

PREPARATION AND CHARACTERIZATION OF POLYMER-STABILIZED METAL NANOPARTICLES FOR SENSOR APPLICATIONS

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Nowadays, synthesis and application of Metal Nano-Clusters (MNC) attract great attention of scientists and technologists due to their unique electrical, magnetic and optical properties that differ from those of the bulk material. Nevertheless metallic nanoparticles are sometimes unstable and their stabilization is a crucial point to be solved in order to design new sensing devices which contain such particles. In this sense, one of most promising solution of MNC stability problems is *in situ* synthesis of MNC in stabilizing polymeric matrix [1].

Our research line is mainly focused on the development of novel routes to synthesize Polymer Stabilized MNC (PSMNC) by the use of both non-functionalized and functionalized polymers as MNC stabilizing media. Modification of polymeric matrices by Solid-Phase-Incorporated-Reagents (SPHINER) allows us to chemically fix metal ions or complexes inside the parent polymeric matrix prior to their reduction. Besides, the incorporation of functional groups into the polymeric chains by chemical grafting (e.g., sulfonic groups addition) permits the loading of metal ions that undergo a reduction reaction to form the desired nanoparticles.

Both stabilization procedures are compatible with chemical or electrochemical reduction when using a soluble (non-crosslinked) polymer. The polymer solutions can be used for casting membranes either on an appropriate support or directly on the surface of the electrode to be used as a sensor. In the first case the reduction of metals proceeds *ex situ*, while in the second one *in situ*, i.e. in the first case after metal reduction the PSMNC containing membrane must be dissolved to prepare a sort of “ink” to be used for the second casting of membrane on the electrode surface while in the second case this step is not required.

Different PSMNC systems have been studied with successful results:

- a) Pt and Pd PSMNC were synthesized inside polyvinyl chloride (PVC) or polysulphone (PS) matrix. The synthesis route includes the following stages: 1) dissolution in Tetrahydrofuran, THF, of the polymer, the plasticizer (n-octylphenylether) and a Pt or Pd tributyl-phosphine oxide complex; 2) casting of the membrane followed by either chemical or electrochemical reduction of Pt and Pd ions; and 3) re-dissolution of the prepared membrane in THF to prepare the “PSMNC-ink”. The PSMNC-based sensors were prepared on the surface of graphite-epoxy composite (GEC) electrodes [2].
- b) 2. The synthesis of mono-metallic Cu and Pt MNC inside sulfonated polyetheretherketone (SPEEK) membranes: 1) membrane loading with metal ions; 2) reduction inside the polymeric matrix. It was shown that repetitive metal loading-reduction procedure of the same membrane permits to accumulate sufficiently high concentration of PSMNC inside the polymer.

The size of MNC in all systems studied was determined by TEM and appeared to be in the range of 6-20 nm (Fig 1). Some of the results of cyclic voltammetric analysis of GEC sensors prepared under different conditions are shown in Figures 2 and 3.

Modification of GEC electrode with PVC-Pt-PSMNC substantially enhances the electroconductivity of membrane in comparison with GEC-PVC (Pt-free) electrode but the

mass-transfer characteristics of the sensor still remain unsatisfactory (Fig. 2). The desired result is achieved when changing the membrane casting technique from drying to the phase inversion technique. Indeed, as follows from the results shown in Figs. 2 and 3, the shape of voltamperograms of GEC-PS-Pt sensors with membranes obtained by different methods differs dramatically from each other. The main reason for such a remarkable difference in the sensors performance is attributed to the different morphology of PS-membrane obtained by using the drying and the phase inversion techniques. Unlike the first technique, the second one permits to obtain PS-membranes with highly developed macroporous structure resulting in a far higher rates of mass transfer. As clearly follows from Figure 3. the composition of the non-solvent bath used in phase inversion technique (i.e. H₂O or H₂O-DMF mixture) results in different behavior of sensors.

Acknowledgements: this work was supported by research grant BIO2003-06087, 2003-2005 from the Ministry of Science and Technology of Spain, which is also acknowledged for financial support of Dmitri N. Muraviev within the Program *Ramon y Cajal*.

References

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Figures:

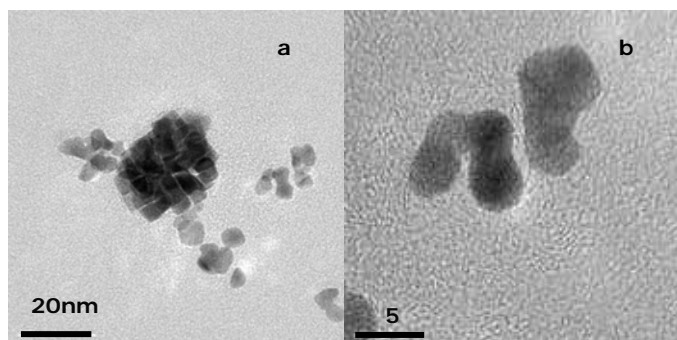


Figure 1. Typical TEM images of structural fragments of

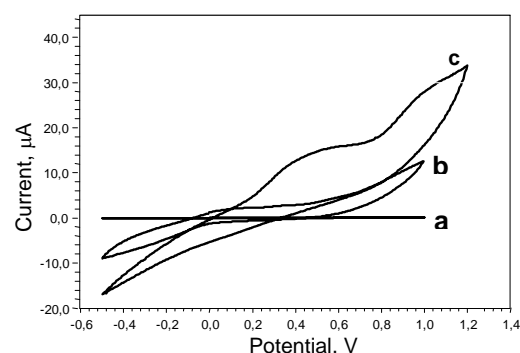


Figure 2. Comparison of cyclic voltammetry of GEC sensors modified with PVC (a); PVC-Pt (b) and PS-Pt (c). Conditions: membranes formation by drying; scan rate 3 mV/s, K₄[Fe(CN)₆] 5 mM in acetate buffer pH 5, KCl 0.1 M. Electrochem. Pt reduction for 10 min. at -1.6 V.

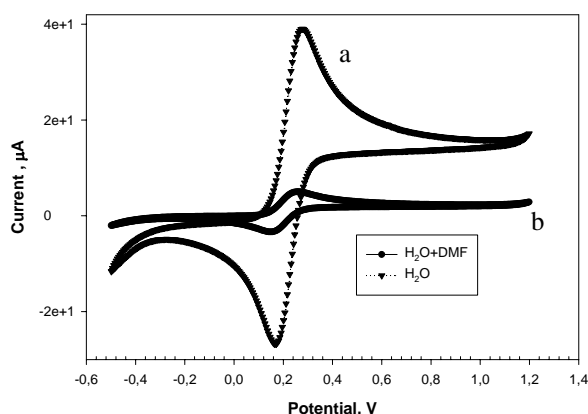


Figure 3. Comparison of cyclic voltammetry of GEC sensors modified with Pt-PS prepared by phase inversion technique a) in water, and b) in water-DMF mixture. Conditions: scan rate 3 mV/s, K₄[Fe(CN)₆] 5 mM in acetate buffer pH 5, KCl 0.1 M. Electrochem. Pt reduction for 10 min. at -1.6 V.