

Multilayer polyelectrolyte films formed with Prussian Blue nanoparticles and reduced graphene oxide as a sensitive tool for H₂O₂ detection

A. Pajor-Świerzy¹, T. Kruk¹, L. Szyk-Warszyńska¹, R. Socha¹, R. Wendelbo²,
P. Warszyński¹

¹Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences,
Niezapominajek 8, 30-239 Krakow, Poland

²Abalonyx AS, Forskningsveien 1, 0314 Oslo, Norway

ncpajor@cyf-kr.edu.pl

Graphene is a new material consisting of single layer of sp² – bonded carbon atoms. 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]. Graphene is now considered as a promising material for application in various technological fields such as transparent conductive films [4], solar cells [5], gas storage media [6], and next generation of electronic devices [7]. Prussian Blue (PB), which is the prototype of mixed-valence transition metal hexacyanoferrates was initially used as a blue pigment only. In 1978 Neff reported that PB can be deposited onto an electrode surface to produce an electroactive coating [8]. In particular the PB films can be used in electrochemical sensors and biosensors because of its catalytic properties toward the detection of hydrogen peroxide [9].

PB nanoparticles with the size 10 nm and ζ-potential –50 mV were synthesized by the reaction of FeCl₃ and K₄[Fe(CN)₆] in the presence of 10⁻² HCl. PB nanoparticles were immobilized in polyelectrolyte (PE) multilayers using the layer-by-layer (LbL) method [10]. Additionally the graphene oxide (GO) was deposited from its aqueous suspension to form additional layers of the film. We found that the thermal reduction of GO at the temperature 180°C is the effective processes leading to formation of sp²-bonded carbon atoms. The examination of XPS spectra indicated that after the ratio of the sp² carbon increased to c.a. 80 at.%. Since, on the other hand the PB nanoparticles remained stable at that temperature; we applied thermal reduction to turn graphene oxide embedded in the multilayer films into its reduced form (rGO). The electric conductivity of films after the reduction was analyzed by the four point surface conductivity measurements, whereas cyclic voltamperometry was used to determine the electroactive properties of multilayer films containing both Prussian blue and rGO.

We noticed that in the presence of rGO sheets the intensity of the redox current of PB embedded in the multilayer films markedly increased due to enhancement of electron transport to the gold electrode surface. In the presence of hydrogen peroxide characteristic peaks from reduction of H₂O₂ to OH⁻ ions and oxidation to O₂ molecules appeared. We found a linear correlation between that redox current density with the number of deposited PB/rGO layers and concentration of hydrogen peroxide in the solution. Therefore, the electrodes covered with composite polyelectrolyte/PB nanoparticles/rGO film enable in-situ sensing of H₂O₂. Presence of rGO in the multilayer structure increases ca. 30 times the sensitivity for hydrogen peroxide with respect to films containing polyelectrolyte and the same number of PB layers only.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, *Nature*, **306** (2004) 666-669.
- [2] J.S. Bunch, A.v.d.Z. Arend, S.V. Scott, W.F. Ian, M.T. David, M.P. Jeevak, G.C. Harold, L. M. Paul, *Science*, **315** (2007) 490-493.
- [3] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.*, **3** (2008) 270-274.
- [4] S. Watcharotone, D.A. Dikin, S. Stankovich, R. Piner, I. Jung, G.H.B. Dommett, et al. *Nano Lett.* **7** (2007) 1888.
- [5] X. Wang, L.J. Zhi, N. Tsao, Z. Tomovic, J.L. Li, K. Mullen, *Angew Chem Int Ed.* **47** (2008) 2990.
- [6] C. Sealy, *Nano Today* **4**(2009) 6.
- [7] C. Gomez-Navarro, R.T. Weitz, A.M. Bittner, M. Scolari, A. Mews, M. Burghard, et al. *Nano Lett.* **7** (2007) 3499.
- [8] V.D. Neff, *J. Electrochem.Soc.* **128** (1978) 886.
- [9] A.A. Karyakin, E.A. Kotel'nikova, L.V. Lukachova, E.E. Karyakina, J. Wang, *Anal. Chem.* **74** (2002) 1597.
- [10] Decher, G.; Hong, J.D.; Schmitt, J. *Thin Solid Films* **210/211** (1992) 831-838.