Electrodeposition of a hybrid material composed by poly(pyrrole) and Prussian blue nanoparticles assisted by ultrasonic radiation.

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Introduction

An interesting approach for material science relies on a synthesis of hybrid materials. In an optimistic view these synergistic materials present the best features of both organic and inorganic individual based materials[1].

Herein, we propose the direct synthesis of a hybrid material composed by poly(pyrrole) (PPy) and Prussian Blue (PB) nanoparticles by a quick and straightforward electrochemical deposition under ultrasonic radiation. The modified electrodes were characterized by electrochemical techniques.

Results and Discussion

The platinum electrode (A = 0.0314 cm^2) were modified by applying +1.0 V in a solution containing 50 mmol L^{-1} of pyrrole, pH=3 controlled by HCl addition. The deposition charge was monitored until the reaction reached 160 mC cm^{-2}. In the synthetic solution was also added 5mL (2 mmol L^{-1}) of $K_4Fe(CN)_6$ and then the same aliquot of $FeCl_3$ (1 mmol L^{-1}), forming by this way the PB. After few seconds of magnetic stirring, the solution was irradiated with ultrasound (Sonics Vibra Cell 20 kHz and amplitude of 60%) and the potential was applied until the final deposition charge was achieved.

Figure 1 shows the response by the hybrid compound formed by PPy/nano-PB in silent and with 60% amplitude of ultrasound radiation.

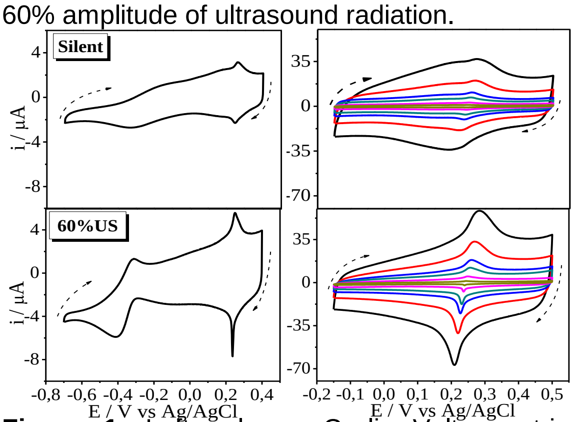

Figure 1. Left column: Cyclic Voltammetries of PPy/nano-PB modified electrodes. Electrolyte: KCl/HCl pH 3 scan rate of 10 mVs^{-1}. Right column: Cyclic voltammetries at different scan rates on a limited potential window (1, 5, 15, 25, 50 and 100 mVs^{-1}).

Under sonication conditions, there are two significant changes in the voltammograms: (i) the PPy redox pair becomes more defined and shifts to -0.40 V and (ii) the PB peaks present a clear narrowing with the increase of the US intensity. The better definition on the voltammograms is an effect of the electrode roughness where the ionic diffusion of both PPy and PB solid matrix become faster.

In Figure 2 are shown the Nyquist diagrams for the PPy/$Fe(CN)_6^{4-}$(silent), PPy/nano-PB(silent) and PPy/nano-PB(60% US) modified electrodes. It can be observed that the poly(pyrrole) interfacial process is dependent on the presence of nano-PB, once the arc at high frequencies is diminished, resulting in an increase in the poly(pyrrole) conductivity.

In order to obtain a quantitative response concerning the modified electrode conductivity, the EIS data were fitted using an equivalent circuit model[2]. By this way the values of R_{ct} for the modified electrodes were found to be as 1063, 670 and 403 kΩcm^2 for the PB/$Fe(CN)_6^{4-}$ (silent), PPy/ nano-PB (silent) and PPy/nano-PB (60%US) respectively.

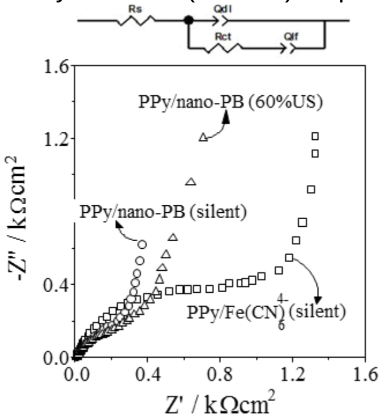

Figure 2. Nyquist diagrams obtained for PPy/$Fe(CN)_6^{4-}$ and PPy/nano-PB electrodes modified under sonication (60% amplitude) and silent conditions, measured at -0.55 V. Electrolyte: KCl/HCl pH 3.

Conclusions

By these results is possible to evaluate that the inclusion of PB itself leads to an increase in the film conductivity furthermore the presence of small PB nanoparticles, obtained under sonication, enhances even more the film conductivity.

The presented modified electrode shows a great potential for the development of many different electrochemical applications.

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2 Marchesi, L.F.; Pereira, E.C. *Synth. Met*. **2014,** 194, 82–87.