



Nanostructured electropolymerized poly(methylene blue) films from deep eutectic solvents. Optimization and characterization



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ABSTRACT

Electropolymerization in deep eutectic solvents (DES) as a new class of “green” solvents, was employed to prepare poly(methylene blue) (PMB) polymers with different nanostructured morphologies. PMB films were synthesized on glassy carbon electrodes by potential cycling from a mixture of 90% ethaline (choline chloride: ethylene glycol) and 10% aqueous solution with different ionic composition, i.e. Na^+ , SO_4^{2-} , ClO_4^- , NO_3^- , Cl^- . The scan rate during polymerization was the key parameter in controlling film structure, confirmed by scanning electron microscopy. Electrochemical characterization of the polymers demonstrated differences in the electrochemical voltammetric and impedance properties of all synthesized PMB films. The PMB film obtained at 150 mV s^{-1} polymerisation scan rate with stirring, formed nanostructured ordered and granular films, was shown to have superior electrochemical properties. Electrochemical quartz crystal microbalance gravimetry was used to quantify the amount of deposited film and probe the polymerization mechanism. PMB film modified electrodes obtained in optimized DES media at different scan rates were tested for ascorbate sensing, in order to establish the most suitable PMB_{DES} film for (bio)sensing applications.

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1. Introduction

The use of redox phenazine polymers has been shown to be efficient in many (bio)analytical applications, and methods to synthesize polymeric films with new nanostructured and controlled structures are still being investigated. Electrochemical methods prevail in the selective modification of electrodes, since they offer the possibility to tailor polymer structure by simply adjusting the electrochemical parameters [1]. Moreover, it has been shown that the medium used for the electrochemical synthesis of conducting/redox polymers has a strong influence on the structure, and therefore the properties of the obtained polymer films, especially the electronic conductivity [2,3].

The use of deep eutectic solvents (DES) has emerged as an alternative in polymer synthesis and has shown to be successful in the preparation of advanced materials with controlled structure [4]. DES are molecular complexes, liquids at ambient temperature,

formed between suitable hydrogen bond donors (HBD) and acceptors mixed in a specific mole ratio to enable the decrease of the resulting mixture's melting point, to a much lower temperature than that of the components. DES have the characteristics of ionic liquids, such as extended working temperature range, wide electrochemical window (important in electrochemical synthesis of polymers, which usually require the generation of radicals at high overpotential) and good chemical stability, but are easier to prepare, cost effective and biodegradable [4,5]. Several nanomaterial syntheses have been reported in DES, namely shape-controlled nanoparticles, electrodeposited films, metal–organic frameworks, colloidal assemblies, hierarchically porous carbons, and DNA/RNA architectures, where DES can act as template, carbon or metal source and as reactant or auxiliary agent for synthetic processes [6]. Some DES parameters, such as viscosity, polarity, surface tension, can have a strong influence on the structure of the synthesized materials, mainly because of their control on species' reactivity and mass transport properties [6]. Recently, it has been shown that addition of water between 5 to 10 wt % to DES improves their mass transport and conductivity characteristics. The addition of water introduces a second HBD and the relative interactions

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between the anion/cation and both HBDs will change the diffusion coefficients of each component [7,8].

In electrochemistry, DES have been mostly employed for the electrodeposition of metals, alloys and semiconductors, in cases where the processes are difficult to achieve in aqueous solutions, since, due to hydrogen evolution, electrodeposition in water is generally limited [9–13]. The electrosynthesis of polymers in DES is still little explored; to the best of our knowledge only 5 papers report the use of DES for polymer electrosynthesis, i.e. for PEDOT [2,14], PANI [3,15], and recently for 3-aminophenylboronic acid, a derivative of aniline [16]. It was highlighted that the resulting polymers synthesized from DES had a higher electronic conductivity than their analogues synthesized in aqueous media.

This work describes for the first time the electrodeposition of the phenazine polymer poly(methylene blue) on glassy carbon electrodes (GCE), in solutions of methylene blue monomer dissolved in ethaline with 10% (v/v) water content and different concentrations and ratios of ions, i.e. Na^+ , SO_4^{2-} , ClO_4^- , NO_3^- , Cl^- . Polymers obtained in different DES media (PMB_{DES}) and at different scan rates from 50 to 500 mV s^{-1} ($\text{PMB}_{\text{DES}}50\text{-}500$) were synthesized and characterized in order to choose the best conditions for PMB film formation. Scanning electron microscopy (SEM) was used to identify the different nanostructured polymer films obtained in the optimized DES composition medium at different scan rates, their structures being correlated with the electrochemical properties observed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). A PMB film-modified electrode was also prepared in optimized aqueous medium for comparison purposes (PMB_{aq}). Electrochemical quartz crystal microbalance (EQCM) studies enabled the determination of the mass deposited during MB polymerization and the polymerization mechanism. Application to ascorbate sensing, evidenced the polymer with best properties for use as (bio)sensors.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade and were used without further purification. Millipore Milli-Q nanopure water (resistivity $\geq 18 \text{ M}\Omega \text{ cm}$) was used for the preparation of all solutions.

Methylene blue, choline chloride, ethylene glycol, L-ascorbic acid (AA), potassium chloride, hydrochloric acid (37%), nitric acid (65%), sodium hydroxide, dibasic potassium phosphate sodium tetraborate, sodium sulphate were purchased from Sigma Aldrich, Germany. Perchloric acid (70%), potassium chloride and monobasic sodium phosphate were obtained from Fluka, Switzerland.

For electrochemical sensing studies, the supporting electrolyte was 0.1 M KCl solution containing 5 mM HCl ($\text{pH} \approx 4$). All experiments were carried out at room temperature ($25 \pm 1 \text{ }^\circ\text{C}$).

2.2. Instrumentation

Electrochemical experiments were performed in a three electrode cell, containing the glassy carbon electrode (GCE-geometric area 0.00785 cm^2) as working electrode, a Pt wire counter electrode and an Ag/AgCl (3.0 M KCl) reference electrode, using a potentiostat/galvanostat μ -Autolab system (Metrohm-Autolab, Netherlands). Before each use, the surface of the GCE was cleaned with diamond spray (1 Micron) and polishing paper (Kemet, UK).

EIS experiments were carried by using a potentiostat/galvanostat/ZRA, (Gamry Instruments, Reference 600). A root mean square (rms) perturbation of 10 mV was applied over the frequency range 65 kHz–0.1 Hz, with 10 frequency values per frequency decade.

An EQCM 10 M, Gamry Instruments, containing a graphite quartz crystal (QC) with 10 MHz central frequency was used for the gravimetric studies.

A scanning electron microscope (SEM) (JEOL, JSM-5310, Japan) was used to characterize the morphology of the different PMB films deposited on carbon film electrodes.

The pH measurements were carried out with a CRISON 2001 micro pH-meter (Crison Instruments SA, Barcelona, Spain).

2.3. Preparation of MB polymerization solution

Ethaline was obtained by mixing a quaternary ammonium salt (choline chloride) with a HBD (ethylene glycol) in a 1:2 molar ratio, heating to $60 \text{ }^\circ\text{C}$, following pre-treatment of the solid choline chloride by heating it up to $100 \text{ }^\circ\text{C}$ to evaporate any water. After cooling down to room temperature, ethaline is ready to use for the preparation of the MB polymerization solution. MB was dissolved first in aqueous solution containing a mixture of NaOH and HClO_4 in different concentrations and ratios (see Table 1). Ethaline was added to this solution, so that the final concentration of monomer was 5 mM in a mixture of 10% v/v aqueous solution: 90% v/v ethaline, which was thoroughly stirred and sonicated in the ultrasound bath.

A uniform and reproducible PMB_{DES} film was obtained by cycling for 30 scans in the potential range -0.6 – $+1.2 \text{ V}$; different scan rates were investigated, between 50 to 500 mV s^{-1} , and the films obtained were designated as $\text{PMB}_{\text{DES}}50\text{-}500$. The polymerization was performed in a stirred solution, with a magnetic stirrer set at 450 rpm. For comparison purposes, PMB was also prepared in aqueous medium, in a solution containing 1 mM MB in $0.025 \text{ M Na}_2\text{B}_4\text{O}_7 + 0.1 \text{ M Na}_2\text{SO}_4$ ($\text{pH} 9.2$), at a scan rate of 50 mV s^{-1} , as in [19].

2.4. Analysis of ascorbate

The analysis of ascorbate analysis was done in a 2 mL cell, the GCE/ PMB_{DES} or GCE/ PMB_{aq} acting as a working electrode. Aliquots of a 50 mM AA standard solution were added, under continuous magnetic stirring, the additions corresponding to 10 or $20 \text{ }\mu\text{M}$ ascorbate in the final volume. The current was recorded at a fixed applied potential of 0.2 V vs Ag/AgCl.

Standard solutions of 10 mM ascorbic acid (AA) were freshly prepared and kept at $4 \text{ }^\circ\text{C}$ in a refrigerator before use.

Table 1

Values of total faradaic current, peak separation and capacitance values (at $+0.6 \text{ V}$) obtained from CVs recorded in (0.1 M KCl + 5 mM HCl) aqueous solution at 50 mV s^{-1} at GCE modified with PMB_{DES} obtained in ethaline with different concentrations of NaOH, HClO_4 and H_2SO_4 in a final mixture of 10% aqueous solution: 90% ethaline.

Acid	[acid]/ M	[NaOH]/ M	$I_{\text{pa}}/$ $\mu\text{A cm}^{-2}$	$I_{\text{pc}}/$ $\mu\text{A cm}^{-2}$	$\Delta E_{\text{p}}/$ mV	C/ $\mu\text{F cm}^{-2}$
HClO_4	0.1	0.1	19.0	21.5	38	665
	0.2	0.1	9.7	7.4	50	912
	0.3	0.1	12.0	10.4	61	448
	0.1	0.25	9.6	9.4	66	876
	0.1	0.4	10.8	10.8	61	1065
H_2SO_4	0.1	0.1	10.8	9.4	52	678
	0.2	0.1	10.3	10.8	66	576
	0.3	0.1	14.6	10.7	72	927
	0.1	0.25	9.6	9.9	89	836
	0.1	0.4	8.4	10.4	61	955

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