Decorating carbon nanotubes with polyethylene glycol-coated magnetic nanoparticles for implementing highly sensitive enzyme biosensors

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Abstract

Last challenges in electrochemical analysis have been predominantly linked to the use of nanosized materials for the construction of sensing electrodes. This trend is justified by the unique structural, physico-chemical and surface-to-volume ratio properties of nanomaterials. In addition, they also offer the possibility to design a wide variety of original tree-dimensional nanoarchitectures at the electrode surface, based on the single or combined use of different nanomaterials [1]. Multi- and single walled carbon nanotubes (SWNT) are among the nanomaterials more widely used in electroanalysis due to their relevant chemical stability, protein adsorption ability, electro-conductive properties and capability to promote fast electron transfer reactions of some enzymatically generated species. In this regards, a large number of nanostructured biosensors based on carbon nanotubes have been reported, in which they have been used alone or combined with other nanomaterials [2]. During las years, special interest have been devoted to prepare carbon nanotubes-based magnetic nanomaterials, not only for analytical applications but also for magnetic data storage, microelectronic, xerography and magnetic resonance imaging. Such kind of hybrid nanomaterials can be prepared by filling the nanotubes with the magnetic material or by coating the outer wall of the nanotubes with magnetic nanoparticles. The later is, by far, the strategy most commonly used because it is easier to manipulate the outer wall surface rather than the inner cavity of nanotubes, offering in this way more experimental alternatives. In general, decoration of carbon nanotubes with magnetic nanoparticles has been accomplished by adsorption, covalent attachment, π-π stacking and coating with polymeric films containing the iron oxide nanoparticles [3].

In this work we propose a novel approach for decorating SWNT with magnetic nanoparticles, based on the non-covalent attachment of monomethoxypolyethylene glycol (PEG)-coated superparamagnetic Fe3O4 nanoparticles on the nanotube surface (Figure 1). For this purpose, superparamagnetic Fe3O4 nanoparticles were first coated with (3-aminopropyl)triethoxysilane and further branched with monomethoxypolyethylene glycol chains. These nanoparticles were employed for the non-covalent surface modification of SWNT, conferring them magnetic properties.

This nanomaterial was employed to immobilize the enzyme xanthine oxidase in order to construct magnetically modified disposable gold screen-printed electrodes as bioelectrodes for the determination of xanthine. The electroanalytical properties of the biosensor were modulated by the nanomaterial composition, being optimal at a SWNT:magnetic nanoparticles ratio of 1:27. The resulting biosensor showed a linear dependence on the xanthine concentration in the 0.25-3.5 µM range with a fast amperometric response in 12 s. The biosensor also showed a noticeable high sensitivity of 1.31 A/M cm2 and a very low detection limit of 60 nM, which can be compared advantageously with other biosensor designs for xanthine.

References

Figure 1. Schematic display of the construction of Fe$_3$O$_4$/APTES-PEG-XO/SWNT magnetic nanomaterials-based biosensors. A) and B): SEM and TEM analysis of the hybrid magnetic nanomaterial, respectively.