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Electrochemical Approach for Constructing a Monolayer of Thiophenolates from Grafted Multilayers of Diaryl Disulfides

Lasse T. Nielsen,[†] Karina H. Vase,[†] Mingdong Dong,[‡] Flemming Besenbacher,[‡]
Steen U. Pedersen,*,[†] and Kim Daasbjerg*,[†]

Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark, and
Interdisciplinary Nanoscience Center (iNANO), University of Aarhus, Ny Munkegade, DK-8000 Aarhus C, Denmark

Received November 17, 2006; E-mail: sup@chem.au.dk; kdaa@chem.au.dk

One of the most widely used procedures for covalent modification of conducting surfaces involves electroreduction of aryldiazonium salts.[1−13] Usually, the electrode derivatization is so effective that intertwined multilayers are formed.[4,7] Although the process to some extent may be controlled through the applied potential and electrolysis time,[11−13] the derivatized surface will seldom be sufficiently well-defined for developing, for example, sensors or molecular devices. To accomplish such a goal, other approaches would usually be required.

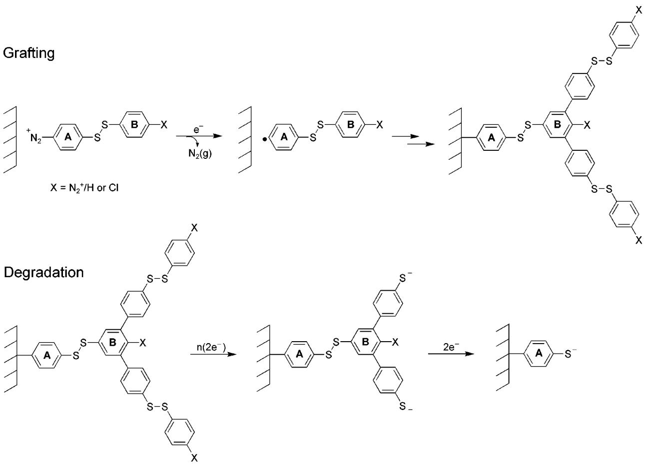
In this communication, we explore the possibility of preparing thin layers on carbon surfaces through a degradation of multilayers formed via reduction of diazonium salts. Rather than controlling the grafting process, the key issue becomes selecting appropriate molecular systems containing cleavable groups. The basic concept involving disulfides is outlined in Scheme 1.

In the first step, a diazonium salt of a diaryl disulfide is reduced electrochemically at a glassy carbon (GC) surface to produce a covalently bonded multilayer. This polymerization process goes through the intermediate formation of reactive aryl radicals which attack either the surface or the aryl rings of already grafted molecules.[4,7] Because of the steric constraints, it is expected that the outer ring **B** will be more accessible to attack than **A**. Subsequent reductive cleavage[14] of the disulfide bonds should, therefore, in principle, lead to the generation of a monolayer of thiophenolates. The formation of such a monolayer would be either impossible or, at least, difficult to obtain through a direct electroreduction of 4-mercaptobenzenediazonium.[15]

The grafting of the surfaces with the two diazonium salts, 4,4′-disulfanediyldibenzenediazonium (**1**)[16] or 4-[(4-chlorophenyl)disulfanyl]benzenediazonium (**2**), was carried out using standard procedures (potentiostatic grafting for 300 s at a potential 200 mV negative of the reduction peak; see Supporting Information). In Figure 1, a cyclic voltammogram recording of a GC electrode derivatized with compound **2** is shown.

The most notable feature on the first cycle is the reduction wave at −1.3 V versus SCE accompanied by the smaller oxidation wave at −0.3 V versus SCE; the latter wave only appears if the first sweep is extended past the reduction wave. We attribute these two signals to the reductive cleavage of diaryl disulfide units, ArSSAr, in the multilayer followed by oxidation of surface-confined ArS^- (Scheme 1). Integration of the waves reveals that about four times as much charge is associated with the reduction as with the oxidation process, indicating that thiophenolates generated in the outer layer during the reductive sweep are able to escape not only the surface but also detection on the oxidative sweep. On the assumption that all disulfides are reduced on the forward sweep and that the reduction proceeds by a two-electron process while the oxidation of the remaining thiophenolates on the reverse sweep is a one-electron process, it may be concluded that the initially formed coating consists of about two layers.

Scheme 1



The second and subsequent cycles give rise to essentially the same oxidative behavior, whereas the reduction wave decreases to the same size as the oxidation wave while shifted in a positive direction by 300 mV. Both the cathodic peak current, $i_{p,c}$, and the anodic peak current, $i_{p,a}$, are found to be proportional to the sweep rate ν (inset of Figure 1).[17] These observations show that the degradation of the outer layers on the first cycle is an efficient process and that the molecules left on the surface constitute a *surface-confined* redox pair, that is, $ArSSAr/ArS^-$. The stability of this pair is surprisingly high as evidenced by the fact that at

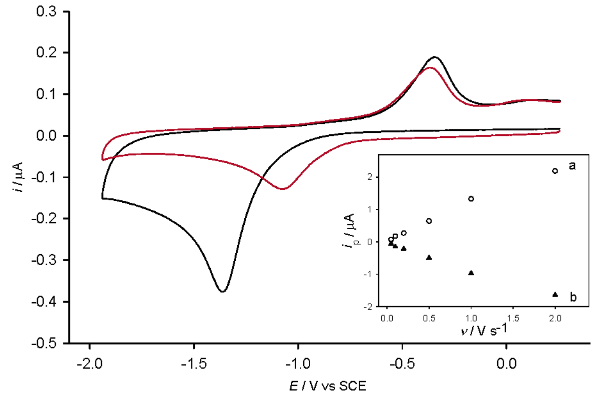


Figure 1. Cyclic voltammograms of a GC electrode derivatized with **2** recorded at a sweep rate ν of 0.1 V s^{-1} in 0.1 M Bu_4NBF_4/*N*,*N*-dimethylformamide; sweep no. 1 (black) and 2 (red). Inset shows plots of (a) anodic and (b) cathodic peak currents measured for the degraded film as a function of ν.

[†] Department of Chemistry.
[‡] Interdisciplinary Nanoscience Center.

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Table 1. XPS Surface Elemental Compositions of Modified Glassy Carbon Plates[a]

entry	electrode	atomic concentration (%)[b]		
		C_{1s}	S_{2p}	Cl_{2p}
1	GC[c]	94.5		
2	GC/**1**[d]	85.5	5.1	
3	GC/**1**/cleaved[e]	89.4	0.9	
4	GC/**2**[f]	84.8	5.3	1.0
5	GC/**2**/cleaved[g]	88.7	0.8	0.0

[a] Average of the results obtained for two GC plates. [b] In addition to the reported elements, the surfaces contained oxygen. [c] Bare GC plate. [d] GC plate modified with **1**. [e] Entry 2 after reduction at −1.7 V vs SCE in 0.1 M Bu_4NBF_4/*N*,*N*-dimethylformamide. [f] GC plate modified with **2**. [g] Entry 4 after reduction at −1.4 V vs SCE in 0.1 M Bu_4NBF_4/*N*,*N*-dimethylformamide.

least 100 cycles at $\nu = 0.1$ V s^{-1} are required to deactivate it electrochemically. Thus, it appears that disulfide bonds can be created between the covalently attached molecules at the surface despite the steric constraints. In fact, the positive shift of the reduction wave observed for the first two cycles could be partly due to differences in the sulfur−sulfur bond strengths; that is, the bonds in the degraded film are more strained and weaker than those in the multilayer film. Also the increase of the heterogeneous charge transfer rate brought about by the formation of a thinner film will induce a shift in this potential direction.[18]

The surface coverage Γ of ArS^- and ArSSAr in the degraded film can be determined from an integration of the current signals to be 4.0 and 2.2×10^{-10} mol cm^{-2}, respectively (obtained at $\nu \leq 2$ V s^{-1}). While this shows that essentially all surface-confined ArS^- surprisingly are able to form a disulfide bridge with a neighbor molecule upon oxidation, Γ is much lower than that calculated for an ideal closed-packed monolayer at a plane surface ($\Gamma_{\text{ideal}} = 12 \times 10^{-10}$ mol cm^{-2}).[19,20] In fact, a study using the smaller 4-nitrobenzenediazonium salt as grafting agent has shown that at least five layers were required to obtain a coverage comparable to Γ_{ideal} on carbon materials and that a single molecular layer would correspond to $\Gamma = 2.5 \times 10^{-10}$ mol cm^{-2}.[21]

To substantiate the proposed reaction scheme, GC plates derivatized with **1** or **2** were analyzed (Table 1) before and after degradation by means of X-ray photoelectron spectroscopy (XPS). In entries 2 and 4, survey spectra of the two modified surfaces are provided. Importantly, they contain nearly the same amount of S (~5.2%). For the surface derivatized with **2**, the amount of Cl (1.0%) is surprisingly small. We suspect that this may be attributed to an *ipso*-attack of the aryl radical at the chlorine substituent in the polymerization reaction followed by an elimination of chlorine.[22] As expected, the sulfur content diminishes considerably after the reductive cleavage (entries 3 and 5) to ~0.9%. This is accompanied by a complete disappearance of chlorine in the case of **2**. These observations are consistent with the proposition that the efficient degradation of the modified surface results in the removal of the outer part, thus leaving the inner ring **A** as the main moiety at the surface.

The film thickness for the GC plates in entries 4 and 5 in Table 1 was determined by atomic force microscopy (AFM) to be 3 ± 1 and 1.5 ± 0.5 nm (Supporting Information). Although the uncertainty on these measurements does not allow a quantitative description of the changes induced by the degradation procedure, they substantiate the view that molecular units of the originally derivatized surface (consisting of 2−3 layers of diaryl disulfides) indeed have been cleaved off.[23] The thickness of a monolayer of thiophenolate is calculated to be only 0.6 nm,[20] so we cannot exclude that larger biphenyl bis(thiolate) units may have been formed during the grafting because of aryl radicals attacking ring **A**. Future work will show to what extent the exact electrolysis conditions and, in particular, the substituent X can be used to affect the proportion of radicals reaching the inner part.

In summary, a versatile electrochemical approach employing diazonium salts of diaryl disulfides has been developed for the construction of a monolayer or near monolayer of ArS^- on glassy carbon surfaces. An extension of the approach to include other cleavable functionalities as well as atomically smooth materials such as Si, metals, or pyrolyzed photoresist films to better exploit the properties of a monolayer seems straightforward. Interestingly, ArS^- may be reversibly oxidized to ArSSAr, thus allowing the establishment of a relatively stable covalently attached $ArSSAr/ArS^-$ redox pair. This feature gives simple access to adjusting and controlling electrochemically the surface properties. For instance, preliminary work has shown that the high reactivity of thiophenolates may be exploited in further reactions to develop more advanced molecular systems. In addition, the prospect in repeating the formation/degradation procedure with the purpose of eliminating pinholes and/or build up surfaces layer by layer is worth pursuing.

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Supporting Information Available: Synthetic details, grafting procedures, and analyses of electrode surfaces by electrochemical methods and AFM. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Delamar, M.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 5883−5884.
(2) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201−207.
(3) Downard, A. J. *Electroanalysis* **2000**, *12*, 1085−1096.
(4) Kariuki, J. K.; McDermott, M. T. *Langmuir* **2001**, *17*, 5947−5951.
(5) Itoh, T.; McCreery, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 10894−10902.
(6) Nowak, A. M.; McCreery, R. L. *J. Am. Chem. Soc.* **2004**, *126*, 16621−16631.
(7) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429−439.
(8) Holm, A. H.; Møller, R.; Vase, K. H.; Dong, M.; Norrman, K.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *New J. Chem.* **2005**, *29*, 659−666.
(9) Brooksby, P. A.; Downard, A. J. *Langmuir* **2005**, *21*, 1672−1675.
(10) Baranton, S.; Bélanger, D. *J. Phys. Chem. B* **2005**, *109*, 24401−24410.
(11) Brooksby, P. A.; Downard, A. J. *J. Phys. Chem. B* **2005**, *109*, 8791−8798.
(12) Anariba, F.; Viswanathan, U.; Bocian, D. F.; McCreery, R. L. *Anal. Chem.* **2006**, *78*, 3104−3112.
(13) Ricci, A.; Bonazzola, C.; Calvo, E. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4297−4299.

(14) The bond cleavage can be accomplished using various chemical approaches, but an electrochemical procedure exploiting the high conductivity of GC seems straightforward.

(15) Harnisch, J. A.; Pris, A. D.; Porter, M. D. *J. Am. Chem. Soc.* **2001**, *123*, 5829−5830.

(16) For the salt **1**, the second N_2^+ group will be reduced off and most likely replaced with a hydrogen atom, this being the reason for presenting the substituent X in Scheme 1 as N_2^+/H.
(17) The slopes of plots of log $i_{p,c}$ and log $i_{a,c}$ versus log ν are 0.87 and 0.92, respectively.
(18) In general, the voltammetric behavior is consistent with that of freely diffusing diaryl disulfide, although the oxidation wave of surface-confined ArS^- appears at a less extreme potential than the solution counterpart (Supporting Information). This might be attributed to an effect such as charge repulsion between the surface-confined thiophenolate ions. The possibility that the inner ring **A** has been attacked by aryl radicals during the grafting process to produce the biphenyl bis(thiolate) system after degradation cannot be excluded.

(19) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254−11259.

(20) Calculations are based on an optimization of the structure using DFT and assuming a perpendicular orientation of the molecules.

(21) Brooksby, P. A.; Downard, A. J. *Langmuir* **2004**, *20*, 5038−5045.
(22) Traynham, J. G. *Chem. Rev.* **1979**, *79*, 323−330.

(23) The thickness of the initially derivatized film is essentially equal to that found under similar grafting conditions in other studies, in which typically 4−5 layers are formed using grafting agents of approximately half the molecular size of our systems.[4,21]

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