

Electrosynthesis, characterization and electrocatalytic properties of Prussian Blue (PB) nanoparticles disposed on a template

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Abstract In the present work, an arrangement of polystyrene (PS) spheres was employed as a pattern for the electrodeposition of nanostructured Prussian blue (PB). The pattern of PS spheres was formed on Indium tin oxide (ITO) glass substrate. The ITO substrate modified by the PS spheres was used as a working electrode for the electrosynthesis of PB. A macroporous PB film constituted by nanoparticles of the compound was obtained after the dissolution of the spheres and was characterized by voltammetric and atomic force microscopy techniques. The electrocatalytic properties of this material were tested in the electrooxidation of hydrazine.

Keywords Prussian blue · Electrocatalysis · Hydrazine · Macroporous electrode · ITO electrodes

Introduction

The first report of the synthesis of Prussian blue (PB) as a film over a solid electrode was done by V.D. Neff [1]. PB

belongs to a series of solid mixed-valence compounds, which can be represented by the following general formula: $A_aM_b[Fe(CN)_6]_c \cdot dH_2O$. In this formula, a, b, c, d stand for stoichiometric numbers, A is an alkali metal cation and M is a metal (Cu, Pd, In, V, Co, Ni, etc.) bonded to nitrogen atom of the cyano group present in the structure. In the case of PB, M corresponds to an iron atom. PB, as its analogs (PBAs), has a zeolitic structure in which the iron center (Fe^{3+}) is octahedrally coordinated to the nitrogen atom of the cyanide ligand. This iron center is designed as high-spin iron atom. The other iron center (Fe^{2+}) which is coordinated to the carbon atom of the cyanide ligand is designed as low-spin iron atom. The 3D structure of PB is attained by the prolongation of this type of interaction along the three Cartesian axes. PB and PBAs are very interesting compounds due to their electrochromic [2–5] and electrocatalytic properties [6]. An interesting review about these compounds relative to the electrosynthesis, characterization, and applications has been previously published [7]. The properties that these compounds present are important because they allow to design sensors [8] or battery electrodes [9], among many other applications [7]. From an electrochemical point of view, PB presents, in electrolyte containing monovalent alkaline cations, a voltammetric behavior which is characterized by the presence of two quasi-reversible waves. The first one, which is located at more negative potentials, is related to the redox response of the high-spin (HS) iron center. The second wave is related to the redox response of the low-spin (LS) iron center. The occurrence of both redox processes involves the exchange of alkaline cations between the solid phase of the PB and the electrolytic solution [10]. Therefore, during the electrooxidation processes, the alkaline cations present in the structure of PB leave the solid matrix and go towards the solution. On the contrary, during the electroreduction

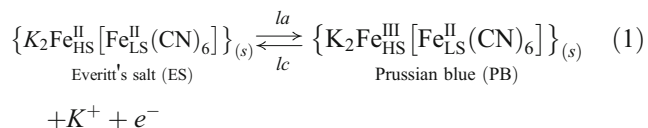
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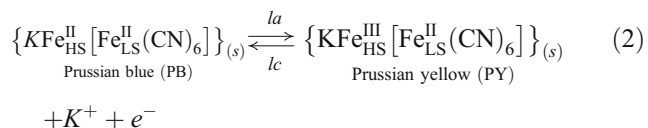
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processes, alkaline cations are incorporated to the solid matrix of PB from the electrolyte. This cation exchange that takes place during the redox processes is necessary in order to maintain the electroneutrality of the solid phase [9]. Both processes can be represented by Eqs. 1 and 2, when the voltammetric experiment is carried out in an aqueous electrolyte containing potassium ions.

High-spin iron:



Low-spin iron:



where (s) denotes solid phases.

A chronocoulometric study of the electrochemistry of PB was carried out [11]. It is important to note that electrodes containing PB can be employed to sense several organic and biochemical species apart from hydrogen peroxide [12]. Besides, nanocomposites of PB electrodes obtained by different procedures were assayed for the H_2O_2 detection [13–15]. In general, the literature shows that the obtention of the PB and PBA nanoparticles, which can be used for varied purposes, can be undertaken by different routes of synthesis. For example, water soluble negatively charged PB nanoclusters with adjustable diameter were obtained employing polyelectrolyte molecules [16]. By using poly(*N*-vinyl-2-pyrrolidone) as protective matrix, stable and well-dispersed PB and PBA nanoparticles with fairly narrow size distribution (45–60 nm) can be prepared [17]. On the other hand, employing a formamide–water mixture as a reaction media, PBA nanoparticles with controllable size can be synthesized [18]. For the synthesis of nanoparticles and superlattices of PB, the reverse microemulsion technique, employing sodium bis(2-ethylhexyl) sulfosuccinate as anionic surfactant, was assayed [19]. On the other hand, negative PB nanoparticles assembled on a positive surface of SiO_2 or multiwall carbon nanotubes, previously modified by a polyelectrolyte, were also prepared. The core-shell structure obtained, when disposed on a glassy carbon electrode, allowed the electrocatalytic reduction of H_2O_2 [20]. Furthermore, using octadecylamine monolayer as a soft template, PBAs nanoparticles can be synthesized as oriented cubic crystals at air–water interface [21] or as polypyrrol–prussian blue (PPy–PB) composite microtubes

by means of a one-step method using methyl orange as reactive self-degraded soft template. The Ppy–PB composite system when it was immobilized on a glassy carbon electrode was used as a sensor for detecting H_2O_2 [22]. Using anodic aluminum oxide [23–25] or polycarbonate membrane [26] as hard templates, highly ordered PB nanowires and PB nanowire array (PBNWA) were obtained by electrodeposition. The PBNWA disposed on a glassy carbon electrode by itself or cross-linked with glucose oxidase was employed in the H_2O_2 reduction or as a biosensor system for glucose [26, 27]. Using a glassy carbon electrode covered with a lyotropic liquid crystalline template, the electrodeposition of nanostructured PB was obtained and employed for detecting H_2O_2 [28]. Due to the fact that two (2D) and three (3D) dimension macroporous materials with micron and submicron scale structures could be important for the design of biosensors [29], several new templating techniques have been developed [30–33]. By means of one of these techniques that employs close packed arrays of polystyrene spheres as the template, highly ordered three-dimensional macroporous compounds can be synthesized in the interstitial spaces left by the polystyrene sphere arrangement. The synthesis procedure of these materials can be chemical (e.g., oxides, salt, composites) [34–37] or electrochemical (e.g., metals, oxides, semiconductors, conducting polymer) [38–51]. In the present work, we synthesized nanoparticles of PB following the down contour left by the polystyrene spheres disposed in a cubic arrangement. The PB macroporous deposit obtained by the template was morphologically and electrochemically characterized by atomic force microscopy (AFM) and cyclic voltammetry measurements, respectively. The electrocatalytic properties of the PB macroporous deposit were proved in the hydrazine oxidation. Nevertheless, further studies could be necessary in order to demonstrate that the current electrodic system can be employed as an adequate electrocatalytic system for the oxidation of hydrazine or as a sensor of it or of other analytes.

Experimental

In the preparation of the spheres template, indium tin oxide glass (ITO; Delta Technologies) was used as a substrate. This represents a modification of the procedure developed by P. Bartlett, initially applied to a gold substrate [46]. The ITO substrate was previously cleaned in isopropanol for 20 min in an ultrasonic bath. The polystyrene sphere templates were assembled by sticking the conducting face of ITO glass (1.0×2.0 cm) with a cover glass (1.0×1.0 cm) using one layer of parafilm as spacer. The space between the two glasses was filled with 10 μL of polystyrene sphere

suspension containing either 350 or 600 nm sphere diameter negatively charged (Duke Scientific Corp). The assembly was held vertically inside an incubator at 30 °C for 24 h. Then, the assembly was carefully dismantled, and the ITO glass with the sphere arrangement was covered by nail enamel, leaving an exposed area of 0.5 cm². This ITO–Polystyrene sphere (ITO–PSS) system was employed as a working electrode. For the electrodeposition of the PB, a conventional electrochemical cell with three compartments was employed, using an Ag/AgCl electrode (saturated with KCl, $E=0.197$ V vs NHE) as a reference electrode and a

platinum wire (0.5 cm²) as an auxiliary electrode. The electrolytic solution employed was composed of 1 mM FeCl₃, 1 mM K₃Fe(CN)₆, and 0.1 M KNO₃. For testing the electrocatalytic property of the electrodeposited PB, a solution of 1 mM hydrazine sulfate prepared in 0.1 M KNO₃, pH 6 phosphate buffer solution, was employed. The electrodeposit of PB was obtained applying to the working electrode, a potential value of –0.1 V. The polarization was maintained until reaching an electrical charge of 18 mC cm^{–2} for the 600-nm diameter spheres arrangement or 1.56 mC cm^{–2} for the 300-nm diameter spheres arrange-

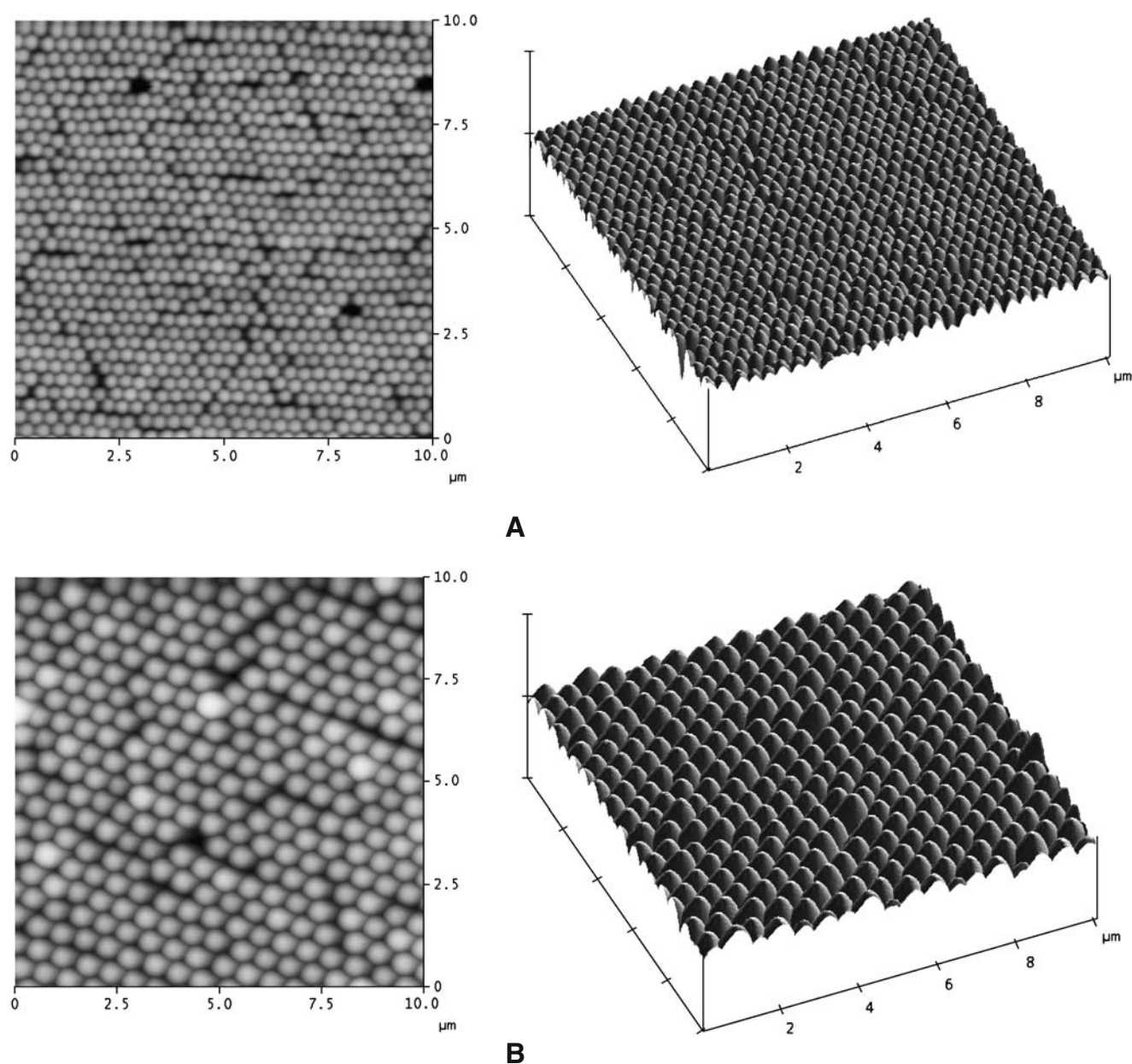


Fig. 1 Two-dimensional and 3D AFM images of the arrangement of polystyrene spheres on ITO glass substrate: **a** 350 nm polystyrene diameter spheres. **b** 600 nm polystyrene diameter spheres

ment. The electrical charge involved in the electroformation of PB was calculated so that the deposit of the compound would reach half the sphere height. Once the PB was deposited on the electrode, this was rinsed with distilled water, and the polystyrene spheres were dissolved submerging the electrode in *N*-methylformamide during 30 min. The electrochemical characterization of the resulting electrode was carried out by the voltammetric technique in an electrolytic solution containing 0.1 M KNO_3 at a scan rate of 0.02 V s^{-1} . The electrochemical experiments were

performed using a Zhaner IM-6e potentiostat-galvanostat. Data acquisition and data analysis were performed using a THALES package from Zahner Elektrik GMBH & Co. Ultra pure water of resistance of $18.2 \text{ M}\Omega$ was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA) and was used throughout the preparation of the solutions.

The morphology of the electrodes was characterized by atomic force microscopy in tapping mode using a Nanoscope IIIa Digital instruments.

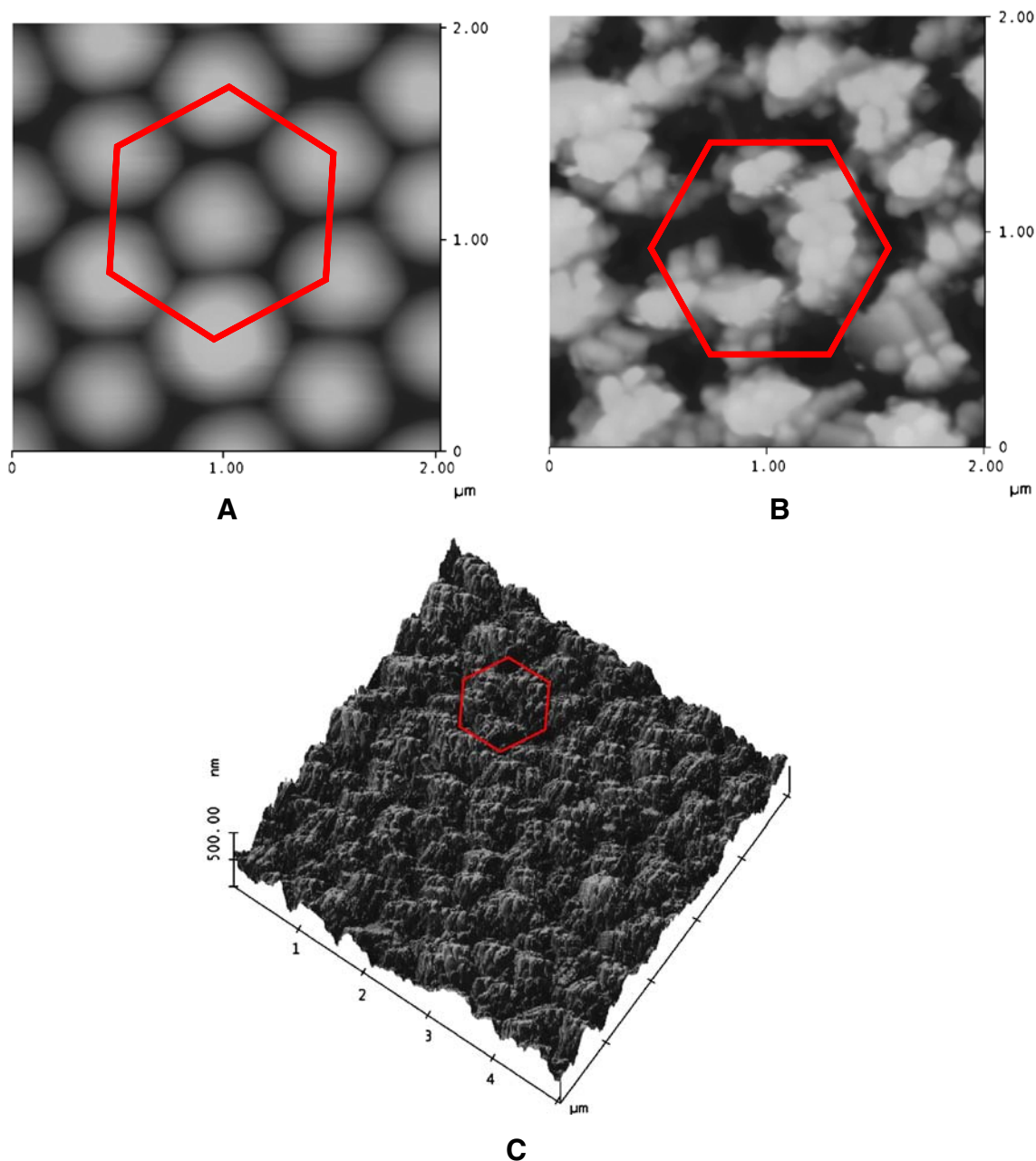


Fig. 2 AFM images **a** pattern arrangement of polystyrene 600-nm diameter spheres on ITO glass substrate. **b** bidimensional PB deposit, after dissolution of the polystyrene spheres arrangement. **c** tridimensional PB deposit, after dissolution of the polystyrene spheres arrangement

Results and discussion

AFM study

After the incubation step, the spheres assembled on ITO were observed by AFM to evaluate the morphology and homogeneity of the sphere arrangement. Figure 1 shows the arrangement obtained with 350-nm (Fig. 1a) and 600-nm (Fig. 1b) diameter spheres. It is appreciated that the best arrangement is obtained with 600-nm diameter spheres. In fact, when the 350-nm diameter spheres are employed, the arrangement shows some uncovered areas. Nevertheless, in both arrangements, a hexagonal disposition of the spheres is observed, but when 600-nm diameter spheres are employed, the arrangement appears more homogeneous. The hexagonal disposition of the spheres is reproduced along the surface, and the empty spaces do not derange the total arrangement, as it is observed in Fig. 1b.

Figure 2 shows the PB deposit on the ITO glass after the dissolution of the polystyrene spheres by the *N*-methylformamide treatment. It is observed that the hexagonal pattern established by the arrangement of the polystyrene spheres is maintained after the dissolution of them. In order to remark this fact, a hexagon was drawn on both pictures as it is shown in Fig. 2.

Figure 2b and c shows a granular morphology of macroporous PB deposit; the average diameter of the particles is close to 100 nm indicating a nanometric character of the PB particles.

Cyclic voltammetry study

Figure 3 shows a stabilized cyclic voltammogram which is designated as profile 1, corresponding to an ITO–patterned PB (p-PB) electrodic system, obtained in an electrolytic media of 1 M KNO₃. In the positive potential scan, two anodic current peaks denoted as I_a and II_a appear located at 0.30 and 0.95 V, respectively. In the negative potential scan, two cathodic current peaks denoted as II_c and I_c are located at 0.87 and 0.22 V, respectively. The peak couples I_a–I_c and II_a–II_c are associated to redox processes represented by the reactions 1 and 2, respectively.

In the following experiment, the macroporous PB deposited on ITO substrate was tested in order to establish its electrocatalytic properties in the hydrazine electro-oxidation. In Fig. 3, the voltammogram of the ITO–p-PB electrodic system in the presence of 0.1 mM of hydrazine is shown and appears designated as profile 2. For comparison, the voltammogram of an ITO electrode in the presence of 0.1 mM of hydrazine and designated as profile 3 is also included. The profile 3 is characterized only by an exponential increase of the current along with the increase of the potential and corresponds to the hydrazine electro-

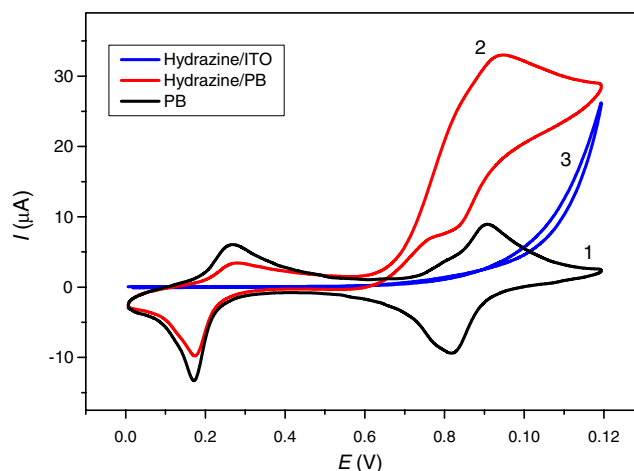
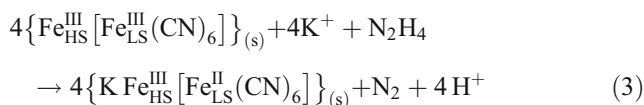


Fig. 3 Comparison of the cyclic voltammograms corresponding to the different electrodes employed. 1 Voltammogram of ITO–p-PB electrodic system in the absence of hydrazine. 2 Voltammogram of ITO–p-PB electrodic system in the presence of 0.1 mM of hydrazine. 3 Voltammogram of ITO electrode in the presence of 0.1 mM of hydrazine. Supporting electrolyte: 1 M KNO₃. Scan rate: 0.02 Vs⁻¹

oxidation process occurring on the ITO electrode. In the same potential range, but in the absence of hydrazine, only a capacitive current is observed with the ITO electrode (profile not shown).

As it can be appreciated, the electrooxidation of hydrazine on the macroporous deposit of PB on ITO electrode is manifested by a remarkable increase of the anodic current, which starts at a potential close to 0.55 V. According to the results shown in Fig. 3, the participation of the low-spin iron of PB in the electrocatalytic process of oxidation of hydrazine is evident. The high-spin iron of the PB apparently does not have any effect on the oxidation of hydrazine. Therefore, the reaction that takes place in the experimental conditions assayed is represented by Eq. 3.



This reaction has been previously studied employing other different hexacyanoferrate compounds [52].

Conclusion

Polystyrene spheres disposed on ITO electrode define a surface pattern which can be employed for the electrosynthesis of macroporous solid compounds with a defined arrangement, after dissolving the spheres. In the current case, PB nanoparticles were deposited in the pattern, and the macroporous electrode resulting was proved for the electrocatalytic oxidation of hydrazine. The present work represents a preliminary study of the properties of a

macroporous electrode of PB. In order to prove the application potentialities of the present electrodic system as an electrocatalyst for the electrooxidation or sensor for sensing hydrazine, as well as other analytes, additional and comparative studies with other electrodic systems should be performed. Further applications of this new electrodic system are subjects of oncoming studies.

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