Simple Route for Intermatrix Synthesis of Polymer Stabilized Core-Shell Metal Nanoparticles for Sensor Applications

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The use of nanometer-sized metal particles (MNP) in sensor and biosensor construction can substantially improve their performance and therefore increase their applications in clinical, biomedical, and environmental research fields. MNP are objects of great interest in the modern chemical research due to their unique physical and chemical properties, which are distinct from both those of the bulk metal and those of isolated atoms and molecules. The main drawback of MNP is their high trend for aggregation. Without stabilization MNP fuse together, losing their special shape and properties. The development of Polymer-Stabilized MNP (PSMNP) is considered to be one of the most promising solutions to the MNP stability problem [1]. In many instances the sensor and biosensor constructions are based on the use of noble MNP as sensing element due to their unique electrocatalytic properties. One of the most important problems in this case is the decrease of the noble metal loading without dramatic change of the performance of sensing element. One of the possible solution of this problem is the use of core-shell PSMNP, which are composed of a cheap metal core covered with a thin noble metal shell.

In this presentation we report the novel simple route for the inter-matrix synthesis and characterization of PSMNP with core-shell structure. The proposed approach is based on the use of functionalized polymeric membranes (FPM) as a nanoreactor for both to synthesize and to characterize the composition and architecture of PSMNP. The desired functionalization is achieved by the chemical grafting of functional groups to the polymeric matrix or by using the physical immobilization of metal-selective extractants inside the polymer. The optimal degree of functionalization provides, on one hand, insolubility of the polymer in water and, on the other hand, its solubility in some organic solvents (e.g., DMF). Due to the presence of functional groups, the polymer matrix is able to chemically fix metal ions or complexes (metal loading stage) prior to their reduction, which results in the formation of PSMNP. After metal reduction the functional groups of the functional polymer appear to be prepared for the next metal loading-reduction cycle. The first cycle permits to form the core-PSMNP of desired size, while the second cycle leads to the coverage of pre-shaped core with the second metal forming the shell.

The proposed approach is illustrated by the results obtained by studying the intermatrix synthesis of Cu-Pt and Cu-Pd core-shell PSMNP of different compositions in the sulfonated poly(etherether ketone) (SPEEK) membranes. MNP-containing SPEEK membranes were characterized by SEM, AFM and TEM (see Fig. 1) techniques to evaluate the morphological changes of the membrane structure and to estimate the MNP size.

The core-shell-MNP loaded membranes were also deposited on the surface of graphite-epoxy composite electrodes [2] to study the electrochemical properties of polymer-PSMNP composites and to estimate their applicability in sensor constructions. The electrochemical response of amperomtric sensors has been shown to increase with the loading of the second (shell-forming) metal (see Fig. 2). The preliminary results shown in Fig. 2 demonstrate that the presence of Pt@Cu-PSMNC inside the membrane not only substantially improves the

electric conductivity of the polymer, but also testifies to manifestation of clearly pronounced strong electrocatalytic activity of Pt@Cu-PSMNC towards analyte under study (H_2O_2).

References:

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[2] A.D. Pomogailo, G.I. Dzhardimalieva, A.S. Rozenberg, D. Muraviev, J. Nanoparticle Res., **5** (2003) 497.
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Figures:

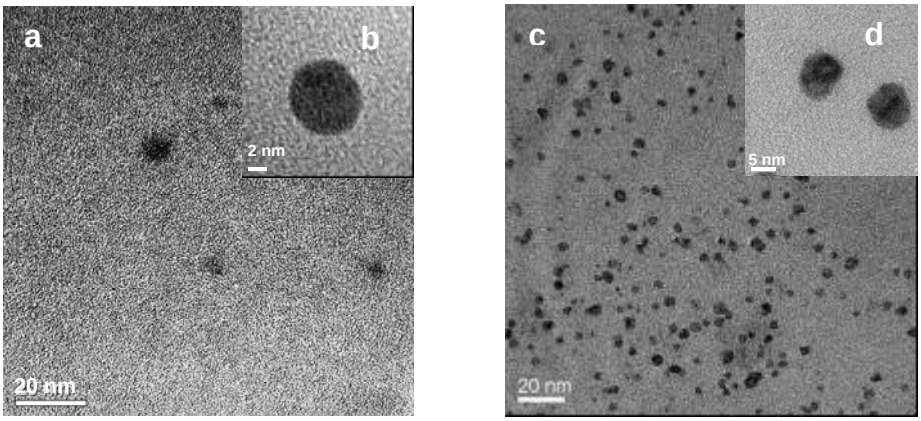

Figure 1. Typical TEM (a, c) and HRTEM (b, d) images of Cu-core PSMNP (a, b) and Pt@Cu-core-shell PSMNP (c, d) for sample with platinum loading of 45 mg/g of initial SPEEK membrane. Diameters of both Cu- and Pt@Cu-PSMNP lie within 5-7 nm range and particles demonstrate quite narrow size distribution.

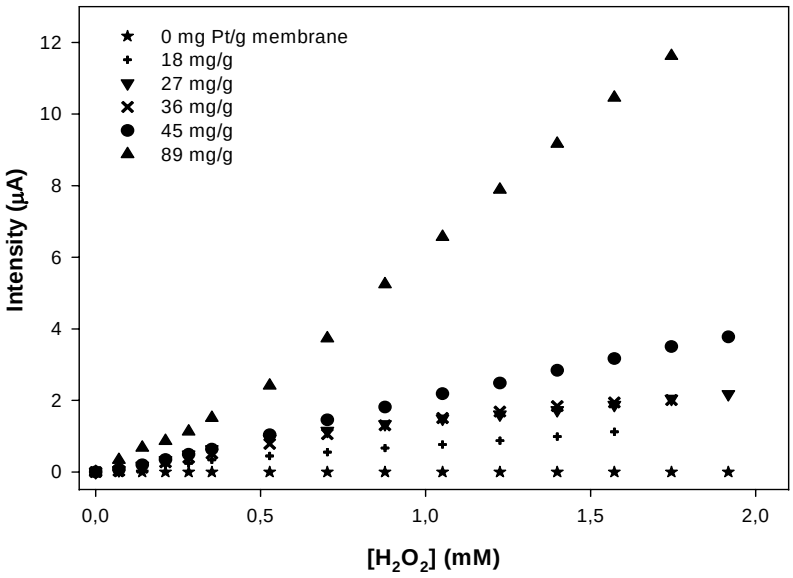

Figure 2. Calibration curves of amperometric sensors prepared by modification of graphite-epoxy composite electrodes with Pt@Cu-PSMNP-SPEEK membranes at different values of platinum loading. Conditions: potential: -250 mV; 0.1 M KCl in 0.1 M acetate buffer, pH = 7.0.