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ARTICLES

Rhenium Nanoclusters as Modifiers of Immunosensors in the Determination of Tricyclic Antidepressants

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Abstract—The properties of hexarhenium chalcogenide nanoclusters ($K_4[\{Re_6S_8\}(OH)_6]\cdot 8H_2O$ and $K_4[\{Re_6S_8\}(CN)_6]\cdot 8H_2O$) in combination with carbon nanomaterials (carbon nanotubes and graphene oxide) are studied by voltammetry, electrochemical impedance spectroscopy, atomic force microscopy, and spectrophotometry and their screening is performed for use as hybrid modifiers of screen-printed graphite electrodes in immunosensors in order to improve analytical characteristics. The high negative charge of nanoclusters can be considered the driving force of the adsorption of clusters in the formation of electrodes modified by hybrid nanomaterials. It was found that hexarhenium chalcogenide nanoclusters possess electrochemical activity, which was first used to register immunochemical interactions. The change in the resistance of electron transfer made it possible to choose the best hybrid nanomaterials. The parameters of the surface roughness of the modified electrodes associated with the height properties of the irregularities were estimated. The use of hexarhenium chalcogenide nanoclusters in combination with carbon nanomaterials as hybrid nanomodifiers has made it possible to develop highly sensitive and selective amperometric and impedimetric immunosensors for the determination of tricyclic antidepressants (amitriptyline, desipramine, and imipramine) in pharmaceuticals and urine. The limit of quantification (LOQ) is at the level $(4–7) \times 10^{-11}$ M. The relative standard deviation does not exceed 5%.

Keywords: immunosensor, tricyclic antidepressants, chitosan, polyether polyol, carbon nanotubes, reduced graphene oxide, hexarhenium chalcogenide nanoclusters

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Currently, an urgent task is to control the quality and identify counterfeit products, determine medicinal substances, including trace amounts, in pharmaceuticals and biological fluids, and also use the data obtained to assess the efficiency of therapeutic prescriptions for various diseases [1–3]. For these purposes, various methods were presented [4–7] for the determination of tricyclic antidepressants (TCA), drastic drugs used for the effective treatment of mainly depression. Chromatographic methods are mainly used, however, they require a long and complex sample preparation and large volumes of high-purity and sufficiently toxic solvents [8–10].

As an alternative, it is promising to use biosensor devices for accessible, rapid, and relatively uncomplicated versions of analysis that are not inferior in sensitivity and selectivity to chromatographic procedures [11–14]. Previously, it was shown that the modification of the transducer surface as a sensor base with various nanomaterials, including carbon (carbon nanotubes, fullerene, and graphene oxides) and metal nanoparticles, promotes the formation and significant enhancement of the analytical signal [12, 13]. The luminescent properties of hexarhenium complexes have been successfully used to create sensors and cell markers [15–17].

For the better immobilization of nanomodifiers on the surface of transducers, polymer compounds were used, in particular, chitosan, which has proven itself well in this regard [17]. Few works were devoted to the use of polyether polyols for these purposes [18, 19].

The aim of this work was to develop electrochemical immunosensors based on screen-printed graphite electrodes modified with hybrid nanomaterials (carbon nanotubes (**CNT**) or graphene oxide (**GO**) in combination with hexarhenium chalcogenide clusters ($K_4[\{Re_6S_8\}(OH)_6]\cdot 8H_2O$ and $K_4[\{Re_6S_8\}(CN)_6]\cdot 8H_2O$) for use in the quality control of medicinal substances in corresponding pharmaceutical preparations