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# Three-dimensional porous electrode based on silver nanowires for hydrogen sulfide detection

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ABSTRACT

A new type of 3D material that allows gas circulation through it composed of polyether sponge, silver nanowires and silver dendrites was built. The material was bonded inside a graphite tube. The silver dendrites were electrochemically deposited on the metallic nanowire network during the recirculation of the electrolyte through the electrode. Air containing 0.89 ÷ 100 ppm $H_2S$ was circulated through the porous electrode. Subsequently, the electrode was characterized by cyclic voltammetry. It exhibited a linear response for concentrations between 3.6 ÷ 28.5 ppm $H_2S$ in air and the detection limit was below 1 ppm. Due to the large electroactive surface and innovative design it was possible to easily obtain sensitivities of $3.9 \cdot 10^4$ nA/ppmv at concentrations lower than 1 ppm $H_2S$ in air.

## 1. Introduction

Hydrogen sulfide is a toxic and flammable gas produced mainly during anaerobic biological processes or in the chemical industry. Colorimetric sensors are used to detect H2S resulted from the decomposition of waste foods [1]. Although the detection limit is below 1 ppmv, the linear response of these non-reversible sensors occurs at higher concentrations [2]. The electrochemical sensors for H2S detection can be regenerated and used in the ppm range. The most employed working principle is the oxidation of sulfide ion to sulfur that often passivates the platinum anode reducing the lifetime of the sensor [3,4]. For this reason, some sensors with long lifetime have a complex multi-chambered structure [5] and triple pulse amperometry (TPA) [3] was utilized to oxidize the elemental sulfur to soluble sulfate ions. In this work, we present for the first time a flexible 3D material based on polyether foam, silver nanowires (AgNws) and electrodeposited silver dendrites ($Ag_{den}$). Sensors based on $Ag_{den}$ [6] or $ZnSnO_3$ [7] deposited on rigid substrates have been previously used for hydrogen peroxide and liquefied petroleum gas detection. By comparison, our 3D structure simultaneously provides mechanical flexibility and good electrical conductivity, whereas the dendrites ensure a significant electroactive surface required to achieve a good sensitivity. Furthermore, this design allows analyte circulation through the porous electrode.

## 2. Experimental section

### 2.1. Synthesis of silver nanowires

For the AgNws synthesis, three solutions were prepared by dissolving: polyvinylpyrrolidone (PVP), Mw 40.000 g/mol in ethylene glycol (EG)-S1, $AgNO_3$ (99.8% Sigma-Aldrich) in EG (99% Sigma-Aldrich)-S2 and $Na_2Sx9H_2O$ (98% Sigma-Aldrich) in EG-S3. After mixing S1 and S2, S3 was added dropwise [8], under vigorous stirring. The final concentrations were: 0.05 M $AgNO_3$, 0.075 M PVP as *N*-vinylpyrrolidone and 0.15 mM $Na_2S$. The yellow–brown suspension was transferred in a PTFE-lined steel autoclave. The autoclave was placed in a preheated oven at 160 °C for 150 min and subsequently allowed to cool naturally. AgNws were separated by centrifugation, washed with ethanol and redispersed in ethanol (96% vol. ChimReactiv).

### 2.2. Electrode fabrication

The polyether foam (Waasoscon) was cut in cylinders with D = 12 mm and H = 6 mm, washed with 96% ethanol, air-dried and treated for 5 min in 25%$O_2$-75%Ar plasma using the 1020 Plasma Cleaner–Fischione. Subsequently, it was immersed in the AgNws suspension then dried in an oven at 150 °C for 3 min. The procedure was repeated until a less than 100 Ω electrical resistance was obtained. The electro-

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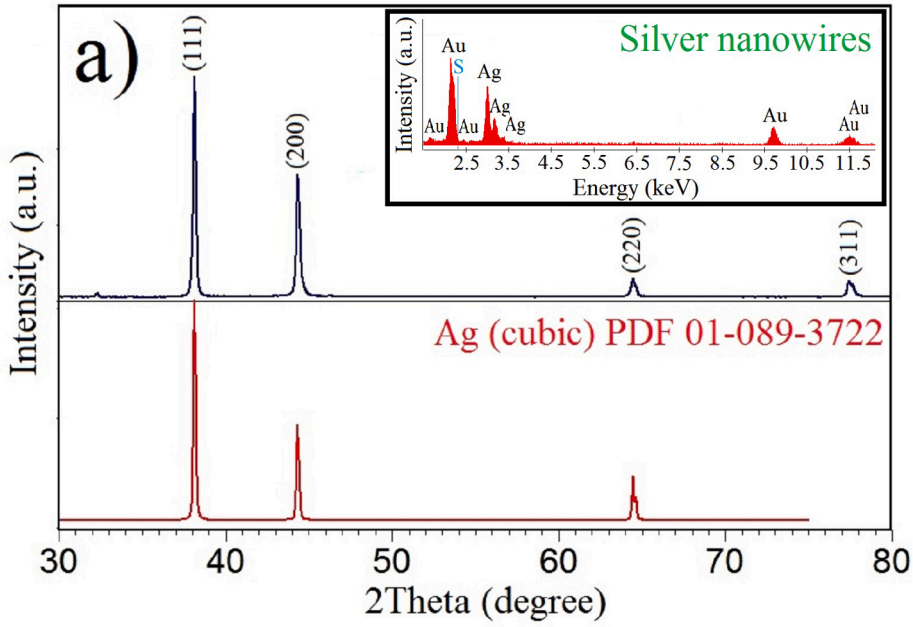


**Fig. 1.** a) XRD pattern of simulated cubic silver and AgNWs with EDX spectrum (inset); b) SEM images of AgNws deposited on gold at low and high (inset) magnifications.

conductive samples were bonded with graphite paste inside externally electrically insulated graphite cylinders. Following a literature method [6], the silver dendrites were electrodeposited at −200 mV *vs.* Ag/AgCl, for 120 s, in a solution of $AgNO_3$ and PVP, and the electrolyte was recirculated at a rate of 19.2 μL/s through the porous electrode using a peristaltic pump.

### 2.3. Characterization

The X'Pert Pro MPD (PanAlytical) diffractometer using CuKα radiation (λ = 1.54 Å) and nickel filter, SEM microscope Quanta FEG 250 (FEI) equipped with EDX and a Voltalab PGZ 402 potentiostat were used for the morphostructural, compositional and electrochemical (in a 0.02 M $HClO_4$-0.08 M $KClO_4$ solution) characterization. Gaseous $H_2S$ was prepared by injecting diluted HCl in $Na_2S$ solution and was stored in a Tedlar gas-bag. The exact concentration of $H_2S$ was determined by gravimetric analysis. The final concentrations were obtained by mixing 1%vol. $H_2S$ with water-saturated air at 294 ± 2 K, in a T–shaped gas mixer. 1.0L ± 1% air having different $H_2S$ concentrations was circulated with a flow rate of 200 mL/min through the porous electrode. After the electrochemical experiments, the electrode was washed, dried using nitrogen and subjected to the next $H_2S$ concentration.

## 3. Results and discussions

### 3.1. AgNws synthesis

$Ag_2S$ immediately precipitates during $AgNO_3$-$Na_2S$ mixing [8]. PVP

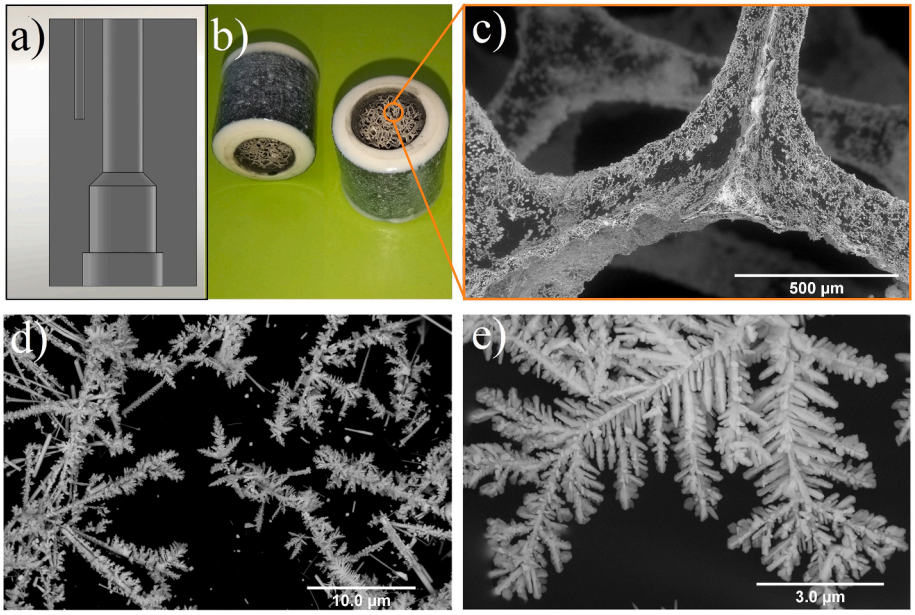


**Fig. 2.** a) Sectional view of the graphite tube; b) Photographic images of the 3D electrodes; c-e) SEM images on the surface of the 3D structure.

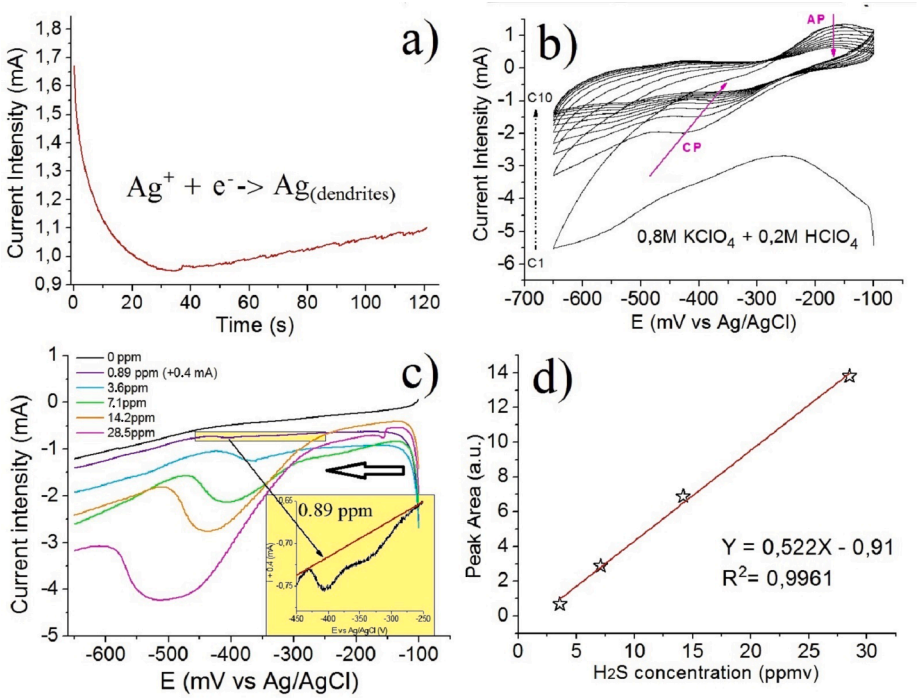


**Fig. 3.** a) Chronoamperogram at −200 mV *vs.* Ag/AgCl, b) First 10 CV cycles of as-synthesized electrode; c) Linear voltammograms after $H_2S$ treatments; d) Calibration curve.

is adsorbed on the surface of the seeds, thus preventing aggregation and precipitation.

EG simultaneously acts both as solvent and as reducing agent [9,10]. Although the oxygen from the autoclave is oxidizing the Ag twinned particles [10], in the presence of $S^{2-}$ ions oxygen scavengers are not required [8].

### 3.2. Compositional and morphostructural characterization

The XRD pattern presented in Fig. 1a shows that silver has cubic crystal structure. $Ag_2S$ is absent from both the XRD pattern and EDX spectrum, due to very low sulphur concentration. The SEM micrographs analyzed with ImageJ software show the growth of angled nanowires forming angles of ≈140°, marked with blue lines in Fig. 1b. The bending of AgNws is probably due to crystal growth inhibition along some crystalline directions {1 1 1} during the growth of the nanowires. The unblocked faces continue to grow in another direction that is conditioned by the angle made with the longitudinal axis of the nanowire [10].

### 3.3. Electrodeposition of Ag dendrites and $H_2S$ chemisorption

The plasma treatment makes the polymer surface hydrophilic, allowing the PVP capped AgNws to bond and ensure its electroconductivity (Fig. 2b-d). The deposition of dendritic silver ($Ag_{den}$) starts at the ends of AgNws and continues on the edges of the pentagonal prisms of each nanowire (Fig. 2d,e). Electrodeposition is difficult on the {1 0 0} faces of the AgNws, where PVP is strongly adsorbed [10]. At the beginning of the electrodeposition (Fig. 3a), the current decreased due to the total surface of the {1 1 1} crystalline faces having the highest energy [10] and to the decrease of the $Ag^+$ concentration at the interface. The current slightly increases after 30 s, because $Ag_{den}$ formation enlarges the electroactive surface.

$H_2S$ chemisorption on $Ag_{den}$ is a pure chemical reaction (r1):

$$H_2S + 1/2O_{2(air)} + 2Ag \rightarrow Ag_2S + H_2O \quad (r1)$$

The very low values of $Ag_2S$ solubility product, $Ksp = 5.92 \times 10^{-51}$ [11] explain silver affinity for $H_2S$, making the sensor selective if $H_2S$ is present with other atmospheric gases. Moreover, silver nanoparticles react faster with $H_2S$ than bulk Ag and the presence of $H_2O$ vapors greatly increases the rate of $Ag_2S$ formation. Thus, the analyte is concentrated by reacting with silver and the $Ag^+$ resulted from the formed $Ag_2S$ is electrochemically reduced.

### 3.4. Analyte detection

The cyclic voltammetry (CV) curves (Fig. 3b-c) show two cathodic processes (CP)-(r2) that overlap almost entirely at concentrations above 3 ppmv and two oxidation processes (AP)-(r3). Compared to an alkaline medium, in an acidic environment the observed number of peaks is smaller and the reduction peaks appear at more positive potentials due to the lower stability of $Ag_2S$ [12].The peak currents are directly proportional to the amount of $Ag_2S$ formed and the reaction rate is limited by the diffusion of $H_2S$ through the sulfide layer deposited on the metal surface. The $Ag_{den}$ increase the reactive surface improving sensor sensibility.

$$(K)\ Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S_{(dissolved)} \quad (r2)$$

$$(A)\ H_2S_{(dissolved)} + 2Ag \rightarrow Ag_2S + 2H^+ + 2e^- \quad (r3)$$

During the potential sweep, the decrease and shift of CP and AP peaks shown in Fig. 3b is due to the decrease in analyte concentration (formed in r2) by diffusion. The CP and AP maxima during the first CV cycles, before the electrode was subjected to the analyte, demonstrates the presence on the AgNws of small amounts of $Ag_2S$ from the synthesis of AgNws that are electrochemically solubilized. The graphite tubular support shown in Fig. 2a allows the rapid elimination of $H_2S$ formed during CP. Due to the large electroactive surface, the amperometric sensor exhibits a good sensitivity of 35.4 μA at a concentration of 0.89 ppmv $H_2S$, as can be seen in Fig. 3c and 3d, and displays a linear response in the range of interest of 5–20 ppmv $H_2S$, as it is specified by Occupational Safety and Health Administration (OSHA).

## 4. Conclusions

A new type of material was synthesized for the detection of $H_2S$. The material is based on AgNws, $Ag_{den}$ and 3D-polyether, it is flexible, light and has a large reactive surface. This particular design allows gas and electrolyte flowing through it. The material was used for the fabrication of an electrode with an innovative form. The 3D structure can be detached from the graphite support and exposed to the contaminated environment in difficult and dangerous conditions. The sampled analyte concentration can then be determined later. The sensor has a detection limit lower than 0.89 ppmv and a linear response in the 3.6–28.5 ppmv concentration range, which is of particular practical importance.

## CRediT authorship contribution statement

**Radu Banica:** Conceptualization, Methodology, Investigation, Writing – original draft. **Bogdan Taranu:** Writing – review & editing, Data curation. **Calin Ladasiu:** Investigation, Writing – review & editing. **Iosif Hulka:** Investigation. **Petrica Linul:** Supervision.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

[1] G. Tian, J. Xi, M. Yeung, G. Ren, Characteristics and mechanisms of $H_2S$ production in anaerobic digestion of food waste, Sci. Total Environ. 724 (2020) 137977–137983.
[2] L. Zhao, L. Zhao, Y. Miao, C. Liu, C. Zhang, A colorimetric sensor for the highly selective detection of sulfide and 1,4-dithiothreitol based on the in situ formation of silver nanoparticles using dopamine, Sensors. 17 (2017) 1–13.
[3] M.D. Brown, J.R. Hall, M.H. Schoenfisch, A direct and selective electrochemical hydrogen sulfide sensor, Anal. Chim. Acta. 1045 (2019) 67–76.
[4] J.R. Hall, M.H. Schoenfisch, Direct Electrochemical Sensing of Hydrogen Sulfide without Sulfur Poisoning, Anal. Chem. 90 (8) (2018) 5194–5200.
[5] A.V. Kroll, V. Smorchkov, A.Y. Nazarenko, Electrochemical sensors for hydrogen and hydrogen sulfide determination, Sensors Actuators B. Chem. 21 (2) (1994) 97–100.
[6] B. Liu, M. Wang, Electrodeposition of dendritic silver nanostructures and their application as hydrogen peroxide sensor, Int. J. Electrochem. Sci. 8 (2013) 8572–8578.
[7] S. Singh, A. Singh, M. Wan, R.R. Yadav, P. Tandon, S.S.A. Rasool, B.C. Yadav, Fabrication of self-assembled hierarchical flowerlike zinc stannate thin film and its application as liquefied petroleum gas sensor Sens, Actuators B-Chem. 205 (2019) 102–110.
[8] D. Chen, X. Qiao, X. Qiu, J. Chen, R. Jiang, Convenient synthesis of silver nanowires with adjustable diameters via a solvothermal method, J. Colloid Interface Sci. 344 (2) (2010) 286–291.
[9] R. Banica, D. Ursu, T. Nyari, A. Kellenberger, Two step polyol-solvothermal growth of thick silver nanowires, Mater. Lett. 194 (2017) 181–184.
[10] P. Zhang, I. Wyman, J. Hu, S. Lin, Z. Zhong, Y. Tu, Z. Huang, Y. Wei, Silver nanowires: Synthesis technologies, growth mechanism and multifunctional applications, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 223 (2017) 1–23.
[11] C. Levard, E.M. Hotze, G.V. Lowry, G.E. Brown Jr., Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity, Environ. Sci. Technol. 46 (2012) 6900–6914.
[12] M. Hepel, S. Bruckenstein, G.C. Tang, The formation and electroreduction of silver sulfide films at a silver metal electrode, J. Electroanal. Chem. 261 (2) (1989) 389–400.