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Electrografting of diazonium salts: A kinetics study

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ABSTRACT

The rates of electrochemical grafting of different diazonium salts on gold are measured by EQCM (Electrochemical Quartz Crystal Microbalance). These rates correlate reasonably well with the σ_{para} Hammett constant, indicating that the partial electrophilic character of the intermediate aryl radical favors attack on the gold surface.

1. Introduction

Surface modification by de-diazonation of aryl diazonium salts (electrochemically, photochemically or chemically) has been the subject of sustained interest for the last 25 years [1,2]. The different studies dedicated to this reaction [3,4,5] have led to: (i) reasonable control of the films that are formed on the surface (chemical functions, thickness, compactness), (ii) demonstration of the covalent bonding of the aryl groups to the surface (on gold [6,7], carbon [8] and oxides [9,10]); (iii) description of the mechanisms involved in the grafting reaction and in the further growth of the film [11]; (iv) many applications in organic electronics [12], supercapacitors and batteries [13,14], sensors [15–19], inks [20], and biomedical devices [21]. The key reactive species in this electrochemical reaction is the aryl radical [22,23] obtained through a concerted electron transfer–homolytic dissociation of the starting diazonium cation (Fig. 1). Unlike thiol self-assembled monolayers (SAMs) on gold, which only produce monolayers, this reaction generally leads to the formation of multilayers through the attack of the radical on the first grafted layer [3,4,5]. In addition to reacting on the surfaces, the radicals also diffuse in solution to give a number of side products (dimers, oligomers as in the Gomberg Bachman reaction [24]) that partly precipitate on the surface.

Therefore, the kinetics of the reaction of the aryl radical on the surface is an important parameter in the control of the reaction; however, few studies have been devoted to this particular topic. This is due to the fact that it is difficult to separate the primary reaction of the radical on the surface from the further attack of the same radical on the first grafted layer and from the deposition of products formed in solution [24].

EQCM makes it possible to follow the kinetics of electrografting of diazonium salts [25]. Using this method, the deposition of 4-X phenyl groups (X = NO₂, COOH, N-(C₂H₅)₂) on a polycrystalline gold electrode has been investigated by the electrochemical reduction of the corresponding 4-substituted phenyldiazonium tetrafluoroborate salts. A two-step deposition process has been demonstrated: first, the deposition of an almost complete monolayer and second, the relatively slower growth of multilayers [26]. The steric effect of para substituents (amino, carboxy, nitro, maleimido, methoxy and trifluoromethyl) on the growth of multilayers has also been investigated [27].

Two interesting studies have dealt specifically with the grafting kinetics of diazonium salts on two amorphous carbon substrates at very low concentrations [28,29]; the experimental data were fitted with first-order reversible Langmuir adsorption curves. The rate constant for the grafting of nitrophenyl groups on a high sp^3 content carbon was found to be $k = 3.1 \, M^{-1} \, s^{-1}$ and $\Delta G = 20.1 \, kJ \, mol^{-1}$. A Langmuir isotherm has also been used to fit the experimental data (obtained by Raman SERS) during the grafting of 4-sulfobenzenediazonium cation on Ag nanoparticles ($k = 13.0 \, M^{-1} \, s^{-1}$) [30]. However, fitting the experimental EQCM data with a Langmuir isotherm requires us to introduce the surface concentration of the aryl radical, which is unknown. Replacing the surface concentration with that of the diazonium salt in the grafting solution is an approximation which probably introduces a significant error.

Moreover, a previous study on HOPG showed that the nitrophenyl radical reacts with the first grafted group faster than with the free surface and the formation of a compact monolayer is never observed [31], making difficult the data exploitation through fitting with Langmuir isotherms.

Furthermore, EQCM mass vs time curves have already been used to determine the rate of grafting of 4-aminobenzyl and aminoethylaniline: 0.029 and 0.025 nmol $s^{-1} \, cm^{-2}$ on a carbon-coated quartz crystal. This rate is larger by one order of magnitude than the rate of reaction of
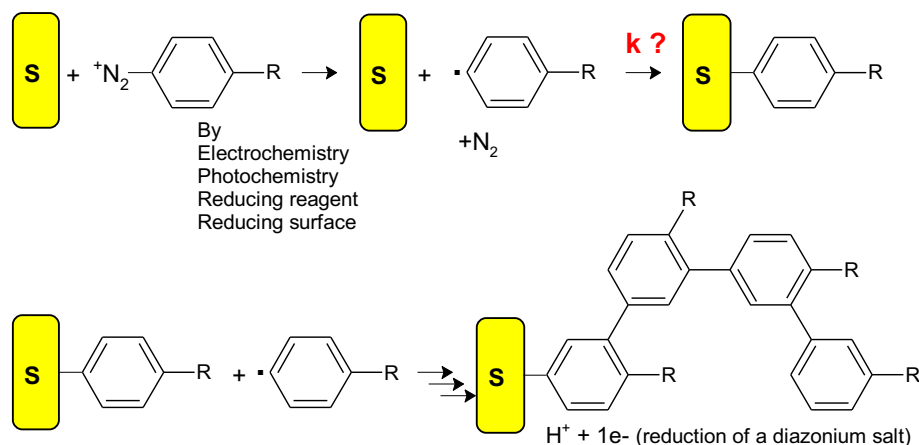
the same radical on the existing film: 0.0027 and 0.0068 nmol s^{-1} cm^{-2}, respectively [32].

In this paper, unlike previous investigations, we measure, by EQCM, the initial rates of electrografting on gold as a function of the substituents on the aryl group. We aim to determine whether a partial nucleophilic or electrophilic character of the radical favors electrografting on gold. These initial rates (in mol s^{-1} cm^{-2}) are obtained from the tangent to the mass vs time curve at time $t = 0$ s – at this time the surface is free from any grafted molecule. In this way, it is possible to eliminate the formation of multilayers or the deposition of products from the solution. These results should shine some light on the electronic parameters that control the reaction between the aryl radical and the substrate. The different substituents of the diazonium salts investigated are 4-NO_2 (DNO2), 4-CF_3 (DCF3), 4-H (DH), 4-OMe (DOMe), and 4-$N(CH_3)_2$ (DNMe2) but also 3,5-bis-*t*-butyl (DdtBu), as the corresponding benzenediazonium salt is known to produce only monolayers due to the steric hindrance of the *t*-butyl groups blocking the attack of the aryl radical on the aromatic ring [31,33].

2. Results and discussion

We first investigated the cyclic voltammetry of the different diazonium salts in ACN + 0.1 M NBu$_4$BF$_4$, on a gold disk electrode. Most of the investigated diazonium salts present two peaks, for example Ep = + 0.22 and 0.00 V/(Ag/AgCl) for DNO2 (Fig. 2A insert), the first one being sharper than the second. The presence of several peaks on gold corresponds to reduction on the different gold facets [34]. The first and second peaks are reported in Table 1.

Fig. 2A shows the voltammogram of DNO2 along with the mass increase on gold-coated quartz. Unlike the disk electrode, a single reduction peak located at 0.3 V/(Ag/AgCl) is observed on the gold-coated quartz. EQCM makes it possible to measure the deposited mass; this value can be transformed into a number of moles which can also be expressed as a number of equivalent monolayers. An approximate value for the surface concentration of a monolayer of DNO2 has been estimated [4]: $\Gamma_{monolayer}$ = 1.25 nmol cm^{-2}. The number of moles deposited on the gold-coated quartz upon reduction of DNO2 (5 mM, cycling the potential from 0.6 to -0.8 V at v = 0.1 V s^{-1}) increases from 0 to ~6.5 nmol cm^{-2} at the end of the cathodic scan. This value corresponds to ~5–6 equivalent monolayers. The increase is slower on the return scan and finally reaches 9.2 10^{-9} mol cm^{-2}, which is equivalent to 7–8 monolayers. After 5 scans the mass increases steadily up to 42 equivalent monolayers. The formation of this thick layer is due to (i) to the fact that the scan encompasses part of the nitrophenyl reduction peak, and the formation of very thick films under such conditions has already been observed and rationalized [35] and (ii) to the reaction products deposited on the surface. This is why it is important to measure the grafting rate at the very beginning of the scan. Unlike
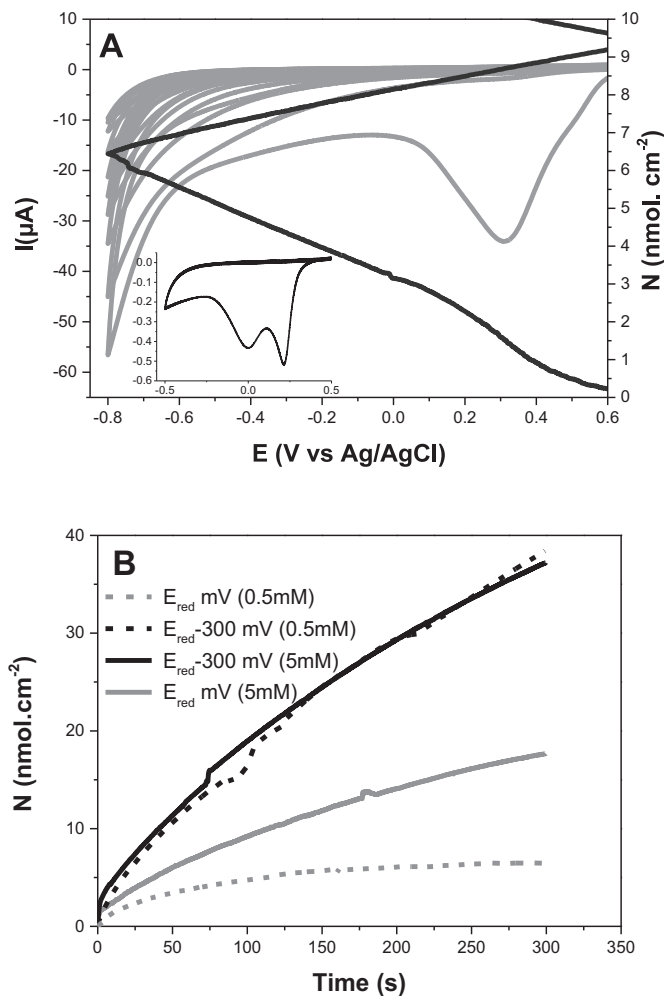

Fig. 2. (A) EQCM measurement: cyclic voltammetry (I vs E) and deposited amount of materials (nmoles vs E) on a gold-coated quartz in an ACN + 0.1 M NBu$_4$BF$_4$ + 5 mM DNO2. v = 0.05 Vs^{-1}; insert: cyclic voltammetry on a gold electrode in ACN + 0.1 M NBu$_4$BF$_4$ + 1 mM DNO2. v = 0.1 Vs^{-1} (B) EQCM measurement by chronoamperometry at the voltammetric peak potential and 0.3 V negative to the peak; in ACN + 0.1 M NBu$_4$BF$_4$ + 5 mM and 0.5 mM DNO2. Ref. Ag/AgCl.

other diazonium salts, DdtBu only produces a monolayer, as shown by ellipsometry and STM [31,33]; in our work a DdtBu monolayer is obtained after approximately 30s during chronoamperometry, the potential being set at the voltammetric peak (Figure not shown).

We then considered the rate of initial grafting under different conditions. We first examined the effect of the potential when