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Formaldehyde detection with chemical gas sensors based on WO_3 nanowires decorated with metal nanoparticles under dark conditions and UV light irradiation

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ABSTRACT

We report results of formaldehyde gas (CH_2O) detection under dark conditions and UV light irradiation with pristine tungsten trioxide nanowires (WO_3 NWs) and metal nanoparticles decorated WO_3 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 WO_3 and on WO_3 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 CH_2O 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 WO_3 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 SnO_2, with actually higher response stability [5]. Since the development of Taguchi's gas sensor based on SnO_2in 1971 [6], many semiconductor materials were investigated and analyzed. Among them, tungsten trioxide (WO_3), 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 (CH_2O) 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 CH_2O is 80 ppb in an indoor environment, while an indoor concentration of 0.1 ppm of CH_2O is considered by experts to be

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harmful to the human health. Moreover, studies have shown that CH_2O emission may cause cancer in humans in the long run [9]. Hence, the rapid real-time monitoring of CH_2O 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 CH_2O by using metal oxide gas sensors. NiO thin film was studied as a sensing layer for CH_2O detection [12] due to its catalytic properties for the oxidation of formaldehyde [10,11,13]. SnO_2 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 CH_2O detection [4]. WO_3 sensors have the advantage of reduced energy consumption for CH_2O detection as they work at lower operating temperatures [16–18].

In the present work, we assess the performance of WO_3 nanowires (NWs), both pristine and decorated with various metal nanoparticles (NPs), grown by the aerosol-assisted chemical vapor deposition (AACVD) method, for CH_2O 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 CH_2O detection with pristine and NPs decorated WO_3 NWs under UV light irradiation and under dark (normal operation) conditions.

2. Materials and methods

2.1. Elaboration of the WO_3 nanowires sensors

The sensing films assessed in this experiment were composed of pristine WO_3 NWs and WO_3 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 WO_3 NWs were prepared using tungsten hexacarbonyl (WC_6O_6) 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/WO_3 NWs, 2.2 μm for pristine WO_3, 0.991 μm for Au/WO_3, 0.762 μm for Pt/WO_3, 0.713 μm for Au/Pt/WO_3, and 0.505 μm for Ni/WO_3. SEM analysis showed that the mean diameter of the pristine WO_3 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/WO_3, 1 wt% of Fe in Fe/WO_3, 6 wt% of Pt in Pt/WO_3, 1 wt% of Au and 7 wt% of Pt in Au/Pt/WO_3, and 1 wt% of Ni in Ni/WO_3; 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 WO_3-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 WO_3, Pt/WO_3 and Au/Pt/WO_3, and to 160 °C for Au/WO_3, Ni/WO_3 and Fe/WO_3 [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/cm^2, 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 (CH_2O 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 CH_2O 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 R_0 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

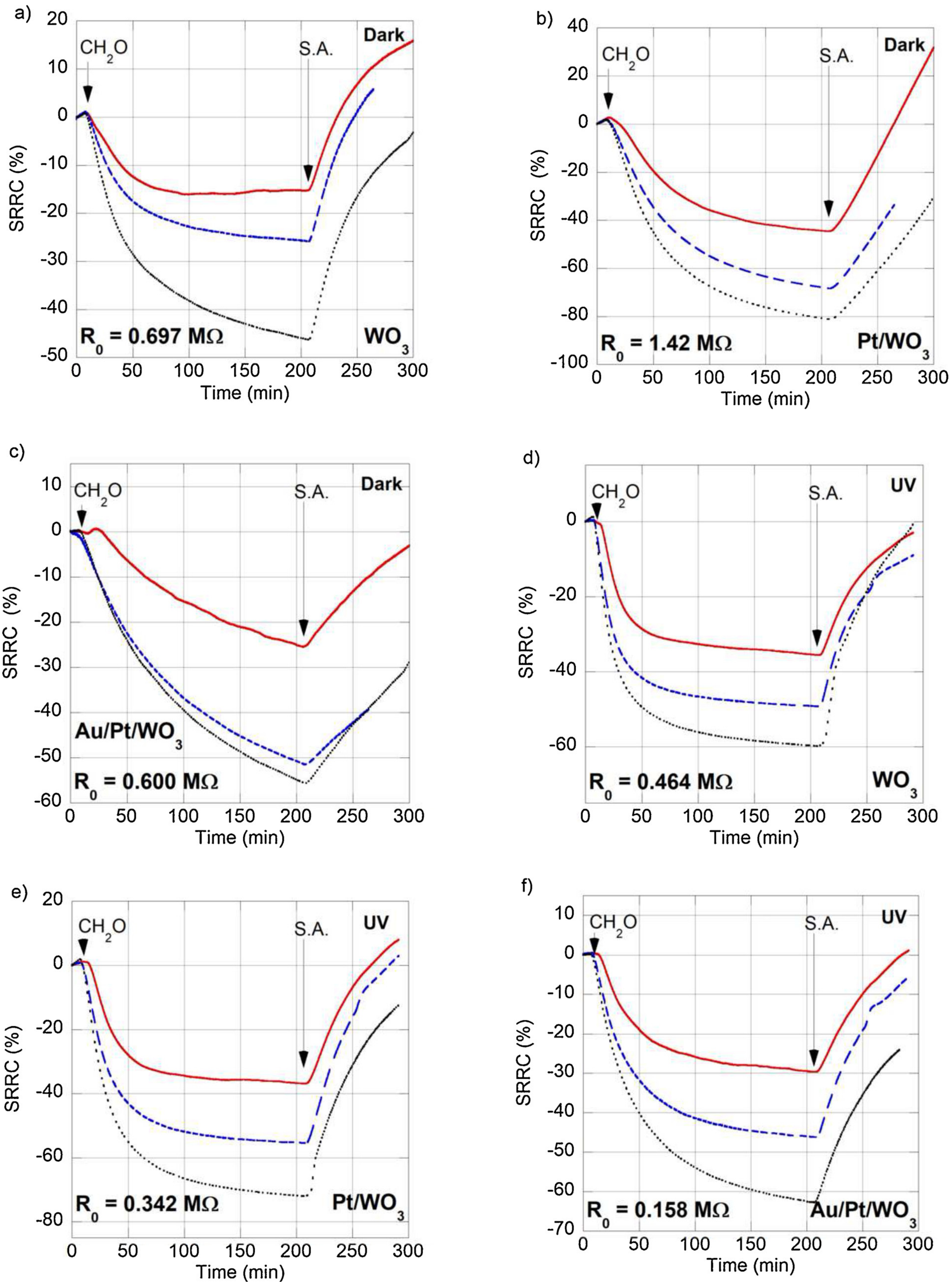

Fig. 1. Sensors relative resistance changes (*SRRC*) towards three selected concentrations of CH_2O: 5 ppm (solid red line); 10 ppm (blue dashed line); 15 ppm (black dotted line), and during synthetic air cleaning achieved under: (a-c) dark (normal operation) conditions; (d-f) UV light irradiation (394 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).

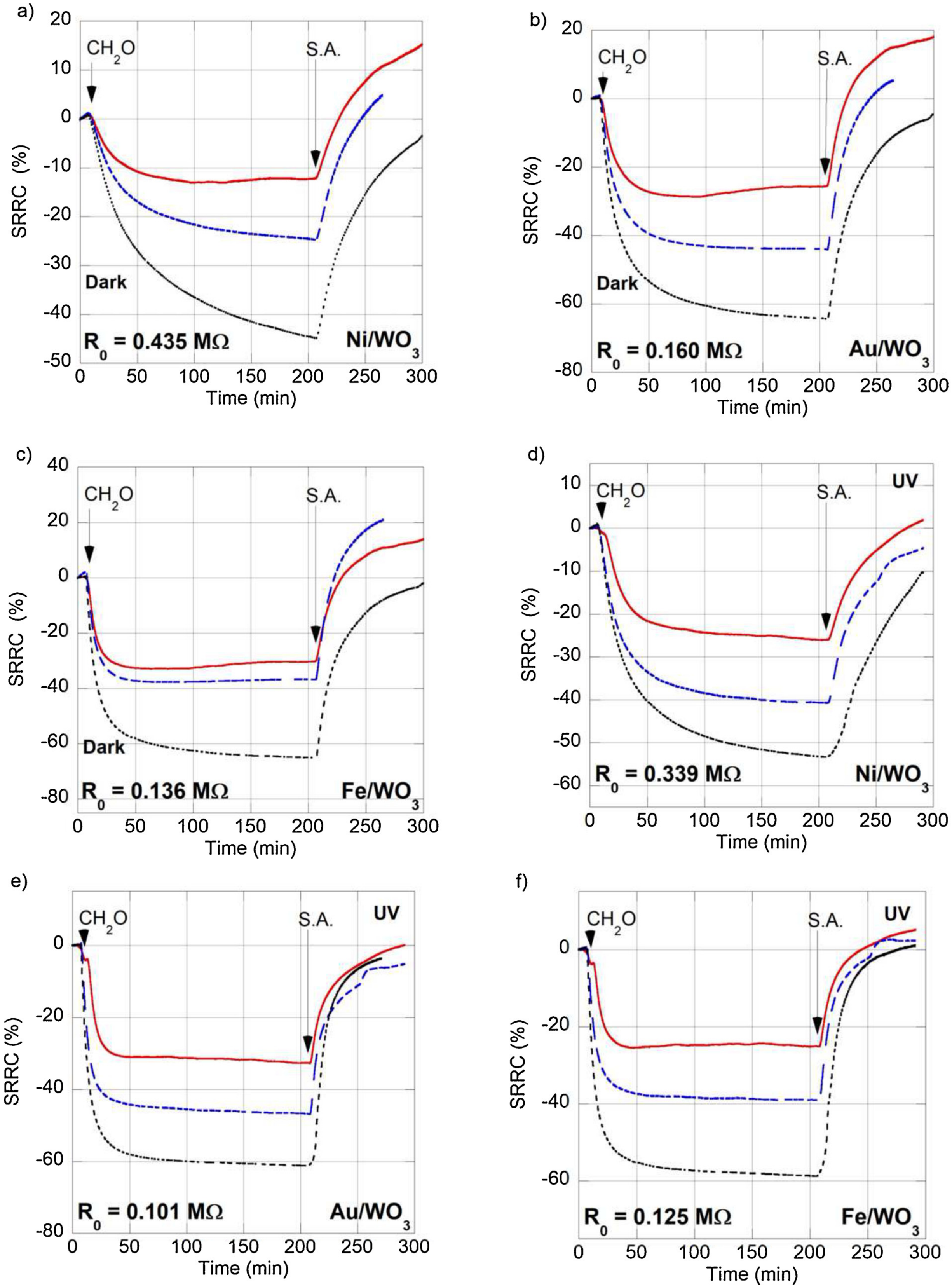

Fig. 2. Sensors relative resistance changes (*SRRC*) towards three selected concentrations of CH_2O: 5 ppm (solid red line); 10 ppm (blue dashed line); 15 ppm (black dotted line), and during synthetic air cleaning achieved under: (a–c) dark (normal operation) conditions; (d-f) UV light irradiation (394 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).

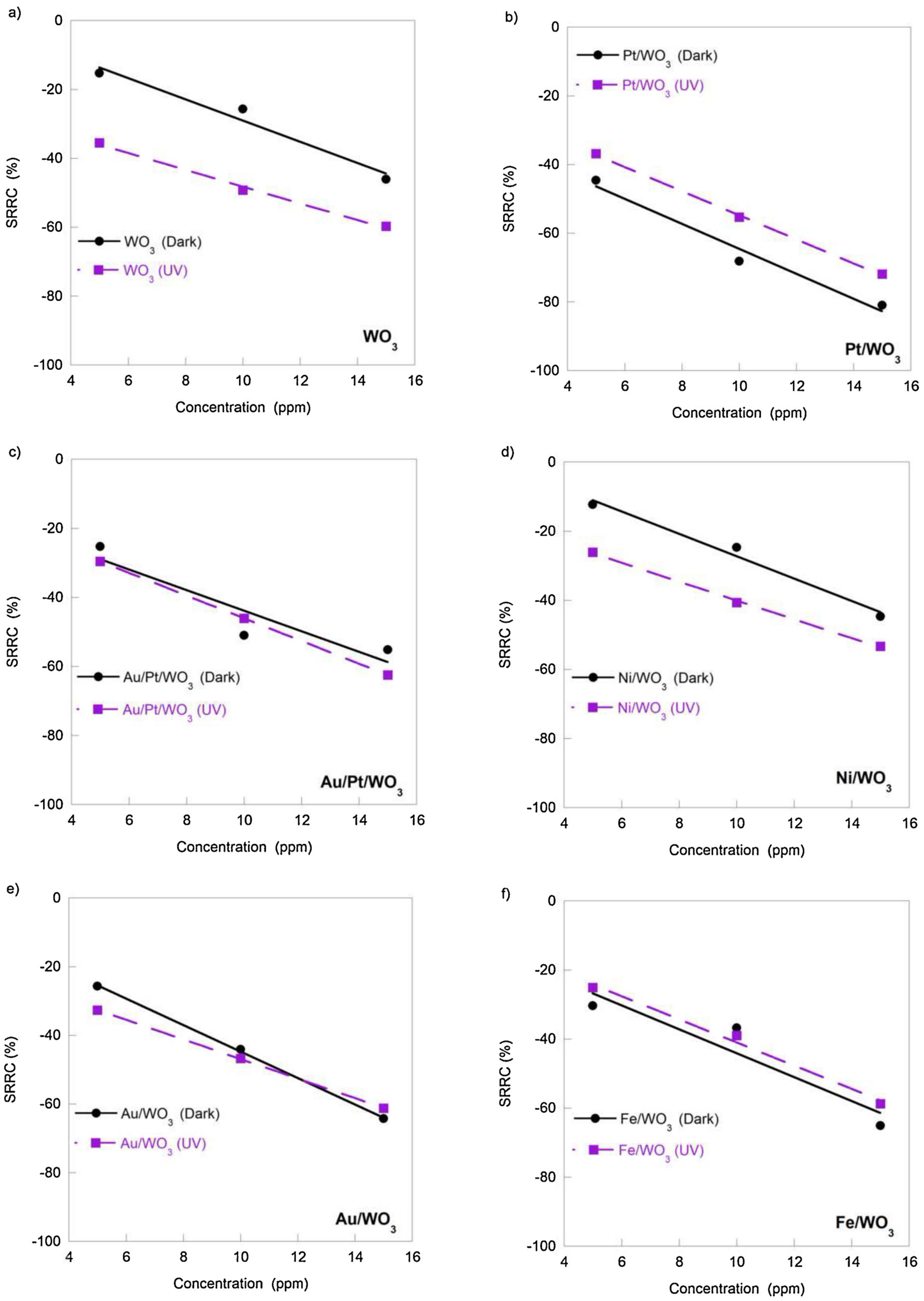

Fig. 3. Relation between sensors relative resistance changes (*SRRC*) and CH_2O exposures when the sensors were operated under dark conditions (black circles) and UV light irradiation at 394 nm (violet squares): (a) pristine WO_3, (b) Pt/WO_3, (c) $Au/Pt/WO_3$, (d) Ni/WO_3, (e) Au/WO_3, (f) Fe/WO_3.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

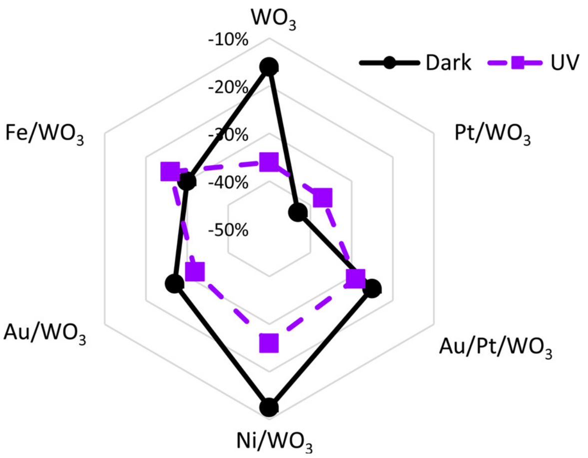

Fig. 4. Radar plot of the sensors relative resistance changes (*SRRC*) values achieved by the gas sensors exposed to 5 ppm CH_2O under dark (black circles) and UV light irradiation (violet squares) operation conditions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

estimated to be ≈ 400 nm for the WO_3 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: $0.167 = \exp(-710\,[\mathrm{nm}]/d)$; 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/WO_3 – *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 WO_3 sensors towards the three selected concentrations of CH_2O 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.

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

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 CH_2O 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/WO_3 sensor, both under dark conditions and UV light irradiation. The use of UV light irradiation enhanced the responses of the pristine WO_3 and Ni/WO_3 sensors, while the responses of the Pt/WO_3 and Fe/WO_3 were higher under dark conditions, as it can be observed from the response values of the sensors to the different CH_2O concentrations analyzed in this study, presented in Fig. 3. The Au/WO_3 sensor showed higher responses under UV light irradiation for the two lowest CH_2O concentrations measured (5 and 10 ppm), while its response to the highest CH_2O concentration (15 ppm) was lower under UV light irradiation than under dark conditions, indicating a saturation tendency at increased CH_2O 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 CH_2O 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 CH_2O 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 CH_2O 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 CH_2O (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 CH_2O exposure highly increased the responses of the pristine WO_3 and Ni/WO_3 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 WO_3 sensor was similar with that of Pt doping of the WO_3 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 synergetic effect.

For assessing the reproducibility of sensors responses, there were performed two repeated measurements of the same gas concentration (10 ppm of CH_2O) 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/WO_3 and $Au/Pt/WO_3$ 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/WO_3 and Au/WO_3 sensors. We suppose that these dopants effectively activated the WO_3 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 WO_3 and Ni/WO_3 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 O_2- occupying the surface of grains of the gas sensing material (e.g., WO_3, TiO_2, ZnO, SnO_2) by releasing the adsorbed oxygen

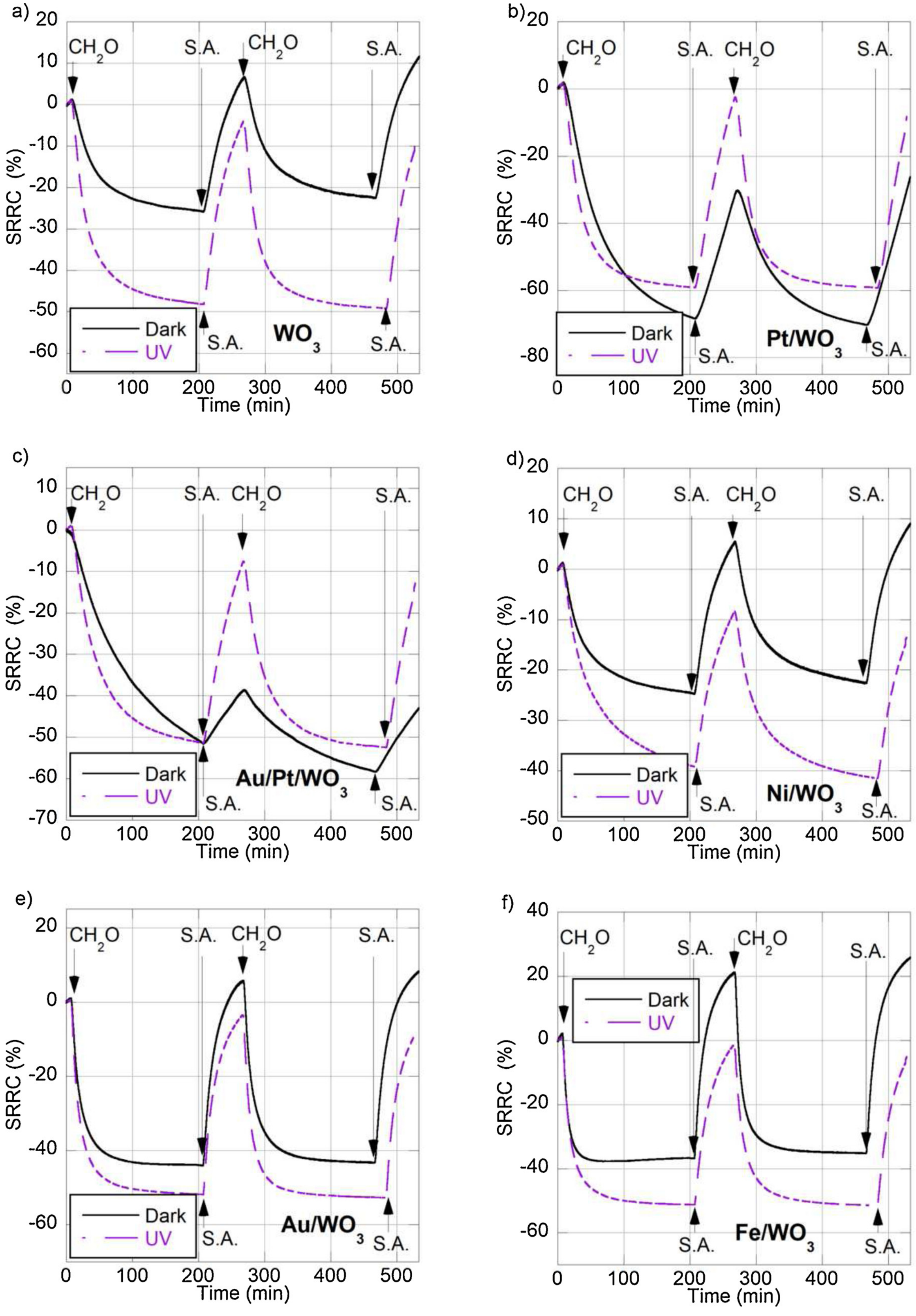

Fig. 5. Repeatability test of gas sensors relative resistance changes (*SRRC*) to two successive exposures to 10 ppm of CH_2O under dark (solid black line) and UV light irradiation (dashed violet line). Operation conditions: (a) pristine WO_3, (b) Pt/WO_3, (c) $Au/Pt/WO_3$, (d) Ni/WO_3, (e) Au/WO_3, (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 [$O_2(g) + e^- \rightarrow O_2\text{-}(h\nu)$]. 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 [$O_2\text{-}(h\nu) + CH_2O \rightarrow CO_2 + H_2O + e^-$]. 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 [$O_2\text{-}(h\nu)$]. 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.

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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.

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