





## Abstract

# Electrochemical Performance of WS<sub>2</sub>-CNT Core-Shell Heterostructures for the Detection of Vitamin B<sub>2</sub><sup>†</sup>

Rayhane Zribi<sup>1,\*</sup>, Muhammad Hamid Raza<sup>2,3</sup>, Nicola Pinna<sup>2</sup> and Giovanni Neri<sup>1,\*</sup><sup>1</sup> Department of Engineering, University of Messina, 98166 Messina, Italy<sup>2</sup> Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, 2, 12489 Berlin, Germany; hamid.raza@hu-berlin.de (M.H.R.); nicola.pinna@hu-berlin.de (N.P.)<sup>3</sup> PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Schwarzschildstrasse 3, 12489 Berlin, Germany

\* Correspondence: razribi@unime.it (R.Z.); gneri@unime.it (G.N.); Tel.: +090-6765297 (R.Z.)

<sup>†</sup> Presented at the XXXV EUROSensors Conference, Lecce, Italy, 10–13 September 2023.

**Abstract:** In this study, a novel electrochemical sensor was developed for the quantitative determination of riboflavin. The tungsten disulfide (WS<sub>2</sub>) layer was deposited on carbon nanotubes (CNTs) by atomic layer deposition (ALD), forming a CNTs-WS<sub>2</sub> core-shell heterostructure. This material was used to modify the commercial screen-printed carbon electrode in order to enhance its electrocatalytic activity toward the detection of vitamin B<sub>2</sub>. Cyclic voltammetry was performed as a preliminary test in the presence of riboflavin. In addition to this, an extensive electrochemical study was performed using differential pulse voltammetry, demonstrating that modified the CNTs-WS<sub>2</sub>/SPCE sensor display superior electrochemical performance compared with bare SPCE. The sensor exhibits a linear response in the concentration range from 0 μM to 45 μM, with remarkably enhanced sensitivity (9 μA μM<sup>−1</sup> cm<sup>−2</sup>) compared with the bare electrode, with a limit of detection (LOD) of 1.24 μM. This enhancement is attributed to the conformal growth of the WS<sub>2</sub> flakes on the CNTs and the high surface area offered by these flakes.

**Keywords:** atomic layer deposition; tungsten disulfide; carbon nanotubes; electrochemical sensor; riboflavin



**Citation:** Zribi, R.; Raza, M.H.; Pinna, N.; Neri, G. Electrochemical Performance of WS<sub>2</sub>-CNT Core-Shell Heterostructures for the Detection of Vitamin B<sub>2</sub>. *Proceedings* **2024**, *97*, 39. <https://doi.org/10.3390/proceedings2024097039>

Academic Editors: Pietro Siciliano and Luca Francioso

Published: 18 March 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Transition metals dichalcogenides (TMDs) have been investigated as sensing layers in electrochemical sensors to detect various analytes such as biomolecules [1], gases [2], and heavy metal ions [3]. Among the compounds of this family, tungsten disulfide (WS<sub>2</sub>) presents a layered structure that makes it attractive for various applications. WS<sub>2</sub> has been investigated as a sensing material in electrochemical sensors due to its unique properties. Carbon nanotubes (CNTs) have also been used in electrochemical sensors due to their excellent electrical conductivity, high surface area, and biocompatibility [4]; CNTs can be combined with WS<sub>2</sub> to develop CNTs-WS<sub>2</sub> heterostructures with improved electrochemical performances.

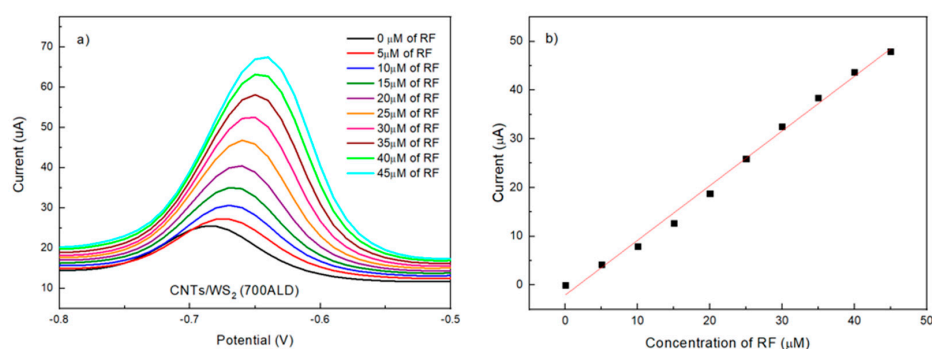
In this respect, here, we investigate the CNTs-WS<sub>2</sub> heterostructure for the detection of riboflavin (vitamin B<sub>2</sub>), a water-soluble vitamin essential for human health. It is involved in many metabolic processes in the body, including the metabolism of carbohydrates, fats, and proteins. Riboflavin is important for maintaining healthy skin, hair, and nails, and is also needed for the production of red blood cells [5]. The improved sensor performances of the CNTs-WS<sub>2</sub> heterostructure are related to the synergy between the WS<sub>2</sub> layer, which provides the active sites for target analyte adsorption, and the CNTs, which provide excellent electron transport properties.

## 2. Materials and Methods

Carbon nanotubes (CNTs) were functionalized as follows: 10 mg of dried powder (80 °C overnight) was dispersed in 2 mL ethanol by ultrasonication (30 min) and drop-cast on an Al foil for ALD-WS<sub>2</sub> deposition. WS<sub>2</sub> films were deposited in the ALD system at 300 °C, using BTBMW (maintained at 80 °C) and H<sub>2</sub>S as precursors.

## 3. Discussion

The good electroanalytical performance of the developed CNTs-WS<sub>2</sub>/SPCE sensor is summarized in Figure 1a, showing the large current variation during the differential pulse voltammetry (DPV) analysis of a solution containing different concentrations of RF, from 0 to 45 µM. Figure 1b shows the corresponding calibration curve, plotting the peak current as a function of the analyte concentration. The sensitivity of 9 µAµM<sup>-1</sup>cm<sup>-2</sup> was computed from a linear fit of the data (red line) and resulted in a limit of detection of 1.24 µM.



**Figure 1.** (a) DPV of CNTs-WS<sub>2</sub>/SPCE in 0.1 M PBS in the presence of different RF concentrations, (b) calibration curve corresponding to the DPV test. (The red line corresponds to the linear fit of the calibration curve).

**Author Contributions:** Investigation, data curation, writing—review and editing R.Z.; data curation, writing—review M.H.R. Supervision N.P. Supervision, writing—review and editing, G.N. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Dataset available on request from the authors.

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

## References

1. Zang, Y.; Nie, J.; He, B.; Yin, W.; Zheng, J.; Hou, C.; Huo, D.; Yang, M.; Liu, F.; Sun, Q.; et al. Fabrication of S-MoSe<sub>2</sub>/NSG/Au/MIPs imprinted composites for electrochemical detection of dopamine based on synergistic effect. *Microchem. J.* **2020**, *156*, 104845. [\[CrossRef\]](#)
2. Neri, G. Thin 2D: The new dimensionality in gas sensing. *Chemosensors* **2017**, *5*, 21. [\[CrossRef\]](#)
3. Cai, J.; Xia, Y.; Gang, R.; He, S.; Komarneni, S. Activation of MoS<sub>2</sub> via tungsten doping for efficient photocatalytic oxidation of gaseous mercury. *Appl. Catal. B Environ.* **2022**, *314*, 121486. [\[CrossRef\]](#)
4. Hu, C.; Hu, S. Carbon Nanotube-Based Electrochemical Sensors: Principles and Applications in Biomedical Systems. *J. Sens.* **2009**, *2009*, 187615. [\[CrossRef\]](#)
5. Powers, H.J. Riboflavin (vitamin B-2) and health. *Am. J. Clin. Nutr.* **2003**, *77*, 1352–1360. [\[CrossRef\]](#) [\[PubMed\]](#)

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.