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Monitoring hydrophilic –hydrophobic character of a surface electrode via TiO_2 nano particles addition as aspect of interface phenomena

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Abstract — **The paper aims on the effect in surface features of TiO_2 nanoparticles addition on the polypyrole coating obtained electrochemically on Au electrode via electrochemical polymerization in LiClO4 as electrolyte. The main surface studied property is the hydrophilic character, which is very important in bioapplication, taking into account that the balance hydrophilic –hydrophobic strongly influence cell adherence, spreading and viability. The hydrophilic character was evaluated from contact angle measurements and surface analysis was completed with scanning electronic microscopy and with atomic force microscopy. For all deposited films Mott Schottky determinations were performed at 1 kHz frequency and potential range from 0 to 1.5 V. The flatband potential has variations as a function of TiO_2 concentrations due probably to nanoparticles agglomeration.**

Keywords – TiO nanoparticle, wettability, polypyrrole, PEG, Mott Schottky

I. INTRODUCTION

The development of nanotechnology is important for many fields able to improve human life, and nanosizing effect of materials become a subject of many studies in the last decade. Regarding the relationship between biomaterials and nanotechnology [1] this aspect was presented clearly in an editorial a couple of years ago. The concept of nanotechnology according to D.F. Williams [1] are concerned with the engineering at the nanoscale and means specifically a measure of 10^{-9} units, independent of the nature of this unit. In this approach a nanomaterial is 'any form of a material that is composed of discrete functional parts, many of which have one or more dimensions of the order of 100 nm or less' and nanocomposite is a 'multi-phase material in which the majority of the dispersed phase components have one or more dimensions of the order of 100 nm or less'. Taking into account that interactions between cells and biomaterial surfaces are assisted by structures on cell membranes and are responsive to signalling processes that take place at very small dimensions, biocompatibility as an expression of the cell behaviour may be strongly depended on the nanotopography features. In this idea well known biomaterials as Ti and Ti alloys properties is related more recently to the possibility to get a better cellular response due to a nanostructure in the entire bulk [2,3] or at surface level [4,5].

As can be seen from literature studies [5-7] nanolevel usually represents a merit size having the potential to positively influence the development of advanced procedures in medicine and biotechnology. Despite this fact some time nanotechnologies represent a demerit being possible that they may be associated with health risks especially related to adverse effects of nanoparticles [8]. Regarding this aspect nanoparticles surface properties as hydrophilic –hydrophobic character which serve as a focus of attention in monitoring cell spreading and viability, became worthy of investigation, and this paper is devoted to this subject, introducing nanoparticles in a Polypyrrole (PPy) coating. In fact PPY has attired the attention more than other conducting polymers due to its high electrical conductivity, stability in air, good redox reversibility and PPy films on various metallic support as Ti and Ti alloys was intensively studied [9, 10] in the last decade. Elaboration of a conducting polymer composites based on PPy leads to new application, being important for its potential use in the next generation of modified electrodes, sensors, batteries, diodes, solar cells, tissue repair. Introducing polyethylene glycol (PEG) as a second component of composite is a way to decrease contact angle of composite [10] and to develop new bioengineering technologies based on enhancement of cell adherence and proliferation, taking into account that the cells usually do prefer hydrophilic surfaces [11,12]. According to other literature data some cell exhibit more proliferation and viability on hydrophobic surfaces [13] and the idea of the present research is based on the possibility to monitorize the hydrophilic hydrophobic balance introducing TiO_2 nanoparticles, able to increase the contact angle.

The present paper is focused on TiO_2 nanoparticles effect on PPy coating deposited on Au electrode via electrochemical polymerization in $LiClO_4$ as electrolyte. The effect of TiO_2 nanoparticles on the polimeric composite coating are quantified as a function of nanoparticle concentration and the balance hydrophilic/hydrophobic, which seems to be clearly important for the variation of flatband potential as well.

II. EXPERIMENTAL

In the experimental procedure we used a three electrodes system for the electrochemical deposition and characterization, composed of: a working gold electrode with an area of $0.07cm^2$, a platinum conterelectrode and an Ag/AgCl, KCl reference electrode on an Autolab PGSTAT 302N potentiostat/galvanostat. The electrochemical data processing was achieved using general purpose GPES and NOVA software. A $LiClO_4$ 0.1M electrolyte was used as support medium for the electrodeposition, with pyrrole (Py) of 0.1M and different quantities of TiO_2 nanopaticles with size <100nm BET or polyethileneglycole (PEG) concentrations. The electrodeposition potential was kept at 0.8V with a deposited surface charge limited to 10mC. Thus a hybrid coating of polypyrrole (PPy) and TiO_2 or PPy and PEG was achieved. The used TiO_2 nanoparticles, PEG and Py were all purchased from Aldrich.

The contact angle measurements were made with CAM 100 hardware and software. The micrographs were obtained using an Environmental Scanning Electron Microscope XL30 ESEM TMP (SEM).

The surface topography and roughness of polypyrrole films was studied with Atomic Force Microscope (AFM) from APE Research, Italy.

III. RESULTS AND DISCUSSION

Electrochemical deposition of polypyrrole hybride coating

Figure 1 presents the chronoamperograms corresponding to polypyrrole / TiO_2 hybride coatings obtained for different concentrations of TiO_2 nanoparticles in electrolyte during electropolymerization process.

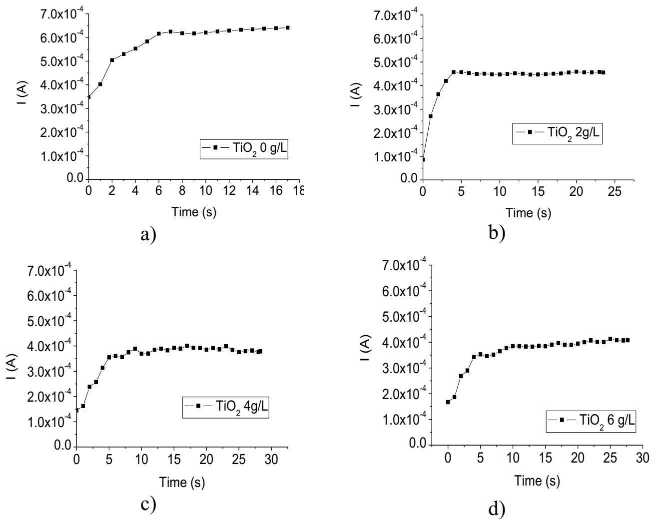
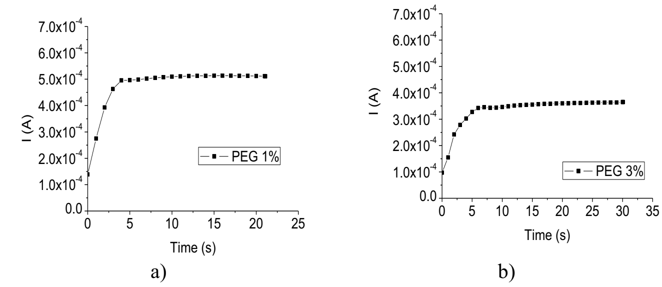


Figure 1. Chronoamperogram obtained at electrochemical deposition of polypyrrole / TiO_2 nanoparticle coating:
a) 2g/L, b) 4 g/L, c) 6 g/L.

The curves can be separated in two stages: a suddenly increase of the current in the first polymerization stage can be observed followed by a current stabilization at an almost constant value. This constant value of the current decreases from 6.5 10^{-4} A for 0g/L TiO_2 to 4.5 10^{-4} A for 2g/L TiO_2 and to 3.9 10^{-4} A and 3.8 10^{-4} A for 4g/L TiO_2 and 6g/L TiO_2, respectively.

This behavior can be attributed to the presence of the semiconducting TiO_2 nanoparticle in the structure of polypyrrole layer.



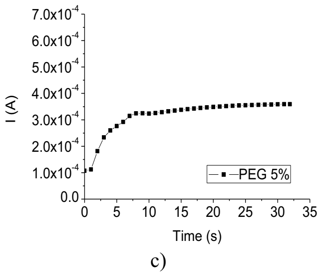


Figure 2. Chronoamperogram obtained at electrochemical deposition of polypyrrole / PEG coating:
a) 1% PEG, b) 3% PEG, c) 5% PEG.

In figure 2, current vs. time curve corresponding to polypyrrole /PEG hybride coatings are presented. The presence of PEG in polymerization solution decrease the current from 6.5 10^{-4} A for 0 % PEG to 3.5 10^{-4} A for 5 % PEG.

This decrease may also be associated with the presence of non-conducting PEG in the structure of polypyrrole conducting polymer.

Evaluation of semiconducting behavior

The Mott-Schottky evaluations were made in a Na_2SO_4 electrolyte with a 1 Hz frequency signal and a potential scan from 0V to 1.5V.

The obtained fitting presents the conductive character of the films that has a tendency towards a *p*-type semiconductor.

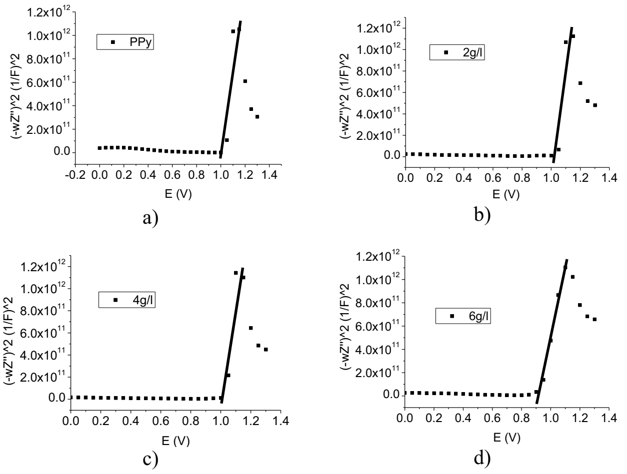
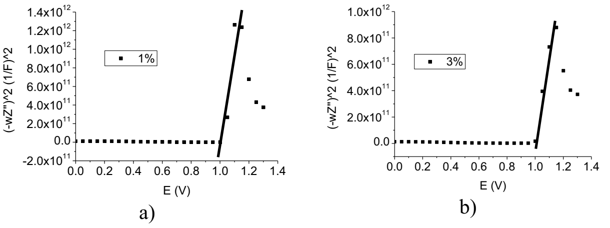


Figure 3. Mott Schottky fitting for Polypyrrole / TiO_2 nanoparticle coating, with a TiO2 nanoparticles content of:

a) 0 g/L b) 2g/L, c) 4 g/L, d) 6 g/L.

For the PPy the Fermi level and the solution redox potential indicates that at 1.009V there is no net charge transfer.



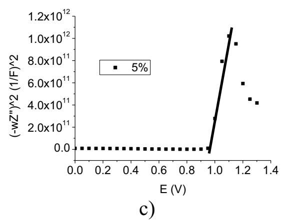


Figure 4. Mott Schottky fitting for Polypyrrole / PEG coating, with a PEG content of:
a) 1%, b) 3%, c) 5%.

With the addition of PEG in the electrolyte, this flatband potential drops until it reaches 0.951V. The same behavior is observed with the addition of TiO_2 nanoparticles.

TABLE I. FLATBAND POTENTIAL

Sample	Flatband potential (V)
PPy	1.009
PPy+PEG1%	1.002
PPy+PEG3%	0.989
PPy+PEG5%	0.951
PPy+TiO2 2g/l	1.011
PPy+TiO2 4g/l	1.002
PPy+TiO2 6g/l	0.910

By the addition of PEG and TiO_2 nanoparticles, interface changes occur. This is observed in Mott-Schottky results as the flatband potential varies, Table I.

Structural analysis

Structure of PPy-PEG Composite Films

The infrared spectra of the samples were recorded in the wavenumber range from 4000 to 400 cm^{-1}. The FT-IR spectra of PEG, PPy and PPy-PEG films are presented in Figure 5. In the IR spectrum of PEG (Fig. 2a) are evidenced: the absorption bands at 3384 cm^{-1} corresponding to stretching vibration of OH group, the band at 2864 cm^{-1} corresponding to stretching vibration of CH2 and the absorption band at 1107 cm^{-1} corresponding to stretching vibration of C-O bond. In the case of PPy spectrum (Fig. 5b), it was observed the NH stretching band of pyrrole ring at 3425 cm^{-1}. The bands between 1000–1600 cm^{-1} show the characteristic polypyrrole absorption. The band at 1626 cm^{-1} is assigned to C=C ring of pyrrole.

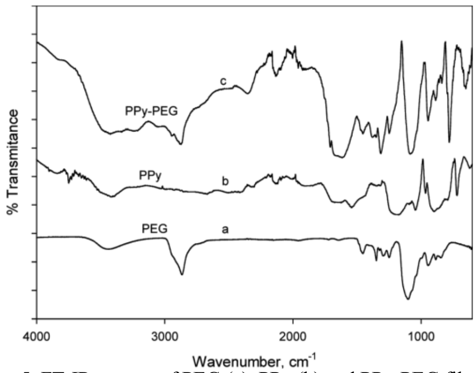


Figure 5. FT-IR spectra of PEG (a), PPy (b) and PPy-PEG films (c).

Figure 5c shows the FT-IR absorption spectrum of PPy-PEG film. This presents peaks that are characteristic both to PPy (3425 cm^{-1}, 1626 cm^{-1}) and to PEG (2864 cm^{-1}, 1107 cm^{-1}), indicating that PEG was incorporated into the PPy film, forming a PPy-PEG composite film.

Structure of PPy-TiO_2 Composite Films

Raman spectra of polypyrrole/ TiO2 nanoparticles hybride coating presented in Figure 6, shows the characteristic peaks of TiO_2 at 500 – 700 cm^{-1} indicating that TiO_2 was incorporated into the PPy film structure.

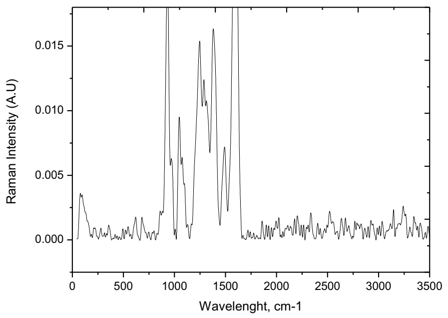
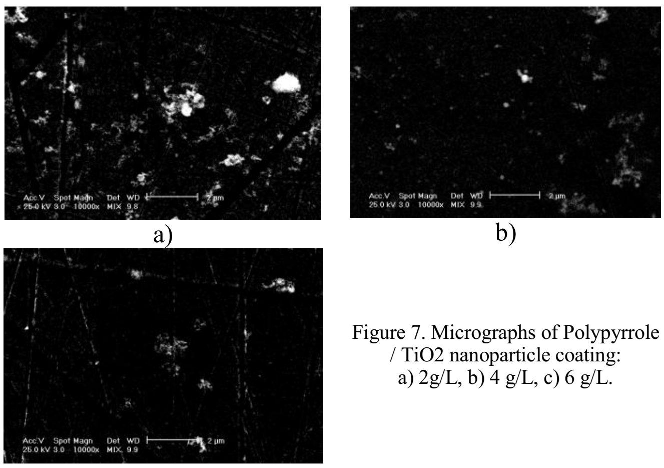


Figure 6. Raman spectra of polypyrrole/ TiO2 nanoparticles hybride coating.

Surface analysis

SEM micrographs preset different aspects of TiO_2 in the film. We evaluated effective surface area of the total of 106µm^2 surface area (Fig. 1).

The measured data indicates that for 2g/L of TiO_2, the agglomeration totalizes an area of 8.87µm^2. With the increase of the TiO_2 quantity to 4g/L the agglomeration drops to 4.45µm^2. The lowest value of 2.85µm^2 is reached for 6g/L TiO_2 in the solution. This is most likely due to the increase of the TiO_2 agglomerates in the electrolyte solution prior and during the experimental electrochemical film formation, thus increasing the mass and decreasing the mobility.



a) b) c)

Figure 7. Micrographs of Polypyrrole / TiO2 nanoparticle coating: a) 2g/L, b) 4 g/L, c) 6 g/L.

SEM images indicate that the TiO_2 agglomerates in the film decrease with the increase of TiO_2 quantity in the solution.

Contact angle

The wettablility of the composite films was appreciated by measuring the contact angle of a drop of water deposited on the film surface.

TABLE II. CONTACT ANGLE

Sample	Contact angle (º)
PPy	32
PPy+PEG1%	24
PPy+PEG3%	18
PPy+PEG5%	7
PPy+TiO2 2g/l	85
PPy+TiO2 4g/l	86
PPy+TiO2 6g/l	81

The values of contact angle is changed from 32 degree in the case of the polypyrrole surface to 24 degree for film deposited in the presence of 1% PEG, 18 degree for film deposited in the presence of 3% PEG to a quasi total spreading of the drop of water in the last case, with 5% PEG (Table II). This behaviour suggests that PEG concentration plays an important role in determining the surface energy, especially in increasing the hydrophilic character.

In contrast the adding of TiO_2 nanoparticle in the structure of polypyrrole coating changes the wettability in the hydrophobic direction but the concentration of TiO_2 nanoparticle in the polymerization solution show no special influence, the contact angle being between 81 to 86 degree.

IV. CONCLUSIONS

1. The elaboration of composites coating based on PPy , PEG and TiO_2 nanoparticles was performed and the balance hydrophilic –hydrophobic was monitorize changing the concentration of PEG and TiO_2.

2. The flatband potential decreases with the increase of PEG or TiO_2 nanoparticles addition, and has variations as a function of TiO_2 concentrations due probably to nanoparticles agglomeration.

3. The addition of PEG and nanoparticles as TiO_2 in PPY composites films permitted a significant change in surface features and leads to potential applications, in the next generation of modified electrodes, sensors, batteries, diodes, solar cells, tissue repair.

ACKNOWLEDGMENT

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