Nanostructured Electrode Surface with Octasilsesquioxane-Ferrocenyl Dendrimer as a sensitive Tryptophan sensor

Lorena fernández[1], M. P. García Armada[1], J. Losada[1], M. Herrero[2], B. Alonso[2], C. M. Casado[2]

[1] Dpto. Ingeniería Química Industrial y M. A., Universidad Politécnica de Madrid,José Gutierrez Abascal, 2,28006 Madrid, Spain
[2] Dpto. Química Inorgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain
pilar.garcia.armada@upm.es

Abstract.
L-Tryptophan is one of the essential amino acids for the human body and a vital constituent of protein biosynthesis of living organisms. In many biochemical processes, it is an essential precursor of hormone for neurotransmitter serotonin and other relevant biomolecules. Due to L-Trp cannot be synthesized directly in human body and the scarce presence in vegetables; it is commonly added to dietary, food products as a food fortifier and to pharmaceutical formulations. However, when improperly metabolized, a waste product will be created in the brain to cause hallucinations and delusions. So, to establish a simple, accurate, rapid and inexpensive method for the determination of l-Trp in food, pharmaceutical products and biological fluids is very necessary [1]. At present, many methods have been proposed for the determination of tryptophan, including high-performance liquid chromatography (HPLC), HPLC with fluorescence detection, liquid chromatography–tandem mass spectrometry, spectrophotometry, spectrofluorometry, capillary electrophoresis technique, and especially infrared optical sensor [2]. Various electrochemical L-Trp sensors based on several nanomateriales have been reported [3-6]. However these new sensors are simple and show better sensitivity than the majority of them.
Ferrocenyl dendrimers based on octasilsesquioxane cores (Figure 1) exhibit the pattern of communicating ferrocenyl sites with two distinct, separated oxidation waves. The dendrimers were also deposited on electrode surfaces which were investigated via CV, showing formation of electroactive films with promising results for the use of these materials in the development of biosensors [7]. The morphologic studies showed that films of this dendrimer offer a globular surface (figure 2) very promising in order to immobilize several materials as well as sensitive sensor with a big effective surface.
In this work we present a novel and selective tryptophan electrochemical sensor, in a nanostructured electrode surface prepared with the electrodeposited octasilsesquioxane-ferrocenyl dendrimer.
Once the modified electrodes were characterized, the kinetics was studied by application of Laviron model. The ΔEp values remained invariable with the increasing scan rate indicating that there are no kinetic limitations [8]. The Developed new sensor oxidizes efficiently the tryptophan at pH = 2 and an applied potential of 0.896 V vs. SCE with a sensitivity of 0.60 mA/mM cm^2 and a detection limit of 318 nM. In addition, the developed sensor allows to measure tryptophan into three consecutive linear ranges: 5 - 54.5 μM, 54.5 – 113 μM and 113 – 325 μM.
The effect of the interferences caused by ascorbic acid, dopamine and uric acid was also studied and a method for the determination of tryptophan in presence of these interfering substances. Also we have carried out the simultaneous determination of tryptophan, ascorbic acid, dopamine and uric acid.
This new biosensor has been applied successfully to determine tryptophan in real samples of a tryptophan – B vitamin pharmaceutical formulation and to simultaneous determination of tryptophan and uric acid in human urine samples.

References

[1] Xi Ba, Liqiang Luo, Yaping Ding, Xiao Liu, Sensors and Actuators B 187 (2013) 27– 32.
[2] Xiaohong Xi, Zhixiang Zheng, Yan Zhang, Xiaojuan Zhao, Chunming Wang, Sensors and Actuators B 192 (2014) 42– 50
[3] H. Beitollahi, M. A. Taher, A. Hosseini, Measurement **51** (2014) 156–163.
[4] C. Wang, R. Yuan, Y. Chai, S. Chen, F. Hu, M. Zhang, Analytica Chimica Acta **741** (2012) 15–20.
[5] P. Deng, Z. Xu, Y. Feng, Materials Science and Engineering **35** (2014) 54-60.
[6] S. Güney, G. Yildiz, Electrochimica Acta **57** (2011) 290–296.
[7] Marta Herrero, Beatriz Alonso, , Pilar García -Armada, and Carmen M. Casado, Organometallics **689** (2004) 2799–2807.
[8] H. D. Abruña, Electrochemical Interfaces: Modern Techniques for in-situ Interface Characterization. VCH Pub. (1991) Florida, U.S.A.

Figures

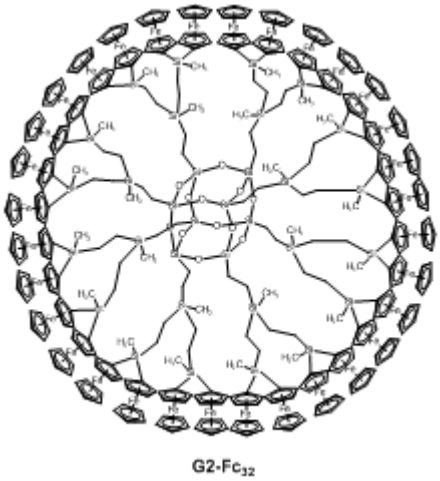

Figure 1. Octasilsesquioxane-Ferrocenyl Dendrimer

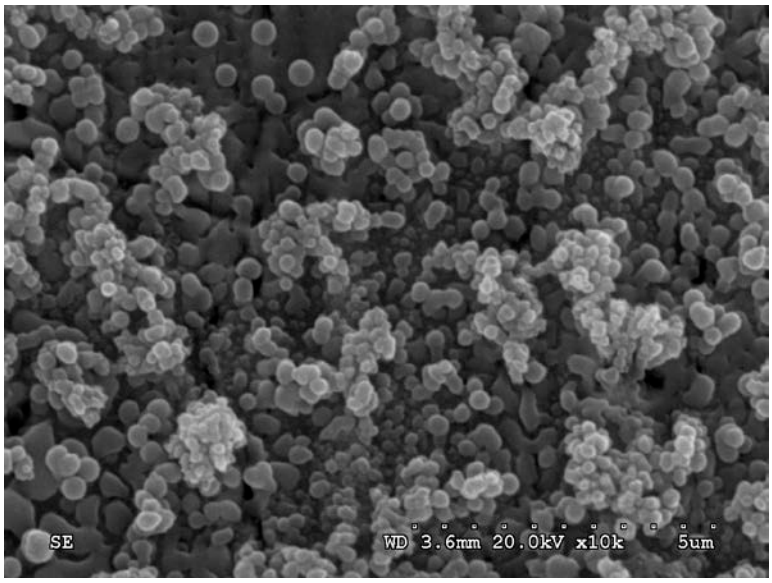

Figure 2. SEM micrographs of Pt wires modified with a actasilsesquioxane-ferrocenyl dendrimer layer.