


Proceeding Paper

# An Inkjet-Printed Amperometric H<sub>2</sub>S Sensor for Environmental Applications <sup>†</sup>

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**Abstract:** Hydrogen sulfide (H<sub>2</sub>S) is a highly toxic chemical capable of causing severe health issues. Due to its environmental impact, it is critical to create effective methods for its monitoring. Inkjet printing technology has become an alternative for sensor fabrication because it is an economic, fast, and reproducible method for mass producing micro-electrodes. Herein, a miniaturized 25 mm<sup>2</sup> inkjet-printed amperometric sensor is presented. A gold electrode coupled with a silver track was modified with two inks: single-walled carbon nanotubes (SWCNTs) and a mixture of SCWCNTs and poly(vinyl alcohol) (PVA). Morphological and electrochemical properties were studied, as well as H<sub>2</sub>S sensor performance. This approach is a suitable option for environmental H<sub>2</sub>S tracking.

**Keywords:** electrochemical sensor; amperometric sensor; H<sub>2</sub>S sensor; single-walled carbon nanotubes



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## 1. Introduction

Environmental equilibrium is a hard-to-preserve resource, dangerously impacted by human heavy industrial activities [1,2]. It is naturally regulated through biogeochemical cycles. Among these, the sulfur cycle is of crucial importance, since it is vital for maintaining the composition of both the atmosphere and soils, as well as most living beings. Nonetheless, even more dangerous is an excess of highly toxic compounds such as water-soluble hydrogen sulfide (H<sub>2</sub>S) gas. This is a poisonous, inflammable, and corrosive chemical, hazardous to human health at concentrations as low as 20 ppm (1.1 µM) for prolonged exposure [3]. Even though it generally appears as a gas, it has labile hydrogens, meaning it coexists as different species in aqueous media. Hydrogen sulfide can appear as different species depending on the pH of its medium, being capable of losing both its protons and transitioning from a gas to ions. It has a pK<sub>a1</sub> of approximately 7 and a pK<sub>a2</sub> of about 13.5, meaning that HS<sup>−</sup> predominates between pH 7.5 and 13. Due to the dangerous nature of H<sub>2</sub>S and its frequent appearance in gas streams, a great need has recently arisen for many biotechnological processes to remove it [4], which require adequate systems for quick and easy tracking.

Nonetheless, many of these removal processes occur in aqueous media, requiring consideration of the environmental pH for adequate quantification. Thus, it is appropriate to incorporate a simultaneous pH measurement with the H<sub>2</sub>S tracking.

In recent years, printed electronics have steadily replaced more traditional electrode fabrication methods. Among these, inkjet printing has the main advantage of not requiring any mask preparation, greatly reducing the time and cost of device fabrication.

Moreover, its low drop volume and precision, added to its capacity for printing metal-based inks, allow for the fabrication of highly reproducible micro-electrodes.

For biotechnological applications, microsensors can be printed on different substrates and their designs can be adapted to the shapes of bioreactors with little cost impact [5]. Therefore, inkjet printing technology is an interesting alternative for the development of a microsensors platform for H<sub>2</sub>S and pH measurements.

Moreover, electrochemical sensors have the advantages of high sensitivity, in situ application, and a broad range of applicable materials. However, H<sub>2</sub>S determination using electrochemical sensors has many design and implementation challenges to solve, such as the pH influence on measurements [6] and electrode passivation by accumulation of S<sup>0</sup> produced from H<sub>2</sub>S oxidation [7].

Among the authors who have developed H<sub>2</sub>S sensors, Yang et al. (2018) [8] fabricated a sensor using Nafion for H<sub>2</sub>S measurement in gaseous samples. This membrane was added to carbon fibers modified with platinum and rhodium nanoparticles. The H<sub>2</sub>S was adsorbed on the platinum, releasing protons that crossed the Nafion membrane while electrons moved through an external circuit. The H<sub>2</sub>S concentration was proportional to the circulating charge. This sensor had a linear range from 2.9 µM to 5.9 mM, and the minimum detectable signal was 2.9 µM. Brown et al. (2019) [9] deposited a thin layer of S<sup>0</sup> on a glassy carbon electrode (GCE) and covered it with electro-polymers to avoid passivation of the electrode via accumulation of S<sup>0</sup>. The H<sub>2</sub>S was measured by constant potential amperometry (CPA), using a potential of 0.3 V vs. Ag/AgCl. This sensor exhibited a high degree of selectivity and a linear range between 0 µM and 15 µM, with lowest and highest detection limits of (9 ± 6) nM and (79 ± 51) nM, respectively.

Furthermore, new carbon materials with excellent electronic properties have become suitable options for electrode development. As an example, Lawrence et al. (2004) [10] modified a GCE with carbon nanotubes (CNTs) deposited on the surface by drop casting a solution of CNTs in dimethylformamide (DMF). The main advantage found was the catalytic capacity that decreased the oxidation potential from 0.4 V to −0.3 V (vs. Ag/AgCl). This allowed amperometric measurements at 0.1 V (vs. Ag/AgCl) in a range between 1.25 µM and 112.5 µM, with a detection limit of 0.3 µM. Li et al. (2017) [6] used cobalt to magnetically attach MoS<sub>2</sub> monolayer sheets to CNTs, which were deposited on glassy carbon electrodes using a Nafion membrane as an adhesive. Analysis was performed by amperometry obtaining a linear range of application from 0.05 µM to 0.6 µM, with a detection limit of 7.6 nM.

Despite authors applying carbon materials for H<sub>2</sub>S sensor development, there are no reports of the use of SWCNTs ink for an inkjet-printed H<sub>2</sub>S sensor. Moreover, several studies have reported poly(vinyl alcohol) (PVA) addition to conductive materials to improve its mechanical and adhesive properties [11–13].

In this study, the fabrication of a H<sub>2</sub>S amperometric microsensor has been studied using both a SWCNTs ink and a SWCNTs–PVA ink for Au electrode modification. Morphological and electrochemical characterizations were carried out for electrode performance analysis.

## 2. Materials and Methods

### 2.1. Inkjet-Printed H<sub>2</sub>S Sensor Fabrication

The printing process for the electrode was performed using Ag NPs ink (SI-J20x Nanosilver Inkjet Printing Ink from Agfa, Mortsel, Belgium), Au NPs ink (Drycure Au-JB 1010B from C-ink, Japan), and SWCNTs ink (Carbon nanotube, single-walled, conductive aqueous ink, SWCNT 1.00 mg/mL from Sigma-Aldrich, Spain). To passivate the electrode, SU8 ink (XP PriElex SU-8 1.0 Inkjettable Dielectric from Kayaku, Westborough, MA, USA) was used. All inks were printed over polyethylene terephthalate (PET) sheets (Q65HA,

Du Pont Teijin Films, Dumfries, UK), using a Dimatix printer (DMP-2831 from FUJIFILM Dimatix, Santa Clara, CA, USA). The SWCNTs–PVA composite ink was prepared by mixing a commercial SWCNTs ink, and a 5 wt.% PVA solution, both acquired from Sigma-Aldrich. For SWCNTs ink and SWCNTs–PVA ink deposition, the drop casting technique was performed on a thermal plate. The applied temperature was a studied parameter. The final electrode dimensions were a 1 mm diameter gold disk with a total length of 26 mm and surface of 25 mm<sup>2</sup>, and an approximately 2 mm diameter SWCNTs disk.

## 2.2. Sensor Characterization

Morphological characterization of the electrodes was carried out via optical microscopy. Images were obtained with a digital microscope (USB microscope AM4815ZTL from DinoLite, Alemere, The Netherlands).

Electrochemical characterization was performed with a PalmSens potentiostat–galvanostat (PalmSens4 from PalmSens, The Netherlands). A three-electrode configuration was used for the electrochemical cell. An Ag/AgCl (1 M KCl) reference electrode (reference electrode with Ag/AgCl in aqueous KCl from ItalSens, PalmSens, Houten, The Netherlands) and a platinum wire counter electrode (counter electrode made of platinum wire from ItalSens, PalmSens, Houten, The Netherlands) were used. The fabricated electrode functioned as the working electrode. Cyclic voltammetry (CV) measurements were carried out using the redox pair  $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$  (0.01 M) at 0.01 V/s from  $-0.1$  V to 0.5 V. Intensity peaks ( $I_p$ ) resulting from redox reactions allowed for electrochemical characterization.

To study the effect of deposition temperature in the SWCNTs–PVA ink, ten layers of PVA were drop casted over a gold inkjet-printed electrode at 90 °C and at room temperature. Intensity-peak values were obtained.

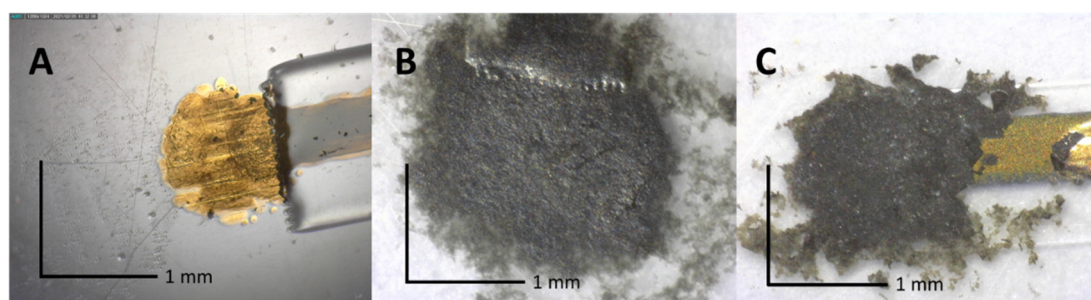
For H<sub>2</sub>S calibration, a stock H<sub>2</sub>S solution (0.1 M) was prepared by dissolving NaS·9H<sub>2</sub>O and NaOH (both from Sigma-Aldrich, Spain) in deionized water (Milli-Q from Millipore Corporation, Burlington, MA, USA). Standardization was carried out according to standard methods [14]. The stock solution was diluted in phosphate-buffered saline solution (PBS) (from Sigma-Aldrich, Madrid, Spain) to obtain a 0.02 M H<sub>2</sub>S solution.

## 3. Results and Discussion

### 3.1. Inkjet-Printed H<sub>2</sub>S Miniaturized Sensor Fabrication

Inkjet-printed micro-electrodes were fabricated by first printing the Ag tracks and pads, drying at 100 °C in an oven, then printing the Au surfaces and connecting tracks, which were later dried at 120 °C. Subsequently, inks were sintered at 150 °C for 60 min to improve their conductivity. Finally, micro-electrodes were passivated by printing an SU8 layer over the tracks, preventing the short circuiting of the electrodes.

Both SWCNTs and SWCNTs–PVA inks were drop casted on a gold electrode, covering it completely (Figure 1). Both inks showed good adhesion to gold, allowing morphological and electrochemical characterization of the microsensors.

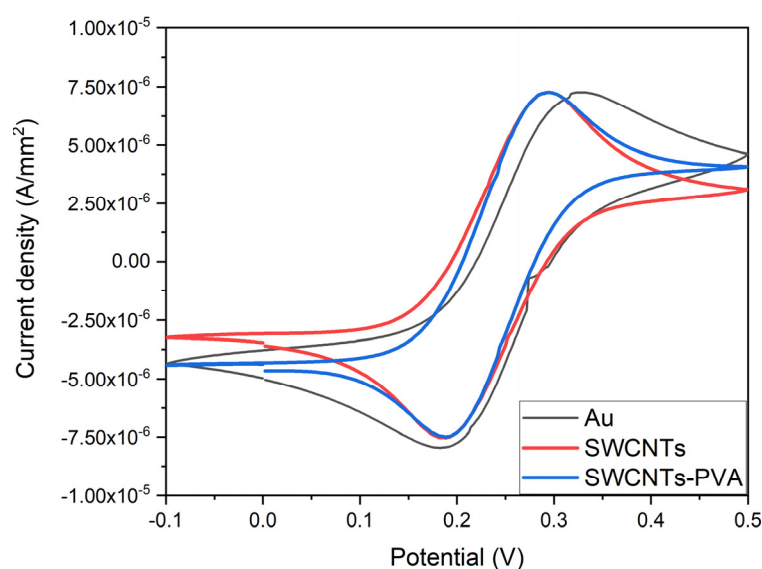


**Figure 1.** Photographs of (A) inkjet-printed Au electrode, (B) SWCNTs drop casted over Au electrode, and (C) drop-casted SWCNTs–PVA over Au electrode.

### 3.2. Microsensor Electrochemical Characterization

Cyclic voltammetry measurements of Au, SWCNTs, and SWCNTs–PVA electrodes were carried out. These allowed verification of whether the applied modifications yielded an electrode with properties of interest that could be used for an  $\text{H}_2\text{S}$  sensor. The main interest was in fabricating a sensor capable of oxidizing  $\text{H}_2\text{S}$  at low voltages and with a high tolerance for sulfur poisoning since it is well known that  $\text{S}^0$  is highly insoluble in water [7] and has a high affinity for Au atoms. Thus, the electrode would gradually deteriorate by accumulating non-conductive layers of sulfur atoms.

Modified electrodes presented a similar current density and a smaller potential gap than bare Au electrodes (Figure 2). The smaller peak separation, specifically due to reducing the potential necessary for ferrocyanide oxidation, meant that SWCNTs and SWCNTs–PVA are both favorable for use as an  $\text{H}_2\text{S}$  sensor, with the added benefit of lowered rates of sulfur deposition on their surfaces due to the less-favorable S–C interaction compared with S–Au.



**Figure 2.** Cyclic voltammetry of Au, SWCNTs, and SWCNTs–PVA electrodes in hexacyanoferrate/hexacyanoferrate (0.01 M).

### 3.3. PVA Deposition Temperature Study

The effect of PVA deposition temperature was studied through the drop casting of 10 layers of PVA on an Au inkjet-printed electrode at 90 °C and at room temperature. Cyclic voltammetry was performed, and current-peak ( $I_p$ ) values were obtained. The results showed that at room temperature, PVA deposition had a smaller passivation effect than at 90 °C, in which case the electrode's current values dropped significantly (Table 1).

**Table 1.** Effect of polymer deposition temperature on Au inkjet-printed electrodes.

Temperature	$I_p$	$I_p$	% $I_p$ Reduction
	Au Electrode ( $\mu\text{A}$ )	Au Electrode + PVA ( $\mu\text{A}$ )	
25 °C	8.12	7.46	8.1
90 °C	3.92	$1.22 \cdot 10^{-5}$	100.0

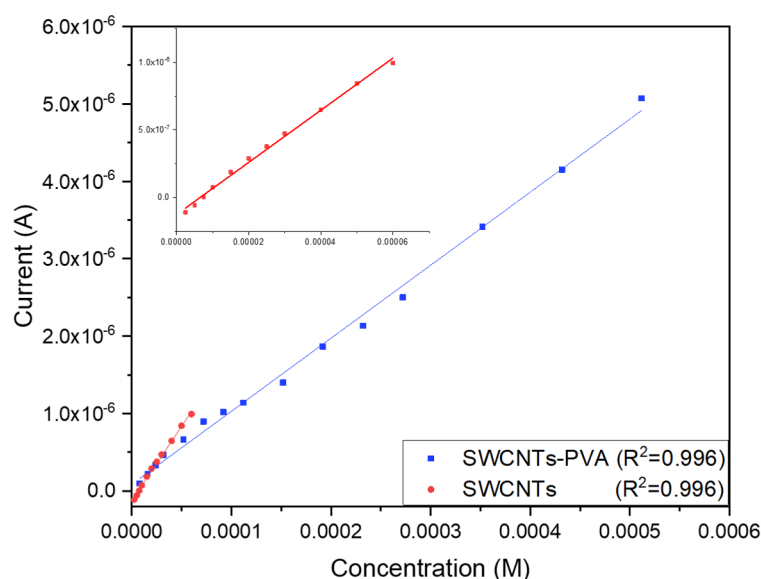
### 3.4. Microsensor Calibration and Analytical Response

Calibration of SWCNTs and SWCNTs–PVA microsensors was performed by adding different volumes of  $\text{H}_2\text{S}$  standard to a PBS solution, measuring a concentration range

between 0 and 600  $\mu\text{M}$ . The chronoamperometry method was used for  $\text{H}_2\text{S}$  oxidation (Equation (1)) at a polarization voltage of 50 mV, and the resulting current was measured.



Calibrations were performed for both SWCNTs and SWCNTs-PVA under the same conditions (Figure 3). The results showed good correlation between the measured current and the analyte concentration, with a similar slope for both sensors but different linear ranges.



**Figure 3.** Calibrations of two different sensors made of Au electrodes modified with SWCNTs and SWCNTs-PVA by drop casting. Inset shows a reduced range of  $\text{H}_2\text{S}$  concentration for the SWCNTs sensor calibration.

While the SWCNTs sensor showed a higher sensitivity ( $19.3 \pm 0.4 \text{ mA/M}$ ) compared to SWCNTs-PVA ( $9.4 \pm 0.2 \text{ mA/M}$ ), it also had a reduced working range. SWCNTs can measure  $\text{H}_2\text{S}$  concentrations from 8  $\mu\text{M}$  to 60  $\mu\text{M}$ , with a limit of detection (LD) of 4.3  $\mu\text{M}$ . On the other hand, SWCNTs-PVA is capable of measuring from 52  $\mu\text{M}$  to 512  $\mu\text{M}$ , with a LD of 34  $\mu\text{M}$ .

#### 4. Conclusions

We demonstrated a novel miniaturized inkjet-printed amperometric  $\text{H}_2\text{S}$  sensor fabricated by modification of a gold electrode with SWCNTs ink. The results showed that the addition of a stabilizing polymer allowed for an increased range of  $\text{H}_2\text{S}$  concentration measurements. Due to the low versatility of the SWCNTs sensor, the addition of PVA was considered, to improve the  $\text{H}_2\text{S}$  sensor performance. However, it was necessary to adapt the fabrication temperature conditions to avoid electrode passivation, limiting the SWCNTs-PVA ink-deposition temperature to 25  $^\circ\text{C}$ . This sensor offers an approach for  $\text{H}_2\text{S}$  tracking with environmental and biotechnological applications.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/CSAC2021-10462/s1>.

**Author Contributions:** Conceptualization, M.B. and G.G.; methodology, F.P.; validation, M.B. and X.G.; formal analysis, F.P. and R.C.; investigation, F.P. and R.C.; resources, G.G. and M.B.; data curation, F.P. and R.C.; writing—original draft preparation, F.P. and R.C.; writing—review and editing, M.B., G.G., and X.G.; visualization, G.G. and M.B.; supervision, M.B., G.G., and X.G.; project administration, M.B.; funding acquisition, M.B. and G.G. All authors have read and agreed to the published version of the manuscript.



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

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