Antioxidants detection with nanostructured electrochemical sensors

M.L. Rodriguez-Mendez[1], C. Garcia-Hernandez[1], C. Medina-Plaza[1], C. Garcia-Cabezon[2], D. Paniagua[1], S. Rodriguez[1], F. Pedrosa[2], J.A. de Saja[3].

[1]Department of Inorganic Chemistry, Engineers School, Universidad de Valladolid, 47011 Valladolid, Spain. E-mail: mluz@eii.uva.es.
[2]Department of Materials Science, Engineers School, Universidad de Valladolid, 47011 Valladolid, Spain.
[3]Department of Condensed Matter Physics, Faculty of Sciences, Universidad de Valladolid, 47011 Valladolid, Spain.

Abstract

The use of quick, reliable and cheap sensors for the detection of chemical compounds represents an important need in the food industry. Antioxidants are among the analytes that must be monitored and measured in order to guarantee the quality of final products. In particular, phenolic and polyphenolic compounds are interesting antioxidants because they inhibit or delay the oxidation processes by blocking the initiation or of oxidizing chain reactions.
Previous works have demonstrated that voltammetric electrodes chemically modified with electrocatalytic materials can be used to detect such compounds in musts and wines [1]. Electrodes chemically modified can be an advantage because the electrocatalytic activity of a variety of modifiers (carbon nanotubes, nanoparticles, porphyrins, phthalocyanines, etc) can reduce the oxidation potential while increasing the intensity of the response. In turn, electrodes can be prepared using a variety of techniques from simple Carbon Paste Electrodes (CPE) or Screen Printed Electrodes (SPE) to extremely sophisticated nanostructured sensors prepared using the Langmuir-Blodgett (LB) or the electrostatic Layer-by-Layer (LbL) techniques.

Nanostructured sensors have the advantage of the enhanced number of active sites producing an increase in the intensity. Moreover, the control of molecular architectures afforded by these techniques can led to the development of a variety of devices where synergy is achieved by combining distinct materials, including organic-inorganic hybrids [2].
For instance, combinations of phthalocyanines with nanoparticles or carbon nanotubes in LB films have been developed and their structures have been analyzed. The films have been used as voltammetric sensors for the detection of compounds of interest in the food industry (i.e. citric acid) (Figure 1). The combination of phthalocyanines with carbon nanotubes (CNT) produced a clear increase in the intensity of the responses due to the synergy promoted by the pi-pi stacking between both components.

Similarly, gold nanoparticles in LB films produced an increase in the sensitivity towards phenols and detection limits of 10^{-7} mol.L^{-1} were attained. Similar detection limits could be obtained by combining phthalocyanines with silver nanoparticles in LbL films.

Finally, voltammetric biosensors have also been prepared using the LB technique (Figure 2). LB films combining phthalocyanines and amphiphilic molecules provided biomimetic environments where enzymes could preserve their functionality. The role of the molecular interactions in the electrocatalytic properties in biomimetic systems has been studied by combining enzymes with different electron mediators and the existence of synergistic effects has been evidenced. Detection limits as low as 10^{-8} mol.L^{-1} towards phenols can be attained for the detection of phenols.

It has been demonstrated that the arrays formed by voltammetric electrodes (voltammetric electronic tongue) modified with phthalocyanines are able to discriminate complex liquids. Arrays of sensors based on MPcs have been successfully used to discriminate wines of different qualities, grape variety or wines prepared using different techniques or aged in different types of oak barrels [3]. The capability of discrimination is due to the sensibility of phthalocyanine sensors towards redox (i.e. polyphenols) and acids present in wines. Their electrocatalytic properties play also an important role in the discrimination capabilities of the array.

References

[1] Rodriguez-Mendez, M.L., Medina, C., De Saja, J.A., Apetrei, C., Muñoz, R. Eds. Lvova, L., Kirsanov, D., Di Natale, C., Legin, A. Pan Stanford Publisheing, Chapter 4 (2012) 70-109.
[2] Pavinatto, F.J., Fernandes, E.G.R., Alessio, P., Constantino, C.J.L., De Saja, J.A., Zucolotto, V., Apetrei, C., Oliveira O.N.Jr., Rodriguez, M.L. J. Mat. Chem. **21** (2011) 4995-5003.
[3] Prieto,N., Gay, M., Vidal, S., Aagaard, O., De Saja, J.A., Rodriguez-Méndez M.L. Food Chem. **129** (2011) 589-594.

Acknowledgements

The authors are grateful to FEDER and to the Spanish Ministry of Science-CICYT (Grant AGL2012-33535), Junta de Castilla y León (VA-032U13) and FPI-UVa for the financial support.

Figures

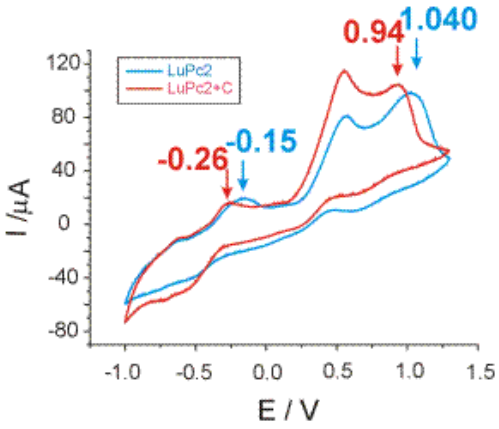

Figure 1. LB film based sensors exposed to 0.1 M citric acid. (Blue) Lutetium bisphthalocyanine films, (red) Lutetium bisphthalocyanine + CNT films.

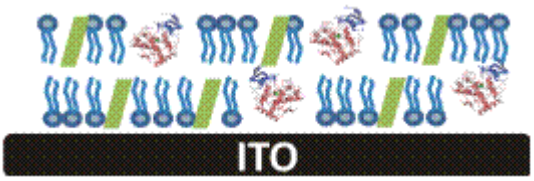

Figure 2. Voltammetric biosensor formed by an amphiphile, a phthalocyanine and an enzyme (tyrosinase).