J|A|C|S
COMMUNICATIONS

General Approach for Monolayer Formation of Covalently Attached Aryl Groups Through Electrografting of Arylhydrazines

Kristoffer Malmos,[†] Joseph Iruthayaraj,[†] Steen U. Pedersen,*[,†,‡] and Kim Daasbjerg*[,†,‡]

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

Received July 23, 2009; E-mail: sup@chem.au.dk; kdaa@chem.au.dk

In recent years pathways for modifying surfaces with organic films have received enormous interest.[1] Among these the most prominent one is the covalent immobilization of aryl groups through electroreduction of diazonium salts on carbon materials and metals.[1,2] The process which involves reactive aryl radicals is highly effective usually leading to multilayered film formation. One essential issue in the further development is to achieve control on the layer structuring, in particular, with the aim of forming monolayers. So far, this goal has been accomplished only in a few specific cases by adjusting the electrolysis potential[3] and time,[4] changing the solvent,[5] or introducing bulky substituents on the aryl ring.[6] Most recently, the so-called "formation−degradation" approach was developed to produce thin layers of benzaldehydes[5] or thiophenolates.[7]

In this communication we present a general approach to covalently immobilize a monolayer of aryl groups by means of mild anodic oxidation of arylhydrazines in water. Previously air oxidation of arylhydrazines at high temperatures has been used to assemble aryl-based films on [60]fullerenes[8] and carbon nanotubes.[9,10] Also a report on the anodic oxidation of biotin hydrazide for patterning purposes has appeared.[11] We will show that electrografting of arylhydrazines forms a monolayer, essentially independent of the experimental conditions used, i.e. substituent, pH, and grafting time and potential.

The grafting agents comprise arylhydrazines having para substituents with both electron-donating and -withdrawing properties [$Z-C_6H_4NHNH_2$; $Z = OCH_3$ (**1a**), Cl (**1b**), COOH (**1c**), or NO_2 (**1d**)] being assembled onto glassy carbon (GC) and Au substrates. Experimental techniques employed are electrochemistry, phase modulated infrared reflection absorption spectroscopy (PM-IRRAS), and ellipsometry.

Figure 1 shows successive cyclic voltammograms of the oxidation wave of **1d** recorded at a GC electrode in aqueous solution. Evidently, repeated sweeping leads to a decrease in the peak current accompanied by a concomitant increase in the anodic peak potential. Upon potentiostatic electrolysis for 300 s at 0.8 V vs SCE, a subsequently recorded voltammogram is essentially featureless. This is consistent with the formation of an electrochemically insulating film on the electrode surface.[12] The same feature, although to a greater extent, is also observed during electrografting of aryldiazonium salts.[1,2,13] The electrografting of **1a**−**c** followed the same procedure as outlined for **1d** (Figure 1S, Supporting Information).

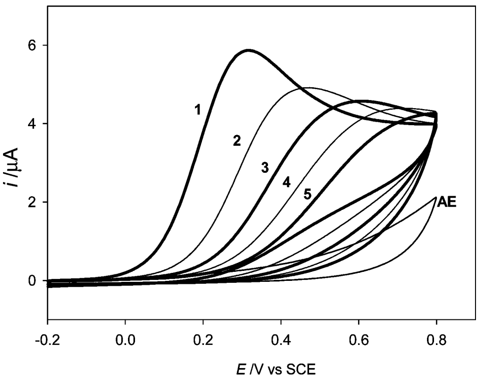
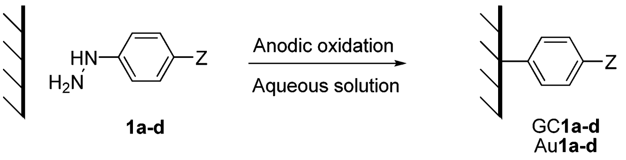


Figure 1. Cyclic voltammograms of 2.0 mM **1d** in 0.1 M aqueous KH_2PO_4 recorded at a GC electrode at a sweep rate of 0.2 V s^{-1}; numerals refer to sweep numbers. The voltammogram "AE" was obtained after potentiostatic electrolysis at 0.8 V vs SCE for 300 s. The solution was stirred in between cycles.

The detailed mechanism of the grafting process was not investigated, but most likely the aryl radical is the grafting agent as suggested for the chemical oxidative pathway[8−10,14,15] with aryldiazene acting as a short-lived precursor.[16,17] As already mentioned the aryl radical is also the key species in the reductive diazonium salt procedure.[1−7] In Scheme 1 the overall grafting process is shown.[18,19]

Scheme 1. Oxidative Electrografting of Arylhydrazines to Afford Aryl-Functionalized GC or Au Films (GC/Au**1a**−**d**)



$Z = OCH_3$ (**a**), Cl (**b**), COOH (**c**), or NO_2 (**d**)

A common electrochemical methodology employed for a first analysis of the properties of surface films is to measure charge transfer properties of a suitable redox probe such as $K_3Fe(CN)_6$. As shown in Figure 2 the charge transfer between GC**1a** or GC**1b** and $Fe(CN)_6{}^{3-}$ is severely hindered, resulting in a complete lack of electrochemical signal from the redox probe. For GC**1c** and GC**1d** quasi-reversible behaviors are observable, which we attribute to a more loosely packed film structure in these cases. Notably, for GC**1c** a small sigmoidally shaped voltammetric signal of $Fe(CN)_6{}^{3-}$ is discernible at 0.2 V vs SCE. Such behavior is consistent with a film which contains small pinholes acting as a collection of ultramicroelectrodes with nonoverlapping diffusion layers.[20]

Further evidence of the presence of the aryl group can be provided by exploiting the electroactivity of the nitrophenyl group in GC**1d**. The inset of Figure 2 shows two successive voltammograms recorded at a GC**1d** electrode (ultrasonically rinsed) in acidic medium. In accordance with other studies[1−5] the first sweep shows

---

[†] Department of Chemistry.
[‡] iNANO.

10.1021/ja905919u CCC: $40.75

a significant reduction peak at −0.55 V vs SCE originating from the reduction of the surface-attached $-C_6H_4NO_2$ to the corresponding $-C_6H_4NHOH$ or $-C_6H_4NH_2$, while on the reverse sweep and subsequent cycle a somewhat smaller redox wave appears at ∼0.3 V vs SCE corresponding to the $-C_6H_4NO/-C_6H_4NHOH$ redox couple.

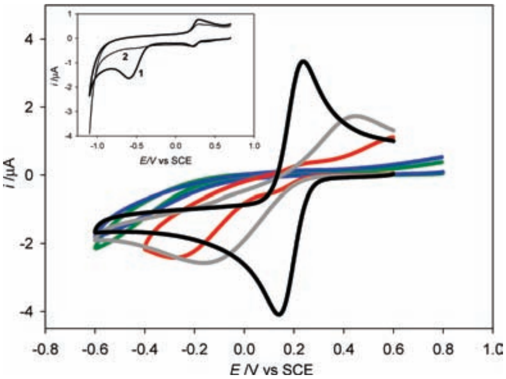


Figure 2. Cyclic voltammograms recorded at the modified electrodes, GC**1a**−**d**, of 2 mM $K_3Fe(CN)_6$ in 0.1 M $H_2PO_4^-/HPO_4^{2-}$ (pH 7) at a sweep rate of 0.2 V s^{-1}; bare (black), GC**1a** (green), GC**1b** (blue), GC**1c** (red), and GC**1d** (gray). Inset: Two successive voltammograms recorded at a GC**1d** electrode in 0.1 M H_2SO_4 at a sweep rate of 0.2 V s^{-1}; numerals refer to sweep numbers.

PM-IRRAS of Au**1d** shows the characteristic peaks corresponding to the symmetric (1349 cm^{-1}) and the antisymmetric stretching (1527 cm^{-1}) of the aromatic nitro group and the phenyl ring stretch at 1598 cm^{-1} (Figure 2S, Supporting Information). The absence of peaks in the 1650−1630 cm^{-1} region shows that there are no NH_2 groups present in the layer (Figures 2S and 3S, Supporting Information). Consequently no physisorption of arylhydrazines takes place during grafting.[13] This information combined with the fact that the film on a GC electrode can withstand sonication (20 min) in both water and ethanol indicates that a covalent bond has been formed between the surface and the aryl ring (see Scheme 1).

From integration of the electrochemical signals the surface coverage (Γ) of the electroactive groups on GC**1a** as well as GC**1d** can be determined (Figure 4S, Supporting Information). These data along with the experimental (d_{exp}) and theoretically estimated (d_{theo}) thicknesses of the films are reported in Table 1.

Table 1. Surface Coverage, Γ, and Experimental, d_{exp}, and Theoretical Thicknesses, d_{theo}, of Grafted GC Samples

sample	Γ (10^{-10} mol cm^{-2})	d_{exp} (nm)	d_{theo} (nm)[a]
GC**1a**	4.5[b]	0.52 ± 0.36	0.72
GC**1b**		0.51 ± 0.14	0.56
GC**1c**		0.71 ± 0.08	0.71
GC**1d**	4.4	0.63 ± 0.16	0.61

[a] Calculated for a monolayer using MM2 calculations in ChemDraw 3D. [b] Assuming a one-electron oxidation process.

First it may be noted that d_{exp} for each film is close to d_{theo} calculated for a single layer of the pertinent aryl groups, which implies that the grafted samples essentially consist of a monolayer. Astonishingly, we also find that d_{exp} is independent of grafting time (300 or 600 s), grafting potential (0.65−0.95 V vs SCE), and pH (2, 5.5, or 12), although thicker films are formed under strongly alkaline conditions (Table 1S, Supporting Information). The reasons for this remarkable feature remain to be clarified, but at this point we may note that both the reaction medium and the mild oxidation conditions, under which the aryl radical are formed, are two key issues.

The $\Gamma \approx 4.5 \times 10^{-10}$ mol cm^{-2} obtained for GC**1a** and GC**1d** is in line with corresponding data reported for thin films of thiophenolates ($\Gamma = 4.0 \times 10^{-10}$ mol cm^{-2})[7] and benzaldehydes ($\Gamma = 3.9 \times 10^{-10}$ mol cm^{-2})[5] on GC surfaces. In comparison, Γ calculated for an ideal close-packed monolayer of 4-nitrophenyl groups is 12 × 10^{-10} mol cm^{-2}.[21] This result substantiates the conclusion from the redox probe and thickness measurements; that is, the grafting process which is governed mainly by the strong driving force for covalent bond formation gives rise to a relatively loosely packed, yet reasonably uniform film structure.

In summary, an approach has been introduced for carrying out controlled modification of carbon and metal surfaces with aryl groups through mild anodic oxidation of arylhydrazines. Electrochemical, PM-IRRAS, and ellipsometrical measurements reveal that monolayers are formed, the thickness of which is essentially independent of the substituent, pH, and grafting time and potential. This astonishing feature makes the approach very tolerant toward variations in the experimental conditions. Hence, this method should be considered as a strong option if the aim is to form thin, well-defined, and covalently assembled aryl layers on surfaces.

Acknowledgment. The Danish Agency for Science, Technology, and Innovation is gratefully acknowledged for financial support.

Supporting Information Available: Experimental procedures, cyclic voltammograms, PMIRRAS spectrum of Au**1d**, and thickness measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Barriére, F.; Downard, A. J. *J. Solid State Electrochem.* **2008**, *12*, 1231–1244, and references therein.
(2) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429–439, and references therein.
(3) Stewart, M. P.; Maya, F.; Kosynkin, D. V.; Dirk, S. M.; Stapleton, J. J.; McGuiness, C. L.; Allara, D. L.; Tour, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 370–378.
(4) Ricci, A.; Bonazzola, C.; Calvo, E. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4297–4299.
(5) Malmos, K; Dong, M.; Pillai, S.; Kingshott, P.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2009**, *131*, 4928–4936.
(6) Combellas, C.; Kanoufi, F.; Pinson, J.; Podvorica, F. I. *J. Am. Chem. Soc.* **2008**, *130*, 8576–8577.
(7) Nielsen, L. T.; Vase, K. H.; Dong, M.; Besenbacher, F.; Pedersen, S. U.; Daasbjerg, K. *J. Am. Chem. Soc.* **2007**, *129*, 1888–1889.
(8) Chen, Z-X; Wang, G.-W. *J. Org. Chem.* **2005**, *70*, 2380–2383.
(9) Liu, J.; Zubiri, M. R. I.; Dossot, M.; Vigolo, B.; Hauge, R. H.; Fort, Y.; Ehrhardt, J.-J.; Mcrae, E. *Chem. Phys. Lett.* **2006**, *430*, 93–96.
(10) Vigolo, B.; Mamane, V.; Valsaque, F.; Le, T. N. Ha; Thabit, J.; Ghanbaja, J.; Aranda, L.; Fort, Y.; McRae, E. *Carbon* **2009**, *47*, 411–419.
(11) Nowall, W. B.; Wipf, D. O.; Kuhr, W. G. *Anal. Chem.* **1998**, *70*, 2601–2606.
(12) Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201–207.
(13) Unlike diazonium salts, which are prone to graft spontaneously onto materials, arylhydrazines are not amenable to such a process. A cyclic voltammogram recorded for a GC electrode upon 30 min of exposure to an arylhydrazine solution shows that there are no blocking effects at all.
(14) Demir, A. S.; Reis, O.; Ozgul-Karaaslan, E. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3042–3045.
(15) Beckwith, A. L. J.; Leydon, R. J. *Aust. J. Chem.* **1966**, *19*, 1381–1390.
(16) Cauquis, G.; Geniès, M. *Tetrahedron Lett.* **1968**, *9*, 3537–3540.
(17) Bond, A. M; Hollenkamp, A. F.; Thompson, S. B.; Bourne, A. R.; Huf, P. A.; Watson, T. G. *Anal. Chem.* **1988**, *60*, 1023–1027.
(18) It is proposed that N atoms in the arylhydrazine are expelled as nitrogen gas during the oxidation, thereby allowing the substate−aryl linkage to become the predominant bonding mode. In contrast for the electrooxidative grafting of primary and secondary alkylamines, covalent attachment at the surface goes through N; see: Adenier, A.; Chehimi, M. M.; Gallardo, I.; Pinson, J.; Vilà, N. *Langmuir* **2004**, *20*, 8243–8253.
(19) X-ray photoelectron spectroscopy measurements confirm that the nitrogens in the hydrazine group are lost during the grafting process.
(20) Amatore, C.; Savéant, J.-M.; Tessier, D. *J. Electroanal. Chem.* **1983**, *147*, 39–51.
(21) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254–11259.

JA905919U