



Electrochemical grafting of heterocyclic molecules on glassy carbon and platinum using heteroaromatic iodonium salts or iodo-substituted heteroaromatics

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ABSTRACT

Electrochemical grafting of aryldiazonium salts has been widely explored for functionalization of conducting surfaces with aromatic molecules. Unfortunately, heteroaromatic diazonium salts are highly unstable and decompose rapidly, precluding, in general, the use of such salts. We show here that pyridine and thiophene based iodonium salts along with iodo-substituted pyridine, thiophene, furan, and pyrrole may find use as suitable grafting agents. The precursors are much more stable than their diazonium analogs but the price to pay is a slower grafting process that takes place at a more extreme potential. The grafted films are characterized electrochemically and spectroscopically by XPS, IRRAS, and Raman.

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1. Introduction

Electrochemical functionalization of conductive surfaces is an important field where surfaces of metals, carbon materials, semiconductors, or conducting polymers can be modified for a wide range of applications such as electronic devices, sensors, fibers for reinforced polymers, and polymer adhesion [1,2]. The procedures used for electrode derivatization include electrochemical generation of aryl radicals via reduction of aryldiazonium [3,4], diaryliodonium [5], and triarylsulfonium [6] salts or by reduction of aryl iodides as shown in a recent study [7]. Oxidative grafting of alkyl amines [8] or alcohols [9] offers another route for surface modification of carbon materials, while on metals this treatment may corrode and, eventually, dissolve the metal surface. Without comparison, the most used method is the electrografting of aryldiazonium salts, exploiting the great availability of these salts via the straightforward diazotation of aryl amines and benefitting from

low potential requirement and a high grafting efficiency. As important the high reactivity is for the success of this efficient grafting process, it is the very same property that gives diazonium salts instability, rendering some systems too unstable to work with. However, in some cases one may resort to in-situ generation of the aryldiazonium salts followed by a subsequent grafting [10,11].

For diazonium salts of heteroaromatic compounds this protocol is challenged to its limit or beyond that. For example, the diazotation of 3-diazopyridine with nitrite and HCl followed by in-situ electrografting from the aqueous solution was feasible, although the diazopyridinium cation decomposed to 3-hydroxypyridine within 10–60 min [12]. The diazotation and electrografting of other heteroaromatic amines derived from furan, thiophene, and pyrrole has, to the best of our knowledge, not been reported. Instead, such heteroaromatic moieties have been introduced as substituents on aryldiazonium salts, e.g. 4-pyrrolylphenyldiazonium or 4-(2-thienyl)benzenediazonium salts [13]. Alternatively, already grafted aryl films may be postmodified to generate heteroaromatic moieties such as triazol groups through click chemistry [14].

In general, iodonium salts should be a more suitable precursor for direct electrografting of heteroaromatic surface films, since they are less prone to decompose spontaneously compared with

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diazonium salts. Recently, He and Swager demonstrated that unsymmetrical pyridyl 2,4,6-triisopropylphenyl iodonium salts are stable precursors which can be employed to functionalize single wall carbon nanotubes (SWCNTs) [15]. Prior to functionalization the SWCNTs were activated through a chemical reduction using sodium naphthalide as the strong reductant. Noteworthy, this process is not an electrografting.

Recently, our group introduced aryl iodides as electrografting agents [7]. The reduction of aryl iodides goes through the aryl radical intermediate, which predominantly is reduced to the corresponding anion at the reduction potential of the parent compounds. Nevertheless, a small fraction of the aryl radicals survives to provide electrografting. Aryl iodides are much less efficient grafting agents compared with diazonium and iodonium salts, but they are readily available (often commercially), possess a high stability, and can form well-defined thin films in a controlled manner.

In this work, we report on the successful electrografting of heteroaromatic multilayered films of pyridine, pyrrole, furan, and thiophene using suitable precursors of iodonium salts and iodo-substituted heteroaromatics. Such films would be very difficult, if not impossible, to prepare by other means. The grafted layers are characterized both electrochemically and spectroscopically and their physical and chemical stability is examined. The electrografted films on glassy carbon (GC) are shown to be stable towards extensive ultrasonication in acetone and they are therefore believed to be covalently anchored to the substrate. Finally, it is shown that an electrografted primer layer of polythiophene on platinum (Pt) enhances considerably the adhesion strength to a top layer of oxidatively electropolymerized polythiophene film.

2. Experimental

2.1. Chemicals

Unless otherwise stated chemicals were obtained from Aldrich and used without further purification. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was synthesized using standard procedures [16]. 3-Bromo-2,4,6-triisopropylphenyl (pyridine-3-yl) iodonium trifluoromethanesulfonate was synthesized in a procedure similar to that given by He and Swager (see supporting information). [15] 2-Iodofuran was synthesized by a two-step literature procedure [17]. *N*-Methyl-2-iodopyrrole was synthesized in the following way: A solution of 1.020 g *N*-iodosuccinimide (4.5 mmol, 1.2 eq.) in 10 mL tetrahydrofuran (THF) was stirred under argon at -40°C . Trifluoroacetic acid (0.09 mL, 0.3 eq.) was added, followed by dropwise addition of *N*-methylpyrrole (0.45 g, 1.0 eq.) during 5 min. The solution turned yellow, then brown and, finally, after 30 min deep green/blue. The reaction was quenched by adding MilliQ water and dichloromethane. The organic phase was separated and washed once with MilliQ water and once with brine. The organic phase was dried with MgSO_4 and concentrated on a rotary evaporator to give a green liquid of ~ 0.5 M solution in THF (based on NMR) in 14% yield. Further evaporation resulted in a violent decomposition of the material into a black solid, which is in accordance with the unstable nature of 2-halogenated pyrroles [18]. In all experiments with *N*-methyl-2-iodopyrrole (**5**) the THF solution containing dichloromethane (2.5 M) was used. ^1H NMR (400 MHz, CDCl_3) δ_{H} 6.71 (dd, $J = 3.2$ Hz, $J = 1.5$ Hz, 1H), 6.21 (dd, $J = 3.4$ Hz, $J = 1.6$ Hz, 1H), 6.01 (t, $J = 3.3$ Hz, 1H), 3.49 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 124.7, 121.0, 118.4, 110.5, 37.9.

2.2. Electrochemical setup

Glassy carbon (GC) (Sigradur G, HTW, diameter = 1 mm) and

platinum rods (Dansk Ædelmetal A/S, diameter = 1 mm) imbedded in epoxy resin or GC plates (Sigradur G, HTW, 10 mm \times 10 mm \times 1 mm) served as working electrodes. The counter electrode was a Pt wire. A silver wire immersed in 0.1 M Bu_4NBF_4 + 0.01 M Bu_4NI /solvent provided the Ag/AgI pseudo-reference electrode, where the solvent is either acetonitrile or dimethyl sulfoxide (DMSO). All electroanalytical experiments were conducted with 2 mM solutions of the parent compound in 0.1 M Bu_4NBF_4 /solvent. The electrolyte solutions were degassed with argon before each experiment. The GC electrodes were carefully polished before each experiment by successive treatments with diamond suspensions (Struers, grain size: 9, 3, 1, and 0.25 μm) followed by thorough rinsing with water and ethanol and, finally, 10 min ultrasonication in HPLC grade acetone. GC plates were cleaned by sonication in Milli-Q water, HPLC grade acetone, and pentane (10 min in each solvent) prior to electrografting. At the end of each experiment the standard potential of the ferrocenium/ferrocene (Fc^+/Fc) couple, $E_{\text{Fc}^+}^0$, was measured, and all potentials were referenced against SCE using the previous determination of $E_{\text{Fc}^+}^0 = 0.41$ vs SCE in acetonitrile and $E_{\text{Fc}^+}^0 = 0.43$ vs SCE in DMSO [19]. Consecutive voltammetric cycles were always recorded with 2 s of stirring in between the cycles.

2.3. Ellipsometry

A rotating analyzer ellipsometer from Dre, Germany was used to measure dry-film thicknesses. The GC plates were measured at 65° angle of incidence. The ellipsometric parameters of the bare (Δ_s, ψ_s) and grafted (Δ_g, ψ_g) substrates were measured in air at ambient temperature, where Δ is the phase shift and $\tan(\psi)$ is the amplitude ratio upon reflection. The complex refractive index of the bare substrate was calculated from the measured Δ_s and ψ_s values. A three-layer optical model consisting of a substrate with a complex refractive index, the grafted layer with a refractive index and thickness and the surrounding medium (air) was used to calculate the overall reflection coefficients for in-plane (R_p) and out-of-plane (R_s) polarized lights. The real and the imaginary parts of the refractive index of the bare substrate were obtained by measuring each clean plate prior to modification. Ellipsometric measurements were performed on the same area of the plates before and after each modification step. Because the measurements are carried out on a dried and, therefore, collapsed film, the refractive index of the layer is fixed at a constant value (real = 1.55; imaginary = 0), independent of the thickness. The average values reported correspond to data points obtained from measuring the thickness at three spots on each plate.

2.4. Profilometry

Profilometric measurements were carried out using a surface profiler (Veeco, Dektak 150 Surface Profiler). A plastic (PE) tweezer was used to scratch a trace (50–100 μm broad) in the organic film. Residual film physisorbed on the surface was removed by 10 min of ultrasonication in HPLC acetone. Depth profiling was made by averaging the first 100 μm before the scratch to the average depth of the scratch.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed with a Kratos Axis Ultra-DLD spectrometer equipped with a 150 W monochromatic Al K_{α} X-ray source with an analysis area of 300 \times 700 μm^2 . Survey spectra were attained by accumulating two sweeps in the 0–1350 eV range at a pass energy of 160 eV. The spectral analysis was made using CasaXPS (Casa Software Ltd, Teignmouth, UK). A Shirley

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