Synthesis of Polymer Stabilized Palladium Nanoparticles by Wet Chemical and Electrochemical Routes

P. Ruiz, J. Macanás, M. Muñoz and D.N. Muraviev
Analytical Chemistry Division, Department of Chemistry, Autonomous University of Barcelona, 08193 Bellaterra, Barcelona, Spain.
Patricia.Ruiz.Nicolas@uab.cat

Synthesis and Characterization of Metal nanoparticles (MNPs) attract great interest of scientists and technologists due to their special physical and chemical properties. A high trend for aggregation is considered to be the main drawback of MNPs, as their coalescence results in the loss of their special shape and properties. The development of Polymer-Stabilized MNPs (PSMNPs) is considered to be one of the most promising solutions to the MNPs stability problem [1, 2]. In many instances the electrochemical applications of MNPs are based on the use of noble metals (Pd, Pt, etc.) due to their well-known unique electrocatalytic properties. The synthesis of PSMNPs can be successfully carried out by using InterMatrix Synthesis (IMS) technique, which consists in sequential loading of the functional groups of the polymer (sulfonated poly(etherether ketone), SPEEK in our case) with the desired metal ions followed by their chemical reduction inside the membrane, what results in the formation of PSMNPs.
In this presentation we report the results obtained by the development of an electrochemical version of IMS technique in the synthesis of Pd-PSMNPs and their comparison with those obtained by using the usual wet chemical route. In the first case Pd-PSMNPs were synthesized by electrochemical reduction of palladium ions inside a SPEEK-membrane deposited onto the surface of an electrode, while in the second case the reduction of palladium ions inside the membrane was carried out by a chemical method (e.g. reduction by a sodium borohydride solution). A third method can be done by successive electrochemical and chemical reduction. All three versions of IMS technique can be classified as “in situ-IMS” method. In all cases the SPEEK-MNP-nanocomposites were characterized by using microscopic and electrochemical techniques in order to evaluate MNPs size and electrocatalytic response of the MNPs-modified electrodes.
Typical TEM images of Pd-MNPs obtained by different versions of IMS method are shown in Fig. 1. As it is clearly seen, the size of Pd-MNPs is higher in the case of chemical reduction (see Fig. 1a). The use of the coupled electrochemical-chemical reduction results in the formation of smaller nanoparticles (see Fig. 1b) what increases the performance of the catalytic material. An additional improvement could be considered if MNPs were formed on both sides of the membrane, thus, enhancing the response of doubly modified electrodes (electrochemical-chemical) in comparison with those obtained when using solely chemical reduction.
In general terms we propose that the electrochemical reduction results in the predominant formation of Pd-PSMNPs on the internal side of the membrane (located on the electrode-membrane interface) whereas the chemical reduction leads to the formation of palladium MNPs mainly on the outer side of the membrane (membrane-solution interface). In the case when using both chemical and electrochemical reduction the formation of Pd-MNPs might proceed by both sides of the membrane.
The results of the amperometric detection of H_2O_2 with Pd-PSMNPs synthesized by different in situ IMS methods (see Fig 2.) clearly testify to the validity of above hypothesis.

References:

[1] A.D. Pomogailo, G.I. Dzhardimalieva, A.S. Rozenberg, D.N. Muraviev, J. Nanoparticle Res., **5** (2003) 497-519.
[2]. D.N. Muraviev, Contribut. Sci. 3(1) (2005) 19-32.

[3] D.N. Muraviev, J. Macanás, M. Farre, M. Muñoz, S. Alegret, Sens. Actuators B, **118(1-2)** (2006) 408-417.
[4] J. Macanas, M. Farre, M. Muñoz, S. Alegret, D. N. Muraviev, Phys. Stat. Sol. (a), 203, **6**, (2006) 1194-1200.
[5] D.N.Muraviev, J. Macanás, P. Ruiz, M. Muñoz, Phys. Stat. Sol. (a), 205, 6, (2008) 1460-1464.
[6] D.N.Muraviev, P. Ruiz, M. Muñoz, J. Macanás, Pure Appl**.** Chem. , 80, **11** (2008) 2425-2437.

Figures:

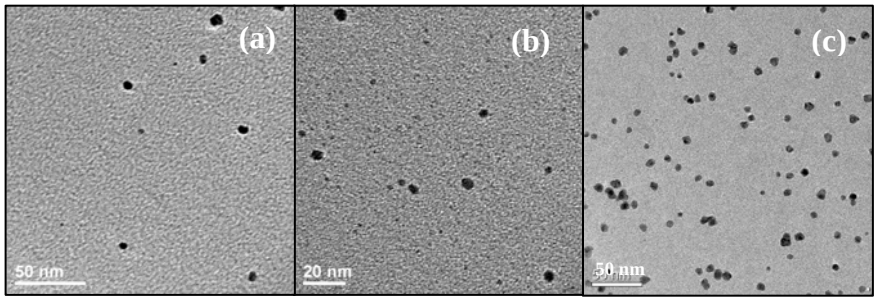

Fig. 1 Typical TEM images of Pd-PSMNPs-SPEEK nanocomposite inks synthesized by "in situ-IMS" (a,b) and "ex situ-IMS" (c), where (a) corresponds to chemical reduction and (b) electrochemical-chemical reduction.

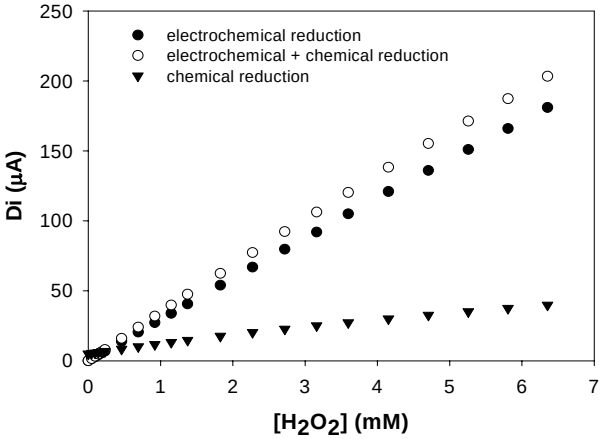

Fig. 2 Calibration curves of electrochemical detection of H_2O_2 concentration with Pd -PSMNP-based amperometric sensors. These PSMNPs have been obtained by using different ways to do the reduction process. Experimental conditions: potential: -250 mV; 0.1 M acetate buffer, pH = 5.0.