

Co₃O₄-NiO Nanocomposites for the Electrochemical Determination of L-Tyrosine

Madiha Khan^{1,*2}, Khoulood Abid^{1,2}, Viviana Bressi¹, Giovanni Neri¹

¹ Department of Engineering, University of Messina, C.da Di Dio, 1-98166 Messina, Italy; madihakhan7121992@gmail.com, khoulood.abid@unime.it, vibressi@unime.it, giovanni.neri@unime.it

² Department of Physics, Air University, PAF complex, E-9, Islamabad, 4400, Pakistan; madihakhan7121992@gmail.com

³ CNR IPCF Istituto per i Processi Chimico-Fisici, viale F. Stagno D'Alcontres 37, Messina, Italy.

Corresponding Author's e-mail address madihakhan7121992@gmail.com

Summary:

Co₃O₄-NiO nanocomposites at different molar ratios have been prepared using a simple sol-gel method. The composite were used as electrode materials for detecting L-tyrosine, modifying a screen printed electrode (SPCE). The electrochemical sensor response to L-Tyrosine (concentration-Tyr) in PBS pH=7.4 and at [0μM–100μM] has been investigated by using cyclic voltammetry (CV). Results obtained demonstrated that the composite Co₃O₄-NiO/SPCE sensors exhibit good electroanalytical performances, with a maximum of sensitivity exhibited at a Co₃O₄:NiO ratio = 1.

Keywords: Cobalt Oxide-Nickel Oxide nanocomposite, Tyrosine, Electrochemical sensor.

Introduction

Tyrosine (Tyr) is an aromatic amino acid critical to the synthesis of compounds such as neurotransmitters and melanin [1,2]. Abnormal Tyr concentrations in plasma/urine can also be used as a biomarker in the detection of various diseases like alkaptonuria, tyrosinemia, and liver disease [3]. Therefore, an easy quantification assay of Tyr is critical. To attend this purpose, researchers have developed numerous analytical methods. However, implementing such methods is expensive and complex, thus, the necessity of the development of a sensitive and low-cost platform for the determination of Tyr is mandatory.

In this study, Co₃O₄-NiO nanocomposites (NCs) are synthesized through the sol-gel method and employed to improve the detection of Tyr by means of electrochemical sensors, modified by NCs of different Co₃O₄-NiO ratios.

Materials and Methods

a. Co₃O₄-NiO preparation

The synthesis of Co₃O₄-NiO NC was carried out as follows: first, 1.19g of Co₃O₄ was dissolved in 10mL of hydrochloric acid (HCl) and continuously stirred at room temperature until the

solution became transparent and uniform. Then, various quantities of pure nickel oxide at 0.186 and 0.37g were dissolved in 2M citric acid (HOC (CO₂H) (CH₂CO₂H)₂) solution and stirred at room temperature till the solution became transparent and uniform.

Subsequently, the Co₃O₄ and NiO solutions were mixed and placed on a heating plate at a temperature of ~350°C. The materials were fully burned, and, in this way, two samples were obtained with different Co₃O₄-NiO molar ratios. At last, the powdered samples were annealed in a glass furnace for 2 hours at 400°C.

b. Electrode preparation.

The modified SPCE electrodes are prepared by a simple drop-casting method with Co₃O₄-NiO NC. Herein, 1mg of Co₃O₄-NiO NC is dissolved in 1mL aqueous solution was assembled through the dispersion of 1 mg Co₃O₄-NiO NC and ultrasonication for 1 hour.

a. Electrochemical tests.

The modified screen-printed carbon electrode (SPCE) were prepared by dispersing the NC electrode materials on the working carbon electrode of SPCE platform (Metrohm-DropSens). All electrochemical analyses were performed using a Metrohm Autolab galvanostatic potentiostat equipped with NOVA 2.1 data acquisition software.

Results and Discussion

XRD patterns are depicted in Figure 1. Reflection peaks of NiO and Co₃O₄ are observed in the diffraction patterns of the composite samples, indicating they are through composites.

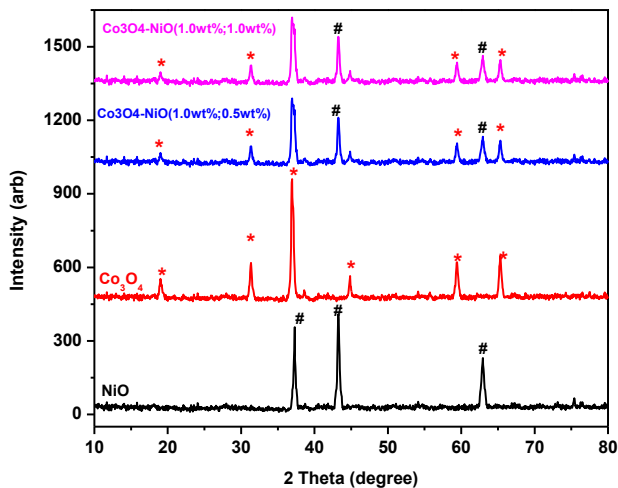


Fig.1. XRD spectra of pure NiO (black line), pure Co₃O₄ (red line), Co₃O₄-NiO(1.0wt%;0.5wt%) (blue line), and Co₃O₄-NiO(1.0wt%;1.0wt%) (pink line)

a. Electrochemical Tests

The L-Tyr determination is performed by voltammetric technique at different concentrations (see Figure. 2a) to compare the sensitivity of the modified electrodes. Calibration curves are plotted and presented in Figure.2b, showing that the composite Co₃O₄-NiO/SPCE sensors exhibit good electroanalytical performances, with a maximum of sensitivity exhibited at a Co₃O₄:NiO ratio = 1.

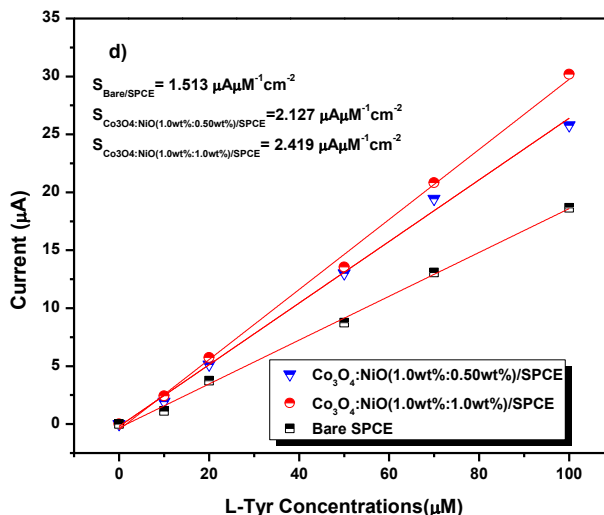
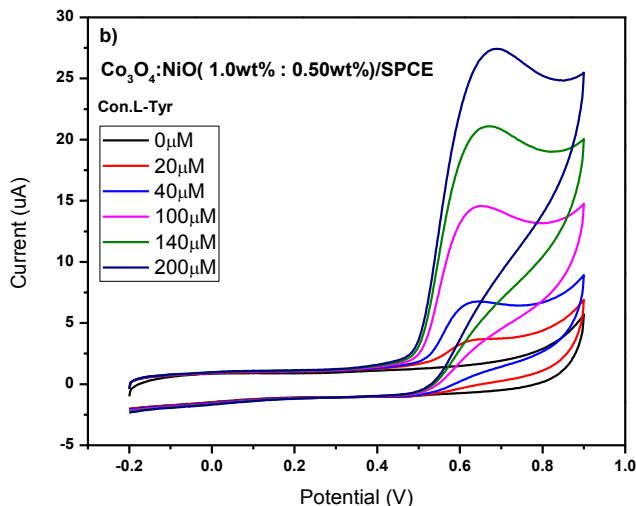


Figure.2. a) CV test in PBS solution containing L-Tyr (0µM-200µM) at 50mV/s scan rate on (a) Co₃O₄LNiO (1.0wt%;0.5wt%) and d) the calibration curve.

Conclusion

Co₃O₄-NiO NCs have been synthesized successfully via the sol-gel method. XRD, SEM and EDX measurements indicate a NC structure and the presence of crystalline metal oxide nanoparticles. More studies are to be done in order to optimize the synthetic approach to improve the quality of Co₃O₄-NiO doped films, which to the best of our knowledge may represent a new electrode material for electrochemical sensing applications.

References

- [1] Alkaws, G., et al., Review of Renewable Energy-Based Charging Infrastructure for Electric Vehicles. Applied Sciences, 2021. **11**(9): p. 3847.
- [2] Hosny, N.M., Synthesis, characterization and optical band gap of NiO nanoparticles derived from anthranilic acid precursors via a thermal decomposition route. Polyhedron, 2011. **30**(3): p. 470-476.
- [3] Danjumma, S.G., Y. Abubakar, and S. Suleiman, Nickel oxide (NiO) devices and applications: a review. Int. J. Eng. Res. Technol, 2019. **8**: p. 12-21.