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Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer

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Abstract: A global strategy to prepare a versatile and robust reactive platform for immobilizing molecules on carbon substrates with controlled morphology and high selectivity is presented. The procedure is based on the electroreduction of a selected triisopropylsilyl (TIPS)-protected ethynyl aryldiazonium salt. It avoids the formation of multilayers and efficiently protects the functional group during the electrografting step. After TIPS deprotection, a dense reactive ethynyl aryl monolayer is obtained which presents a very low barrier to charge transfer between molecules in solution and the surface. As a test functionalization, azidomethylferrocene was coupled by "click" chemistry with the modified surface. Analysis of the redox activity highlights a surface concentration close to the maximum possible attachment considering the steric hindrance of a ferrocenyl group.

Selective and robust attachment of functional molecules onto graphitic substrates is of fundamental importance because of the numerous applications of carbon-based interfaces.[1] Efficient strategies for immobilizing functional entities are often based on two-step procedures. An anchoring layer or a specific reactive group is first grafted on the surface, followed by its postfunctionalization. The immediate interest is an easier control of the properties of the anchoring layer that could be separately optimized. Among the possible methods to prepare such an anchoring platform, electroreduction of aryldiazonium salts is becoming a more and more popular method.[2] The functionalization is based on the electrochemical generation of reactive aryl radicals by reduction of the aryldiazonium salt (ArN$_2^+$) that covalently bind onto the substrate, leading to robust layers. The procedure can be executed on a variety of conducting or semiconducting substrates[2] and permits patterning of the film.[3] Different chemical groups can be introduced on the diazonium salt, allowing the use of most classical coupling reactions.[2b,4−7]

The major drawbacks of this method remain in the difficulties of controlling the extent of reaction and getting a high density of immobilized functional groups. Aryl radicals are highly reactive species that rapidly add to the substrate electrode where they are produced but also react with already-grafted aryl layers.[2b] This generally leads to multiple attachments and formation of disordered polyaryl multilayers, but it also can lead to possible radical degradation of the reactive groups. This last point could explain the relatively low yields of the second postcoupling step when we compare the active group surface concentration and the quantity of grafted materials.[6] Introduction of bulky substituents on the ArN$_2^+$ moieties limits the secondary radical reactions.[2b] Ultrathin organic layers with thickness close to a single monolayer were obtained by electroreduction of substituted ArN$_2^+$ when the 3,5-positions were hindered with *tert*-butyl groups.[8] An alternative solution was recently explored by Daasbjerg et al., who successfully used a two-step formation−degradation procedure to obtain thin thiophenolate or benzaldehyde films.[5]

On the basis of these concepts, we explore the possibility of obtaining dense reactive aryl alkyne monolayers that could serve as a platform to immobilize molecules onto various carbon substrates with controlled selectivity and morphological properties. Our approach took advantage of the protective effect of bulky silyl groups that were linked through a triple-bond bridge to the ArN$_2^+$ salt. We expect a minimization of the multilayer formation and, moreover, a strong protection of the acetylene functional group during the grafting process. After deprotection, an ethynyl aryl layer could be obtained. This opens a route for easy immobilization of most azide-terminated molecules[4c] using mild conditions via the extremely selective and high-yielding "click" reaction (Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition).[9] For this purpose, the triisopropylsilyl (TIPS) moiety was selected as an efficient bulky group (see below).

The precursor 4-((triisopropylsilyl)ethynyl)benzenediazonium salt (TIPS-Eth-ArN$_2^+$) was synthesized in two steps as described in the Supporting Information. The organic deposit layer was obtained by potential cycling (cyclic voltammetry) in a solution containing the diazonium salt. Different carbon substrates were treated according to the general procedure depicted in Figure 1: a glassy carbon electrode (GC) and pyrolyzed photoresist film (PPF) for AFM imaging. PPF layers present reactivity similar to that of GC

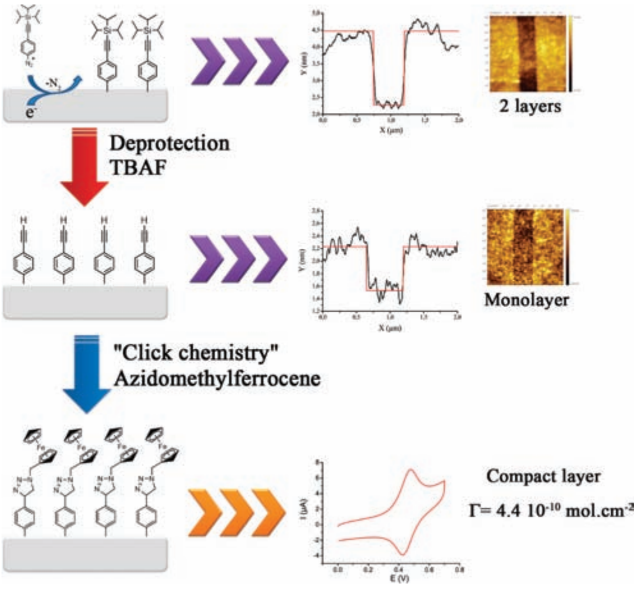

Figure 1. Principles of the different modification steps.

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but are more suitable for AFM experiments because of a lower roughness. X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and cyclic voltammetry (CV) studies were used to characterize the modified carbon surfaces.

As observed by CV, the reduction peak current of a TIPS-Eth-ArN_2^+ solution (recorded on a clean GC electrode) rapidly decreases after one cycle, indicating an inhibition of the electrode (see Supporting Information, Figure S1). The blocking properties of the layer were characterized by recording the CV of the oxidation of ferrocene in acetonitrile after each modification step. As can be seen in Figure 2, the current response is considerably modified after the electrodeposition. The voltamogram is typical of a totally blocked electrode. Examination of a similarly modified PPF layer by AFM indicates the formation of a compact layer with a granular structure similar to that of the neat PPF layer. To evaluate the layer thickness, we used the AFM “scratching” technique, which was shown to provide reliable estimation.[10] It involves ploughing the organic layer with the AFM tip in contact mode and then imaging the scratch to get the depth profile. If the applied force is sufficient to disrupt the organic layer but not damage the substrate, it is possible to “carve out” a rectangular trench in the deposit layer. After electrodeposition, a thickness value of 2.06 ± 0.5 nm is estimated from this technique. This indicates the formation of a thin coating corresponding to about two layers, considering a value of 1.01 nm for the size of a grafted unit. For comparison, we also made a modification in the same experimental conditions for the PPF surface by electroreduction of 4-(ethynyl)benzenediazonium salt (Eth-ArN_2^+), which is the same precursor but without the TIPS protecting group. “AFM scratching” provides an estimation of the layer thickness around 6 nm, which indeed corresponds the formation of multilayers (10 monolayers, 0.66 nm for one monomer) when TIPS is not present.

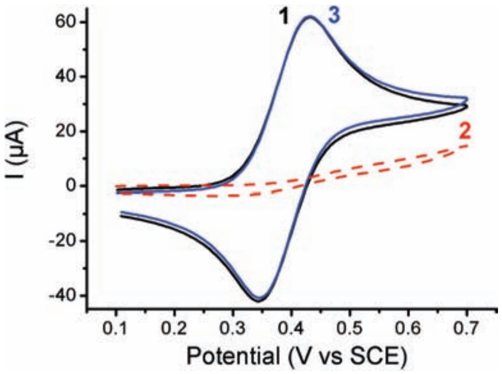

Figure 2. Cyclic voltammetry in ACN + 10^{-3} M Fc + 0.1 M NBu_4PF_6 solution of (1) bare GC electrode, (2) GC electrode modified by TIPS-Eth-ArN_2^+, and (3) GC electrode modified by TIPS-Eth-ArN_2^+ after deprotection. Scan rate, 0.1 V/s.

In a second step, the modified surfaces were immersed in a 0.05 $mol \cdot L^{-1}$ tetrabutylammonium fluoride (TBAF) solution in THF at room temperature and allowed to react for about 20 min. This is a soft technique classically used in organic synthesis to deprotect TIPS moieties.[11] Examinations of the deposited layer by XPS show that silicon peaks corresponding to the presence of TIPS that were visible after electroreduction of TIPS-Eth-ArN_2^+ have totally disappeared after TBAF treatment (see Supporting Information, Figures S3 and S4). Measurement of the thickness by AFM scratching confirms that the deprotected layer is much thinner. A thickness value of 0.65 ± 0.18 nm is estimated, which corresponds to the dimension of a monolayer. In a parallel manner, the CV of the ferrocene oxidation was recorded on the modified GC electrode that was deprotected. Remarkably, the voltamogram of the ferrocene oxidation became almost indiscernible from that obtained on a freshly polished GC electrode (see Figure 2).[12] Ferrocene molecules in solution could easily reach the carbon surface, as the current is not considerably affected by the presence of the grafted layer, indicating not only a very thin layer but also that the layer presents a very low barrier for charge transfer between the molecule and the substrate. McCreery et al. also observed a similar low barrier for charge transfer on a nitrophenyl-modified GC electrode.[13] They also demonstrated that this behavior is redox probe dependent.

The last point to consider concerns the activity of immobilized ethynyl groups. For this purpose, the deprotected GC substrate was treated by “click” chemistry using azidomethylferrocene that was chosen as an example of redox functionality. The functionalized electrode was then analyzed in an ethanolic blank solution containing only the supporting electrolyte. The electrode shows the well-defined ferrocene/ferrocenium system, characteristic of immobilized molecules (see Supporting Information, Figure S8). By integration of the electrochemical current, we derived a surface concentration, Γ_{Fc}, of grafted ferrocene of 4.4×10^{-10} $mol \cdot cm^{-2}$. We should emphasize that this value is close to the maximum possible attachment considering the steric hindrance of a ferrocenyl group, showing the high reactivity of the ethynyl aryl layer.[14] The same treatment was performed on the film obtained after electrodeposition of the unprotected diazonium Eth-ArN_2^+. In agreement with literature,[9] a Γ_{Fc} around 2.2×10^{-10} $mol \cdot cm^{-2}$ was derived, which is around half the previous value, despite a much thicker film. Additionally, a broader electrochemical response is visible in this case, suggesting that TIPS protecting groups induce a better organization of the final film.

These preliminary investigations show all the prerequisites of a global strategy to prepare versatile and robust platforms with controlled morphology on carbon substrates based on TIPS protection. We could highlight the possibility of obtaining a high density of reactive groups, balanced with a monolayer character of the anchoring coating. Because of the general character of the aryldiazonium salt electrografting method, it is likely that similar strategies could be developed for many other different substrates.

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Supporting Information Available: Experimental section; electrochemical, AFM, and XPS details. This material is available free of charge via the Internet at http://pubs.acs.org.

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