Amperometric Dopamine Sensor Based on Gold Nanoparticles Synthesized Within an Electrodeposited Dendrimer as Template

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Abstract.

A novel and selective electrochemical sensor, based on Au nanoparticles (AuNPs) obtained with a DAB-ferrocenyl dendrimers [1] as template previously electrodeposited on a Pt electrode, has been developed for the determination of dopamine (DA). In this work, the kinetics and analytical properties of the modified electrodes are described.

In a similar way than in homogeneous media [2], inter-dendritic Au nanoparticles have been obtained when electrodes modified with the first generation dendrimer were used. In this work, we show that well-dispersed non-aggregated Au nanoparticles having diameters of less than 5 nm can be obtained by this way.

The AuNps were obtained from a 0.1 mM $HAuCl_4$ solution and subsequent chemical reduction with $NaBH_4$. The direct reduction of Au (III) by the amidoferrocenyl groups in the dendrimer [3] does not occur because $HAuCl_4$ is reduced much more slowly to gold nanoparticles due to the anodic shift of the redox potential compared to that of the parent aminoferrocenyl dendrimer. The formation of AuNps was followed by UV-Vis spectrophotometry by the appearance of the plasmon band at 530 nm in modified ITO electrodes [4]. The AuDEN modified electrodes were characterized by Scanning Electron Microscopy (SEM), which let us estimate the nanoparticles size and to prove that none aggregate is formed in the film.

Once the modified electrodes were characterized, the kinetics of AuDEN was studied and a k_{obs} of 4.65 s^{-1} was obtained from the variation of peak potentials with increasing scan rates by application of Laviron model. The k_{obs} obtained with electrodes modified without AuNPs was 2.98 s^{-1}. These constants indicate that the electrocatalytic material is confined on the electrode surface and the electronic transfer in fast enough. In addition, the composite AuDEN shows better electron transfer properties than the DEND alone.

The AuDEN electrode showed excellent electrocatalytic activity toward the oxidation of DA in the phosphate buffer solution (pH 7.0). The Koutecky-Levich studies with rotary electrode let us know the kinetics of the electrooxidation of dopamine and determine the rate constant, $K = 1.7 \times 10^4$ $M^{-1}s^{-1}$, which indicates a better electrocatalytic behavior than those of other related electrochemical dopamine sensors.

The good electrocatalytic behavior has allowed us to develop an efficient sensor capable of measuring DA from +0.15 V (vs. SCE). The linear relationship between the current response and the concentration of DA ranging from 0 to 100 μM was obtained with a detection limit of 257 nM at pH 7.0, sensitivity of 0.102 A M^{-1} cm^{-2} and higher values for increasing applied potentials, reaching a linear range from 0 to 500 μM at a measuring potential of 0.30 V with sensitivity of 0.499 A M^{-1} cm^{-2} and detection limit of 80 nM. In order to test possible applications for the AuDEN sensor, the interferences caused by ascorbic acid (AA) and uric acid (UA) were studied by cyclic voltammetry and differential pulse voltammetry. The obtained electrochemical sensor could effectively minimize these interferences using sodium dodecyl sulfate micelles as masking agent. DA can be determined in the presence of ascorbic acid (AA) because both compounds were well-separated with a potential difference of 0.22 V on the modified electrode. The UA does not interfere because its oxidation process occurs at a potential of 0.56 vs. SCE.

Based on its excellent electrochemical performance and easiness of preparation, the proposed electrode may provide a promising alternative in routine sensing applications.

At present, we are studying the application of the sensor to real samples.

References

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Figure 1. Scheme of the developed Dopamine sensor.

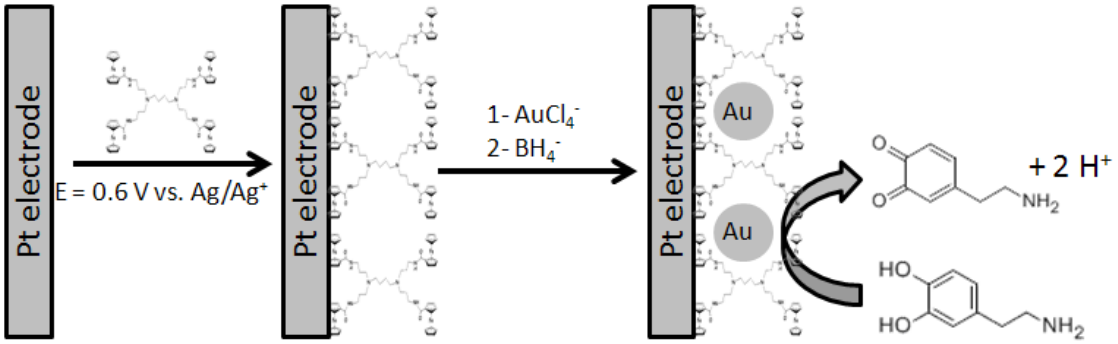

Figure 2. Cyclic voltammograms of the AuDEN sensor in absence and presence of Dopamine 0.5 mM. Supporting electrolyte: $NaClO_4$ 0.1 M/ phosphate buffer 0.01 M, pH=7.0. Scan rate 20 mV s^{-1}.