



Electrochemical and spectroscopic characterization of a gold electrode modified with 3,4',4'',4''' copper(II) tetrasulphonated phthalocyanine

Karolien De Wael¹, Karl Peeters, David Bogaert, Hans Buschop, Laszlo Vincze, Annemie Adriaens*

Department of Analytical Chemistry, Ghent University, Krijgslaan 281-S12, B-9000 Ghent, Belgium

Received 31 August 2006; received in revised form 26 January 2007; accepted 8 February 2007

Available online 15 February 2007

Abstract

This paper describes an electrochemical and spectroscopic study of a gold electrode modified with 3,4',4'',4''' copper(II) tetrasulphophthalocyanine tetrasodium salt (CuTSPc). Its electrochemical behaviour is compared to that with random CuTSPc and cobalt(II) tetrasulphophthalocyanine tetrasodium salt (CoTSPc). In addition electrochemical and synchrotron radiation X-ray fluorescence measurements were performed to characterize the adsorbed copper surface concentration.

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Keywords: Gold; Modification; Phthalocyanine; Copper; SR-XRF; Cyclic voltammetry; UV-Vis; XPS

1. Introduction

Many chemical reactions, although thermodynamically very favorable, do not always occur at a significant rate. For such reactions to be useful, it is necessary to find a catalyst which will increase the reaction rate. Likewise, in the absence of a catalyst, many electrode reactions occur, if at all, only at very high overpotentials because of poor kinetics; i.e. such electrode reactions have a low exchange current density. In view of this, the development of chemically modified electrodes (CMEs) has become essential. The emphasis of this approach has been on improving the selectivity, efficiency and sensitivity of electroanalytical measurements, providing therefore an alternative pathway with lower activation energy and hence to permit such electrode reaction to occur at high current densities close to the

equilibrium potential [1]. The basic feature of a CME is that generally quite a thin film of a selected chemical is bound to or coated on the electrode to provide the electrode with the desired electrochemical, optical, electrical, transport or other properties [2–4].

Especially transition metallo phthalocyanines have lately attracted a wide research interest as electrocatalysts. Soluble sulphonated phthalocyanines have namely shown to be able to form layers on different types of supporting material, including electrodes [5–8]. Their aromatic ring structure is completely flat which enables the phthalocyanines in the deposited layer to form columnar aggregates, in which π -stacking interactions between the molecules dominate. It is desirable to have ordered, well-packed and well-oriented molecular layers of phthalocyanines on the electrodes. The aggregation of phthalocyanines has been the subject of intensive study over many decades [9–11]. More than 70 different metal ions can form a complex by coordinating with the phthalocyanine ring [12], each leading to specific electrocatalytic properties.

This article focuses on the immobilization characteristics of a 3,4',4'',4''' copper(II) tetrasulphonated phthalocyanine

* Corresponding author. Tel.: +32 9 264 4826; fax: +32 9 264 4960.

E-mail address: Annemie.Adriaens@UGent.be (A. Adriaens).

¹ Postdoctoral Fellow of the Research Foundation – Flanders (Belgium).

tetrasodium salt (CuTSPc) on gold electrodes. A comparison will be made with previously obtained results involving the modification of gold using a random copper(II) tetrasulphonated phthalocyanine tetrasodium salt (CuTSPc) and a cobalt(II) tetrasulphonated phthalocyanine tetrasodium salt (CoTSPc).

2. Experimental

The 3,4',4'',4'''CuTSPc sodium salt was purchased with Sigma–Aldrich (USA). It has four sulphonated groups on fixed positions, more specifically on the 3, 4', 4'' and 4''' positions of a phthalocyanine ring.

Electrochemical experiments were performed in a three-electrode cell using a saturated calomel reference electrode (SCE) containing two compartments (Radiometer Analytical, France) and a carbon counter electrode. The working electrodes were gold electrodes with a diameter of 1.6 mm (BAS, UK) which were pretreated by mechanical and electrochemical polishing according to the following procedure. Before its first use the electrode surface was briefly scoured by a silicon carbide emery paper of 1200 grit to obtain a fresh surface. To smoothen the resulting relatively rough surface it was further subjected to sequential polishing by polishing cloth covered with alumina powder of 1, 0.3 and 0.05 μm particle size (Buehler, USA) for, respectively, 5, 10 and 20 min. To remove any adherent Al_2O_3 particles the electrode surface was rinsed thoroughly with doubly deionised water and cleaned in an ultrasonic bath containing deionised water (Branson 3210, USA) for 2 min. Finally, the electrode was pretreated by an electrochemical potential cycling technique in a 0.1 mol L^{-1} $\text{Na}_2\text{HPO}_4/\text{NaOH}$ buffer solution, pH 12 (VWR, Belgium) between -1.2 and 0.6 V vs. SCE until five subsequent scans were identical. A PGSTAT20 potentiostat controlled by GPES 4.9 005 software package running (ECO Chemie, The Netherlands) was used to record voltammetric curves. Prior the start of each measurement, the pH of the solution was measured using an Orion Benchtop pH-meter model 420A (Thermo Fisher Scientific, USA). Prior to each experiment, pure nitrogen was bubbled through the cell solution for 20 min.

Modification was performed by recording successive cyclic voltammetric scans (100 scans) in a potential window from -1.2 to 0.6 V vs. SCE in a $\text{Na}_2\text{HPO}_4/\text{NaOH}$ pH 12 buffer solution containing 4×10^{-3} mol L^{-1} CuTSPc. After each modification procedure, the electrode was immersed in a $\text{Na}_2\text{HPO}_4/\text{NaOH}$ pH 12 buffer solution (not containing CuTSPc) while voltammetric scans were taken in order to study the electrochemical behaviour of the modified electrode and to obtain information about the amount of CuTSPc deposited on the gold surface.

Scanning micro-SR-XRF (synchrotron radiation induced X-ray fluorescence) experiments were performed at Beam Line L of the DORIS-III storage ring, HASYLAB (Hamburg, Germany) [13]. This beamline is dedicated to micro-XRF experiments using either white or monochro-

matic bending magnet excitation and mono- or polycapillary focusing, with routinely available beam sizes of 10–30 μm . The primary X-ray beam is generated by a 1.2 T bending magnet source which, given the machine energy of 4.465 GeV, provides a polychromatic spectral distribution with a critical energy of 16.6 keV. After initial low-energy filtering and collimation, the beam was monochromatized by a Ni/C multilayer monochromator ($\Delta E/E \approx 10^{-2}$) and further collimated by a motorized cross-slit system. After monochromatization the beam was focused by a monolithic polycapillary half-lens (X-ray Optical Systems Inc., USA), designed specifically for parallel primary beams hence suitable for the focusing of low-divergence synchrotron beams. A microbeam size of about 20 μm (FWHM) was obtained at the excitation energy range of 9.3 ± 0.1 keV, which was used to excite selectively the Cu $\text{K}\alpha, \beta$ fluorescent-lines without exciting Au-L lines from the (spectroscopically infinitely thick) gold substrate. The nominal working distance of the polycapillary optic was 5 mm.

Experimental difficulty of the CuTSPc thin-film uniformity studies included the determination of low-amounts of Cu (ca. 0.1–0.5 pg, assuming a 20 μm incident beam) in the presence of partially overlapping Compton and Au X-ray resonant Raman peaks. During the CuTSPc uniformity studies 31×31 scanning XRF maps were recorded with 20 μm step-size, using a data collection time of 10 s per data point. Absolute detection limits for Cu were estimated to be 5–6 ng cm^{-2} using a measuring time of 20 s. In order to determine the level of uniformity of the deposited CuTSPs thin-film, the scanning and subsequent data reduction strategy described by Kempenaers et al. was applied [14].

UV–Vis measurements were performed with a Specors 200 spectrophotometer (Analytical Jena, Germany). XPS measurements were performed with a Perkin–Elmer Phi ESCA 5500 system equipped with a monochromated 450 W Al $\text{K}\alpha$ source. The base pressure of the XPS system was below 1×10^{-7} Pa. Experiments were recorded with 220 W source power and an angular acceptance of $\pm 7^\circ$. The analyser axis made an angle of 45° with the specimen surface. The C_{1s} , O_{1s} and Au_{4f} and metal core levels were recorded with a step of 0.125 eV and a pass energy of 117.4 eV.

3. Results and discussion

3.1. Electrochemical behaviour of 3,4',4'',4'''CuTSPc during the modification

Fig. 1 shows a selection of the 100 cyclic voltammetric scans (i.e. scans 10, 20, 30, 40, 60, 80 and 100) recorded at a gold electrode in a pH 12 buffer solution (curve 1) and a solution containing 4.0×10^{-3} mol L^{-1} 3,4',4'',4'''CuTSPc (curves 2–8). The voltammogram shows two well-defined oxidation and reduction peaks. The oxidation peak (I_a) at 0.50 V can be determined as the oxidation of the gold surface and is linked to the reduction process (I_c) at

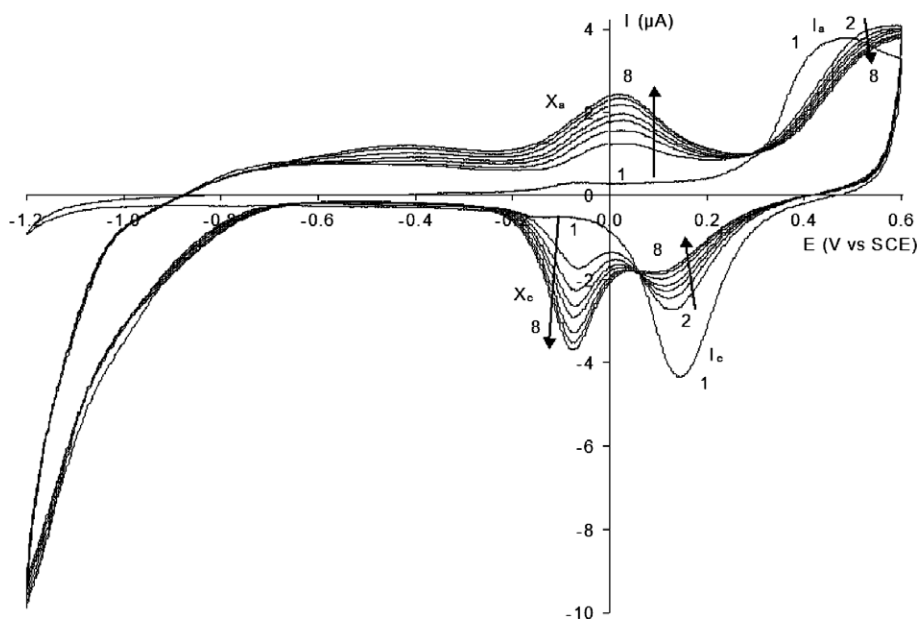
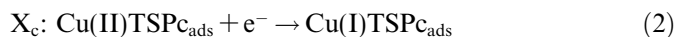


Fig. 1. Current–potential curves recorded at a gold electrode in a pH 12 buffer solution in the absence (1) and presence of $4.0 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc (2–8) at a scan rate of 50 mV s^{-1} and a temperature of 298.0 K as a function of scan number. Scan number is (2) 10, (3) 20, (4) 30, (5) 40, (6) 60, (7) 80 and (8) 100.

0.15 V. The latter can in its turn be explained as the reduction of the gold oxides formed during surface oxidation [15].

Besides these two peaks, new oxidation and reduction processes appear, respectively, at 0.05 V (X_a) and -0.1 V (X_c). They can be explained as the oxidation and reduction of adsorbed 3,4',4'',4'''CuTSPc as shown, respectively, in Eqs. (1) and (2):



Both peaks grow during the first 100 scans. This growth with increasing scan number is due to the deposition of 3,4',4'',4'''CuTSPc on the gold surface. A second indication of adsorption is the decrease and the shift of the AuO formation peak around 0.5 V (I_a) and its related reduction signal at 0.15 V (I_c). The latter indicates that the 3,4',4'',4'''CuTSPc molecules immobilized on the gold electrode prevent the oxidation and reduction of the gold surface. Similar to the electrochemistry of CoTSPc, the processes observed in the potential range from -0.4 to -1.2 V can be explained as ring processes of 3,4',4'',4'''CuTSPc in solution [5,7].

The variation of the peak current at -0.1 V (X_c) as a function of scan number is represented in Fig. 2 (curve A). Based on the fact that the slope decreases as a function of scan number, it can be stated that the adsorption becomes more difficult as a function of time. Curve B in Fig. 2 shows the relationship between the peak current of the reduction process at 0.15 V (I_c) and the scan number. The slope of this curve decreases in a way similar to curve A. However, the shift in peak potential to less positive val-

ues (Fig. 1) is an indication that the process is not exclusively associated with the gold oxide reduction. The peak maximum shifts towards less positive potentials with increasing scan number, despite the fact that the peak intensity decreases. An opposite effect is expected when the peak is only attributed to the gold oxide reduction. Therefore, the reduction process at 0.15 V can be explained as the gold oxide superimposed by another redox process. Probably an interference with the increasing peak X_c occurs. Another potential explanation of this phenomenon is the occurrence of an interference with the ring reduction of adsorbed 3,4',4'',4'''CuTSPc.

3.2. Electrochemical proof of deposition

Based on the above results, a 3,4',4'',4'''CuTSPc modified gold electrode can be formed by recording successive cyclic voltammograms in a pH 12 buffer solution containing 3,4',4'',4'''CuTSPc. The electrochemical proof of deposition was further obtained by bringing the modified electrode in a blank buffer solution and recording a set of cyclic voltammograms. Fig. 3 represents the voltammogram of a blank gold electrode (curve 1) and scan 10 of a 3,4',4'',4'''CuTSPc modified gold electrode (curve 2). The 3,4',4'',4'''CuTSPc adsorption peaks appear at the same potentials as in a buffer solution containing $4.0 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc, ca. -0.1 and 0.05 V.

A small redox system can be observed at ca. -1.1 V. In a buffer solution containing $4.0 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc (Fig. 1) a large reduction peak, explained as a ring reduction of 3,4',4'',4'''CuTSPc in solution, is seen at this potential. It is postulated that the small redox process in the 3,4',4'',4'''CuTSPc free buffer solution after

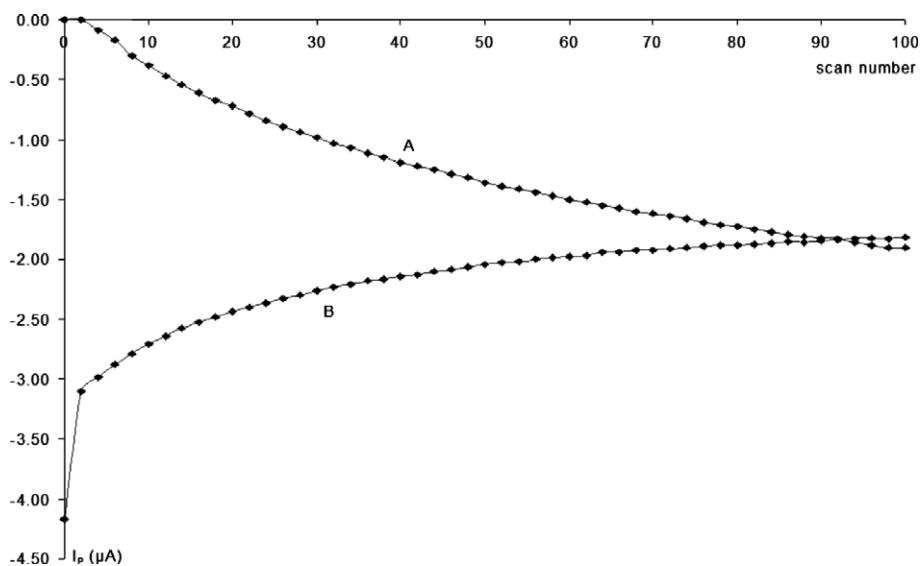


Fig. 2. Relationship between peak current of process X_c at -0.1 V vs. SCE (A) or I_c at 0.15 V vs. SCE (B) in a pH 12 buffer solution containing 4.0×10^{-3} mol L^{-1} 3,4',4'',4'''CuTSPc and scan number.

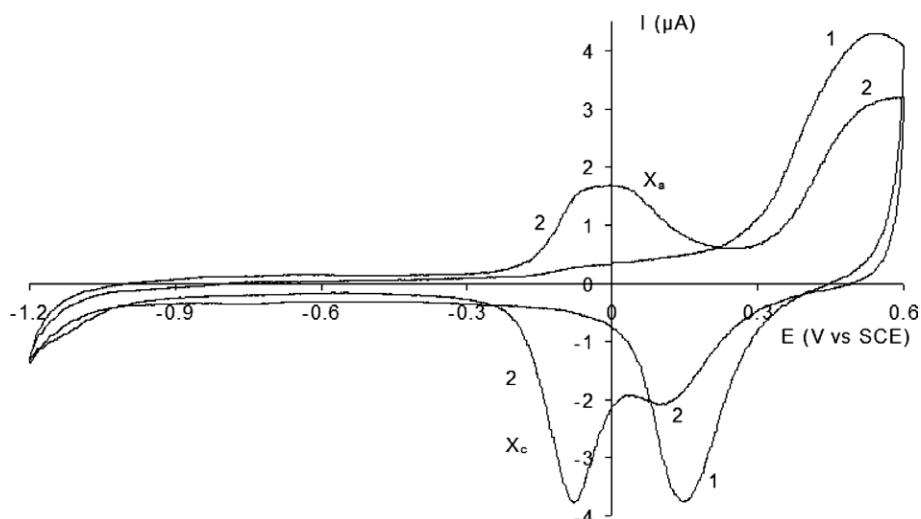


Fig. 3. Current–potential curves recorded at a blank gold electrode in a pH 12 buffer solution (1) and current–potential curves of a continuous cyclic scanning experiment recorded at a gold electrode modified with 3,4',4'',4'''CuTSPc in a pH 12 buffer solution (2).

modification (Fig. 3) can be explained as the ring reduction of adsorbed CuTSPc that electrocatalyses the ring reduction of 3,4',4'',4'''CuTSPc in solution.

The influence of the scan rate on the peak current was investigated to confirm the adsorption electrochemically. A slope of the relationship between the logarithm of the peak current ($\log I_p$) and the logarithm of the scan rate ($\log \nu$) equals to 1 corresponds to oxidation and reduction of 3,4',4'',4'''CuTSPc adsorbed at the gold electrode, while a slope of 0.5 rather indicates a rate determining diffusion of 3,4',4'',4'''CuTSPc towards the electrode surface [1]. Fig. 4 shows the relationship between $\log I_p$ and $\log \nu$ for peak X_a and X_c . The slope for the redox processes is, respectively, 0.911 and 1.012, indicating the occurrence of redox processes of particles adsorbed on the electrode surface.

3.3. Comparison with random CuTSPc

Random CuTSPc is a related salt which can be considered as a complex mixture with every possible substitution having the sulphonated groups randomly placed on the isoindole groups. The difference in electrochemical behaviour between 3,4',4'',4'''CuTSPc and random CuTSPc at a gold electrode is shown in Fig. 5. The modification procedure was similar as before in that sense that the electrodes were modified either with random CuTSPc (curve 2) [8] or 3,4',4'',4'''CuTSPc (curve 3) by recording successive cyclic voltammetric scans in a potential window from -1.2 to 0.6 V (50 mV s^{-1}) using a pH 12 buffer solution containing 4×10^{-3} mol L^{-1} CuTSPc. Scan 20 is shown in Fig. 5. The background curve (curve 1) is the 10th cyclic voltammogram measured in a pH 12 buffer solution. The

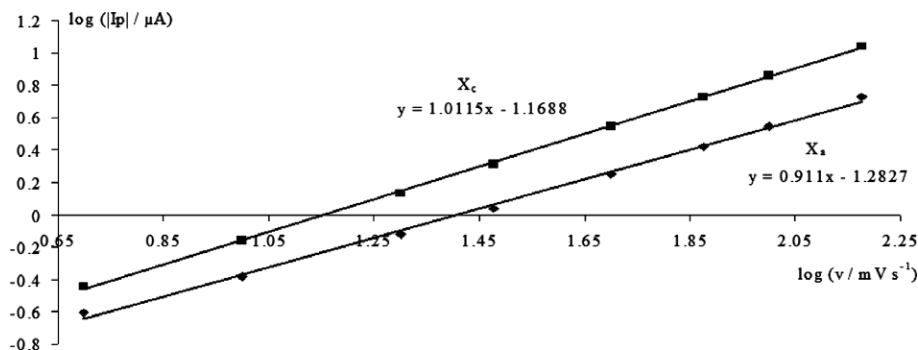


Fig. 4. Relationship between \log of the peak current (I_p) and \log of the scan rate (v) for peak X_a and X_c (same experimental conditions as in Fig. 3).

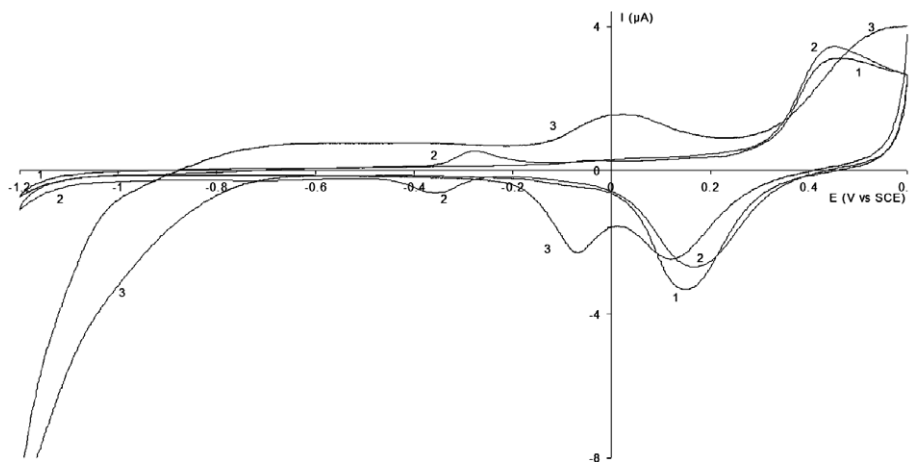


Fig. 5. Current–potential curves recorded at a gold electrode in a pH 12 buffer solution (scan 10) (1) in a pH 12 buffer solution containing $4 \times 10^{-3} \text{ mol L}^{-1}$ random CuTSPc (scan 20) [8] (2) or in a pH 12 buffer solution containing $4 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc (scan 20) (3) at a scan rate of 50 mV s^{-1} and a temperature of 298.0 K .

oxidation and reduction peaks at -0.29 and -0.36 V (curve 2) are attributed to the random $\text{Cu(II)TSPc}_{\text{ads}}$ /random $\text{Cu(I)TSPc}_{\text{ads}}$ redox system [8]. The data in Fig. 5 clearly demonstrate that 3,4',4'',4'''CuTSPc shows a different electrochemical behaviour. The redox processes in curve 2, however, are very analogous to the processes observed when modifying gold electrodes with other tetrasulphonated phthalocyanines such as iron tetrasulphophthalocyanine (FeTSPc) and aluminium tetrasulphophthalocyanine (AlTSPc) [8].

3.4. Comparison with cobalt(II) tetrasulphonated phthalocyanine

The electrochemistry of 3,4',4'',4'''CuTSPc is different as compared to the behaviour of CoTSPc at a gold electrode especially in the potential range from -1.2 V to 0.6 V [5,6]. Characteristic for the voltammetric behaviour of CoTSPc at gold is the occurrence of a breaking point at which a maximum coverage is reached. In the CoTSPc study, it was seen that the ring reactions of CoTSPc in solution (from -0.4 to -1.2 V vs. SCE) changed considerably after a maximum coverage was obtained [5,6]. These changes were explained in the past as the reorganization of the

deposited layer to form, from a thermodynamic point of view, a more stable layer consisting of columnar aggregates. Fig. 1 shows that not any change or evolution of the ring processes is observed during the first 100 scans cycling in a 3,4',4'',4'''CuTSPc pH 12 buffer solution. The latter indicates that the deposition of 3,4',4'',4'''CuTSPc is considered to be different as compared to the immobilization of CoTSPc. This means that as of scan 1, the 3,4',4'',4'''CuTSPc molecules are stacked in their definitive position resulting in a stable electrochemical signal.

The different electrochemical behaviour of CoTSPc in comparison to that of 3,4',4'',4'''CuTSPc during electrochemical modification can be explained by the fact that 3,4',4'',4'''CuTSPc, when brought in solution, forms immediately stable dimer structures. The latter can be confirmed by the UV–Vis data of the two phthalocyanines, which are shown in Fig. 6. The monomer peak for the phthalocyanine species in a pH 12 buffer solution is located at 661 nm , while the dimer peak is observed at 634 nm [10,11]. The figure shows that even at very low concentrations ($4 \times 10^{-6} \text{ mol L}^{-1}$) 3,4',4'',4'''CuTSPc (curve 1 in Fig. 6) forms a much higher amount of dimer species than CoTSPc (curve 2 in Fig. 6) which can be explained by the fact that six coordinate species, such as CoTSPc,

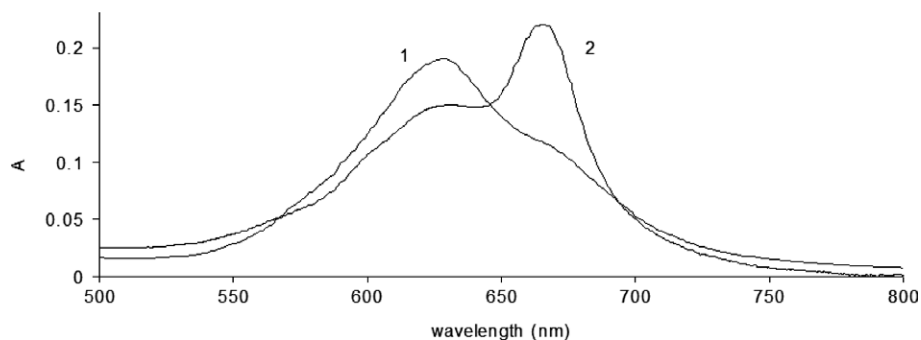


Fig. 6. Absorbance spectra of a pH 12 buffer solution containing $4 \times 10^{-6} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc (1) or CoTSPc purchased at Rhodes University of Grahamstown (2).

generally do not aggregate because the species are kept apart by the axially bound ligands [16]. Therefore CoTSPc forms at low concentrations mainly monomers. At higher concentrations such as $4.0 \times 10^{-3} \text{ mol L}^{-1}$, however, the concentration in which the electrodeposition occurs, there are dimers present next to the dominating amount of monomers. Given the fact that the monomer concentration of CoTSPc in solution cannot be neglected, it can be assumed that in the beginning of the CoTSPc modification process there is a competition between the monomers and dimers. The difference in equilibrium between monomers and dimers explains the difference in voltammetric behaviour and the reorganization of the layer.

In contrast to CoTSPc it is expected that mainly CuTSPc dimers are formed at low and high concentrations [17]. As copper prefers a four-coordination, dimers are formed very easily. The monomer concentration is negligibly low in the case of CuTSPc and it is seen that a stable 3,4',4'',4'''CuTSPc thin layer is formed from the first scan on during electrodeposition. The latter indicates that the 3,4',4'',4'''CuTSPc dimers, as well as the monomers are electrochemically active.

3.5. Spectroscopic characterization of the adsorbed thin-film

X-ray photoelectron spectroscopic analyses of the 3,4',4'',4'''CuTSPc modified electrode were carried out and a coverage value of 67% could be calculated. Compared to the 18.3% coverage in the case of random CuTSPc [8], a significantly higher value is obtained for the well ordered 3,4',4'',4'''CuTSPc. A potential explanation for this difference is the fact that the well ordered 3,4',4'',4'''CuTSPc is able to form stable columnar aggregates. Because of the conjugated π -systems of two CuTSPc molecules, in which the sulphonate groups take part, and the preference for four coordination, the ring structures can approach each other very closely resulting in strong π - π interactions. A dense packing of random CuTSPc is more difficult because of the randomly oriented sulphonate groups.

Micro-SR-XRF measurements were performed to provide further experimental evidence of the formation of the adsorbed 3,4',4'',4'''CuTSPc layer at the gold electrodes

and to study the uniformity of the formed thin film in a quantitative manner. Fig. 7 shows a typical elemental map from a $600 \times 600 \mu\text{m}^2$ area and the corresponding intensity distribution of the detected Cu K α obtained by SR-XRF measurements after normalization with the gold M line. This figure provides not only direct evidence of the occurrence of adsorbed 3,4',4'',4'''CuTSPc but also gives an estimate of the amount of adsorbed 3,4',4'',4'''CuTSPc. The micro-SR-XRF measurements were performed after different number of scans cycling in a $4.0 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc buffer solution. Table 1 shows the copper surface concentrations derived from the XRF measurements as well as those derived from the electrochemical measurements. The average copper intensity, its relative standard deviation and the copper surface concentration of each SR-XRF measurement and the charge caused by the Cu(II)_{ads}/Cu(I)_{ads} oxidation process and its calculated surface concentration are presented for different scan numbers. Both techniques give similar results for the copper surface concentration indicating that 3,4',4'',4'''CuTSPc monomers are electrochemically active as well as the dimers. The amount of adsorbed 3,4',4'',4'''CuTSPc grows with scan number. It is clear that the increase in surface concentration slows down at higher scan

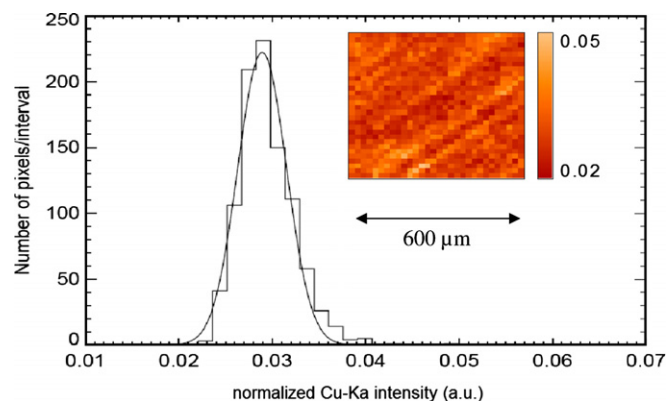


Fig. 7. Elemental map and intensity distribution of copper on a gold electrode electrochemically modified during 60 scans in $6 \times 10^{-3} \text{ mol L}^{-1}$ 3,4',4'',4'''CuTSPc.

Table 1
SR-XRF and electrochemical data

Number of voltammetric scans	$\langle I_{\text{Cu}} \rangle$ (counts s ⁻¹)	$\delta_{\text{Cu}}/\bar{I}_{\text{Cu}}$ (%)	Surface concentration ($\mu\text{g cm}^{-2}$) measured by SR-XRF	Charge (μC)	Surface concentration ($\mu\text{g cm}^{-2}$) measured by voltammetry
5	75.8	25.3	0.045 ± 0.010	1.1 ± 0.2	0.034
10	92.4	27.4	0.064 ± 0.015	1.6 ± 0.2	0.053
17	121.8	25.9	0.072 ± 0.017	1.9 ± 0.2	0.061
30	132.3	21.5	0.076 ± 0.016	2.8 ± 0.3	0.093
60	152.1	19.1	0.103 ± 0.022	3.9 ± 0.3	0.128
100	228.4	23.7	0.142 ± 0.032	3.8 ± 0.2	0.124

First column is the number of voltammetric scans. Next three columns show the SR-XRF data, respectively, the average copper intensity, its relative standard deviation and the copper surface concentration. The last columns show the electrochemical data, respectively, the charge due to the Cu(II)/Cu(I) oxidation peak and the calculated surface concentration.

number. Probably, further adsorption is slightly obstructed by the initially adsorbed molecules.

4. Conclusion

This paper has discussed the electrochemical modification of gold electrodes with 3,4',4'',4'''CuTSPc and has compared the electrochemical behaviour with that of random CuTSPc and CoTSPc. The voltammograms demonstrate that the position of the sulphonate groups on the phthalocyanine has an influence on its electrochemistry and thus on the characteristics of the modified electrode. It was shown that a better modification was obtained with 3,4',4'',4'''CuTSPc as compared to with random CuTSPc. A study of the deposited CuTSPc layer by XPS allowed us to derive the coverage value and showed that this was much higher for the 3,4',4'',4'''CuTSPc (67%) in comparison to that of random CuTSPc (18%). Compared to CoTSPc, both phthalocyanines have a different UV–Vis spectrum resulting in different monomer–dimer equilibrium which has its influence on the electrochemistry.

In addition, it can be postulated that the 3,4',4'',4'''CuTSPc monomer species are electrochemically active as well as the dimer species which is in contrast with the CoTSPc monomer and dimer species.

Acknowledgments

This work was supported by the European Community – Research Infrastructure Action under the FP6 “Structuring the European Research Area” Programme (through the Integrated Infrastructure Initiative “integrating Activity on Synchrotron and Free Electron Laser Science”). The

authors gratefully acknowledge G. Falkenberg (Hamburger Synchrotronstrahlungslabor at Deutsches Elektronen-Synchrotron, Germany).

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