



Formaldehyde detection with chemical gas sensors based on WO₃ nanowires decorated with metal nanoparticles under dark conditions and UV light irradiation

Benachir Bouchikhi^{a,*}, Tomasz Chludziński^b, Tarik Saidi^a, Janusz Smulko^b, Nezha El Bari^c, He Wen^d, Radu Ionescu^e

^a Sensor Electronic & Instrumentation Group, Moulay Ismail University of Meknes, Faculty of Sciences, Department of Physics, B.P. 11201, Zitoune, Meknes, Morocco

^b Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, Gdańsk, Poland

^c Biotechnology Agroalimentary and Biomedical Analysis Group, Moulay Ismail University of Meknes, Faculty of Sciences, Department of Biology, B.P. 11201, Zitoune, Meknes, Morocco

^d College of Electrical and Information Engineering Hunan University, PR China

^e The Ångström Laboratory, Department of Solid State Physics, Uppsala University, 75121, Uppsala, Sweden

ARTICLE INFO

Keywords:

WO₃ nanowires gas sensors
Metal nanoparticles doping
UV light irradiation
Formaldehyde detection

ABSTRACT

We report results of formaldehyde gas (CH₂O) detection under dark conditions and UV light irradiation with pristine tungsten trioxide nanowires (WO₃ NWs) and metal nanoparticles decorated WO₃ NWs gas sensing layers. The resistive layers were deposited by one step aerosol assisted chemical vapor deposition (AACVD) on commercial alumina substrates with 10-pair interdigitated platinum electrodes. The elaborated gas sensors, based on pristine WO₃ and on WO₃ decorated with Au, Pt, Au/Pt, Ni and Fe nanoparticles, were investigated towards three concentrations of formaldehyde gas (5, 10 and 15 ppm) under dark conditions and under UV light irradiation at the wavelength of 394 nm. Two main effects were observed: firstly, under UV light irradiation the response time for CH₂O desorption was significantly reduced with the exception of the nanomaterial with Fe NPs dopant; secondly, the gas induced baseline shift was reduced under UV light irradiation conditions. These results can be explained by the additional energy induced by the UV light, accelerating the adsorption-desorption processes. The results obtained confirmed that both the decoration of WO₃ NWs with selected metal nanoparticles as well as sensors operation under UV light irradiation are a practical and affordable way to enhance gas sensing towards formaldehyde detection, although both strategies applied together did not introduce an amplified synergetic effect.

1. Introduction

Since the 1960s, metal oxide semiconductor (MOS) gas sensors were developed as electronic devices whose electrical resistance changes as a function of the ambient/gaseous surrounding. These sensitive structures were designed to detect gaseous molecules at low concentrations [1,2]. This effect was firstly demonstrated in 1953 for Ge [3]. Later on, it was shown that the conductivity of ZnO thin film heated at ~300 °C was sensitive to the presence of traces of reactive gases in the air [4]. Similar properties were reported for SnO₂, with actually higher response stability [5]. Since the development of Taguchi's gas sensor based on SnO₂ in 1971 [6], many semiconductor materials were investigated and analyzed. Among them, tungsten trioxide (WO₃), with a bandgap of ~2.8 eV [7], is one of the essential n-type MOS, and was

extensively assessed as a gas sensing material for volatile organic compounds (VOCs) detection [8].

Formaldehyde (CH₂O) is one of the dangerous gases that is commonly generated in our environment, being a pollutant substance causing chemical contamination in indoor and outdoor environments [9,10]. It is used in industry to manufacture materials for medical laboratories, in the production of plastics and resins, and other material processes. As a result, it may be present in low concentrations in human being environments [3]. The Occupational Safety and Health Administration (OSHA) established a concentration of 2 ppm as exposure limit for formaldehyde, whereas it is a tendency to decrease its permissible exposure limit to ppb levels in various countries [11]. Currently, the permissible level of CH₂O is 80 ppb in an indoor environment, while an indoor concentration of 0.1 ppm of CH₂O is considered by experts to be

* Corresponding author.

E-mail address: janusz.smulko@pg.edu.pl (B. Bouchikhi).

<https://doi.org/10.1016/j.snb.2020.128331>

Received 12 February 2020; Received in revised form 8 May 2020; Accepted 18 May 2020

Available online 25 May 2020

0925-4005/ © 2020 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license

(<http://creativecommons.org/licenses/by/4.0/>).

harmful to the human health. Moreover, studies have shown that CH₂O emission may cause cancer in humans in the long run [9]. Hence, the rapid real-time monitoring of CH₂O traces is urgent and faced as a great challenge for researchers in the field of low-cost chemical gas sensing.

A large variety of sensing films were proposed and studied to detect CH₂O by using metal oxide gas sensors. NiO thin film was studied as a sensing layer for CH₂O detection [12] due to its catalytic properties for the oxidation of formaldehyde [10,11,13]. SnO₂ gas sensors were also of interest for formaldehyde detection [14,15]. Other studies revealed that Fe doping into the surface of ZnO improves its gas sensing performance efficiently and narrows the bandgap of ZnO, and a gas sensor based on Fe-doped ZnO nanosheet-spheres was demonstrated for CH₂O detection [4]. WO₃ sensors have the advantage of reduced energy consumption for CH₂O detection as they work at lower operating temperatures [16–18].

In the present work, we assess the performance of WO₃ nanowires (NWs), both pristine and decorated with various metal nanoparticles (NPs), grown by the aerosol-assisted chemical vapor deposition (AACVD) method, for CH₂O detection. Previous studies demonstrated that the gas sensing properties can be significantly improved by decorating MOS surface with dopants of noble metals [19,20]. Moreover, irradiating gas sensors surface with UV light appears as an exciting option for activating chemical reactions at the metal oxide surface without the necessity of running the sensors at elevated operating temperatures [21–24]. In this experimental study, we report CH₂O detection with pristine and NPs decorated WO₃ NWs under UV light irradiation and under dark (normal operation) conditions.

2. Materials and methods

2.1. Elaboration of the WO₃ nanowires sensors

The sensing films assessed in this experiment were composed of pristine WO₃ NWs and WO₃ NWs decorated with platinum (Pt), bimetallic gold-platinum (Au/Pt), gold (Au), nickel (Ni) and iron (Fe) nanoparticles, grown by AACVD according to a previously reported procedure [25–28]. Alumina substrates with Pt interdigitated electrodes on the front-side and a Pt meander heater on the backside (CeramTec®, Marktredwitz, Germany) were employed as substrates. The substrates were successively cleaned with ethanol, acetone and distilled water and dried with nitrogen flow before placing them inside the AACVD reactor. The WO₃ NWs were prepared using tungsten hexacarbonyl (WC₆O₆) as a precursor. After nanomaterials synthesis, the deposited films were annealed in a conventional oven (Carbolite BWF 1200 °C) at 500 °C during 180 min under a constant flow of 200 mL/min of synthetic air. This step was carried out in order to clean the surface from the deposition residues and to stabilize and crystallize the structure of the grown nanomaterials [29].

2.2. Sensing films characterization

The gas sensing layers were characterized by different microscopic techniques: Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy Dispersive X-ray (EDX-ray). The full results obtained were reported in detail in ref. [26]. However, for a more convenient following of the present study, the most important characteristics of the sensing films are briefly presented below.

AFM analysis revealed that the maximum thickness of the sensing films were 3.4 μm for Fe/WO₃ NWs, 2.2 μm for pristine WO₃, 0.991 μm for Au/WO₃, 0.762 μm for Pt/WO₃, 0.713 μm for Au/Pt/WO₃, and 0.505 μm for Ni/WO₃. SEM analysis showed that the mean diameter of the pristine WO₃ NWs was about 159 nm at 500 °C, while the catalysts reduced the diameter of the NWs: addition of Pt and Au nanoparticles and bimetallic Au/Pt decreased the widths of the NWs to a range between 45 and 57 nm, Fe atoms kept the NWs in the broader range

between 47 and 126 nm, while Ni dopant induced randomly distributed NWs with mean diameters below 10 nm. TEM analysis demonstrated porous polycrystalline structures of spherical or cylindrical morphologies with visible NWs and metal nanoparticles of different sizes: 11 nm for Pt, 4.63 nm for bimetallic Au/Pt, 3.97 nm for Au, 39 nm for Ni, and 8.22 nm for Fe. EDX studies confirmed the presence of the dopant atoms at different concentrations in the sensing layers: 2 wt% of Au in Au/WO₃, 1 wt% of Fe in Fe/WO₃, 6 wt% of Pt in Pt/WO₃, 1 wt% of Au and 7 wt% of Pt in Au/Pt/WO₃, and 1 wt% of Ni in Ni/WO₃; the higher Pt concentration as compared with the other NPs is explained by the additional cross-influence of the platinum connectors from sensors substrates.

2.3. Gas sensing measurements

Gas sensing measurements were simultaneously performed with the six WO₃-based gas sensors placed inside a metal test chamber of 1 L volume. Based on a previous optimization process, the operating temperatures of the sensors were set to 100 °C for pristine WO₃, Pt/WO₃ and Au/Pt/WO₃, and to 160 °C for Au/WO₃, Ni/WO₃ and Fe/WO₃ [27], by connecting the sensors heaters to separate current sources. PT100 temperature sensor attached to the sensor substrate was used to determine the right current for obtaining the desired operating temperature for each sensor. The temperature in the gas chamber was furthermore monitored with a temperature sensor LM35DZ during the experiments to confirm stable conditions.

The sensors were operated once under dark conditions, and then under UV light irradiation provided by six independent UV LEDs with a wavelength of 394 nm (OSV4YL5451B type, OptoSupply). The optical power of the emitted radiation was equal for all sensors by setting the same distance of 1.5 cm between the UV LED and the sensing layers and by biasing the diodes with the same current set to 10 mA. The optical power of UV light irradiation on the surface of the sensing layer was equal to 0.764 mW/cm², measured by Melles Griot broadband power meter, model 13PEM001/J.

The measurements were performed in the presence of three concentrations of formaldehyde gas (5, 10 and 15 ppm). The gas concentration was set by diluting a calibration gas of formaldehyde (CH₂O stabilized in nitrogen, and made by Linde Gas) in synthetic air by means of two mass flow controllers (Analyt-MTC, GFC17 type). The sensing films were pre-heated for 17 min prior to starting the measurements, and then the sensors were exposed for 200 min to the diluted CH₂O concentration in a continuous flow of 180 mL/min, followed by 80 min cleaning with synthetic air at 90 mL/min flow rate.

The voltage across the gas sensors was recorded at a sampling frequency of 1 Hz with a National Instruments data acquisition board (NI USB-6212 type). Each sensor was connected in series with the selected resistor divider. 5 V dc voltage was supplied to each divider circuit from a Keysight E3648A power supply. The PC, data acquisition board and mass flow controllers were turn on 30 min before starting the measurements for heating up and reaching stable working conditions. The recorded voltages across the gas sensors were used to estimate their resistances which decreased when exposed to the ambient atmosphere of formaldehyde. We observed the changes of dc resistances of the investigated sensors induced by the gas introduced to the gas chamber or UV light irradiation. The voltage dividers used the resistors (390 kΩ, 150 kΩ, 47 kΩ), selected such that to accurately capture sensors resistance variations during formaldehyde exposure (see Table S1 from Supplementary Material). The values of R₀ were included in Figs. 1 and 2.

3. Results

The AFM studies revealed that the thickness of all sensors produced in this batch was higher than the UV light penetration depth for the applied 394 nm UV light wavelength. The penetration depth was

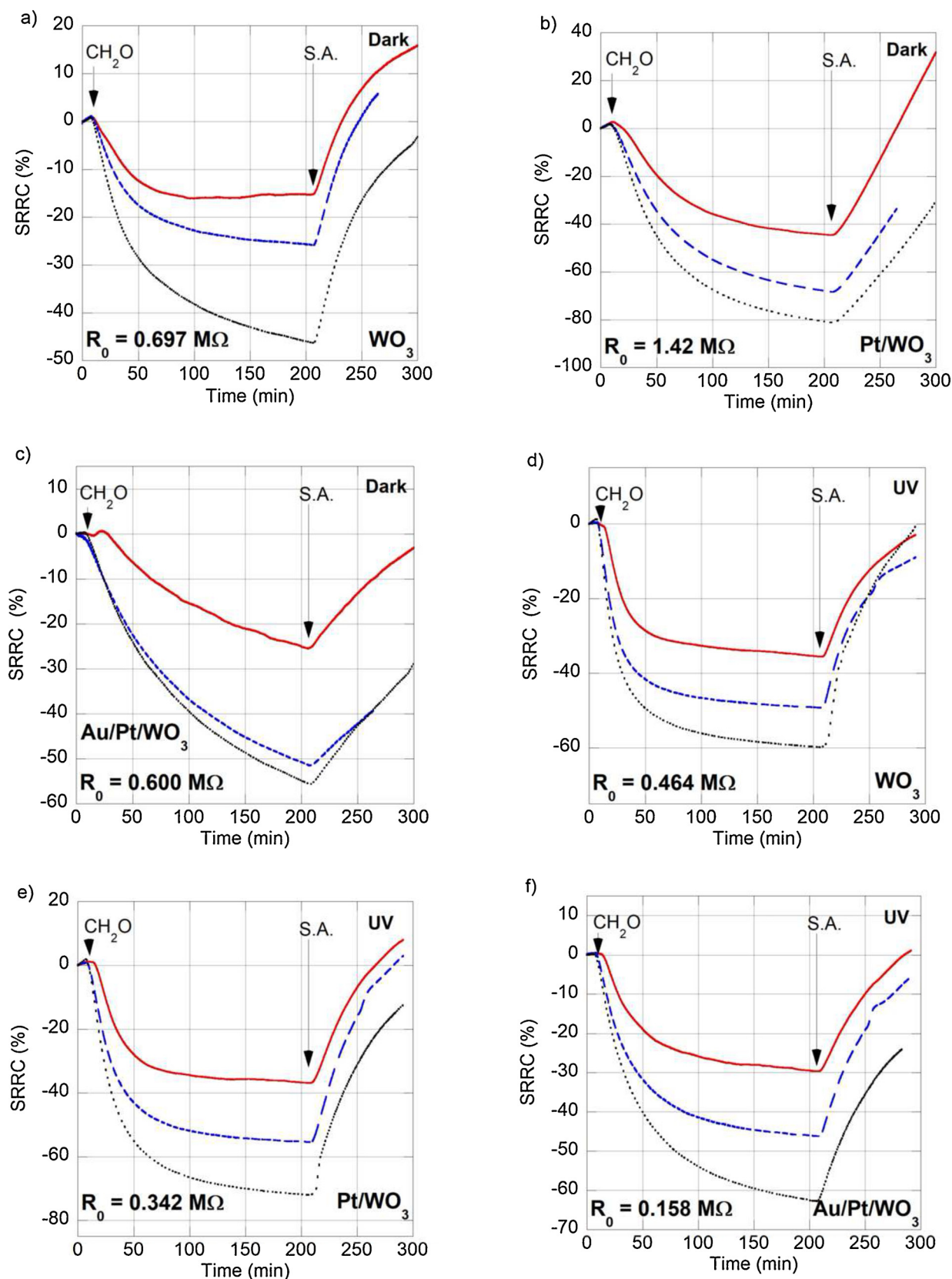


Fig. 1. Sensors relative resistance changes (SRRC) towards three selected concentrations of CH_2O : 5 ppm (solid red line); 10 ppm (blue dashed line); 15 ppm (black dotted line), and during synthetic air cleaning (SRRC) towards three selected concentrations of CH_2O : 5 ppm (solid red line); 10 ppm (blue dashed line); 15 ppm (black dotted line), and during synthetic air cleaning (SRRC) achieved under: (a-c) dark (normal operation) conditions; (d-f) UV light irradiation (394 nm). Sensing layers: (a) and (d) pristine WO_3 ; (b) and (e) Pt/WO_3 ; (c) and (f) $Au/Pt/WO_3$. S.A. states for synthetic air. DC resistance R_0 was measured at the ambient atmosphere of S.A. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

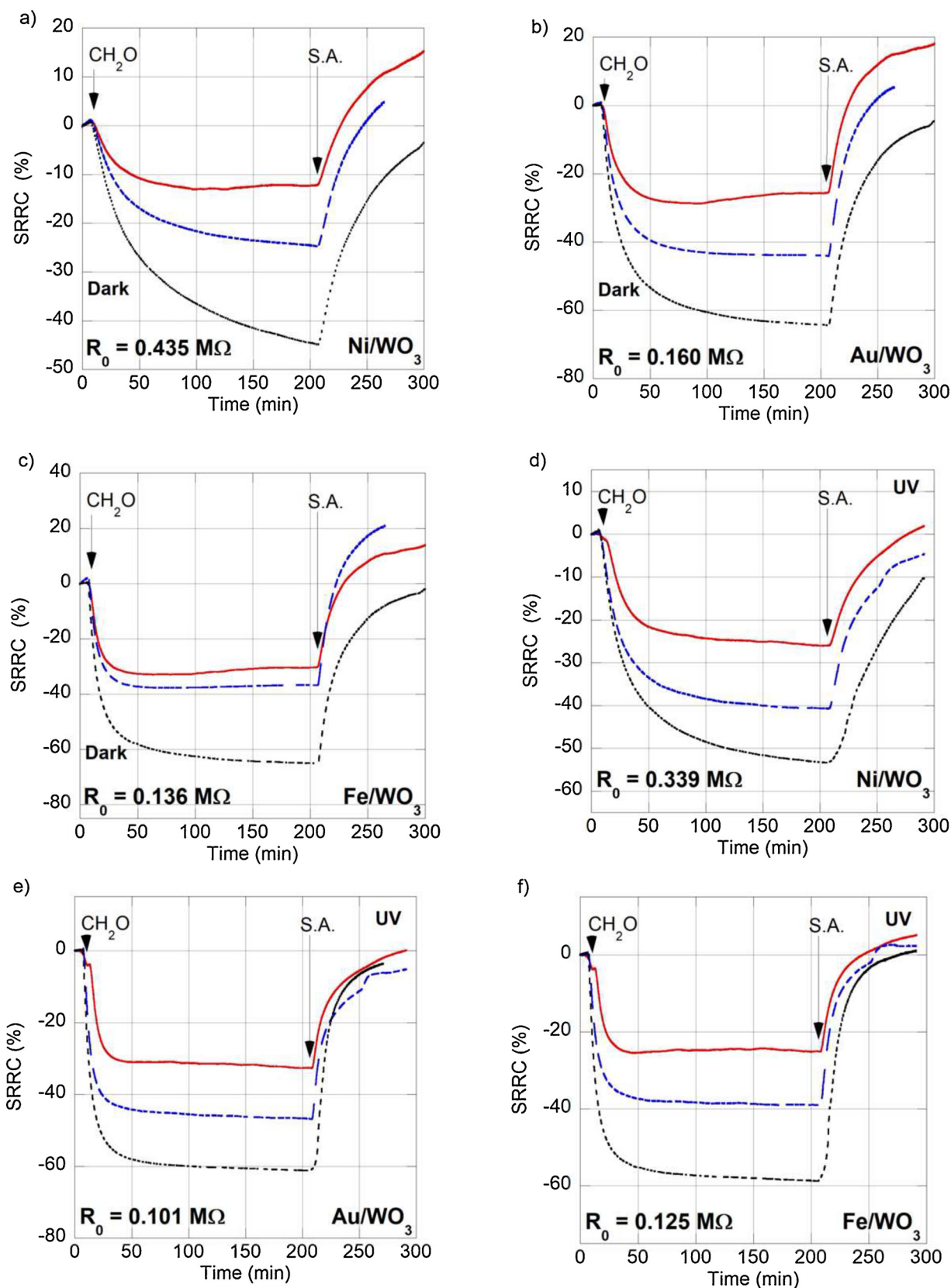


Fig. 2. Sensors relative resistance changes (SRRC) towards three selected concentrations of CH_2O : 5 ppm (solid red line); 10 ppm (blue dashed line); 15 ppm (black dotted line), and during synthetic air cleaning achieved under: (a–c) dark (normal operation) conditions; (d–f) UV light irradiation (394 nm). Sensing layers: (a) and (d) Ni/WO_3 ; (b) and (e) Au/WO_3 ; (c) and (f) Fe/WO_3 . S.A. states for synthetic air. DC resistance R_0 was measured at the ambient atmosphere of S.A. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

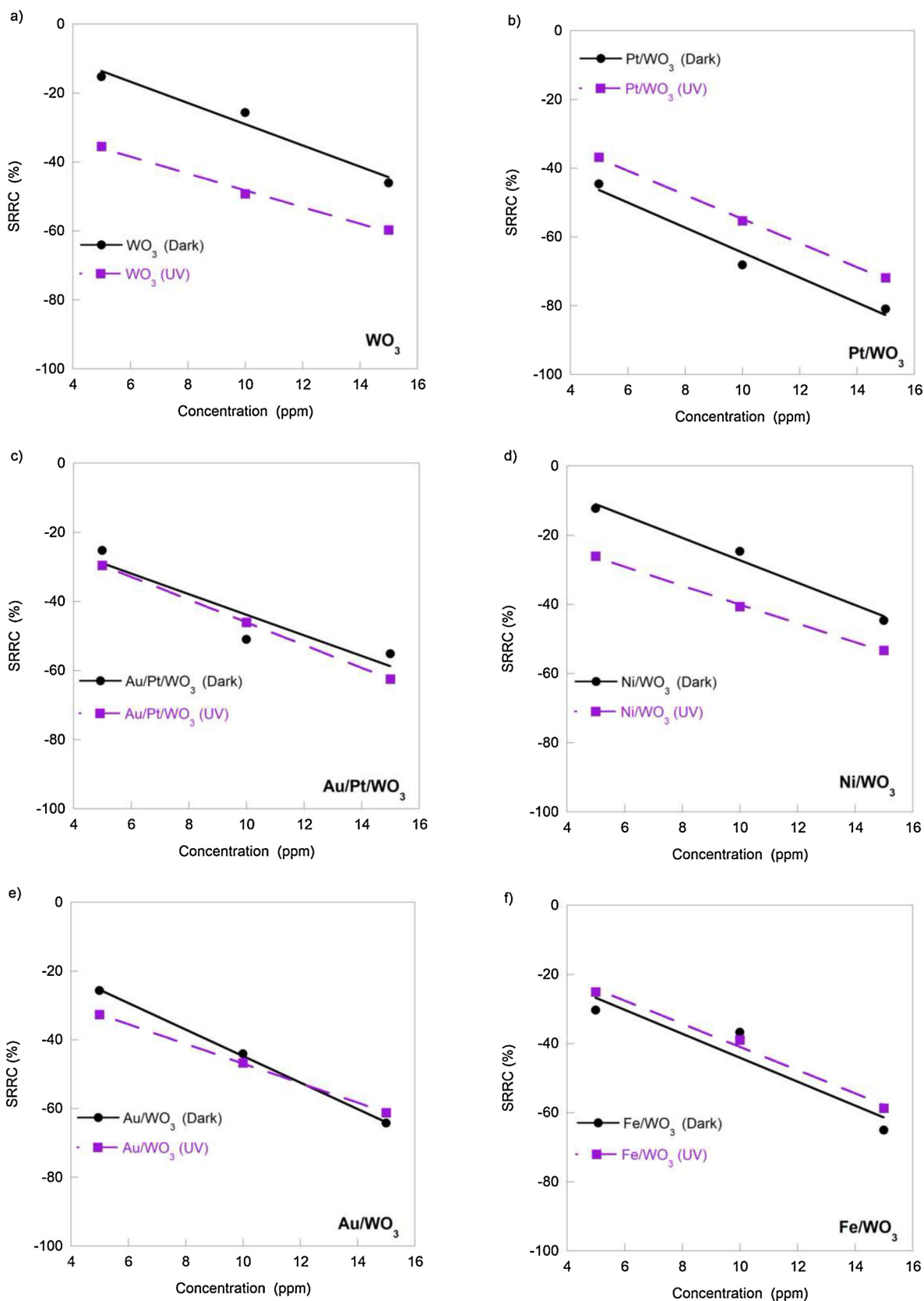


Fig. 3. Relation between sensors relative resistance changes (SRRC) and CH_2O exposures when the sensors were operated under dark conditions (black circles) and UV light irradiation at 394 nm (violet squares): (a) pristine WO_3 , (b) Pt/WO_3 , (c) $\text{Au}/\text{Pt}/\text{WO}_3$, (d) Ni/WO_3 , (e) Au/WO_3 , (f) Fe/WO_3 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

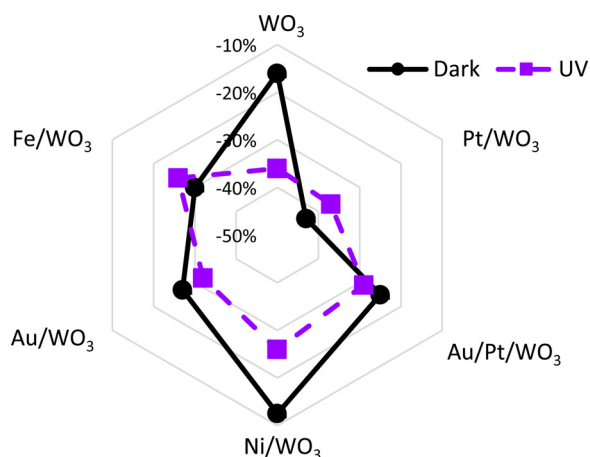


Fig. 4. Radar plot of the sensors relative resistance changes (SRRC) values achieved by the gas sensors exposed to 5 ppm CH₂O under dark (black circles) and UV light irradiation (violet squares) operation conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

estimated to be ≈ 400 nm for the WO₃ layer, by assuming that the absorbance of the thickest film (710 nm from the reference data presented in [30]) equals 0.167 by using the equation: $0.167 = \exp(-710[\text{nm}]/d)$; thus, penetration depth $d = -710/\ln(0.167)$ nm ≈ 400 nm [30], whereas the thinnest gas sensing layer from the investigated batch had a thickness of 505 nm (Ni/WO₃ – see Section 2.2). Therefore, the thickness of all gas sensing layers was higher than the penetration depth of UV light.

The gas sensing properties of the prepared WO₃ sensors towards the three selected concentrations of CH₂O were investigated under dark conditions and under 394 nm UV light irradiation. Sensors relative resistance changes (SRRC) are presented in Figs. 1 and 2, where SRRC was calculated as the relative change of the sensor resistance (R) measured during gas exposure (diluted formaldehyde flow) or the cleaning process (synthetic air flow) with regard to sensor resistance (R_0) measured in synthetic air in the stationary state prior to the start of the measurement, in conformity with Eq. (1). Both resistances R and R_0 were measured under dark conditions and when the sensors were irradiated with UV light, respectively.

$$SRRC = \frac{R_{(\text{dark or UV})} - R_{0(\text{dark or UV})}}{R_{0(\text{dark or UV})}} \times 100\% \quad (1)$$

As it can be deduced from Figs. 1 and 2, the resistance of the six sensors, both under dark conditions and UV light irradiation, decreased sharply upon CH₂O exposure and increased during the cleaning with synthetic air, which reveals the expected n-type semiconductor behavior of the devices, since formaldehyde is a reducing gas.

The highest responses were recorded by the Pt/WO₃ sensor, both under dark conditions and UV light irradiation. The use of UV light irradiation enhanced the responses of the pristine WO₃ and Ni/WO₃ sensors, while the responses of the Pt/WO₃ and Fe/WO₃ were higher under dark conditions, as it can be observed from the response values of the sensors to the different CH₂O concentrations analyzed in this study, presented in Fig. 3. The Au/WO₃ sensor showed higher responses under UV light irradiation for the two lowest CH₂O concentrations measured (5 and 10 ppm), while its response to the highest CH₂O concentration (15 ppm) was lower under UV light irradiation than under dark conditions, indicating a saturation tendency at increased CH₂O level when the sensor was operated under UV light irradiation. The use of two doping NPs (Au and Pt) led to an unpredictable competing effect between them for CH₂O sensing, without a clear response enhancement or worsening under UV light irradiation with regard to dark conditions.

Although the use of UV light irradiation didn't enhance the response

of all sensors, it was able to largely counteract the drift of the sensors baseline condition, which is an important drawback for the MOS gas sensors, favoring the desorption of the CH₂O molecules from the active surface of the sensing layers. On the other hand, UV light irradiation showed in general a tendency to reduce the response time of the gas sensors. These effects might be explained by the uniform irradiation of the gas sensing layer on its whole surface, limiting the necessity of deep gas diffusion inside the sensing layer for changing its resistance.

In order to see if there are pattern differences in the detection of CH₂O among the investigated sensing layers, in Fig. 4 it was plotted the radar plot of the responses (SRRC) of all gas sensors analyzed towards the lowest concentration of CH₂O (5 ppm), measured under dark conditions and UV light irradiation. The radar plot was constructed using the steady state value of sensors resistances at the end of the gas exposure period for calculating the SRRC values. The lowest investigated concentration of formaldehyde was considered in this plot because of faster stabilization of sensors responses than at higher gas concentrations. As it can be seen in Fig. 4, the application of UV light irradiation during CH₂O exposure highly increased the responses of the pristine WO₃ and Ni/WO₃ sensors, whereas for the other dopants (Au, Au/Pt, Pt and Fe) did not have a noticeable effect. Importantly, the effect of UV light irradiation on SRRC value achieved by the pristine WO₃ sensor was similar with that of Pt doping of the WO₃ NWs when the later sensor was operated under dark conditions (these sensors achieving the highest SRRC, in absolute values, under dark and UV light operation, respectively), which indicates that metal doping can be replaced by using UV light irradiation to reach the same sensitivity to formaldehyde. Nevertheless, both factors (NPs doping and UV light irradiation), when applied together, did not introduce an amplified synergistic effect.

For assessing the reproducibility of sensors responses, there were performed two repeated measurements of the same gas concentration (10 ppm of CH₂O) under the same operation conditions (both under dark conditions and UV light irradiation), whose results are shown in Fig. 5. Under UV light irradiation all but Ni/WO₃ and Au/Pt/WO₃ sensors showed good performance in terms of reversibility and stability of their responses to the considered gas exposure, while under dark conditions the best reproducibility was achieved by far by the Pt/WO₃ and Au/WO₃ sensors. We suppose that these dopants effectively activated the WO₃ gas sensing layers at the employed low operating temperatures, assuring the reproducibility of gas sensing by accelerated adsorption-desorption even without UV light.

The presented results were obtained for the fabricated batch of gas sensing layers. The applied technology can be characterized by the unavoidable differences between gas sensing films parameters produced in different batches, as observed for other MOS technologies. This issue requires more studies to show detailed conclusions about repeatability of the applied technology and distribution of the most important parameters (e.g., dc resistance, thickness, roughness, etc.) of the gas sensing layers.

4. Discussion

The results obtained in this study showed that UV light irradiation highly enhanced the sensing behavior of the pristine WO₃ and Ni/WO₃ layers. Previous gas sensing tests showed that the UV light increases the density of free carriers in MOS and contributes to the migration of additional carriers and hence to the increase of sensors responses [31], accelerating also the absorption-desorption of gas molecules by the sensing layer [12].

The mechanisms of photocatalytic-activated gas sensing for some gases and materials were presented elsewhere [32–35]. Gas sensing accelerates under irradiation because the photons generate electron-hole pairs [$h\nu \rightarrow e^- + h^+$]. The holes h^+ decrease the depletion layer of oxygen ions O₂⁻ occupying the surface of grains of the gas sensing material (e.g., WO₃, TiO₂, ZnO, SnO₂) by releasing the adsorbed oxygen

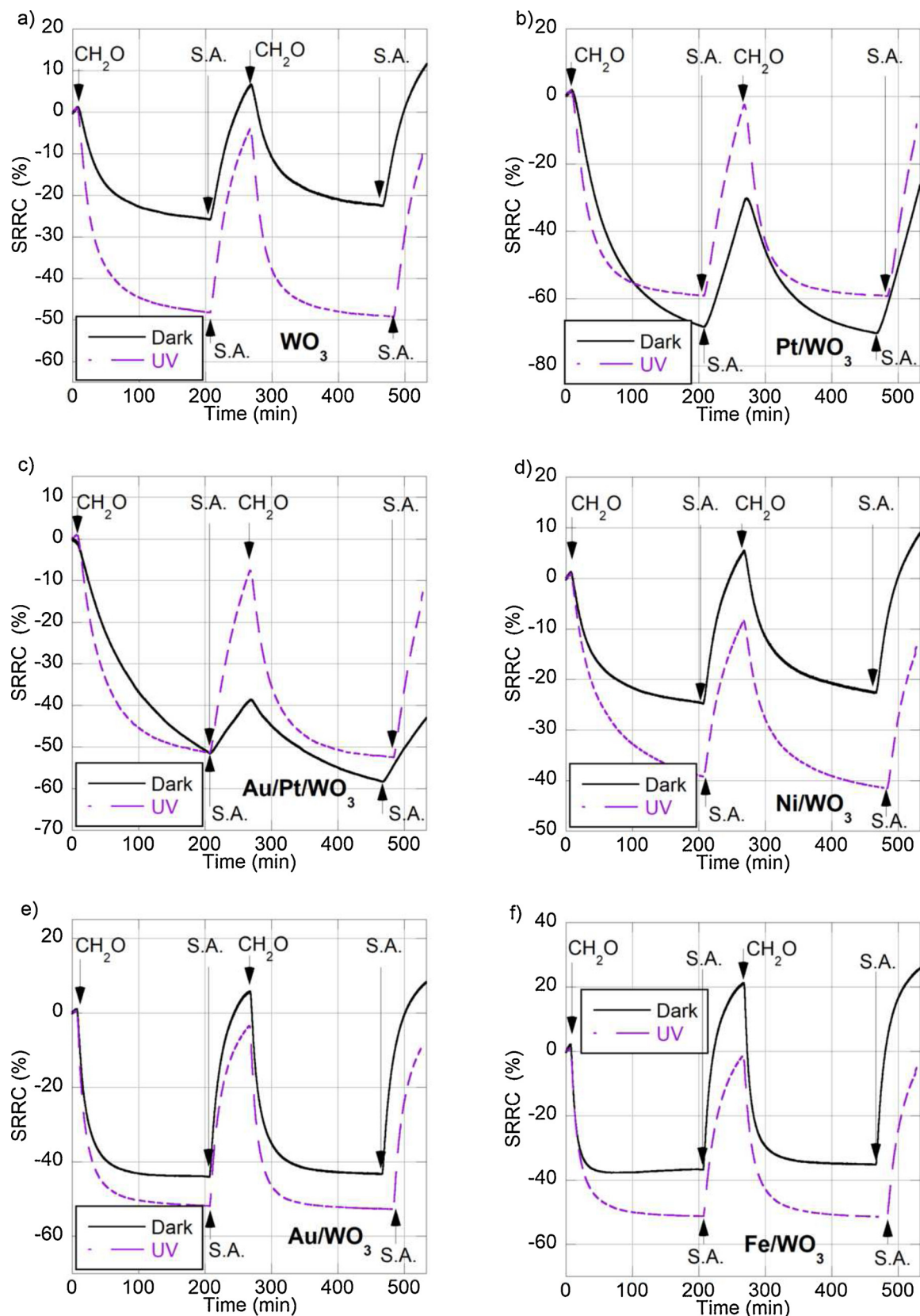


Fig. 5. Repeatability test of gas sensors relative resistance changes (SRRC) to two successive exposures to 10 ppm of CH_2O under dark (solid black line) and UV light irradiation (dashed violet line). Operation conditions: (a) pristine WO_3 , (b) Pt/WO_3 , (c) $\text{Au}/\text{Pt}/\text{WO}_3$, (d) Ni/WO_3 , (e) Au/WO_3 , (f) Fe/WO_3 . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ions [$h^+ + O_2^- \rightarrow O_2(g)$]. Next, the released $O_2(g)$ reacts with photo-activated electrons and creates oxygen ions [$O_2(g) + e^- \rightarrow O_2^-(h\nu)$]. These ions are much weakly bounded to the grains than the chemisorbed O_2^- ions, accelerating the oxidation-reduction reaction with the formaldehyde gas molecules [$O_2^-(h\nu) + CH_2O \rightarrow CO_2 + H_2O + e^-$]. This reaction ultimately increases the conductance of the sensor [32]. The photo-degradation of formaldehyde gas molecules includes the formation of the intermediate product $-O-HC-O-$, which is converted to H_2O and CO_2 by photo-induced ions [$O_2^-(h\nu)$]. The kinetics of this reaction depends on the formaldehyde concentration and light intensity, as presented in detail in the literature [32]. The number of $O_2^-(h\nu)$ depends on various factors: the active surface area that provides reacting sites, and the ability of photons absorption by the gas sensing material. These factors are conditioned by the wavelength of the applied UV-light, the morphology of gas sensing material and eventual dopants.

The faster response to formaldehyde in the case of most of the NPs-doped WO_3 NWs and UV light irradiated sensing films might be explained by the fact that volume phenomena determines the gas sensing in the doped films. A longer time is required for gas molecules diffusion than in the case of the mechanism induced by UV light irradiation in the pristine WO_3 film, as UV light irradiation is mainly limited to the surface of the gas sensing layer. The observed effect could be influenced by the wavelength of the applied UV light and the thickness of the gas sensing layer, as UV light wavelength determines the depth of irradiation that penetrates the gas sensing films. Actually, the ratio between the gas sensing layer thickness and UV light penetration depth regulates the impact of UV light on gas sensing, and both parameters need to be considered for enhancing the influence of UV light on sensors performance.

On the other hand, sensors response time could be further decreased by increasing the formaldehyde exposure flow rate and/or reducing the volume of the test chamber. Importantly, it is to note that the bias current of the UV LEDs (10 mA) was kept low for avoiding to induce changes in the structure of the irradiated gas sensing layers, but in the same time it was sufficiently high for ensuring a correct operation.

5. Conclusions

This experimental study aimed at assessing the sensing performances of both pristine and metal NPs-doped WO_3 NWs towards formaldehyde detection under dark (normal operation) conditions and UV light irradiation. All sensors responded in ascending order to increasing concentrations of formaldehyde in the range 5–15 ppm. On the other hand, sensor response was significantly enhanced by UV light irradiation for the gas sensing layers made of pristine WO_3 and Ni/WO_3 , while in the case of the other sensors it didn't have a noticeable effect or even decreased. Furthermore, when the sensors were operated under UV light irradiation, the drift effect was greatly counteracted, and it was a general tendency of reducing the response time. Moreover, the responses of most of the sensors (with the exception of Pt/WO_3 and Au/WO_3) were more repeatable and reversible than under dark operation conditions, when good reproducibility was achieved by the Pt/WO_3 sensor only.

These results were explained by a higher probability of activation of adsorption-desorption processes in the sensing layers, increased by the generated oxygen ions $O_2^-(h\nu)$ under UV light irradiation. These ions were weakly bounded to the porous sensing layer when compared with the chemisorbed O_2^- ions. The UV light modulates only a relatively thin external gas sensing layer and therefore gives faster responses to the ambient atmosphere than the gas sensing in the porous volume of the film that requires gas molecules diffusion. The presented results open new opportunities for gas sensing improvement by using thinner sensing layers when employing UV light irradiation during sensors operation, which could result in enhanced gas sensing at reduced operating temperatures and at lower production costs. We expect that

using various wavelengths of UV LEDs irradiating thin gas sensing layers could lead to similar performances in gas sensing as the use of different metal dopants. Nevertheless, this emerging direction in MOS gas sensors requires further in-depth studies.

CRedit authorship contribution statement

Benachir Bouchikhi: Writing - original draft, Project administration. **Tomasz Chludziński:** Visualization, Investigation. **Tarik Saidi:** . **Janusz Smulko:** . **Nezha El Bari:** Conceptualization. **He Wen:** Data curation, Validation. **Radu Ionescu:** Writing - review & editing, Funding acquisition.

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.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement no. 645758.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.snb.2020.128331>.

References

- [1] P. Camagni, G. Faglia, P. Galinetto, C. Perego, G. Samoggia, G. Sberveglieri, Photosensitivity activation of SnO_2 thin film gas sensors at room temperature, *Sens. Actuators B Chem.* 31 (1996) 99–103.
- [2] S. Mishra, C. Ghanshyam, N. Ram, R.P. Bajpai, R.K. Bedi, Detection mechanism of metal oxide gas sensor under UV radiation, *Sens. Actuators B Chem.* 97 (2004) 387–390.
- [3] W.H. Brattain, J. Bardeen, Surface properties of germanium, *Bell Syst. Tech. J.* 32 (1953) 1–41.
- [4] W. Guo, Design of gas sensor based on Fe-doped ZnO nanosheet-spheres for low concentration of formaldehyde detection, *J. Electrochem. Soc.* 163 (2016) B517–B525.
- [5] N. Yamazoe, N. Miura, Some basic aspects of semiconductor gas sensors, *Chem. Sensor Technol.* 4 (1992) 19–42.
- [6] N. Taguchi, Gas-detecting device, US Patent 3,631,436 (1971).
- [7] G. Yun, M. Balamurugan, H.-S. Kim, K.-S. Ahn, S.H. Kang, Role of WO_3 layers electrodeposited on SnO_2 inverse opal skeletons in photoelectrochemical water splitting, *J. Phys. Chem. C* 120 (2016) 5906–5915.
- [8] S.S. Shendage, V.L. Patil, S.A. Vanalakar, S.P. Patil, N.S. Harale, J.L. Bhosale, J.H. Kim, P.S. Patil, Sensitive and selective NO_2 gas sensor based on WO_3 nanoplates, *Sens. Actuators B Chem.* 240 (2017) 426–433.
- [9] A. Blair, R. Saracci, P.A. Stewart, R.B. Hayes, C. Shy, Epidemiologic evidence on the relationship between formaldehyde exposure and cancer, *Scand. J. Work Environ. Health* (1990) 381–393.
- [10] C.-Y. Lee, C.-M. Chiang, Y.-H. Wang, R.-H. Ma, A self-heating gas sensor with integrated NiO thin-film for formaldehyde detection, *Sens. Actuators B Chem.* 122 (2007) 503–510.
- [11] I. Castro-Hurtado, G.G. Mandayo, E. Castaño, Thickness influence on gas sensing characteristics of NiO thin films for formaldehyde detection, *Proc. of the 8th Spanish Conf. on Electron Devices, CDE' (2011)* 1–4.
- [12] K. Anothainart, M. Burgmair, A. Karthigeyan, M. Zimmer, I. Eisele, Light enhanced NO_2 gas sensing with tin oxide at room temperature: conductance and work function measurements, *Sens. Actuators B Chem.* 93 (2003) 580–584.
- [13] J.A. Dirksen, K. Duval, T.A. Ring, NiO thin-film formaldehyde gas sensor, *Sens. Actuators B Chem.* 80 (2001) 106–115.
- [14] D.-S. Lee, J.-K. Jung, J.-W. Lim, J.-S. Huh, D.-D. Lee, Recognition of volatile organic compounds using SnO_2 sensor array and pattern recognition analysis, *Sens. Actuators B Chem.* 77 (2001) 228–236.
- [15] A.K. Srivastava, Detection of volatile organic compounds (VOCs) using SnO_2 gas-sensor array and artificial neural network, *Sens. Actuators B Chem.* 96 (2003) 24–37.
- [16] L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, C. Xie, Visible-light activate mesoporous WO_3 sensors with enhanced formaldehyde-sensing property at room temperature, *Sens. Actuators B Chem.* 163 (2012) 260–266.

- [17] H. Yu, J. Li, Z. Li, Y. Tian, Z. Yang, Enhanced formaldehyde sensing performance based on Ag@ WO₃ 2D nanocomposite, *Powder Technol.* 343 (2019) 1–10.
- [18] F.E. Annanouch, S. Vallejos, T. Stoycheva, C. Blackman, E. Llobet, Aerosol assisted chemical vapour deposition of gas-sensitive nanomaterials, *Thin Solid Films* 548 (2013) 703–709.
- [19] W. Zeng, C. Dong, B. Miao, H. Zhang, S. Xu, X. Ding, S. Hussain, Preparation, characterization and gas sensing properties of sub-micron porous WO₃ spheres, *Mater. Lett.* 117 (2014) 41–44.
- [20] M.-H. Chen, Lu C.-S, Wu R.-J, Novel Pt/TiO₂-WO₃ materials irradiated by visible light used in a photoreductive ozone sensor, *J. Taiwan Inst. Chem. Eng.* 45 (2014) 1043–1048.
- [21] L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, C. Xie, Visible-light activate mesoporous WO₃ sensors with enhanced formaldehyde-sensing property at room temperature, *Sens. Actuators B Chem.* 163 (2012) 260–266.
- [22] Q. Geng, Z. He, X. Chen, W. Dai, X. Wang, Gas sensing property of ZnO under visible light irradiation at room temperature, *Sens. Actuators B Chem.* 188 (2013) 293–297.
- [23] Y. Gui, S. Li, J. Xu, C. Li, Study on TiO₂-doped ZnO thick film gas sensors enhanced by UV light at room temperature, *Microelectron. J.* 39 (2008) 1120–1125.
- [24] S. Zhang, L. Zhang, Research on the formaldehyde gas detection based on grass like WO₃, *J. Nanoelectron. Optoelectron.* 12 (2017) 1203–1206.
- [25] M.U. Qadri, F.E. Annanouch, M. Aguilo, F. Diaz, J.F. Borull, M.C. Pujol, E. Llobet, Metal decorated WO₃ nanoneedles fabricated by aerosol assisted chemical vapor deposition for optical gas sensing, *J. Nanosci. Nanotechnol.* 16 (2016) 10125–10132.
- [26] T. Saidi, D. Palmowski, S. Babicz-Kiewlicz, T.G. Welearegay, N. El Bari, R. Ionescu, J. Smulko, B. Bouchikhi, Exhaled breath gas sensing using pristine and functionalized WO₃ nanowire sensors enhanced by UV-light irradiation, *Sens. Actuators B Chem.* 273 (2018) 1719–1729.
- [27] F.E. Annanouch, Z. Haddi, S. Vallejos, P. Umek, P. Guttmann, C. Bittencourt, E. Llobet, Aerosol-assisted CVD-grown WO₃ nanoneedles decorated with copper oxide nanoparticles for the selective and humidity-resilient detection of H₂S, *ACS Appl. Mater. Interfaces* 7 (2015) 6842–6851.
- [28] A. Thamri, H. Baccar, F.E. Annanouch, E. Llobet, A. Abdelghani, Methanol, ethanol and acetone sensing using AACVD-grown tungsten oxide nanoneedles, *J. Nanomed. Nanotechnol.* 7 (2016) 1–6.
- [29] T. Saidi, T.G. Welearegay, O. Zaim, O.G. León, R. Ionescu, N. El Bari, B. Bouchikhi, Ability of discrimination of breath from smoker and non-smoker volunteers by using an electronic nose based on WO₃ nanowires and SnO₂ sensors, *Olfaction and Electronic Nose (ISOEN)*, ISOCs/IEEE International Symposium On. IEEE, 2017, pp. 1–3.
- [30] Y. Shigesato, Photochromic properties of amorphous WO₃ films, *J. Appl. Phys.* 30 (1991) 1457–1462.
- [31] L. Lentka, J. Smulko, Methods of trend removal in electrochemical noise data—overview, *Measurement* 131 (2019) 569–581.
- [32] L. Deng, X. Ding, D. Zeng, S. Tian, H. Li, C. Xie, Visible-light activate mesoporous WO₃ sensors with enhanced formaldehyde-sensing property at room temperature, *Sens. Actuators B Chem.* 163 (2012) 260–266.
- [33] S.W. Fan, A.K. Srivastava, V.P. Dravid, UV-activated room-temperature gas sensing mechanism of polycrystalline ZnO, *Appl. Phys. Lett.* 95 (2009) 142106.
- [34] E. Espid, F. Taghipour, UV-LED photo-activated chemical gas sensors: a review, *Crit. Rev. Solid State Mater. Sci.* 42 (2017) 416–432.
- [35] S. Zhang, T. Lei, D. Li, G. Zhang, C. Xie, UV light activation of TiO₂ for sensing formaldehyde: how to be sensitive, recovering fast, and humidity less sensitive, *Sens. Actuators B Chem.* 202 (2014) 964–970.

Benachir Bouchikhi received his Ph.D degree at Aix-Marseille University in 1982, France, and his Dr. Sc. Degree in 1988 at the University of Nancy I, France, specialising in measuring instruments. He is working as Professor at Moulay Ismail University, as a Research Scientist at the Faculty of Sciences of Meknes, Morocco. He is the Director of the Laboratory of Electronics, Automatic and Biotechnology. His research concerns the development of electronic sensing and biosensors for applications related to food safety, biomedical diagnostics and environmental monitoring. He has published over 110 scientific papers. During the last 15 years he has managed about 20 national and international bilateral projects in the area of food safety, biomedical diagnostics, and control of the climate parameters and drip fertigation under greenhouse. He supervised 12 doctoral theses, 5 in preparation, 3 Dr Sc-Degree, and 4 Habilitations. He is member of the H2020-MSCA-RISE-2014 project TROPSENSE: "Development of a non-invasive breath test for early diagnosis of tropical diseases" (Reference No: 645758). His work has been cited more than 1920 times, and the Hirsch index is 25 (source Google Scholar database, 20-01-2020).

Tomasz Chludziński received his M.Sc. (2015) Degree in Biomedical Engineering from Gdańsk University of Technology (Poland) where he is currently a Ph.D. student in the field of Electronics at the Department of Metrology and Optoelectronics. His research interests are environmental measurements with a focus on gas detection, VOCs and biomarkers diseases in the exhaled breath. He uses for gas detection e-nose systems utilizing Fluctuation-Enhanced Sensing (FES) method, for non-invasive disease diagnosis.

Tomasz Chludziński was involved in the TROPSENSE-EU project "Development of a non-invasive breath test for early diagnosis of tropical diseases". He was responsible for preparation of the e-nose system utilizing prototype gas sensors.

Tarik Saidi received his doctorate degree in electronics and artificial intelligence from the University of Moulay Ismail (Meknes, Morocco) in 2018, while his Master degree in electronic, electrical engineering, automatic and industrial computing from the University of Hassan II (Casablanca, Morocco) in 2013. His research interests include sensors networks based electronic noses/tongues for non-invasive biomedical analysis.

Janusz Smulko received his M.Sc., Ph.D. and D.Sc. degrees in electronics from Gdańsk University of Technology, Poland, in 1989, 1996 and 2007, respectively. Presently, he is a full professor (since 2016), Head of the Metrology and Optoelectronics Department (since 2012). He had also conducted scientific research in short-term positions in Texas A&M University (2003), Uppsala University (2006/07), Massachusetts Institute of Technology (2011, 2013). As a researcher, he focuses on the applications of 1/f noise for gas sensing and reliability assessment of electronic components and structures, the influence of noise on detection efficiency in Raman spectroscopy systems. He was Vice-Rector for Research of the Gdańsk University of Technology (in the term 2016–2019), member of the Committee on Metrology and Scientific Instrumentation of the Polish Academy of Science (two terms: 2013–2019) and Editor-in-Chief of Metrology and Measurement Systems Journal (two terms: 2013–2019), Chair of IEEE Chapter Computer Society Gdańsk (two terms: 2014–2017). Professor chaired three International Conferences on Noise and Fluctuations issues and managed seven research projects. He co-authored more than 100 papers and was a member of the H2020-MSCA-RISE-2014 project TROPSENSE: "Development of a non-invasive breath test for early diagnosis of tropical diseases" (No.: 645758).

Nezha El Bari is currently a full Professor at the Biology Department at Moulay Ismail University of Meknes in Morocco since 1990. She was awarded a PhD in Biology Applied to Nutrition and Biotechnology in 1989 from the Nancy 1 University and the Doctorat d'Etat Es-Sciences in Biology from Moulay Ismail university in 1995. From 1997–2003 she was the instigator and a head of professional bachelor in dairy industry. Her background is also the physico-chemical analysis of milk and the cheese technology and she is an Expert in this field (Technopole Saint-Brieuc ARMOR, France, 2003). She was an instigator and a head of Applied Bachelor, "Milk Engineering and Derivatives" from 1997–2003 at the Faculty of Sciences of Meknes. She is the head of the Biotechnology, Agroalimentary and Biomedical Analysis group since 2005. Her current research combines biotechnology and sensing technology especially Biosensors, Molecularly Imprinted Polymers, Electronics Tongue and Nose in food quality control, in biomedical application and environmental monitoring. She has been involved in several European and national projects as a coordinator or a member (University of Rovira and Virgili, University of Malaga, University of Claude Bernard of Lyon 1, INRAP of Tunis University, The New University of Lisboa....). She was a member of the H2020-MSCA-RISE-2014 project TROPSENSE: "Development of a non-invasive breath test for early diagnosis of tropical diseases" (No.: 645758). She is co-authored more than 70 papers. Her researchgate score is 29.81 and hirsch index is 17. She was awarded the Best Researcher in Agricultural Sciences in Morocco (Research Excellence Awards) by Web of Science Group, Clarivate analytics on July 3th, 2019.

He Wen was born in Hunan, China, in 1982. He received the B.Sc., M. Sc., and Ph.D. degrees in electrical engineering from Hunan University, Hunan, China, in 2004, 2007, and 2009, respectively. He is currently a professor with the College of Electrical and Information Engineering, Hunan University, China. His present research interests include electrical contact reliability, wireless communications, power system harmonic measurement and analysis, power quality, and digital signal processing. Also, he is the deputy director of Hunan Province Key Laboratory of Intelligent Electrical Measurement and Application Technology. He is an Associate Editor of the IEEE Transactions on Instrumentation and Measurement, and a Member of Editorial Board of Fluctuation and Noise Letters.

Radu Ionescu is affiliated with the Division of Solid State Physics, The Angström Laboratory, Uppsala University, Sweden. He received his degree in Electrical Power Engineering from the Polytechnic University of Bucharest, Romania, in 1998, and his Ph.D. degree in Electronics Engineering from the Polytechnic University of Catalonia, Barcelona, Spain, in 2003. Previously, Dr. Radu Ionescu was postdoctoral researcher at Rovira i Virgili University, Tarragona, Spain, experienced researcher (FP6 Marie Curie Transfer of Knowledge Actions) at Mediterranean University of Reggio Calabria, Italy, EC Senior Researcher at the Technion – Israel Institute of Technology, Haifa, Israel, and Research Director at the Institute of Macromolecular Chemistry Petru Poni, Romania. Dr. Radu Ionescu's research focuses on the development of chemical gas sensors for VOCs detection and diseases diagnosis through volatile samples analysis. Dr. Ionescu was the Scientific Coordinator of the EU funded projects H2020-MSCA-RISE-2014 "Development of a non-invasive breath test for early diagnosis of tropical diseases" – TROPSENSE, and H2020-MSCA-RISE-2017 "Volatolomics test for the diagnosis of bovine tuberculosis" – BTB-Test.