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Pascal Viel, Xuan Tuan Le, Vincent Huc, Jennifer Bar, Alessandro Benedetto, et al.. Covalent grafting onto self-adhesive surfaces based on aryldiazonium salt seed layers. *Journal of Materials Chemistry*, Royal Society of Chemistry, 2008, 18, pp.5913-5920. 10.1039/B811299A . cea-01056529

**HAL Id: cea-01056529**

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Submitted on 20 Aug 2014

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# Covalent grafting onto self-adhesive surfaces based on aryldiazonium salt seed layers

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Received 2nd July 2008, Accepted 17th September 2008

First published as an Advance Article on the web 5th November 2008

DOI: 10.1039/b811299a

The chemistry of aryldiazonium salts has been thoroughly used in recent years to graft in a very simple and robust way ultrathin polyphenylene-like films on a broad range of surfaces. We show here that the same chemistry can be used to obtain “self-adhesive surfaces”. This target was reached in a simple way by coating various surfaces with chemisorbed organic films containing active aryldiazonium salts. These “self-adhesive surfaces” are then put into contact with various species (molecules, polymers, nanoparticles, nanotubes, graphene flakes, etc.) that react either spontaneously or under activation with the immobilized aryldiazonium salts. Our self-adhesive surfaces were synthesized following a simple aqueous two-step protocol based on *p*-phenylenediamine diazotisation. The first diazotisation step results in the robust grafting of thin polyaminophenylene (PAP) layers onto the surface. The second diazotisation step changed the grafted PAP film into a “poly-aryldiazonium polymer” (PDP) film. The covalent grafting between those self-adhesive surfaces and the target species was achieved by direct contact or by immersion of the self-adhesive surfaces in solution. We present in this preliminary work the grafting of multi-wall carbon nanotubes (MWCNTs), flakes of highly oriented pyrolytic graphite (HOPG), various organic compounds and copper nanoparticles. We also tested these immobilized aryldiazonium salts as electropolymerization initiators for the grafting-to process.

## Introduction

The need for chemically controlled functionalization of surfaces with robust adhesion is important in a large number of technological fields, such as biocompatibility for bio-implants, wettability on car windscreens, protection against corrosion, etc. The covalent grafting of organic thin films is likely to improve performance in harsh conditions. Very robust coatings are derived from various methods, either physical with plasma depositions,<sup>1–3</sup> or chemical with silane chemisorption<sup>4–6</sup> or electrochemical grafting.<sup>7–9</sup> In the latter case, electrografting of aryldiazonium salts has been extensively studied for more than a decade, following Pinson's pioneering work.<sup>10,11</sup> The use of aryldiazonium salt chemistry for surface modification is now quite common, and two different routes can be followed to achieve this objective, which are briefly described below.

- Electrografting: Electron transfer on aryldiazonium salts subsequent to the electrochemical reduction leads to extremely reactive moieties, which generally graft onto the electrode surface *via* a covalent bond. Up to now, a significant number of functional groups borne by the aryl ring (OCH<sub>3</sub>, NO<sub>2</sub>, SH, COOH)

have been grafted on surfaces in this way.<sup>9,12</sup> The coating thickness is tuneable by varying the working conditions. There is an excellent review on the subject by Doppelt *et al.*<sup>13</sup>

- Redox grafting: Electroless coating has also been achieved on several carbeneous materials such as graphite, glassy carbon, CNTs<sup>14,15,16</sup> or metallic surfaces such as nickel, zinc, iron and copper.<sup>17,18</sup> This versatile procedure is much simpler than the electrochemical process, thanks to the high standard redox potentials and the strong electrophilic properties of aryldiazonium salts.

The latter method, which is based on spontaneous reactions between diazonium groups and various surfaces, can be reversed to immobilize various chemical species onto diazonium-rich surfaces. Indeed, if aryldiazonium salts are able to be spontaneously grafted on many surfaces or molecular objects, surfaces bearing active diazonium salts could spontaneously react with analogous chemical functions and lead to covalent immobilization. Two different routes have already been proposed for that purpose.

In the first route, diazo-resins (DARs),<sup>19</sup> i.e. polymers containing positively charged aryldiazonium salts as lateral groups, were exploited in a layer-by-layer (LbL) method to build molecular assemblies with negatively charged porphyrins,<sup>20</sup> phtalocyanines,<sup>21</sup> enzymes<sup>22</sup> or fullerols.<sup>23</sup> The resulting diazonium-rich coatings were shown to undergo reticulation under UV irradiation, which strengthens the multilayer structure.<sup>19</sup> However, the DAR was not used in those cases for covalent bonding of the multilayer structure on the solid substrate: the authors used the standard silane coupling agents or thiols to get the required adhesion.<sup>19–23</sup>

In the second route, bis-aryldiazonium salts were synthesized to immobilize designated molecules onto various surfaces. Rigid

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linear molecules, bearing either two aromatic amines (which are standard precursors for diazonium salts) or diazonium groups, were used as “linkers” between a solid surface and various nano-objects such as carbon nanotubes.<sup>24–26</sup> The present paper presents an alternative synthetic strategy for that second route.

The one-step electrografting of bis-aryldiazonium salts upon surfaces has already been proposed by Pinson.<sup>24</sup> The idea consisted in electrografting one aryldiazonium function without altering the second one, but it was experimentally difficult to control the selective reduction of only one aryldiazonium group, as shown by the recorded voltammograms. Furthermore, insulating surfaces cannot be modified in this way. Tour tried the electroless grafting of a bis-aryldiazonium salt on the Si–H surface through a radical mechanism,<sup>25</sup> but the results were not satisfactory: after reaction with the silicon surface, no XPS signal from the remaining aryldiazonium group could be observed, although no “looping” was possible with the rigid OPE (oligo phenylene ethylene) molecular structure. The authors suggested that the origin of the loss of the second diazonium group was the spontaneous one-electron reduction of the Si surface. Thus, it appears quite difficult to graft molecules bearing more than one diazonium salt, either electrochemically or *via* an electroless process.

An alternative method is thus to graft a precursor of the diazonium group, and synthesize it *in situ*. Conversion of aniline moieties with NOBF<sub>4</sub> in organic solvent or NaNO<sub>2</sub> in aqueous acidic medium are quite effective for that purpose.<sup>13,16,28–31</sup> Tour recently proposed another method with triazene groups converted in aryldiazonium groups under HF or HBF<sub>4</sub> treatment.<sup>25–27</sup>

That latter method was cleverly used by Tour to graft an aniline-terminated OPE onto Si–H substrates: the starting molecule bears an  $\alpha$ -triazene on one end of the linear conjugated OPE backbone, and an aniline group at the other end.<sup>25,27</sup> The triazene group was *in situ* converted into aryldiazonium using 2% HF followed by spontaneous grafting to the Si–H surface. As expected, this treatment did not affect the aniline group. Then the grafted aniline groups were converted into grafted aryldiazonium by reaction with NOBF<sub>4</sub> or alkyl nitrite in organic medium. The resulting grafted diazonium groups were successfully used to immobilize SWNTs or fullerenes.<sup>25,27</sup> However, the pH conditions used for the first diazonium salt formation did not prevent the free aniline group reacting with the already-formed diazonium groups, which is likely to decrease the yield and the covering ratio.

We propose in this paper a much simpler method, which relies on commercial compounds and aqueous medium reactions. Previously, Lyskawa *et al.* had shown that *p*-phenylenediamine could be reacted with an equivalent quantity of NaNO<sub>2</sub> in 0.5 M HCl to form the aminophenyl diazonium salt, which was then electrografted onto a carbon surface as a “polyaniline-like” (PAP) film.<sup>29,30,32,33</sup> We recently improved and extended that strategy by replacing electrografting with redox grafting. This process, called Diazonium Induced Anchoring Process (DIAP), provides a very simple way to modify any surface (either metallic, semiconductor or insulating) of any complex geometry with robust polyphenylene-like films.<sup>34,35</sup> When applied to the *p*-phenylenediamine precursor, DIAP provides on any kind of surface a dense and homogeneous grafted “polyaniline-like” film.

Starting from that result, we show here that the grafted aniline groups can be easily converted into grafted aryldiazonium salts, either in aqueous or organic medium. Then, the resulting

“diazotised surfaces” (PDP) were put into contact (dry or wet) with various materials that eventually graft onto the surface. The “diazotised surfaces” thus act as “self-adhesive surfaces”.

The present paper focuses on describing: (1) the preparation protocol of self-adhesive surfaces through aryldiazonium salts chemistry; (2) the characterisation of the self-adhesive surfaces and the investigation of the chemical stability of the grafted aryldiazonium groups; (3) the demonstration of efficient grafting with our self-adhesive surfaces on various examples: simple organic molecules, polymers, dendrimers, copper nanoparticles, multi-wall carbon nanotubes and graphene flakes; (4) a new “grafting-from” process using self-adhesive surface as chemical initiators.

## Experimental section

### General methods

The synthesis of self-adhesive surfaces was performed at open air in a simple flask. The grafting and growing of the PAP primer layer was promoted by heating the flask at 35 °C. The second step (converting PAP into PDP) was carried out at room temperature. The experiments were mainly conducted in acidic deionized water (pH  $\leq$  2 due to poor stability of aryldiazonium salts at high pH). Chemicals were purchased from Sigma Aldrich and used as received. *p*-phenylenediamine, ethyl-4-pyridylacetate, NaNO<sub>2</sub>, PAMAM (generation 4, 10% in methanol), P<sub>4</sub>VP, HEA16Cl, CuSO<sub>4</sub>, NaBH<sub>4</sub> were of research grade. Iron particles were purchased from VWR (98%, mean particle size 45–100  $\mu$ m). MWCNT (pure CVD furnished by Nanocyl), HOPG (from Advanced Ceramics Corporation, grade ZYH) were used as received. Gold substrates were obtained by metallic evaporation of 5 nm of chromium and 200 nm of gold on microscopic slides. All the samples obtained after grafting were submitted to an ultrasonic treatment in order to discard any ungrafted matter.

### Spectroscopy studies

The scanning electron microscopy images of MWCNT and copper nanoparticles were obtained using a FEI XL30S field emission gun scanning electron microscope (FEG-SEM). The pictures were acquired with an accelerating voltage of 5 kV using a through-the-lens SE detector (TLD) in the ultra high resolution (UHR) mode, a working distance of 5 mm, and an electron beam diameter of about 16 nm and beam current of 100 pA corresponding to spot 3 on the instrument. Graphene flakes were simply imaged with a binocular microscope.

Infrared spectra were recorded on a Bruker Vertex 70 spectrometer equipped with an ATR Pike-Miracle accessory. The detector was a MCT working at liquid nitrogen temperature. The spectra were obtained after 256 scans at 2 cm<sup>-1</sup> resolution.

MicroRaman spectra were recorded by a Jobin-Yvon T64000 spectrometer using a 100X objective. The excitation is settled at 514.5 nm by an Argon laser (~1mW of incident power on the sample).

### Electrochemical method

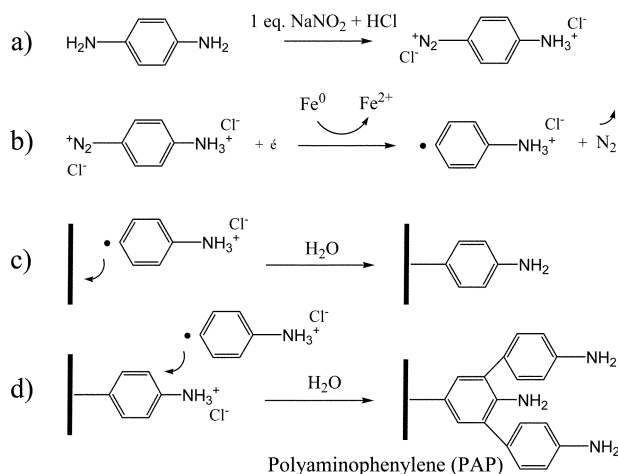
Cyclic voltammetry was recorded with a potentiostat EGG model 273. The substrate and the solution were placed in a typical three-electrode electrochemical cell: a working electrode

at which the electropolymerization takes place, an auxiliary electrode (graphitic plate) and a reference electrode (Ag/AgClO<sub>4</sub>). The solvent was acetonitrile in the presence of 0.05 M of tetraethyl ammonium perchlorate (TEAP). Monomer was distilled methyl methacrylate (MMA) to remove polymerization inhibitor. All products were of electrochemical grade and purchased from Sigma Aldrich and apart the MMA used as received.

## Results and discussion

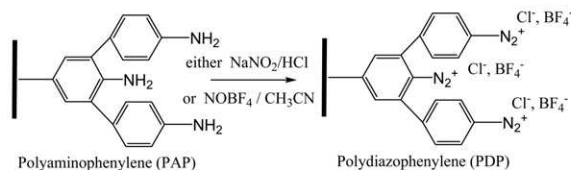
### Mechanistic models to achieve “self-adhesive surfaces”

The self-adhesive surfaces can be obtained by the following two-diazotisation-step protocol based on *p*-phenylenediamine. The first step aimed at the synthesis of polyaminophenylene layer (PAP) on the desired substrates according to a chemical route in aqueous medium as presented in Fig. 1. For step (a), the addition of one equivalent of NaNO<sub>2</sub> leads to the conversion of only one of the two amine groups to aryldiazonium salt. It is important to point out that the acidic medium protects the remaining amine group from reactive diazonium salts, which is likely to improve both the overall yield of grafting and the covering ratio. Note that the resulting PAP films are stable in ambient conditions. The upper part of Fig. 2 shows the proposed chemical mechanism for conversion of the grafted amine groups to grafted aryldiazonium salts (PDP). This conversion should be done just before “using” the self-adhesive surfaces to limit spontaneous decomposition of the grafted aryldiazonium salts. Finally, direct contact between self-adhesive surfaces and desired compounds achieves covalent grafting. The lower part of Fig. 2 accounts for the adhesion step. With some metallic, carbonaceous materials or strongly nucleophilic compounds, a spontaneous mechanism is expected.<sup>14–18</sup> However, for the less reactive materials, thermal, photochemical or electrochemical activation was necessary. The precise mechanism that takes place at the interface between the self-adhesive surface and the materials to be grafted will not be discussed in this work. It has already been shown that diazonium salts evolve

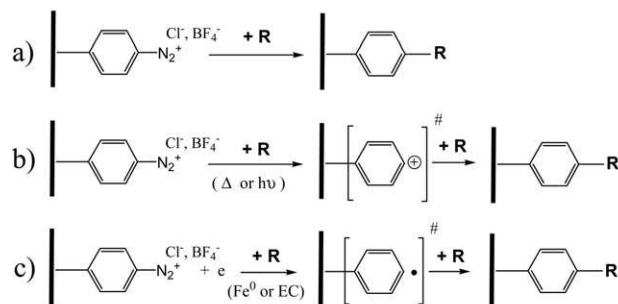


**Fig. 1** Chemical route to produce grafted polyaminophenylene (PAP) as primer layer: (a) Diazotisation of the *p*-phenylenediamine in solution, (b) Reduction of the aryldiazonium group through redox mechanism with iron particles, (c) Grafting of the resulting aryl radicals onto the surface, (d) Growing of PAP multilayer.

### Chemical route to produce “self-adhesive surfaces” bearing grafted diazonium salts



### Chemical route to grafting materials on “self-adhesive surface”



R = 1/ Chemical compounds as molecule, macromolecule, polymer, or 2/ Solid compounds as CNT, Graphene, metallic particles, .....

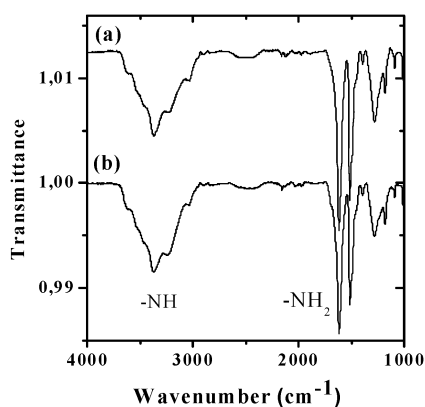
**Fig. 2** Upper part: Chemical route to produce “self-adhesive surfaces” bearing grafted aryldiazonium salts. Lower part: Schematic views of proposed chemical routes of the grafting step between “self-adhesive surfaces” and various compounds: (a) Spontaneous reaction between the aryldiazonium grafted salt and nucleophilic compounds (Ex: pyridine based compounds), (b) Physical activation by thermal or UV irradiation, the intermediate should be a phenyl cation (c) Chemical activation through electron transfer by redox (copper particles) or electrochemical way (graft electropolymerisation).

as radicals or cations depending on the conditions.<sup>37</sup> Work is in progress to explore the rich chemistry of aryldiazonium salts in our PDP films.

### Preparation of primer polyaminophenylene layers

The aryldiazonium salts were synthesized *in situ* from the corresponding amines. The grafting of polyaminophenylene (PAP) onto gold surfaces was realized according to the following process: 3 mL of 0.1M sodium nitrite was added dropwise to the same volume of a 0.1M solution of *p*-phenylenediamine in 0.5M HCl (pH = 0.3). The solution turned from orange to red wine. After homogenizing the solution, 200 mg of iron powder were added to reduce the aryldiazonium salt in solution. Once the solution bubbled because of dihydrogen and dinitrogen evolution, we introduced the gold substrates. Then, the temperature was adjusted to 35 °C and maintained during 2 hours. The samples were then rinsed with pure water and acetone in an ultrasonic bath for 5 minutes.

As schematized on Fig. 1, spontaneous reduction of *in situ* generated aryldiazonium salts by iron particles formed aryl radicals that eventually graft onto gold and grow a PAP film on the surface. After rinsing with deionised water, the ammonium groups switch to amines. The resulting PAP films were analyzed by IR-ATR as shown on Fig. 3. Film stability was tested under ultrasonic treatment and no evolution was observed. Bands at 1515, 1617 and 3370 cm<sup>-1</sup> are respectively attributed to phenyl



**Fig. 3** IR-ATR spectra of polyaminophenylene (PAP) film acting as primer. Reaction time 40 minutes, followed by rinsing with pure water: (a) Before ultrasonic treatment with acetone, (b) After ultrasonic treatment with acetone.

ring vibrations,  $\text{NH}_2$  deformation and  $\text{NH}$  stretching vibration. The general features of the IR spectra of the corresponding PAP are reproducible and similar to the PAP film obtained by electrografting by Lyskawa *et al.*<sup>29</sup>

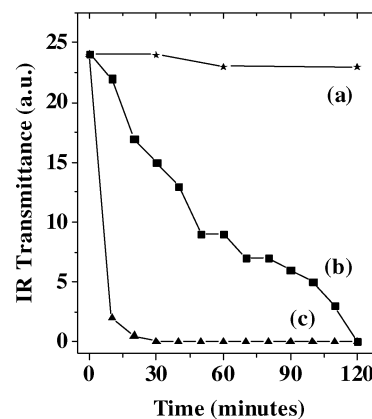
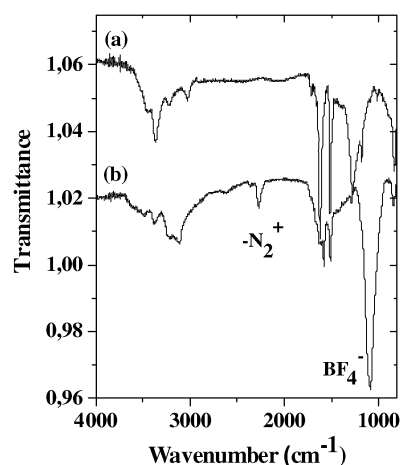
#### Diazotisation of the PAP films: “self-adhesive surfaces” preparation

The diazotisation of the grafted PAP layer obtained on the gold substrates was performed either in aqueous or in organic medium. In aqueous medium, the PAP layer was soaked for 60 s in an equal volume of  $\text{NaNO}_2$  0.1 M and  $\text{HCl}$  0.5 M, then rinsed with dry DMF.

The resulting polydiazophenylene (PDP) films were analyzed by IR-ATR as shown on Fig. 4. Bands at  $2270$  and  $1088\text{ cm}^{-1}$  are respectively attributed to aryldiazonium stretching and to the  $\text{BF}_4^-$  group vibration when treated in acetonitrile with  $\text{NOBF}_4$ . When treated in aqueous medium with  $\text{NaNO}_2/\text{HCl}$  the band at  $1088\text{ cm}^{-1}$  is of course absent since the counter-ion is now the IR-silent chloride ion. In both cases the almost complete disappearance of the  $\text{NH}_2$  ( $1617\text{ cm}^{-1}$ ) and  $\text{NH}$  ( $3370\text{ cm}^{-1}$ ) bands confirms the diazotisation.

#### Stability versus activation of polydiazophenylene

Since aryldiazonium salts are generally unstable compounds, storage in a cold and dark place is required. Therefore, it is important to evaluate the lifetime of grafted aryldiazonium salts. The results are shown in Fig. 4. Two hours at  $50^\circ\text{C}$  are enough to observe complete disappearance of the IR signals from the aryldiazonium salts previously formed on the surface. Few minutes under UV light (200W) give the same result. The mechanism probably proceeds *via* phenyl cations which give phenols *via* interaction with ambient water in air.<sup>15,36,37</sup> At room temperature, a sample left for 24h at  $22^\circ\text{C}$  and 45% RH (relative humidity) exhibited no remaining aryldiazonium signature. Consequently, it is advisable to use only freshly prepared aryldiazonium-rich surfaces. Otherwise, self-adhesive surfaces should at least be stored in dry atmosphere in a cold and dark place. That poor thermal stability may however be used to



**Fig. 4** Upper part. IR-ATR spectra of: (a) Polyaminophenylene (PAP), (b) Polydiazophenylene (PDP) film acting as self-adhesive surface. Lower part. Stability versus activation of self-adhesive surfaces. Graph shows the IR aryldiazonium band intensity. (a) At room temperature ( $22^\circ\text{C}$  and 45% RH), (b) Heated at  $50^\circ\text{C}$ , (c) Irradiated with UV light (200 W).

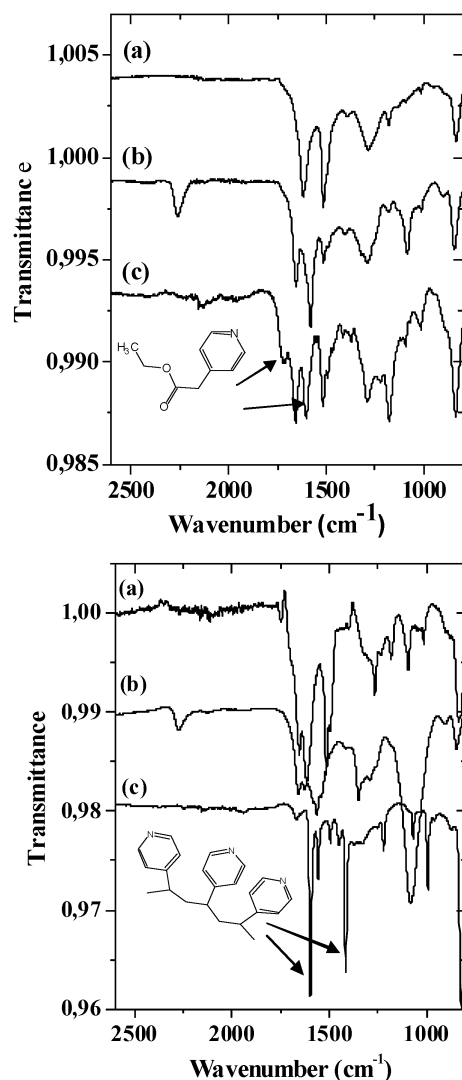
advantage to deliberately decrease the amount of grafted diazonium salts on the surface. Indeed, a simple moderate heating step followed *in situ* by IR absorption will result in an accurate control of the final surface coverage. That property may be useful when a limited number of anchoring sites is required, as for graphitic compounds (nanotubes or graphene flakes), for which conductivity may be significantly affected by a high density of covalent attachments to the surface.

#### Grafting of nitrogenated organic compounds

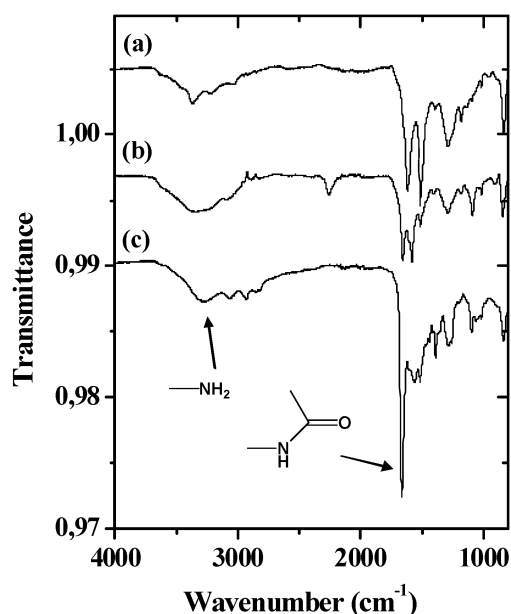
Electrophilic properties of aryldiazonium-rich surfaces were used to graft pyridine-based compounds and polyamidoamine (PAMAM) dendrimers. The well-known spontaneous reactivity of aryldiazonium salts towards pyridine allowed us to successfully graft 4-vinyl pyridine, acetyl pyridine, ethyl-4-pyridylacetate and poly-4-vinyl pyridine ( $\text{P}_4\text{VP}$ ) onto self-adhesive gold substrates. The freshly prepared self-adhesive surfaces were simply soaked for 30 s in the pyridine derivative (either pure or diluted in non-reactive solvent as acetonitrile). With  $\text{P}_4\text{VP}$ , a spin coating procedure was carried-out: a spin cast solution of  $\text{P}_4\text{VP}$  2% in DMF was added dropwise on the self-adhesive surface just

before spinning (2000 rpm, 120 s). In all cases, IR analyses were performed after ultrasonic treatment with various solvents (alcohol, acetone, acetonitrile, DMF) to discard any ungrafted matter. Fig. 5 gives the resulting spectra for ethyl-4-pyridylacetate and P<sub>4</sub>VP, which confirm the immobilization of the corresponding moieties together with the corresponding disappearance of the IR signature of the aryldiazonium salts: The characteristic IR bands at 1600 cm<sup>-1</sup> for pyridine ring and 1730 cm<sup>-1</sup> for acetate group are easily observed and resist the rinsings. Results are similar with 4-vinyl pyridine and acetyl pyridine (not shown).

In the case of the PAMAM dendrimer, the reactivity of aryldiazonium salt with amine groups was turned to account. The commercial PAMAM solution (10% in methanol) was added dropwise on a fresh aryldiazonium-rich sample and left for



**Fig. 5** Upper part. IR-ATR spectra of: (a) Polyaminophenylene (PAP) initial surface, (b) Polydiazophenylene (PDP) surface treated with NaNO<sub>2</sub> in acidic water, (c) Spectra of grafted ethyl-4-pyridylacetate on PDP surface. Lower part. IR-ATR spectra of: (a) Polyaminophenylene (PAP) initial surface, (b) Polydiazophenylene (PDP) surface treated with NOBF<sub>4</sub> in acetonitrile, (c) Spectra of grafted poly-4-vinylpyridine on PDP surface.



**Fig. 6** IR-ATR spectra of (a) Polyaminophenylene (PAP) initial surface, (b) Polydiazophenylene (PDP) surface treated with NaNO<sub>2</sub> in acidic water, (c) Spectra of grafted PAMAM on PDP surface.

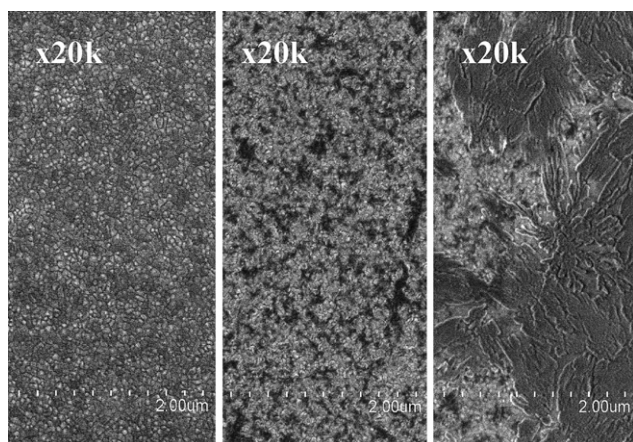
1 minute. After abundant rinsing with DMF, IR analysis shown on Fig. 6 exhibited characteristic bands at 3272 and 1666 cm<sup>-1</sup> for respectively amine and amide groups and no peak at 2270 cm<sup>-1</sup>, which indicates that aryldiazonium salts reacted with amine groups from PAMAM.

We thus showed that nucleophilic compounds such as pyridine derivatives or amines could be easily immobilized on to gold surfaces *via* spontaneous reaction with primer aryldiazonium-rich films. The chemical mechanisms for those reactions are out of the scope of this article and will not be discussed. However, RMN studies are in progress to assess whether copulation, electrophilic addition or S<sub>N</sub>1 mechanisms are involved when similar reactions are performed in solution.<sup>19,36,38</sup>

### Grafting of copper nanoparticles

As already shown by Pinson,<sup>18</sup> aryldiazonium salts spontaneously graft on copper surfaces. It would thus make sense that copper particles react with aryldiazonium-rich surfaces and graft following the same redox mechanism.

Copper nanoparticles were synthesized by the following procedure: in a flask, 50 ml CuSO<sub>4</sub> aqueous solution (250 mg CuSO<sub>4</sub>·5H<sub>2</sub>O in 50 mL H<sub>2</sub>O) was mixed with 2 g of surfactant HEA16Cl (N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl) ammonium chloride) under magnetic stirring for several minutes to obtain a homogeneous solution. Then, we introduced the NaBH<sub>4</sub> solution (previously prepared by dissolving 150 mg NaBH<sub>4</sub> in 2 ml pure water) into the flask. The agitation was stopped after obtaining a blue-black solution. Once the colour changed to red-black, the diazotised samples were soaked into the solution for a given time (5, 10, 30 s, respectively) and then were rinsed with pure water. Reference surfaces (pristine gold surface and gold/PAP surface) were treated similarly to check if any spontaneous immobilization of copper nanoparticles occurs. Resulting SEM



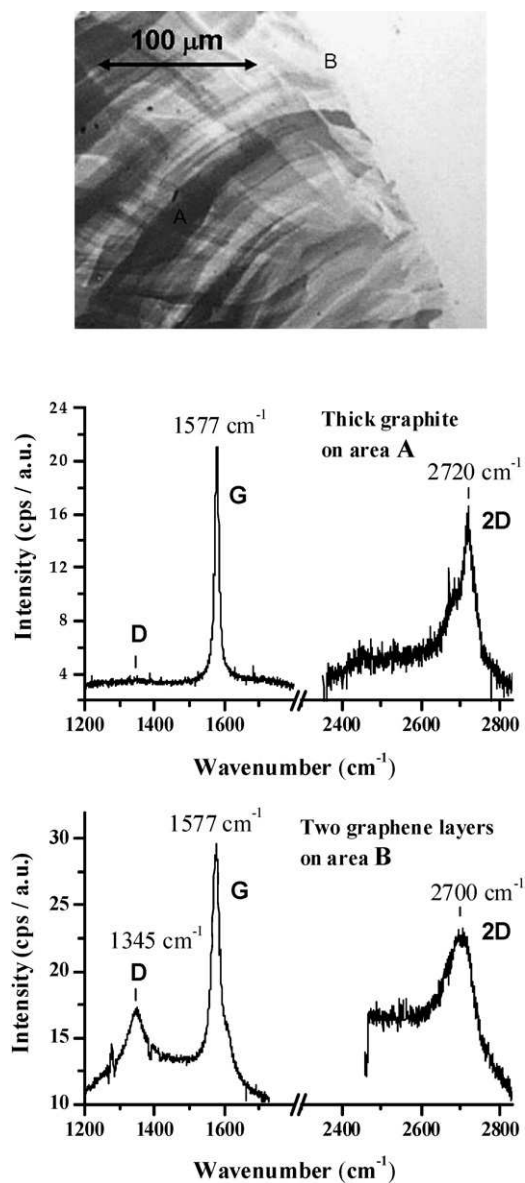
**Fig. 7** SEM images of grafted copper nanoparticles. All surfaces have been immersed in copper nanoparticles solution. From left to right: Pristine gold polymicrocrystalline surface, primer PAP surface, PDP surface (from treatment of the PAP surface with  $\text{NaNO}_2$  in acidic water for 30 s).

images are showed on Fig. 7. The diazotised surface clearly shows dendritic copper features, which are absent on both reference surfaces. Although the deposition is obviously inhomogeneous (resulting from non-optimized conditions), this result undoubtedly proves the efficiency of self-adhesive surfaces for metallic nano-objects immobilization. The process may for example be extended to palladium particles as catalyst for further electroless metallization.

### Grafting of graphene sheets and MWCNTs

Carbon nanotubes and graphene are currently exhibiting growing interest as potential future components of nano-electronic devices. Various methods for controlled immobilization of those carbon-based nano-objects have already been proposed,<sup>25,39,40</sup> which generally rely on preliminary chemical modification. Self-adhesive surfaces could provide an easier way to graft carbon-based nano-objects on surfaces, and avoid pre-treatments of the nano-object surfaces themselves. The following text shows that diazonium-rich surfaces prepared as described above are efficient for carbon-based nano-object immobilization. Multi sheets of graphene ( $1 \times 1$  cm) were adhesively transferred from a commercial block of HOPG onto a desk adhesive tape. Then these graphene sheets were applied directly to a Au/PDP surface. A simple adjustable pinch clip was used to exert a mechanical pressure and the system was placed in a drying oven at  $100^\circ\text{C}$  for one hour. With this treatment, graphene sheets were transferred on the surface and were optically detectable. Treatment by ultrasound in acetone allowed exfoliation of the thickest parts and left blocks of few tens of graphene flakes, as estimated by mechanical profilometer.

Fig. 8 shows the on top microscope view of the specific superposed drapery shape of multilayer graphene flakes deposited on the surface. RAMAN spectra registered on area “A” (seen as dark on Fig. 8) shows band centred at  $1577\text{ cm}^{-1}$  (G-band) and  $2720\text{ cm}^{-1}$  (2D second order band) attesting the presence of pure graphite.<sup>38</sup> On this place, thickness was sufficient to fit graphite characteristics. RAMAN spectra registered



**Fig. 8** Upper part. microscope view of graphene flakes grafted on self-adhesive surfaces. Lower part. MicroRaman spectrum registered on area “A” and “B”.

on area “B” (seen as light grey on Fig. 8) shows an additional band at  $1344\text{ cm}^{-1}$  (D-band) together with the band at  $1577\text{ cm}^{-1}$ . Moreover, the high-energy band was shifted to  $2700\text{ cm}^{-1}$ . This latter feature stems for the presence of only few graphene layers. According to Ferrari’s work, that shift is consistent with a two-graphene-layer thickness in the area “B”.<sup>41</sup> Furthermore, the peak at  $1344\text{ cm}^{-1}$  was typically attributed to a disorder-induced band and is not present in the Raman spectrum of single-crystal graphite. Concerning HOPG the grafting on  $\text{sp}^2$  orbitals have been discussed together with the relative ability to edge-plane sites or basal-plane sites to form bonds with aryl radical species.<sup>42</sup> Pinson also observed when electrografting diazonium salts that graphite carbon surface (with crystallographic defaults) is more reactive than the basal plane of HOPG (with no or few defaults). But at the end the diazonium salts are found strongly attached

both on graphite carbon and HOPG.<sup>43</sup> More recently numerous studies were performed on CNT using Raman spectroscopy. The disorder-induced D-band intensity undoubtedly increases with the functionalization with diazonium salts,<sup>44,45</sup> i.e. with the  $sp^2$  to  $sp^3$  transition. Although CNTs are known to be more reactive than flat HOPG, because of the torsion, we consider that HOPG can react with diazonium salts heated up to 100 °C (our experimental conditions). Therefore, we consider that this band at 1344  $cm^{-1}$  may be the Raman signature of defects on the  $sp^2$  framework corresponding to the grafting sites with the underlying polyphenylene primer.

Multi-wall carbon nanotubes (MWCNTs) of external diameter ranging between 4 and 15 nm were suspended at 0.3 mg/ml in N-methylpyrrolidinone then exposed to ultrasound (100 W) for 6 hours to lead to a stable dispersion. Centrifugation at 7000 rpm separated the larger aggregates. An Au/PDP surface was immersed in 10 ml of the supernatant. The medium was gradually heated at 5 °C/mn up to 100 °C under stirring. After 12 hours, the sample was withdrawn then thoroughly rinsed with ethanol and acetone. Surfaces thus treated were analyzed by SEM. Fig. 9 clearly shows MWCNTs immobilized on the substrate.

#### Grafted aryldiazonium salts as electropolymerization initiator

The chemistry of aryldiazonium salts is not limited to coupling reactions. Indeed, aryldiazonium salts are also considered as good electropolymerization initiators.<sup>46</sup> That property was turned into account in our recent publications, where “free” aryldiazonium salts were used as initiators for vinylic polymerization in the SEEP and DIAP electrografting processes.<sup>34,35,47</sup> With aryldiazonium-rich surfaces, “grafting-from” polymerization processes can be promoted provided the aryldiazonium salts evolution is triggered. Hence, grafted aryldiazonium salts could be electrochemically reduced (in acid aqueous medium or organic medium) to generate grafted radicals able to initiate a “grafting from” polymerization process. For better chemical stability of the diazotised surfaces, we worked in acetonitrile. Methyl methacrylate (MMA) was selected as monomer. The

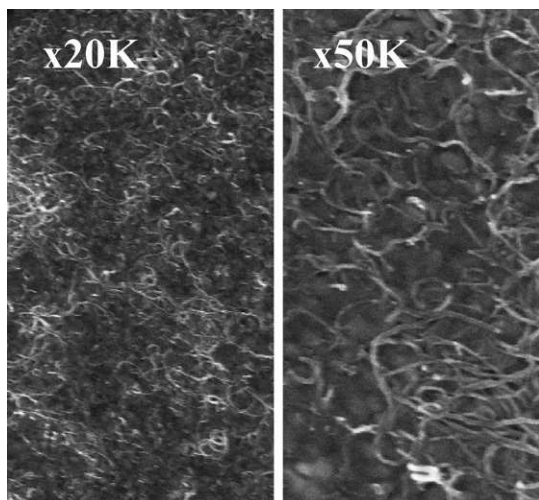


Fig. 9 FEG-SEM images of grafted MWCNT on self-adhesive surfaces.

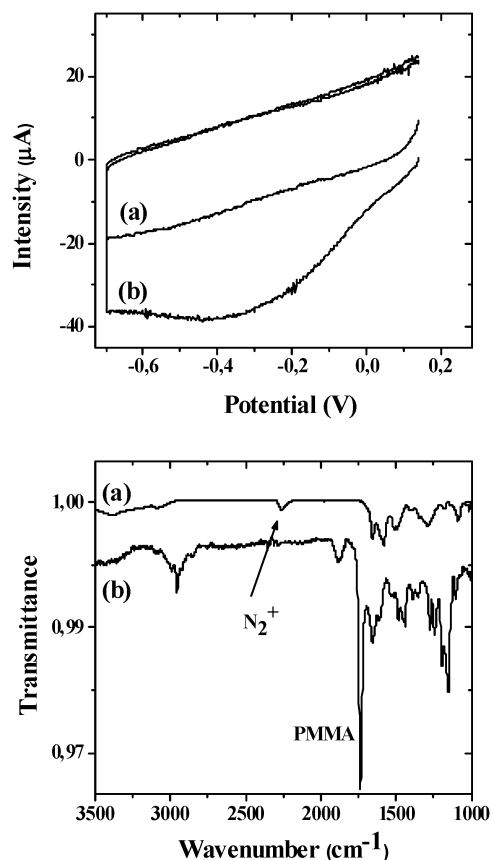


Fig. 10 Upper part. (a) Voltammogram obtained on a gold initial surface, (b) Voltammogram obtained on a self-adhesive surface. Lower part. (a) IR spectra of the initial polydiazophenylene (PDP) surface, (b) IR spectra of the grafted surface from electro-induced polymerization of MMA after ultrasound treatment. (Estimated thickness of the grafted film: 20 nm).

voltammograms recorded on a non-diazotised and on a diazotised surface are given on Fig. 10. In the latter case the peak at  $-0.4V$  is attributed to the aryldiazonium reduction. The recorded intensity and the corresponding estimated Coulombic charge roughly correspond to the reduction of few compact layers of aryldiazonium.<sup>48</sup> The final cathodic potential was high enough to avoid direct electropolymerization, which generally requires potentials below  $-2V$ .<sup>49</sup> Fig. 10 gives the IR spectra recorded on the pristine diazotised surface and the same after electropolymerization with MMA. The latter clearly demonstrates PMMA grafting, with a  $C=O$  peak at  $1745\text{ cm}^{-1}$  and no remaining peak in the aryldiazonium salt region. A PMMA thickness of about 30 nm could be estimated from the IR intensity. MMA polymerization was thus initiated at the surface by species resulting from immobilized aryldiazonium salts reduction. These preliminary results demonstrate a new graft polymerisation route based on easily immobilized precursors.

#### Conclusion

We have described in this article a new, simple and powerful method to obtain surfaces grafted with aryldiazonium groups. These “self-adhesive surfaces” take advantage of the versatile



chemical reactivity of aryldiazonium salts to graft various chemical materials such as molecules, macromolecules, polymers, copper nanoparticles as well as MWCNT and graphenes. Electro-initiated “grafting-from” polymerization was also demonstrated with the same “aryldiazonium-rich” surfaces. Aryldiazonium-based “self-adhesive surfaces” thus constitute a new versatile platform for nano-object immobilization and tailor-made surface modification that ensures both robustness and homogeneity.

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