Modified graphene materials for electrochemical sensing applications

Abstract

Nowadays, due to an increased awareness in the field of health state monitoring and environment protection, great research interest has been focused on the development of novel techniques for appropriate sensing of several analytes as neurotransmitters and pharmaceuticals. Electrochemical sensors appear as promising alternatives for currently applied methodologies as High-Performance Liquid Chromatography (HPLC) or spectroscopy techniques. The key element in achieving a suitable electrochemical sensing setup is the working electrode. Traditionally, non-modified working electrodes are characterized by weak current responses originated from redox processes of analytes of interest. One of the approaches to enhance recorded currents and resulting sensor working parameters is the development of novel and efficient active electrode materials. Moreover, great efforts have been focused on miniaturizing currently used setups, which would enable to test small sample volumes in real analysis time.

The aim of this work was develop and apply graphene-based materials and their composites as GCE modifiers, for electrochemical detection of dopamine (DA), ascorbic acid (AA), uric acid (UA) and diclofenac (DCF), which enable detection of above-mentioned analytes in low concentrations with high sensitivity. Three groups of materials based on reduced graphene oxide (RGO) were synthesized. The first group was based on nitrogen-doped RGO (NRGO) and its composites with gold nanoparticles (AuNPs/NRGO), the second group includes composites of thermally reduced RGO (TRGO) with polyaniline (PANI/TRGO), and the last group of materials covered binary and ternary RGO composites with iron and tin oxides and PANI (FSG and PFSG).

Synthesized composites and their components were thoroughly investigated using advanced analytical methods (FESEM, HRTEM, XPS, EA, N_2 sorption, XRD, sheet resistance measurements). The impact of the morphology and chemical composition of composites on the detection of above mentioned analytes using cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) was defined, including determination of sensor working parameters such as limit of detection (LOD), linear range (LR), sensitivity, selectivity and long-term stability.

Beneficial impact of nitrogen doping of the graphene material on the homogenous distribution of AuNPs and resulting electrochemical properties was revealed. Moreover, the amount of PANI in the PANI-TRGO composites was optimized and the impact of reduction

temperature of TRGO on the PANI distribution was determined. |A synergistic effect between composite counterparts of PFSG was demonstrated. The most improved sensor working parameters in electrochemical DA detection were recorded on PFSG/GCE (LOD = 76 nM). The lowest LOD values in AA and UA detection were obtained for GCEs modified with AuNPs/NRGO (LOD = 44 μM) and FSG15:85 (LOD = 328 nM), respectively. Whereas, in simultaneous detection of DA, AA and UA, AuNPs/NRGO/GCE was the most effective. In case of DCF detection the lowest LOD was recorded on GCE modified with TRGO700 (LOD = 61 nM).

Moreover, a novel miniaturized setup using inkjet-printed electrodes for DCF detection was designed. Inkjet printed electrodes were prepared using graphene-based ink (GO) printed on Kapton® and then subsequently thermal reduction process was performed. The high effectiveness of reduction of GO on Kapton® was revealed.

The results of this thesis open a new line of research on novel electrochemical sensor based on modified graphene materials.