



Electrochemical signature of the grafting of diazonium salts: A probing parameter for monitoring the electro-addressed functionalization of devices

Fabien Le Floch^a, Jean-Pierre Simonato^b, Gérard Bidan^{c,*}

^a LETI/DIHS/LCMS, CEA-Grenoble 17 rue des martyrs, 38054 Grenoble cedex 9, France

^b LITEN/DTNM/LCH, CEA-Grenoble 17 rue des martyrs, 38054 Grenoble cedex 9, France

^c INAC/DIR, CEA-Grenoble 17 rue des martyrs, 38054 Grenoble cedex 9, France

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ABSTRACT

The reciprocal influence of the phenylsubstituents and diazonium groups allows to monitor the diazonium reactivity and to electrochemically detect the grafting reaction. Extended understanding concerning the grafting of *para* substituted tetrafluoroborate aryl diazonium salts p -(R-Ph-N₂⁺, BF₄⁻) was obtained by studying comparatively four compounds (R = NO₂, NEt₂, NHPh, NPh₂) by electrochemistry. For R = NEt₂, the grafted molecules showed no reversible electroactivity whereas for the aminophenyl substituents, the first oxidation process induced chemical modification of the deposited layers before being totally reversible. The compound with electron withdrawing group (NO₂) was the only one able to create spontaneous covalent bonding with the glassy carbon electrode (GCE). We observed that the substituent directly acts upon the diazonium reactivity. This effect can be directly monitored through the potential onset value of the diazonium reduction. In addition, the elimination of the diazonium group during electrografting induces a cathodic shift of the electroactivity of the aminodiphenyl and aminotriphenyl groups covalently attached onto the carbon electrode surface. The shift between these electrochemical values may be considered as a signature of the grafting reaction.

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1. Introduction

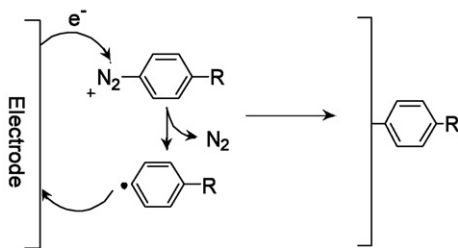
Specific properties of materials are determined mainly by the surface composition and in this field modified electrodes represent a pertinent illustration of this phenomenon [1]. Surface modification of conducting or semiconducting substrates can be used for the production of new superior products in terms of increased corrosion resistance, better biocompatibility, improvement of optical and electrical/electronic properties, electrocatalysis, sensing, etc. Obviously, the best functionalization route occurs through covalent coupling which ensures a stable strong grafting of the desired molecules. In this option, aryl diazonium salts are promising candidates for introducing molecular tools by surface modifications. In particular, the fast and versatile diazonium reactivity explored by Pinson [2–4] has been demonstrated using a wide variety of substituted aryl derivatives to create functionalities in multidisciplinary fields. Thanks to this reactivity, grafting of biological species becomes very favourable and leads to obtain high quality biosensors [5–13]. Diazonium reactivity is also extensively employed for side-wall functionalization of carbon nanotubes [13–26], to induce functionalization or to help solubilisation. More generally, a large

panel of surface modification of various electrode substrates has been reported [27–38,64–67].

Briefly, it has been established that following one electron reduction and a subsequent elimination of dinitrogen, aryl diazonium salts provide highly reactive radicals allowing the formation of covalent bonds with surfaces (Scheme 1). Though the main reduction process is caused by electrochemical induction and polarization of the material aimed to modify, grafting can also be initiated using a reducing chemical agent such as hypophosphorous acid [39] and iron powder [40], or in acidic conditions as used for in situ grafting [41,42]. Apart from those methods, spontaneous grafting in aprotic media without introducing other reactant than the diazonium salt has been recently identified by Pinson and Vautrin-UI's group [43,44]. Spontaneous grafting behaviours of different substituted diazonium salts were studied (R = H, NO₂, CF₃, Br, NMe₂, NEt₂, COOPh) and electroless grafting efficiency was correlated with the reactivity of the metallic supports (Fe, Ni, Zn, Cu). More favourable grafting results were obtained on the more reducing metals assigned by the open-circuit potential (OCP) values. It was also noted that indication on the influence of the substituent could be deduced from the electrochemical behaviour of diazonium salts in the sense that electron withdrawing substituents (NO₂, COOPh) were found to graft faster and more easily, while no grafting was observed with the more electron donating substituent NEt₂ (DDEA) on the less reducing metals such as Ni [43,44].

* Corresponding author. Tel.: +33 4 3878 4841; fax: +33 4 3878 5153.

E-mail address: gerard.bidan@cea.fr (G. Bidan).

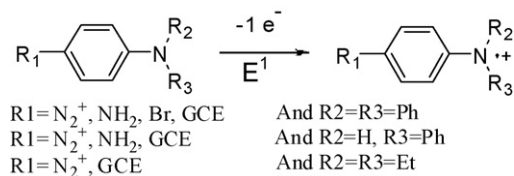


Scheme 1. Diazonium grafting route.

Since grafting was shown to be either electroinduced or spontaneous it is of the highest importance to anticipate how a compound would react when one wants to functionalize accurately only one element in an array of multiplexed electrodes [6–9,21], of transistors [45,46] or nanoelectromechanical systems (NEMS) [47], and especially for sensing applications. To develop a one-step locally addressed grafting method with a possible controlled density of specific elements, spontaneous binding should be anticipated.

The aim of this study was to approach the electrochemical and chemical relationship that could exist between each diazonium salt and the grafting parameters while widening the panel of grafted molecules. All studied molecules are drawn in Fig. 1.

To understand the general trends of the grafting behaviour of diazonium salts and to establish grafting conditions enforceable to all kinds of diazonium derivatives (*i.e.* with non-electroactive grafted molecules) on carbon substrates, we have compared the grafting behaviour of NBD with another commercial diazonium salt DDEA and with two synthesized *p*-amino substituted phenyl compounds; diazonium diphenylamine DDPA and diazonium triphenylamine DTPA. These molecules were chosen both for the contrasted electronegativity (electro-withdrawing nitro group, electro-donating amino groups) of the *para* substituents and their electroactivity after grafting. A strong change of the reduction potential of the diazonium group (Scheme 1) was obtained according to the electronic character of the substituent. Vice versa, the electroactivity of the amino-phenyl groups (Scheme 2) was also compared depending on whether these amino-phenyl groups were part of the diazonium salts or precursors ATPA, BrTPA and ADPA used for their synthesis or they are linked to the glassy carbon electrode, GCE, surface. The surface modification was confirmed by electrochemical signals related to the immobilized moieties obtained both by CV and square-wave voltammetry (SWV), a very



Scheme 2. Electrooxidation of *p*-aminophenyl compounds. R1=GCE means the aminophenyl group is grafted on the glassy carbon electrode.

sensitive method to detect electroactive species on electrode surfaces. These redox signals and their shifts from their values in solution to those in the grafted state constitute a straightforward signature. New points have been raised concerning the grafting ability of the diazonium salts in correlation with the electronic nature of the substituents in the *para* position of the phenyl ring and the cathodic wave potentials obtained during their reduction (Scheme 2).

2. Experimental

2.1. Material

All products were purchased from Aldrich. 4-Nitrobenzene-diazonium tetrafluoroborate NBD (97%, 294438) and 4-diazo-N,N-diethylaniline tetrafluoroborate DDEA (97%, D28205) were used without any further purification and kept in the freezer. Anhydrous acetonitrile ACN (99.8%, 27,100-4) and anhydrous dioxane (296306) were used as received and stored in glove box. Tetra-*n*-butylammonium tetrafluoroborate Bu_4NBF_4 (99%, 21,796-4) was dried under vacuum at 60 °C for 3 days. Nitrosyl tetrafluoroborate $NOBF_4$ (74010), N-phenyl-*p*-phenylenediamine ADPA (07920), 4-bromotriphenylamine BrTPA (643831), lithium bis(trimethylsilyl)amide solution 1.0 M in tetrahydrofuran LiHMDS (225770), Tris(dibenzylideneacetone)dipalladium(0) $Pd_2(dba)_3$ (683345), (2-biphenyl)dicyclohexylphosphine DCHPBP (638099) were used as received.

Distilled water was obtained from an Elgastat water purification system (18 MΩ cm). 1H and ^{13}C NMR spectra were carried out using a Bruker Avance AC 200 MHz spectrometer. Chemical shifts are reported in ppm downfield from TMS and referenced to solvent. FT-IR spectra were recorded on a Vertex 70 from Bruker.

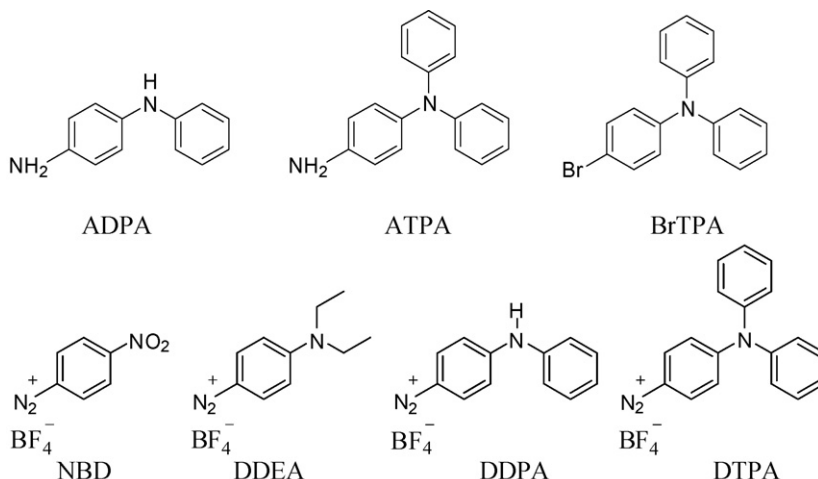


Fig. 1. Chemical structures of the studied products.

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