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Dopamine assessment on conductive polymers/gold NPs with appended metalloporphyrins composites

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Summary:

The potential of gold nanoparticles with appended metalloporphyrin synthesized through one-pot sono-synthesis and incorporated in conductive PANI and PPy polymeric coatings deposited on SPEs for catalytic oxidative detection of dopamine (DA) has been evaluated. The CV and LSV studies of developed composite materials have demonstrated their specific response to DA n in 2.5×10^{-5} – 1.0×10^{-3} M concentration range. The morphology of electropolymerized PPy and PANI polymeric coatings bearing ZnTPP(CO_2)$_4$@AuNPs and ZnTPP(SO_3)$_4$@AuNPs were tested my SEM and spectroscopic methods.

Keywords: electrochemical dopamine detection; gold nanoparticles; porphyrin catalytic center; conductive PANI and PPy polymeric coatings; composite materials.

Background, Motivation and Objective

Dopamine (DA) is a primary neurotransmitter, synthesized in the brain and involved in many functions: it is responsible for feelings of pleasure, motivation, and gratification, and is also involved in processes such as movement, memory, and attention [1]. DA is one of the most important biomarkers of the brain diseases, its measurable changes in body fluids, as for instance in urine, may be associated with a physiological or pathophysiological processes [2]. Hence the development of analytical systems permitting the fast and effective DA levels control in biological liquids is a challenging task. Chemical sensors, and in particular electrochemical sensors based on electrocatalytically active nanohybrid materials have been reported for the oxidation of different biological materials, and for DA detection in particular [3-5].

In this work, 4 conductive PANI and PPy polymeric coatings obtained through co-polymerization with gold nanoparticles, AuNPs, with appended water-soluble Zn-porphyrin complexes synthesized through one-pot sono-synthesis were tested in comparison to non-modified PANI and PPY for catalytic dopamine assessment.

The coatings were obtained on carbon black SPE from with from aniline or pyrrole monomer solutions, and doped either with ZnTPP(CO_2)$_4$@AuNPs or with ZnTPP(SO_3)$_4$@ AuNPs through Cyclic Voltammetry (CV) electropolymerization process in standard 3-electrode cell, with Pt wire counter and SCE reference, Table 1. Film electrolymerizations were run for 10-20 cycles, scanning the potential from -0.3 to 1.1 V range, with 100 mV/s scan rate. The water-soluble Zn(II) complexes of tetrakis-(4-sulfonatophenylporphyrin), ZnTPP(SO_3)$_4$, or tetrakis-(4- carboxy-phenyl porphyrin, ZnTPP(CO_2)$_4$, appended on AuNPs and bearing negative charge served as counterions for positively charged PPy and PANI polymeric backbone upon electropolymerization. Further, the catalytic effect of AuNPs on DA oxidation was tested for obtained films in comparison to bare carbon black (CB) material of SPE working electrode, CB coated either with PPy (and ClO_4^- - counter anions), or PANI (Cl^- counter anions), and for CB/ZnTPP(SO_3)$_4$@AuNPs coating.

Tab. 1: Composition of tested polymeric coatings for oxidative DA assessment.

N	Coating	Deposition solution
1	-	-
2	PPy	**Sol.1:** 0.15M pyrrole in ACN, 0.1M TBClO$_4$
3	PANI	**Sol.2:** 0.15M aniline in 1M HCl
4	PPy/ ZnTPP(CO_2)$_4$ @AuNPs	**Sol.1** : 5mM ZnTPP(CO_2)$_4$ @AuNPs = 1:1
5	PPy/ ZnTPP(SO_3)$_4$ @AuNPs	**Sol.1** : 5mM ZnTPP(SO_3)$_4$ @AuNPs = 1:1
6	PANI/ ZnTPP(CO_2)$_4$ @AuNPs	**Sol.2** : 5mM ZnTPP(CO_2)$_4$ @AuNPs = 1:1
7	PANI/ ZnTPP(SO_3)$_4$ @AuNPs	Sol.2 : 5mM 2ZnTPP(SO_3)$_4$ @AuNPs = 1:1

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Results

As it is shown in Figure 1 the higher currents indicating the formation of highly conjugated conductive coating were obtained for PANI films doped with $ZnTPP(SO_3)_4$@AuNPs served as counter-ions for positively charged PANI-backbone during electropolymerization.

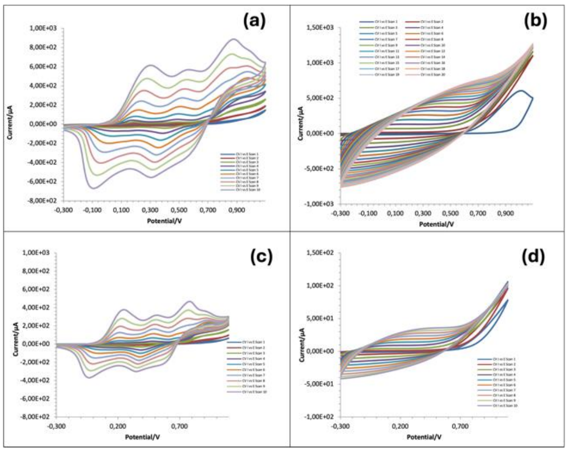

Fig. 1. CV electropolymerization of (a) PANI/ $ZnTPP(SO_3)_4$@AuNPs, *coating 7; (b)* PPy/$ZnTPP(SO_3)_4$ @AuNPs, *coating 5; (c)* PANI/$ZnTPP(CO_2)_4$@AuNPs, *coating 6; (d)* PPy/$ZnTPP(CO_2)_4$@AuNPs, *coating 4. CV 10-20 cycles from -0.3 to 1.1V, 100 mV/s scan rate.*

The morphology of electropolymerized PPy and PANI polymeric coatings bearing $ZnTPP(CO_2)_4$ @AuNPs and $ZnTPP(SO_3)_4$@AuNPs were tested by SEM microscopy and spectroscopic methods. As it may be seen from Figure 2(a) and magnified insert, the more uniform film with well distributed AuNPs was registered for coating 7: PANI/ $ZnTPP(SO_3)_4$@AuNPs.

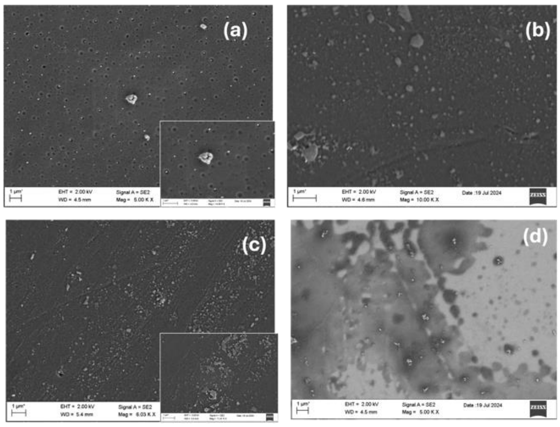

Fig. 2. SEM images of (a) PANI/ $ZnTPP(SO_3)_4$@AuNPs, *coating 7; (b)* PPy/$ZnTPP(SO_3)_4$ @AuNPs, *coating 5; (c)* PANI/$ZnTPP(CO_2)_4$@AuNPs, *coating 6; (d)* PPy/ZnTPP $(CO_2)_4$@AuNPs, *coating 4.*

CV and Linear Sweep Voltammetry (LSV) studies of developed composite materials have demonstrated the specific response to DA neurotransmitter in a $2.5 \times 10^{-5} – 2.0 \times 10^{-3}$ M concentration range, with LDL of 50 µM. The best performance has shown coating 7, based on PANI and doped with $ZnTPP(SO_3)_4$@AuNPs, Fig. 3.

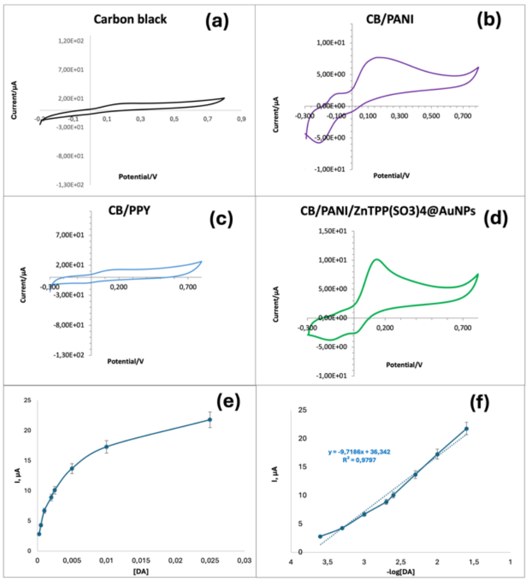

Fig. 3. (a) CV of DA detection at (a) CB; (b) CB/PANI; (c) CB/PPy; (d) PANI/ $ZnTPP(SO_3)_4$@AuNPs, *coating 7. Calibration curves od DA response obtained for c* PANI/ $ZnTPP(SO_3)_4$@AuNPs, *coating 7: (e) current vs DA concentration, (d) – current vs -log[DA].*

The detailed discussion on influence of conductive polymeric matrix, AuNPs and metalloporphyrin complexes properties on sensitivity and selectivity properties of the composite materials, as well as examples of real samples analysis, will be provided in our presentation.

References

[1] Iversen, S.D.; Iversen, L.L. Trends Neurosci., 2007, 30, 188.
[2] An, M.; Gao, Y. Genomics Proteomics Bioinformatics, 2015, 13, 345.
[3] Kim, D.S.; Kang, E.S.; Baek, S. et al., Sci Rep, 2018, 8, 14049.
[4] Anuar, N.S.; Basirun, W.J.; Shalauddin, Md.; Akhter, S. RSC Adv., 2020,10, 17336.
[5] Lakard, S.; Pavel, I.A.; Lakard, B. Biosensors, 2021, 11, 179.