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PROPANOL DETECTION DEVICE FOR THE PURPOSE OF MONITORING THE QUALITY OF THE ENVIRONMENT

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Abstract. The aim of this study was to develop and characterize CuO/Cu_2O functionalized with AgPt nanostructures for gas sensing applications. Environmental pollution remains a pressing global concern, requiring effective detection methods. Metal oxide nanostructures, such as those based on copper oxides, offer promising solutions due to their sensitivity and selectivity for various gases. The research investigated the morphology and structure of the nanostructures using techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectroscopy. In addition, the nanostructures were functionalized with noble metals such as silver and platinum to enhance their sensory properties. The deposition of polymer layers has been investigated as a method to improve sensor selectivity. The gas sensing properties of the $CuO/Cu_2O/AgPt$ nanostructures were evaluated using the Keithley 2400 source meter and showed high sensitivity to gases such as propanol, acetone, hydrogen, and ammonia at elevated temperatures. The results showed that higher operating temperatures result in faster response and recovery times. In addition, the nanostructures exhibited saturation in response at higher concentrations of certain gases. These results highlighted the potential of $CuO/Cu_2O/AgPt$ nanostructures in environmental monitoring applications, particularly in industries prone to gas emissions. Overall, this research contributes to the advancement of gas sensing technology for pollution prevention and control efforts.

Keywords: *sensors, propanol, nanostructutres, functionalized.*

Rezumat. Scopul acestui studiu a fost explorarea, dezvoltarea și caracterizarea nanostructurilor CuO/Cu_2O funcționalizate cu AgPt pentru aplicații de detectare a gazelor. Poluarea mediului rămâne o preocupare globală presantă, necesitând metode eficiente de detectare. Nanostructurile de oxizi metalici, cum ar fi cele pe bază de oxizi de cupru, oferă soluții promițătoare datorită sensibilității și selectivității lor pentru diferite gaze. Cercetarea a investigat morfologia și structura nanostructurilor folosind tehnici precum microscopia electronică de scanare (SEM), difracția de raze X (XRD) și spectroscopia Raman. În plus, nanostructurile au fost funcționalizate cu metale nobile, cum ar fi argintul și platina, pentru a le îmbunătăți proprietățile senzoriale. S-a investigat depunerea de straturi de polimeri ca metodă de îmbunătățire a selectivității senzorilor. Proprietățile de detectare a gazelor ale nanostructurilor $CuO/Cu_2O/AgPt$ au fost evaluate cu ajutorul aparatului de măsură cu sursă Keithley 2400 și s-a demonstrat o sensibilitate ridicată la gaze precum propanol, acetonă, hidrogen și amoniac la temperaturi ridicate. Rezultatele au arătat că temperaturile de funcționare mai ridicate duc la timpi de răspuns și de recuperare mai rapizi. În plus, nanostructurile au prezentat o saturație a răspunsului la concentrații mai mari de anumite gaze. Aceste rezultate au evidențiat potențialul nanostructurilor $CuO/Cu_2O/AgPt$ în aplicațiile de monitorizare a mediului, în special în industriile predispuse la emisii de gaze. În general, această cercetare contribuie la progresul tehnologiei de detectare a gazelor pentru eforturile de prevenire și control al poluării.

Cuvinte cheie: *senzor, propanol, nanostructuri, funcționalizat.*

1. Introduction

The development of humanity today has led to one of the biggest global problems, environmental pollution. For this purpose, to prevent this phenomenon, the researchers started the active study on gas detectors based on different nanostructures of metal oxides such as SnO_2, In_2O_3, WO_3, ZnO, Fe_2O_3 and many others [1]. The performance of gas sensors is determined by the following factors such as sensitivity, selectivity, response and recovery times, stability, repeatability and others. The structure and morphology of CuO/Cu_2O nanostructures were characterized using techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. The sensitivity of the nanostructures to gas was tested, where the generation of the p-type response was observed for such gases as propanol, acetone, hydrogen and at relatively higher temperatures for ammonia as well. Similar researches were also carried out by other authors [2,3]. The detection of volatile organic compounds (VOC) by the researched nanostructures of $CuO/Cu_2O/AgPt$ makes it possible to use them in such areas as monitoring the quality of the environment with the aim of preventing pollution, such as in factories, paint factories, pharmaceuticals and others. Doping and functionalizing nanostructures with noble metals such as Ag, Au, Pt and others, proved to be an effective method for improving sensor properties such as sensitivity, selectivity, response and recovery times, stability over time and others [4]. In this work, the nanostructures based on copper oxide functionalized with Ag and Pt were studied. Another technology quite often encountered lately is the deposition of polymer layers with the aim of improving the selectivity of the sensor, acting as a sieve for the gas molecule [5]. Similarly, to improve the properties of the sensor, a layer of PV3D3 polymer was deposited, where the difference was observed before and after the deposition of the polymer.

2. Materials and Methods

The CuO/Cu_2O structures were obtained by the chemical method, which is a simple and cost-effective method to implement [6,7]. To enhance the sensory properties of the obtained nanostructures, they were functionalized with noble metals like silver and platinum. The functionalization of noble metals can enhance the sensory properties of nanostructures [8], including sensitivity, selectivity, response and recovery time, repeatability, and others. Another effective method for improving the selectivity of nanostructures is the deposition of polymers that function as a flat net over the nanostructures, which enables the filtering of gas molecules by permitting their passage with smaller sizes [9].

For the determination of the sensory properties of $CuO/Cu_2O/AgPt$ nanostructures, the Keithley 2400 source meter was used, which has high accuracy. The data obtained from the source meter was processed and displayed using LabView software (from National Instruments). The following formula was used to transform the data obtained into percentages:

$$S = \frac{G_{gas} - G_{air}}{G_{air}} * 100\%, \quad (1)$$

where: S is the sensitivity of nanostructures, G_{gas} represents the electrical conductivity of nanostructures when exposed to gas, and G_{air} represents the electrical conductivity of nanostructures when exposed to air [10].

The average crystallite size (D_{hkl}) were determined using Debye-Scherer equation [11]:

$$D_{hkl} = \frac{0.9\lambda}{\beta cos\theta}, \quad (2)$$

where: λ − X-ray wavelength, β − full width at half maximum of the diffraction peak and θ − Bragg angle. Determined Dhkl was ~28.07 nm and ~42.84 for (111) Cu_2O plane and (-111) CuO plane, respectively.

Dislocation density (δ) was calculated using average crystallite size, as following relation:

$$\delta = \frac{1}{D_{hkl}^2} \quad (3)$$

For (111) Cu_2O plane and (-111) CuO plane was obtained 0.0013 and 0.0006 nm^{-2}.

3. Results and Discussion

3.1. Morphological and Strucutral Analysis of CuO/Cu_2O/AgPt

Morphology of the CuO/Cu_2O/AgPt sample was studied at different magnifications after gas tests, observing that nanostructures are deposited uniformly on the surface (Figure 1a, b). At higher magnification (Fgure 1c) nanodots of AgPt are visible, compared to the the SEM images before the deposition of nanodots. Average diameter of the AgPt nanodot was approximatively 20 nm, as observed in Figure 1d.

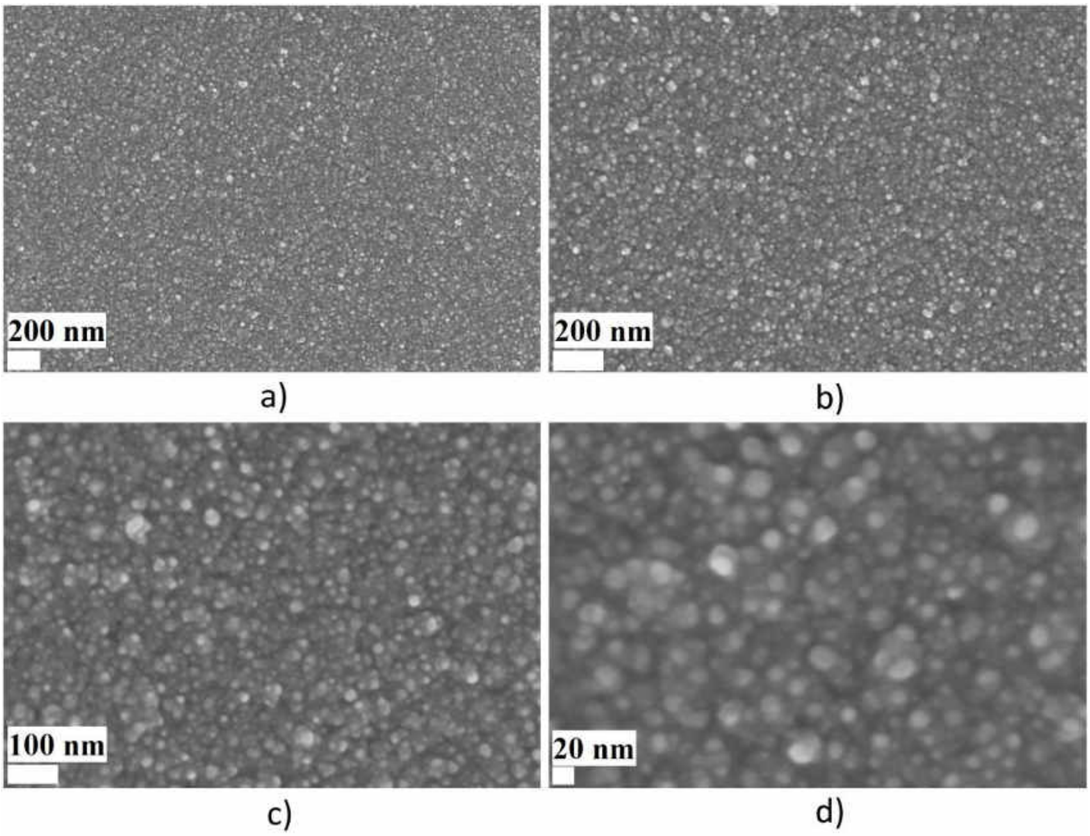

Figure 1. SEM images of the CuO/Cu_2O/AgPt after gas tests at different magnifications: a) 200 nm; b) 200 nm; c) 100 nm; d) 20 nm.

Figure 2 shows SEM images of the CuO/Cu_2O sample after coating with PV3D3. After comparing with Figure 1, it can be observed the same granular nanostructures, the only difference being the PV3D3 polymer layer deposited in Figure 2, so it is possible to observe a smoothening of the surface layer due to the uniform deposition of polymer on the sample, as previously observed in [9].

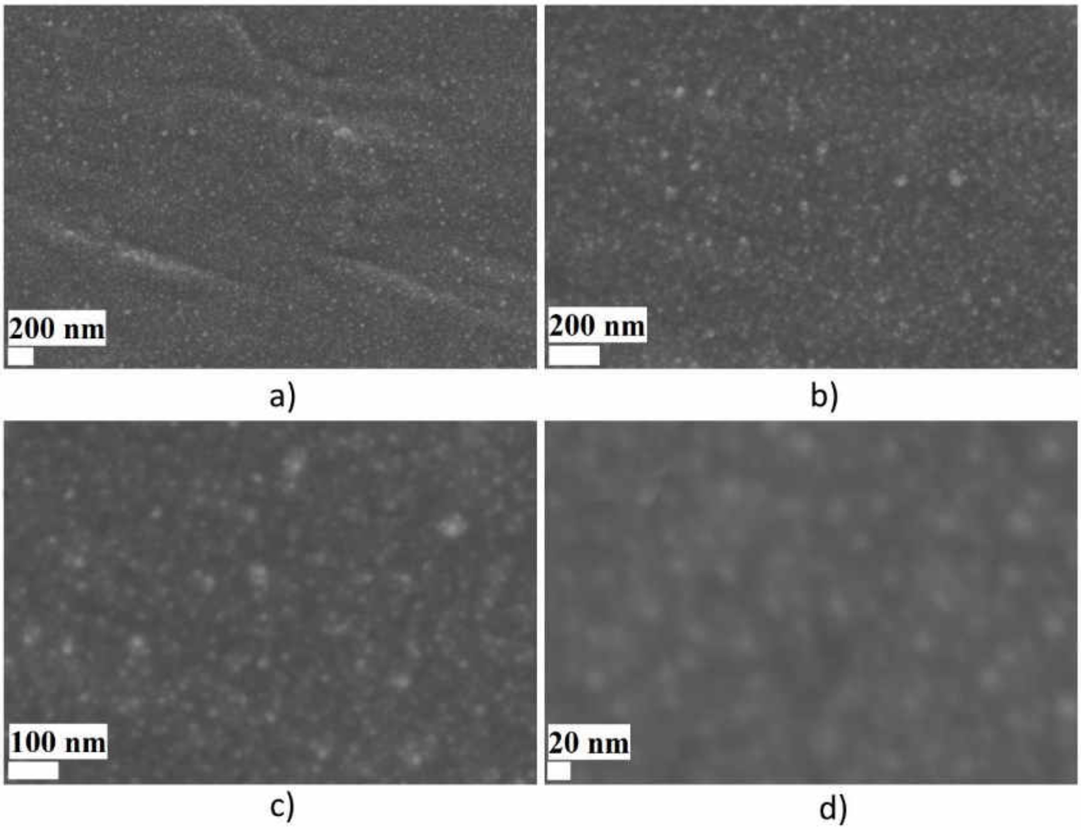

Figure 2. SEM images of the CuO/Cu_2O/AgPt after gas tests and after being coated with PV3D3 layer at different magnifications: a) 200 nm; b) 200 nm; c) 100 nm; d) 20 nm.

XRD pattern of the sample was studied in the 10-90° 2θ values, with the results in the interval 30-80° 2θ presented in Figure 3.

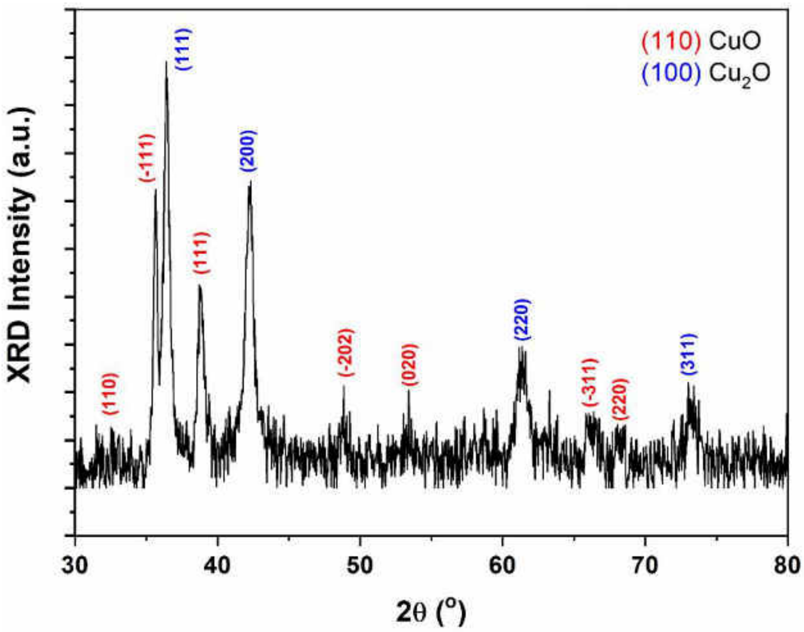

Figure 3. XRD pattern of the CuO/Cu_2O:AgPt sample.

There have been detected multiple CuO and Cu_2O peaks, according to CuO_00-005-0661 and Cu_2O_050667, respectively. Cu_2O cuprite peaks (111) and (200) have a higher intensity compared to tenorite peaks, which can be due to the slow formation of the CuO on top of Cu_2O layers [11]. Strong and sharp diffraction peaks indicate high cristallinity of the sample [12].

In Figure 4 is presented Raman spectra of the CuO/Cu_2O sample, observing multiple CuO peaks at 286 cm^{-1}, 335 cm^{-1} and 599 cm^{-1}, coresponding to the Ag and Bg, which are in accordance with the results of other authors [13,14]. A Cu_2O peak has been detected at 1040-1090 cm^{-1}, corresponding to multi-phonon transitions according to [15,16].

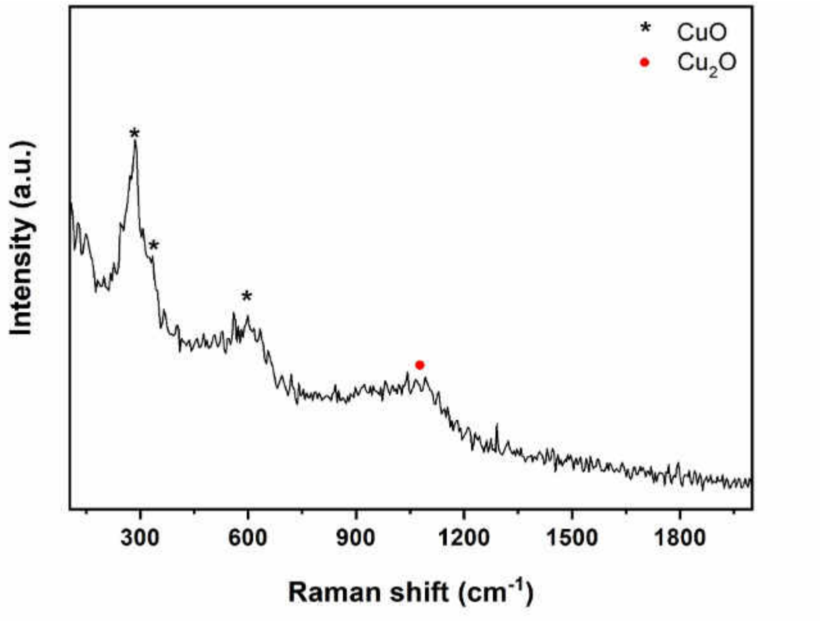

Figure 4. RAMAN spectra of the CuO/Cu_2O:AgPt sample.

3.2. Gas sensing properties of CuO/Cu_2O/AgPt

Figure 5 shows the operational response of the CuO/Cu_2O/AgPt nanostructures under the influence of the application of gases such as acetone, methane, hydrogen, ammonia, propanol and carbon dioxide with a concentration of 100 ppm.

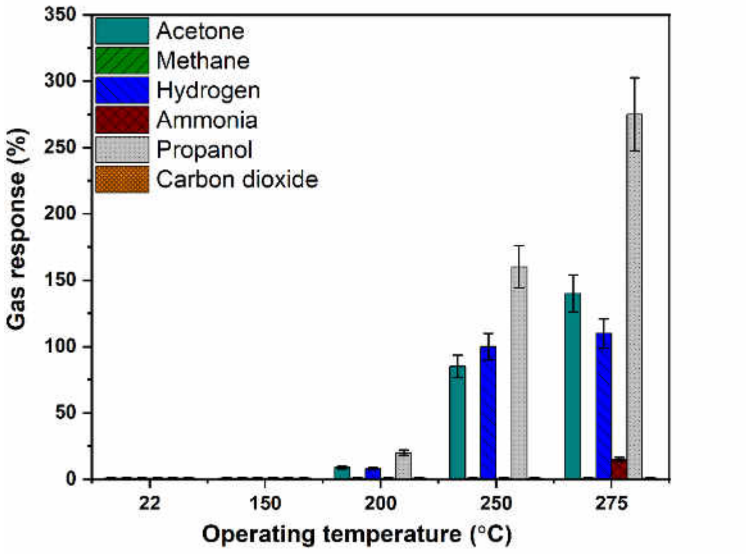

Figure 5. The dynamic response to all gases with 100 ppm concentration at RT, 150 °C, 200 °C, 250 °C, 275 °C.

It can be seen from the figure that the responses of these nanostructures appear at relatively high operating temperatures (200 – 275 °C). Starting with the temperature of 200 °C, a high sensitivity to propanol with a value of 20 % is observed. At a temperature of 250 °C, a more pronounced response to propanol appears, thus we have a sensitivity of 160 % to propanol. Hydrogen has a sensitivity of 100 %, and acetone 85 %. At the temperature of 275 °C we have a high sensitivity to propanol with the value of 275 %. Hydrogen has a response of 110 % while at this operating temperature the nanostructures already have a greater response to acetone with a value of 140 % and a response to ammonia of 15 % appears.

Figure 6 shows the dynamic response for propanol with a concentration of 100 ppm for different temperatures. According to these data, the response time of the AgPt:Bb nanostructures to propanol at the temperature of 200 °C is approximately 21.72 s, while the recovery time has a value greater than 41.4 s. At a temperature of 250 °C, the response time is approximately 22.6 s, and the recovery time is more than 76 s. At a temperature of 275 °C, the response time is 20.4 s, and the recovery time is approximately 75.2 s. From these results we can conclude that by applying a higher operating temperature we have a faster response and recovery time.

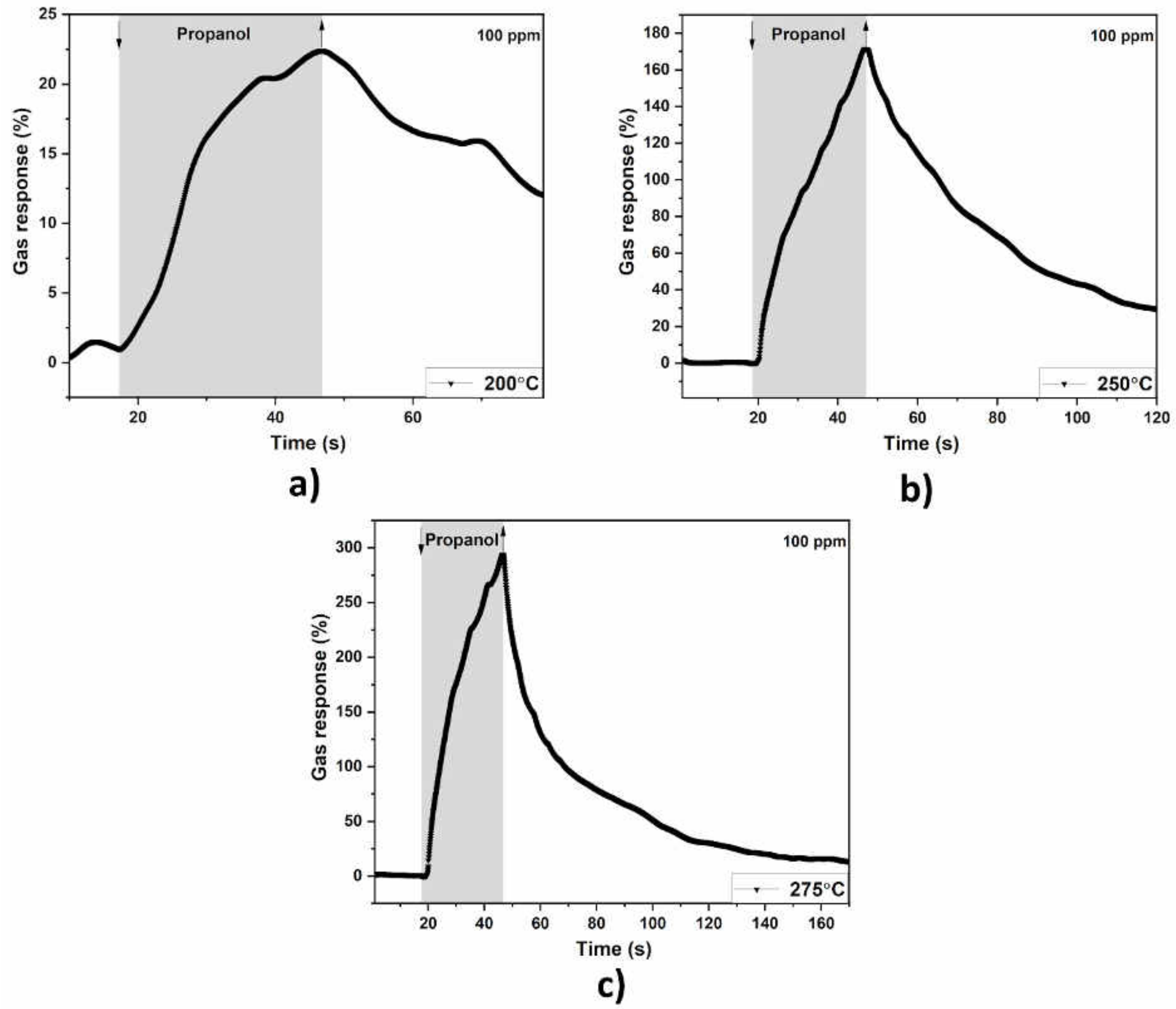

Figure 6. The dynamic response to propanol 100ppm at different operating temperatures: a) 200 °C, a) 250 °C, a) 275 °C.

Figure 7 shows the response of the nanostructures at the 300 °C operating temperature of different concentrations of propanol (1 ppm, 5 ppm, 10 ppm, 50 ppm, 100 ppm, 500 ppm, 1000 ppm). Thus, at a concentration of 1 ppm, the response time is approximately 18.71 s, and the recovery time approximately 38.86 s. At 5 ppm the response time is about 15.2 s and the recovery time is about 40 s. At 10 ppm the response time is approximately 21.55 s and the recovery time approximately 37.9 s. At the concentration of 50 ppm the response time is approximately 20.31 s and the recovery time approximately 42.78 s. At 100 ppm the response time is about 19.1 seconds and the recovery time about 57.2 s. At 500 ppm the response time is approximately 14.79 seconds and the recovery time approximately 64.45 s. At 1000 ppm the response time is approximately 19.99 s and the recovery time approximately 77.94 s. In Figure 7 can be seen that at concentrations higher than 500 and 1000 ppm the response value S of the sensor enters saturation. There is also a significant increase from 50 ppm to 500 ppm in the value of the S response.

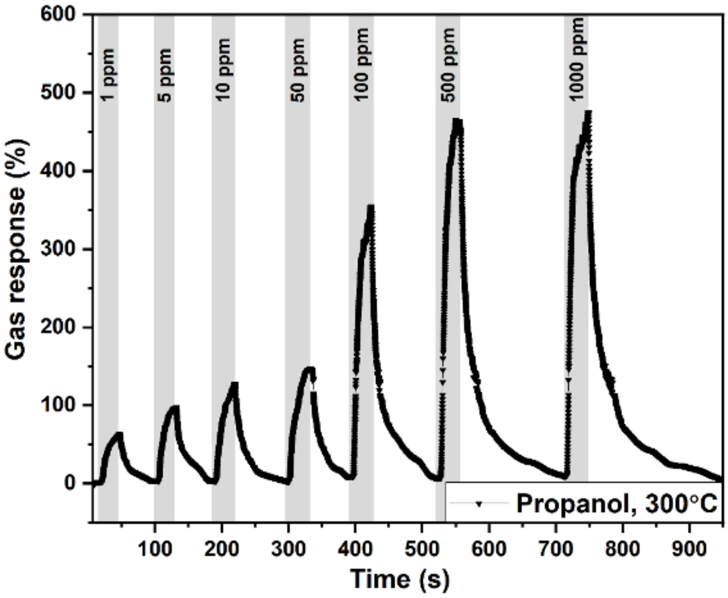

Figure 7. The dynamic response to propanol at 300 °C at different concentrations.

Like the previous figure, Figure 8 represents the response of nanostructures at a temperature of 300°C, but to acetone with concentrations of 1 ppm, 5 ppm, 10 ppm, 50 ppm, 100 ppm, 500 ppm, 1000 ppm.

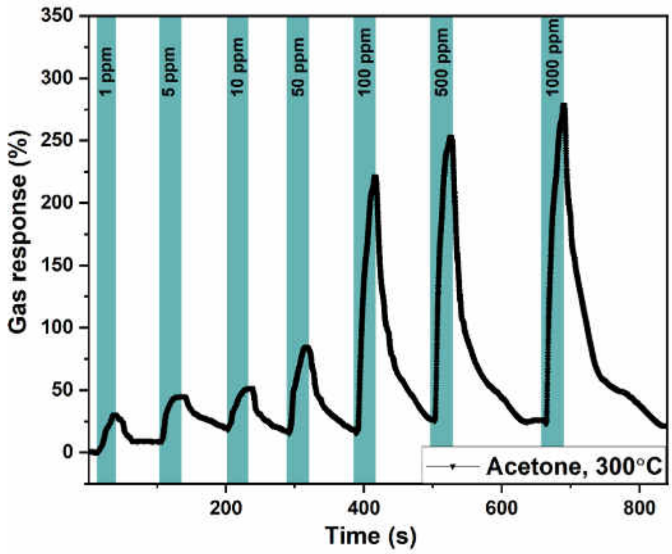

Figure 8. The dynamic response to acetone at 300 °C at different concentrations.

Likewise, in this case, the response and recovery times were determined, where it was observed that in the case of the response time, the best result at 50 ppm was 13.2 s, and in the case of the recovery time at 1 ppm, it was 24.47 s. It can also be observed that at higher concentrations of 500 ppm and 1000 ppm the nanostructures enter saturation, having an insignificant increase in the response.

4. Conclusions

The research conducted on CuO/Cu_2O functionalized with AgPt nanostructures for gas sensing applications provides significant insight into their potential utility in environmental monitoring and pollution prevention. Through careful characterization using SEM, XRD, and Raman spectroscopy, the morphology and structure of the nanostructures have been elucidated, providing a fundamental understanding of their functionality. The deposition of noble metals such as silver and platinum, as well as polymer layers, has been shown to improve sensor properties, including sensitivity and selectivity.

The gas sensing properties of the nanostructures show remarkable sensitivity to various gases such as propanol, acetone, hydrogen and ammonia, especially at elevated temperatures. In addition, the observed trends in response and recovery times underscore the importance of operating temperature in optimizing sensor performance. The saturation effects observed at higher concentrations of certain gases further highlight the need for nuanced calibration and sensitivity adjustments in practical applications.

Overall, this research contributes to the advancement of gas sensing technology and offers promising avenues for the development of efficient and reliable monitoring systems in industries susceptible to gas emissions. By harnessing the capabilities of $CuO/Cu_2O/AgPt$ nanostructures, we can potentially reduce environmental pollution and protect human health. Future studies could delve deeper into optimization strategies and real-world deployment scenarios to further validate the efficacy of these nanostructures in practical environmental monitoring contexts.

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Conflicts of Interest: The authors declare no conflict of interest.

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