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Optical, electrical and photoelectrochemical characterization of electropolymerized poly methylene blue on fluorine doped tin oxide conducting glass

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ABSTRACT

This paper describes the poly methylene bleu (PMB) electrodeposition on fluorine doped tin oxide (FTO) conducting glass and its optical, electrical and photoelectrochemical characterization. The deposited film shows a good electric conductivity which is well confirmed by the low gap value determinated optically by UV–vis spectroscopy. Like all polymers the PMB presents an absorption difference in the visible range function of the polarization potential, it is expressed by the strong conjugation at oxidized state but is weakened with leucoform formation at reduced state. The electrochemical behaviour of the film allows us, to confirm the polymerization of the methylene blue (MB), to observe the oxidation and the reduction states of as prepared layer and to locate the energy levels HOMO and LUMO of this polymer. A photocurrent of some μA has been observed when the film is photosensitized with white light source.

1. Introduction

These last decades conducting polymers have been a subject of great interest for their promising applications such as for Polymer Light Emitting diodes (PLEDs) [1], Polymer Field-effect Transistors (FETs) [2] and Polymer Solar Cells [3,4], they are also used in electronics and optoelectronics. With a good method of preparation and through a careful designing of the structure of conjugated polymers, their electronics and optoelectronics properties can be modified to achieve polymers with high electronic affinity (n-type) [5] or to produce a stable polymer matrix, with good electron donor/acceptor properties, from which to build a new generation of biosensors [6].

Among the most studied polymers, there are heterocyclic polymers such as: polythiophene [7,8], polypyrrole and polycarbazole [9].Owing to electron-rich heteroatoms like sulphur and nitrogen, polyphenothiazines are good electron donors and thus good hole transport materials. They have, therefore, been investigated for their application in PLEDs [1,5]. However, the applications of the polyphenothiazines in the electronic devices and the study of their photovoltaic properties are very limited. According to Weihua Tang et al. [10] there is a possibility to reduce the gap and obtain interesting results when incorporating phenothiazine nucleus, a fact which motivated our present study.

The choice of deposition technique can also play an important role on the properties of a conjugated polymer. The electropolymerization, one of the elaborating techniques of conducting polymer films, is studied since few years particularly that using compounds such as: aniline, pyrrole, thiophene and carbazol. Elaboration of such compounds appears among predilection subjects of many laboratories all over the world.

Various types of organic compounds permit to form electronic conducting polymers by this technique, for example, substituted derivatives of benzene, organometallic complexes and heteroatomic compounds. The latter compounds are the basis of our selected polymer which is the poly methylene blue belonging to the phenanthiazine family (Fig. 1). This polymer has been synthesized very recently; however, its structure has not yet been elucidated. The application of this new polymer was used particularly in biology and medicine. For exemple A. Siliber and N.Hampp [11] prepared conducting films of PMB on gold electrodes for the electrocatalytic oxidation of the NADH and its applications in the glucose biosensors.

In order to monitor the growth of the PBM films on gold electrode, V. Kertész et al. [12] used an electrochemical quartz crystal microbalance and cyclic voltammetry. The response of the polymer films is significantly separated from that of the monomer species in solution, it has been proved that anion sorption/desorption

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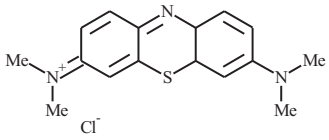

Fig. 1. Methylene blue (MB) structure.

(doping/dedoping) occur during the redox transformation of the polymer, and that the cations play no role.

In another publication, Kertesz et al. [13], followed the formation of PMB films using Electrospray Mass Spectroscopy, Where, MB dimers and trimers observed at *m*/*z* values consistent with either "nitrogen-to-ring" coupling of the monomer or with "ring to ring" coupling of demethylated monomers during the electropolymerization. They proved that "nitrogen-to-ring" coupling is the dominant process.

In this paper we describe the conditions of depositing methylene blue by electropolymerization. The originality of our work lies in the fact that the deposit of this polymer is carried out on conducting glass substrate which make its optical characterization easier and possible. It is obvious that nature substrate plays a big role in structural, optical, electric and/or electrochemical properties. The gap, and either the energy levels HOMO and LUMO have been estimated. The thickness and the conductivity of the prepared layers have been investigated as well as the electrochemical and photoelectrochemical behaviour on the transparent substrates. Such layers are probably appropriated for different uses than the same layers prepared on opaque or metallic substrates. The field application of such films of polymer is widespread and is more convenient for use in solar cells and photovoltaic devices.

2. Experimental

2.1. Chemicals

FTO (fluorine-doped tin oxide) electrodes were obtained from EPFL (Ecole federale of Lausane). Methylene blue MB, acetone, absolute ethanol, Na_2HPO_4, KH_2PO_4 and Na_2SO_4 were purchased from Aldrich and Sigma–Aldrich and used as received. Phosphate Buffer aqueous solution (PBS pH 7.4) was prepared from 0.1 mol dm^{-3} of (Na_2HPO_4, KH_2PO_4). The preparation of aqueous solutions was done with distilled deionized water.

2.2. Preparation and characterization techniques

Cyclic voltammetry (CV) and all electrochemical measurements were performed in a Radiometer Analytical system model PGZ 301 potentiostat with VoltaMaster 04 software. A conventional three-electrode cell consisting of an Ag/AgCl/KCl_{sat} reference electrode and Pt wafer of 0.5 cm^2 as a counter electrode were used. All the potentials have been reported versus the Ag/AgCl/KCl_{sat} reference electrode (+220 mV vs normal hydrogen electrode). The working electrode was FTO wafer of 1 cm^2 treated with acetone and ethanol.

The electrochemical impedance spectroscopy (EIS) measurements were performed in the same electrochemical cell which has been used in the voltammetric experiments with the same PGZ 301 Voltalab. Measurements have been done at stationary conditions in electrolytic solution 0.1 mol dm^{-3} PBS within a frequency range between 100 kHz and 20 mHz with a decreasing scanning frequency order. The ac amplitude was 10 mV. The fitting of the recorded impedance spectra and the estimation of the EIS parameters have been done using a software Z VIEW (Solartron). Mott-Shotky curves have been drawn using inverse square capacitances extrapolated from Nyquist plots and investigating a range of potentials values from −350 to 0 V/Ag/AgCl/KCl_{sat}.

UV–vis absorption spectra were recorded with a Unicam UV 300 with Vision 32 Software. Absorption spectra of electrodes were referenced against a blank FTO electrode. Photoelectrochemical measurements were carried out using a 500 watt white light lamp. The film's thickness were determined using an ELX 01 DRE Germany elipsometer with two laser lamps He and Ne λ = 632.8 nm. Film's resistances were measured with a CMT Series CHANG MIN four points instrument.

3. Results and discussion

3.1. Electropolymerization of MB

Methylene blue was electropolymerized from a solution of 10^{-3} mol dm^{-3} of monomer in 10^{-1} mol dm^{-3} Phosphate Buffer (PBS pH 7.4) containing 10^{-1} mol dm^{-3} Na_2SO_4 as electrolyte, by cycling electrodes between −500 and +1200 mV vs Ag/AgCl/KCl_{sat} at a sweep rate of 50 mV/s and performing 100 cycles. Poly Methylene Blue film was grown on the glassy FTO electrode according to the process described by Karayakin et al. [14]. After electropolymerization the electrode was thoroughly rinsed with PBS + Na_2SO_4 solution to remove any remaining monomeric traces. Fig. 2 shows a typical cyclic voltammogram obtained during film growth. The voltammetric profile is similar to that obtained on gold and on platinum Pt [11,12,15–17], it is also similar to the curves obtained on glassy carbon [16] and not very different from the cyclic voltammograms elaborated on carbon fibre [18,19]. The first cycle of this voltammogram Fig. 3 shows an initial reversible ox/red wave couple situated at −150 mV and −200 mV due to the monomeric oxidation and reduction states respectively and an oxidation wave

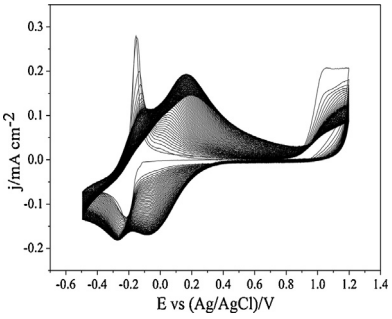

Fig. 2. Cyclic voltamogram of 0.1 M PBS (Na_2HPO_4, KH_2PO_4), 0.1 M Na_2SO_4 and 10^{-3} M methylene blue solution on FTO glass electrode vs Ag/AgC/KCl_{sat} reference, 100 cycles, sweeping rate 50 mV/s.

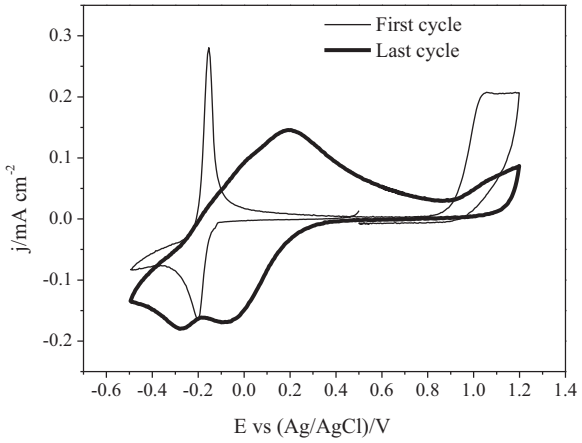

Fig. 3. Cyclic voltamograms of methylene blue electropolymerization (—) first cycle, (▬) last cycle.