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An Inkjet-Printed Amperometric H_2S Sensor for Environmental Applications †

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Abstract: Hydrogen Sulfide (H_2S) 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^2 inkjet-printed amperometric sensor is presented. A gold electrode, coupled with a silver track, is modified with two inks: Single-Walled Carbon Nanotubes (SWCNTs), and a mixture of SCWCNTs with Poly(VinylAlcohol) (PVA). Morphological and electrochemical properties were studied, as well as H_2S sensor performance. This approach is a suitable option for environmental H_2S tracking.

Keywords: electrochemical sensor; amperometric sensor; H_2S sensor; single-walled carbon nanotubes

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1. Introduction

Environmental equilibrium is a hard to preserve resource, dangerously impacted by human's heavy industrial activities [1,2]. It is naturally regulated through the biogeochemical cycles. Among these, sulfur cycle is of crucial importance, since it is vital for maintaining the composition of both atmosphere and soils, as well as most living beings. Nonetheless, of even more danger is the excess of highly toxic compounds, such is the water-soluble hydrogen sulfide (H_2S) gas. It is a venomous, 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 gas to ion. It has a pka_1 of approximately 7 and a pka_2 of about 13.5, meaning that HS^- predominates between pH 7.5 and 13. Due to H_2S' dangerous nature, and its frequent appearance in gas streams, a large need for many biotechnological processes to remove it has recently arisen [4], which require adequate systems for quick and easy tracking.

Nonetheless, many of these removal processes happen in aqueous media, which requires considering its environment pH for adequate quantification. Thus, it is suitable to incorporate a pH measurement simultaneous to the H_2S 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 the capacity of printing metal-based inks, allow for the fabrication of highly reproducible microelectrodes.

Regarding biotechnological applications, microsensors can be printed on different substrates and their designs can be adapted to the shape of bioreactors with little cost impact [5]. Therefore, inkjet printing technology is an interesting alternative for the development of a microsensors platform for H_2S and pH measurements.

Moreover, electrochemical sensors have the advantages of high sensitivity, in situ application and a broad range of applicable materials. However, H_2S determination using electrochemical sensors has many design and implementation challenges to solve as pH influence in measurements [6] and electrode passivation by accumulation of S^0 produced from H_2S oxidation [7].

Among the authors who have developed H_2S sensors, Yang et al. (2018) [8], fabricated a sensor using Nafion for H_2S measurement in gaseous samples. This membrane was added to platinum and rhodium nanoparticles modified carbon fibers. The H_2S was adsorbed on platinum releasing protons that went across Nafion membrane while electrons moved through an external circuit. The H_2S concentration was proportional to circulating charge. This sensor had a linear range from 2.9 μM to 5.9 mM and minimum detectable signal was 2.9 μM. Brown et al. (2019) [9] deposited a thin layer of S^0 on a glassy carbon electrode (GCE) and covered it with electropolymers to avoid passivation of the electrode by accumulation of S^0. The H_2S 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, a linear range between 0 μM and 15 μM, with a lowest and a 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 catalytic capacity that decreased 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_2 monolayer sheets to CNTs, which were deposited on glassy carbon electrodes using a Nafion membrane as 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 there being authors applying carbon materials for H_2S sensor development, there are no reports of SWCNTs ink usage for an inkjet-printed H_2S sensor. Moreover, several works reported Poly(VinylAlcohol) (PVA) addition to conductive materials to improve its mechanical and adhesive properties [11–13].

In this work the fabrication of a H_2S amperometric microsensor has been studied using both a SWCNTs ink and a SWCNTs-PVA ink for Au electrode modification. Morphological and electrochemical characterization were carried out for electrode performance analysis.

2. Materials and Methods

2.1. Inkjet-Printed H_2S Sensor Fabrication

The printing process of the electrode was performed using Ag NPs ink (SI-J20X Nanosilver Inkjet Printing Ink from Agfa, 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, USA) was used. All inks were printed

over a polyethylene teraphtalate (PET) sheets (Q65HA, Du Pont Teijin Films, USA) and using a Dimatix printer (DMP-2831 from FUJIFILM-Dimatix, USA). SWCNTs-PVA composite ink was prepared by mixing SWCNTs commercial ink, and a 5% wt. PVA solution, both acquired from Sigma-Aldrich. For SWCNTs ink and SWCNTs-PVA ink deposition, drop casting technique was performed on a thermal plate. Applied temperature was a studied parameter. Final electrode dimensions make for a 1 mm diameter gold disk, with a total length of 26 mm and surface of 25 mm^2, and an approximately 2 mm diameter SWCNTs disk.

2.2. Sensor Characterization

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

Electrochemical characterization was performed with a PalmSens potentiostat-galvanostat (PalmSens 4 from PalmSens, Netherlands). For the electrochemical cell a three-electrode configuration was used. An Ag/AgCl (1 M KCl) reference electrode (Reference electrode with an Ag/AgCl in aqueous KCl from ItalSens, PalmSens, Netherlands) and a platinum wire counter electrode (Counter electrode made of platinum wire from ItalSens, PalmSens, 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 (Ip), resulting from redox reactions, allowed for an electrochemical characterization.

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

For H_2S calibration a stock H_2S solution (0.1 M) was prepared dissolving $NaS{\cdot}9H_2O$ and NaOH (both form Sigma-Aldrich, Spain), in deionized water (Milli-Q from Millipore Corporation, USA). Standardization was carried out according to standard methods [14]. The stock solution was diluted in phosphate buffered saline solution (PBS) (from Sigma-Aldrich, Spain) to obtain a 0.02 M H_2S solution.

3. Results and Discussion

3.1. Inkjet Printing H_2S Miniaturized Sensor Fabrication

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

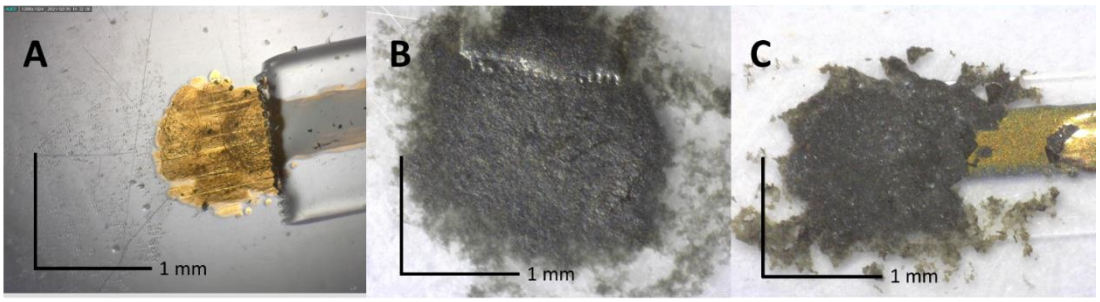

Figure 1. Photographs of **a**) inkjet-printed Au electrode, **b**) SWCNTs drop-casted over Au electrode, **c**) drop-casted SWCNTs-PVA over Au electrode.

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

3.2. Microsensor Electrochemical Characterization

Cyclic voltammetry measurements of Au, SWCNTs and SWCNTs-PVA electrodes were carried out. These allowed to verify if the applied modifications yielded an electrode with properties of interest that could be used for an H_2S sensors. The main interest was in fabricating a sensor capable of oxidizing H_2S at low voltages and with a high tolerance for sulfur poisoning since it is well-known that 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 similar current density and a smaller potential gap than Au bare electrodes (Figure 2). The smaller peak separation, specifically by reducing the potential necessary for ferrocyanide oxidation, meant that SWCNTs and SWCNTs-PVA are both favorable for an H_2S sensor, with the added benefit of lowered rates of sulfur deposition on their surfaces due to the less favorable interaction S-C against S-Au.

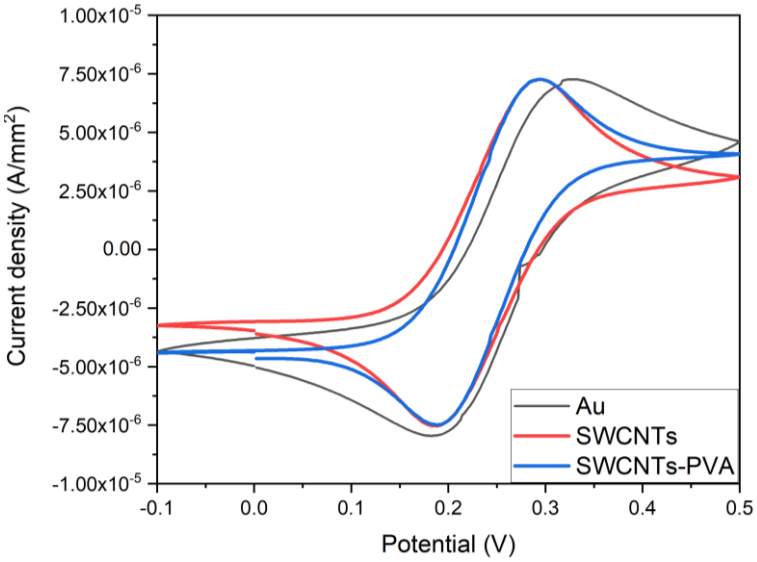

Figure 2. Cyclic voltammetry of Au, SWCNTs, SWCNTs-PVA electrodes in hexacyanoferrate/hexacyanoferrate 0.01 M.

3.3. PVA's Deposition Temperature Study

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 (Ip) values were obtained. 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. Polymer's deposition temperature effect on Au inkjet-printed electrodes.

Temperature	Ip Au electrode (μA)	Ip Au electrode + PVA (μA)	% Ip Reduction
25 °C	8.12	7.46	8.1
90 °C	3.92	$1.22 \cdot 10^{-5}$	100.0

3.3. Microsensor Calibration and Analytical Response

Calibration of SWCNTs and SWCNTs-PVA microsensors was performed by adding different volumes of H_2S standard to a PBS solution to measure at a concentration range between 0 and 600 μM. Chronoamperometry method was performed for H_2S oxidation (eq. 1) at a polarization voltage of 50 mV and the resulting current was measured.

$$H_2S \rightarrow S^0 + 2e^- + 2H^+ \quad (1)$$

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

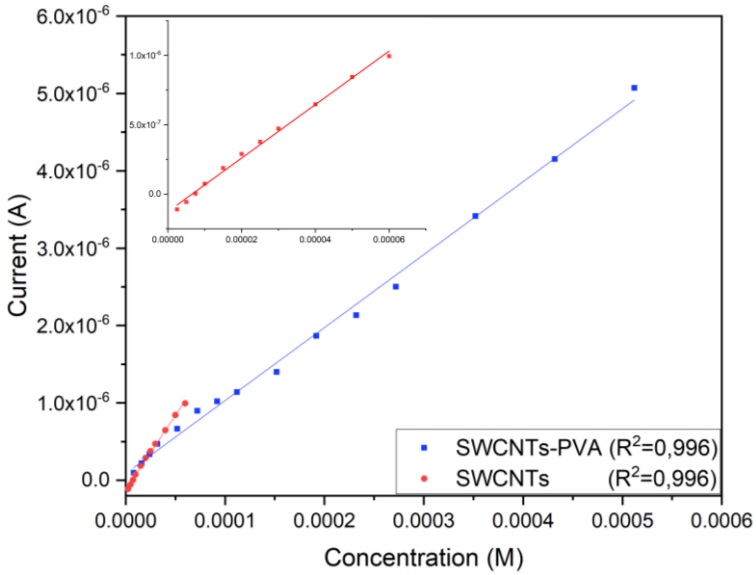

Figure 3. Calibrations of two different sensors, made of Au electrodes modified with SWCNTs and SWCNTs-PVA by drop casting. Inset shows a reduced range of H_2S concentration for the SWCNTs' sensor calibration.

While SWCNTs sensor shows a higher sensitivity, (19.3±0.4) mA/M compared to SWCNTs-PVA's (9.4±0.2) mA/M, it also has a reduced working range. SWCNTs can measure H_2S concentrations from 8 μM to 60 μM, with a limit of detection (LD) of 4.3 μM. On the other hand, SWCNTs-PVA is capable of measuring from 52 μM to 512 μM, with a LD of 34 μM.

4. Conclusions

We demonstrated a novel miniaturized inkjet-printed amperometric H_2S sensor fabricated through a gold electrode modification with SWCNTs ink. Results show that the addition of a stabilizing polymer allows for an increased range of H_2S concentration measurement. Due to the low versatility of the SWCNTs sensor, the addition of PVA became an alternative to improve H_2S sensor performance. However, temperature's fabrication condition was necessary to adapt to avoid electrode passivation, limiting SWCNTs-PVA ink deposition to 25 °C. This sensor is an approach for H_2S tracking with environmental and biotechnological applications.

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Guimera.; project administration, Mireia Baeza; funding acquisition, Mireia Baeza and Gemma Gabriel. All authors have read and agreed to the published version of the manuscript.

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