Inter-matrix synthesis of polymer stabilised metal nanoparticles for sensor applications

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Resum

Les partícules metàl·liques de mida nanomètrica o *Metal NanoParticles* (MNP) són objecte de gran interès en la recerca química actual a causa de les seves especials propietats elèctriques, magnètiques i òptiques, entre d'altres, que són diferents de les del material macroscòpic i, a la vegada, diferents de les dels àtoms i les molècules en forma aïllada. No obstant això, les MNP poden ser força inestables, fins al punt que si les superfícies es troben en contacte, poden combinar-se i provocar una pèrdua de la forma i de les propietats. El desenvolupament de nanopartícules metàl·liques estabilitzades mitjançant un polímer o *Polymer-Stabilized Metal NanoParticles* (PSMNP) és una de les solucions més prometedores per a resoldre el problema d'estabilitat de les MNP.

Aquest treball revisa les principals propietats dels PSMNP i les àrees on es podrien aplicar, incidint especialment en la utilització de nanocompostos polímer-metall per a sensors i biosensors electroquímics. També es descriuen i es comenten les noves tècniques per a la síntesi de PSMNP. Una d'aquestes tècniques es fonamenta en la utilització de fases sòlides amb reactius incorporats o *Solid-Phase-Incorporated-Reagents* (SPHINER) i l'altra empra membranes polimèriques funcionalitzades com a nanoreactors. Ambdós sistemes són capaços d'immobilitzar ions metàl·lics o complexos metàl·lics dins les matrius polimèriques abans de la seva reducció per a la formació de PSMNP. Els resultats obtinguts amb l'estudi de PSMNP de platí i pal·ladi a dins de matrius de clorur de polivinil (PVC) o polisulfona (PS) i de PSMNP de coure a dins de poli(èter èter cetona) sulfonada (SPEEK) confirmen l'aplicabilitat dels mètodes esmentats per a produir nanopartícules metàl·liques estabilitzades amb la composició i l'arquitectura desitjades. Els resultats preliminars d'anàlisi de nous elèctrodes preparats en diferents condicions mitjançant tècniques com ara la voltamperometria cíclica o l'amperometria confirmen l'aplicabilitat de sistemes amb PSMNP per a sensors i biosensors.

Abstract

Nanometer-sized metal particles or Metal NanoParticles (MNP) are objects of great interest in modern chemical research due to their unique electrical, magnetic, optical and other 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 will 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.

This paper reviews the main properties of PSMNP and the areas of their potential application mainly focusing on the use of polymer-metal nanocomposites in electrochemical sensors and biosensors. The novel approaches to synthesize PSMNP are also described and discussed. One of them is based upon the use of Solid-Phase-Incorporated-Reagents (SPHINER) and the other one uses the functionalized polymeric membrane (FP) as a nanoreactor. Both SPHINER and FP systems are able to chemically fix metal ions or complexes inside the parent polymeric matrix prior to their reduction and formation of PSMNP. The results obtained by studying the synthesis of Pt– and Pd-PSMNP inside polyvinyl chloride (PVC) or polysulphone (PS) matrix and Cu-PSMNP inside sulphonated poly(ether ether ketone) (SPEEK) confirm the applicability of these approaches to produce PSMNP of given composition and architecture. The preliminary results of cyclic voltammetric and amperometric analysis of electrodes prepared under different conditions confirm the usability of PSMNP systems in sensors and biosensors.

Paraules clau: Nanopartícules metàl·liques, polímers, estabilització, sensors, biosensors.

Keywords: Metal nanoparticles, polymers, stabilization, sensors, biosensors.

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1. Introduction

About 150 years ago scientists first began to understand that objects in the nanometer size range have special properties and behavior. The name «*colloid*» was given in 1861 by Scottish scientist Thomas Graham to objects in this size range, which, due to the dominance of surface forces in these materials, tend to be *sticky* or *adhesive*. A colloid or colloidal dispersion, is a form of matter intermediate between a true solution and a mixture (e.g., suspensions). Microscopic particles of one substance, said to be in the dispersed or solute phase, are distributed throughout another, said to be in the dispersing, continuous, or solvent phase. Colloidal sizes range from 0.001 to 1 micrometers in dimension. The electrostatic repulsion stabilizes a colloid because usually different phases generally have different charge affinities, so that a charge double-layer forms at any interface (see Fig.1a).

In the last 20 years a new focus has been initiated to control and to better understand these nanometer-size objects due to appearance of a new interdisciplinary field, which is known now as Nanoscience and Nanotechnology, which can also be called Nanomaterial Science. The main goal of Nanoscience and Nanotechnology is the creation of useful/functional materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties (physical, chemical and biological) at that scale

The nanometer-size objects are those, which have the nanometer size at least in one dimension (*D*). In this regard they can be subdivided in three following groups:

1) *1D* nanometer-size objects (such as e.g., thin films);
2) *2D* nanometer-size objects (e.g., nanowires, nanorods and nanotubes), and
3) *3D* nanometer-size objects (e.g., nanoparticles and/or nanoclusters).
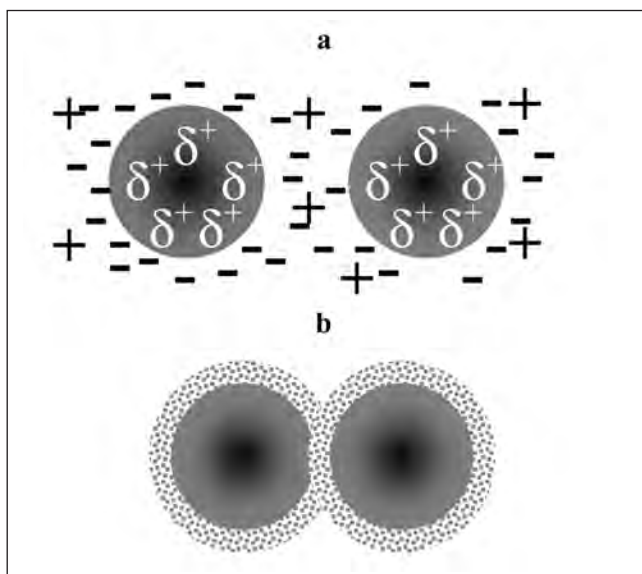

Figure 1. Stabilization mechanisms of MNP: (a) electrostatic stabilization (due to adsorption of ions to MNP surface and creation of electrical double layer, which results in Coulombic repulsion force between individual particles), and (b) steric stabilization (due to surrounding metal particle by layers of material that are sterically bulky).
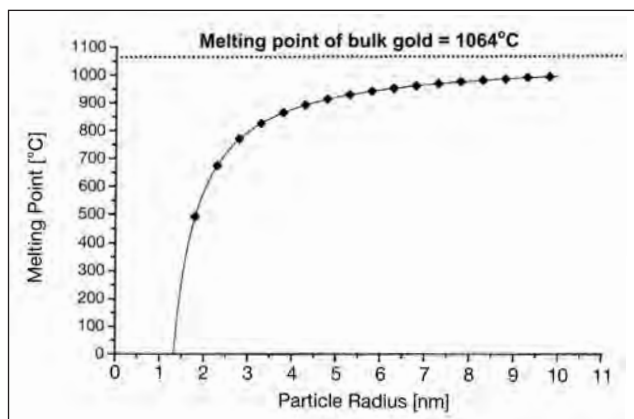

Figure 2. Dependence of melting point temperature on size of gold nanoparticles.

On the other hand, with regard to their size, metal particles can also be divided into three following groups:

1) Nanometric or ultradispersed: from 1 to 30–50nm;
2) Submicrometric or highly dispersed: from 30–50 to 100–500 nm, and
3) Micrometric: from 100–500 to 1000 nm

Nanometer-sized metal particles or Metal NanoParticles (MNP) are objects of great interest in modern chemical research [1–5] due to their unique physical and chemical properties (e.g., electrical, magnetic, optical, ionization potentials, etc.), which are distinct from both those of the bulk metal and those of isolated atoms and molecules. This can be illustrated clearly by the dependence of gold melting temperature on the size of gold nanoparticles, which is shown in Fig.2 [6].

MNP find wide application in such diverse fields as photochemistry, electrochemistry, catalysis, optics, medicine amongst others [7–16]. MNP can be so fragile and unstable that if their surfaces touch, they will 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, and as such, they attract great attention of scientists and technologists. PSMNP possess both a high stability and the unique combination of their properties [17–19]. Composite PSMNP materials, which find industrial applications, are mainly known as resin-stabilized MNP [9–11], which are obtained through the anchoring of suitable precursors (metal ions or complexes) to properly designed functional resins followed by their reduction inside the polymeric network. For example, they are used as active supports of palladium metal in the preparation of bi-functional catalysts comprising the acid as well as the hydrogenation-active centers. Such catalysts are currently employed in at least four industrial processes. Nevertheless, the areas of potential applications of PSMNP can be substantially widened due to the unique combination of their properties and a great deal of scientific experience accumulated in this particular area [17–21].

In general, the catalytic efficiency of supported catalysts (in the case of both polymeric and carbon or inorganic supports) is primarily determined by the accessibility of the catalytically ac-
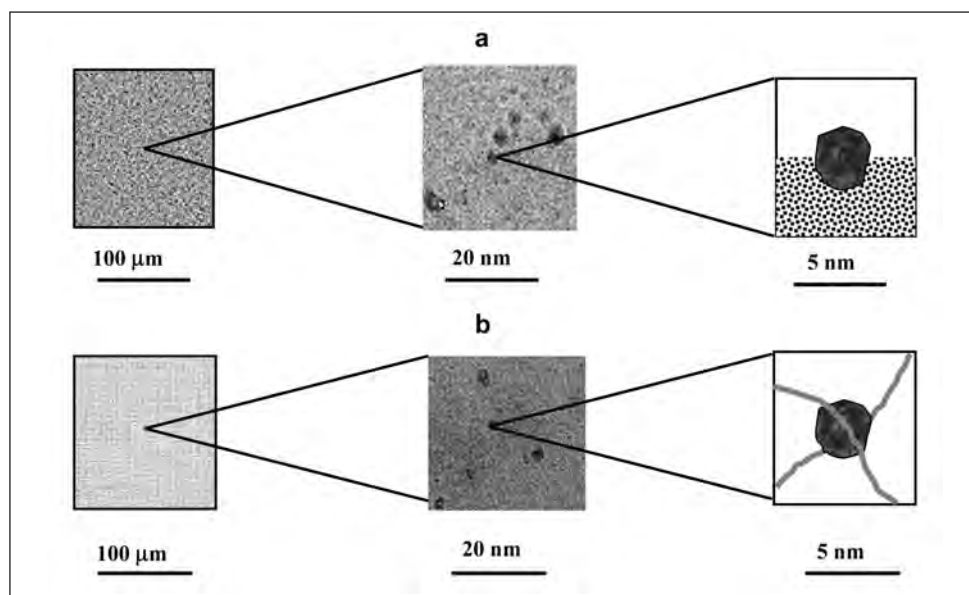
Figure 3. Comparison of accessibility of catalytically active MNP supported on inorganic supports (a) or in polymeric matrix (b).

tive MNP to reactants. A comparison of location of MNP-catalysts supported on inorganic and polymeric resin supports is shown in Fig.3. As seen in Fig. 3, supported MNPs inside the pores of an inorganic support are in direct contact with a surrounding liquid phase. Although only a part of the MNP surface is accessible to reactant molecules. In the case of the PSMNP the accessibility of the MNP surface is evidently higher. At the same time PSMNP are located inside a polymer matrix and therefore their contact with reactant molecules is mediated by the swelling of polymer networks in the liquid phase. Reagents involved in a given metal-catalyzed reaction must be able to enter the swollen resin, where the reaction proceeds. As a consequence, the physico-chemical features of the polymeric support can be (and must be) designed and controlled in such a way to enhance the mass-transfer inside the polymer gel microreactor. This must be also taken into account when designing the sensor or biosensor systems based upon the use of PSMNP.

2. MNP magic numbers

The properties of MNPs (such as, ionization potential and bonding energy per metal ion, interatomic distances, optical and magnetic properties, electron conductivity, electron-substrate interactions among others) are size-dependent and change non-monotonically with cluster size. This non-monotonic dependence is determined by the «magic numbers», i.e. a discrete set of number of atoms, corresponding to the formation of energetically favorable MNPs. Indeed, clusters containing certain special number of atoms occur more frequently than the others. For example, clusters of 3 (forming a triangle), 4 (forming a tetrahedron), 6 (forming a octahedron), and 8 atoms (forming a cube) are far more common than clusters of 5, 7, or 9 atoms. Teo and Sloane [22] have proposed equations, which permit calculation of the total number of atoms (Gn) and the number of surface atoms (Sn) for clusters (or MNPs in our case) of different structure. For examples, for

MNPs which form tetrahedronal or cubic structures G_n and S_n values are determined by the following expressions:

Tetrahedron

$$G_n = \frac{1}{6}(n+1)(n+2)(n+3) \tag{1}$$

$$S_n = 6n^2 + 2 \tag{2}$$

Cube

$$G_n = (n+1)^3 \tag{3}$$

$$S_n = 6n^2 + 2 \tag{4}$$

where n in the above equations stands for the atom rows. Table 1 shows examples of calculation of G_n and S_n values for MNPs of different structure and size (for different n values).

Table 1. G_n and S_n values for MNP of different structure and size[*].

Tetrahedron								
n	1	3	5	6	7	8	9	10
G_n (equation 1)	4	20	56	84	120	165	220	286
S_n (equation 2)	4	20	52	74	100	130	164	202
$S_n/G_n \times 100$, %	100	100	93	88	83	79	75	71
G_n (equation 3)	8	64	216	343	512	729	1000	1331
S_n (equation 4)	8	56	152	218	296	386	488	602
$S_n/G_n \times 100$, %	100	88	70	64	58	53	49	45

* Adapted from Ref. [21].

As it is clearly seen from the results shown in Table 1, the fraction of surface atoms, $S_n/G_n \times 100$, for clusters of different structure decreases with size. Nevertheless, even for MNPs with n=10, which can be estimated to correspond to the clusters of ~ 4nm in diameter (for an average unit cell parameter of 0.4nm) the fraction of surface atoms remains sufficiently high (~70% for a tetrahedron and 45% for a cube).

3. MNP stability problem

The above estimation helps to understand the main reason for MNP instability and therefore the necessity of their stabilization. The stabilization of MNP is required, for example during their growth to protect nanoparticles from Oswald ripening. The Oswald ripening is the growth mechanism where small particles dissolve, and are consumed by larger particles. As a result the average nanoparticle size increases with time and the particle concentration decreases. As particles increase in size, their solubility decreases. Generally speaking the stabilization of MNP is required for a number of reasons: 1) to prevent the uncontrollable growth of particles, but also 2) to prevent particle aggregation; 3) to control the particles growth rate; 4) to control particle size, and finally 5) to allow particle solubility in various solvents.

The stabilizing agent can be either some ligands, capping agents and passivating agents or surfactants and polymers. In the last case the stabilization mechanism can be qualified as steric stabilization as nanoparticles appear to be surrounded by the layers of material that are sterically bulky as is shown in Fig.1b.

Figure 4 illustrates the results of MNP synthesis with and without stabilization. Figs.4a and 4b show TEM images of Pt-MNP synthesized inside the PVC matrix by using the Solid Phase Incorporated Reagents (SPHINER) technique (see below) after reduction with aqueous formaldehyde solution. As is seen, the size of platinum nanoparticles does not exceed 5–7 nm. The particles are well separated from each other due to stabilization with PVC chains inside the polymeric matrix, which prevents them from aggregation. Figures 4c and 4d illustrate the case of platinum MNP formation outside the PVC matrix, i.e. in the solution of reducing agent (formaldehyde), which occurs in the course of the same experiment due to the partial extraction of platinum ions from the polymer surface by transfer to formaldehyde solution. As it is seen in Fig.4c, in the absence of stabilizing agent the size of Pt-MNP exceeds by almost one order of magnitude that of Pt-PSMNP (approx. 40–50 nm vs 5–7 nm). Moreover, non-stabilized Pt-MNPs tend to aggregate in the solution phase so that finally they form bigger particle clusters (see Fig. 4d).
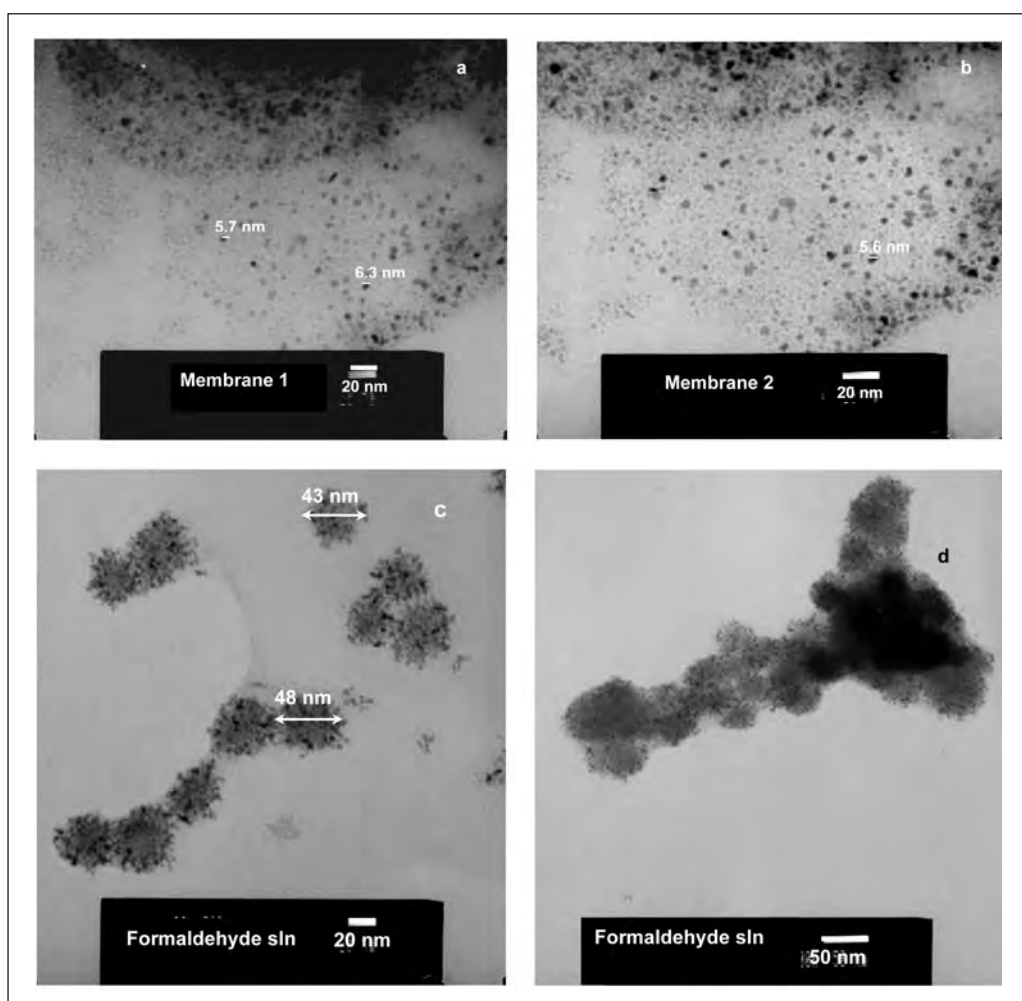

Figure 4. Formation of Pt-MNP with (a, b) and without (c, d) stabilization. Conditions: (a, b) synthesis of Pt-MNP by SPHINER technique (see text below) inside PVC matrix; (c) formation of big Pt-MNP in aqueous solution of reducing agent (formaldehyde); (d) further aggregation of Pt-MNP in formaldehyde solution.

The mechanism of MNP stabilization with polymers can be explained by using the following two approaches:

1) Substantial increase of viscosity of the immobilizing media (the polymer matrix).

As follows from the Smoluchowsky equation, the rate constant of particle coagulation, k_c, is inversely proportional to the viscosity of the media, η, i.e.:

$$k_c = \frac{4kT}{\eta} \qquad (5)$$

Here k stands for the Boltzman constant, and T is the temperature. A similar conclusion follows from the Stokes-Einstein equation, which permits to determine the diffusion coefficient of a spherical particle of radius r in a viscous medium:

$$D = \frac{kT}{6\pi\eta r} \qquad (6)$$

Nevertheless, as it has been shown elsewhere [23] the mobility of Au nanoparticles in poly(t-butyl acrylate)/gold composite decreases by 2 or 3 orders of magnitude compared with that predicted by Stokes-Einstein equation. The authors ascribe this discrepancy to strong bridging interactions between Au-MNPs and the chain segments of the stabilizing polymeric matrix. As a result, the mobility of nanoparticles inside the polymer substantially decreases and the matrix, in turn, appears to be a somewhat "crosslinked" so that effective viscosity of the polymer increases by a factor of ~ 4 [24].

2) Substantial decrease of the energy of particle-particle interaction in PSMNP systems (e.g., in polymer-MNP composites) versus non-stabilized MNP dispersions.

The potential energy of attraction (Ur) between two spherical particles of radius *r* can be approximately described by the following simplified expression:

$$U_r \approx \frac{Ar}{12l_0} \, at \, r \gg l_0 \qquad (7)$$

where *A* is the effective Hamaker constant having the dimensions of energy, and *l_o* is the minimum distance between particle surfaces. The value of the Hamaker constant A is known to be close to *kT* for polymer particles, while for the metal dispersions it is far higher. This is illustrated by the data given in Table 2 [25].

Table 2. Values of effective Hamaker constant for particles of different materials*.

Material of particle	Effective Hamaker constant, $A \times 10^{20}$, J
Poly(methyl methacrylate)	6.3
Polysterene	6.15
Al_2O_3	15.5
Silver	40

* Adapted from Ref. [18].

4. Application of PSMNPs in sensors and biosensors

The areas of practical application of metal-polymer composites is very wide. Applications are found as electroconductive pastes and glues, special coatings, paints and varnishes, rheomagnetic fluids, antifrictional polymeric coatings, construction materials in aviation and space technology, catalysis and many others. PSMNP s containing polymeric membranes are used as electroconductive and optical materials, supported catalysts and also as active elements in sensors and biosensors.

The development of sensors and biosensors for detection and quantitative determination of various inorganic, organic and biomolecules has a great potential for application in: clinical, biomedical, and environmental research fields. In basic terms, a biosensor is an analytical device that incorporates a biological sensing (recognition) element integrated in very close proximity to a signal transducer, thus combining the absolute selectivity of the biological system with the processing power of modern electronics. A successful chemical sensor must have good sensitivity, selectivity, reversibility, speed, and longevity toward the desired analyte while consuming minimal power and volume. Additionally it must be able to be manufactured from inexpensive materials using economical batch methods.

The PSMNPs do not find yet a wide use in the field of sensors and biosensors although in some recent publications one can find a clear conformation of their applicability in different sensing systems [26–28]. For example, as it has been shown by Sergeev et al [29–30] the electroresistivity of Pb-poly-(p-xylylene) nanocomposite film (with the size of Pb nanoparticles of 30 nm) in the presence of NH_3 in the air changes dramatically; as is clearly seen from Table 3. The applicability of the sensing system based upon the data shown in Table 3 is quite evident. Indeed, the sensing systems this type can find wide application for control of the ammonia content in the indoor air of animal farms to control of the release of contaminated air to the atmosphere through the farm ventilation systems [31].

Another route to use PSMNPs for the development of sensors and biosensors deals with the enhancement of the biosensor performance. This clearly follows from the possibility to substantially improve the electron-transfer in amperometric biosensors. The electron-transfer mechanisms in biosensors of this type have been recently reviewed by Habermüller et al. [32]. They distinguish several possible electron-transfer mechanisms such as, direct electron transfer

Table 3. Change of electroresistivity of Pb-poly-(p-xylylene) nanocomposite film in presence of NH_3 in the air [28].

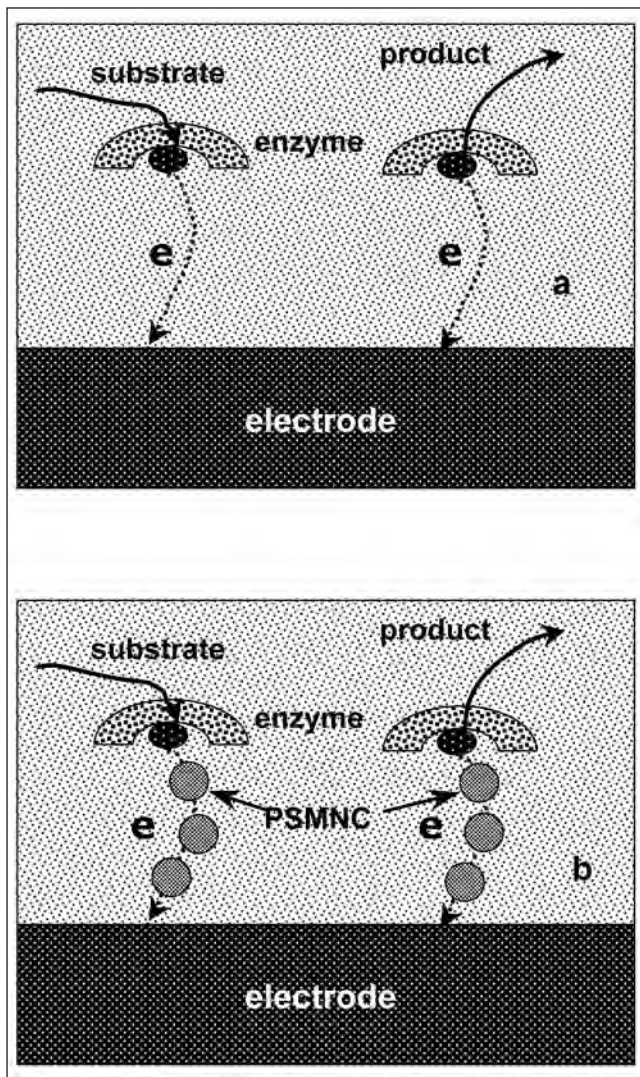| Pb content, %	R_o (0 ppm NH_3, v/v), $\Omega\,cm^{-2}$	R (13 ppm NH_3, v/v), $\Omega\,cm^{-2}$
0.5	10^{16}	4×10^{10}
2.0	10^{16}	2×10^{10}
4.5	10^{15}	3×10^9
7.5	10^{14}	2×10^7

Figure 5. Electron-transfer mechanisms in amperometric biosensors: (a) direct electron transfer (tunneling mechanism) from active site of enzyme to electrode surface, (b) improved direct electron transfer from active site of enzyme to electrode surface in PSMNP containing matrix.

Figure 6. Electron-transfer mechanisms in amperometric biosensors: (a) electron transfer via redox mediator used as "electron-transfer shuttle", and (b) electron-hopping mechanism in a mediator-modified immobilization matrix.

(tunneling mechanism) (see Fig. 5) and mediated electron transfer with the use of redox mediators, which can serve either as "electron-transfer shuttles" (see Fig.6a) or as a sort of "electron trampolines" in case of electron-hopping mechanism (see Fig.6b).

Introduction of PSMNCs into the enzyme immobilizing matrix can substantially improve the electron conductivity of the matrix and, therefore enhance the electron transfer from the enzyme molecule to the surface of the electrode as it is shown schematically in Fig. 5b. The same effect can be expected in the case of mediated electron transfer systems due to the shortening of the electron-hopping distance.

5. Preparation of PSMNPs by using Solid-Phase-Incorporated-Reagents (SPHINER)

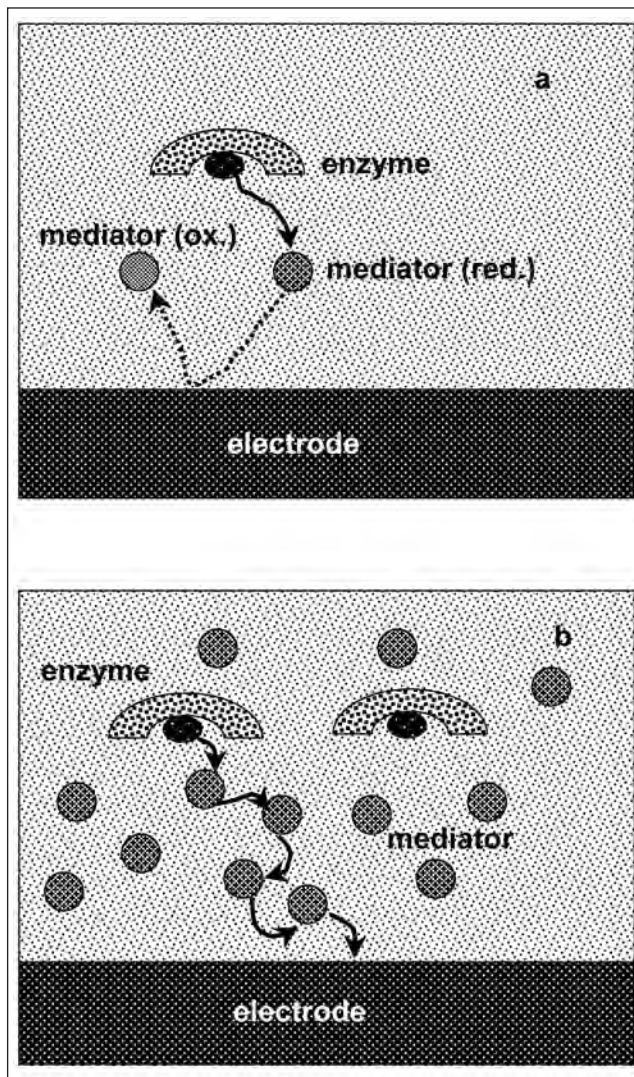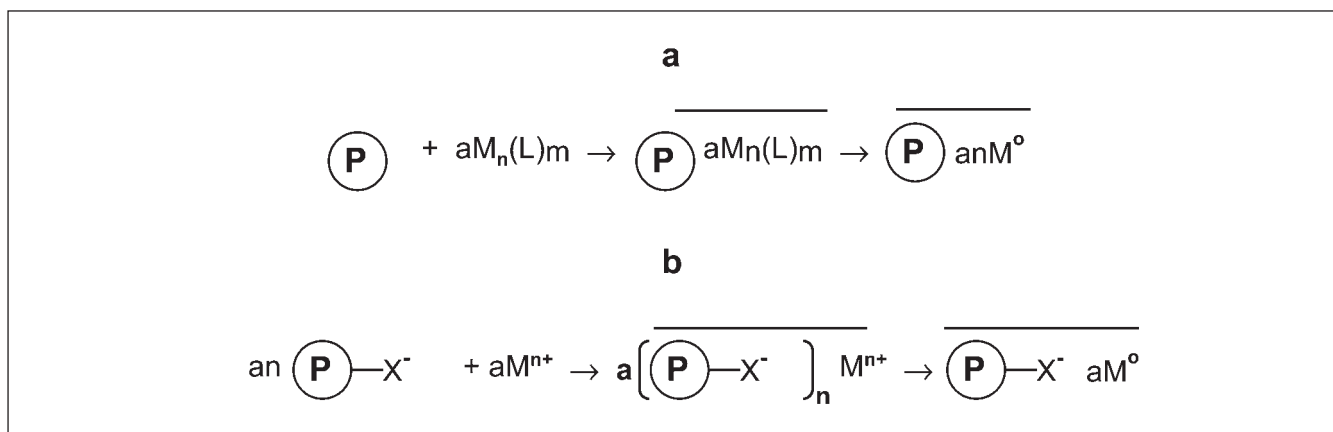The general methods for preparation of PSMNP can be divided into two main groups [17–21], namely, the physical (main-ly based on condensation techniques), and the chemical ones (mainly based on reduction of metals inside polymer). Examples of physical methods are cryochemical deposition of metals on polymeric supports and simultaneous plasma-induced polymerization and metal evaporation techniques. The chemical methods include, for example, thermal decomposition of precursor compounds in polymer, formation of PSMNP at the polymerization stage, and intermatrix synthesis of PSMNPs. This last method will be considered below more in detail.

The intermatrix synthesis of PSMNPs can be based on the following two approaches:

1) The use of Solid-Phase-Incorporated-Reagents, which permit immobilization of metal ion or metal complexes in non-functionalized polymeric matrices followed by metal reduction as illustrated by Scheme 1a.

2) The second approach is based on the use of functionalized polymers, where matrices bear the desired functional

a

$$\text{P} + aM_n(L)m \rightarrow \overline{\text{P} \, aMn(L)m} \rightarrow \overline{\text{P} \, anM^o}$$

b

$$an \, \text{P}-X^- + aM^{n+} \rightarrow a\overline{\left[\text{P}-X^-\right]_n M^{n+}} \rightarrow \overline{\text{P}-X^- \, aM^o}$$

Scheme 1. PSMNC formation in pre-shaped polymer matrix by using SPHINER technique (a) and functionalized polymers (b).

groups (cationic or anionic). The PSMNP preparation procedure in this case includes sequential loading of the polymer functional groups with metal ions and their reduction inside the polymer as shown in Scheme 1b.

The Solid-Phase-Incorporated-Reagents (SPHINER) are mainly known as extraction chromatographic materials (ECM) [33–36], solvent impregnated resins (SIR) [37–43] and intercalates (IC) [44–46]. The main difference between SPHINER systems of these types is illustrated by Figure 7. In all above cases the reagent (e.g., extractant) is immobilized on the surface of a solid support (as in case of ECM) or inside a supporting organic polymeric (SIR) or layered inorganic matrix (IC). Only some of SPHINER systems under discussion (IC) start to be applied to the preparation of PSMNP [47, 48].

The solid supports in the majority of SPHINER systems of known types are usually pre-shaped matrices (organic or in-

organic) of different physical forms (mainly granulated or powdered). The polymeric supports in majority of SPHINER systems represent crosslinked polymers, which are insoluble either in organic solvent or in water. This makes it hardly possible to change the physical form of the support which is sometimes required in the design of sensors and biosensors.

This problem can be successfully solved by using non-crosslinked polymers, which are on one hand soluble in organic solvents and, on the other, insoluble in water, as supports for SPHINER and therefore for PSMNP produced by this means. The polymers of this type such as, for example, poly(vinyl chloride), PVC, are used as both matrices for the synthesis of PSMNP [49] and enzyme immobilization matrices for biosensors of different types [50–52]. The types of SPHINER used for incorporation in soluble polymers and therefore for the intermatrix synthesis of PSMNP can be extractants, which are selective of the desired metals [53]. In this case the synthe-
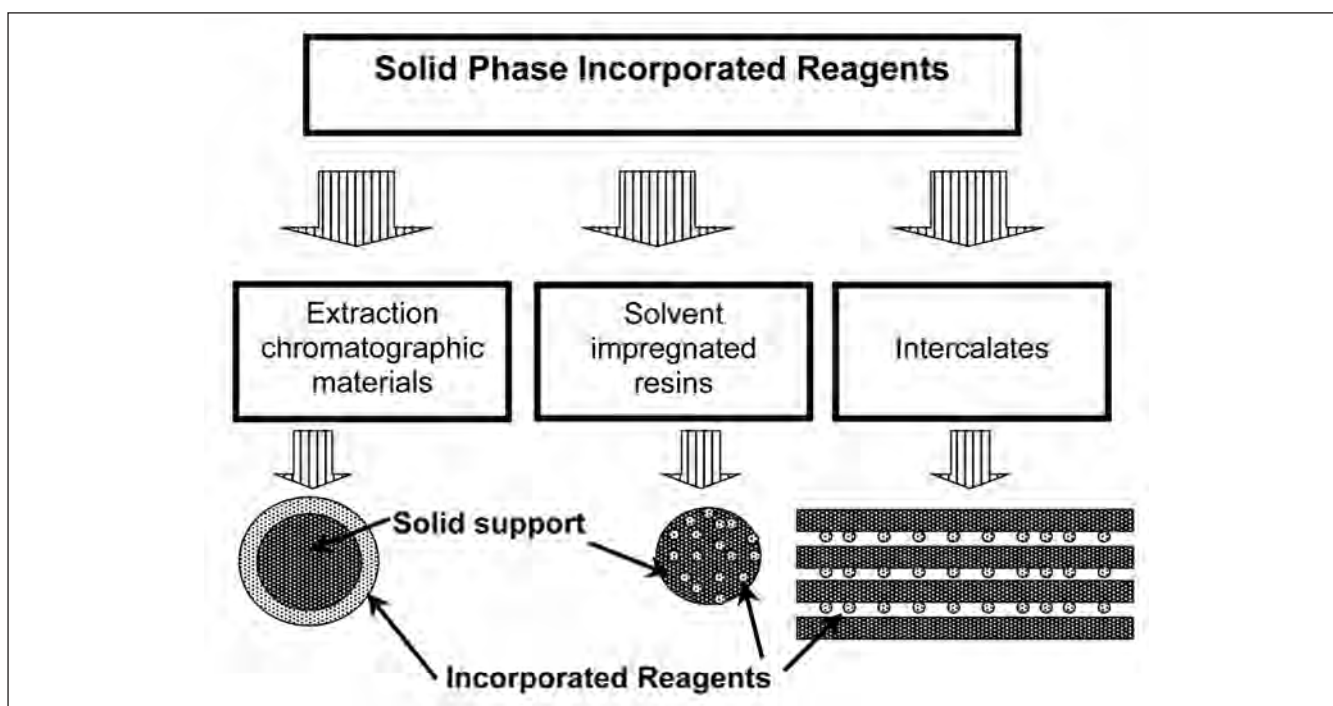

Figure.7. Solid Phase Incorporated Reagent (SPHINER) systems of different type.
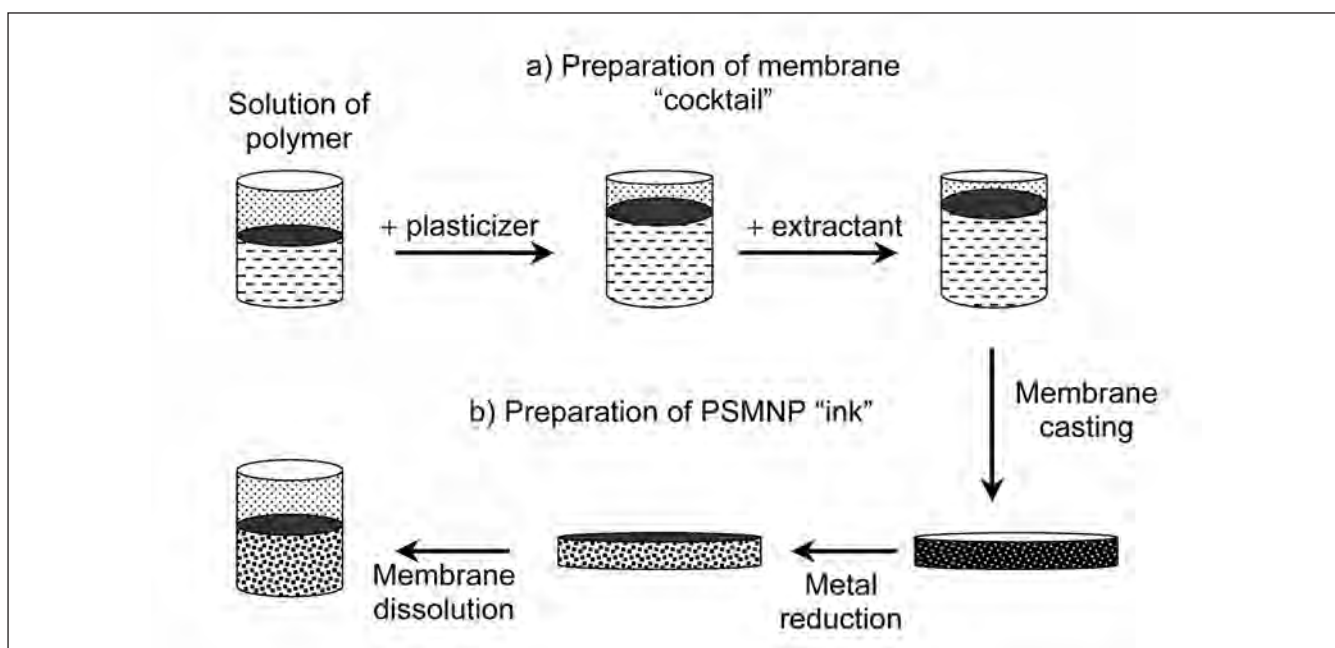
Figure 8. Scheme of preparation procedure for synthesis of PSMNP "ink" by using SPHINER systems.

sis of PSMNP can follow the procedure shown schematically in Fig. 8.

As seen in Fig. 8, the procedure includes the following sequential stages: 1) preparation of the membrane casting solution (membrane "coctail"); 2) membrane casting; 3) reduction of metal ions inside the polymer (intermatrix synthesis of PSM-NP), and 4) dissolution of PSMNP-containing membrane in an appropriate solvent to produce the PSMNP "ink", which can be deposited of the surface of an electrode to study the electro-chemical properties of the polymer-PSMNP composite. The same ink can be used for characterization of PSMNP particles by Transmission Electron Microscopy (TEM).

6. Intermatrix synthesis of PSMNP using non-functionalized polymer-SPHINER systems

The intermatrix synthesis of PSMNP using non-functionalized polymer-SPHINER systems can be illustrated by the results obtained by studying PVC-tributyl-phosphine oxide (TBPO) SPHINER system to synthesize platinum and palladium PSM-NP [54]. The experimental procedure included the following stages (see Fig.8):

1) Extraction of Pt or Pd ions with tributyl-phosphine oxide (TBPO) under conditions described elsewhere [53];
2) Preparation of membrane "cocktail": PVC + plasticizer (o-ni-trophenyl-octyl-ether) + TBPO pre-loaded with Pt or Pd ions;
3) Preparation of solid polymeric membrane followed by chemical reduction of Pt or Pd ions;
4) Dissolution of the membrane in THF to prepare Pt– or Pd-MNP "ink", and
5) Examination of ink samples by TEM to determine the size and structure of Pt and Pd PSMNP.

Figures 4 (see above), 9 and 10 show the typical TEM images of Pt (see Figs. 4 and 9) and Pd (see Fig. 10) PSMNP synthesized in a stabilizing PVC matrix. As is evident, the size of both
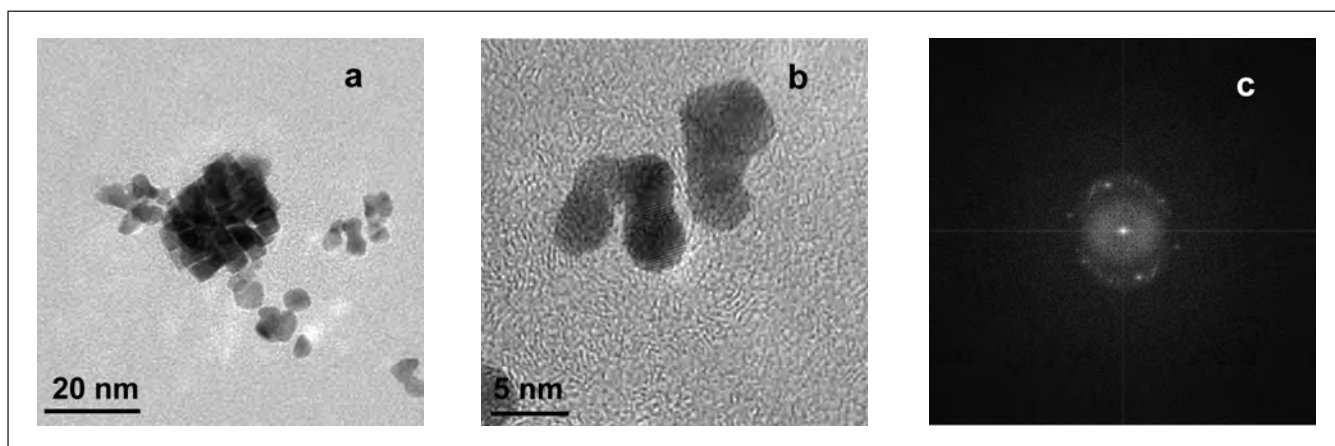

Figure 9. TEM images of PVC immobilized Pt-PSNMP (a, b) and diffraction pattern of Pt nanoparticles shown in b.
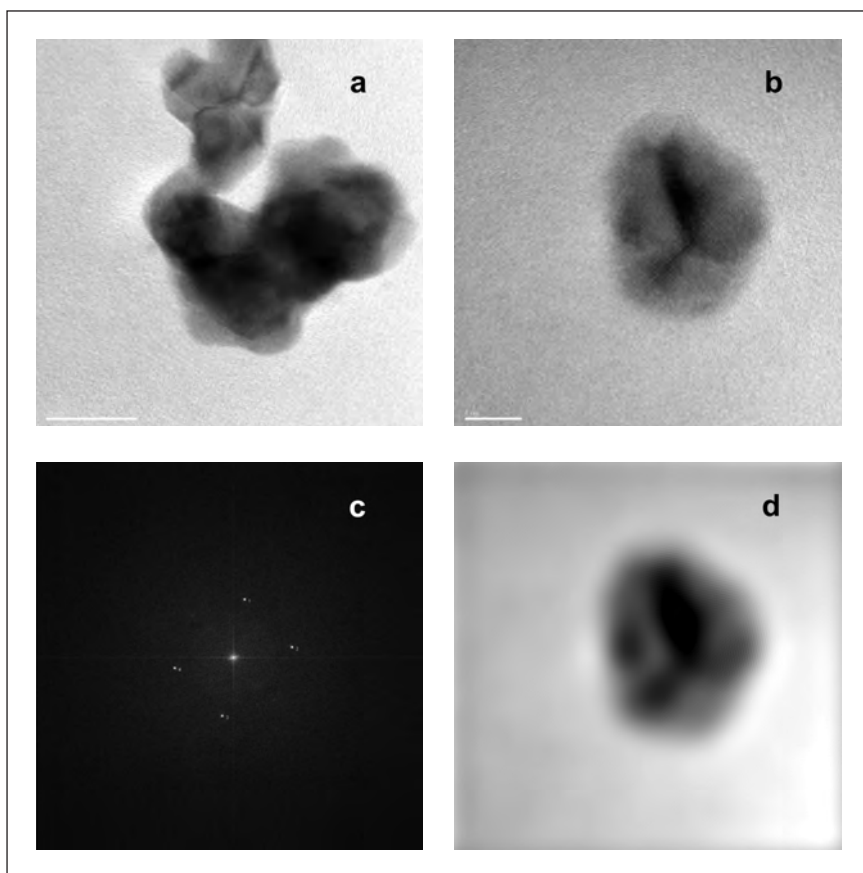
Figure 10. (a, b) TEM images of PVC immobilized Pd-PSNMP, (c) diffraction pattern of Pd nanoparticles shown in (b), and (d) inverse FFT image of Pd particle shown in (b).

Pt and Pd nanoparticles is at the level of 6–7 nm, although the formation of MNP clusters is also observed in some instances (see Fig. 9a).

The PSMNP-ink can also be used to deposit PSMNP-containing membranes on the surface of graphite-epoxy composite (GEC) electrodes [55] to study the performance of PSMNP-modified electrodes by, for example, cyclic voltammetry and other electrochemical techniques. In this case GEC electrodes serve as a conventional tool for studying the properties of polymer-MNP composites of different types. Some exam-

ples of comparative studies of Pt-MNP-poly(vinyl chloride) (PVC) and Pt-MNP-polysulfone (PS) composite membranes deposited on GEC electrodes by cyclic voltammetry are shown in Figs. 11, 12 and 13 [54].

Fig. 11 shows a comparison of the performance of GEC electrodes modified with a metal-free PVC membrane (see curve 3) and electrodes modified with Pt-PSMNP-PVC-composite membranes (see curves 1 and 2). In all cases membranes were formed on the electrode surface by drop-by-drop deposition of the corresponding membrane "cocktail" contain-
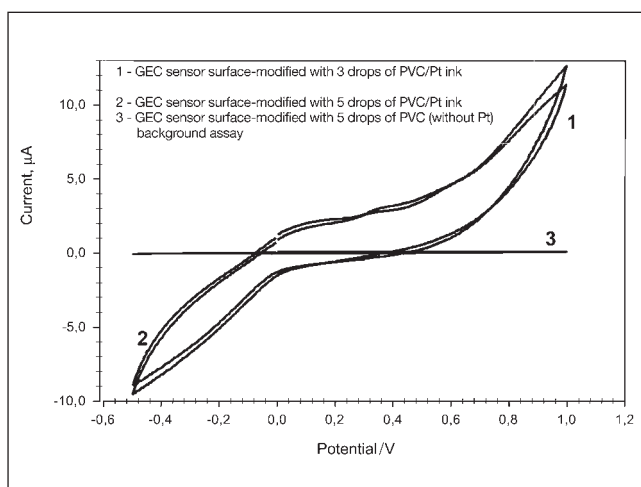

Figure 11. Cyclic voltammetry of GEC sensors modified with PVC-Pt-MNP (curves 1 and 2) and MNP-free PVC (curve 3) membranes. Conditions: scan rate 3 mV/s, $K_4[Fe(CN)_6]$ 5 mM, acetate buffer pH 5, KCl 0.1 M. Electrochemical Pt reduction during 10 minutes at -1.6 V.
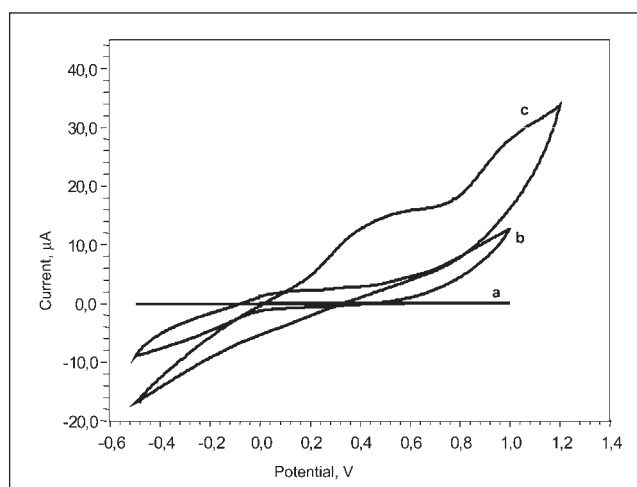

Figure 12. Comparison of cyclic voltammetry of GEC sensors modified with PVC (a); PVC-Pt (b) and PS-Pt (c). Conditions: membranes formation by drying; scan rate 3 mV/s, $K_4[Fe(CN)_6]$ 5 mM in acetate buffer pH 5, KCl 0.1 M. Electrochem. Pt reduction for 10 min. at -1.6 V.
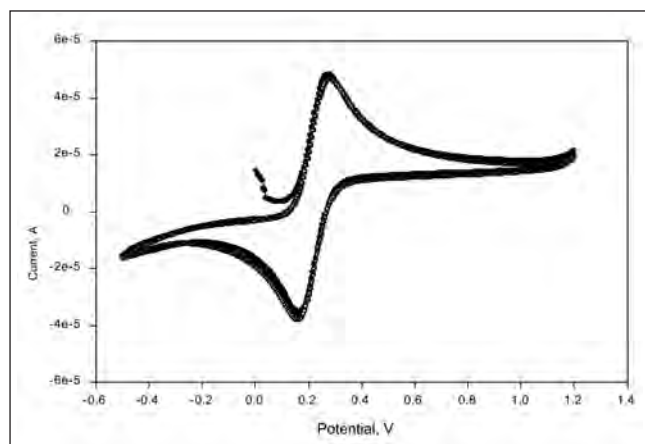
Figure 13. Cyclic voltammetry of GEC sensors modified with Polysulfone/Pt-MNP. Conditions: membranes formation by phase inversion mechanism; scan rate 3 mV/s, $K_4[Fe(CN)_6]$ 5 mM in acetate buffer pH 5, KCl 0.1 M. Electrochem. Pt reduction for 10 minutes at -1.6 V.

Scheme 2. Schematic structure of repetitive units of poly (ether ether ketone) (PEEK) and sulfonated PEEK (SPEEK).

ing either platinum-free extractant (tributyl-phosphine oxide in this case) or extractant pre-loaded with platinum ions followed by drying at 40°C. Note that unlike the procedure shown in Fig. 8, Pt-PSMNP-PVC-composite membranes were formed in this case by *in situ* electrochemical reduction of platinum inside the polymer matrix. As can be seen, the presence of Pt-MNP inside the PVC matrix dramatically changes the membrane electroconductivity, it increases by several orders of magnitude. Nevertheless, the mass-transfer properties of the membrane appear to be insufficiently improved which follows from the absence of clearly pronounced oxidation-reduction peaks of the analyte being studied ($K_4[Fe(CN)_6]$).

Although the situation improves when moving from PVC-Pt to polysulfone (PS)-Pt membranes, which clearly follows from the comparison of curves b and c in Fig. 12, the mass-transfer characteristics of the sensor still remain unsatisfactory. The desired result is achieved when changing the membrane casting technique from drying to the phase inversion. Indeed, as follows from the results shown in Figs.12 (see curve c) and 13, the shape of voltammerograms of GEC-PS-Pt sensors with membranes obtained by different methods differs dramatically from one another. The first (and most likely 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 PS-membranes with highly developed macroporous structure resulting in a far higher rates of mass transfer [40] to be obtained. The second reason is associated with higher hydrophilicity of the PS matrix in comparison with PVC. This conclusion clearly follows from the structure of repeated units of PS chains.

7. Intermatrix synthesis of PSMNP by using functionalized polymer-SPHINER systems

Application of functionalized polymers for the intermatrix synthesis of PSMNP and their further practical use dictates certain
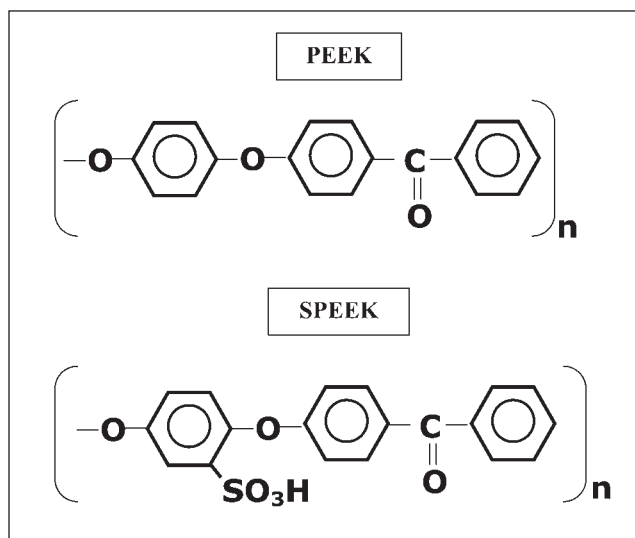
necessary requirements to the parent matrix (inside which the MNP must be synthesized), which in general depend on the technical or technological features of the field of their particular application. For example, in case of their use in sensor or biosensor constructions, which are to be applied to the analysis of aqueous solutions, the polymer must be insoluble in water. On the other hand, to provide sufficient permeability of the PSMNP-containing membrane for analyte ions or molecules it must either slightly swell in water or at least be hydrophilic. In addition it must also be soluble in some organic solvents to allow for the preparation of membrane "cocktails" or PSMNP "inks".

One of the polymers, which meets the above requirements is sulfonated poly(ether-ether ketone) . The structures of the initial poly(ether-ether ketone) (PEEK) and sulfonated PEEK (SPEEK) are shown schematically in Scheme. 2.

The sulfonation degree is the most important factor, which determines the solubility of SPEEK both in water and in organic solvents [56, 57]. Thus complete sulfonation of PEEK (one sulfonic group per benzene ring, 100% sulfonation degree) results in quite good solubility of SPEEK in hot water [56], which is undesired. At lower sulfonation degrees (around 60%) SPEEK appears to be insoluble in water (up to ~60°C) while it is soluble in some organic solvents such as, for example, dimethyl formamide (DMF).

The presence of sulfonic groups in the polymer matrix permits us to load them with metal cations by using conventional ion-exchange mechanism. Further reduction of the metals inside the SPEEK matrix with, for example, sodium borohydride ($NaBH_4$) solution, results in the formation of MNP stabilized by SPEEK polymer chains (i.e., PSMNP). The size of metal particles obtained by intermatrix synthesis technique appears to be at the same scale as in SPHINER systems. This is seen in Fig. 14 [58], where TEM and high resolution TEM images of Cu-PSMNP synthesized in the SPEEK matrix are shown.

At the same time, after metal reduction the functional groups of the polymer are converted in the Na-form. This per-
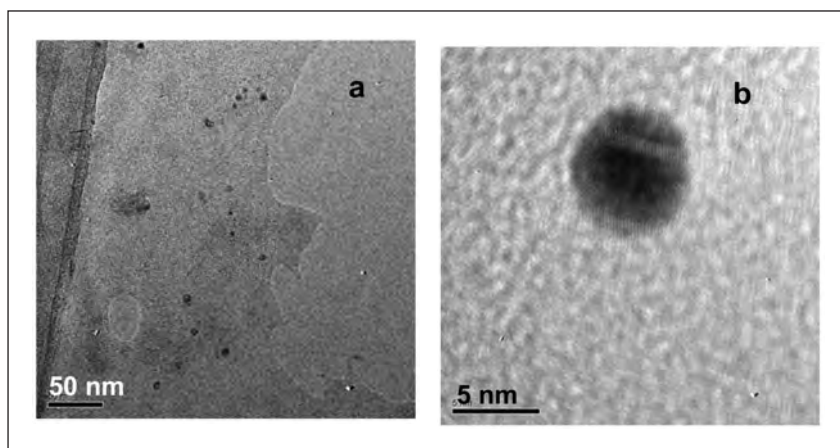
Figure 14. TEM (a) and high resolution TEM (b) images of Cu-PSMNP synthesised inside SPEEK matrix.

Table 4. Results of sequential loading of SPEEK with Cu.

No. Cycle	Cu content, mmol/g SPEEK	Cu content, mg/g SPEEK
1	1.02	6.5
2	1.85	11.7
3	1.96	12.5

mits repetition of the metal loading-reduction cycle and therefore, to increase PSMNP content in the polymer. The results of three sequential loading reduction cycles of SPEEK matrix with Cu PSMNP are shown in Table 4 [58].

As can be seen from the data shown in Table 4, the content of Cu-PSMNP in SPEEK substantially increases in the course of repetitive metal loading-reduction cycles.

Besides the electroconductivity, the morphology of the membrane changes dramatically in the course of the loading with PSMNP. This is clearly seen in the SEM images presented in Fig.15 [58]. Indeed, comparison of the image shown in Fig. 15a with those

shown in Figs. 15b and 15c indicate that initially smooth gel structure of SPEEK membrane surface transforms to the "worm-like" structure after membrane loading with Cu-PSMNP. These morphological changes are to be evidently associated with the inter-membranes mechanical stress, resulting from a strong interfacial interaction between Cu nanoparticles and the SPEEK chains. Similar changes to the polymer structure were observed for some other polymer-MNP composites [59].

The morphological changes observed must substantially improve the mass-transfer properties of the SPEEK-Cu-PSMNP composite membranes in comparison with the initial (copper-free) polymer due to the appearance of clearly visible macropores (see Fig. 15d). In the case of GEC electrodes, the surface of which is modified with SPEEK-Cu-PSMNP composite membranes, these morphological changes must, in turn, substantially enhance the transport of the analyte molecules to the electrode surface improving its sensing performance. The results shown in Figure 16 confirm this conclusion. Indeed, as
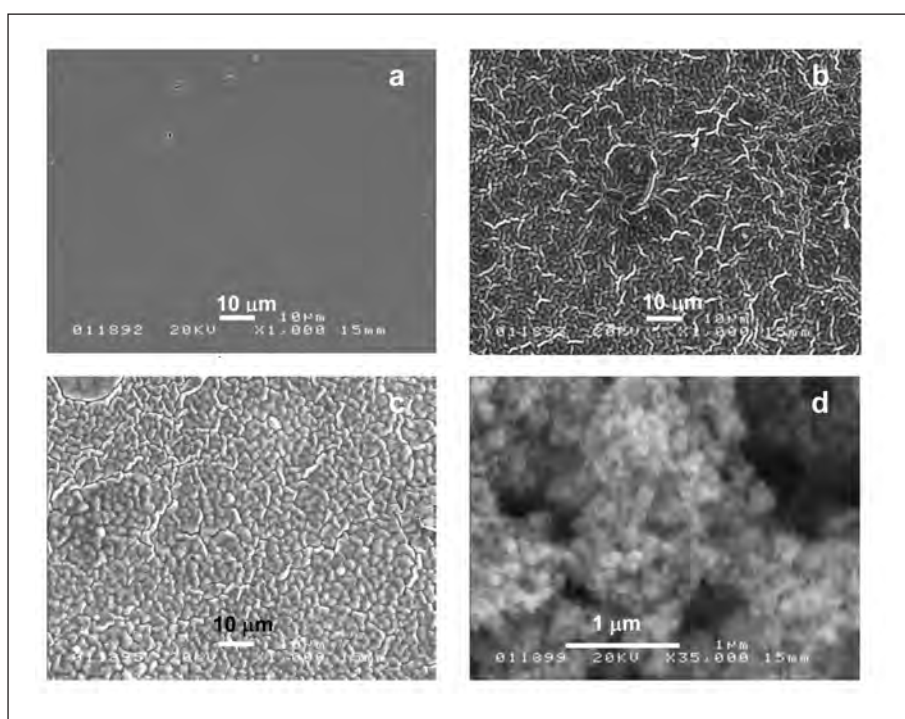

Figure 15. SEM images of initial SPEEK membrane (a) and same membrane after first (b) and second (c) metal (Cu) loading-reduction cycle. (d) Internal macroporous structure of Cu-PSMNP-loaded membrane.

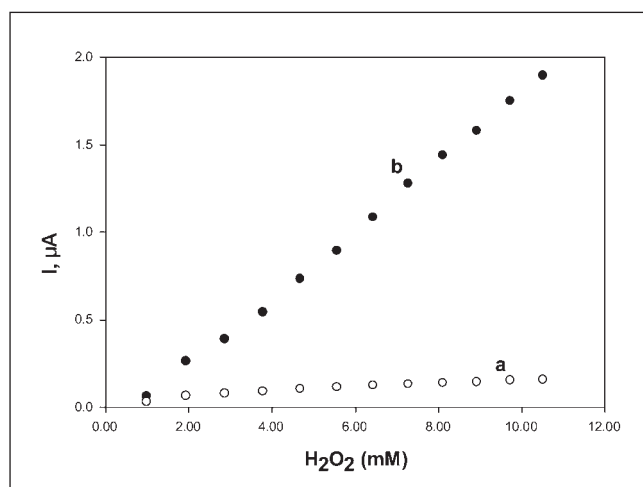can be seen, the presence of Cu-PSMNP inside the membrane substantially

Figure 16. Calibration curves of GEC sensor modified with the initial metal-free SPEEK (a) and SPEEK-Cu-PSMNP composite membranes (b). Conditions: potential = –100mV, 0.1 M KCl in 0.1 M phosphate buffer at pH = 7.0.

improves the electrical conductivity of the polymer PSMNP composite in comparison with initial polymer (similar to that observed in PSMNP-PVC and PSMNP-PS systems, see above). A far stronger response of the GEC-SPEEK-Cu sensor in comparison with GEC-SPEEK one testifies to manifestation of clearly pronounced strong catalytic activity of Cu-PSMNP for the analyte under study (H_2O_2). These results appear to be in a good agreement with those obtained for metallic copper electrodes [60]. The same results testify to quite obvious applicability of SPEEK-Cu-PSMNP composite membranes for biosensor constructions. In this case Cu-MNP must play a dual function acting both as mediators and electron "trampolines" improving the electron transfer of the enzyme immobilizing matrix (see above, Fig. 6). Nevertheless, further experimental work is required to confirm this conclusion.

Acknowledgements

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