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Functionalized conducting polymers for chemical sensors – An *in situ* ESR/UV-Vis-NIR voltammetric study

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SUMMARY: The redox and optical properties of various well defined polymer and copolymer films containing pyrrole or thiophene units were studied. The *in situ* ESR/UV-Vis-NIR spectroelectrochemistry was applied to investigate polymers and copolymers deposited both electrochemically or by a special chemical procedure using adhesion promoter onto the optically transparent indium-tin-oxide (ITO) electrodes.

The spectroelectrochemical responses of chemically and electrochemically prepared polythiophenes on ITO were compared and the electronic structures of both polymers found to be similar. *In situ* ESR/UV-Vis-NIR voltammetric studies on electrochemically prepared copolymers containing pyrrole units and various N,N'-ethylene-bis(salicylidenimine) (salen) transition metal complexes indicate the presence of both polysalen and polypyrrole redox active centers in the copolymer.

Introduction

Preparation of conducting polymers on electrode surfaces for applications such as chemical sensors, electrocatalysts or electronic and optical devices still remains an active field of research. It is of great significance to clarify the optical, electrochemical and ESR properties of these polymers. Thus a better understanding of the processes of charge transfer to the polymer is obtained.

We are currently engaged in the design and spectroelectrochemical characterization of new conducting polymer architectures containing salen complexes with transition metals and their copolymers with pyrrole [1] as well as polythiophenes containing complexing substituents [2,3]. The aim of these activities is to prepare all-solid-state sensors that allow

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selective recognition of molecules and transduction of the chemical signal into an electric signal in the solid state [4].

The ESR/UV-Vis-NIR spectroelectrochemical setup [5] and laminated optically transparent electrodes [6] were used to monitor simultaneously ESR and optical spectra of the polymers at the electrode surfaces during the polymer redox cycling and to estimate the absolute numbers of free spins formed in the polymer [7]. Here this technique is used for electrochemically prepared polymer structures containing salen moieties and well defined thin polythiophene layers chemically synthesized onto ITO. The results are compared with the previous *in situ* spectroelectrochemical studies on polypyrrole [8], polyaniline [9] and $(Py)_n(Ni\text{-}bpsalen)_m$ [1].

Experimental

The polythiophene layers were deposited chemically [2,3] onto a special laminated ITO working electrode [8]. The ITO surface was coated with adhesion promoter 11-(3-thienyl)undecyltrichlorsilane (TUTS) by inserting the substrate in a 3 mM TUTS solution in bicyclohexyl for 60 min. The chemical polymerization was done at room temperature using 0.05 M thiophene monomer in acetonitrile by adding 0.25 M $FeCl_3$ (anhydrous) oxidation reagent acetonitrile solution. The polymer film of a typical thickness of 100 to 200 nm was grown after a polymerization time of 60 min. The oxidizing agent $FeCl_3$ was extracted by dipping the substrate for 60 min in methanol. Electrochemical deposition of polythiophene was done by potentiostatic electrolysis at 1.9 V *vs.* Ag/AgCl starting from 0.05 M / 0.1 M tetrabuthylammonium tetrafluoroborate ($TBABF_4$) acetonitrile solution.

N,N'-ethylene-bis(salicylidenimine) Cu(II) (Cu(II)-salen) was polymerized on ITO by repetitive cyclic voltammetry between 0 and 1.15 V *vs.* Ag/AgCl in 0.8 mM monomer and 0.1 M support electrolyte [tetrabuthylammonium perchlorate (TBAP), tetraethylammonium tosylate (TEATos) or $TBABF_4$ acetonitrile solution]. The corresponding salen-pyrrole copolymer was electrochemically synthesized applying 'prepulse' technique [1]. All electrochemical preparation experiments were carried out in a standard one compartment cell providing with three electrode system.

The preparation of laminated ITO working electrode and the spectroelectrochemical cell for *in situ* ESR/UV-Vis-NIR cyclovoltammetry are described elsewhere [5-9]. Spectro-cyclovoltammetric measurements with up to 41 spectra during one single scan in cyclic voltammetry were done. For UV-Vis and UV-Vis-NIR spectra InstaSpec II (LOT Oriel) or UV-Vis-NIR (TIDAS, J&M GmbH, Germany) diode array spectrometers were used and linked to the HEKA potentiostat PG 390 or PG 285. For ESR X-band spectrometers EMX or ESP 300 (both Bruker) were used.

Results

In Figs.1 and 2 the spectroelectrochemical studies on electrochemically (Fig.1) and chemically (Fig. 2) prepared polythiophene on ITO are summarized.

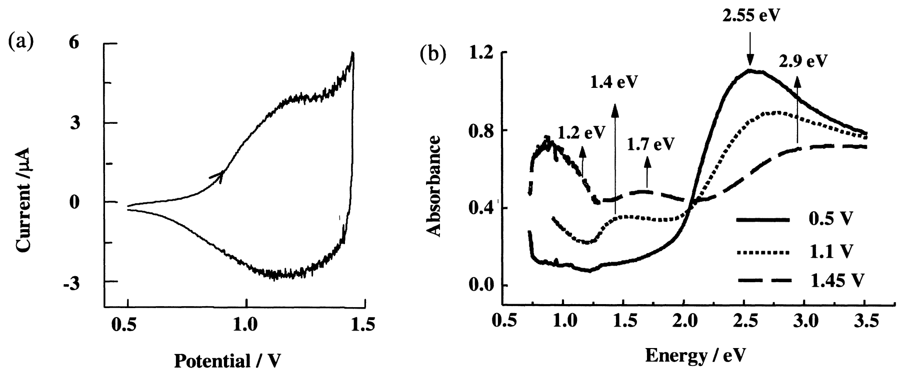

Figure 1. (a) Cyclic voltammogram (potential referred to Ag/AgCl) and (b) UV-Vis-NIR spectra of electrochemically prepared polythiophene on ITO (0.1 M $TBABF_4$ acetonitrile solution, scan rate: 5 mV s^{-1}).

The spectrocyclovoltammogram of polythiophene deposited onto ITO by the anodic oxidation measured in 0.1 M $TBABF_4$ acetonitrile (Fig. 1) exhibits similar characteristics as previously observed for PPy [8] and polyaniline [9]. The results can be interpreted assuming neutral, mono-charged and double-charged states, where the mono-charged units exhibit well known polaronic single ESR line ($g = 2.0027$, $\Delta H_{pp} = 0.2$ mT) with the corresponding visible band at 1.4 eV. In the fully oxidized state double-charged segments which are ESR silent (bands at 2.9 eV, 1.7 eV and 1.2 eV) dominate. Very similar behavior was observed in the case of chemically prepared polythiophene on ITO (Fig. 2) indicating an analogous chemical structure causing the same electrochemical and optical properties as for electrochemically prepared films. This implies that the special chemical procedure used (as described above) is suitable for the preparation of well defined thin polythiophene layers with the same characteristics as those polythiophenenes obtained electrochemically. Therefore the electronic structures of both chemically and electrochemically prepared polythiophene are similar.

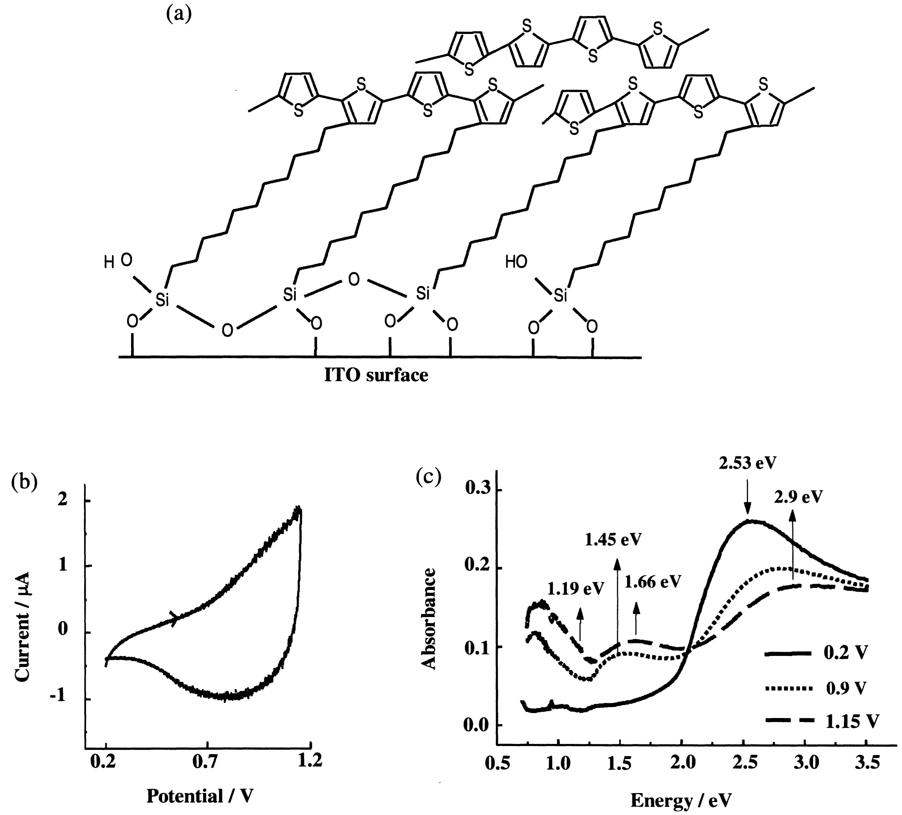

Figure 2. (a) Schematic structure of chemically deposited polythiophene on ITO, (b) corresponding cyclic voltammogram (0.2-1.15 V vs. Ag/AgCl) and (c) UV-Vis-NIR spectra (measured in acetonitrile / 0.1 M TBABF$_4$ solution).

Copolymer layers containing salen subunits attract much attention due to their ability to exchange the central metal ion easily and due to their sensitivity to specific organic or inorganic analytes [10,11]. In our previous work [1] the spectroelectrochemical studies on newly prepared pyrrole/Ni-bpsalen stable copolymer were presented. As the stability of the salen subunits plays a crucial role in sensor applications we are focussing on the optimization of the polymer preparation conditions in order to form stable salen polymers by using simple salen monomers. In this work the new spectroelectrochemical results on N,N'-ethylene-bis(salicylidenimine) Cu(II) monomer (Fig.3a) and its polymer (Fig.3b) are presented. During oxidation polymer consisting of the Cu-salen complex displayed characteristic features of the Cu(II)/Cu(III) redox couple within the polymer film, as was previously observed by Audebert et al. [12,13]. During the cyclovoltammetric scan poly(Cu-salen) exhibit remarkable changes in UV-Vis spectra (Fig. 3) with corresponding optical bands for poly(Cu(II)-salen) at 3.83 eV and for (Cu(III)-salen) polymer at 3.26 eV. An increase of the single ESR line ($\Delta H_{pp} = 0.9$ mT) intensity resulting from a state in the polysalen π-backbone (optical band at 2.6 eV) was observed at higher potentials. The stability of films prepared using the simple salen-complex with Cu(II) is similar to stable poly(Ni-bpsalen) [1] and increases using TEAP acetonitrile dry electrolyte [12]. In previous studies on $(Py)_n(Ni\text{-}bpsalen)_m$, $(Py)_n(Ni\text{-}salen)_m$ films on ITO [1] the presence of both polypyrrole- and polysalen- redox centers and their copolymeric nature were proved. Similar results we obtained for $(Py)_n(Cu\text{-}salen)_m$ with both polymer redox centers which will be published elsewhere.

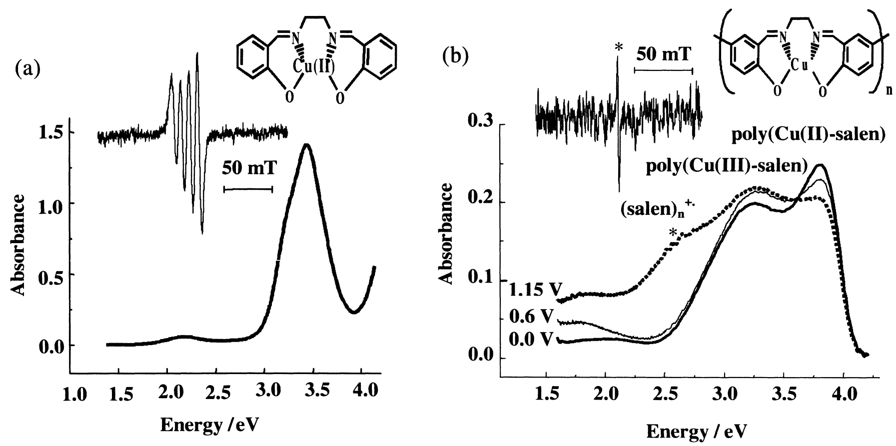

Figure 3. (a) Structures, UV-Vis-NIR bands and ESR spectra of investigated Cu(II)salen monomer and (b) its corresponding polymer on ITO in various oxidation states (0.1 M TBAP acetonitrile electrolyte, CV scan: from 0 V to 1.15 V *vs.* Ag/AgCl, scan rate 3 mV s^{-1}; ESR: sweep width 150 mT).

Conclusions

Polythiophene films deposited on ITO optically transparent working electrodes were prepared chemically using an adhesion promoter as well as by standard electrochemical procedure. In this manner we were able to compare their redox and optical properties applying *in situ* UV-Vis-NIR cyclovoltammetry. In both cases a very similar redox behavior is observed.

Applying special electrochemical procedures stable and well defined Cu-salen polymer and copolymer (with pyrrole) films on ITO can be prepared in acetonitrile/$TBABF_4$ solutions.

Combining of optically transparent electrodes and reactive polymers and copolymers, chemically bounded at the electrode surface, is a new route for the use of conducting polymers in sensor applications. Especially polymer and copolymer films consisting of polypyrrole or polythiophene subunits and selective complexation parts (salen complexes, thiophene derivatives containing complexing substituents) are promising materials for all-solid state sensors. They combine the metal ion or gas-vapor recognition with still good electrical conductivity of the polymer. Such copolymeric structures allow a very efficient transduction of the chemical signal into an electric signal.

Acknowledgements

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