Fluctuation enhanced gas sensing using UV irradiated Au-nanoparticle-decorated WO_3-nanowire films

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Abstract—**WO_3 nanowires (WO_3-NWs) decorated with gold nanoparticles (AuNPs) were utilized in resistive gas sensor devices to detect ethanol by use of fluctuation enhanced sensing (FES). The experimental system records both DC resistance and fluctuations of the sensing film. Our data verify that the sensitivity and selectivity of the gas sensor are improved by applying FES when the sensor is stimulated with a combination of UV light and heating. We conclude that UV light can produce improved gas sensing at low operating temperatures for the investigated AuNP-decorated WO_3-NWs films.**

Keywords: AuNP-decorated WO_3 nanowires; fluctuation enhanced sensing; UV light; noise

I. INTRODUCTION

A commonly used method for gas sensing involves DC resistance measurements on a single resistive gas sensor or on an array of such sensors. The gas sensing element comprises a semiconducting film deposited on the alumina or ceramic substrate of the sensing chip, which is also provided with an integrated heater. The sensor conductivity changes in the presence of the detectable gas, in proportion with its concentration. Specifically, the sensing film is reduced or oxidized by the gas, which leads to modifications in the DC resistance via an alteration of the charge carriers' mobility, concentration, or a combination of both of these factors [1]. An electrical circuit converts conductivity changes to an output signal, which corresponds to the gas concentration. This method often suffers from insufficient sensitivity and selectivity for the detection of various gases, which is the main reason to further develop the technology [2, 3], as discussed below.

Improved sensitivity can be achieved by fluctuation-enhanced sensing (FES), which records low-frequency fluctuations in the resistance instead of, or in addition to, changes in the DC resistance. It has been shown that the gas detection ability, especially for some nanoparticle film sensors [4, 5], can be significantly improved by employing the FES method, and noise spectroscopy provided a more efficient gas detection when compared with DC resistance measurements only [6–10].

Importantly, a gas sensor responds to the presence of particular gases from its surrounding environment when it is stimulated by an external energy necessary to activate chemical processes, such as adsorption and desorption. The easiest and most commonly used way to provide this energy is to heat the sensor to a specified temperature in the range of hundreds of ºC. Generally, the heat exchange process is time dependent due to thermal inertia, and therefore some period of time is required to stabilize the sensor's temperature and other parameters after switching on the heater. Moreover, heating requires energy and it also limits some gas sensing applications (e.g., detection of explosives or combustible gases).

However, there are other ways than thermal to transfer energy to a sensor, one of these being UV light generated by a cheap UV semiconductor diode [8, 11]. In the present study, we used light, instead of heating, to improve the selectivity of Au-nanoparticle (NP)-decorated WO_3-nanowires (NWs) gas sensors. The pros and cons of using UV light wave instead of, or combined with, heating to stimulate the sensor are discussed in some detail.

II. MEASUREMENT SYSTEM

Fig. 1 shows the measurement system that was set up to determine the DC resistance and the fluctuations of the investigated AuNP-decorated WO_3-NWs film irradiated with a controlled UV light source. The hardware comprises a low-noise voltage amplifier, heat and light drivers, a sensor bias current (I_s) driver, a power supply and a computer to acquire the data and control the measurement system [10]. The collected data were processed using Mathworks Matlab scripts and built-in functions. The resolution of the analog–digital converters was

24 bits in both measurement channels. Time-dependent waveforms of resistance fluctuations were sampled using 2 kHz sampling rate and were registered as consecutive records of 10^6 samples.

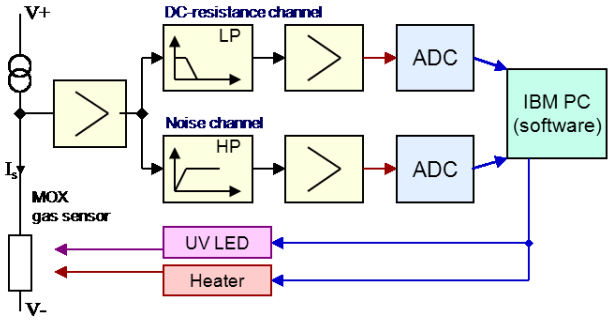

Figure 1. Block diagram of the measurement system. I_s denotes the DC current flowing through the studied gas sensor. Low-pass (LP) and high-pass (HP) filters were applied to measure DC resistance and its fluctuations, respectively, by analog–digital converters (ADCs)

III. GAS SENSING AUNP-DECORATED WO_3-NWS FILM

Nanotechnology is able to produce quasi-one-dimensional nanomaterials on a large scale, such as metal-decorated WO_3-NWs with excellent sensing properties upon exposure to different gases [12, 13]. Many techniques can be used to grow WO_3 nanowires doped with metal nanoparticles; in our case, we use a deposition method based on aerosol-assisted chemical vapor deposition (AACVD). As shown by our previous results [14, 15], this is a versatile, inexpensive and high-yield technique for growing metal oxides with remarkable gas sensing properties. Moreover, the synthesis of nanostructures, as well as the decoration with metal NPs and the integration in the structure of a device, can be realized in a single processing step. AuNP-decorated WO_3-NWs films were grown at 350 ºC by AACVD directly on the electrode area of alumina gas sensor substrates using tungsten hexacarbonyl and hydrogen tetrachloroaurate as precursors. Full details on the deposition conditions can be found elsewhere [14]. The average size of the AuNPs was 10 nm, while the WO_3-NWs were ~5 µm in length and 60–120 nm in width.

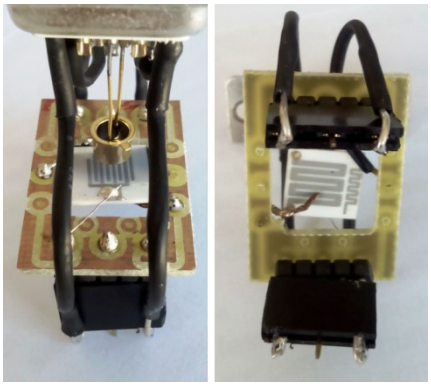

Figure 2. Gas sensing AuNP-decorated WO_3-NWs film and a T5F UV LED diode. Left and right panels show top side with the diode T5F and bottom side with the heater, respectively

Fig. 2 depicts the AuNP-decorated WO_3-NWs gas sensor together with the UV LED diode employed for irradiation. The T5F UV diode has its peak wavelength at 365 nm, which corresponds to photons of 3.1 eV energy. Therefore the change in sensor conductance after irradiating the AuNP-decorated WO_3-NWs material can be expected to depend mainly on interband electronic transitions (for photon energies greater than the energy band gap of 2.56 eV). Additionally, the plasmonic resonance on the surface of gold nanoparticles can increase penetration of the UV light into the sensing layer [16].

IV. EXPERIMENTAL RESULTS

A. *Sensing by DC resistance changes*

The main difference between energy transfer by UV light and by heating is related to the impact area: the heating affects the entire volume of the gas sensor, while the UV light impacts mainly on its surface. Both factors might potentially be used to improve gas detection, but they have different efficiency. Thus, in order to compare both features we have measured the sensor's DC resistance in ambient atmospheres of synthetic air (s.a.) and 200 ppm of ethanol (Fig. 3) when the sensor was heated to different temperatures. Additionally, UV light irradiated the sensor to accelerate adsorption and desorption processes. We can conclude that the investigated AuNP-decorated WO_3-NW film is sensitive to ethanol, and its sensitivity depends on both temperature and UV light.

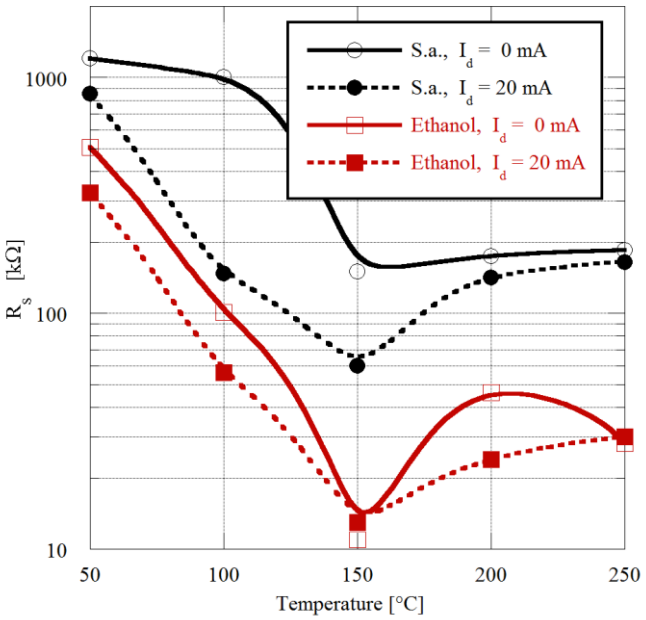

Figure 3. DC resistance R_S of an AuNP-decorated WO_3-NWs gas sensing film *versus* temperature in synthetic air (s.a.) and in 200 ppm of ethanol. I_d denotes the DC current of the UV LED diode used to irradiate the sensing film; the diode was placed ~5 mm from the gas sensing film

At low temperatures, below 150 °C, we observed that the UV light induces significant changes in the sensor's DC resistance, of up to as much as one order of magnitude. The difference in DC resistance of the AuNP-decorated WO_3-NWs film with and without UV light depends on the sensor's ambient atmosphere.

In the presence of ethanol vapor, the change of DC resistance caused by UV light becomes less pronounced. At higher temperatures, above 150 °C, we noticed much lower DC resistance changes induced by UV light than at lower temperatures. This fact is in fact as expected, because adsorption–desorption processes are so intense at high temperatures that the additional energy introduced by UV light does not change the conditions within the gas sensing film to any significant degree. A similar argument could be used to explain why UV light does not change the DC resistance as much at temperatures below 150 °C in the presence of ethanol as it does in the case of synthetic air: The DC resistance of an AuNP-decorated WO_3-NWs film in synthetic air is relatively high because the activation energy of oxygen ions captured at the WO_3 grains is higher than the activation energy of ethanol molecules. Thus the extra energy of the UV light makes the potential energy between the grains comparatively much lower for synthetic air than for ethanol.

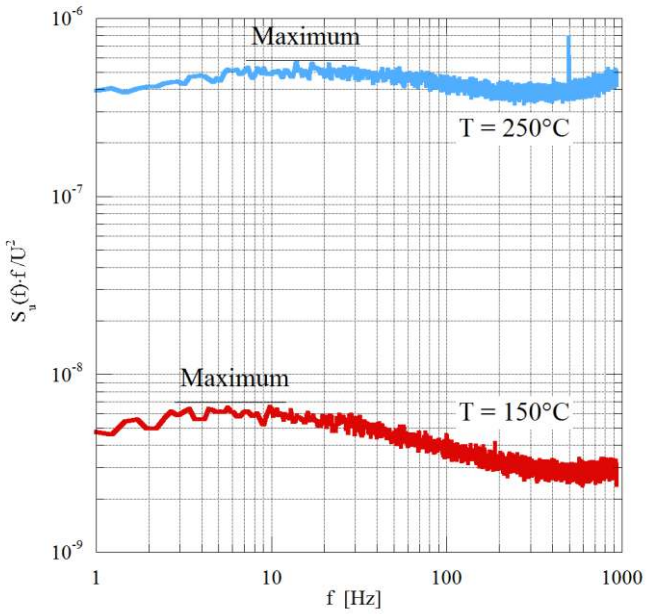

Figure 4. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across an AuNP-decorated WO_3-NWs sensor biased by the DC voltage U *versus* f. Data were taken at the shown temperatures T with the sensor placed in the dark in synthetic air

B. Sensing by low-frequency fluctuations

Benefits of using UV light to stimulate the AuNP-decorated WO_3-NWs gas sensor can be clearly seen when low-frequency noise is analyzed. The results of noise measurements in an ambient atmosphere of synthetic air, and under dark conditions, are presented in Fig. 4. The $1/f$ noise component was observed within at least three frequency decades up to 1 kHz and depended strongly on the sensor temperature. We observed a crossover frequency in the spectra whose value shifted upon temperature rise from a few Hz to about 20 Hz. The crossover frequency was identified as the local maximum of the product $S_u(f)\cdot f/U^2$ (*cf.* Fig. 4).

When UV light irradiation was applied—as indicated in Fig. 5 for $I_d = 20$ mA—we noticed at the lower sensor temperature (150 °C) that the crossover frequency was shifted towards lower frequencies and that the $1/f$ noise component dominated up to 40 Hz. This means that the UV light can be a very efficient factor for determining the intensity of low frequency noise and helping to establish what kind of gas is present in the sensor's ambiance.

Similar results were observed when the sensor was placed in 200 ppm of ethanol, as shown in Fig. 6. There is again a crossover frequency similar to that of the noise observed in the dark and in synthetic air but having lower intensity in the case of ethanol. When UV light is applied the crossover frequency shifts towards lower frequencies. We expect that this frequency shift is characteristic for the gas present in the ambient atmosphere, but a firm conclusion on this issue requires additional experimental studies. Nevertheless, the presented results confirm that FES is very informative when the properties of the gas sensing film are modulated by UV light.

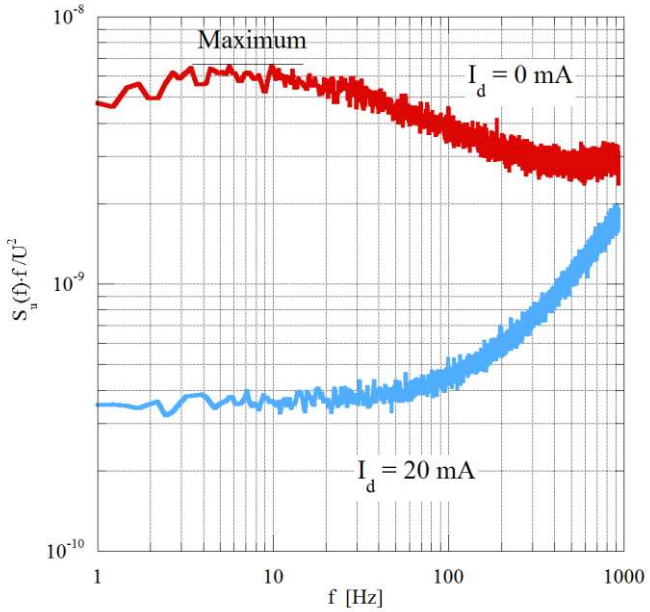

Figure 5. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across an AuNP-decorated WO_3-NWs sensor biased by the DC voltage U *versus* f. Data were taken at 150 °C and in synthetic air. UV light irradiation was accomplished by a UV LED diode with the shown values of DC current I_d

V. Results and Discussion

The experimental data were acquired with the purpose of determining which detection method was preferable under different conditions. Fig. 7 confirms that the effect of low frequency noise changes caused by UV light is very strong at low concentrations of ethanol. This conclusion is consistent with the data reported in Figs. 5 and 6, which show that the noise change induced by UV light was largest in an atmosphere of synthetic air. Thus noise modulated by UV light should be very efficient for ethanol detection at low concentrations. Furthermore, the effect caused by UV light starts to saturate very fast at low intensities of UV light. At the given distance between the gas sensing film and the applied UV diode (*cf.* Fig. 2) we observed that a DC current of 3 mA was sufficient to saturate

noise changes, and a further increase of the UV light intensity did not alter the low-frequency noise.

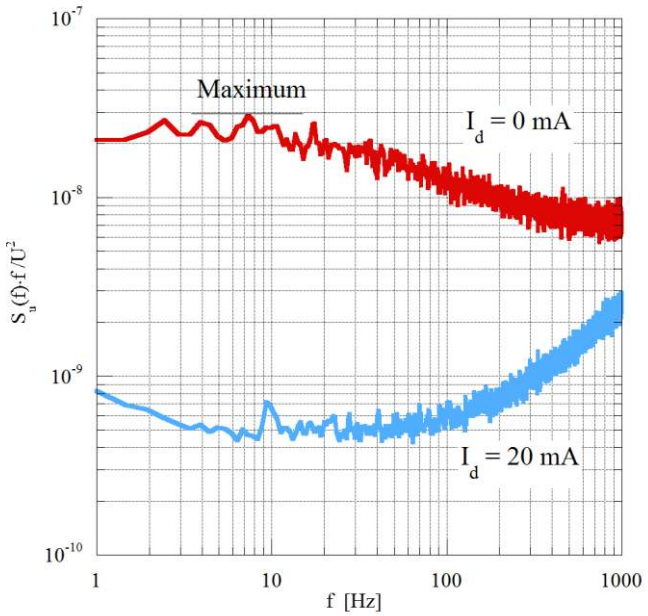

Figure 6. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across an AuNP-decorated WO_3-NWs sensor biased by the DC voltage U *versus* f. Data were taken at 150 °C in 200 ppm of ethanol. UV light irradiation was accomplished by a UV LED diode with the shown values of DC current I_d

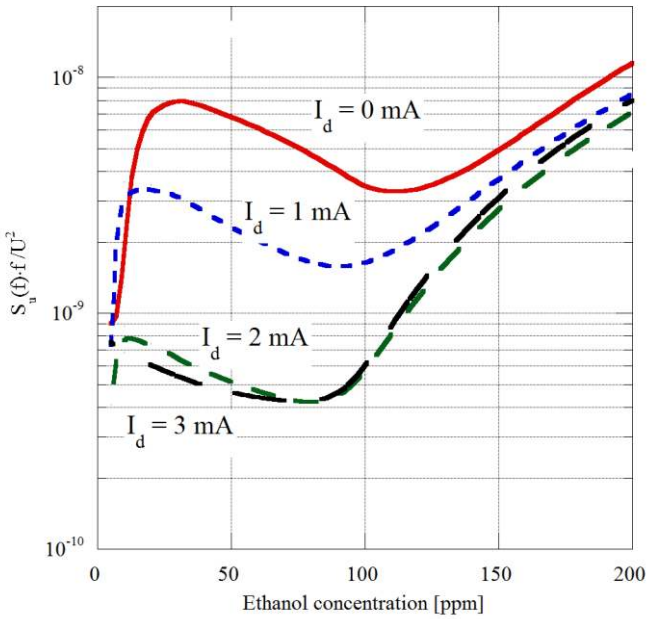

Figure 7. Normalized product of frequency f and power spectral density $S_u(f)$ of voltage fluctuations across an AuNP-decorated WO_3-NWs sensor biased by the DC voltage U *versus* ethanol concentration. Data were taken at f = 100 Hz and 150 ºC. UV light irradiation was accomplished by a UV LED diode with the shown values of DC current I_d

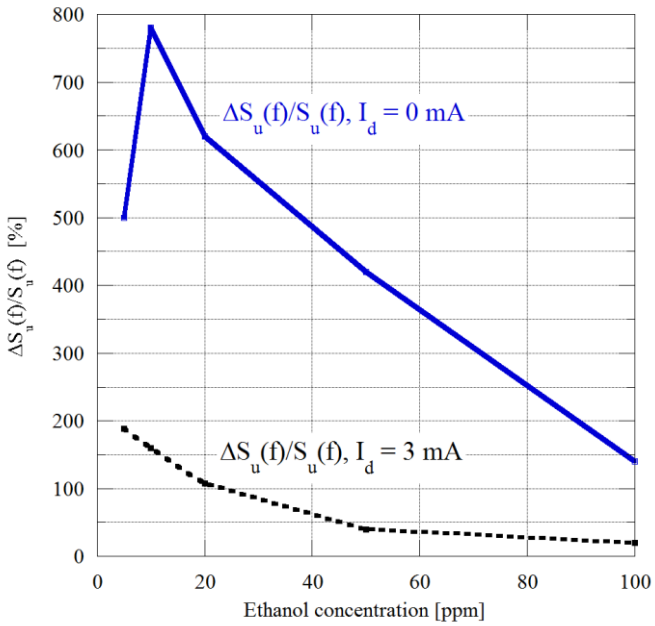

Figure 8. Relative noise level difference, as discussed in the main text, *versus* ethanol concentration. Data were taken at f = 100 Hz and 150 ºC. UV light irradiation was accomplished by a UV LED diode with the shown values of DC current I_d

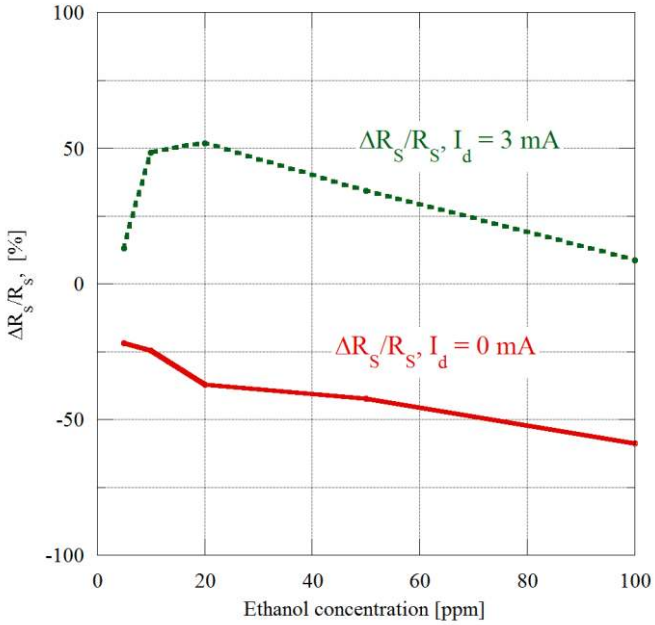

Figure 9. Relative resistance difference, as discussed in the main text, *versus* ethanol concentration. Data were taken at 150 ºC. UV light irradiation was accomplished by a UV LED diode with the shown values of DC current I_d

Fig. 8 shows relative changes of power spectral density $\Delta S_u(f)/S(f)$ of voltage fluctuations at f = 100 Hz. Fig. 9 shows relative changes of DC resistance $\Delta R_S/R_S$. Both figures compare these data in order to establish which method is most sensitive to ethanol. The relative changes of the noise are seen to be several times stronger than the relative changes in the DC resistance when the sensor was in the dark. The measurements

were performed at 150°C, when we observed the crossover frequency in the low-frequency range of the spectra. This significant change of noise intensity was due to the shift of that frequency. When the UV light was switched on (I_d = 3 mA), the noise intensity did not change as much with ethanol concentration, because the additional energy of UV light altered the noise component identified by the crossover frequency and responsible for the previously noticed intense noise changes. This means that the best sensitivity can be guaranteed by low-frequency noise when the temperature and the UV light are carefully selected to assure a shift of the crossover frequency in the spectra. Thus low-frequency noise can be an important source of information and improve gas sensing in photo-catalytic materials, as suggested previously when noise was applied to predict the reliability of similar materials in optical applications [17].

VI. CONCLUSIONS

The investigated AuNP-decorated WO_3-NWs gas sensing film was sensitive to ethanol, and gas sensing could be modulated by UV light to gather more information about the ambient atmosphere. We found that a cautiously selected operating temperature could significantly increase the sensitivity for low-concentration ethanol gas detection. Moreover, the operating temperature of the gas sensing film can be reduced to limit energy consumption, and the sensor can be gas activated by UV light.

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REFERENCES

[1] G. Korotcenkov, “Gas response control through structural and chemical modifications of metal oxide films: State of the art and approaches,” Sensors and Actuators B: Chemical, vol. 107, 2005, pp. 209–232.

[2] P. Heszler, R. Ionescu, E. Llobet, L. F. Reyes, J. Smulko, et al., “On the selectivity of nanostructured semiconductor gas sensors,” Physica Status Solidi B, vol. 244, 2007, pp. 4331–4335.

[3] S. R. Morrison, “Selectivity in semiconductor gas sensors,” Sensors and Actuators, vol. 12, 1987, pp. 425–440.

[4] B. Ayhan, C. Kwan, J. Zhou, L. B. Kish, K. D. Benkstein, et al., “Fluctuation enhanced sensing (FES) with a nanostructured, semiconducting metal oxide film for gas detection and classification,” Sensors and Actuators B: Chemical, vol. 188, 2013, pp. 651–660.

[5] J. Smulko, C. G. Granqvist, L. B. Kish, “On the statistical analysis of noise in chemical sensors and its application for sensing,” Fluctuation and Noise Letters, vol. 1, 2001, pp. L147–L153.

[6] A. W. Stadler, Z. Zawiślak, A. Dziedzic, D. Nowak, “Noise spectroscopy of resistive components at elevated temperature,” Metrology and Measurement Systems, vol. 21, 2014, pp. 15–26.

[7] L. B. Kish, R. Vajtai, C. G. Granqvist, “Extracting information from noise spectra of chemical sensors: Single sensor electronic noses and tongues,” Sensors and Actuators B: Chemical, vol. 71, 2000, pp. 55–59.

[8] M. Kotarski, J. Smulko, Hazardous gases detection by fluctuation-enhanced gas sensing,” Fluctuation and Noise Letters, vol. 9, 2010, pp. 359–371.

[9] J. Ederth, J. Smulko, L. B. Kish, P. Heszler, C. G. Granqvist, “Comparison of classical and fluctuation-enhanced gas sensing with Pd_xWO_3 nanoparticle films,” Sensors and Actuators B: Chemical, vol 113, 2006, pp. 310–315.

[10] M. Kotarski, J. Smulko, “Noise measurement setups for fluctuations enhanced gas sensing,” Metrology and Measurement Systems, vol. 16, 2009, pp. 457–464.

[11] A. Giberti, C. Malagùa, V. Guidia, “WO_3 sensing properties enhanced by UV illumination: An evidence of surface effect”, Sensors and Actuators B: Chemical, vol. 165, 2012, pp. 59–61.

[12] F. Chávez, G. F. Pérez-Sánchez, O. Goiz, P. Zaca-Morán, R. Peña-Sierra, A. Morales-Acevedo, et al., “Sensing performance of palladium-functionalized WO_3 nanowires by a drop-casting method,” Applied Surface Science, vol. 275, 2013, pp. 28–35.

[13] J. Kukkola, M. Mohl, A. R. Leino, J. Mäklin, N. Halonen, A. Shchukarev, et al., “Room temperature hydrogen sensors based on metal decorated WO_3 nanowires,” Sensors and Actuators B: Chemical, vol. 186, 2013, pp. 90–95.

[14] S. Vallejos, P. Umek, T. Stoycheva, F. Annanouch, E. Llobet, X. Correig, P. De Marco, C. Bittencourt, C. Blackman, “Single-step deposition of Au- and Pt-nanoparticle-functionalized tungsten oxide nanoneedles synthesized via aerosol-assisted CVD, and used for fabrication of selective gas microsensor arrays”, Advanced Functional Materials, vol. 23, 2013, pp. 1313–1322.

[15] F. E. Annanouch, S. Vallejos, T. Stoycheva, C. Blackman, and E. Llobet, “Aerosol assisted chemical vapour deposition of gas-sensitive nanomaterials,” Thin Solid Films, vol. 548, 2013, pp. 703–709.

[16] M. A. Vincenti, D. De Ceglia, V. Roppo, V., M. Scalora, “Harmonic generation in metallic, GaAs-filled nanocavities in the enhanced transmission regime at visible and UV wavelengths,” Optics Express, vol. 19, 2011, pp. 2064–2078.

[17] C. G. Granqvist, S. Green, E. K. Jonson, R. Marsal, G. A. Niklasson, et al., “Electrochromic foil-based devices: Optical transmittance and modulation range, effect of ultraviolet irradiation, and quality assessment by 1/*f* current noise,” Thin Solid Films, vol. 516, 2008, pp. 5921–5926.