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Adsorption of polyanions on nanostructured polypyrrole submonolayer grafted on semiconducting transparent support

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Abstract Polypyrrole submonolayers are formed on three different supports: indium oxide (In_2O_3), indium tin oxide (ITO) and tin oxide (SnO_2). It is seen that this formation is a function of the nature of the substrates. Nanometric film scale has been checked by AFM measurements. These polypyrrole submonolayers allowed self-assembling with polyoxometalate $SiMo_{12}O_{40}^{4-}$ and played a determining role in the adsorption characteristics.

Introduction

Since some decades, conducting organic polymer is a field which has been considerably studied. This is due to their wide range of possible applications in electrocatalysis, molecular electronics, energy conversion, for example [1]. Among all the choices of conducting polymers, polypyrrole (PPy) attracted attention because it presents high stability and its preparation is simple [2]. On the other hand, polyoxometalates (POM) are known to be a very rich family of inorganic metal oxide clusters which presents also, due to their structural and electronic versatility, a wide range of applications such as electrocatalysis [3], photochromism [4], for example. Both are involved in the formation of films on supports to dispose of objects with desirable physical properties. Based on their electrostatic interaction, POM are used to form films of nanometric scale [3, 5]. When Polypyrrole is deposited electrochemically, often it presents films with thicknesses from several hundreds of nanometers to microns. Moreover, when polypyrrole is employed with POM, mainly, the deposition of films is realized from a mix of the two components [6–10]. As expressed by Onada et al. [11], it is more interesting and challenging to contract films with a supramolecular architecture in which the individual component could be incorporated into individual layers. Recently, a new approach has been proposed to make the formation of films involving polypyrrole and POM more supramolecular [12]. In our work, we proposed another way, based on the electrochemical deposition, which allows the formation of polypyrrole films of some nanometer thickness. Keeping the principle of layer-by-layer deposition, the polypyrrole-covered electrode is dipped into a solution of POM to execute the adsorption. We studied these phenomena on three different supports (SnO_2, ITO and In_2O_3) to dispose of several data on substrate which present, in theory, similar properties.

Experimental section

Materials

Polyoxometalate $H_4SiMo_{12}O_{40}$ ($SiMo_{12}$), 37% hydrochloric acid, potassium chloride and pyrrole were purchased

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from Aldrich Chemical Co. Pyrrole was distilled prior to use and all the other compounds were used as received. Hydrochloric acid solutions for electrochemical measurements were prepared by dilution of the appropriate proportion of commercial hydrochloric acid solution to a solution 1 M KCl in ultrapure water of 18.2 MΩ cm^{-1} (ELIX-Synergy Millipore Station) for a solution at pH = 4. The pyrrole monomer was dissolved at a concentration of 0.1 M in a 1-M ultrapure water solution of KCl. This solution was stored in argon atmosphere at 4 °C in the dark before use. The semi-conducting oxide working electrodes were a glass piece of 1 cm × 2 cm covered by an oxide layer of about 500-nm thickness and having the structure G/Ox, where G corresponds to glass and Ox to In_2O_3 or ITO or SnO_2. These substrates were purchased from Diamond Coatings Limited Company (UK), Sagem (Fr) and Saint Gobain (Fr), respectively. For all the substrates, only 1 cm^2 was dipped in the different solutions.

Instrumentation

Cyclic voltammetry

Cyclic voltammetry experiments were carried out at ambient temperature (20 ± 2 °C) in a two-compartment cell connected to an autolab model PGSTAT 20 potentiostat. The aqueous electrolyte was bubbled with argon for at least 10 min prior to use. All potentials were measured versus a commercial (Tacussel) calomel reference electrode (SCE) (KCl sat.). The platinum wire used as an auxiliary electrode was placed in a separate compartment to avoid contamination of the electrolytic solution by electrogenerated species. The working electrodes were cleaned with ethanol and dried under argon. The pH of the solutions was monitored with a pH meter Tacussel minisis 6000 and a regular glass electrode (Radiometer).

Atomic force microscopy (AFM)

AFM analyses were performed with a Standalone SMENA NT MDT microscope in a constant contact force mode. The images were collected in ambient atmosphere, and each of them was digitized into 256 × 256 pixels with a scanning frequency of ~1 Hz. The cantilever was made of a commercial Si3Ni4 tip with nearly 20-nm apex radius bearing a spring constant of 0.12 N m^{-1}.

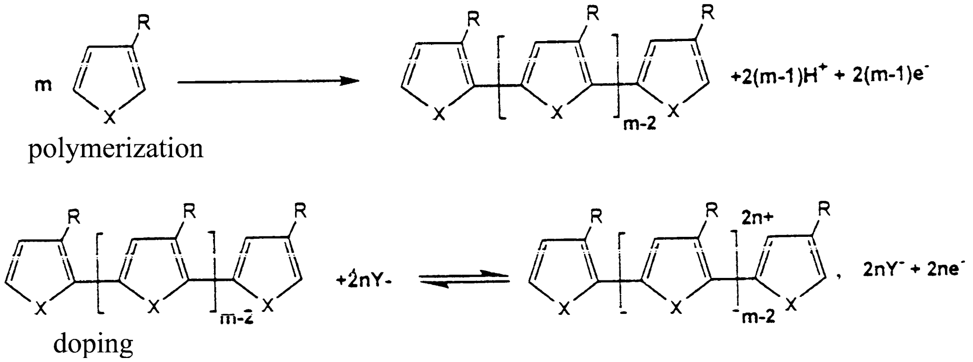
Film formation

The polypyrrole sublayer was prepared by electrochemical oxidation at constant potential (1.1 V vs. SCE) for 0.7 s in the pyrrole monomer solution (first bubbled for 30 min with argon). The electrode was then washed with water. Taking into account the potentiostat limit response of 15 ms and the measurement reproducibility at time up to 40 ms, the i-t curves start at 50 ms.

The adsorption of polyoxometalate was performed by dipping the two types of electrodes, uncoated and coated with polypyrrole, for 10 min in an aqueous solution of $H_4SiMo_{12}O_{40}$ (the concentration of polyanion was such that the pH was equal to about 4). The electrode was then transferred into HCl solution (pH = 4) for 5 min. The washed electrode was transferred into the electrochemical cell and voltammograms were recorded.

Results and discussion

Figure 1 presents the chronoamperometric curves at +1.1 V vs. SCE for $t = 0.7$ s characterizing the polypyrrole submonolayer electrochemical grafted on the three supports: SnO_2, ITO and In_2O_3, whose formation was schematized by: (with R = H, CH_3 or C_2H_5; x = N and Y = Cl^-.)



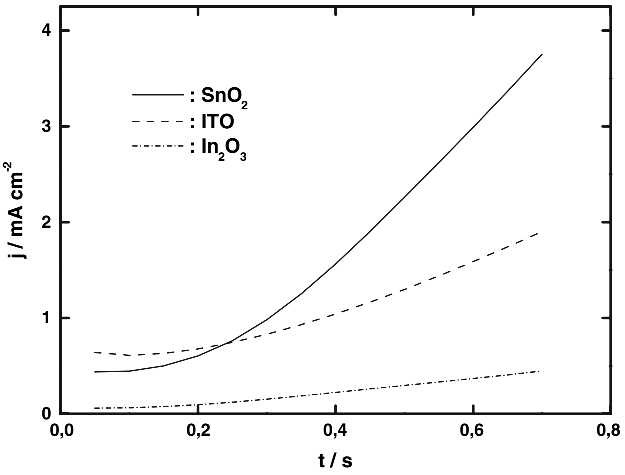


Fig. 1 Chronoamperometric curves for the electrodeposition of polypyrrole for SnO_2 (——), ITO (- - - -) and In_2O_3 (-·-·-·-·). The imposed potential is 1.1 V vs. SCE and imposed time is 0.7 s. The pyrrole concentration is 0.1 M in KCl 1 M

It is known that [13, 14] the nucleation and growth mechanisms of conducting polymers are very similar to those of metals. According to different authors, the current responses related to the nucleation process of polypyrrole on Al [14] and gold/highly oriented pyrolytic graphite (Au/HOPG) [13] were under diffusional control and generally represented by

$$J = Bt^{-1/2}[1 - \exp Ct] \qquad (1)$$

where $B = zFD^{1/2}c\pi^{-1/2}$ and $C = \pi KND$. D and c are the diffusion coefficient and concentration of pyrrole monomer, respectively, K is a constant dependent on the applied potential and N is the number of nucleation sites. This relation implies that current response passes through a maximum. In case of Au/HOPG, some authors [13] suggested that PPy nuclei form a monolayer and for an electrical charge equal to 10.53 mC cm^{-2}; for PPy electropolymerization, the thickness is around 5 nm. In our case, the electrodeposition was stopped before the maximum current is reached. On the other hand, the electrical charge passed was 10^{-3} C, 3.6×10^{-4} and 1.46×10^{-4} C cm^{-2} for SnO_2, ITO and In_2O_3, respectively. The estimated thickness using the empirical relation, e(μm) = 2.5Q(C cm^{-2}), proposed by Diaz et al. [15, 16] did not exceed 2.5 nm. In these conditions, we can suggest that the polypyrrole electrochemical grafted on SnO_2, ITO and In_2O_3 substrates was in submonolayer form. Even if these values do not represent the reality, they confirm the nanometric scale of the polypyrrole deposition.

When the oxidation potential is fixed, the recorded current represents the kinetic characteristics of polymerization. As observed in Fig. 1, the polymerization rate is quite dependent on the support: the kinetic for In_2O_3 is low compared to that of SnO_2 (the highest) and ITO. To have an idea how the polypyrrole has been deposited, the samples were studied by AFM. Figure 2 presents the 3D topographies of the bare substrates and of the polypyrrole-grafted surfaces. It is possible to say that the degree of changes follows the chronoamperometric variations. For In_2O_3, the modification of the morphology, due to the presence of polypyrrole, is very low, while for ITO and SnO_2, some comments could be made. On ITO, the surface appears more flat with the presence of some grains (as on In_2O_3). The polypyrrole should be deposited as a relatively uniform layer. That is also the case for SnO_2 but with a more pronounced effect. The grain density is decreased, and the grain feature turns to a more round morphology. This shows that several grains are covered by polypyrrole to form a new grain type which presents a more important size (as the could be thought for ITO also). Of course, the entire surface does not present this characteristic; it is possible to find the area without observable polypyrrole. This confirms the submonolayer notion.

We have submitted these three types of electrodes covered by polypyrrole to adsorption to polyoxometalate $SiMo_{12}O_{40}^{4-}$ ions. We remember that it was carried out by a simple dipping step (10 min) in a solution of POM.

The electrochemical behaviour of $SiMo_{12}O_{40}^{4-}$ could be summarized as follows [3]:

$$SiMo_{12}O_{40}^{4-} + 2e^- + 2H^+ = H_2SiMo_{12}O_{40}^{4-}$$

$$H_2SiMo_{12}O_{40}^{4-} + 2e^- + 2H^+ = H_4SiMo_{12}O_{40}^{4-}$$

$$H_4SiMo_{12}O_{40}^{4-} + 2e^- + 2H^+ = H_6SiMo_{12}O_{40}^{4-}$$

Figure 3 (inset) gives an example of the electrochemical behaviour for $SiMo_{12}O_{40}^{4-}$ 10^{-4} M, for SnO_2, which is similar to the other type of electrodes such as ITO, carbon and so on. Three equivalent two-electron steps are obtained.

Figures 3, 4 and 5 show the results of different substrates in the presence and in the absence of polypyrrole submonolayer grafted in the same experimental conditions. If we consider each substrate individually, the comparison between the adsorption of POM on the bare electrode and that covered by the polypyrrole submonolayer (Fig. 4) revealed that the submonolayer polypyrrole grafted, enhanced the POM adsorption process keeping its redox characteristics. As for SnO_2 substrate, its presence did not modify the adsorption process. However, the electrochemical response of the adsorbed POM is quite different from the one recorded on bare SnO_2 substrate. In the presence of polypyrrole, the adsorbed POM electrochemical characteristics are similar to those observed for POM species in solution. Such behaviour is not observed for POM directly adsorbed on bare SnO_2. Concerning In_2O_3 (Fig. 5), the polypyrrole effect on the adsorbed POM

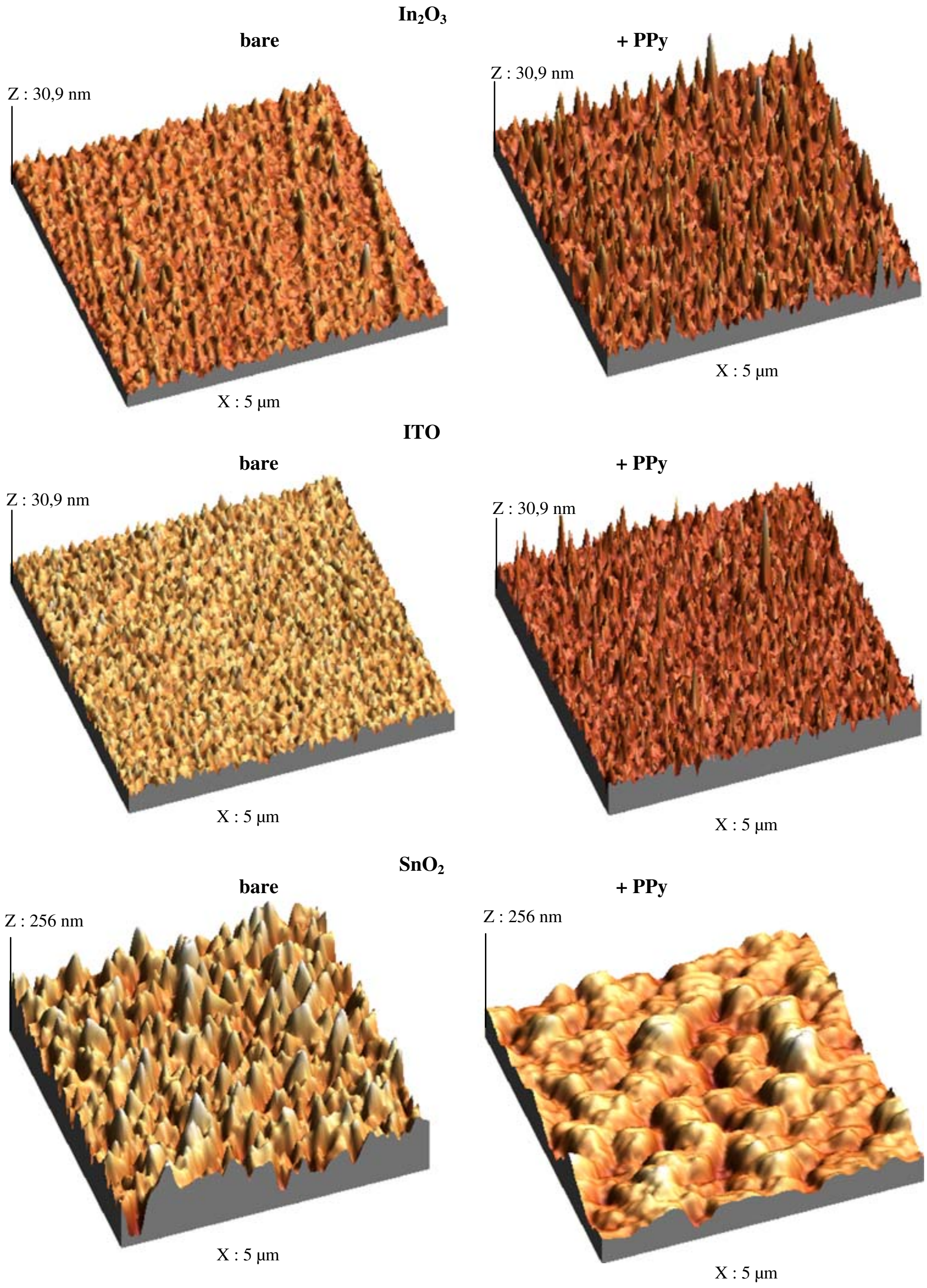


Fig. 2 AFM 3D topographies of bare substrates (left column) and polypyrrole-modified substrates (right column)

electrochemical properties is quasi nil. These results suggest the possibility of self-assembling between Polypyrrole and POM. The more polypyrrole was formed, the more self-assembling occurred. Such possibility explains not only the differences in electrochemical responses recorded on In_2O_3 and those observed on ITO and SnO_2, but also the important change in electrochemical behaviour of the absorbed POM on the last one in the presence of polypyrrole. Indeed, the augmentation of self-assembling between POM and polypyrrole on SnO_2 might modify the surface characteristics and reduce also the possibility of POM clusters formed in the pores of SnO_2 [17]. This is why the electrochemical characteristics observed on POM adsorbed for SnO_2 in the presence of polypyrrole and those recorded for POM in solution are similar.

Conclusion

This work shows that the nature of semiconducting transparent supports plays a determining role in the polypyrrole submonolayer formation. The adsorption processes of

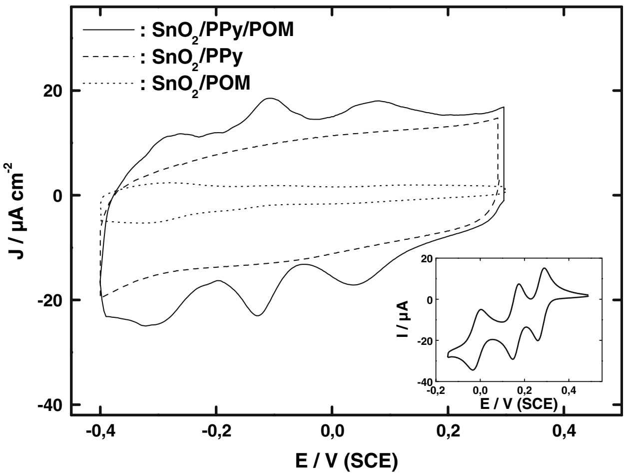


Fig. 3 Cyclic voltammograms showing responses for SnO_2/POM (⋯⋯), SnO_2/PPy (- - - -) and SnO_2/PPy/POM (——). $v = 0.05$ V s^{-1}. KCl 1 M, HCl pH = 4. The inset shows the electrochemical response, $v = 0.02$ v s^{-1}, for SnO_2, of $SiMo_{12}O_{40}^{4-}$ 10^{-4} M in HCl 1 M

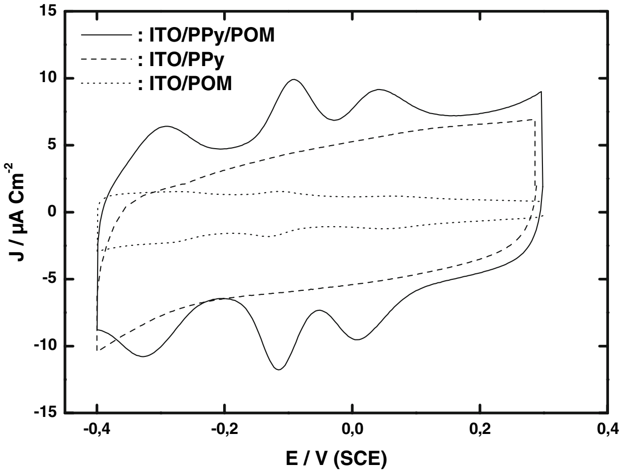


Fig. 4 Cyclic voltammograms showing responses for ITO/POM (⋯⋯), ITO/PPy (- - - -) and ITO/PPy/POM (——). $v = 0.05$ V s^{-1}. KCl 1 M, HCl pH = 4

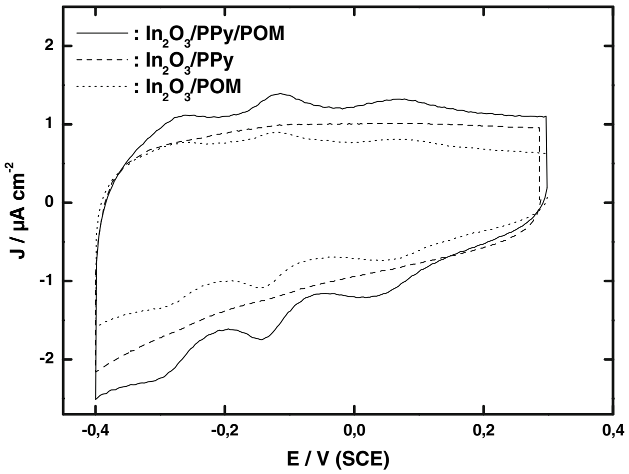


Fig. 5 Cyclic voltammograms showing responses for In_2O_3/POM (⋯⋯), In_2O_3/PPy (- - - -) and In_2O_3/PPy/POM (——). $v = 0.05$ V s^{-1}. KCl 1 M, HCl pH = 4

polyoxometalate on these substrates are noticeably modified and the self-assembling between polyoxometalate and polypyrrole is favoured, which might reduce the cluster polyoxometalate formation in the pores of SnO_2. It seems that the Sn^{4+} ions might play the main role in the adsorption processes and the nucleation of polypyrrole. Experiments are currently running in our laboratory to clarify this point.

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