NOVEL APPROACHES FOR INTER-MATRIX SYNTHESIS AND CHARACTERIZATION OF POLYMER STABILIZED METAL NANO-PARTICLES FOR MOLECULAR RECOGNITION SYSTEMS.

Dmitri N. Muraviev, Jorge Macanás, Marinella Farre, Maria Muñoz and Salvador Alegret
Analytical Chemistry Division, Department of Chemistry, Autonomous University of Barcelona, 08193 Bellaterra, Barcelona, Spain.
Dimitri.Muraviev@uab.es

Molecular Recognition Devices (MRD) such as sensors and biosensors have a great application potential for clinical, biomedical, and environmental research fields. The use of Nanometer-sized Metal Particles (MNP) in MRD construction can substantially improve their performance. MNP are objects of great interest in 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. MNP can be so unstable that if their surfaces touch, they fuse together, losing their special shape and properties. The development of Polymer-Stabilized MNP (PSMNP) is one of the most promising solutions to the MNP stability problem [1].

In this presentation we report novel approaches for the inter-matrix synthesis and characterization of PSMNP. The proposed approaches are based on the use of a Functionalized Polymeric Membrane (FPM) as a nanoreactor for both to synthesize and to characterize the composition and architecture of PSMNP. The desired functionalization is achieved by either chemical grafting of functional groups to the polymeric matrix or by using the physical immobilization of metal-selective extractants inside the polymer (Solid-Phase-Incorporated-Reagents, SPHINER). In both cases the polymer matrix is able to chemically fix metal ions or complexes prior to their reduction resulting in the formation of PSMNP. After metal reduction the functional groups of SPHINER or those of functional polymer appear to be prepared for the second metal loading-reduction cycle. This permits either to increase the content of PSMNP inside the polymer or to synthesize PSMNC of different composition and architecture.

The approaches under discussion are illustrated by the results obtained by studying the intermatrix synthesis of Cu, Pt, Pd, Co and Ni PSMNP of different structures and compositions with an average diameter of 7-20 nm. MNP-containing membranes were characterized by Scanning Electron Microscopy, SEM, (see Fig. 1) and Transmission Electron Microscopy, TEM, (see Fig. 2) techniques to evaluate the morphological changes of polymer structure and to estimate the MNP size. In case of MNP-loaded FPM it seems possible to study some chemical properties of PSMNP such as, for example the kinetics of MNP dissolution in different acids (see Fig. 3).

The MNP loaded membranes were also deposited on the surface of graphite-epoxy composite electrodes [2] in order to study the electrochemical properties of polymer-PSMNC composites and to estimate their applicability MRD constructions. In all cases the electrical conductivity of membranes increased by several orders of magnitude in comparison with metal-free polymer. Certain PSMNP demonstrate abnormal chemical activity permitting to directly use them in MRD. The preliminary results shown in Fig. 4 demonstrate that presence of Cu-PSMNC inside the membrane not only substantially improves the electric conductivity of the polymer, but also testifies to manifestation of clearly pronounced strong catalytic activity of Cu-PSMNC towards analyte under study (H_2O_2).

References:

[1] A.D. Pomogailo, G.I. Dzhardimalieva, A.S. Rozenberg, D. Muraviev, J. Nanoparticle Res., **5** (2003) 497.
[2] M.I. Pividori, S. Alegret, Anal. Lett., **36** (2003) 1669.

Figures:

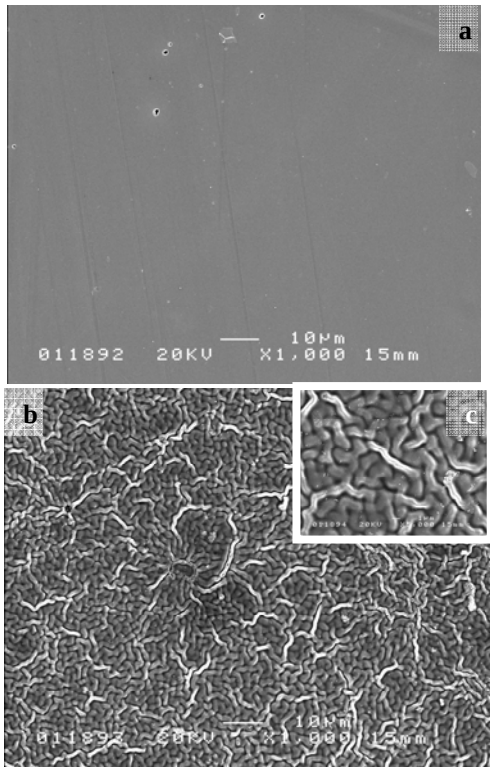

Fig1: Typical SEM images a) unmodified sulfonated polyetheretherketone SPEEK, 1000X;, b) SPEEK Copper loaded, 1st cycle, 1000X, c) SPEEK Copper loaded, 1st cycle, 5000X

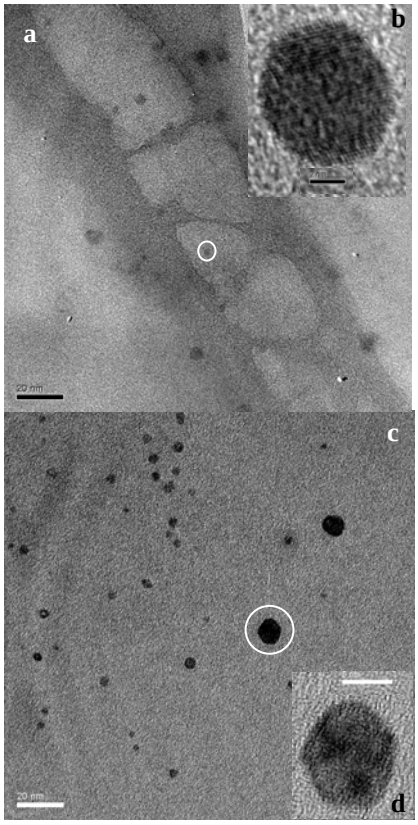

Fig2: Typical TEM images, a) TEM of Cu-PSMNC in SPEEK; b) TEM of single Cu nanoparticle; c) TEM of Cu-Pt-PSMNC in SPEEK; d) TEM of single Cu-Pt nanoparticle

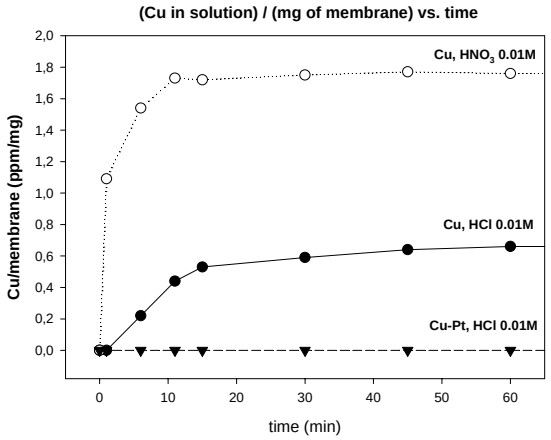

Fig 3: Kinetics of dissolution of Cu-PSMNC and Pt@Cu-PSMNC in HCl and HNO3. As it is seen platinum coated copper MNP appears to be stable against acid treatment.

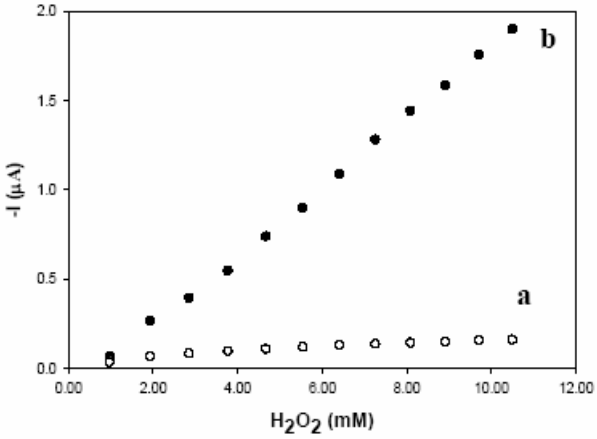

Fig4: Calibration curves of GEC sensor modified with the initial SPEEK (a) and SPEEK-Cu-PSMNC (b) membranes. Conditions: potential = –100mV, 0.1 M KCl in 0.1M phosphate buffer at pH = 7.0.