Functional multilayer films formed with reduced graphene oxide

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Graphene - a new material consisting of single layer of sp^2 – bonded carbon atoms with unique two-dimensional nanostructure attracts attention of many specialists from various branches of science. Since its discovery in 2004 [1], graphene has emerged as the "material of the future" due to its unique nanostructure and electrical, thermal and mechanical properties [2,3]. It is considered as a promising material for application in various technological fields such as transparent conductive films [4], solar cells [5], gas storage media [6] or next generation of electronic devices [7].

Sequential adsorption of charged nanoobjects, as polyelectrolytes, micelles, nanoparticles or proteins (known also as the "Layer by layer" (LbL) deposition method) [8], is considered as one of the most promising techniques of surface modification and formation of highly tailored functional thin films for the wide range of possible applications, including: selective membranes, biosensors and drug delivery systems. As graphene is a hydrophobic material, it cannot be directly used for construction of multilayer films with the LbL method. Therefore, in this work we have proposed to use suspension of graphene oxide (GO) for formation of such films and its subsequent reduction to the reduced graphene oxide (rGO). Since GO is negatively charged it can be easily suspended in water and used as an anionic layer for the film formation.

For the formation of multilayer films we deposited sequentially, at various substrates (gold, polyimide), layers of polycation polyethylene imine (PEI) or poly(allylamine hydrochloride) (PAH) and GO. Then we compared several reduction methods to turn GO into reduced graphene oxide, e.g. thermal reduction, UV irradiation, chemical reduction by hydrazine and electrochemical reduction. We noticed that the thermal reduction of GO above the temperature 180^{o}C is the most effective process leading to formation of sp^2-bonded carbon atoms. The examination of XPS spectra indicated that after the reduction the ratio of the sp^2 carbon increased to c.a. 80 at.%. The atomic ratios of carbon to oxygen for GO before and after reduction determined by XPS were corroborated by EDS analysis. The structure and properties of the films before and after reduction were investigated also using ellipsometry, ATR-FTIR spectroscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

By measuring surface conductivity with the four point method we showed that using the proposed method it is possible to obtain ultrathin conductive films on quartz and polyimide (PI) plates. Formation of such films on PI allows creating flexible electrodes, which can find applications in biomedicine as disposable, electroactive sensors. The same methodology was applied to obtain the electroactive films containing PAH/Prussian blue nanoparticles/rGO at the gold electrode surface. We demonstrated that such sensor layers can be used for the electrochemical detection of hydrogen peroxide.

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