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Abstract

Surface Enhanced Raman Scattering (SERS) for the Detection of Oxidative Stress Markers Using Si Nanowires (SiNWs)/Ag Nanostructures Fabricated by Metal Assisted Chemical Etching (MACE) †

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† Presented at the XXXV EUROSENSORS Conference, Lecce, Italy, 10–13 September 2023.

Abstract: In this work, silicon nanowires were constructed by metal-assisted chemical etching and decorated with silver nanoparticles and used as substrates for the SERS determination of oxidative stress markers, namely glutathione, malondialdehyde and catalase. The assays were sensitive, with detection limits of 50 and 3.2 nM for glutathione and malondialdehyde, respectively, and 0.5 μg/mL for catalase, indicating the capability of the proposed substrates to be implemented for the determination of various oxidative stress markers.

Keywords: SERS; MACE; oxidative stress; glutathione; malondialdehyde; catalase

Citation: Kochylas, I.; Kanioura, A.; Geka, G.; Likodimos, V.; Gardelis, S.; Dimitriou, A.; Papanikolaou, N.; Kakabakos, S.; Petrou, P. Surface Enhanced Raman Scattering (SERS) for the Detection of Oxidative Stress Markers Using Si Nanowires (SiNWs)/Ag Nanostructures Fabricated by Metal Assisted Chemical Etching (MACE). *Proceedings* **2024**, *97*, 170. https://doi.org/10.3390/proceedings2024097170

Academic Editors: Pietro Siciliano and Luca Francioso

Published: 9 April 2024

1. Introduction

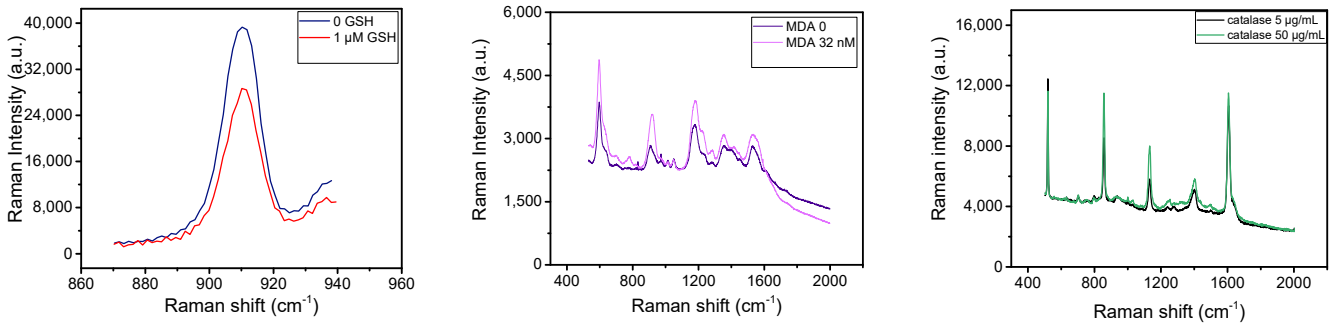
Oxidative stress is characterized by the increase of reactive oxygen species in cells and tissues. It affects almost all cellular functions, leading to severe pathological situations [1]. For the determination of the oxidative stress status, several markers are used in clinical practice, such as malondialdehyde (MDA), glutathione (GSH) and catalase [2]. In the present work, silicon nanowires decorated with silver nanoparticles fabricated by the MACE technique were evaluated as substrates for the determination of various oxidative stress markers using Surface-Enhanced Raman Spectroscopy.

2. Materials and Methods

SERS substrates were fabricated on a p-type silicon wafer by MACE, with the immersion of silicon wafers in a mixture of AgNO3/hydrofluoric acid (HF), as described previously [3]. Raman was performed using 532 and 785 nm excitation lasers. For the detection of GSH, the substrates were firstly incubated with an aqueous solution of 3 μg/mL crystal violet (CV) for 30 min and then with aqueous solutions of GSH at different concentrations for another 30 min [4]. MDA was detected by incubating on the surfaces for 20 min; different concentrations of MDA were determined upon derivatization with thiobarbituric acid (TBA) [4]. Finally, catalase was determined by a 30 min incubation of different concentrations onto the SERS substrates.

3. Discussion

GSH was determined by monitoring the decrease of the Raman signal produced from CV upon incubation with glutathione solutions of increasing concentration. In the case of malondialdehyde detection, derivatization was conducted with 2-thiobarbituric acid prior to incubation with the substrate. Finally, a direct measurement was carried out for the detection of catalase. In Figure 1a–c, the Raman spectra of zero calibrators along with the Raman spectra of different calibrators regarding GSH, MDA and catalase are presented. The limits of detection achieved for the specific markers were 50 nM and 3.2 nM for glutathione and malondialdehyde, respectively, and 0.5 μg/mL for catalase, indicating the ability of the SERS substrates to detect those oxidative markers with high sensitivity, in a short assay time, paving the way for on-site applications.



(**a**) (**b**) (**c**)

Figure 1. (**a**) SERS spectra of CV upon incubation with 0 (dark blue line) and 1 μM GSH (red line). (**b**) SERS spectra of TBA-MDA adduct for 0 (blue line) and 32 nM MDA (purple line). (**c**) SERS spectra of catalase at concentrations of 5 (black line) and 50 μg/mL (green line).

Author Contributions: Conceptualization, V.L., S.G., N.P. and P.P.; methodology, A.K., A.D. and P.P.; formal analysis, A.K. and A.D.; investigation, A.K., G.G., I.K. and A.D.; resources, V.L., S.G., N.P., S.K. and P.P.; data curation, A.K., I.K. and A.D.; writing—original draft preparation, A.K., I.K. and A.D. All authors have read and agreed to the published version of the manuscript.

Funding: This research was co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation under the call RESEARCH-CREATE-INNOVATE (project code: T2EΔK-03746 BioNanoDiagnostiki). I.K. was supported by Greece and the European Union (European Social Fund-ESF) through the Operational Program "Human Resources Development, Education and Lifelong Learning" in the context of the Act "Enhancing Human Resources Research Potential by undertaking a Doctoral Research", Sub-Section 2: IKY Scholarship Program for PhD candidates in Greek Universities.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy issues.

Conflicts of Interest: The authors declare no conflicts of interest.

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