

Is the Enhanced Adhesion of PEDOT Thin Films on Electrodes Due to Sulfur - Gold Interaction? - An XPS Study

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Abstract: Electrode materials obtained through electropolymerization of 3,4-ethylenedioxythiophene (EDOT) have sparked interest toward applications in neuroscience and neuroprosthetics due to their favorable electrochemical properties and their biocompatibility. However, insufficient mechanical stability had been an unresolved issue and hindered practical applications, until recent research by our group demonstrated proper adhesion of poly(3,4-ethylenedioxythiophene) (PEDOT) to a gold surface. In the present study, X-ray photoelectron spectroscopy (XPS) was employed and in particular the chemical shift of the S2p band, which is indicative of binding between sulfur and gold, was used to assess the degree of interaction between 3,4-ethylenedioxythiophene (EDOT), thiophene, and 3-thiophenecarboxylic acid (thiophene-COOH), with the gold surface. The results of the XPS investigations indicate a covalent bond between EDOT and gold, which should indeed contribute to improved adhesion.

Keywords: PEDOT, XPS, thiophene, adhesion, gold electrode.

INTRODUCTION

Neuroscience and the development of neuroprostheses require means for electrical stimulation and recording of living cells and tissues by electronic devices [1]. The interface between cells and the stimulation/recording device represents a critical component with respect to its electrochemical properties as well as its biocompatibility [2]. Typically, microelectrodes manufactured from materials such as platinum, gold, or titanium nitride have been used for this purpose [1, 3-5]. As the electrical coupling between chip and tissue is capacitive by nature, a large effective surface area is necessary to provide sufficient charge transfer capacity. On the other hand, high spatial resolution of electric stimulation and recording requires small electrodes. These conflicting requirements have been reconciled using nanoporous electrode materials exhibiting an effective surface area many times larger than their apparent geometric size [5]. More recently, electroactive materials such as poly(3,4-ethylenedioxythiophene) (PEDOT) and composites thereof with carbon nanotubes (CNT) also have been investigated as electrode materials [2]. These materials have been demonstrated to provide charge transfer stemming from electrochemical conversion of the electrode material in addition to mere surface size effects as are observed with porous materials [6-8]. However, while numerous reports had demonstrated favorable electrochemical properties, the mechanical stability and in particular the adhesion of PEDOT to electrode substrates clearly were insufficient for any of the practical applications mentioned above [9, 10]. Only recently, we were able to demonstrate PEDOT and

PEDOT-CNT electrodes with excellent mechanical stability and adhesion to the underlying gold substrate [6].

As PEDOT contains a sulfur atom in every unit, and sulfur and gold are known to build strong self-assembled covalent bonds [11, 12], the question arose of whether this thiol-gold chemistry is also found at the PEDOT-gold interface and could contribute to the mechanical stability of the coatings. While there is a vast number of studies on the interaction of thiols with gold [13-19], knowledge is limited with respect to thioethers such as thiophene or 3,4-ethylenedioxythiophene (EDOT). For thiophene and its oligomers, somewhat contradictory results have been published. Noh *et al.* [20] and Ishida *et al.* [21] clearly claim a covalent bond between the sulfur of thiophene and gold, Ishida even for bithiophene; however Schwieger *et al.* [22], Elfeninat *et al.* [23] and Honda *et al.* [24] state that no chemical bond is formed between gold and thiophene or its oligomers. They explain that any interaction, if it occurs, would be due to the aromatic ring system when the molecules lie flat on the surface. Indeed, the situation for oligomers could be completely different in comparison to monomers, firstly for steric reasons and secondly because aromatic systems do also interact with gold surfaces [25].

X-ray photoelectron spectroscopy (XPS) measurements of EDOT on gold in comparison to other similar molecules are expected to provide indications about the nature of the PEDOT-gold interface. Therefore, gold surfaces were immersed in dioxane containing either EDOT, thiophene, or 3-thiophenecarboxylic acid (thiophene-COOH), and were measured after rinsing and drying (Fig. 1). Thiophene was chosen as a reference and to enable comparison with the literature data. Thiophene-COOH was chosen because the COOH group on the thiophene provides a contrasting chemical environment in comparison to the ethylenedioxy

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residue in EDOT: the COOH has a negative mesomeric (-M) and electron withdrawing (-I) effect, the ethylenedioxy group is electron donating resulting in a positive mesomeric (+M) and electron donating (+I) effect [26].

XPS enables evaluation of the chemical interaction between sulfur and gold by measurement of the S2p band at 161-162 eV in the XPS spectra.

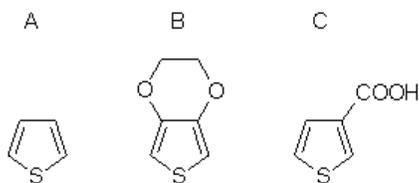


Fig. (1). Chemical structures of the three thioethers examined on gold surfaces with XPS. **A)** thiophene, **B)** EDOT, **C)** thiophene-COOH.

MATERIALS AND METHODS

Gold surfaces were immersed in dioxane solutions containing either EDOT, thiophene, or thiophene-COOH (dilution 1:500 v/v), and were measured after extensive rinsing in dioxane and subsequent drying under nitrogen stream.

XPS was performed on a Quantera SXMTM by PHI (Physical Electronics, Inc., USA) equipped with an X-ray Al K α source ($E = 1486.6$ eV). The diameter of the X-ray beam was 10 to 200 μm . Survey spectra were recorded from 1360 to 0 eV, using a pass energy of 224 eV and a step size of 0.4 eV. Detail spectra were measured from 178 to 158 eV with a pass energy of 55 eV and a step size of 0.1 eV. Ten spectra were measured and averaged.

Analysis of the spectra was carried out using the software Multipak V.9.0 by PHI. To assign quantities to the different states of sulfur, i.e. physisorbed, chemisorbed or oxidized, detail spectra were fitted with standard fitting procedures: Three S2p doublet peaks were employed at three positions (161-162, 163-164 and 168 eV) with a branching ratio of 2:1 for S2p $_{3/2}$ to S2p $_{1/2}$ of each doublet, a spin-orbit splitting of 1.2 eV and the same full width at half maximum (FWHM) for every peak. More details are explained in the results section.

RESULTS

Fig. (2) shows survey spectra of the three substances coated on gold substrates. The gold signals (Au4f, Au4p, Au4d, Au4s) from the substrate as well as carbon (C1s) and oxygen (O1s, O2s) signals from the organic layers can be clearly recognized. The relevant sulfur signals (S2p, S2s) appear as very weak peak features on an intense background. Even after coating with the monomers, a strong gold signal remains (with 30 to 40% atomic concentration), indicating a very thin or not fully covering layer of the organic molecules.

The peak area gives the atomic concentration of the different elements present on the surface and is expressed in percent [27]. The ratio of the sum of organic elements (sum of peak areas from C, O, N, and S) versus gold is similar in all three cases with 1.83 for thiophene, 1.44 for thiophene-COOH and 1.48 for EDOT (Table 1) but higher compared to

the reference gold sample without coating (1.00). The increase in organic/gold ratio underlines the presence of a compound on the surface as opposed to commonly observed surface contamination. The ratio also indicates that there is a higher concentration of thiophene present in comparison to the others, as it exhibits the highest organic amount despite possessing the lowest molecular weight.

Regarding sulfur, quantitative evaluations may be performed despite the unfavorable signal-to-background ratio. However, the determined concentrations provide only nominal values reflecting relative amounts of adsorbed atomic species on the gold surface rather than concentrations as in a homogeneous mixed sample. All three substances show sulfur concentrations of 1.75 to 2.5% on the surface, which is much higher than the value of 0.09% found on the reference sample (Table 1). This indicates that the sulfur-containing compounds are somehow adsorbed or bound to the surface and retained there even after rinsing of the surface.

EDOT shows a similar amount of sulfur (2.48%) to thiophene (2.43%), whereas the sulfur concentration on the surface is lower for thiophene-COOH (1.75%). These results suggest a similar behavior of EDOT and thiophene. However, as the quantities are close to the technical limits of the instrument (about 1% atomic concentration, depending on the element) one may obtain qualitative information yet must be careful with quantitative statements.

As can be seen in the inset of Fig. (2), all three samples show broad sulfur signals in the range from 160 to 170 eV, which exhibit well-separated peak structures at low (mainly below 164 eV) and high (mostly above 166 eV) binding energies. Additional information regarding the presence and chemical binding state of sulfur is elucidated by investigation of these S2p chemical shifts. A finding which is consistent throughout the literature is that covalent bonding to gold shifts the sulfur signal to lower binding energies, i.e. 161-162 eV, whereas unbound sulfur of organic molecules evokes a signal at 163-164 eV [13-24]. However, part of the signal at 163-164 eV may also originate from radiation damage due to extensive irradiation with X-rays [17]. Oxidized sulfur, as in sulfonate, is detected at even higher binding energies of 168 eV [13, 21]. The detail spectra were analyzed according to these peak positions.

To assign quantities to the three types of sulfur (chemisorbed, physisorbed, and oxidized), detail spectra were fitted with three S2p doublets at the three positions (161-162, 163-164 and 168 eV, respectively) with a branching ratio of 2:1 for S2p $_{3/2}$ to S2p $_{1/2}$ of each doublet, a spin-orbit splitting of 1.2 eV and the same full width at half maximum (FWHM) for every peak. Original data and fitted data are displayed in Fig. (3), and results are presented in Table 1. As the original data are noisy due to the low sulfur signal, the fitting can give qualitative indications while quantification must be taken cautiously. Keeping this in mind, results show that thiophene exhibits the highest amount of chemisorbed sulfur (at 161-162 eV) while EDOT shows a higher amount as compared to thiophene-COOH. The signal at 161-162 eV strongly indicates that some of the observed sulfur is covalently bound to the gold surface.

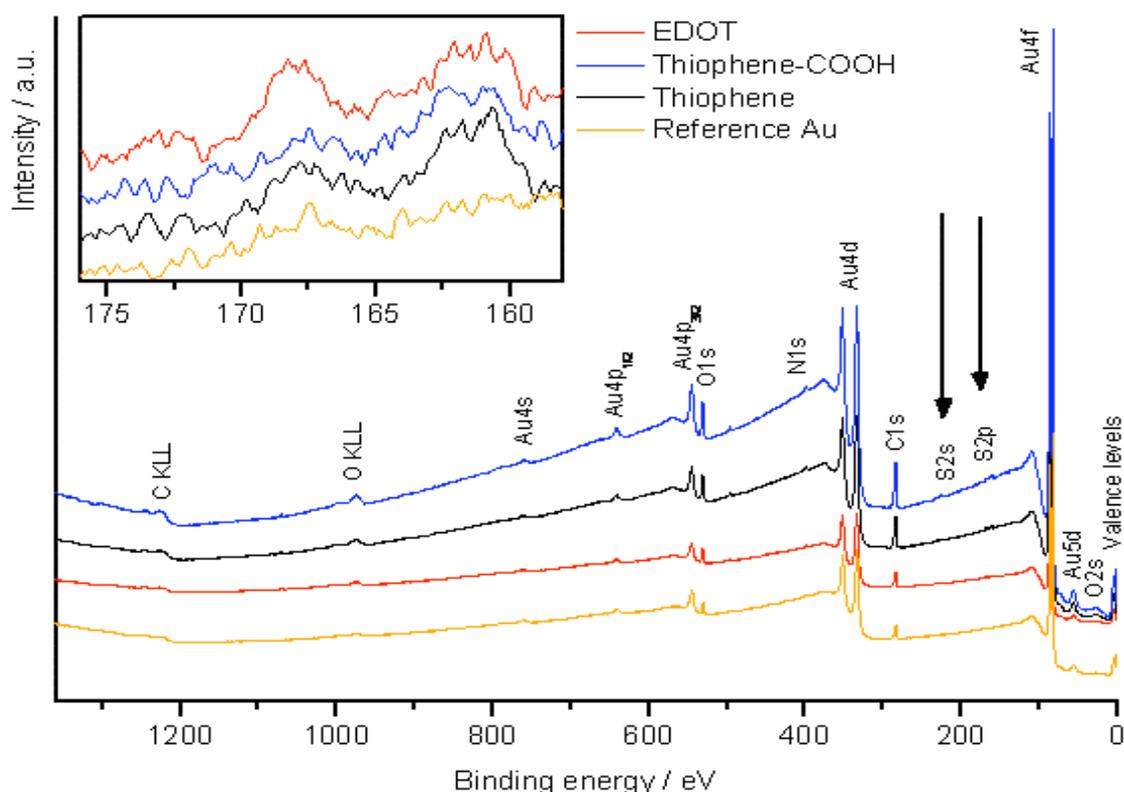


Fig. (2). XPS spectra of EDOT (red), thiophene (black) and thiophene-COOH (blue) on gold substrates. The substrates were immersed in dioxane containing the thioether overnight and rinsed and dried before measurements. The spectrum obtained from the bare Au reference is displayed in orange. The inset shows detailed spectra of the same samples. All three substances show sulfur signals in the region of 160 to 170 eV. The reference only shows a very small sulfur peak located mostly at higher energy near 167 eV.

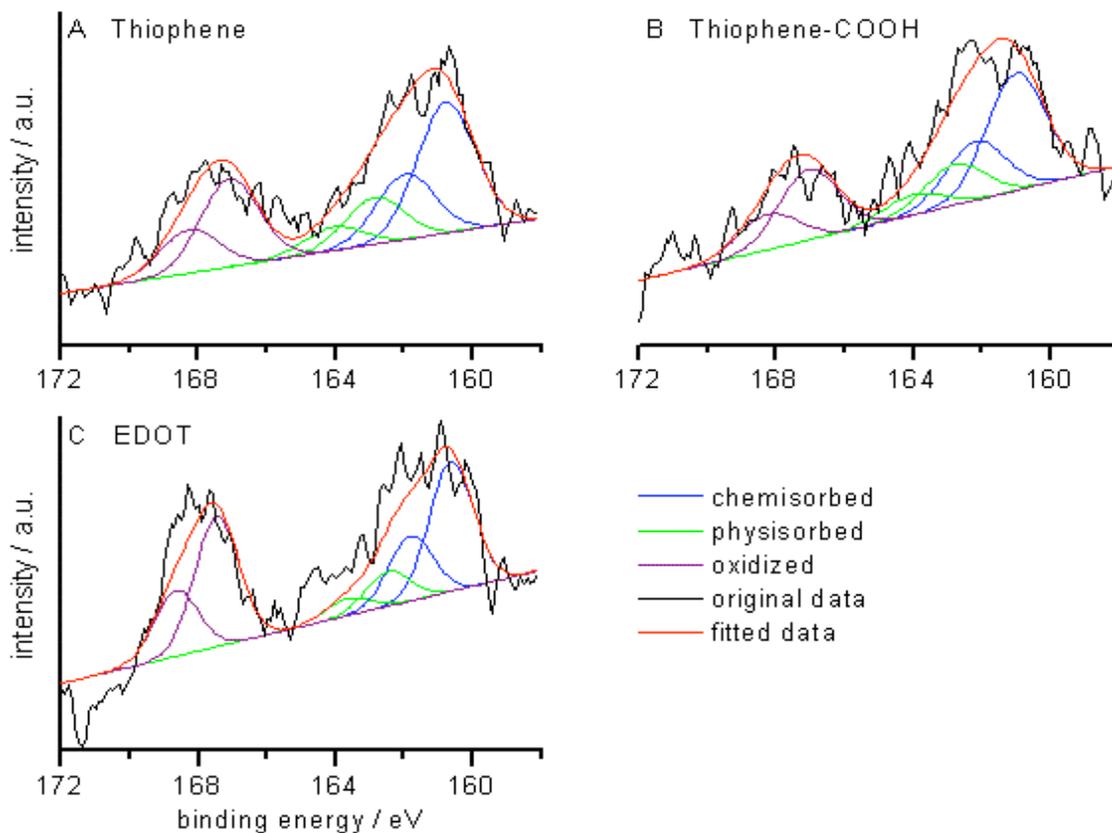


Fig. (3). Detail spectra of the S_{2p} region of sulfur from the three different thioethers on Au: thiophene (A), thiophene-COOH (B) and EDOT (C). Data was fitted using three doublets representing chemisorbed (blue), physisorbed (green) and oxidized (purple) sulfur.

Table 1. Data from XPS Spectra of Three Different Thioethers on Au. The First Column Contains the Ratio of the Sum of Organic Elements (C, O, N, S) to Gold. The Following Columns Contain the Surface Sulfur Concentration in Total as Well as Assigned to the Different Oxidation States of Sulfur: Chemisorbed, Physisorbed and Oxidized

	Ratio Organic Elements/Gold	Sulfur Concentration / %	Chemisorbed S @ 161-162 eV / %	Physisorbed S @ 163-164 eV / %	Oxidized S @ 168 eV / %
Ref Au	1.00	0.09	-	-	0.09
EDOT	1.48	2.48	0.91	0.53	1.04
thiophene	1.83	2.43	1.19	0.39	0.84
thiophene-COOH	1.44	1.75	0.74	0.50	0.51

DISCUSSION & CONCLUSIONS

In summary, the results of the XPS investigations indicate a chemical bond between EDOT and gold, which should contribute to improved adhesion. Further research is required to examine whether these results obtained with monomer compounds indeed can be transferred to the polymer, where steric effects as well as the influence of an applied voltage during electropolymerization come into play. Steric effects could inhibit the sulfur in oligomers and polymers reaching the gold surface. However, work on self-assembly of sulfur-modified polymers has indicated the formation of covalent bonds between sulfur and gold even in the case of polymers [28-29]. In addition, the electronic state of the molecule could be changed through the applied potential favoring or hindering a covalent bond to gold.

AUTHOR CONTRIBUTIONS

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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ABBREVIATIONS

PEDOT = Poly(3,4-ethylenedioxythiophene)
 EDOT = 3,4-ethylenedioxythiophene
 CNT = Carbon nanotube
 XPS = X-ray photoelectron spectroscopy

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