



**HAL**  
open science

## When ionic liquids meet diazonium salts to generate thin layers of modified surfaces

Quentin Lenne, Zaynab Atyf, Jalal Ghilane

### ► To cite this version:

Quentin Lenne, Zaynab Atyf, Jalal Ghilane. When ionic liquids meet diazonium salts to generate thin layers of modified surfaces. *Current Opinion in Electrochemistry*, 2023, 40, pp.101338. 10.1016/j.coelec.2023.101338 . hal-04255164

**HAL Id: hal-04255164**

**<https://hal.science/hal-04255164>**

Submitted on 23 Oct 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## When ionic liquids meet diazonium salts to generate thin layers modified surfaces

Quentin Lenne, Zaynab Atyf, Jalal Ghilane\*

*Université Paris Cité, ITODYS, CNRS, UMR 7086, 15 rue J-A de Baïf, F-75013, Paris, France.*

\*Corresponding author e-mail: [jalal.ghilane@u-paris.fr](mailto:jalal.ghilane@u-paris.fr)

### Abstract

Immobilization of thin organic layers bearing specific functional groups onto materials is one of the main strategies to modulate their properties and develop task specific surfaces. Besides that, ionic liquids (IL's) and their peculiar physicochemical properties have been a major topic of academic research and are now attracting industrial interest. This short review highlights the growing attention given to the encounter between the ionic liquids and diazonium compounds for building organized interfaces. The review explore the different grafting procedures of diazonium in ionic liquid including the electrochemical assisted grafting. Particular emphasis will be devoted to the properties of the generated layers in ionic liquid and the added value of the IL as a grafting medium.

### Introduction

Ionic liquid and their derivatives have attracted a lot of interest from the scientific world and have become a real multidisciplinary field. According to the common definition, an ionic liquid is a molten salt with a melting temperature below 100 °C.[1] The characteristics that can be attributed to ionic liquids are a wide liquid range, very low vapor pressure, and thermal stability with unusual solvent properties.[2] Overcome with knowledge about ionic liquids at this time, researchers' and scientists' imaginations make ILs more useful than only being used in organic synthesis. Thus, the limits are being further pushed to tailor the physical-chemical properties of ionic liquids by generating new structures for use in the field of electrochemistry, in which the development of this type of compound becomes unlimited.[3] The interest of ionic liquids in electrochemistry is much more considerable than just being limited to their use as a solvent–electrolyte. Recently, new families of ionic liquids known as “task specific ionic liquids” have been introduced that are based on ionic liquids bearing functional groups.[4,5]

From laboratory research to real-life applications, the role of surface modification with organic layers is always crucial. The properties of surfaces are dictated by the intrinsic characteristic of the material. Tuning the properties of the surface enable to extend their potential applications. To this end, surface modifications by the attachment of thin organic layers have been proposed to add new functionalities to the surface. Numerous strategies are reported in the literature and several reviews were devoted to this topic as well as the potential applications of the modified surfaces in various fields including, molecular electronics, energy storage and conversion and sensor devices.[6–11] All the described strategies for the immobilization of organic layers share a common principle, thus, the molecule should contain anchoring groups (SH, NH<sub>2</sub>, Si(OR)<sub>3</sub>, COOH, N<sub>2</sub><sup>+</sup>..) and the desired functional groups that will be attached to the extreme electrode interface.

Among the various surface modification strategies, the reduction of diazonium derivatives was widely employed.[12,13•] Diazonium grafting can be initiated by several methods depending

on the nature and the size of the substrates. For instance, chemically and radiatively induced reduction newly led to functional fabric and polymers under very smooth conditions.[14,15] More recently, the plasmon-assisted grafting of diazonium allowed to obtain multifunctional anisotropic objects, such as nanorods or nanocrosses by simply tuning the wavelength to the corresponding plasmon resonances.[16,17] Combining properly defined nanostructures and confinement effect even led to inhomogeneous growth of diazonium films on isotropic gold nanoparticles.[18] However, the most common reductive method remains the electrochemical assisted grafting. It is observed at soft reducing potential ranging from (0 to -0.6 V/SCE) which makes the grafting suitable over a wide range of conductive surfaces (metal, carbon-based materials, semiconductors). [13•] One should note that, while vastly explored, different aspects of this electrochemical reduction were only recently unveiled. For instance, this reduction was widely accepted to be a concerted mechanism. However, recent electrochemical spectroscopy coupled with ultrafast voltammetry measurements evidenced the presence of diazenyl radical species intermediate, suggesting that the diazonium electroreduction occurs through a stepwise mechanism.[19,20]

Thanks to these multiple modification strategies, we reached a point where almost any desired molecules moieties could be grafted with diazonium chemistry, either directly or through post-functionalization.[21,22] Subsequently, particular efforts were made in the recent years to tune the geometry of these immobilized layers to finely modulate the properties of the modified surfaces. While obtaining dense and thin layers is possible through the optimization of experimental parameters (time / scan rate, concentration, potential),[23–25] more efficient strategies were reported over the last years to obtain monolayers. Namely, it could either be performed using sterically hindered ligands (protecting groups, calix[4]arenes),[9,26] redox inhibitors,[27] long alkyl chains,[28] enantioselective species,[29] or simply through ascorbic acid mediated dediazonation.[30]

Although countless methods have been developed to modify surfaces through diazonium chemistry and finely tune the geometry of the grafted layer, one should notice that all the investigations are performed in classical solvents (water and acetonitrile). However, as discussed above, non-conventional solvents such as ionic liquids exhibit very favorable properties for the modification of surfaces using diazonium chemistry. This review focuses on the recent achievements that combine ionic liquids as solvent and the surface functionalization through diazonium molecules.

### **Ionic liquids as solvent for the electrochemical grafting**

The possibility to perform the electrochemical grafting of diazonium compound in ionic liquid has been reported for the first time by Ghilane et. al.[31] In this work, the nitrophenyl diazonium was electrochemically reduced in the presence of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM] [NTf<sub>2</sub>] (Scheme 1 in Figure 1). The electrochemical grafting, performed by cyclic voltammetry, displays the classical irreversible monoelectronic wave of diazonium reduction followed by its disappearance after successive cycles. This behavior is similar to that observed in classical solvent confirming the occurrence of the grafting in the ionic liquid. However, the peak current was found to be lower in ionic liquid due to its high viscosity. The presence of the attached nitrophenyl layer was evidenced by electrochemical measurement in ionic liquid, through the redox signal of the immobilized

nitrophenyl (Scheme 2 in Figure 1). Interestingly, the authors report that the radical anion of the immobilized NO<sub>2</sub>-phenyl, in the ionic liquid [EMIM], undergoes rapid protonation leading to the formation of NHOH-phenyl (4e<sup>-</sup> reduction process) and NH<sub>2</sub>-phenyl groups (6e<sup>-</sup> reduction process) due to the presence of acidic proton at the position 2 in the ionic liquid cation. It is therefore possible that the ionic liquid cation exchange protons with the reduced NO<sub>2</sub>-phenyl. Thereafter, the same group performed a systematic study to investigate the electrochemical grafting of diazonium in various dry ionic liquids (100-200 ppm H<sub>2</sub>O) (Figure 1a and b).[32••]

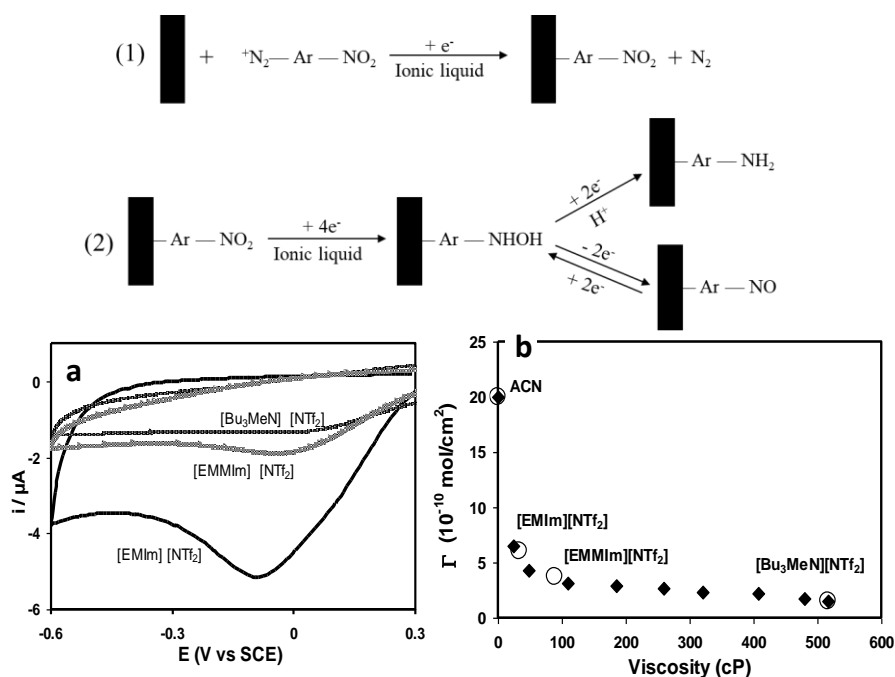


Figure 1. Scheme illustrating the electrochemical grafting of diazonium in ionic liquid (1) and the redox reaction of the immobilized nitrophenyl groups in ionic liquid (2) (Reprinted with permission from ref. [31]. Copyright 2008 Elsevier). (a) CV of the electrochemical reduction of diazonium on a carbon electrode in ionic liquids, 1-ethyl-3-methylimidazolium [EMIm][NTf<sub>2</sub>], 1-ethyl-2,3-dimethylimidazolium [EMMIm][NTf<sub>2</sub>] and N-tributyl-N-methylammonium [Bu<sub>3</sub>MeN][NTf<sub>2</sub>]. (b) Variation of the surface concentration of the attached layer (electrochemical characterization in 0.1 M H<sub>2</sub>SO<sub>4</sub>) with the viscosity of the grafting media. (♦) grafting in [Bu<sub>3</sub>MeN][NTf<sub>2</sub>] with the addition of various amount of ACN co-solvent. (○) grafting in three different ionic liquids and ACN. (Reprinted with permission from ref. [32]. Copyright 2010 American Chemical Society).

For all the investigated ionic liquids, the reduction of diazonium displays an irreversible reduction wave corresponding to the reduction of diazonium in the ionic liquid (Figure 1a). The comparison of the CV's display a current decreases of the diazonium reduction peak from 20  $\mu\text{A}$  in ACN (0.34 cP) to 5.5  $\mu\text{A}$  in [EMIm][NTf<sub>2</sub>] (32 cP) and finally reaches a value around 1.5 - 2  $\mu\text{A}$  in more viscous media ( $\approx$ 100-500 cP). Upon continuous cycling, this wave disappears suggesting the attachment of nitrophenyl layers onto the electrode surface. The performed electrochemical characterization of the modified electrode leads to estimate the surface concentration obtained in different ionic liquids. The surface concentration ( $\Gamma$ ) was calculated using the formula  $\Gamma = Q/nFS$ , where Q corresponds to the charge of the immobilized redox

moieties measured by integration of the redox peak,  $n$  is the number of electron involved,  $F$  is the Faraday constant and  $S$  represents the surface area. As an important result, the change in viscosity from 0.34 to 100 cP leads to a rapid decrease of the surface concentration, while, for a viscosity greater than 100 cP, the surface concentration reaches a constant value around  $10^{-10}$  mol.cm<sup>-2</sup>. A linear correlation between  $\ln(\Gamma)$  as a function of  $\ln(1/\eta)$  was proposed. This work strongly supports the established hypothesis that the surface concentration of the immobilized molecules depends on the viscosity of the grafting medium. The use of ionic liquids as a grafting medium results in modulating the quantity of the attached layer and in forming a thin layer compared to the conventional solvent. Even though, the reason of the self-limitation of layer growth in ionic liquids remain somewhat unclear, the origin could be ascribed to several factors including the high viscosity of the IL which lower the diffusion of the diazonium, the reaction between the radical diazonium and the imidazolium cation, and the effect of the ionic liquid double layer.

In the literature, the electrochemical grafting of diazonium is performed using direct electrochemical reduction of diazonium compounds or using in-situ generated diazonium in the electrochemical cell. The latter is based on the use of amino-phenyl derivatives followed by the addition of the necessary chemical compounds (generally NaNO<sub>2</sub> and HClO<sub>4</sub>) to perform the diazotation reaction.[33] One should note that this strategy avoids the synthesis and the isolation of diazonium salts (caution: risk of explosion). D. Bélanger et al. have investigated the possibility to generate in-situ diazonium in the presence of protic ionic liquid (Scheme in Fig 2).[34]

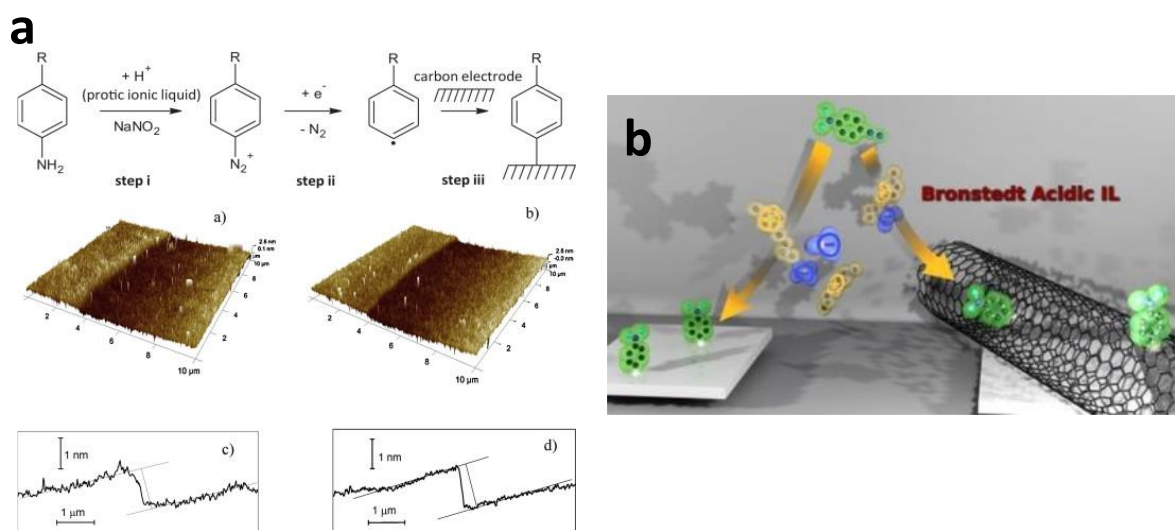


Figure 2. (a) Scheme illustrating the in-situ generation of diazonium in protic ionic liquid followed by the electrochemical grafting and the AFM images as well as the line profile of the grafted nitrophenyl. (Reprinted with permission from ref. [34]. Copyright 2013 Elsevier). (b) Electrochemical grafting of diazonium onto glassy carbon and multi-walled carbon nanotubes using in-situ generated diazonium in ionic liquid. (Reprinted with permission from ref. [35]. Copyright 2016 Wiley).

The occurrence of the grafting was confirmed by electrochemical measurements and by surfaces analysis. As an important result, the attached layer presents characteristic close to that expected for a monolayer (AFM images in Fig 2). The measured thickness 1.5 nm corresponds

to the formation of 1-2 layers of nitrophenyl groups which is found to be thinner than what was obtained in classical solvents (water or acetonitrile). To explain this difference, the authors proposed two hypotheses. First, this phenomenon might arise from the high viscosity of protic ionic liquid and thus lowering the diffusion coefficient of the diazonium. Secondly, it was postulated that the presence of larger ionic liquid ions within the electrochemical double layer may limit the growth of the grafted film to a few layers.

In another study, Lagrost et al. investigated the reduction of diazonium cations, produced in-situ in the presence of the acidic ionic liquid, onto glassy carbon electrode and multi-walled carbon nanotubes (MWCNTs) (Figure 2b).[35] In this work, the electrochemical characterization of the modified electrode displays higher surface concentrations than those obtained from the conventional HCl electrolyte. This finding is different than that reported earlier, however, this result was determined by following the electrochemical response of the attached redox group. It is well known that this electrochemical measurement provides only an estimation of the surface concentration due to the presence of silent redox groups. This difference was clarified when considering the AFM results where a thinner layer is obtained in the presence of the acidic ionic liquid compared to aqueous HCl. Overall, taking into account all the results, thinner and dense layers are probably produced in the presence of the ionic liquid when compared to classical solvent. Similar procedure was successfully performed to generate modified MWNTs for their potential use in energy storage applications with increased electrochemical performance.

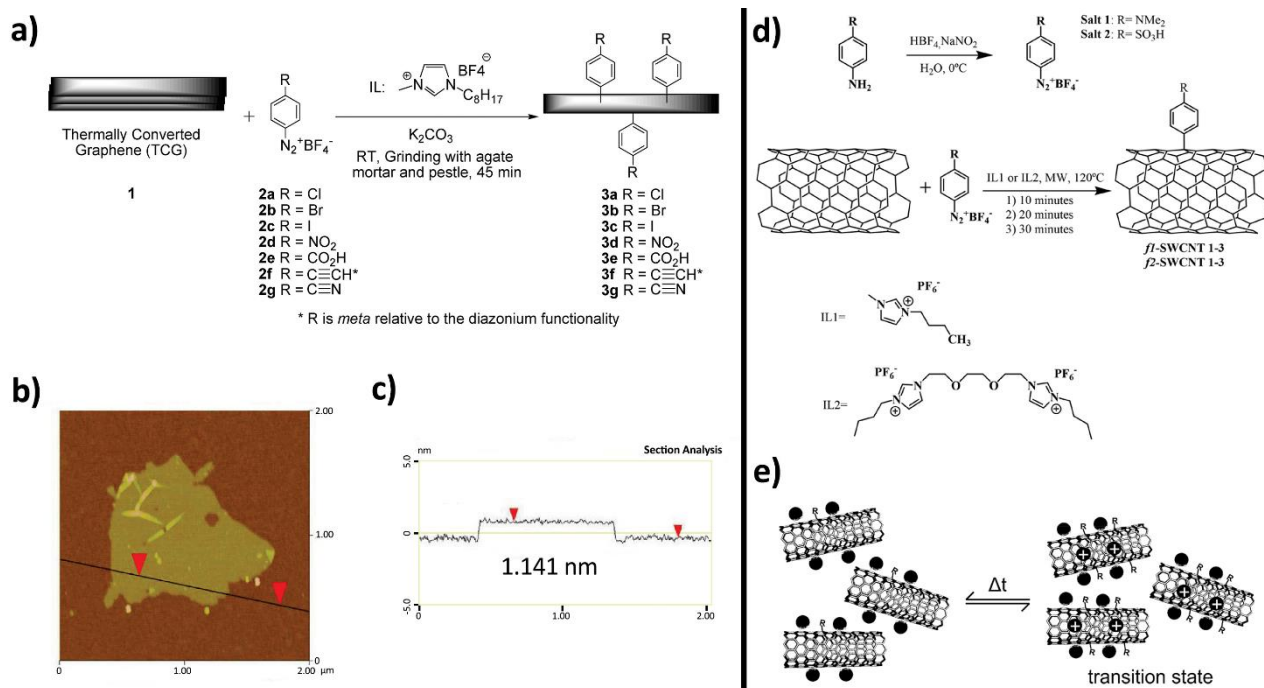
It is worthy to note that this functionalization strategy in ionic liquid is not only limited to carbonaceous surfaces as it was successfully applied to gold surfaces. [36] First, benzenediazonium salt was electrochemically reduced to generate a thin layer of poly(para-phenylene) (PPP) covalently bound to gold substrate. Next, on top of this layer, a thicker layer of poly(para-phenylene) (PPP) is grown by oxidative electro-polymerization of biphenyl in 1-butyl-3-methylimidazolium hexafluorophosphate [BMIm][PF<sub>6</sub>]. The generated material was characterized by various surface analyses methods including IR, ToF-SIMS and fluorescence spectroscopies demonstrating the formation of well regular PPP layers that are covalently linked to the gold substrate. The key role of the ionic liquid in the structuration of the polymer is emphasized. As a consequence, combining IL and diazonium chemistry led to extremely robust and organized films. [36] In another study, electrochemical response of 4-nitrobenzene layers previously dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([BMP]NTf<sub>2</sub>) was measured on gold surfaces, evidencing the grafting process. Similarly to what is observed on carbon surfaces, the use of ionic liquid as a grafting media resulted in thinner layers, supporting the idea that viscosity has an influence over compactness.[37]

Thanks to the flexible synthesis of ionic liquid, it has also been possible to develop a unique example of diazonium-based IL consisting of p-butylbenzenediazonium ions and bis(trifluoromethanesulfonyl) imide (NTf<sub>2</sub>).[38] This flaccidity of the NTf<sub>2</sub> anions renders the resulting diazonium to be liquid at ambient temperature. By soaking a graphitic rod in this hybrid liquid ionic, it was possible to observe a covalently grafted organic layer on the surface of the carbonaceous material, either by thermal (85°C overnight) or electrochemical activation (-0.8V vs Pt during 10 min).[38] However, the study underlines that electrochemical grafting resulted in a more homogeneous organic film, as a result of milder conditions. This class of task-specific ionic liquid therefore makes the use of solvent obsolete for the functionalization of material through diazonium chemistry.

## Surface functionalization without electrical bias

While the coupling of electrochemistry and the presence of ionic liquid has been proven to be a powerful strategy, alternative techniques emerged for the covalent grafting of diazonium moieties onto surfaces without any external electrical bias.

In this regard, ILs were first employed to generate nano-carbon materials such as single wall carbon nanotubes (SWCNTs) and graphene using exfoliation process since they have been found to be particularly efficient to overcome the cohesive forces in these materials.[39,40]



Exfoliation process coupled with the presence of diazonium salt led to a reasonable amount of functionalized carbon sites after a simple grinding step which allowed to obtain highly dispersible CNTs and single graphene sheets (Figure 3). The absence of ILs chemical components in the XPS analyses confirmed that the ILs only served as dispersive media and not grafted/adsorbed onto modified carbon nanomaterials. For such application, ILs with long alkyl chains (1-octyl-3-methylimidazolium tetrafluoroborate, OMIBF<sub>4</sub>) are more favorable as they have been shown to improve the debundling of the stacked 1D/2D objects. The versatility of this strategy has been evidenced by monitoring the solubility of the modified nano-objects as a function of the functional groups located at the interface, which were all better than their unmodified counterparts. Depending on the nature of the ionic liquid used, this method could then be an interesting environmentally friendly alternative for the functionalization of 1D/2D nano-carbon and could easily be implemented in an up-scalable setup thanks to its simplicity.

Figure 3. a) Exfoliation and functionalization of graphene sheets by grinding thermally converted graphene (TCG) in ionic liquid in the presence of a diazonium salt. b) AFM image of TCG sheet functionalized with 2a in OMIBF<sub>4</sub> on a mica surface and c) its corresponding sectional analysis from 3b. (Adapted from Ref. [40]). d) Diazonium salt addition to CNTs yielding different modified CNTs under microwave radiations in different ILs. e) Schematic representation of the reversible functionalization/retro-functionalization process. (Adapted from Ref. [42]).

The inherent conductivity of ionic liquid can also be a powerful tool to induce the necessary electron transfer for the diazonium reduction processes. For instance, boron doped diamond has been successfully modified with a thin layer of 4-nitroazobenzene, by simply stirring of diazonium salts at room temperature in the presence of hydrophobic and hydrophilic ionic liquid.[41•] The electrochemical characterizations of the attached layers confirm that the modified electrodes in hydrophilic and hydrophobic ionic liquids have similar electrochemical characteristics. However, the use of hydrophilic ionic liquid leads to the generation of more compact layers. In another study, imidazolium based ionic liquids were investigated using the thermal grafting of diazonium salts and led to the covalent grafting of organic moieties onto SWCNTs (Figure 3c).[42••] However, during classical heating procedures, no disruptive improvement could be observed when using ionic liquid rather than classical solvents. Interestingly, in the same study, the introduction of microwave radiations led to a tunable functionalization/retro-functionalization of SWCNTs depending on the reaction time. This phenomenon, taking place at high surface coverage, was explained by the concomitant action of the hot spots generated by the microwave irradiations in ionic liquids, causing the detachment of the ligands, and the presence of aryl radicals acting as “inhibitors”, preventing the re-attack of the surface (Figure 3d).[42••] Those properties are quite unusual in diazonium chemistry where the radical grafting is not a reversible process. Such observations are promising to promote the restoration of the  $\pi$ -conjugated structure of CNTs, even if a subtle choice of IL / diazonium couple is needed for a fine tuning of the retro-functionalization process.

### **Concluding remarks**

Using ionic liquid as an electrolyte for diazonium grafting offers various possibilities for the functionalization of different surfaces. While the inherent conductivity of ILs is an indisputable advantage for electrochemistry, the tunable properties of these non-conventional solvents (structure, viscosity) allow to finely modulate the resulting grafted layers. Overall, this review highlights the possibility to use ionic liquid media for the electrochemical grafting of thin layers based on the reduction of diazonium molecules. Compared to classical solvent, the use of IL leads to generate thinner layers which is attributed to several factors including the high viscosity of the ILs and the interaction between the highly reactive aryl radical and the ionic liquid cation. However, the parameters regulating this phenomenon need further rationalization and additional investigations are necessary to elucidate the role of the ionic liquids including the grafting mechanism, the role of the electrochemical double layer and the self-termination of the grafting. Moreover, several studies in this short review show that the use of ILs was not limited to the electrochemical grafting and report the successful grafting of diazonium using thermal, radiative, or even spontaneous activation on several surfaces. Given the number of available ILs and the functional diazonium salts and/or in-situ generated diazonium salts, one can easily imagine that the work reported here is just the mere beginning of this research area, especially if the upcoming progress in materials-genome prediction and design is dedicated to target the most promising ionic liquids candidates.

### **Acknowledgements**

This work was funded by ANR (pHSELECT, ANR-22-CE04-0006-02).

### **References and recommended reading**



Papers of particular interest, published within the period of review, have been highlighted as:

- Paper of special interest.
- Paper of outstanding interest.

- [1] Fabre E, Murshed S: **A review of the thermophysical properties and potential of ionic liquids for thermal applications.** *J Mater Chem A* 2021, **9**: 15861-15879.
- [2] Minea AA, Cherecheş EI: **State of the art on the development of 1-Butyl-3-methylimidazolium tetrafluoroborate ionic liquid and its nanocolloids.** *J Mol Liq* 2022, **368**: 120691.
- [3] Hapiot P, Lagrost C: **Electrochemical reactivity in room-temperature ionic liquids.** *Chem Rev* 2008, **108**: 2238–2264.
- [4] Pillai P, Maiti M, Mandal A: **Mini-review on Recent Advances in the Application of Surface-Active Ionic Liquids: Petroleum Industry Perspective.** *Energy and Fuels* 2022, **36**: 7925–7939.
- [5] Watanabe M, Thomas ML, Zhang S, Ueno K, Yasuda T, Dokko K: **Application of Ionic Liquids to Energy Storage and Conversion Materials and Devices.** *Chem Rev* 2017, **117**: 7190-7239.
- [6] Li D, Luo Y, Onidas D, He L, Jin M, Gazeau F, Pinson J, Mangeney C: **Surface functionalization of nanomaterials by aryl diazonium salts for biomedical sciences.** *Adv Colloid Interface Sci* 2021, **294**: 102479.
- [7] Hetemi D, Noël V, Pinson J: **Grafting of diazonium salts on surfaces: Application to biosensors.** *Biosensors* 2020, **10**: 4.
- [8] Lenne Q, Leroux YR, Lagrost C: **Surface Modification for Promoting Durable, Efficient, and Selective Electrocatalysts.** *ChemElectroChem* 2020, **7**: 2345–2363.
- [9] Mishyn V, Rodrigues T, Leroux YR, Aspermaier P, Happy H, Bintingier J, Kleber C, Boukherroub R, Knoll W, Szunerits S: **Controlled covalent functionalization of a graphene-channel of a field effect transistor as an ideal platform for (bio)sensing applications.** *Nanoscale Horizons* 2021, **6**: 819.
- [10] Cao L, Wu Y, Hang T, Li M: **Covalent Grafting of Dielectric Films on Cu(111) Surface via Electrochemical Reduction of Aryl Diazonium Salts.** *Langmuir* 2022, **38**: 14969–14980.
- [11] Olloqui-Sariego JL, Calvente JJ, Andreu R: **Immobilizing redox enzymes at mesoporous and nanostructured electrodes.** *Curr Opin Electrochem* 2021, **26**: 100658.
- [12] Pinson J, Podvorica FI: **Surface modification of materials: Electrografting of organic films.** *Curr Opin Electrochem* 2020, **24**: 44–48.
- [13] Belanger D, Pinson J: **Electrografting: a powerful method for surface modification.**
  - *Chem Soc Rev* 2011, **40**: 3995–4048.

This review summarizes a series of methods to generate modified surface and describes the

electrochemical and the spontaneous grafting.

- [14] Li W, Wang X, Wu Y, Chen M, Li Z: **One-step spontaneous grafting via diazonium chemistry for the fabrication of robust bionic multifunctional superhydrophobic fabric.** *Surf Coatings Technol* 2021, **407**: 126802.
- [15] Chernozem R V., Guselnikova O, Surmeneva MA, Postnikov PS, Abalymov AA, Parakhonskiy B V., De Roo N, Depla D, Skirtach AG, Surmenev RA: **Diazonium chemistry surface treatment of piezoelectric polyhydroxybutyrate scaffolds for enhanced osteoblastic cell growth.** *Appl Mater Today* 2020, **20**: 100758.
- [16] Therien DAB, McRae DM, Mangeney C, Félidj N, Lagugné-Labarthe F: **Three-color plasmon-mediated reduction of diazonium salts over metasurfaces.** *Nanoscale Adv* 2021, **3**: 2501–2507.
- [17] Olshtrem A, Guselnikova O, Postnikov P, Trelin A, Yusubov M, Kalachyova Y, Lapcak L, Cieslar M, Ulbrich P, Svorcik V, Lyutakov O: **Plasmon-assisted grafting of anisotropic nanoparticles-spatially selective surface modification and the creation of amphiphilic SERS nanoprobe.** *Nanoscale* 2020, **12**: 14581–14588.
- [18] Nguyen LL, Le QH, Pham VN, Bastide M, Gam-Derouich S, Nguyen VQ, Lacroix JC: **Confinement effect of plasmon for the fabrication of interconnected aumps through the reduction of diazonium salts.** *Nanomaterials* 2021, **11**: 1957.
- [19] Pichereau L, Gautier C, Breton T: **Real-time spectroelectrochemical monitoring of the diazonium electrografting.** *J Mater Chem C* 2022, 7111–7118.
- [20] Pichereau L, Fillaud L, Kostopoulos N, Maisonhaute E, Cauchy T, Allain M, Noël J-M, Gautier C, Breton T: **Highly Reactive Diazenyl Radical Species Evidenced during Aryldiazonium Electroreduction.** *J Phys Chem Lett* 2022, **13(51)**: 11866–11871.
- [21] Wu T, Fitchett CM, Brooksby PA, Downard AJ: **Building Tailored Interfaces through Covalent Coupling Reactions at Layers Grafted from Aryldiazonium Salts.** *ACS Appl Mater Interfaces* 2021, **13**: 11545-11570.
- [22] Gautier C, López I, Breton T: **A post-functionalization toolbox for diazonium (electro)-grafted surfaces: Review of the coupling methods.** *Mater Adv* 2021, **2**: 2773–2810.
- [23] Phal S, Shimizu K, Mwanza D, Mashazi P, Shchukarev A, Tesfalidet S: **Electrografting of 4-carboxybenzenediazonium on glassy carbon electrode: The effect of concentration on the formation of mono and multilayers.** *Molecules* 2020, **25**: 1–12.
- [24] Kang SJ, Kim S, Lee K, Shin I-S, Kim Y-R: **Tunable Electrochemical Grafting of Diazonium for Highly Sensitive Impedimetric DNA Sensor.** *J Electrochem Soc* 2020, **167**: 087504.
- [25] Daukiya L, Teyssandier J, Eyley S, Kazzi S El, Candelaria M, González R, Pradhan B, Thielemans W, Hofkens J, De Feyter S: **Covalent functionalization of molybdenum disulfide by chemically activated diazonium salts †.** *Nanoscale* 2021, **13**: 2972.
- [26] Mattiuzzi A, Lenne Q, Carvalho Padilha J, Troian-Gautier L, Leroux YR, Jabin I, Lagrost C: **Strategies for the Formation of Monolayers From Diazonium Salts:**

**Unconventional Grafting Media, Unconventional Building Blocks.** *Front Chem* 2020, **8**: 1–6.

- [27] Cesbron M, Dabos-Seignon S, Gautier C, Breton T: **Enhanced electrocatalytic activity on TEMPO mixed film grafted by diazonium reduction.** *Electrochim Acta* 2020, **345**: 136190.
- [28] Shkirskiy V, Billon J, Levillain E, Gautier C: **From Monolayer to Multilayer: Perylenediimide Diazonium Derivative Acting Either as a Growth Inhibitor or a Growth Enhancer.** *Langmuir* 2021, **37**: 12834–12841.
- [29] Zong Y, Zhang C, Cao H: **Chiral functionalization of solid surfaces with amino acid derivatives: diazonium grafting regulated by enantioselective processes.** *Dalt Trans* 2022, 14906–14911.
- [30] Rodríguez González MC, Brown A, Eyley S, Thielemans W, Mali KS, De Feyter S: **Self-limiting covalent modification of carbon surfaces: diazonium chemistry with a twist.** *Nanoscale* 2020, **12**: 18782.
- [31] Ghilane J, Martin P, Fontaine O, Lacroix JC, Randriamahazaka H: **Modification of carbon electrode in ionic liquid through the reduction of phenyl diazonium salt. Electrochemical evidence in ionic liquid.** *Electrochem Commun* 2008, **10**: 1060–1063.
- [32] Fontaine O, Ghilane J, Martin P, Lacroix JC, Randriamahazaka H: **Ionic liquid viscosity effects on the functionalization of electrode material through the electroreduction of diazonium.** *Langmuir* 2010, **26**: 18542–18549.

This paper presents the first in depth investigations of the diazonium electrochemical grafting in ionic liquid and highlight the possibility to tune the thickness of the attached layer by modulating the viscosity of the ionic liquid.

- [33] Salehzadeh H, Nematollahi D, Khakyzadeh V, Mokhtari B, Henderson LC: **General approach for electrochemical functionalization of glassy carbon surface by in situ generation of diazonium ion under acidic and non-acidic condition with a cascade protocol.** *Electrochim Acta* 2014, **139**: 270–280.
- [34] Shul G, Ruiz CAC, Rochefort D, Brooksby PA, Bélanger D: **Electrochemical functionalization of glassy carbon electrode by reduction of diazonium cations in protic ionic liquid.** *Electrochim Acta* 2013, **106**: 378–385.
- [35] Carvalho Padilha J, Noël J-M, Bergamini J-FF, Rault-Berthelot J, Lagrost C: **Functionalization of Carbon Materials by Reduction of Diazonium Cations Produced in Situ in a Brønstedt Acidic Ionic Liquid.** *ChemElectroChem* 2016, **3**: 572–580.

Intersting work of in-situ generated diazonium in ionic liquid and electrochemical grafting onto glassy carbon and carbon nanotube.

- [36] Descroix S, Hallais G, Lagrost C, Pinson J: **Regular poly(para-phenylene) films bound to gold surfaces through the electrochemical reduction of diazonium salts followed by electropolymerization in an ionic liquid.** *Electrochim Acta* 2013, **106**: 172–180.

- [37] Vacca A, Mascia M, Rizzardini S, Palmas S, Lai S, Napoli C, Barbaro M: **Functionalization of polycrystalline gold through the electroreduction of aryldiazonium salts in ionic liquids.** *Chem Eng Trans* 2014, **41**: 79–84.
- [38] Liang C, Huang JF, Li Z, Luo H, Dai S: **A diazonium salt-based ionic liquid for solvent-free modification of carbon.** *European J Org Chem* 2006, 586–589.
- [39] Price BK, Hudson JL, Tour JM: **Green chemical functionalization of single-walled carbon nanotubes in ionic liquids.** *J Am Chem Soc* 2005, **127**: 14867–14870.
- [40] Jin Z, Lomeda JR, Price BK, Lu W, Zhu Y, Tour JM: **Mechanically assisted exfoliation and functionalization of thermally converted graphene sheets.** *Chem Mater* 2009, **21**: 3045–3047.
- [41] Actis P, Caulliez G, Shul G, Opallo M, Mermoux M, Marcus B, Boukherroub R, Szunerits S: **Functionalization of glassy carbon with diazonium salts in ionic liquids.** *Langmuir* 2008, **24**: 6327–6333.

Covalent grafting of aryldiazonium salts in the presence of hydrophylic or hydrophobic ionic liquids and the effect on the compactness of the layer.

- [42] Barrejón M, Syrgiannis Z, Prato M: **Ionic liquids plus microwave irradiation: A general methodology for the retro-functionalization of single-walled carbon nanotubes.** *Nanoscale* 2018, **10**: 15782–15787.

The paper describes a versatile concept for potential reversibility of the grafting of diazonium compound by coupling microwave-radiation and ionic liquid.