

Conductimetric Gas Sensors for Hydrogen Leakage Detection Based on Copper Phthalocyanine Decorated by Palladium Nanoparticles.

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Summary:

This study introduces the development of conductimetric gas sensors for hydrogen leakage detection, implementing copper phthalocyanine decorated with palladium nanoparticles as sensitive materials. These sensors are devoted to improve the performance of hydrogen sensors through focusing on a novel approach to enhance sensitivity and response time. The sensors also achieve a detection limit of 0.07% at ambient temperatures, demonstrating a significant breakthrough in hydrogen detection capabilities. These performances allow positioning them as a promising solution for industrial safety applications.

Keywords: Copper Phthalocyanine, Palladium Nanoparticles, Hydrogen Micro-sensors, Leakage Detection, Industrial Safety

Motivation and Objective

In the context of global warming, research on alternative energy sources distinct from fossil fuels is becoming essential. To this end, the use of hydrogen energy has emerged as a major priority in the current quest for clean and sustainable energy sources [1]. However, despite its many potential advantages, the deployment of hydrogen as an energy vector presents considerable challenges. Hydrogen, being a colorless and odorless gas, exhibits an explosiveness range between 4% and 75% in air. Coupled with its low minimum ignition energy of 0.017mJ, high heat of combustion (142 kJ/g), and significant burning velocity, along with an ignition temperature of 560°C, hydrogen's physical and chemical properties necessitate rigorous safety protocols [2]. Given these inherent risks, the development of highly sensitive and rapid-response hydrogen sensors is crucial, not only to protect against potential catastrophic explosions but also to support the efficient and secure integration of hydrogen into our energy systems. Thus, our research focuses on advancing microsensor technology that meets the metrological requirements for safer use of hydrogen, such as detecting low hydrogen concentrations with increased reliability and precision, low cost, low power consumption, and low sensitivity to environmental parameters (relative humidity, pressure, etc.) [3][4].

Sensor Elaboration and Test Protocol

Original conductimetric micro-sensors implementing Metallophthalocyanine decorated by metallic nanoparticles have been realized. Unsubstituted copper phthalocyanine has been chosen because of its nanostructured morphology associated to a high specific surface area and a low intrinsic conductivity leading to high gas adsorption capacity and high electronic conductivity modulation even by low gas concentrations. In order to favor sensitivity to hydrogen, palladium has been chosen as metallic nanoparticles because of its well-known catalytic power for hydrogen dissociation. The conductimetric transducer consist of platinum interdigitated electrodes (IDEs) screen printed on an alumina substrate. The substrate is also equipped, on the rear face, with a screen-printed platinum resistor that enables the temperature regulation of the structure. Initially, 100 nm of copper phthalocyanine is deposited on the IDEs through thermal evaporation. Subsequently, palladium nanoparticles are deposited on the copper phthalocyanine film through wet chemical deposition. This method allows for the creation of large adsorption sites facilitated by the copper phthalocyanine nano structuration, while the palladium nanoparticles contribute to enhanced selectivity and sensitivity towards hydrogen. To our knowledge, this is the first time that CuPc are decorated with PdNPs to ensure the building of

nanocomposites materials that enable such performances. The presence of the PdNPs and the nanostructuration of the CuPc allows to tune the conductivity while benefiting from large adsorption sites and catalytic effect of the NPs.

Results

Figure 1 represents the electrical resistance of Pd-decorated copper phthalocyanine at room temperature consecutively exposed to hydrogen concentration during 5 minutes then maintained under clean air during 15 minutes. Results highlight the high sensitivity of microsensors to H₂ in the [0.2%-1.2%] concentration range, with a high signal-noise ratio. The correlation between micro-sensor responses and H₂ concentration is manifest, with a good level of repeatability. The response and recovery times determined at room temperature are estimated to 2.5 minutes and 7 minutes, respectively.

Figure 2 represents the variation of sensor resistance measured during exposure steps versus H₂ concentration at room temperature. This calibration curve is extracted from results depicted in figure 1. Such sensors exhibit a linear calibration curve, a sensitivity close to 200Ω per percent as well as a very low hysteresis. Based on noise magnitude measured during sensor stabilization under clean air and sensitivity, the limit of detection has been estimated to 0.07% (700ppm) at ambient temperatures. This emphasizes the significant improvement by combining CuPc with nanoparticles for conductimetric sensors. While these results are promising, further investigation are required. The impact of nanoparticle density on sensing performances, the impact of the nature of phthalocyanine on response, the effect of temperature on sensing mechanisms, the cross-sensitivity of devices to water vapor and interfering gases must be investigated. These ongoing developments aim to ensure that the sensors meet the rigorous requirements for leak detection across various industrial applications. All these points will be discussed.

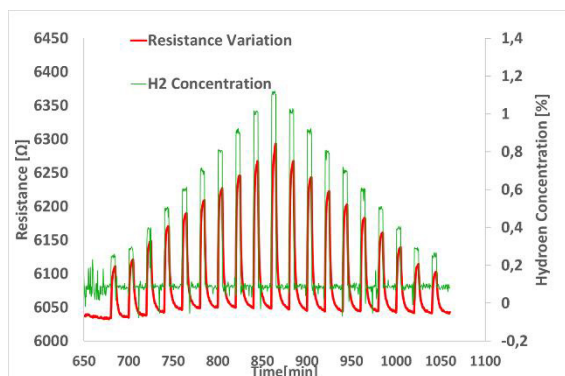


Fig. 1. Electrical resistance of Pd-decorated CuPc conductimetric sensor towards different concentration of Hydrogen at ambient temperature. Time of exposure and recovery steps was set to 5min and 15min respectively.

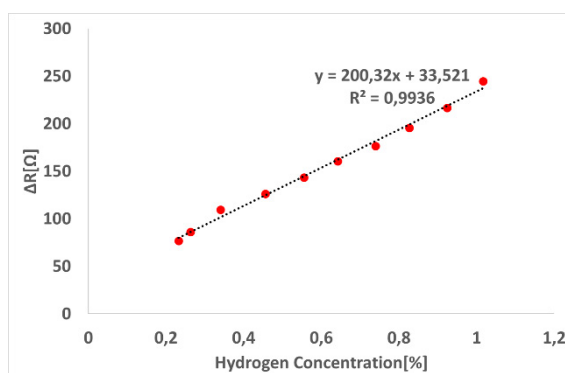


Fig. 2. Resistance variations of Pd-decorated CuPc conductimetric sensor versus H₂ concentration at room temperature. Datas are extracted from measurements depicted in figure 1.

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