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Enhancement of the Electrocatalytic Properties of Prussian Blue Containing Multilayer Films Formed by Reduced Graphene Oxide

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ABSTRACT

In our work we focused on the electroactive and electrocatalytic properties of multilayer films formed from polyelectrolytes (PE) and Prussian blue nanoparticles (PBn), enhanced by addition of reduced graphene oxide (rGO). Films containing poly(allylamine hydrochloride) (PAH) and PBn were constructed using the layer-by-layer adsorption method. Graphene oxide (GO) was deposited from its aqueous suspension forming additional layers of the film. Then they were exposed to the elevated temperature, 180 °C to turn graphene oxide into its reduced form. We demonstrated, by cyclic voltamperometry, that the presence of conductive rGO greatly enhanced the electroactive properties of the PE/PB multilayer films. Simultaneously, they were also up to 40 times more effective for the electrocatalytic redox processes of hydrogen peroxide.

The layer-by-layer (LbL) deposition technique is an efficient method for obtaining functional multilayer films. In the standard LbL process substrates are sequentially dipped in the solutions containing positive or negative polyelectrolytes, which adsorb onto the charged support mainly via electrostatic interactions [1]. The properties of obtained multilayer films largely depend on the type of polyelectrolytes used, number of deposition cycles and conditions of film formation [2]. In addition any charged nano-objects can be incorporated into polyelectrolyte multilayer structure, including biological molecules (e.g. DNA, proteins, viruses, polypeptides) or inorganic nanoparticles (e.g. silica, clays, gold, magnetite, silver, graphene) [2–5] that allows generation of new functional properties of film covered surfaces.

Prussian blue (PB) as a mixed-valence hexacyanometalate salt is one of the longest known coordination compound. In 1978 Neff reported that PB can be deposited onto electrode surface forming an electroactive layer [6]. Since then the PB films have been extensively studied for the construction of electrochemical sensors and biosensors, in particular for measuring hydrogen peroxide concentration [7]. The control of H_2O_2 concentration is an important issue in many areas such as environmental protection, medicine or food quality control. Efficient detection of hydrogen peroxide is a key factor for the development of biosensors, as H_2O_2 is the product of reactions catalyzed by oxidase enzymes [8]. By monitoring the electrochemical response of H_2O_2, the concentration of the enzymatic substrate can be determined [9].

Graphene is a new material consisting of a single layer of sp^2 — bonded carbon atoms. Since its discovery in 2004 [10], graphene has emerged as the "material of the future" due to its unique nanostructure, electrical, thermal and mechanical properties [11,12]. It is considered as a promising material for application in various technological fields such as transparent conductive films [13], solar cells [14], electrochemical sensors [15], and for the next generation of electronic devices [16].

Combining the unique properties of graphene with Prussian blue nanoparticles in nanocomposite film may result in the improved sensitivity of electrochemical sensor for hydrogen peroxide, due to the synergistic effect between graphene and PB nanoparticles as it has been already observed [17,18]. In particular, Li et al. deposited PB/graphene nanocomposite film on glassy carbon electrode with an electrochemical deposition method. The PB/graphene/GCE exhibited high electrocatalytic activity for H_2O_2 detection [17]. Mao et al. used LbL deposition technique to form multilayer films of PB nanoparticles together with cationic polyelectrolyte-functionalized ionic liquid decorated graphene sheets on gold surfaces. They were obtained from GO by reduction with hydrazine. SPR optical signals and electrochemical current responses were monitored upon injecting hydrogen peroxide [18]. In our work we have studied the electroactive properties of the polyelectrolyte multilayer films formed with PB nanoparticles and thermally reduced graphene oxide using cyclic voltamperometry.

Prussian blue nanoparticles were synthesized by the reaction of $FeCl_3$ and $K_4[Fe(CN)_6]$ in the presence of 10^{-2} HCl according to the recipe given in [19]. The size of the Prussian blue nanoparticles was determined by dynamic light scattering (DLS) using the Zetasizer Nano ZS from Malvern Instruments Ltd. The average PB particle size was around 10 nm with the polydispersity index (PDI) less than 0.2. The zeta potential of the Prussian blue nanoparticles was measured by the laser Doppler velocimetry (LDV) technique using Malvern Zetasizer Nano ZS apparatus. The obtained nanoparticles were negatively charged with the average zeta potential around −50 mV.

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The multilayer films were formed by the layer-by-layer adsorption method. As first, anchoring layer branched poly(ethyleneimine) (PEI, MW ~ 750 kDa, Sigma-Aldrich) was deposited at the gold surface (electrode or gold plate) from 500 ppm solution at pH = 7. The other polycations used for multilayers construction was PAH (MW ~ 70 kDa, Sigma-Aldrich). The negatively charged Prussian Blue nanoparticles and graphene oxide (Abalonyx AS, Norway), zeta potential ~−40 mV, were deposited as anionic layers in the sequence $(rGO/PAH/PB/PAH)_n$. After the formation of multilayer films they were heated in 180 °C by 12 h to obtain reduced form of graphene oxide [20]. The reduction of graphene oxide was confirmed by the change in the FTIR spectra shown in Fig. 1A. The spectrum of graphene oxide (blue line) shows the presence of peaks corresponding to carboxyl ($\upsilon_{C=O}$ at 1723 cm^{-1}), hydroxyl (υ_{-OH} at 1616 and 1220 cm^{-1}) and epoxy groups (υ_{C-O-C} at 1049 cm^{-1}). After the reduction process (red line), the height of all those peaks decreased. The SEM images of the PEI/rGO/PAH/PB/PAH/rGO/PAH/PB multilayer are presented in Fig. 1B. The 10 nm PB nanoparticles can be clearly seen in the graphene sheet background.

The electroactive properties of the nanocomposite multilayer films containing Prussian blue nanoparticles and rGO were analyzed by the cyclic voltamperometry method using Autolab rotating disk electrode and potentiostat/galvanostat (PGSTAT302N) in 0.1 M KCl supporting electrolyte. The details of experimental procedure are given elsewhere [21]. Fig. 2 presents the voltammograms obtained for gold electrode covered with PE/PB multilayer films modified with reduced graphene oxide. They exhibit characteristic peaks, located at around 0.2 V, vs. Ag/AgCl electrode, corresponding to the redox reaction of Prussian Blue in the films, i.e., to the reduction of Prussian Blue (PB) to Prussian White (PW) and to the reverse oxidation process [19,22].

$$\underset{PB}{Fe_4^{III}\left[Fe^{II}(CN)_6\right]_3} + e^- \longleftrightarrow \underset{PW}{Fe_4^{II}\left[Fe^{II}(CN)_6\right]_3} \quad (1)$$

The separation potential of the peaks was around 35 mV, slightly higher than the theoretical value (30 mV) [23], indicating the fast charge transfer between Prussian blue nanoparticles and the electrode surface.

To compare the electroactive properties of $PEI/PB/(PAH/PB)_n$ multilayers with ones for films containing rGO, we determined the current density in the maximum of both reduction and oxidation peaks. The CV measurements were performed for various numbers of PB layers in the films. Fig. 3 illustrates the dependence of the current density, J_{rGO}, in the reduction and oxidation peaks for $PEI/(rGO/PAH/PB/PAH)_n/rGO/PAH/PB$ (part A) and of the ratio of J_{rGO}/J (part B), where J is current density of $PEI/PB/(PAH/PB)_n$ films, on the number of deposited PB layers. It can be observed that J_{rGO} increases almost linearly with the number PB layers. The ratio of redox current densities, J_{rGO}/J, is practically independent on the number of those layers. It is around 50 for cathodic and 40 for anodic currents respectively. That means that reduced graphene oxide improves the electroactive properties of studied films. This improvement is the result of the synergistic effect between rGO and PB nanoparticles due to the enhancement of electron transfer between surface of PB nanoparticles and gold electrode.

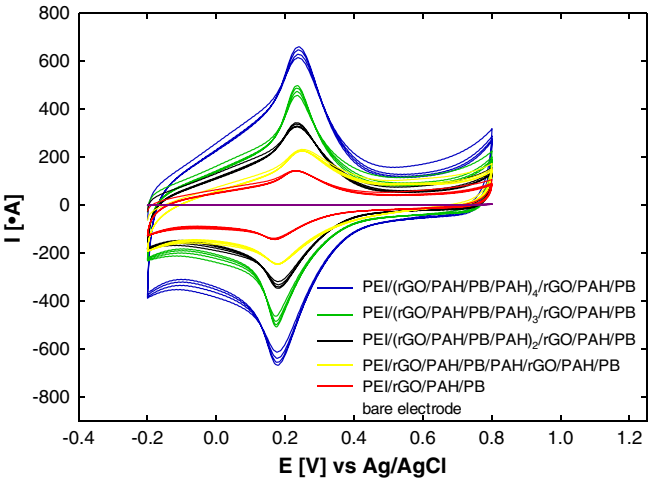

Fig. 2. Voltammetric curves of PE/PB multilayer film modified by rGO with different numbers of layers deposited on gold electrode at a scan rate of 0.1 V/s.

Gold electrodes modified with PE/PB multilayers and the ones containing additionally rGO were used for the evaluation of their electrocatalytic properties towards redox reaction of hydrogen peroxide. For that purpose we compared the CV curves for $PEI/PB/(PAH/PB)_4$ and $PEI/(rGO/PAH/PB/PAH)_4/rGO/PAH/PB$ multilayer films deposited on gold electrode, measured in the mixture of 5 mM H_2O_2 in 0.1 M pH = 7 phosphate buffer solution (PBS, obtained from $NaH_2PO_4 \times 2H_2O$ and $Na_2HPO_4 \times 12H_2O$). The voltammograms exhibited characteristic peaks of H_2O_2 oxidation at the anodic potential of about 1.0 V and reduction at cathodic potential about −0.9 V, were observed for the $PEI/PB/(PAH/PB)_4$ multilayer films. For the PE/PB films modified by

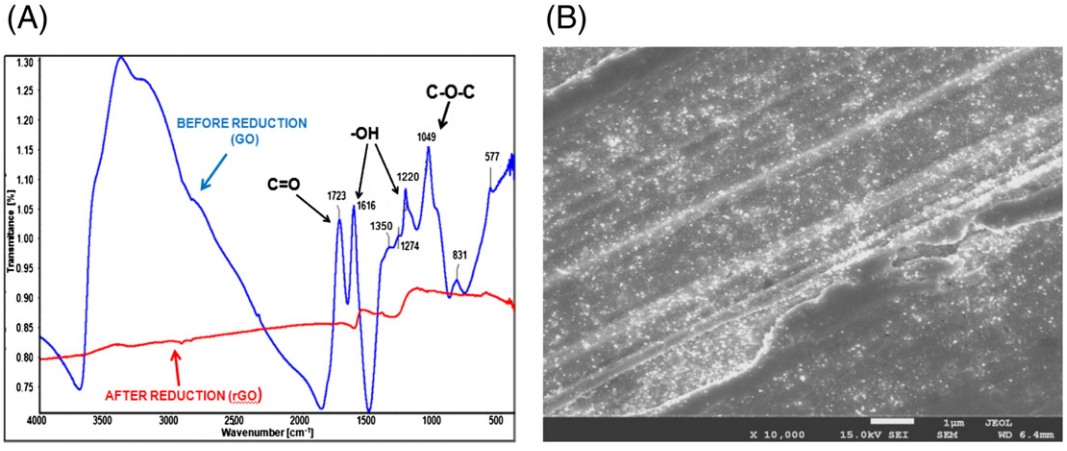

Fig. 1. (A) FTIR spectra of graphene oxide before (blue line) and after the temperature reduction in 180 °C by 12 h (red line). (B) SEM images of PEI/rGO/PAH/PB/PAH/rGO/PAH/PB films (10 000× magnification).