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Abstract

Optimizing Polyaniline-Based Gas Sensors for Hydrogen Sulfide Detection: The Crucial Role of Solvent Choice †

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Abstract: Hydrogen sulfide (H_2S) gas poses a significant risk and thus demands continuous monitoring using reliable sensors. Chemiresistive sensors can serve this purpose, and the utilization of conducting polymeric materials, particularly polyaniline (PAni), has demonstrated significant potential. To fabricate chemiresistors based on PAni, the materials must be dispersed in an organic solvent like dimethylformamide (DMF), which has several hazardous properties. Fortunately, dimethyl sulfoxide (DMSO) is a safer alternative with similar properties to DMF, and may be used instead of DMF. In this study, we aim to compare the efficacy of DMF and DMSO solvents in fabricating PAni and metal chloride composite films for detecting H_2S gas.

Keywords: gas sensor; hydrogen sulfide; polyaniline; tin chloride; thin film; sensor development

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1. Introduction

Emitted from both natural and anthropogenic sources, H_2S gas is a dangerous substance even at sub-ppm levels. To monitor and control the risks associated with this gas in real time, researchers have been developing sensors with good properties and stability for decades [1]. Among the most commonly used H_2S sensors, the chemiresistive sensor stands out as the simplest transducer, measuring the resistance of sensitive material in contact with two electrodes to convert chemical fluctuations into an electrical signal. While metal oxides (MOx) are the predominant sensitive material used for gas detection, they suffer from low selectivity and high-temperature operation [2]. Conductive polymers such as PAni present a promising alternative to MOx [3]. PAni has controllable conductivity through redox and acid/base reactions, and has been used in various gas-sensing applications, especially in the detection of ammonia. Among the methods used to make PAni selective towards H_2S, adding metal chloride has shown a higher potential [4]. This work focuses on the fabrication of PAni and tin chloride composite films from dispersions in DMF and DMSO, with the aim of evaluating the impact of the solvent on their response to H_2S exposure at sub-ppm levels in order to replace the actual hazardous DMF with a safer substitute.

2. Materials and Methods

The active layer of the sensor consisted of two components: PAni emeraldine-base, obtained from Sigma-Aldrich (USA), and $SnCl_2$, obtained from Alfa Aesar (Karlsruhe, Germany). The solvents used were DMF from Sigma-Aldrich and DMSO from Acros Organics (Germany). The H_2S gas was obtained from Messer (10 ppm in N_2, Mitry-Compans, France). To facilitate a comparison between the two composite dispersions, we prepared them as follows: we mixed 50 mg of PAni and 50 mg of $SnCl_2$ in 10 mL of solvent (DMF or DMSO). The processing steps, including stirring speed, temperature, sonication parameters, and time, were carried out following the protocol described in [4]. Next, the

dispersions of PAni:$SnCl_2$ in DMF and DMSO were deposited on interdigitated electrodes using a drop-casting method, and the resulting films were dried in an oven at 90 °C under vacuum for 5 days.

To characterize the performances of the sensors, we placed them inside a Teflon exposure chamber at room temperature (~20 °C) monitored by a Sensirion SHT21 temperature and relative humidity sensor. Throughout the experiment, we maintained a flow rate of 4 L/min while controlling the H_2S concentration (ranging from 200 to 1000 ppb) and relative humidity (RH, ranging from 40 to 70%) using mass flow controllers from MKS Instruments (model 647C, Munich, Germany). We measured the concentration of H_2S inside the chamber and the variation in resistance of each sensor in real time using the H_2S Analyzer-Model T101 from TELEDYNE Envicontrol T series (USA) and the Data Acquisition/Switch Units Agilent 34970A, respectively.

3. Discussion

Drop-cast films of PAni-50%:$SnCl_2$-50% fabricated from a DMSO dispersion exhibited significantly higher electrical resistance, ranging from two to ten times higher than those prepared from a DMF dispersion. In tests conducted with these devices, the resistance of the films decreased when exposed to H_2S. This effect can be attributed to the reaction between H_2S and $SnCl_2$, which releases HCl, thereby doping and decreasing the resistance of PAni. The films deposited from DMSO dispersions showed similar relative responses to H_2S compared to those from DMF, with a significant improvement observed after three tests. This suggests that the DMSO dispersion-based sensors have comparable sensing capabilities and can exhibit improved performance over time. By the last test, the films prepared from DMSO dispersion had increased in resistance, and some of the samples were out of the resistance range of the Agilent 34970A. Although these results suggest that changing solvents from DMF to DMSO is feasible, further research is necessary to develop sensors with longer lifespans using our current experimental setup.

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