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Silver Nanomaterials as Rlectron Mediators in a Bio-Electronic Tongue Dedicated to the Analysis of Milks. The role of the Aspect Ratio of Nanoparticles vs. Nanowires †

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Abstract: The integration of silver nanomaterials as electron mediators in electrochemical biosensors can be crucial to improve the affinity with biomolecules and the electrochemical response. In this work, two voltammetric bioelectronics tongues (bioET) formed by biosensors based on the combination of enzymes with silver nanoparticles (AgNPs) (bioET-1) or silver nanowires (AgNWs) (bioET-2) have been developed and used to analyze milks. Each array was formed by four biosensors formed by enzymes (glucose oxidase, galactose oxidase, β-galactosidase and a blank), capable to detect compounds usually found in milks. Principal component analysis (PCA) has revealed the ability of both biosensor systems to discriminate between milk samples with different fat contents, but with some differences, attributed to the structure employed in the detection.

Keywords: silver nanowires, silver nanoparticles, electronic tongue, electrochemical biosensor, enzymes, milk

1. Introduction

Milk is an essential component of human diets, although its composition varies depending on the brand, storage period, animal origin, and the components that make milk up. As a result, it is vital to assess the composition and quality of milk from the time it is obtained to the time it is consumed [1].

The implementation of biosensors in food industry has taken an essential role due to the fact that these devices are able to provide qualitative information with high specificity and selectivity with the advantages of being portable, miniaturizable, cheap, stable, fast and show effective on-line response [2,3].

The use of nanomaterials in electrochemical sensors and biosensors has attracted researchers' attention. However, using specialized sensors in the analysis of complicated matrices to determine specific parameters, is insufficient to generate useful data. The development of arrays of sensors may be the solution to avoid irrelevant information. For this reason, the implementation of electronic tongues (ET) may be the solution to determine important parameters and properties of complex samples and to be able of discriminate between them [4]. Metallic nanostructures are excellent sensing materials due to their high surface area, high aspect ratio, electrical conductivity, and electrocatalytic characteristics, which provide good sensing properties for the detection of a wide range of analytes. Moreover, it has been demonstrated that their morphology is essential on the electrochemical response and their ability to improve the electron mobility.

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Furthermore, due to their large specific surface area and high surface free energy, metallic nanomaterials may strongly adsorb biomolecules maintaining their bioactivity due to their biocompatibility [5].

This research aims to create a bioelectronic tongue (bioET) for milk analysis. Two electrochemical biosensor arrays in which AgNPs (bioET-1) or AgNWs (bioET-2) have been deposited as enzyme supports, were created and tested for their capacity to differentiate between milk samples with variable fat and nutritional content. For this purpose, unsupervised (PCA) multivariate classification methods were used to assess the bioETs' performance. Finally, the discrimination abilities of both sensor arrays were evaluated to determine which silver nanomaterial provided the best results.

2. Results and discussion

2.1. Sensors development

Metallic nanomaterials previously synthetized were deposited onto BDD substrates by a cast of 25 µL suspension of AgNPs or AgNWs. After drying, 25 µL of the corresponding enzyme (5 mg/mL) was drop-casted onto the modified electrode. Finally, 25 µL of Nafion® was drop-casted and let dry overnight at room temperature.

2.2. Milk samples

The samples collection consisted of 6 groups of milks purchased in the supermarket, including milks with different fat content (skimmed, semi-skimmed and whole), and different nutritional content (classic and lactose-free).

2.3. Electrochemical characterization

The electrochemical responses of the bioETs were studied by cyclic voltammetry in a 50% diluted milk 0.1 M KCl solution.

Figure 1 illustrates the electrochemical response of the developed sensor arrays with the bioETs for one type of milk (Classical Whole milk). As it can be observed, when the biological material is immobilized on the modified electrode surfaces, the increase in the intensity of the cathodic and anodic peaks is more pronounced in the presence of nanowires in the AgNWs bioET.

The results demonstrate that silver nanowires outperform silver nanoparticles in terms of electrocatalytic activity because the electrical conductivity and the electrocatalytic properties of the developed sensors have been enhanced when AgNWs are used as electron mediators. Furthermore, because AgNWs have a high surface-to-volume ratio, they have more surface active sites, allowing for improved enzyme immobilization [5].

As is well known, the ultimate electrocatalytic activity of electrode materials was impacted by surface shape, nanoparticle size, and fabrication technique. For this reason, it can increase electrode surface area depending on the chosen morphology, but mass transport behavior of silver nanoparticles, for example, is difficult to define because nanoparticles are randomly spread or aggregated, whereas nanowires, increased in high proportion the electrical conductivity and mass transport in comparison with them [6].

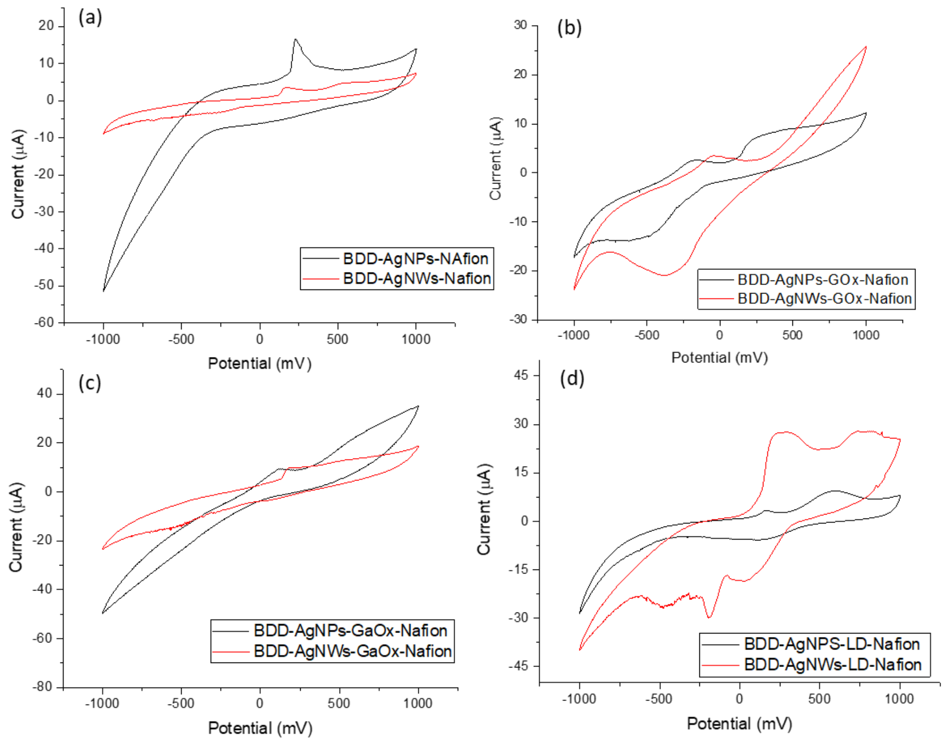

Figure 1. Electrochemical response of the sensors of AgNPs bioET (black) and AgNWs bioET (red) in a 50% diluted Classical Whole Milk in 0.1 M KCl solution.

Multivariate data analysis was used to evaluate the responses of the proposed bioETs in order to discriminate between different types of milks.

Data were evaluated using principal component analysis for this purpose (PCA).

Figure 2 shows the scores plot of both bioETs. As Figure 2.a shows the accumulated explained variance for the two first components of AgNWs bioET was distributed in 49% (PC-1) and 30% (PC2) and for the AgNPs biET (Figure 2.b) was 49% (PC1) and 19% (PC2). As it can be shown in the figure, the scores plot of the array that uses nanoparticles displays certain overlapping between Classical Skimmed milks and Classical Whole, appearing in the same quadrant, it is obvious that the AgNPs bioET presents difficulties to effectively discriminate milks based on their fat content. However, in both cases a clear discrimination of milks according the nutritional contents was achieved. This result indicates that the AgNWs bioET provides a higher proportion of the explained variance for the same number of PCs.

These findings can be explained by the fact that immobilizing the enzyme on nanomaterials improves the enzyme's catalytic effectiveness greatly due to its operational stability. However, it has been demonstrated that the size, morphology and charge distribution of the nanomaterial can variate the effects on enzyme structure and corresponding activity [7]. When nanowires are used as support for enzyme immobilization, different reactivity and good enzyme immobilization is obtained through easier interactions between enzyme and material surface due to providing higher surface / volume ratio in comparison with nanoparticles, thus could be the reason why the discrimination capability of the bioET is higher when AgNWs are used as electrocatalytic material.

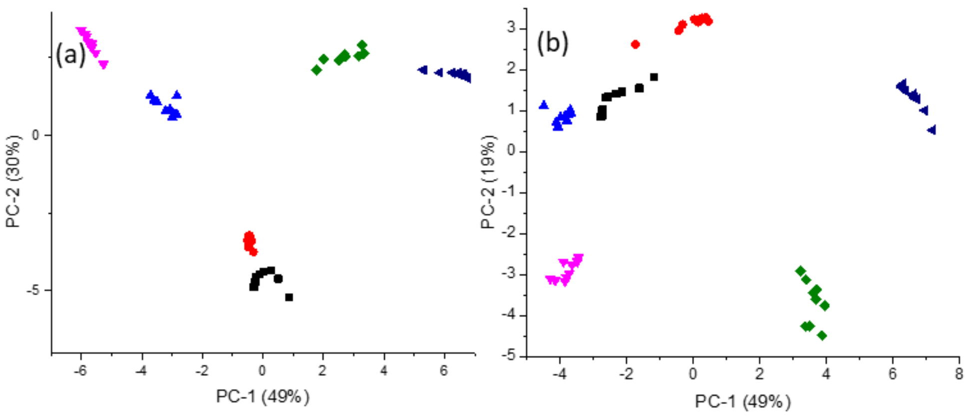

Figure 2. PCA score-plot analyzed using a 4 sensors array (a) AgNWs bioET or (b) AgNPs bioET, of the 6 milks of different fat content and nutritional characteristics: Classical Skimmed (black), Classical Skimmed Lactose free (red), Classical Whole (blue), Classical Whole Lactose free (pink), Classical Semi Skimmed (green) and Classical Semi Skimmed Lactose free (dark blue).

3. Conclusions

In this work, two bioelectronics tongues modified with AgNWs or AgNPs has been developed to discriminate between milks with different nutritional composition. The electrochemical responses based on cyclic voltammetry, of the two different bioETs have been crucial to evaluate the influence of the morphology of the conductive material. Furthermore, the statistical analysis based on PCA loading plots have demonstrated the high capability of the sensors arrays to discriminate between milks.

Finally, it can be concluded that the use of AgNWs could be a better choice because their excellent electrocatalytic properties.

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Conflicts of Interest: Authors must identify and declare any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results. Any role of the funders in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript, or in the decision to publish the results must be declared in this section.

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