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# Surface modification of materials: electrografting of organic films

Jean Pinson,<sup>a</sup> Fetah I. Podvorica<sup>b</sup>

## Abstract

The modification of surfaces is possible through a number of reagents (silanes, thiols, phosphonic acids, amines...) among which diazonium salts have gained an increasing importance, this short review highlights the new achievements in this field.

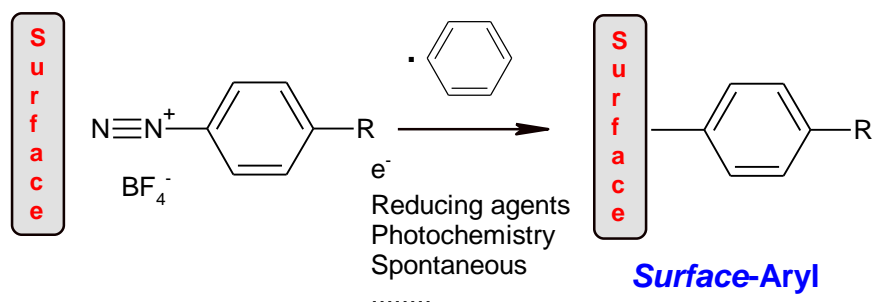
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## Introduction

Upon dediazonation (spontaneous or through reduction) diazonium salts provide highly reactive aryl radicals that bind very strongly to substrates surface through covalent bonds to give composite materials as shown on Scheme 1:



**Scheme 1.** Grafting of diazonium salts, the basic reaction.

Since the first described electrografting of diazonium salts in 1992 [1], their use has included i) more and more materials to which they have been attached, ii) more and more methods available for the reaction, iii) improved descriptions of the structure and formation mechanism of the films, iv) involvement in new reactions and v) an increased number of possible and real-life applications. In this opinion we review recent advances in the field. This reaction has been the subject of many reviews [2] including two Current Opinions [3,4].

## New material modified by reduction of Diazonium Salts

Carbon, metals and oxides, semiconductors, polymers have been modified with diazonium salts. Boron nitride is particularly non-reactive, however with prior hydroxylation under very harsh conditions, it has been functionalized with diazonium salts, albeit with a low surface

coverage [5]. The surface modification of polymers has been described in a book, including reactions with diazonium salts [6]. During the last years there has been an increased interest in nanomaterials such as nanoparticles, nanotubes but also layered materials such as graphene, MXenes, black phosphorus.

*2D Materials* such as MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, WSe<sub>2</sub>, Sb<sub>2</sub>S<sub>3</sub> and Bi<sub>2</sub>S<sub>3</sub> can be exfoliated into nanosheets or nanoribbons and modified by diazonium salts (under sonication) [7]. Black phosphorous has been exfoliated with *n*-BuLi and the negatively modified nanosheets modified with 4-nitrobenzenediazonium to improve their stability under ambient conditions; the mechanism has been discussed including either an homolytic or an heterolytic dediazonation leading respectively to a radical or a carbocation [8].

### **New methods for surface modification.**

Many different methods have been used for the modification of surfaces: electrochemistry, reducing reagents or surfaces, sonication,... In spite of its wide use in the organic chemistry of diazonium salts, photochemistry has been seldom used for surface modification. Recent results include the photochemical cleavage of iodonium salts Ar-I<sup>+</sup>-Ar' [9] (under visible light in the presence of a sensitizer) and azosulfones Ar-N=N-SO<sub>2</sub>CH<sub>3</sub> [10] (under UV light). With the first reaction it is possible to pattern gold surfaces by using a mask, with the second one it is possible to attach both the aryl group and the sulfone to the surface.

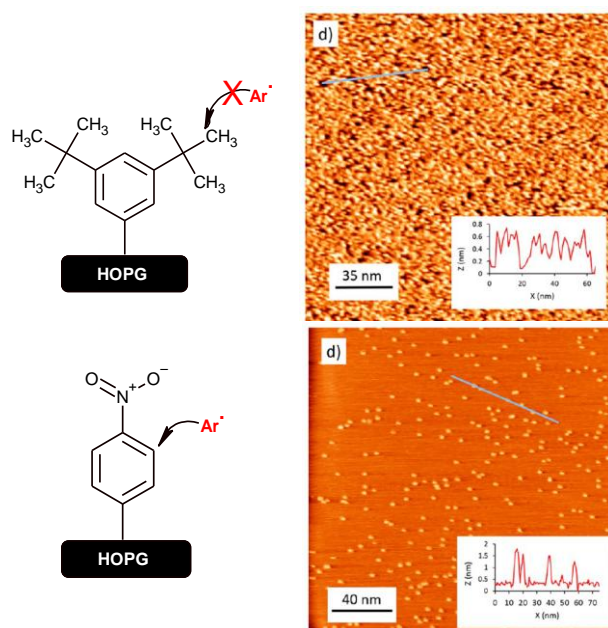
So called "hot electrons" can be produced on structured surfaces or nanoparticles by photochemical excitation of surface plasmons. These hot electrons are able to reduce diazonium salts and provide modified nanoparticles and nanodisks [11]. When nanodisks are irradiated by a polarized laser beam along one direction grafting by a diazonium salt provides modified spots at the extremities of one diameter, by rotating the beam by 90° another diazonium salt can be grafted, therefore this makes possible a regioselective functionalization of the nanodisk.

### **Controlling the structure of organic films**

One of the drawbacks of aryl diazonium salts compared to SAMs is the formation of oligomeric films so-called "multilayers" due to the ability of aryl radicals to attack not only the surface but also already attached aryl layers. There have been a lot of attempts to control the growth of the aryl layer and in particular to obtain monolayers. This topic has been the

subject of a Current Opinion [3]. More recently, a novel approach was devised to prepare a monolayer by use of a redox mediator (compounds that present a fast, outer-sphere, reversible redox couple). The method is based on a fast redox cross-reaction in the diffusion layer between the diazonium compound and the reduced form of the selected inhibitor. This reaction favors the formation of aryl radicals far enough from the surface so that they do not attack the first layer [12]. With this method the measured thickness of a film of iodophenyl groups ( $0.6 \pm 0.2$  nm) on an atomically flat carbon surface (PPF) fits excellently with that expected for a monolayer (0.55 nm).

The use of diazonium salts with bulky substituents on the benzene ring such as 3,5-bis-*t*-butyl 13, calix[4]arene [14], bulky Ru(II) complex [15] permits to obtain monolayers, and even structured organized monolayers in the last example. In the case of 3,5-bis-*t*-butylbenzenediazonium, a thickness was measured by ellipsometry ( $1 \pm 0.3$  nm) [3]. High resolution STM images [16] confirm the formation of a uniform monolayer on HOPG (Figure 1). However, if 4-nitrobenzenediazonium is grafted on the same substrate, a very different image is obtained where small oligomers are dispersed on the surface of HOPG, this indicates a faster attack of the radical on the first grafted group than on the substrate. In this case even if the film appears as a monolayer on a  $\mu\text{m}$  scale by AFM or ellipsometry, it is not a real monolayer. In addition, grafting of the same 4-nitrobenzenediazonium cation on a different type of carbon (PPF) provides a real monolayer as shown by AFM [17]. Therefore, the formation of real monolayers is a complex problem, the result depends both on the diazonium salt and the substrate and there does not seem to be a general method.



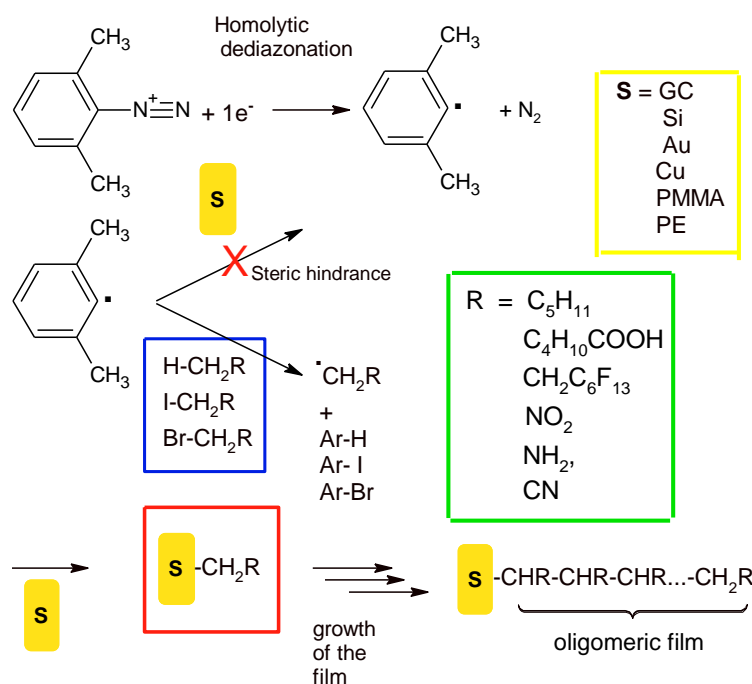
**Figure 1.** STM images after grafting of 3,5-bis-*tert*-butylbenzenediazonium and 4-nitrobenzenediazonium salts on HOPG.

The above methods: redox mediators or bulky substituents permit to limit the growth of the film by either controlling the concentration or limiting the reaction of aryl radicals with already attached aryl groups but these very reactive species are able to abstract hydrogen atoms and longer reaction times would certainly lead to multilayers. A different method permits to obtain a monolayer, it is based on the simultaneous transfer of an octadecylamine (ODA) monolayer Langmuir film on a gold surface and its oxidative electrografting [18]. In this case, the formation of the monolayer *Au*-ODA, with a local order, is “by construction” and the formation of “multilayers” impossible.

### Extending the scope of diazonium grafting

Aryl radicals react with surfaces, but they can undergo other reactions among which atom abstraction (hydrogen, bromine, iodine) from organic molecules (RH, RX). This results in the formation of a new radicals  $R'$  that are able to react with surfaces. If the aryl radical is prevented from reacting on the surface, one will obtain a surface modified with R groups only. This has been achieved using 2,6-dimethylbenzenediazonium (2,6-DMBD); due to the two methyl groups ortho of the radical, the steric hindrance prevents its reaction with surfaces, but does not prevent atom abstraction from different species in solution [19] (Scheme 2). By electrochemical reduction of 2,6-DMBD in  $\text{CH}_3\text{CN}$  it was possible to obtain cyanomethyl radicals issued from the solvent after the H atom abstraction. These radicals react on surfaces to give *Au*, *Cu*, *Si*- $[\text{CH}_2\text{-C}(\text{NH}_2)]_n$  surfaces [20]. If a 40% aqueous solution of  $\text{CH}_3\text{NH}_2$  is used as a solvent, one obtains highly aminated surfaces *Au*- $[\text{CH}(\text{NH}_2)]_n$  [21].

Alkyl iodides and bromides (RBr, RI) are reduced at potentials more negative than -2 V/SCE to give *GC*-, *Au*-, *Cu*-R electrodes (GC = Glassy Carbon). The reaction can be performed at much less negative potential (with a gain > 1.7 V) in the presence of 2,6-DMBD following the atom abstraction mechanism of Scheme 2. This reaction leads to different modified surfaces *GC*-  $\text{C}_6\text{H}_{13}$  or *GC*- $(\text{CH}_2)_2\text{C}_6\text{F}_{13}$  [22], *Au*, *PMMA*, *PE*- $\text{C}_5\text{H}_{10}\text{-COOH}$  [23,24] (PMMA= polymethylmethacrylate, PE = polyethylene). The activation of C-I bonds is also possible with aryl iodides at the reduction potential of 2,6-DMBD [25].



**Scheme 2.** Grafting through C-H, C-I, C-Br activation with a sterically hindered aryl radical obtained by reduction of the corresponding diazonium salt.

When using other aryldiazonium salts (4-nitrobenzenediazonium, for example) in the presence of an alkyl halide ( $\text{I}-(\text{CH}_2)_2\text{C}_6\text{F}_{13}$ , for example) bifunctional alkyl-aryl layers with a complex structure are obtained [26]. These reactions expand the field of the molecules that can be grafted on surfaces, in fact, most organic molecule with a C-H bond can be grafted on surfaces, not taking in account specific problems such as solubility, stability and steric hindrance.

## Conclusion.

Nearly 30 years after its discovery, the surface reaction of diazonium salts is still a very active field. Future challenges involve the grafting of complex molecules such as proteins and nucleic acid with a perfect control of the positions to be attached on the surface and the development of industrial applications in addition to the existing ones: inks and paints [27], copper interconnects and TSV in microelectronics [28], drug eluting stents ( $\text{BuMA}^{\text{®}}$ ) [29], polymer brush coating and adhesion technology [30], molecular junction overdrives [31].

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