Nitrogen doped reduced graphene oxides as electrode material of electrochemical sensors

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ABSTRACT

The development of new methods for the determination of catecholamine neurotransmitters is very important due to the need to improve of diagnosis and therapy of specific diseases associated with the abnormal level of these compounds in human body. A promising direction is the improvement of electrochemical sensors using a wide range of new carbon nanomaterials as electrode materials such as carbon nanotubes and graphene materials.
The aim of this work was to synthesize reduced nitrogen-doped graphene oxides and their composites with gold nanoparticles for electrochemical sensors of dopamine and epinephrine. X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (FESEM, SEM-EDX) were used to characterize the obtained graphene nanomaterials. N-doped graphene materials (N-rGO) were synthesized in a hydrothermal process using graphene oxide and compounds containing nitrogen in their structure such as amitrole, urea and julolidine. Depending on the type of nitrogen precursor, N-rGOs with the dominant ratio of pyridine, pyrrole or amide and amine groups were obtained. The synthesis conditions for obtaining N-rGO with similar distribution of nitrogen type bonds, but with different oxygen content, were also elaborated using amitrole as a nitrogen precursor. The resultant N-rGOs were used to modify the glassy carbon electrode (GCE) for the detection of dopamine (DA) and epinephrine (EP). Cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were applied in the evaluation of electrochemical sensors. The role of oxygen and particular nitrogen groups in the DA and EP detection process was determined and the optimal composition of the electrode material was established. The best electrochemical detection parameters such as the detection limit of 335 nM and sensitivity of 3.51 μA/μM for DA and 0.62 μA and 1.45 μA/μM for EP were obtained by modifying the GCE electrode with a N-rGO of pyrrolic character of nitrogen functionalities and the oxygen content in the range of 11-12 at. %. Electrochemical sensors with the GCE modified using N-rGO with comparable contribution of different nitrogen groups, but with different oxygen content, were also investigated. The best sensor performance was revealed when N-rGO with the lowest oxygen content was used. DA detection was possible in a linear concentration range from 0.5 to 150 μM with a detection limit of 410 nM. Further improvement of the sensor parameters was achieved by deposition Au nanoparticles on the surface of the N-rGO from the $HAuCl_4$ solution using CV technique. Very low LOD values of 173 nM for DA and 0.53 μM for EP were obtained via modifying the GCE electrode with N-rGO/Au. In addition, the presence of pyrrolic nitrogen secured high detection sensitivity of 2.66 and 0.81 μA/μM for DA and EP, respectively.
The results presented in the dissertation pave the way for research aimed at developing a highly effective electrode material for electrochemical DA and EP sensors using N-rGO and Au nanoparticles. Furthermore, the studies allow for in-depth understanding of the role of individual nitrogen groups in DA and EP detection, and thus facilitate the design process of an analytical device with the desired parameters.