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Ni-DOPED CuO SENSORS WITH CONTROLLED SELECTIVITY AT HIGH OPERATING TEMPERATURES FOR HYDROGEN DETECTION

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Abstract. Gas sensors are of major importance in today's industrial, chemical, agricultural, energy and household fields, and their development for general consumer use is an area of growing interest. This study explores the development and hydrogen sensing performance of CuO nanostructures synthesized via a cost-effective chemical solution method. The nanostructures, composed of copper oxide granules uniformly coated with nickel nanoparticles, were deposited on a glass substrate and thermally treated using rapid thermal annealing (RTA) to minimize defects. The resulting sensors exhibited high hydrogen sensitivity, with responses of 60-70% at elevated temperatures of 300 °C and 350 °C. The uniform deposition of Ni on CuO played a critical role in enhancing both sensitivity and selectivity towards hydrogen gas, while minimizing interference from other gases such as acetone, methane, and ammonia. The sensor demonstrated rapid response and recovery times, further confirming its potential for efficient hydrogen gas detection. These findings suggest that CuO nanostructures offer a promising, cost-effective solution for hydrogen gas sensing applications, particularly in safety-critical environments where hydrogen leaks need to be rapidly detected.

Keywords: nanostructures, doped, sensor, hydrogen.

Rezumat. Senzorii de gaz sunt de o importanță majoră în domeniile industrial, chimic, agricol, energetic și casnic de astăzi, iar dezvoltarea lor pentru uzul general al consumatorilor este un domeniu de interes crescând. Acest studiu explorează dezvoltarea și performanța de detectare a hidrogenului cu ajutorul nanostructurilor de CuO sintetizate printr-o metodă de soluție chimică rentabilă. Nanostructurile, compuse din granule de oxid de cupru acoperite

uniform cu nanoparticule de nichel, au fost depuse pe un substrat de sticlă și tratate termic post-depunere folosind tratarea termică rapidă (RTA) pentru a reduce defectele cristalului. Senzorii rezultați au prezentat o sensibilitate ridicată la hidrogenul gazos, cu răspunsuri de 60-70% la temperaturi relativ ridicate de 300 °C și 350 °C. Depunerea uniformă de Ni pe CuO a jucat un rol esențial în creșterea atât a sensibilității, cât și a selectivității față de hidrogenul gazos, minimizând în același timp interferențele din partea altor gaze, cum ar fi acetona, metanul și amoniacul. Senzorul a demonstrat, de asemenea, timpi de răspuns și recuperare rapizi, confirmând în continuare potențialul său pentru detectarea eficientă a hidrogenului gazos. Aceste cercetări sugerează că nanostructurile de CuO dopate cu impurități oferă o soluție promițătoare și rentabilă pentru aplicațiile de detectare a hidrogenului, în special în medii critice pentru siguranță, unde scurgerile de gaz trebuie detectate rapid.

Cuvinte cheie: *nanostructuri, dopat, senzor, hidrogen.*

1. Introduction

According to the Global Hydrogen Review 2023, there is a global growth in the use of this gas, concentrated in traditional uses but also in the chemical field, being produced largely from unburned fossil fuels [1]. Hydrogen is considered to be one of the green gases of the 21st century due to its diverse sources of production but also due to its conductivity and high calorific value which makes it a good substitute for fossil fuels and reduction of CO₂, widely used today with negative effects on the environment [2]. With urbanization, increasing industrial production and the amount of CO₂ emitted, agricultural land as well as its quality is continuously decreasing. An important factor that influences the quantity and quality of produce is plant disease. For example, hydrogen enriched water is used as a chemical-free and safe method of plant treatment [3,4].

Although hydrogen has diverse applications in various fields [5], it holds the potential to be used as a renewable green energy source and can positively impact agricultural production. However, it is an odorless, colorless gas and is considered one of the most explosive gases. In the context of the widespread development of hydrogen utilization, methods for stationary and portable hydrogen storage are being developed. The realizability of the stationary hydrogen storage method is somewhat simpler compared to the portable storage method, due to the gravimetric and volumetric densities that need to be taken into account during storage [6]. For this reason, it is crucial to have devices and systems that can quickly and efficiently detect small quantities of hydrogen leaks in order to prevent explosions in areas where hydrogen is used. Equally important is that these systems are accessible to the global market, that is why cost-effective ways of obtaining gas sensors are being sought. One of the cost-effective methods for obtaining gas sensors, including those for hydrogen detection, is the sensitization of nanostructures based on semiconducting metal oxides from chemical solutions with different metal ions [7,8].

Gas sensors play a crucial role in modern technology due to their ability to detect, monitor, and quantify the presence of hazardous, flammable, or environmentally impactful gases in real-time. Their importance spans across numerous sectors including environmental monitoring, industrial safety, energy systems, agriculture, healthcare, and domestic applications making them an essential component in efforts to protect both human health and infrastructure. One of the most pressing reasons for the deployment of gas sensors is safety. Many gases, such as hydrogen (H₂), carbon monoxide (CO), methane (CH₄), and ammonia (NH₃), are either toxic, highly flammable, or both [9]. Because these gases are often

colorless and odorless, their undetected release can result in life-threatening explosions, poisoning, or environmental disasters. For instance, hydrogen, while being promoted as a clean energy source, is highly explosive even at low concentrations, necessitating precise and rapid leak detection to prevent accidents. In the environmental domain, gas sensors are instrumental in monitoring greenhouse gases (e.g., CO₂, NO₂) and pollutants, enabling governments and industries to comply with regulations, minimize emissions, and combat climate change. They are also used in agriculture to track gases like ethylene (C₂H₄), which influences plant growth and ripening, or to detect the release of gases that indicate soil contamination or plant disease. Gas sensors are also critical in the medical field, where they are used in breath analysis for non-invasive diagnostics, such as detecting acetone in diabetic patients or ammonia in those with liver dysfunction. Furthermore, as the world transitions toward renewable energy sources, particularly hydrogen, the need for efficient, selective, and cost-effective gas sensors has become more urgent. These sensors ensure the safe storage, transportation, and utilization of hydrogen, supporting its integration into fuel cells, industrial processes, and smart energy grids.

Nickel-doped CuO nanostructures have been synthesized using a variety of methods, each offering specific advantages in terms of cost, control over morphology, and material quality. One widely used technique is the co-precipitation method, often employed with natural stabilizers or bio-extracts to enable green synthesis. For example, Etape et al. demonstrated a green synthesis route using carambola fruit juice as a bio-reducing agent for the preparation of spherical Ni-doped CuO nanoparticles, yielding well-defined and stable nanostructures with tunable optical properties [10]. Similarly, Ibrahim and Alamry synthesized Ni-CuO nanoparticles using Arabic gum as a biopolymer template, which provided effective dispersion and prevented agglomeration during synthesis [11]. Another common method is solution combustion synthesis, known for producing highly crystalline nanoparticles rapidly and at low cost. This method is effective for achieving uniform Ni incorporation into the CuO lattice and for scalability in sensor fabrication. Additionally, sol-gel methods and hydrothermal/solvothermal synthesis are employed when better control over particle size, crystallinity, and dopant concentration is required. For thin-film applications, spray pyrolysis and chemical bath deposition (CBD) are also reported for CuO:Ni coatings, especially when substrate uniformity is needed.

In this work, nanostructures based on CuO:Ni metal oxide semiconductors are presented which have hydrogen gas response of about 70-80% at elevated temperatures of 300 and 350 °C. The process of their fabrication is briefly described as well as how the hydrogen gas selectivity of these structures was determined. Nickel-doped copper oxide nanomaterials have shown significant promise for gas sensing applications due to their tunable electronic properties, enhanced surface activity, and improved structural stability [12,13]. Ni doping into the CuO matrix alters its crystal lattice and increases the number of active sites for gas adsorption, thus enhancing sensitivity and selectivity, particularly for toxic and flammable gases [14].

2. Materials and methods

In order to obtain the studied nanostructures based on CuO:Ni, the cost-effective chemical solution synthesis (SCS) method was used. A glass substrate after surface cleaning was used on which the CuO structures were deposited. On the obtained structures an ultrathin layer of Ni was deposited by sputtering followed by rapid thermal annealing at 600 °C for 2

min to form nanoparticles. Afterwards, nickel diffused into the nanostructure after thermal annealing at 600 °C for 2 h and the final structures were obtained. The obtained samples underwent thermal annealing with a 1 h ramp to minimize surface defects obtained during the sample making process. The duration of the thermal process was 2 hours at a temperature of 600 °C in air followed by natural cooling, such a process and mechanism has been previously reported in our work [14].

The sample measurement process involves a Keithley Series 2400 source meter (from Tektronix). This source-meter was chosen because it has a very high accuracy, being able to measure currents in the order of nano amperes, and apply voltages of hundreds of volts. The obtained data was recorded by professional software of our own production. The following formula was used to illustrate the percentage data [15]:

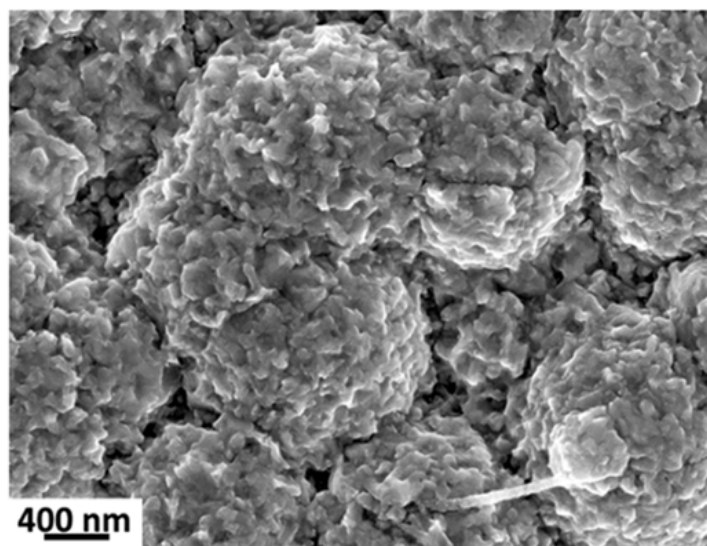
$$S = \frac{G_{gas} - G_{air}}{G_{air}} * 100\%, \quad (1)$$

where: S is the gas response of the sensor, G_{gas} is the electrical resistance when gas is applied to the sample and G_{air} is the electrical resistance when the gas is stopped.

3. Results and Discussion

3.1. Morphological characterization of CuO:Ni

The investigation of the surface morphology of CuO:Ni nanostructures was analyzed using a scanning electron microscope (SEM) with a 25K \times magnitude. SEM is a critical characterization technique that enables high-resolution imaging of surface topographies at the nanometer scale, making it ideal for examining the structural integrity and uniformity of nanomaterial coatings. The SEM image of the obtained surface of the CuO:Ni layer is shown in Figure 1. In Figure 1a was observed the nanostructures at a scale of 400 nm, and in Figure 1b was observed the same nanostructures at a scale of 2 μ m. A uniform deposition of Ni nanoparticle coated copper oxide granules on the glass substrate was observed tentatively. This enhanced surface area allows more hydrogen molecules to adsorb onto the sensor surface, improving its sensitivity by promoting efficient charge transfer between the gas molecules and the sensing material [16].



a)

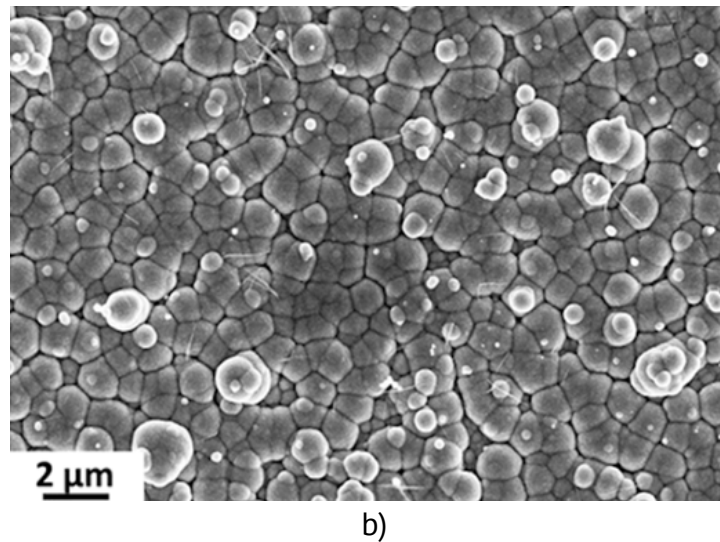


Figure 1. SEM images of CuO:Ni nanostructures at different scales:
a) – 400 nm; b) – 2 μm .

3.2. Measurements of sensor structures

The ampere-voltage (I-V) characteristics of gas sensors are essential for understanding how they operate under different conditions, particularly temperature. Figure 2 shows the I-V characteristics of sensor elements at different operating temperatures.

Gas sensors, especially those based on semiconducting oxide materials (like CuO, ZnO, etc.), exhibit changes in their electrical conductivity based on the surrounding temperature and gas adsorption for gas detection. As temperature increases or decreases, the energy levels of electrons and holes in the material change, affecting how easily current flows through the sensor. I-V characteristics measured at different temperatures of developed sensor help in mapping this behavior [17].

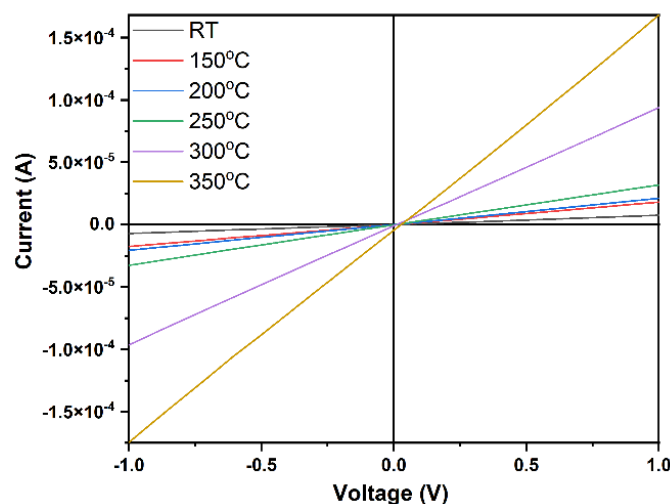


Figure 2. I-V characteristics of nanostructures at different operating temperatures: room temperature (RT), 150 °C, 200 °C, 250 °C, 300 °C and 350 °C, respectively.

3.3. Sensing properties of CuO:Ni

Figure 3 shows the sensor signal of Ni-doped copper oxide nanostructures for the tested gases, namely acetone, methane, hydrogen, ammonia, 2-propanol, n-butanol, ethanol, carbon dioxide at a concentration of 100 ppm for operating temperatures of 22 °C, 150 °C,

200 °C, 250 °C, 300 °C and 350 °C. The best sensitivity for hydrogen gas is observed at approximately 60% at operating temperatures of 300 °C and 350 °C. At 350 °C the same response to hydrogen gas as for the operating temperature of 300 °C is observed and there is a lack of gas response to other species tested in our experiments, which demonstrates the saturation of the nanostructures and a considerable increase in selectivity [18].

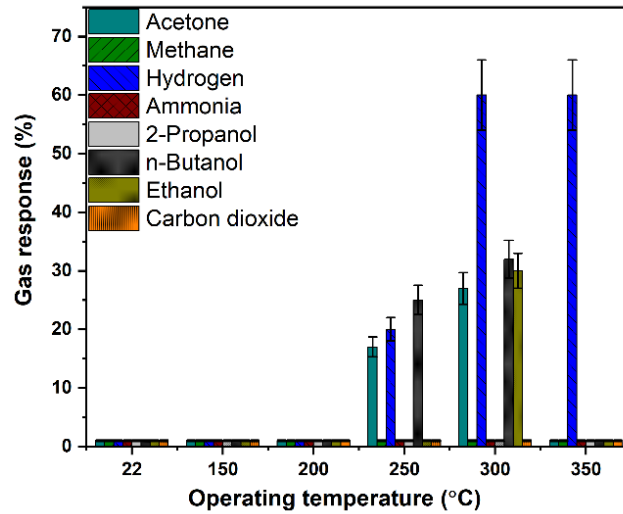


Figure 3. The response of CuO:Ni nanostructures to the investigated gases: acetone, methane, hydrogen, ammonia, 2-propanol, n-butanol, ethanol, carbon dioxide with concentration of 100 ppm for the operating temperatures of 22 °C, 150 °C, 200 °C, 250 °C, 300 °C and 350 °C, respectively.

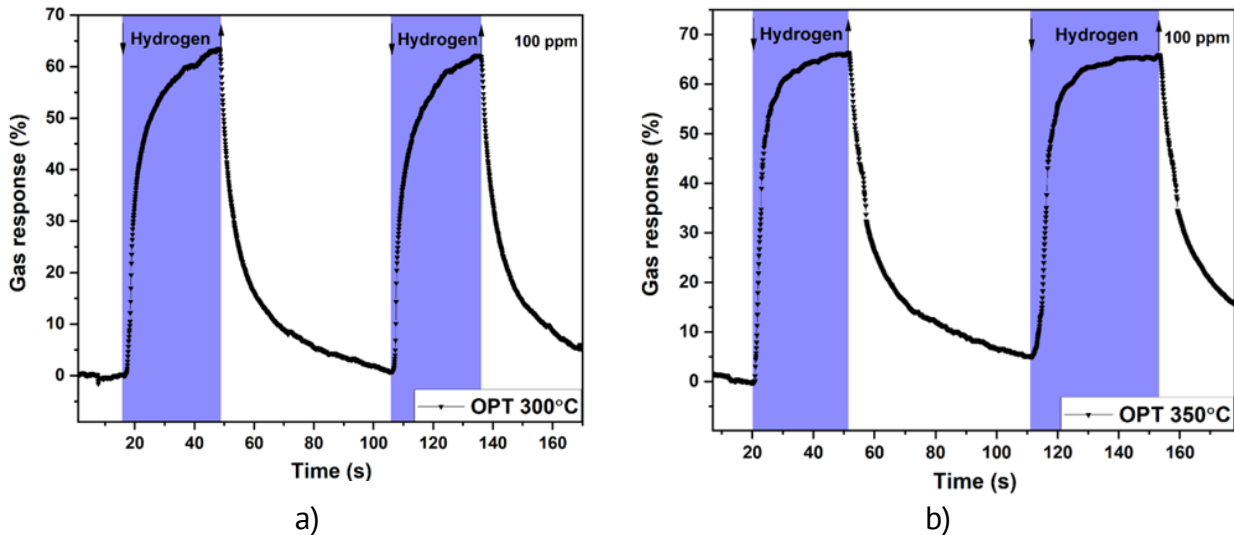


Figure 4. Dynamic response of CuO:Ni nanostructures to H₂ gas at 100 ppm concentration for operating temperatures: a) 300 °C nm; b) 2 μm of 350 °C.

Figure 4 shows the dynamic response of Ni-doped copper oxide nanostructures at operating temperatures of 300 °C (Figure 4a) and 350 °C (Figure 4b) by applying 2 pulses for 30 s each to investigate their repeatability at hydrogen gas concentration of 100 ppm. For both operating temperatures a sensor response of approximately 60% was obtained. The response and recovery times were determined. The response time represents the time in which the response of sensor S increases from 10% to 90% and is determined from the data obtained, while the recovery time is the time in which the response of S decreases from 90%

to 10% and is also determined from the data obtained. At 300°C the response time was about 10.5 s and the recovery time was approximately 29.3 s. At 350°C, the response time was 5.71 s with a recovery time of 51 s.

4. Conclusions

This study presents the successful development and characterization of Ni-doped CuO nanostructures for hydrogen gas sensing applications, emphasizing both scientific advancement and practical relevance. Utilizing a low-cost chemical solution synthesis method followed by controlled rapid thermal annealing at 600 °C, the fabricated nanostructures exhibited uniform surface morphology and enhanced sensing characteristics. Scanning Electron Microscopy confirmed a well-distributed Ni coating on CuO nanocrystallites, which contributes significantly to increasing the effective surface area for gas interaction. Electrical and sensor measurements conducted across a range of operating temperatures revealed a strong and selective response to hydrogen gas, particularly at 300 °C and 350 °C, with a sensitivity range of 60–70%. At these elevated temperatures, the sensors demonstrated minimal interference from other gases such as methane, acetone, ethanol, and ammonia, indicating excellent selectivity and saturation behavior. Additionally, the response and recovery times were found to be favorable, with response times as low as 5.7 seconds, suggesting fast and repeatable detection capabilities. The enhanced performance can be attributed to the presence of Ni dopants, which not only modify the electronic band structure and surface chemistry of CuO nanocrystallites, but also promote catalytic activity and charge carrier mobility - key parameters in achieving high-performance sensing. These findings validate the effectiveness of transition metal doping in tailoring semiconductor oxides performances for advanced sensor applications. Beyond the laboratory, the implications of this work are significant. As hydrogen becomes central to clean energy strategies worldwide, especially in transportation, industry, and agriculture, the need for affordable, scalable, and sensitive hydrogen sensors becomes increasingly vital. Ni-doped CuO structures represent a compelling solution due to their material abundance, fabrication simplicity, and excellent gas sensing properties. Looking ahead, future work should investigate long-term stability, humidity resistance, and real-world deployment in dynamic environments such as hydrogen fuel stations, pipelines, biomedical, and agricultural facilities. Moreover, the integration of these sensors into portable electronic platforms or IoT-based detection systems could greatly expand their usability and impact. This research not only advances our understanding of Ni-doped CuO nanostructures, but also contributes to the development of practical, low-cost gas sensors capable of supporting the global transition toward safer and cleaner hydrogen energy infrastructure.

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

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