partially occupies the defective sites by metal nanoparticles, so the water molecules have fewer adsorption sites at the graphene surface. Thus, a humid atmosphere (RH = 40 % is a commonly existing humidity value in indoor areas) does not entirely limit the sensitivity of the Au-G-TiO₂. Its most significant advantages are confirmed long-term stability and the sensor responsivity maintained in ambient conditions. This type of hybrid ink-printed sensor is worth

considering for practical applications, e.g., environmental and air quality monitoring.

3.3. Low-frequency noise measurements

Noise measurements were realized for G-TiO₂ and Au-G-TiO₂ sensors at RT in the dark, under green light that excites LSPR in Au, and under UV light that enhances the sensing layers photocatalytic activity. NO₂ was the primary target gas for low-frequency noise studies, as the sensors exhibited selectivity to this gas in DC resistance measurements. Fig. 7a and b show noise spectra of voltage fluctuations collected for both sensors in the dark. G-TiO₂ sensor exhibits $\sim 1/f$ noise in the considered frequency range, and the noise amplitude does not correlate with the concentration of the admitted NO₂ gas. A more interesting situation was observed for the Au-G-TiO₂ sensor, for which the deviation from the $1/f$ dependence was observed in the form of a characteristic Lorentzian with the corner frequency f_c between 100 and 200 Hz in S.A. It is worth mentioning that such characteristic shape of the spectrum measured in the air was repeatedly observed during a few months of investigating the prototype sensors, once again confirming the high stability of the proposed devices. After multiplying the noise spectrum with frequency (Fig. 7c), it is visible that this Lorentzian vanishes with increasing NO₂ concentration, and the multiplied spectrum becomes flat for concentrations 3–7 ppm (Fig. 7d) in contrast to the G-TiO₂ sample (see Figure A.7a for the corresponding multiplied spectra). There are two main conclusions when comparing non-decorated and Au-decorated samples operating in the dark. The first one is that Au, mainly occupying the graphene defective sites, is responsible for the specific charge fluctuations dominant at frequencies between 100 and 200 Hz when the sensor is in S.A. The second is that when a higher concentration of NO₂ molecules occupies adsorption sites in the sensing layer, the barrier

between Au and graphene changes and deactivates these sites from charge fluctuations.

The same measurements were repeated for one of the reducing gases (NH₃) investigated earlier via DC responses to see if there is any impact of NH₃ adsorption on the observed fluctuations. Fig. 8 confirms that the effect of NH₃ is uncorrelated with gas concentration for G-TiO₂ and weak for Au-G-TiO₂, as the adsorption of reducing molecules barely influences the amplitude or the Lorentzian position. It suggests that this reducing gas barely affects DC resistance and resistance fluctuations. Similar results were obtained for NH₃ under green and UV light; therefore, only results for NO₂ sensing for the irradiated Au-G-TiO₂ sample are discussed further. See Figure A.7, Figure A.8, and Figure A.9 for the noise spectra collected for the G-TiO₂ sensor with NH₃ in the dark, under green and UV light, and Figure A.10 for the noise spectra collected for Au-G-TiO₂ sensor with NH₃ under green and UV light. All supplementary spectra collected in the NH₃ atmosphere confirm that noise features do not correlate with the reducing gas concentration, and only minor changes in noise amplitude or spectrum shape were observed.

Noise measurement for the Au-G-TiO₂ sensor and NO₂ under green (515 nm) and UV light (275 nm) resulted in other intriguing observations. Fig. 9 shows that the incident wavelength impacts the shape of the spectrum. Under green light and in S.A., the Lorentzian has a lower intensity than in the dark, but it appears in a similar range of frequency (100–200 Hz). The lower amplitude of low-frequency fluctuations can be ascribed to the induction of LSPR. When the incident wavelength satisfies the resonance condition and the plasmonic effect is induced, the collective charge movement occurs within the AuNPs and their vicinity. We suppose that the sensing surface (mostly the parts covered with AuNPs) reduces the low-frequency fluctuations generated in graphene because the AuNPs operate as charge warehouses, which take over low-

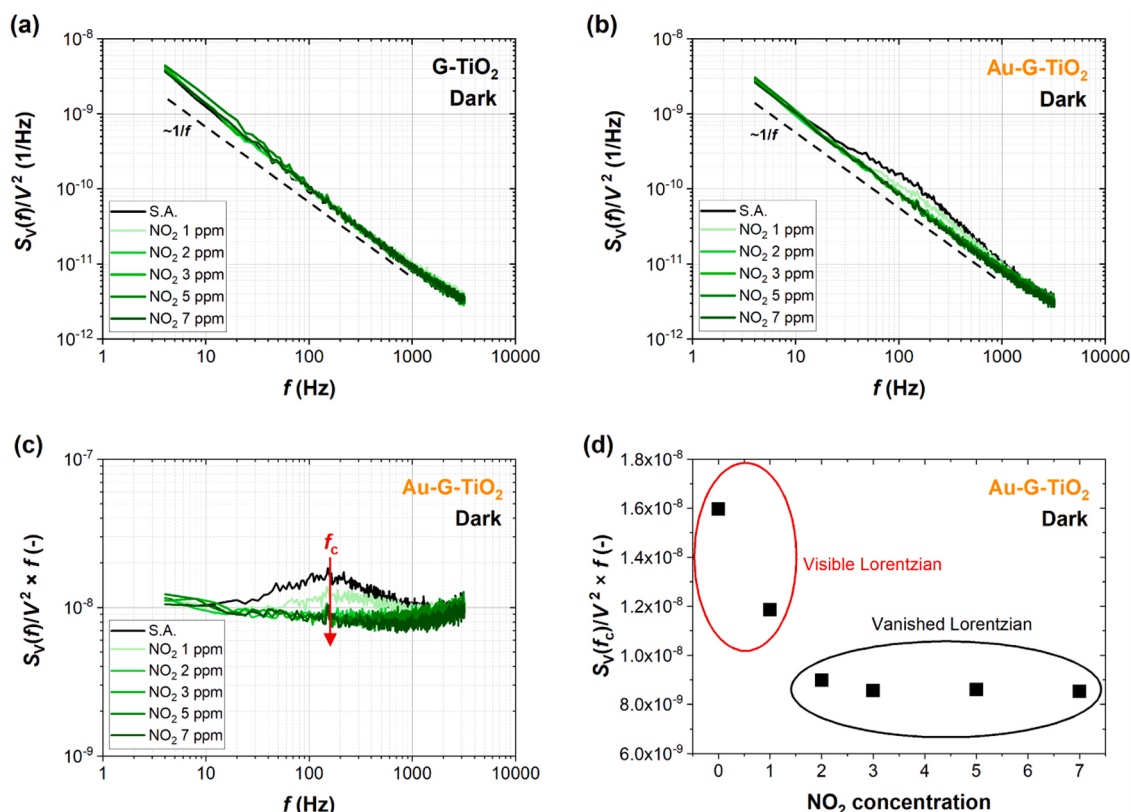


Fig. 7. Power spectral density of voltage fluctuations $S_V(f)$ normalized to the squared voltage across the sensor V^2 measured in the dark in NO₂ (1–7 ppm) (a) for G-TiO₂ and (b) for Au-G-TiO₂ sensor, and (c) multiplication product of $S_V(f)/V^2$ and frequency f showing the characteristic Lorentzian for Au-decorated sensor. Dashed lines indicate the $1/f$ dependence. The points shown in (d) are derived from noise spectra product $S_V(f)/V^2 \times f$ in (c) by averaging over the frequency range of 100–200 Hz.

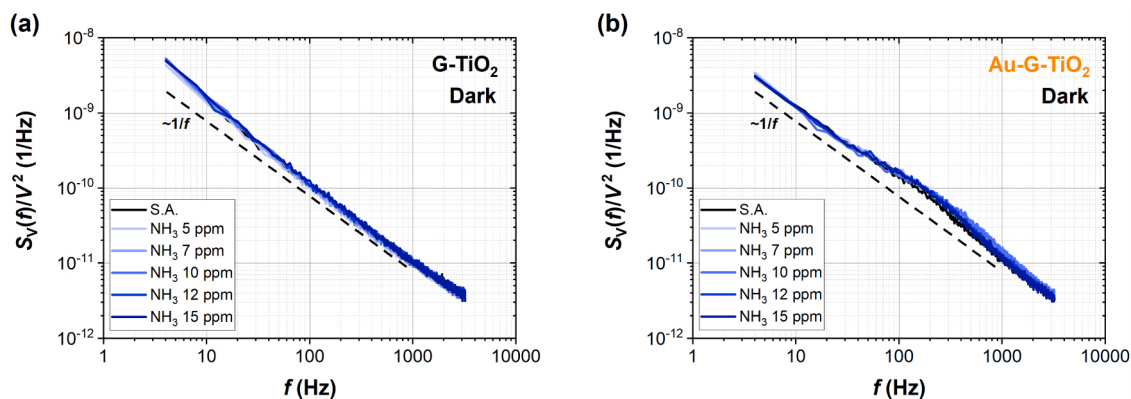


Fig. 8. Power spectral density of voltage fluctuations $S_V(f)$ normalized to the squared voltage across the sensor V^2 measured in the dark in NH_3 (5–15 ppm) (a) for G-TiO₂ and (b) for Au-G-TiO₂ sensor.

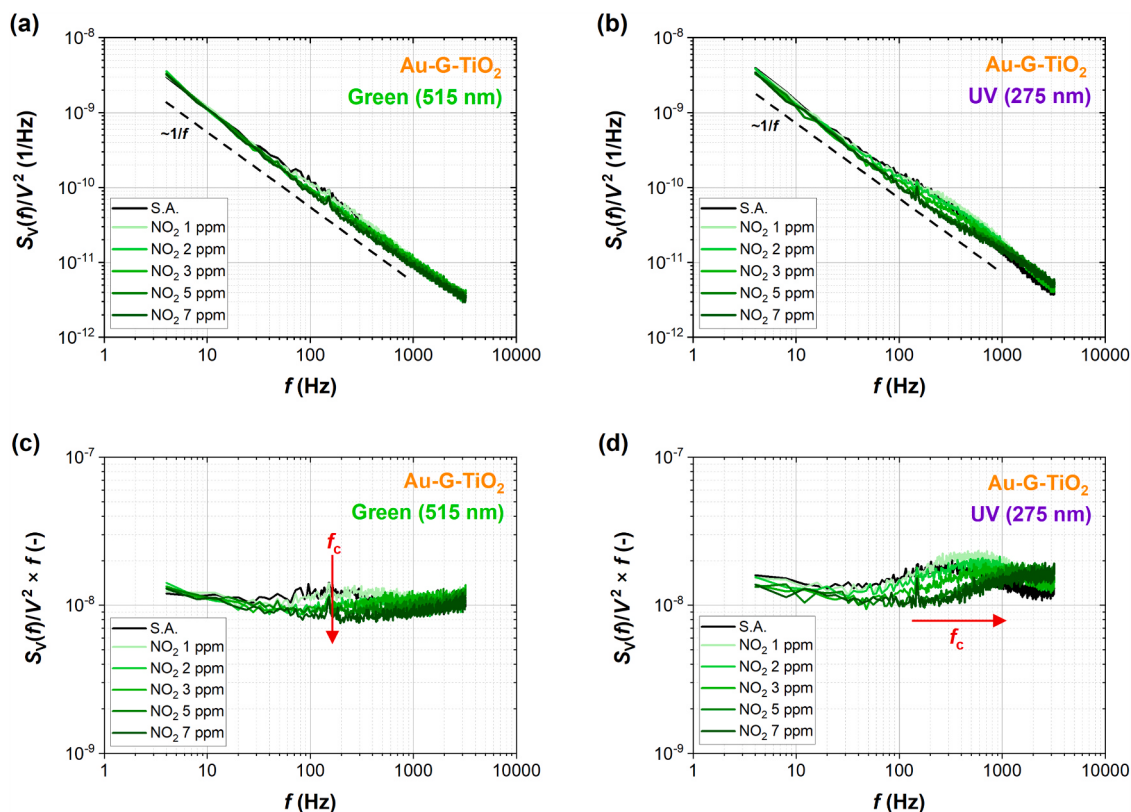


Fig. 9. Power spectral density of voltage fluctuations $S_V(f)$ normalized to squared voltage across the sensor V^2 measured (a) under green light (515 nm) or (b) UV light (275 nm) for NO_2 (1–7 ppm) for Au-G-TiO₂ sensor; and multiplication product of $S_V(f)/V^2$ and frequency f showing the characteristic Lorentzian for Au-decorated sensor (c) under green light (515 nm) or (d) UV light (275 nm). Dashed lines indicate the $1/f$ dependence.

frequency charge fluctuations generated by mobility fluctuations dominating the graphene structure [30]. The effect of low-frequency noise attenuation was observed in various materials decorated with AuNPs [31,32]. Similarly to the dark case, the Lorentzian vanishes with increasing NO_2 concentration (Fig. 9c); however, the decrease is relatively gradual compared to dark conditions. The less rapid change in noise intensity can be ascribed to the fact that when more carriers are excited due to LSPR, any local changes in carrier concentration during NO_2 adsorption produce a relatively lower effect on overall fluctuations than when the plasmon resonance is not involved.

Furthermore, shorter UV wavelengths had a completely different effect on the shape of the noise spectra in S.A. and NO_2 . It is clear from Fig. 9d that higher NO_2 concentrations shift the characteristic frequency

f_c from a few hundred up to ~ 3000 Hz. In this case, the characteristic Lorentzian does not disappear but is shifted to higher frequencies (higher energies) during detection. The shift can be explained by activating more defect sites in the sensing layer due to the cleaning effect of UV light and by photoactivation of TiO₂ nanoparticles that have increased absorbance near 275 nm and change in the Au-TiO₂ interface barrier. Consequently, the characteristic fluctuations are shifted, but still, they are visible only in the Au-G-TiO₂ sample, so AuNPs are crucial for observing the distinct shape of the spectrum.

Fig. 10 summarizes how the noise intensity and shape depend on the NO_2 concentration for the Au-G-TiO₂ sensor. Overall, the mean value of the noise intensity product $S_V(f)/V^2 \times f$ in the selected frequency range, between 100 and 200 Hz, can determine the NO_2 concentration when

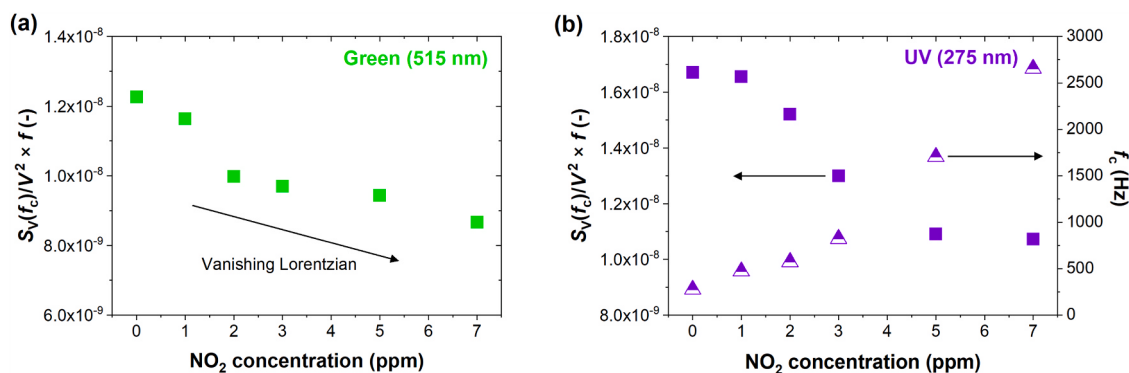


Fig. 10. Multiplication product of $S_V(f)$ normalized to V^2 and multiplied by f for the frequency range 100–200 Hz for Au-G-TiO₂ sensor under (a) green light (515 nm) and (b) UV light with the dependence between NO₂ concentration and position of corner frequency f_c for the UV light case. The f_c points in (b) are derived as the maximum points from the polynomial function fitted to the noise spectra product $S_V(f)/V^2 \times f$. Full-filled squares represent $S_V(f_c)/V^2 \times f$ values (left axis), and half-filled triangles symbolize f_c values (right axis).

green or UV light photoactivates the sensing surface. However, under UV light, the Lorentzian positions and f_c shift are additional informative spectrum features that correlate directly with NO₂ concentration. This way, DC responses and noise spectra features can be utilized to analyze gas responses and quantitatively detect NO₂.

Single graphene layers were reported before to exhibit Lorentzians characteristic for the selected gases (organic vapors) [33,34]. It was indicated that the defects occurring at the surface of graphene were responsible for distinct fluctuations of charges during specific gas molecules adsorption/desorption. In the case of the Au-decorated sensor, AuNPs are chemically affined to selected defect types at the surface of graphene and induce specific fluctuations of charge carriers there. In contrast, the G-TiO₂ sensing layer exhibits $1/f$ noise in the considered low-frequency range without any dominating Lorentzian component. Detection limits estimated from the noise data were 80 ppb, 360 ppb, and 350 ppb for dark, green, and UV light conditions, respectively. DL for the UV light case was even lower (100 ppb) when the shift of f_c was considered. The low DL for dark conditions is due to the abrupt change in noise amplitude for the lowest considered concentrations (Fig. 7d). However, it is worth mentioning that DL for noise data can be even lower when non-linear responses are considered [35].

Consequently, low-frequency noise spectra indicate that a few independent regions responsible for gas sensing can be activated in the graphene sensor by Au and TiO₂ decoration and adjusting the wavelength of incoming radiation. The AuNPs are accountable for the observed Lorentzian (100–200 Hz range in S.A., dark). Graphene, TiO₂, or the G-TiO₂ junctions are not correlated with this broad Lorentzian and lack sensitivity to NO₂ in the FES method. During the excitation of LSPR, AuNPs collect part of low-frequency oscillations in graphene. In this case, most AuNPs and G-Au junctions are activated with green light and are responsible for gas detection. The graphene surface is cleaned during UV irradiation, and TiO₂ becomes photocatalytically active. Since the impact on the characteristic Lorentzian (its corner frequency f_c) is different than under green light, the UV-activation of TiO₂-Au junctions is presumably responsible for sensor performance (shift of f_c). Table 1 summarizes the distinguished regions of gas sensing activity in the

Table 1

Active regions in the hybrid Au-G-TiO₂ (G-TiO₂) sensor under green (515 nm) or UV (275 nm) irradiation based on the collected low-frequency noise spectra.

Sensor component	Irradiation	
	Green (515 nm)	UV (275 nm)
Graphene (G)	-	+
G-TiO ₂	-	+
G-Au	+	+
G-TiO ₂ -Au	+	+

hybrid sensors induced by green or UV light. FES results obtained for G-TiO₂ and Au-G-TiO₂ devices confirm that AuNPs and their junctions with graphene and TiO₂ are the components of the hybrid sensor that drive the sensitive and selective NO₂ detection. Fig. 11 illustrates which parts of the hybrid sensor become active during irradiation with green and UV light – the glow of the particles indicates their activity (LSPR or photoexcitation). It is also worth mentioning that after a few months of storing the Au-G-TiO₂ sensor in ambient air (RH of 30–40 %), the Lorentzian vanished, probably due to humidity adsorption. However, it reappeared shortly after refreshing the sensor under UV light (275 nm). It confirms the reproducibility of the characteristic noise features of the Au-decorated sensor.

4. Conclusions

Au decoration of hybrid sensing layers comprised of graphene flakes and TiO₂ nanoparticles improved the gas sensing properties of the investigated chemiresistors. The effect of chemical sensitization increased sensitivity and selectivity to NO₂ when the printed sensors were irradiated with UV light (275 nm). This resulted in 2.4 times enhancement in DC responses, DL = 10 ppb, and noise features correlated with gas concentration. UV light influences two components of the hybrid sensor – it cleans the graphene surface, creates more sites for molecular adsorption, and generates extra charge carriers within the TiO₂ matrix. This way, more charges participate in the surface processes of gas molecules adsorption/desorption, which results in faster sensing and recovery visible in DC resistance measurements. Plasmonic properties of Au can be activated with green light (515 nm), which also increases sensitivity to NO₂ compared to dark conditions. However, visible light is not sufficiently energetic to support the improved recovery of the sensing surface as it does not influence the electronic properties of TiO₂ nanoparticles and graphene as significantly as shorter wavelengths. Notably, visible light and LSPR have a lower impact on sensing performance measured through monitoring DC resistance and noise spectra than UV light. Low-frequency noise measurements revealed that noise features of the Au-G-TiO₂ sensor are affected by varied NO₂ concentrations. Notably, the irradiated sensor can serve as a sensitive and selective tool toward NO₂ when the intensity of the characteristic Lorentzian (green and UV light) and the local maximum amplitude position are concerned (UV light). Noise studies support analyzing selected elements of the hybrid sensor activated selectively with green or UV light. Au decoration explicitly enhances sensor sensitivity and selectivity to NO₂ by inducing characteristic fluctuations with features dependent on the gas concentration. Green light activates parts of the sensing surface covered with Au; however, under UV light, the TiO₂-Au interface also becomes sensitive to NO₂.

Both DC and noise components of sensor resistance enhance the

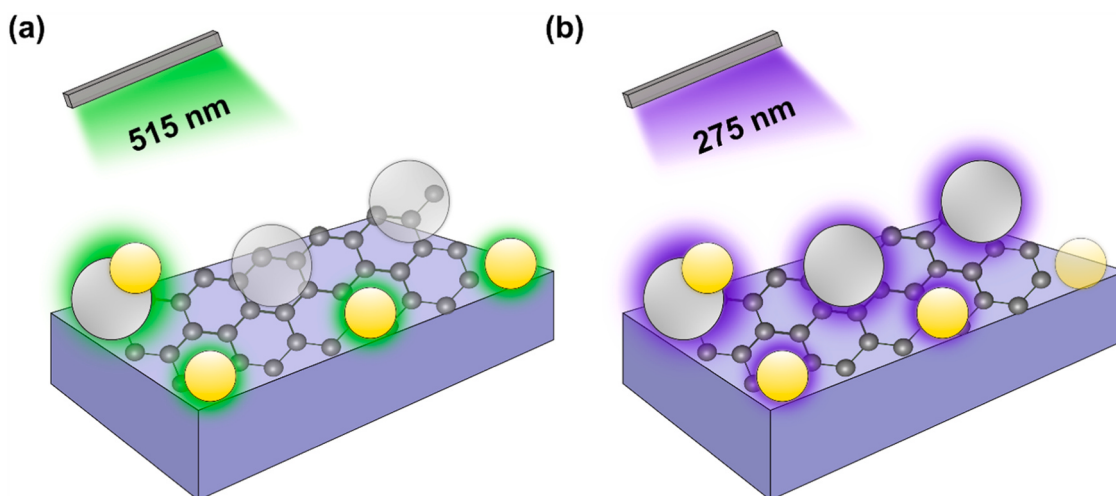


Fig. 11. Schematic representation of the light activation in the hybrid Au-G-TiO₂ sensor: (a) under green light (515 nm), AuNPs and their junctions with graphene lattice or TiO₂ particles are active with induced plasmon resonance; (b) under UV light, graphene lattice and TiO₂ become active, so all the junctions with these elements are photoexcited – only individual AuNPs are not active under UV wavelength (275 nm). Yellow and gray beads signify Au and TiO₂ particles. Semi-transparent particles illustrate inactive adsorption-desorption centers of the hybrid surface, and glowy, opaque circles mark active centers (Au-graphene, TiO₂-Au-graphene, or TiO₂-graphene structures). The scheme does not represent the actual difference in size between TiO₂, Au nanoparticles, and carbon atoms.

sensing performance of the hybrid device composed of a 2D material (graphene), photocatalytic (TiO₂), and plasmonic (Au) nanoparticles. The demonstrated analysis improves understanding of the surface activity of the hybrid graphene-based sensor and enables controlling different regions of its surface activity by ambient light. Long-term stability in baseline resistance and noise spectra features, sensitivity to target gases, selectivity to NO₂, and straightforward fabrication method make Au-G-TiO₂ sensors promising for gas detection and exploitation in ambient conditions. The activation of different sensing areas can be similar when the layer is deposited with traditional coating methods, as mainly the junctions between specific materials are responsible for selective activation with light. However, the size of the deposited droplet and thickness of the layer are better controlled in printing, and the presented technique is more suitable for automated mass production. The studies on the effect of light, temperature, humidity, and aging demonstrated in this work show the attractiveness of the hybrid nanostructured sensors based on photocatalytic and plasmonic effects. This work demonstrates a promising gas sensing platform with controlled sensing features using combined DC resistance and FES measurements.

CRediT authorship contribution statement

Drozdowska Katarzyna: Writing – review & editing, Writing – original draft, Visualization, Validation, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Smulko Janusz:** Writing – review & editing, Supervision, Formal analysis, Conceptualization.

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.2025.137764](https://doi.org/10.1016/j.snb.2025.137764).

Data availability

Data will be made available on request.

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