Synthesis, Stability and Electrocatalytic Activity of Polymer Stabilized Monometallic Pd and Pt and Bimetallic Pd@Cu and Pt@Cu Core-shell Nanoparticles

Dmitri N. Muraviev, Jorge Macanás, Patricia Ruiz and Maria Muñoz.
Analytical Chemistry Division, Department of Chemistry, Autonomous University of Barcelona, 08193 Bellaterra, Barcelona, Spain.
Contact e-mail: Dimitri.Muraviev@uab.es

Platinum-group metal (PGM) nanoparticles (MNPs) find wide application in various catalytic and electrocatalytic processes (such as, for example hydrogen and methanol fuel cells, sensors, biosensors, etc.). In many instances application of MNPs is based on the use of their unique properties (electrical, magnetic, optical, ionization potentials, etc.), which are distinct from those of the bulk metal and isolated atoms. On the other hand, they require stabilization to prevent coalescence and aggregation, and hence to save their special size and properties. The development of Polymer-Stabilized MNPs (PSMNPs) is one of the most promising solutions to the MNPs stability problem [1-3]. Another important problem concerning the use of noble metal nanocatalysts is the decrease of PGM loading without dramatic change of their catalytic properties. One of the possible solutions of this problem is the use of core-shell PSMNPs, which are composed of a cheap metal core coated with a thin PGM shell [4].

In this presentation we report the results obtained in a comparative study of electrocatalytic properties of Pt and Pd (monometallic) and Pt@Cu and Pd@Cu (core-shell bimetallic) PSMNPs, which have been synthesized under identical conditions inside the polymeric membranes. The intermatrix synthesis of MNPs included the loading of sulfonated poly(etherether ketone) (SPEEK) with desired metal ions followed by their reduction (intermatrix synthesis stage), what resulted in formation of PSMNPs of required composition and structure. PSMNPs-containing membranes were characterized by different methods (SEM, AFM, TEM and others) to evaluate the structural features of polymer-metal composite membrane and to estimate the MNPs size. Typical TEM images of the Pt- and Pt@Cu-MNPs are shown in Fig. 1. As it is seen, the shape and size of monometallic Pt-MNPs differs dramatically from those of Pt@Cu nanoparticles, although the value of platinum loading in both cases is the same. Pt-MNPs are characterized by a far larger size and absolutely irregular shape. This makes practically impossible to estimate their diameters, while the majority of Pt@Cu-MNPs have almost spherical shape with diameters of 3-6 nm. As the result, the surface area of Pt@Cu-MNPs appears to be far higher than that of Pt-MNPs. In case of Pd- and Pd@Cu-MNPs the difference in particle form and surface area is not so dramatic.

The MNP-loaded membranes dissolved in DMF followed to produce a sort of PSMNP-inks. The inks were used to evaluate the stabilizing efficiency of SPEEK matrix against MNPs aggregation and to study the electrochemical properties of polymer-PSMNP nanocomposites. The results of these experiments are demonstrated in Figs. 2 and 3. Fig. 2 shows the side distribution histograms of Pd@Cu-MNPs when determined for freshly prepared ink and the same ink after 9 months of storage. As it is seen, the distribution of MNP sizes essentially does not change that indicates a very high stabilizing efficiency of SPEEK matrix towards MNPs. Fig. 3 shows the calibration curves of amperometric detection of H_2O_2 with Pt- and Pt@Cu-MNP-based sensors. As it is seen, the sensitivity of sensors based on the use of Pt- and Pt@Cu-MNPs with the same platinum loading differs dramatically from each other. A possible reason for this difference is quite different values of surface areas of Pt@Cu- and Pt-MNPs.

References:

[1] A.D. Pomogailo, G.I. Dzhardimalieva, A.S. Rozenberg and D.N. Muraviev, J. Nanoparticle Res., **5** (2003) 497.
[2] D.N. Muraviev, Contributions to Science, **3(1)** (2005) 17.
[3] D.N. Muraviev, J.Macanás, M. Farre, M. Muñoz and S. Alegret, Sensors & Actuators B, **118(1-2)** (2006) 408.
[4] S. Zhou, B. Varughese, B. Eichhorn, G. Jackson and K. McIlwrath, Angew. Chem. Int. Ed., **44** (2005) 4539.

Figures:

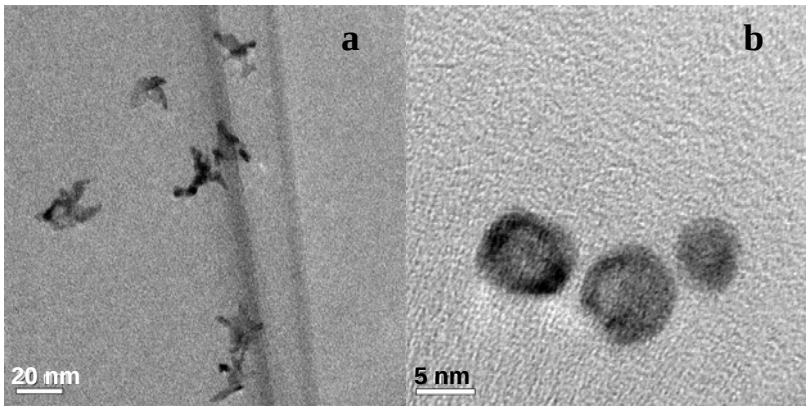

Figure 1. (a) Typical TEM images of Pt-(a) and Pt@Cu- PSMNPs (b) immobilized in SPEEK matrix.

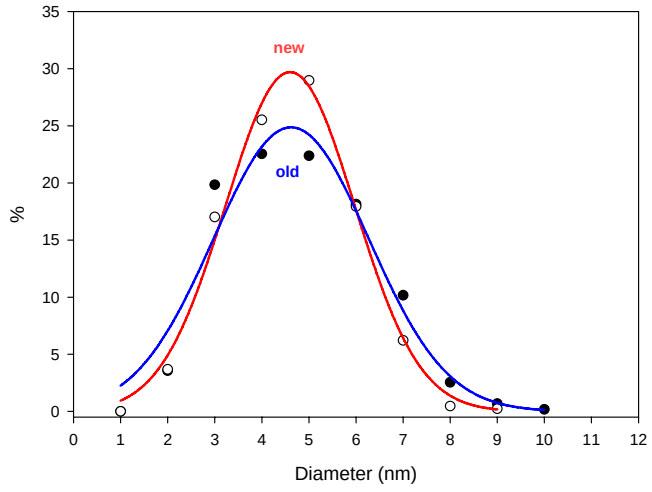

Figure 2. Typical size distribution histograms of Pd@Cu- PSMNPs in freshly prepared ink (new) and in same ink after 9 months of (old) storage.

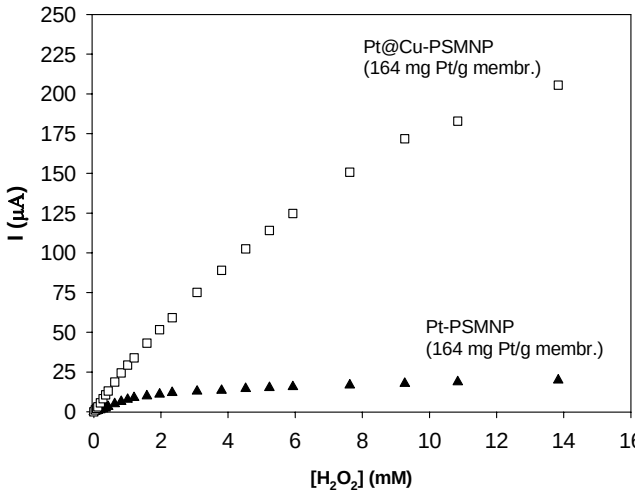

Figure 3. Calibration curves of amperometric sensors prepared by modification of graphite-epoxy composite electrodes with Pt-(black triangles) and Pt@Cu-PSMNP-SPEEK membranes (white squares) at identical values of platinum loading. Conditions: potential: -250 mV; 0.1 M KCl in 0.1 M acetate buffer, pH = 7.0.