



## Rapid Communication

# 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.

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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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> is the product of reactions catalyzed by oxidase enzymes [8]. By monitoring the electrochemical response of H<sub>2</sub>O<sub>2</sub>, the concentration of the enzymatic substrate can be determined [9].

Graphene is a new material consisting of a single layer of sp<sup>2</sup> – 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<sub>2</sub>O<sub>2</sub> 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<sub>3</sub> and K<sub>4</sub>[Fe(CN)<sub>6</sub>] in the presence of 10<sup>−2</sup> 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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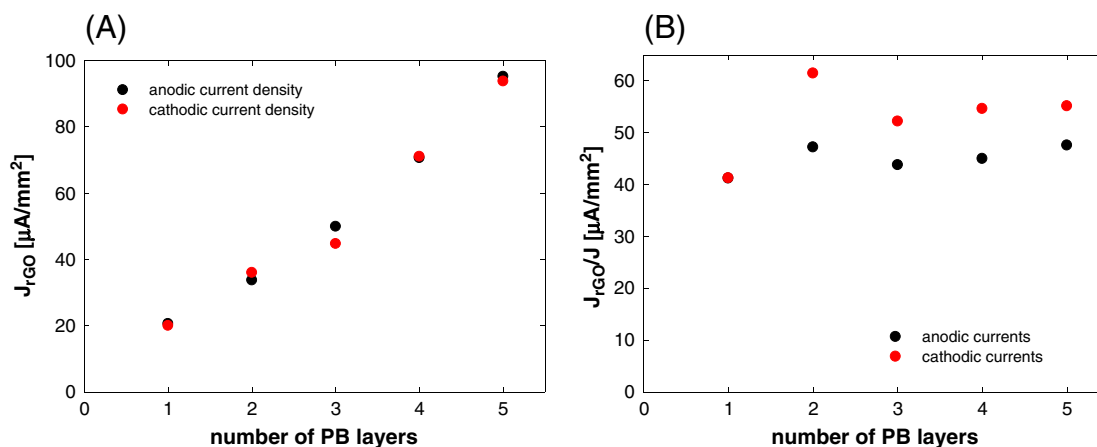


Fig. 3. The dependence of redox currents density ( $J_{rGO}$ ) for the PEI/(rGO/PAH/PB/PAH)<sub>n</sub>/rGO/PAH/PB film on gold electrode (part A) and the ratio of those current densities to ones obtained for PEI/PB(PAH/PB)<sub>n</sub> ( $J_{rGO}/J$ ) (part B) on the number of deposited PB layers (experimental error does not exceed the symbol size).

rGO, the oxidation peak was observed at potential about 0.25 V and the reduction one at  $-0.6$  V. The overall reaction for the electrocatalytic oxidation and reduction process can be written as [24]:



and:



The value of  $H_2O_2$  redox currents for the PEI/PB/(PAH/PB)<sub>4</sub> multilayer films was around 200  $\mu A$  and was more than one order of magnitude lower than the respective values for PEI/(rGO/PAH/PB/PAH)<sub>4</sub>/rGO/PAH/PB film. Therefore, the presence of reduced graphene oxide in the multilayer structure increases the CV response of the PB covered electrode in the presence of hydrogen peroxide.

We determined the hydrogen peroxide redox current density using the value of current in the reduction and oxidation peaks in the second CV cycle. Fig. 4 presents the dependence of that current densities for gold electrode modified with PEI/(rGO/PAH/PB/PAH)<sub>n</sub>/rGO/PAH/PB (part A) and of the ratio of  $J_{rGO}/J$  (part B) on the number of deposited PB layers. Here  $J$  denotes the respective current densities measured for the films with the same number of PB layers but without rGO. It can be noticed that  $J_{rGO}$  for oxidation and reduction of hydrogen peroxide increases almost linearly with the number of deposited PB layers. It

means that the sensitivity of this kind of electrocatalytic sensors can be controlled by the number of adsorbed Prussian blue layers. The values of  $H_2O_2$  cathodic current density for the PE/PB multilayer films modified with reduced graphene oxide were around thirty times (fifteen times for anodic) higher than the ones for films without it. The ratio  $J_{rGO}/J$  seems to slightly increase with the number of layers that indicates that thicker films are more effective as hydrogen peroxide sensor layers.

Fig. 5 presents the results of cyclic voltamperometry measurements obtained for multilayer films containing four layers of PB nanoparticles deposited on gold electrode, in various concentrations of hydrogen peroxide in phosphate buffer solution. The measurements were performed for concentration of  $H_2O_2$  ranging from 0.2 to 10 mM for PEI/PB/(PAH/PB)<sub>3</sub> films and from 0.01 to 10 mM for the ones modified with rGO. For the concentrations below 0.2 mM the current densities for films without rGO were below the detection limit.

The current densities for oxidation and reduction of hydrogen peroxide increase with growing concentration of hydrogen peroxide. The nonlinear increase can be the result of the consumption of hydrogen peroxide in the redox reactions, which cannot be compensated by its transport from the bulk. Some kinetic limitations can be the alternative reason of the nonlinear behavior. When the redox reaction of peroxide with PB is relatively slow, it could limit a rate of electrocatalytic process and thus, nonlinear dependence of the reduction and oxidation current on the concentration of  $H_2O_2$  should be observed [25].

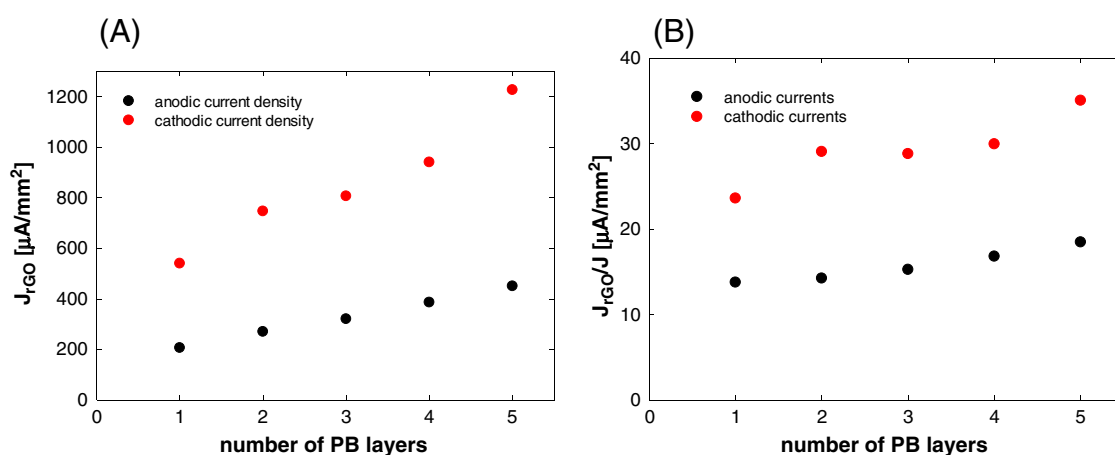
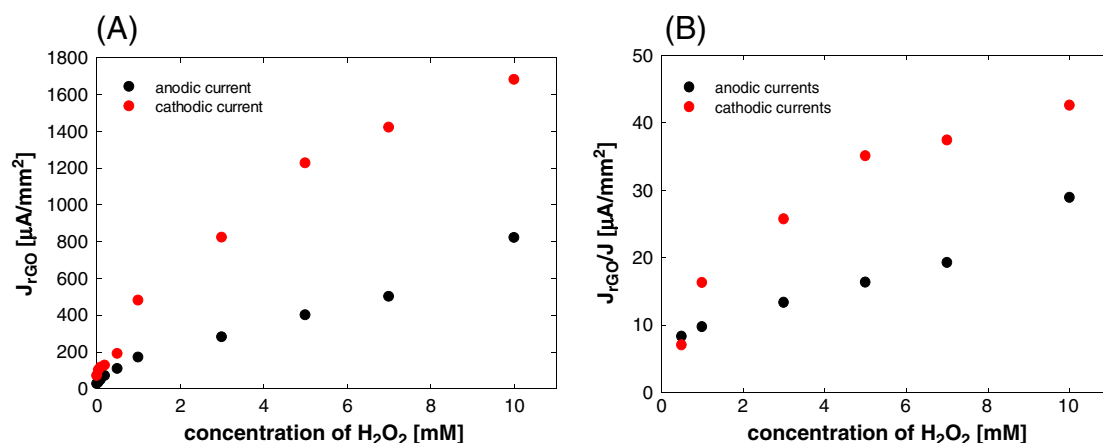


Fig. 4. The comparison of the hydrogen peroxide oxidation (black circle) and reduction (red circle) current density of PEI/(rGO/PAH/PB/PAH)<sub>n</sub>/rGO/PAH/PB (part A) and  $J_{rGO}/J$  (part B) on the number of deposited PB layers. The results were obtained in pH = 7 phosphate buffer solution in the presence of 5 mM  $H_2O_2$ , (experimental error does not exceed the symbol size).



**Fig. 5.** The dependence of the current density for PEI/(rGO/PAH/PB/PAH)<sub>3</sub>rGO/PAH/PB film modified gold electrode (part A) and  $J_{red}/J_{ox}$  (part B) for the oxidation (black circle) and reduction (red circle) of hydrogen peroxide on the concentration of  $H_2O_2$ , obtained in pH = 7 buffer solution (experimental error does not exceed the symbol size).

The values of current densities obtained for films with rGO are much higher (around 20–40 times, cf. Fig. 5B) than the ones received for multilayers without this compound. Moreover, for the  $H_2O_2$  concentration below 0.5 mM the redox currents could still be measured over the background level down to practically 5  $\mu M$ . Reduced graphene oxide is by itself electrocatalytically active towards hydrogen peroxide but the redox currents for the films PAH/rGO were at least four times lower (data not shown). Thus, the multilayers containing both Prussian blue nanoparticles and reduced graphene oxide are more electrocatalytically active towards  $H_2O_2$ , which indicates the possibility of the application of those hybrid PE/PB/rGO multilayers as the effective sensor layers for the electrochemical detection of hydrogen peroxide.

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