Materials Letters 323 (2022) 132574

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Tetrahedrally modified $MnMe_{0.1}Co_{1.9}O_4$ (Me = Zn, Mg, Li) spinels for non-enzymatic glucose sensing

Krystian Lankauf [a,*], Katarzyna Ostrowska [a], Karolina Górnicka [b], Jakub Karczewski [b], Piotr Jasiński [a], Sebastian Molin [a]

[a] *Advanced Materials Center, Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland*

[b] *Advanced Materials Center, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland*

ARTICLE INFO

Keywords:
Spinel
Cation substitution
Glucose sensor

ABSTRACT

In this work, tetrahedrally modified $MnMe_{0.1}Co_{1.9}O_4$ (Me = Zn, Mg, Li) spinels were prepared via the sol–gel synthesis method with subsequent ball-milling fragmentation. The prepared samples were evaluated as glucose–sensing catalyst. The reference $MnCo_2O_4$ spinel exhibited a sensitivity of 49 $\mu A\ mM^{-1}\ cm^{-2}$ and a nonlinearity error of 5.2% in the response range from 0.02 to 1 mM. The partial substitution of cobalt in the reference spinel enhanced the glucose–sensing abilities, and the sample with Li was found to be the most active catalyst, exhibiting a sensitivity of 73.1 $\mu A\ mM^{-1}\ cm^{-2}$. Finally, the proposed material was tested for selectivity in the presence of interfering sucrose.

1. Introduction

According to World Health Organization (WHO) data, Diabetes Mellitus, commonly known as diabetes, was the ninth leading cause of death in 2019 [1]. It is a metabolic disease that causes high blood sugar, which, if untreated, can damage the nerves, eyes, kidneys, and other organs. Frequent monitoring of physiological blood glucose levels is a key factor in avoiding diabetic emergencies and introducing effective treatment.

Glucose sensors can be divided into enzymatic and non-enzymatic sensors. Enzymatic glucose biosensors based on glucose oxidase (GOD) enzyme, initially developed by Clark and Lyons in the 1960s, exhibit high sensitivity and selectivity and have been successfully used over the years [2]. However, enzymatic sensors suffer from disadvantages such as complex manufacturing, high price, and instability [3]. Due to the rising number of patients with diabetes and the subsequent increasing number of premature deaths, the development of more reliable glucose sensors is crucial.

The principle of operation of the non-enzymatic sensors is based on the glucose oxidation directly at the electrocatalyst surface. Two models are proposed to explain the electrocatalytic processes of these sensors, the Activated Chemisorption model and the Incipient Hydrous Oxide Adatom Mediator (IHOAM) model [4]. Noble metals-based (Pt or Au) non-enzymatic sensors have been widely studied and found to exhibit promising performance for direct electrochemical glucose oxidation [5]. Disposable glucose sensors based on bimetallic NiPt nanosheet arrays electrodeposited on carbon papers were proposed by Zhou et al. [6]. Nevertheless, finding more abundant and less expensive materials for glucose sensing is an important and open subject.

Among the many materials proposed as non-enzymatic glucose sensors, transition metal oxides demonstrate favourable performance along with high accessibility [7,8]. Spinels with the formula AB_2O_4 (where A and B are metal ions) are a promising group of materials to be applied in the sensor manufacturing field. Due to the vast range of elements that can occupy the crystal structure sites, spinels exhibit outstanding catalytic, electrical and magnetic properties [9]. Recently, $ZnCo_2O_4$ spinel microrods grown on nickel foam for non-enzymatic glucose sensing were prepared by Liu et al. via a hydrothermal method and subsequent annealing process [10]. Zhang et al. proposed a graphene decorated spinel $MnCo_2O_4$ composite nanofibres-based (GMCFs) biosensor, which exhibited excellent electrocatalytic activity towards glucose oxidation [11]. Only binary spinels seem to have been studied so far.

In this work, a series of $MnMe_{0.1}Co_{1.9}O_4$ spinels, where the Co is partially substituted by Zn, Mg or Li, were prepared by sol–gel synthesis for the purpose of non–enzymatic glucose sensing. The structure,

---

[*] Corresponding author.
E-mail address: krystian.lankauf@pg.edu.pl (K. Lankauf).

https://doi.org/10.1016/j.matlet.2022.132574
Received 8 February 2022; Received in revised form 11 May 2022; Accepted 3 June 2022

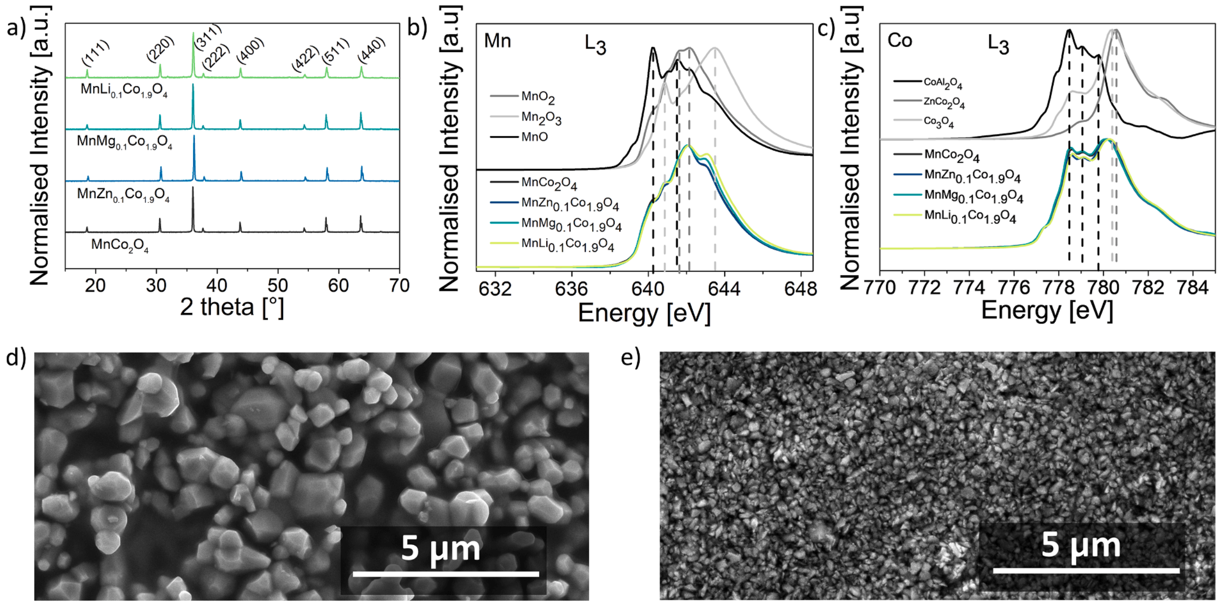

Fig. 1. (a) pXRD patterns of t-MCO powders, XANES spectra of (b) Mn, and (c) Co L_3-edge, SEM image (x10,000) of (d) as-synthesised and (e) ball-milled $MnCo_2O_4$ powder.

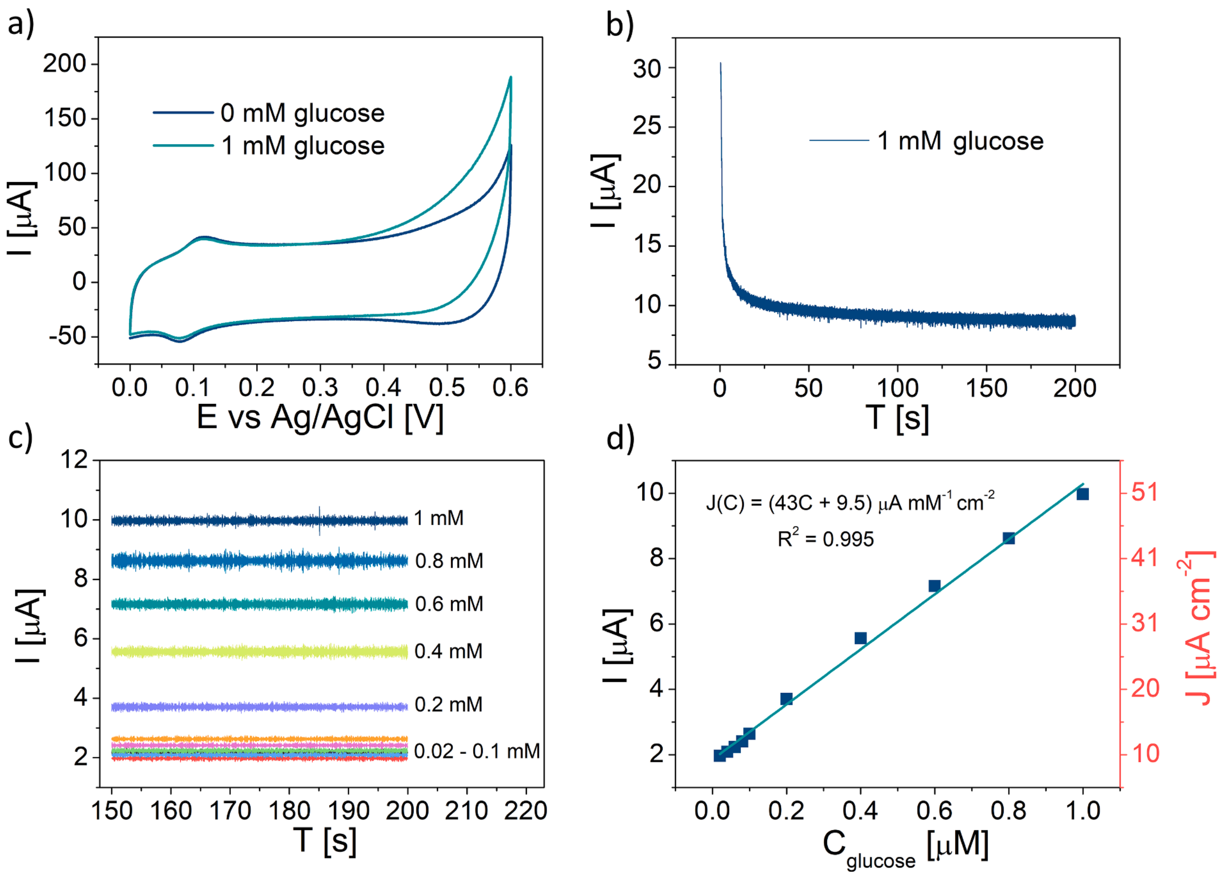

Fig. 2. (a) CVs of the $MnCo_2O_4$-coated electrodes in the absence and presence of 1 mM glucose at a scan rate of 100 mV s^{-1}, (b) exemplary amperometric response of the $MnCo_2O_4$ in the presence of glucose at 0.5 V vs Ag/AgCl, (c) steady-state amperometric responses to the increasing glucose concentration, and (d) corresponding calibration curve. All tests were performed in 0.2 M KOH.

morphology and electrochemical glucose sensing performance were studied.

2. Experimental

Tetrahedrally substituted manganese cobaltite spinel oxides were prepared by the sol–gel EDTA–Citric Acid method described in the

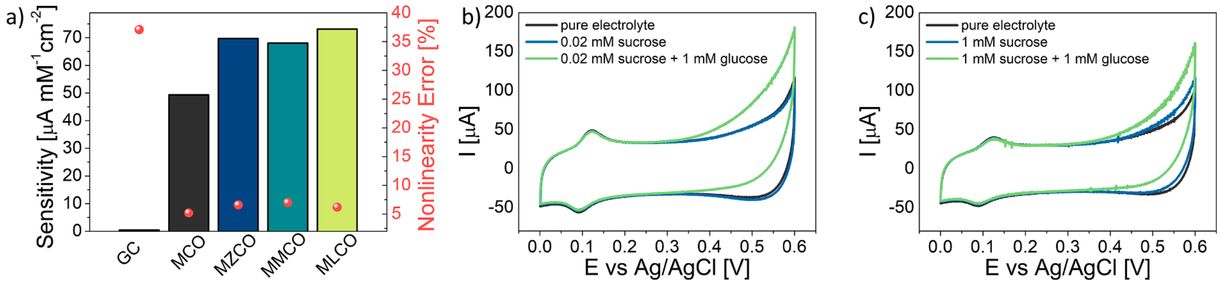

Fig. 3. (a) Comparison of sensitivity and characteristics of nonlinearity towards glucose sensing obtained for t-MCO catalysts, interference test CVs of the $MnLi_{0.1}Co_{1.9}O_4$ performed in the presence of (b) 0.02 mM and (c) 1 mM sucrose. All tests were performed in 0.2 M KOH.

Supplementary Information.

3. Results and discussion

The pXRD patterns collected for all of the synthesised t-MCO powders are pictured in Fig. 1(a). The peaks indicate a well crystallised spinel cubic structure (space group Fd–3 m, No. 227). The measured peak positions: 18.6°, 30.6°, 36°, 37.7°, 43.8°, 54.4°, 58°, 63.7°, fit with standard $MnCo_2O_4$ (PDF #00–023–1237). In Fig. 1 (b), the Mn L_3-edge XANES spectra of $MnCo_2O_4$ doped with Zn, Mg or Li in tetrahedral positions are presented.

The substitution with Zn^{2+} has a negligible influence on the Mn valence in the spinel crystal, since the $MnZn_{0.1}Co_{1.9}O_4$ spectrum overlaps with one of $MnCo_2O_4$. A growing shoulder at 643.5 eV indicates the incorporation of Mg^{2+} and, even more so, Li^{1+}, forces more Mn cations into the +4 oxidation state. The Co L_3-edge spectra presented in Fig. 1 (c) showed minor changes for samples doped with Zn and Li, revealing the higher ratio of Co^{3+}/Co^{2+}. The obtained results show that even a small addition of elements in the tetrahedrally coordinated sites may have a strong influence on the valence of other constituent elements, making it possible to tune the material's physicochemical properties.

Fig. 1 (d) presents the morphology of the as-synthesised pure $MnCo_2O_4$ powder, characterised by micrometre-sized particles. The ball-milling process was applied to reduce the sample's particles size and thus increase the specific surface area. As is shown in Fig. 1 (e) and Fig. S1, the agglomerated particles were crushed, which provided more available surface active sites for electrocatalysis.

Fig. 2 (a) presents the cyclic voltammetry (CV) curves recorded for the pure $MnCo_2O_4$-coated electrode without and with the addition of glucose. The electrocatalytic current response increases in the presence of glucose. Fig. 2 (b) shows the amperometric response at 0.5 V vs Ag/AgCl in electrolyte with a 1 mM glucose concentration. The visible current changes are due to the applied polarisation (from OCV to 0.5 V). The steady–state response is reached at around 200 s. For the purpose of a calibration curve, the series of amperometric response measurements were performed with increasing glucose concentration from 0.02 to 1 mM and analysed after 150 s (Fig. 3 (b)). The obtained calibration curve presented in Fig. 2 (d) indicates a linear glucose oxidation response with a nonlinearity error of 5.2% and sensitivity of 43 $\mu A\ mM^{-1}\ cm^{-2}$ (average sensitivity for 3 electrodes is 49 $\mu A\ mM^{-1}\ cm^{-2}$) two orders of magnitude higher than for uncoated Glassy Carbon (GC) electrode (Fig. S2).

To further improve the glucose–sensing ability, the additional elements were incorporated into the tetrahedrally coordinated sites of the spinel structure. As is depicted in Fig. 3 (a), the introduction of small amounts of Zn^{2+}, Mg^{2+} or Li^{1+} cations into the crystal structure resulted in increased sensitivity with preserved low calibration curve nonlinearity error. Among the studied materials, the best results are seen for $MnLi_{0.1}Co_{1.9}O_4$ with a sensitivity of 73.1 $\mu A\ mM^{-1}\ cm^{-2}$. The detection of glucose is achieved through electron transfer by oxidation of glucose. As revealed by XANES studies, the sample with incorporated Li^{1+} cations is characterised by a higher ratio of $Mn^{4+}/(Mn^{3+}$ and $Mn^{2+})$ and Co^{3+}/Co^{2+} synergistically influencing the adsorption of reaction species, charge transfer and oxidation of glucose [12,13].

The applicability of this new material was then tested with a selectivity test. The CVs were recorded in electrolytes with concentrations of interfering sucrose of 0.02 mM and 1 mM. As is depicted in Fig. 3(b), the smaller sucrose content had a negligible impact on the glucose sensing ability. The higher sucrose concentration produced a visible current at oxidising potentials (Fig. 3 (c)), however, glucose oxidation-related current was still pronounced. The extended selectivity behaviour test, including the influence of ascorbic acid, fructose, urea is presented in Fig. S3. These tests show good selectivity of the spinels towards glucose, which possibly can be further increased by materials tailoring.

4. Conclusions

To summarise, a series of tetrahedrally modified $MnMe_{0.1}Co_{1.9}O_4$ spinels was prepared by the sol–gel synthesis method and subsequent ball–milling process. The obtained powders were tested as electrocatalysts for the non-enzymatic glucose sensor application. Among the prepared samples, the one with cobalt partially substituted for lithium exhibited the highest sensitivity with preserved low nonlinearity error of the calibration curve. Moreover, the proposed $MnLi_{0.1}Co_{1.9}O_4$ preserved the glucose-sensing ability with the presence of an interfering agent, i.e. sucrose. These results demonstrate that the spinels can be tailored via chemical modifications and the proposed catalyst could be used to prepare a promising non-enzymatic glucose sensor based of abundant elements.

CRediT authorship contribution statement

Krystian Lankauf: Conceptualization, Methodology, Investigation, Data curation, Validation, Writing – original draft. **Katarzyna Ostrowska:** Investigation, Methodology, Validation, Formal analysis. **Karolina Górnicka:** Investigation, Validation. **Jakub Karczewski:** Investigation, Validation. **Piotr Jasiński:** Methodology, Supervision, Resources. **Sebastian Molin:** Conceptualization, Methodology, Supervision, Writing – review & editing, Resources, Funding acquisition.

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.

Acknowledgements

The presented research is part of the “Nanocrystalline ceramic materials for efficient electrochemical energy conversion” project, carried out within the First TEAM programme of the Foundation for Polish Science (grant agreement nr. POIR.04.04.00-00-42E9/17-00), co–financed by the European Union under the European Regional Development Fund. Funding from the Statutory Funds of WETI PG is also acknowledged.

This publication was developed under the provision of the Polish Ministry of Education and Science project: “Support for research and development with the use of research infrastructure of the National Synchrotron Radiation Centre SOLARIS” under contract nr. 1/SOL/2021/2.

We acknowledge the SOLARIS Centre for the access to the Beamline PIRX, where the measurements were performed.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2022.132574.

References

[1] WHO, Diabetes (2021). https://www.who.int/news-room/fact-sheets/detail/diabetes.

[2] L.C. Clark, C. Lyons, Electrode Systems for Continuous Monitoring in Cardiovascular Surgery, Ann. N. Y. Acad. Sci. 102 (1962) 29–45, https://doi.org/10.1111/j.1749-6632.1962.tb13623.x.

[3] M.H. Hassan, C. Vyas, B. Grieve, P. Bartolo, Recent advances in enzymatic and non-enzymatic electrochemical glucose sensing, Sensors. 21 (14) (2021) 4672.

[4] H. Zhu, L. Li, W. Zhou, Z. Shao, X. Chen, Advances in non-enzymatic glucose sensors based on metal oxides, J. Mater. Chem. B. 4 (2016) 7333–7349, https://doi.org/10.1039/C6TB02037B.

[5] C. Chen, Q. Xie, D. Yang, H. Xiao, Y. Fu, Y. Tan, S. Yao, Recent advances in electrochemical glucose biosensors: A review, RSC Adv. 3 (2013) 4473–4491, https://doi.org/10.1039/c2ra22351a.

[6] J. Zhou, H. Yin, L. Wang, H. Zhao, Z. Zhang, J. Gong, Y. Zheng, Q. Nie, Electrodeposition of bimetallic NiPt nanosheet arrays on carbon papers for high performance nonenzymatic disposable glucose sensors, J. Mater. Sci. Mater. Electron. 32 (2021) 22493–22505, https://doi.org/10.1007/s10854-021-06735-3.

[7] R.X. Zhang, P. Yang, Y.X. Zhang, A novel high-sensitivity non-enzymatic glucose sensor via Cu2O@CuO@NiCo2O4 nanowires as catalyst, Mater. Lett. 272 (2020), 127850, https://doi.org/10.1016/j.matlet.2020.127850.

[8] R. Madhu, V. Veeramani, S.M. Chen, A. Manikandan, A.Y. Lo, Y.L. Chueh, Honeycomb-like Porous Carbon-Cobalt Oxide Nanocomposite for High-Performance Enzymeless Glucose Sensor and Supercapacitor Applications, ACS Appl. Mater. Interfaces. 7 (2015) 15812–15820, https://doi.org/10.1021/acsami.5b04132.

[9] K. Lankauf, K. Cysewska, J. Karczewski, A. Mielewczyk-Gryń, K. Górnicka, G. Cempura, M. Chen, P. Jasiński, S. Molin, MnxCo3-xO4 spinel oxides as efficient oxygen evolution reaction catalysts in alkaline media, Int. J. Hydrogen Energy. 45 (29) (2020) 14867–14879.

[10] S. Liu, W. Zeng, Y. Li, Synthesis of ZnCo2O4 microrods grown on nickel foam for non-enzymatic glucose sensing, Mater. Lett. 259 (2020), 126820, https://doi.org/10.1016/j.matlet.2019.126820.

[11] Y. Zhang, S. Liu, Y. Li, D. Deng, X. Si, Y. Ding, H. He, L. Luo, Z. Wang, Electrospun graphene decorated MnCo2O4 composite nanofibers for glucose biosensing, Biosens. Bioelectron. 66 (2015) 308–315, https://doi.org/10.1016/j.bios.2014.11.040.

[12] T. Wang, Y. Sun, Y. Zhou, S. Sun, X. Hu, Y. Dai, S. Xi, Y. Du, Y. Yang, Z.J. Xu, Identifying Influential Parameters of Octahedrally Coordinated Cations in Spinel ZnMnxCo2- xO4 Oxides for the Oxidation Reaction, ACS Catal. 8 (2018) 8568–8577, https://doi.org/10.1021/acscatal.8b02376.

[13] L. He, J. Cao, J. Li, X. Li, P. Fan, Y. Yang, Highly efficient non-enzymatic glucose biosensor based on Ni0.5Co0.5(OH)2 microflowers adorned glassy carbon electrode, Mater. Lett. 301 (2021) 1–4, https://doi.org/10.1016/j.matlet.2021.130197.