Poster

Polymer-Stabilized Monometallic Pd and Pd@Cu Core-Shell Nanoparticles: Preparation, Characterization and Electroanalytical Applications

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Metal nanoparticles (MNP) attract great interest of scientists and technologists due to their unique physical and chemical properties, which are distinct from both those of the bulk metal and those of isolated metal atoms. A high trend for aggregation is considered to be the main drawback of MNP, which substantially limits their practical application, as due to MNP coalesce, they lose 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, 2]. In many instances the electrochemical applications of MNP are based on the use of noble metals 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. A possible solution of this problem is the use of core-shell PSMNP, which are composed of a cheap metal core coated with a thin noble metal shell [3, 4].

In this presentation we report the results obtained by the comparative studying electrocatalytic properties of bimetallic (core shell) Pd@Cu -MNPs with their monometallic analogs (Pd-MNPs), which have been synthesized under identical conditions by using the polymeric membranes as a nanoreactor. The intermatrix synthesis of MNPs was carried out by sequential loading of the functional groups of sulfonated poly(etherether ketone) (SPEEK) with desired metal ions followed by their reduction inside the membrane, what resulted in formation of PSMNPs of required composition and structure. Metal nanoparticles were characterized by TEM, XRD and EDS techniques to evaluate the MNPs structure and composition and to estimate their size. Typical TEM images of the Pd- and Pd@Cu-MNPs are shown in Fig. 1. As it is seen, the size of monometallic Pd-MNPs is higher than that of Pd@Cu nanoparticles, although the value of palladium loading in both cases is the same. This also clearly follows from the respective MNP size distribution histograms shown in Fig. 2. Comparison of histogram of the initial core Cu-MNPs (also shown in Fig. 2) with that of Pd@Cu-MNPs indicates that an average size of core-shell MNPs is lower than that of the core nanoparticles.

PSMNP-inks (prepared by dissolution of MNP-containing membranes in organic solvent) were deposited on the surface of graphite-epoxy composite electrodes to study the electrochemical properties of polymer-PSMNP nanocomposites and to evaluate their electrocatalytic activity. The results of these experiments are shown in Fig. 3, where the calibration curves of amperometric detection of H_2O_2 are presented. As it is seen, the sensitivity of sensors based on the use of Pd- and Pd@Cu-MNPs synthesized by using the same value of palladium loading differs from each other. Indeed, the amperometric response of the later is higher than that of the former at the same concentration of hydrogen peroxide. One of the possible reasons for this difference is different values of surface areas of Pd@Cu- and Pd-MNPs. Another reason can be the influence of the core-metal on the catalytic activity of the shell. However, this point requires additional clarification and we continue our research in this direction.

References:

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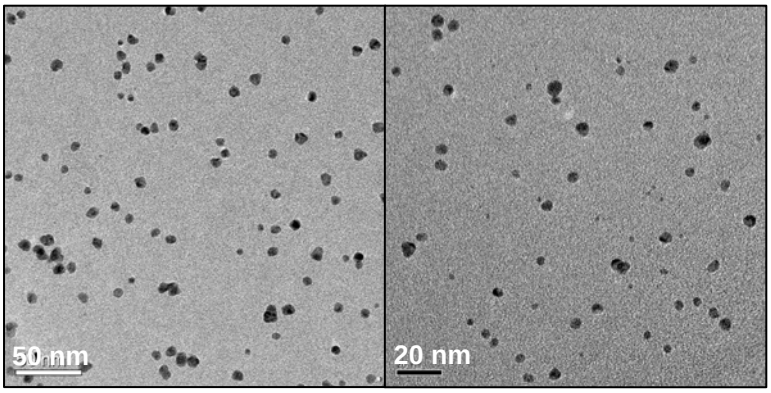
[4] J. Macanas, M. Farre, M. Muñoz, S. Alegret, D. N. Muraviev, Phys. Stat. Sol. (a), 203, **6**, (2006) 1194-1200.

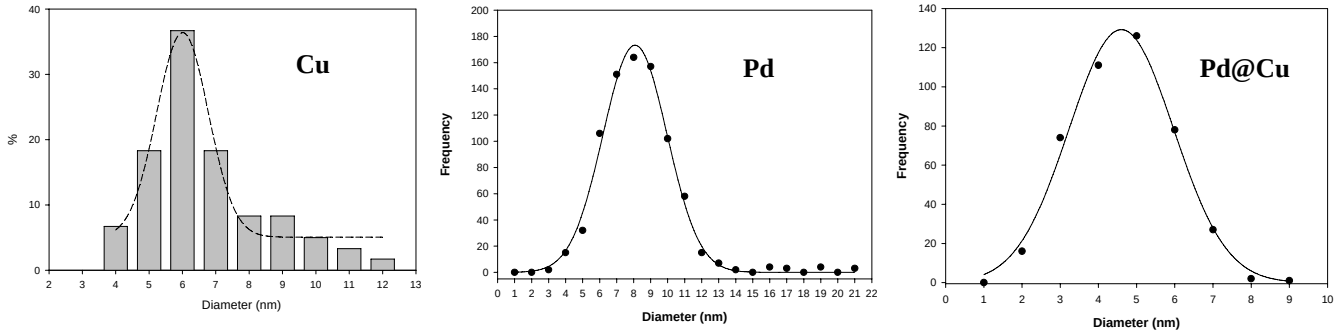
Figures:



(a) (b)

Fig. 1: *Typical TEM image of Pd- (a) and Pd@Cu-PSMNPs (b) prepared by intermatrix synthesis technique.*

Fig. 2: *Typical size distribution histograms of monometallic Pd-, Cu- and bimetallic core-shell Pd@Cu-PSMNPs.*



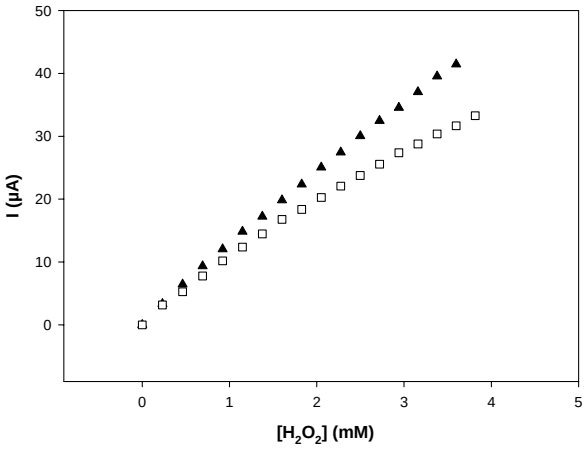


Fig. 3: *Figure 3. Calibration curves of amperometric sensors prepared by modification of graphite-epoxy composite electrodes with Pd- (white squares) and Pd@Cu-PSMNP-SPEEK membranes (black triangles) at identical values of palladium loading. Conditions: potential: -250 mV; 0.1 M acetate buffer, pH = 5.0.*