



Prime importance of the supporting electrolyte in the realization of molecularly imprinted polymers

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Abstract:

This study concerns the highlighting of the role of supporting electrolyte in the realization of stable and reproducible molecular imprinted polymer (MIP), as it is one of the key elements which can affect the MIP's morphology, and thus the corresponding electrochemical response. Here we have designed a MIP with pyrrole, as functional monomer, and prostate specific antigen (PSA) as template. Several electrolytes were tested at a fixed concentration of 0,16 M: phosphate buffer solution (PBS), NaCl, KCl and LiClO₄ in PBS solutions. Square wave voltammetry was investigated to get information about the most appropriate electrolyte. The follow up of variations of PSA peak currents indicates that the MIPs realized in LiClO₄ give the better electrochemical response. The morphological analyses of the electropolymerized MIPs, investigated with atomic force microscopy, confirm the electrochemical results and permitted to highlight the role of anions and cations in MIP's design.

Keywords: Molecularly imprinted polymer; polypyrrole; supporting electrolyte; square wave voltammetry; Atomic force microscopy

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1. Introduction

Molecularly imprinted polymers (MIPs) are attracting considerable attention nowadays, due to their "relative ease" of concept and the possibility of their use in several applications varying from drug release, protein and DNA sensing, to quenchers in SERS experiments. Molecular imprinting principle is based on the

creation of specific and selective cavities in a 3D-polymeric network, which are complementary in size and shape of target species, providing thus interaction points and a coordination sphere around the template molecule.

Among the large panel of functional monomers, we have chosen pyrrole, due to its biocompatibility, the possibility of its use at neutral pH in either aqueous or organic solvents, and mainly the relative ease of its polymerization. Because of the rapidity of polypyrrole (PPy) electropolymerization, several synthesis mechanisms were proposed in literature [1]. The most consensual one is that presented by Genies et al [2]: the electropolymerization is initiated by

2. Results and Discussion

Previous studies have demonstrated that the supporting electrolyte play an important role in the PPy electropolymerization process [4-5]. The most appropriate one corresponds generally to a compromise between several parameters, mainly the solubility, the electrochemical stability and the interaction with reaction intermediate.

Here, we have chosen to investigate four electrolytes at a fixed concentration of 0,16 M: NaCl, KCl and LiClO₄ (in PBS solution) and PBS.

Square wave voltammetry was carried out to follow up the oxidation peak of PSA.

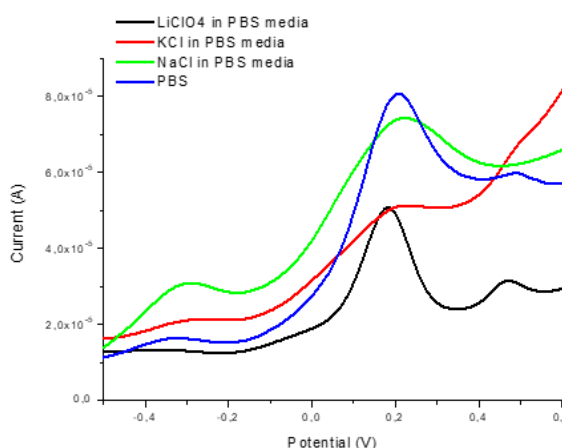


Figure 1. Characterization by square wave voltammetry of MIPs with different supporting electrolytes.

Square wave voltammograms presented in Figure. 1 indicate that the oxidation peak of PSA is more intense in a PBS solution, but it is less resolved than that of LiClO₄ in PBS.

Broad peaks were recorded in KCl/PBS and NaCl/PBS supporting electrolytes. This result is in good agreement with the previous publications relating the role of counter ions in the process of electropolymerization and electrical conductivity

the generation of radical cations monomers at the surface of the electrode and then followed by a rapid growth of the PPy chain. However, there are many factors that can interfere in the polymer synthesis such as solvent nature, pH, temperature and mainly supporting electrolyte [3].

This study is devoted to highlighting the role of the supporting electrolyte in the design of PPy molecular imprinted polymer. Prostate Specific Antigen was investigated as template molecule.

of the PPy [4-7]. LiClO₄ in PBS was thus chosen to realize the PSA/MIPs.

NaCl, KCl and LiClO₄ molecularly imprinted polymers topographies were investigated by means of atomic force microscopy. Figure. 2 shows an obvious difference between the realized MIPs. In fact, MIPs realized with ClO₄ ions are more uniform than those made with Cl⁻ small ion. These results confirm the role of counterion in the structure regularity and morphology of PPy films [8-9].

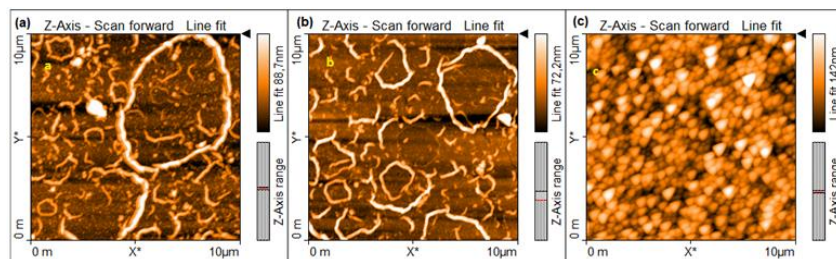


Figure 2: AFM images corresponding to MIPs realized in PBS solutions containing a) NaCl, b) KCl and c) LiClO₄ supporting electrolytes

The comparison between Figure 2a and 2b indicates that the cations can also play a role in MIPs morphology. In fact, and despite the fact that NaCl and KCl based MIPs present “rings like structures”, those of NaCl are more regular and are regularly distributed on the surface. Note that this is not a salt effect accumulated on surfaces, as the electrodes were copiously rinsed with DI water prior to AFM analysis. This results very interesting, as electrochemical studies concerns generally only the influence of the nature of the counter ion.

3. Materials and Methods

Sulfuric acid (H₂SO₄, 95%), hydrogen peroxide (H₂O₂, 30%), lithium perchlorate (LiClO₄), sodium chloride (NaCl), potassium chloride (KCl) and phosphate buffer solution (PBS) were purchased from Sigma Aldrich and used as received. Pyrrole (Py) was purified before its use by filtering through basic alumina column and stored in dark at 4°C.

Prior to any measurement, a drop of a piranha solution (98% H₂SO₄ / 30% H₂O₂ 1:1 V/V) was deposited, during 20 min, on the gold sensing areas of the gold electrodes. The substrates were then copiously rinsed with deionized double distilled water, then with ethanol before being dried under ambient air.

Before MIP deposition, a thin barrier PPy layer was electropolymerized by CA at a constant potential of 1.05 V vs SCE during 2 s.

4. Conclusions

This study permits to highlight the role of the supporting electrolyte on both electrochemical response and structural morphology of a molecular imprinted polymer. Square wave voltammetry results indicate that LiClO₄ (in a PBS solution) is the most appropriate supporting electrolyte. AFM topographic studies showed

MIPs were then prepared by CA at the fixed potential of 1.05 V vs SCE during 7s with the following concentrations: [PPy] = 10⁻² M, [PSA] = 5x 10⁻⁶ M and [supporting electrolyte] = 0.16 M.

Chronoamperometry and Square wave voltammetry measurements were carried out with a CHI 650E potentiostat with the following parameters: increment = 5 mV, amplitude = 25 mV, frequency = 25 Hz, and sensitivity = 1.10⁻⁴. A three-electrodes configuration was used: a gold electrode, a saturated calomel electrode (SCE) and a platinum wire as the working, the reference and the auxiliary electrodes respectively.

AFM measurements were investigated with a Nanosurf easyScan 2 Flexsystem.

that varying the counterion (ClO₄⁻ vs Cl⁻) modify the MIPs morphology, and that ClO₄⁻ anions permitted to obtain more uniform microscopic structure than Cl⁻ ones.

Further investigations are necessary to establish the cations effects on the electrical conductivity of PPy based MIPs.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest

References and Notes

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Notes:

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