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Sensing Effects for Bioapplications in Electroconducting Conjugated Polymers

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Straightforward and easy electrodeposition of electroconducting conjugated polymers (ECPs) and their functionalization either by entrapment of anions or by covalent grafting make these materials attractive candidates for fabrication of a sensitive layer at the surface of an electrode. This approach is exemplified in a NO_2^--sensitive poly(N-methylpyrrole) layer, single-stranded DNA-derivatized polypyrrole film and a reservoir electrode based on a polypyrrole with host β-cyclodextrins.

Conjugated Polymers

The sensing part of a sensor consists of a chemical recognition element coupled with a transducer that converts the recognition event into a measurable electronic signal. Electroconducting conjugated polymers (ECPs), may act as the direct transducer (conductance, impedance or redox potential monitoring) and/or as a sensitive layer containing the catalyst, or the recognition element.[1] The versatility for sensor applications of such an ECP-based modified electrode is exemplified as follows.

(1) Heteropolyanions (HPAs) of the Keggins type $(XMe_{12}O_{40})^{4-}$ with $n = 4$ or 3, where X = Si or P and Me = W or Mo, can be inserted as dopants during the electrodeposition, in acetonitrile or water, of various conducting films such as polypyrrole (Ppy),[2] poly(N-methylpyrrole) (PMePy),[3] poly(3-methylthiophene),[4] and polyaniline.[5] These ECP-derivatized films exhibit an electrochemical response corresponding to the superimposition of the contributions of the two electroactive partners. Considering their size, these HPAs cannot be expelled during the reduction of the polymer. We recently showed[6,7] that the iron-substituted heteropolytungstate $[Fe^{III}SiW_{11}O_{39}(H_2O)]^{5-}$ ($FeSiW_{11}$) retains its electrocatalytic activity towards the reduction of NO_2^- anions in NH_4^+ cations[8] (Fig. 1), providing that the ECP matrix is PMePy. As a matter of fact,

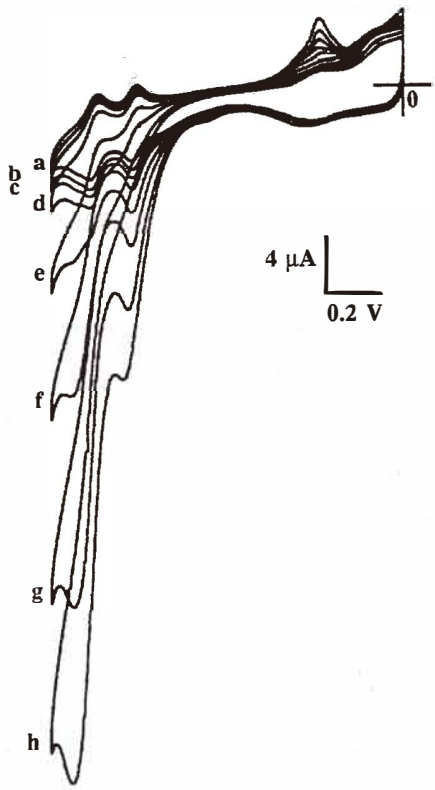


Fig. 1. Cyclic voltammograms at 10 mV/s of a glassy carbon electrode ($S = 0.07$ cm^2) modified with a poly(N-methylpyrrole) film doped with $[H_2OFe^{III}PW_{11}O_{39}]^{4-}$. Supporting electrolyte: 0.1 M CH_3COOH + 0.1 M CH_3COONa (pH=4.6). The film is prepared by electrolysis at 0.60 V (vs Ag/Ag^+ 10^{-2} M) with an acetonitrile solution containing 5×10^{-2} M tetrabutylammonium salt of $[H_2OFe^{III}PW_{11}O_{39}]^{4-}$ and 10^{-2} M N-methylpyrrole, so that 1.7×10^{-8} mol cm^{-2} of $[H_2OFe^{III}PW_{11}O_{39}]^{4-}$ is incorporated into the polymer film. In the absence of $NaNO_2$ (a) and in the presence of 5×10^{-4} (b), 10^{-3} (c), 2×10^{-3} (d), 5×10^{-3} (e), 10^{-2} (f), 2×10^{-2} (g) and 3×10^{-2} M $NaNO_2$ (h).

derivatized poly(3-methylthiophene) or polyaniline films are electro-inactive and PPy/$FeSiW_{11}$ displays limited catalytic activity. These different behaviors induced by the ECP matrices can be explained on the basis of the formation of an iron-nitrosyl complex during the catalytic reaction. The PMePy/$FeSiW_{11}$-modified electrode is sensitive to nitrite ions and exhibits a linear response between catalytic currents (at $E = 1.2$ V vs $Ag/Ag^+ 10^{-2}$ M) and NO_2^- concentration over the 5×10^{-5} to 3×10^{-2} M range (Fig. 2).

(2) The immobilization of a single-stranded DNA sequence in a PPy film by chemical grafting results in a genosensor assembly. The use of radioactive hybridization indicators shows that the immobilized DNA probe hybridizes selectively with its target sequence with a signal-to-noise ratio of about 1000 (Table 1). Preliminary results show that successive hybridization and denaturation experiments (at 60°C in 8×10^{-2} M Na^+ in H_2O) can be carried out. The fourth hybridization is still 30% of the first hybridization experiment considering the DNA-target content.

(3) The trapping/delivering of neutral drugs based on host-guest interaction was attempted by the incorporation of host heptasulfonated cyclodextrines (β-$CDSO_3^-$) as dopants into PPy.[9,10] In this manner entrapment of neutral N-methylphenothiazine (as a drug model) into a (PPy^+, β-$CDSO_3^-$) film is simply achieved by molecular encapsulation (Fig. 3). In order to verify the reservoir ability of a (PPy^+, β-$CDSO_3^-$)-modified electrode, the following procedure has been carried out.

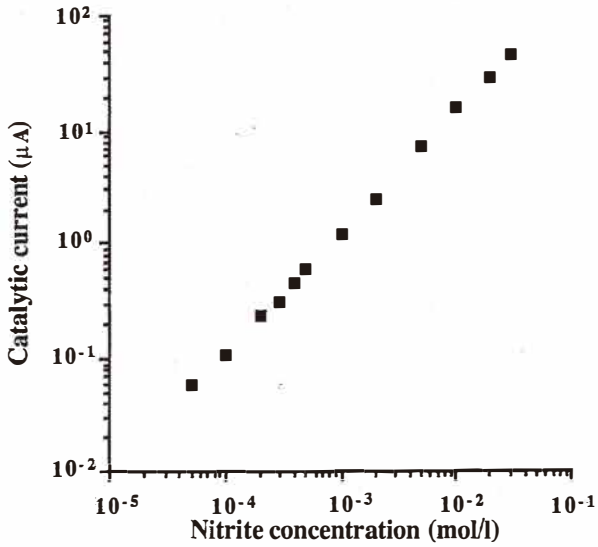


Fig. 2. Catalytic current $I_{cat.}$ vs nitrite concentration. $I_{cat.}$ is measured at –1.20 V from cyclic voltammograms obtained using the same modified electrode as in Fig. 1.

Table 1
Hybridization of a PPy film (S = 1 cm^2) grafted by a twentymer-DNA sequence. The content level is about 4×10^{-12} mol cm^{-2}. Control experiment: aqueous medium, pH 7.4 (sodium salt phosphate EDTA buffer), 0.5 % sodium dodecyl sulfate and 6600 pM noncomplementary labelled DNA sequence (radioactivity: 828000 c.p.m.). Hybridization: same aqueous solution but containing 6600 pM of the target-labelled DNA sequence (radioactivity: 795000 c.p.m.). The measured radioactivity values are obtained after careful rinsing with an aqueous-buffered solution.

	Starting radioactivity (c.p.m.)	End radioactivity (c.p.m.)
Control experiment	0	370
Hybridization experiment	0	249545

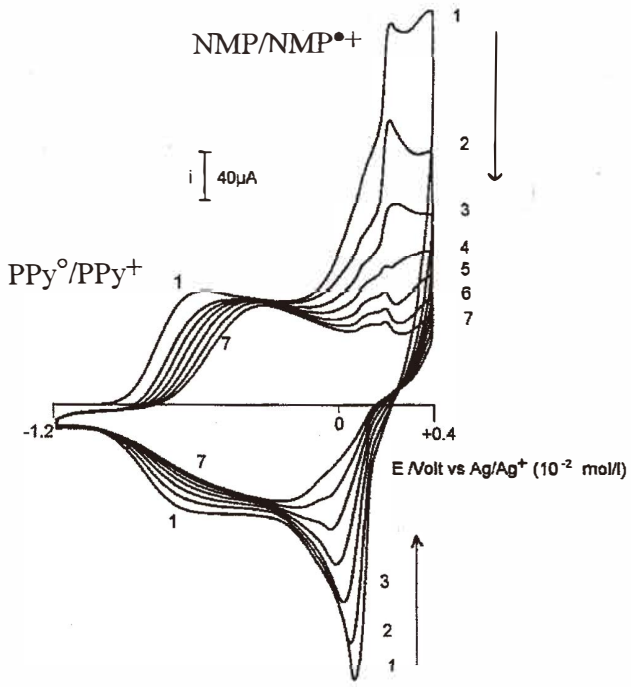


Fig. 3. Voltammetric curves at 20 mV s^{-1} in aq. 0.5 M $LiClO_4$ of a (PPy^+, β-$CDSO_3^-$ [NMP])–modified electrode prepared by dipping a (PPy^+, β-$CDSO_3^-$) film (0.3 C cm^{-2}) in CH_3CN 0.1 M in NMP for 1.5 hours, then rinsing in CH_3CN and aq. 0.5 M in $LiCiO_4$ for 45 minutes.

After electrodeposition of a (PPy^+, β-$CDSO_3^-$) film (q_s = 0.3 C cm^{-2}) from an aqueous solution of 10^{-1} M pyrrole and 10^{-2} M β-$CDSO_3Na$ at E = +0.4 V, the modified electrode is immersed for 90 minutes in a 10^{-1} M NMP solution in CH_3CN, and thoroughly rinsed in CH_3CN and then in aq. 0.5 M $LiClO_4$ for 45 minutes.

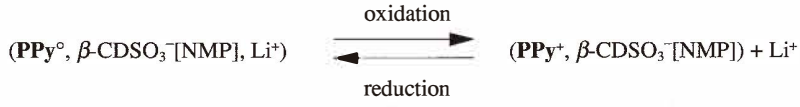
Figure 3 shows the first seven cycles of cyclic voltammetry of the (PPy^+, β-$CDSO_3^-$)-modified electrode incorporating NMP (PPy^+, β-$CDSO_3^-$[NMP]). Two well-separated systems appear, corresponding to the PPy and NMP electroactivities (Scheme 1).

The stimulation for the release of $NMP^{\bullet+}$ from the guest-preloaded polymer might be triggered electrochemically by applying an appropriate potential to the polymer-modified electrode.

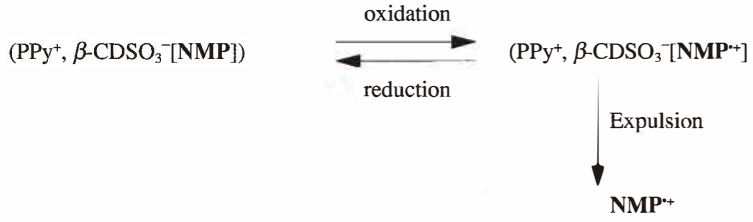
Due to their easy one-step electrodeposition and functionalization, low cost, electrical wiring ability and straightforward response time, ECPs appear to be appropriate materials to fabricate the sensing component of electrochemical sensors or activators for various bioapplications.

Scheme 1. PPy and NMP electroactivities. The oxidation of NMP appears in potentials when PPy is in its heavily doped state.

1. **PPy** electroactivity:



2. **NMP** electroactivity:



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