Mixed diazonium/PEDOT-functionalized graphene electrode for antioxidant biomarkers detection: proof-of-concept for integration on silicon substrate

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During the last two decades, a growing number of research works has been devoted to oxidative stress, which represents a major problem with respect to healthiness, as it is known to be involved in ageing processes and has been suggested to be one of the potential causes for cataract, cancers, cardiovascular and degenerative diseases (Parkinson, Alzheimer) and even male infertility [1]. Among the low molecular weight antioxidant species, ascorbic (AA) and uric (UA) acids are of particular interest since they are present in most biological fluids and thus may be considered as biochemical markers in a lot of pathologies related to oxidative stress (preeclampsia disease, neonatal hypoxia, coronary heart diseases...) [2].

Recently, we have reported on a sensor based on a gold electrode functionalized by an electrogenerated polymer, namely poly[3,4-ethylenedioxythiophene] (PEDOT), for the simultaneous assay of UA and AA [3-5]. This sensor exhibited very good analytical performances including selectivity. We further improved the sensor by using a glassy carbon (GC) electrode functionalized by successive electrodeposition of 4-thiophenylbenzene diazonium (TBD) and (PEDOT) [6]. The use of the TBD layer induced an enhancement of the sensitivity, a lower detection limit for AA and an improved lifetime of the sensor. However, GC is hardly compatible with the silicon technologies required for a cost-effective mass production of integrated microelectrodes and the associated electrochemical microcells.

In the present work, we have developed the proof-of-concept of a mixed TBD/ PEDOT functionalized graphene electrode integrated on a silicon substrate for the simultaneous detection and assay of UA and AA. The catalytic chemical vapour deposition (CVD) synthesis of graphene on either platinum (Pt) foils or thin films will be detailed, together with its electrochemical functionalization by both TBD salt grafting and EDOT electropolymerization. The characterization of the resulting modified electrodes by Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cyclic voltammetry (CV) will be presented. The analytical performances obtained for AA and UA detection and quantification will be also discussed, and a focus will be given to graphene advantages over GC in terms of selectivity and sensitivity.

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