Electrografting of methylamine through C-H activation or oxidation to give highly aminated surfaces

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Abstract.

Three different methods are proposed to obtain surfaces (glassy carbon, gold, iron, copper) modified with either primary or secondary amino groups. The electrochemical C-H activation of CH_3NH_2 gives *Surface*-(CHNH_2)_n structures. The same reaction applied to CH_3NO_2 leads to *Surface*-(CHNO_2)_n that can be electrochemically reduced to *Surface*-(CHNH_2)_n. The C-H activation takes place by H abstraction from CH_3NH_2 or CH_3NO_2 by the 2,6-dimethyl phenyl radical, which does not react with surfaces and therefore does not interfere in the surface modification. The electrochemical oxidation of methylamine provides *Surface*-(NHCH_3)_n. These films are characterized by electrochemistry, IR, XPS and AFM.

Graphical abstract

Highlights

• Highly aminated surfaces

- Electrografting of nitromethane and methylamine
- Indirect electrografting via 2,6-dimethyl benzenediazonium

Keywords: Electrografting, nitromethane, methylamine, H-abstraction, diazonium.

1. Introduction

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Amination of surfaces is used in several domains such as adhesion/antifouling of proteins [1], surface bonded complexing groups [2], catalysis [3], drug release [4] and formation of hybrid materials [5]. The attachment of these groups can be achieved starting from diazonium salts, thiols, silanes, cysteine and plasmas. This paper presents three methods to obtain highly aminated surfaces: i) the C-H activation of CH_3NH_2 , ii) the same reaction applied to CH_3NO_2 followed by reduction and, iii) the direct oxidative electrografting of CH_3NH_2 .

Activation of C-H bonds is the subject of much current interest in organic chemistry [6]; it generally involves transition metal catalysts, but radical chemistry also permits it, *i.e.* hydrogen abstraction from RH by $\text{Ar}^\bullet$ to give ArH and a new radical $\text{R}^\bullet$ [7]. The generation of radicals can be achieved through oxidation and loss of a proton [7], and also by reduction and loss of a neutral molecule (*i.e.* from diazonium salts) or an anion (*i.e.* from organic halides) [8]. Upon homolytic cleavage, diazonium salts (ArN_2^+) provide an interesting source of aryl radicals ($\text{Ar}^\bullet$) [9]; this cleavage can be accomplished by electrochemistry [10], photochemistry [11] (*i.e.* $\text{Ar}^\bullet$ reacts with alkynes [12] or porphyrins [13]), by thermal activation (*i.e.* $\text{Ar}^\bullet$ reacts with aniline and pyrroles [14]) or basic medium [15].

The activation of C-H and also C-Br, C-I bonds towards radical chemistry can be used in surface chemistry. The $\text{Ar}^\bullet$ radicals obtained from the homolytic dediazonation of diazonium salts can activate $\text{R-CH}_2\text{-H}$, $\text{R-CH}_2\text{-Br}$, $\text{R-CH}_2\text{-I}$ bonds through H, I or Br abstraction to produce new $\text{R-CH}_2^\bullet$ radicals that react with surfaces to give functionalized surfaces (**Surface-CH₂-R**), as shown in Scheme 1A. To graft $\text{R-CH}_2^\bullet$ only, $\text{Ar}^\bullet$ must be prevented from reacting on the surface. This is possible by taking advantage of steric effects owing to the 2,6-dimethylbenzenediazonium (2,6-DMBD) that leads to the 2,6-dimethylphenyl radical. This radical does not react with surfaces due to the steric hindrance of the two methyl groups [16]. When reducing 2,6-DMBD different compounds such as CH_3CN (acetonitrile, ACN) [17], ICH_2CN [18], $\text{I(CH}_2)_2\text{C}_6\text{F}_{13}$ (1-iodo-1H,1H,2H,2H-perfluorooctane), $\text{I(CH}_2)_5\text{CH}_3$ (iodohexane) [19], $\text{Br(CH}_2)_5\text{-COOH}$ (bromovaleric acid) [20,21] can be grafted to carbon, gold, and polymer surfaces. The use of other aryldiazonium salts instead of 2,6-DMBD permits the formation of bifunctional alkyl-aryl layers [22]. The activation of C-I bonds was also performed starting from aryl iodides at the reduction potential of 2,6-DMBD, which is

much more positive than those of the aryl iodides [23,24]; the resulting aryl radicals were attached on gold and glassy carbon (GC) surfaces.

In the present paper, we report the indirect grafting, through C-H activation, of $\text{CH}_3\text{-NH}_2$ (Scheme 1A, $\text{R} = \text{NH}_2$) where the same carbon atom will be bonded to the surface and to the functional NH_2 group. Further reaction of $\cdot\text{CH}_2\text{NH}_2$ should lead to highly aminated surfaces

through hydrogen atom abstraction (either by $\cdot\text{CH}_2\text{NH}_2$ or the 2,6-DMBD radical). We

compare this reaction to the activation of CH_3NO_2 followed by reduction of the nitro to amino group (Scheme 1B). Finally, we compare these films with that obtained by electro-oxidation of methylamine (Scheme 1C). The homolytic dediazonation of 2,6-DMBD (Scheme 1A), the reduction of the nitro to amino group (Scheme 1B) and the oxidation of methylamine (Scheme 1C) were performed by electrochemistry. The reactions presented in Scheme 1 are based on previous indirect grafting experiments [17-23] and on the mechanism established for the electrografting of amines [25-27]. The substrates are Au, Cu, Fe and GC. The modified surfaces (GC for example) will be referred as $\text{GC-CH}_2\text{NO}_2$, as $\text{GC-CH}_2\text{NH}_2$ after reduction and as GC-NHCH_3 when obtained by oxidation.

Scheme 1. Grafting through A, B) C-H, C-I, C-Br activation with a sterically hindered aryl radical obtained by reduction of the corresponding diazonium salt. C) oxidation of methylamine.

2. Experimental

2.1. Chemicals

CH_3NH_2 (40% w/w in water), CH_3NO_2 , 2,6-dimethylaniline and trifluoroacetic anhydride were obtained from Sigma Aldrich. Nitromethane was purified by passing through a silica column. Acetonitrile was purified with a PureSolv system. To prepare 2,6-DMBD, on one hand 40 mmol (4.84 g) of 2,6-dimethylaniline were dissolved in 100 mL of 25% HBF_4 in H_2O and on the other hand 48 mmol (3.30 g) of NaNO_2 were dissolved in the minimum amount of water; both solutions were cooled in an ice bath. Upon dropwise addition of NaNO_2 a pale yellow precipitate was obtained. It was rinsed with ether (cooled at -20°C). The solid was dried under vacuum. [19] The purity of the compound was about 60% (measured by NMR).

2.2. Surfaces.

The Au coated (100 nm) Si wafers were obtained from Sigma-Aldrich. Before modification, they were rinsed in concentrated sulfuric acid, ultrasonicated in Milli-Q water for 8 min, cleaned with pure ethanol, and dried under a stream of argon. The GC plates were obtained from Sigradur (Germany). Cu and mild steel plates (Fe) were commercial samples. They were polished with a $0.04\ \mu\text{m}$ alumina slurry, rinsed in pure ethanol and dried under a stream of nitrogen. The Fe plates must be used immediately to prevent oxidation. The electrodes for cyclic voltammetry were GC rods (3 mm diameter, Tokai, Japan) gold, copper and mild steel wires (1 mm diameter) sealed in glass. They were polished as above.

2.3. Electrografting

It was performed in a 3 electrodes cell with a carbon paper as counter electrode and a saturated calomel electrode (SCE) as a reference. Both voltammetry and electrografting experiments were performed with an EG&G 263A potentiostat/galvanostat and Echem v 4.30 software. All experiments were carried out in ACN, H_2O or CH_3NO_2 solutions deoxygenated with nitrogen. After electrografting all the surfaces were sonicated in EtOH for 3 min to remove any adsorbed material and kept under Ar to prevent reaction of the amino groups with CO_2 . Different samples were left in boiling toluene for 1 h without significant loss of the grafted film. The pH of 5 mM 2,6-DMBD + 20 mM CH_3NH_2 in aqueous solution is 11.5.

2.4. IR

The IRRAS and ATR spectra of modified plates were recorded using a purged (low CO_2 , dry air) Jasco FT/IR-6100 Fourier Transform InfraRed spectrometer equipped with MCT

(mercury–cadmium–telluride) detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm^{-1} . The background recorded before each spectrum was that of a bare substrate. ATR and IRRAS spectra were recorded with Jasco accessories (ATRPR0470-H equipped with a germanium crystal and RAS PRO410-H, respectively).

2.5. XPS

XPS measurements were performed using a K Alpha system (Thermo Fisher Scientific, East-Grinstead, UK) fitted with a microfocused and monochromatic Al K α X-ray source (1486.6 eV, spot size: 400 μm). The pass energy was set to 150 and 40 eV for the survey and the high-resolution spectra, respectively. The spectra were calibrated against the C–C/C–H C 1s component set at 285 eV. The chemical composition was determined with version 5.9902 Advantage software, by using the manufacturer sensitivity factors. The spectra were calibrated against C 1s set at 285 eV.

2.6. Ellipsometry

Thicknesses of the films on Au were measured with a mono wavelength ellipsometer Sentech SE400. The following values were taken for gold: $n_s = 0.17$, $k_s = 3.43$; they were measured on the clean surfaces before grafting. The film thicknesses were determined from the same plates after modification, taking $n_s = 1.46$, $k_s = 0$ for the organic layer.

2.7. AFM

AFM images were recorded with a NT-MDT Solver pro equipment. AFM topography was performed in the intermittent contact mode with standard silicon cantilevers. Image analysis was achieved with the free software WSxM.

2.8 Modeling

The surface model used was either a C(111) [supercell dimensions of: $15.133 \times 15.133 \times 6.135\text{ Å}^3$] or an Au(111) [supercell dimensions of: $11.535 \times 11.535 \times 7.844\text{ Å}^3$] plane with 4 slab layers and a 20 Å vacuum layer on the C axis (containing one monomeric grafted nitromethane moiety). The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof functional (PBE) at PBE level of calculation under periodic boundary conditions as implemented in Dmol3 software. All electron, spin unrestricted calculation employed a double numeric polarized (DND) basis set.

3. Results and Discussion

3.1. Surface modification with CH_3NH_2 in the presence of 2,6-DMBD

3.1.1. Cyclic voltammetry and redox probes

The indirect electrografting of CH_3NH_2 was carried out in ACN and aqueous solutions. The electrochemical behavior of Au and GC electrodes in ACN + 20 mM 2,6-DMBD + 100 mM CH_3NH_2 is shown in Fig. 1. Upon repetitive scanning the irreversible reduction wave of 2,6-DMBD decreases and comes close to the background after 3 cycles. Since it has been shown previously that the radical obtained after reduction of 2,6-DMBD cannot react with the surface [16] this means that another reaction takes place that blocks the electrode.

The GC grafted electrode was transferred to an ACN + 0.1M NBu_4BF_4 solution. A weak oxidation wave at 0.97 V vs SCE is assigned to the oxidation of the amino group (Fig. S1 in SI).

The same treatment applied to a gold plate leads -after ultrasonic rinsing- to an attached film, $\text{Au-CH}_2\text{NH}_2$, the thickness of which, measured by ellipsometry, is 6.1 ± 0.7 nm, indicating the formation of multilayers; since a molecular model indicates that a fully extended oligomer with 10 CH-NH_2 groups is 1.5 nm long, the thickness of the film corresponds to ~ 40 repeating units. The presence of a passivated layer on the grafted GC and Au electrodes is attested by redox probes (Fig. S2 in SI): the electrochemical signal of ferricyanide is inhibited on the modified electrodes.

Fig. 1. Cyclic voltammetry of 20 mM 2,6-DMBD + 100 mM CH_3NH_2 + 0.1 M NBu_4BF_4 in ACN on A) a GC electrode ($d = 3$ mm); a) 1st; b) 2nd; c) 3rd and d) 4th scan. B) an Au electrode ($d = 1$ mm); a) 1st, b) 2nd scan. $v = 0.1$ V/s. e) in the absence of 2,6-DMBD.

3.1.2. IRRAS

The IRRAS spectrum of $\text{Au-CH}_2\text{NH}_2$ ($s = 1 \text{ cm}^2$, Fig. 2Ab) (prepared in aqueous solution) and recorded immediately after grafting (to prevent reaction with CO_2) presents a band at

1590 cm^{-1} attributed to the NH deformation of methylamino groups grafted on the gold surface (by comparison, methylamine: 1605 cm^{-1} [28]). A band at 1470 cm^{-1} is attributed to the scissoring of methylene groups. In the absence of 2,6-DMBD, these IR bands are much weaker (Fig. 2Aa). The NH stretching vibration is difficult to observe due to the presence of adventitious bands in this region. However, if the $\text{Au-CH}_2\text{NH}_2$ plate is left overnight in trifluoroacetic anhydride, $\text{Au-CH}_2\text{-NH-C=O-CF}_3$ is formed; it is characterized by strong bands at 1789, 1696 cm^{-1} (C=O, by comparison, C=O bands in trifluoroacetic acid: 1783, 1670 cm^{-1}) and 1219, 1169 cm^{-1} (CF_3 , by comparison, bands in trifluoroacetic anhydride: 1244, 1191 cm^{-1}) [28].

Fig. 2. IRRAS spectrum of A) a gold plate ($s = 1 \text{ cm}^2$) modified with methylamine (20 mM) Aa) in the absence, Ab) in the presence of 2,6-DMBD (5 mM) in $\text{H}_2\text{O} + 0.1\text{M KCl}$, 20 scans between 0.3 V and -0.8 V/SCE, $v = 0.1 \text{ V/s}$; spectra recorded immediately after grafting. B) the same plate left overnight in trifluoroacetic anhydride (200 μL in 10 mL THF).

The redox potential of Fe or Cu ($E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.68 \text{ V/SCE}$ and $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.10 \text{ V/SCE}$) permits the spontaneous reduction of 2,6-DMBD and consequently the grafting of methylamine. A polished Cu or Fe plate was immersed for 1 h in 40% CH_3NH_2 aqueous solution in the presence of 50 mM 2, 6-DMBD; the IRRAS spectra presented in Fig. S3 in SI indicate the success of the grafting reaction.

3.1.3. XPS

The XPS survey spectra of $Au-CH_2NH_2$ (prepared in aqueous solution) and $Au-CH_2NHC(=O)CF_3$ (maintained under argon before recording) (Fig. 3A) are presented in Table 1. **Au4f is present in agreement with the thickness of the film (<10nm).** C1s presents three components due to CH_2 , C-O and C-N, C=O (due to some carbonyl groups of unknown origin and the carbonyl group of $Au-CH_2NHC(=O)CF_3$) and CF_3 . N1s presents a single component due to the amine and the amide. F1s is observed in $Au-CH_2NHC(=O)CF_3$. For comparison, the spectrum of an unmodified gold plate is presented in Fig. S4 in SI.

Table 1. XPS spectra of $Au-CH_2NH_2$ and $Au-CH_2NHC(=O)CF_3$

	$Au-CH_2NH_2$ eV (%)	$Au-CH_2NHC(=O)CF_3$ eV (%)	Assignment
Au4f	84.2 (34.9)	84.2 (24.9)	Substrate
C1s	285.2 (41.7)	285.0 (34.2)	CH_2 , contamination
	286.9 (7.8)	286.7 (10.2)	C-O, C-N
	288.9 (3.2)	289.2 (4.8)	C=O
		293.0 (2.2)	CF_3
N1s	400.5 (3.7)	400.7 (4.9)	NH_2 , $NHC(=O)CF_3$
F1s		688.9 (8.6)	CF_3
O1s	532.9 (8.8)	532.4 (10.2)	OH, C=O, contamination

The spontaneous grafting of Au is confirmed even if less efficient, as indicated by the lower % of N1s (400.1 eV, 2.3%, Table S2 and Fig. S5A in SI). Such spontaneous grafting is likely due to the homolytic cleavage of either the diazohydroxide salt (derived from diazonium in a basic medium) or of the triazene obtained by nucleophilic attack of the amine on the diazonium salt [15]. The XPS spectrum of $CuCH_2NH_2$ obtained by spontaneous grafting is presented in Table S2 and Fig. S5B in SI. The N1s contribution can be deconvoluted with two signals at 400.0 and 398.3 eV, the last one corresponds to a nitride (by comparison 397.7 eV for Ni-N [29]) indicating a direct attack of the NH_2 group of methylamine on the Cu surface ($CuNHCH_3$) as already observed [30] in competition with the radical reaction.

Fig. 3. A,B) XPS survey spectra of A) $Au-CH_2NH_2$ plate modified with methylamine (20 mM) + 2,6-DMBD (5 mM) in $H_2O + 0.1M KCl$, 20 scans between 0.3 V and -0.8 V/SCE, $v = 0.1 V/s$; insert N1s contribution B) $Au-CH_2-NH-C=O-CF_3$ plate; insert F1s contribution.

3.1.4. AFM

The AFM images of $Au-CH_2NH_2$ (Fig. S6A-C in SI) also point to the modification of the surface; on the bare electrode the nano-crystalline domains of the PVD deposited gold are clearly visible, they are blurred after modification while high protruding features are observed. These different results support the grafting of CH_2-NH_2 groups on the surface.

3.2. Surface modification with CH_3NO_2 in the presence of 2,6-DMBD

3.2.1. Cyclic voltammetry

Nitromethane [31] can be used as an electrochemical solvent in spite of its limited cathodic electroactivity domain down to $\sim -1 V/SCE$ (Fig. S7 in SI). This domain is large enough to record the voltammograms of 2,6-DMBD (20 mM) on GC and Au electrodes (Fig. 4A and B) and on Cu and Fe electrodes (Fig. S8 in SI). Note that with Cu and Fe electrodes the voltammetric scan must be started at a potential more negative than their ocp due to their

redox potentials [32]. In the four cases, the reduction wave of 2,6-DMBD decreases upon repetitive scanning and comes close to the background after 4 cycles.

Fig. 4. Cyclic voltammetry of 20 mM 2,6-DMBD + 0.1 M NBu_4BF_4 in CH_3NO_2 on A) a GC electrode ($d = 3$ mm) and B) Au electrode ($d = 1$ mm) a) first cycle, b) successive cycles and c) in the absence of 2,6-DMBD. $v = 0.1$ V/s.

The voltammogram of a GC modified electrode transferred to an ACN + NBu_4BF_4 solution (Fig. 5, $E_{\text{pc}} = -1.73$ V/SCE) was compared to that of CH_3NO_2 in the same solvent (irreversible, $E_{\text{pc}} = -1.82$ V/SCE, $n = 1$ by comparison with ferrocene); the similarity of the peak potentials indicates the grafting of nitromethane on the surface.

Fig. 5. Cyclic voltammetry in ACN + 0.1 M NBu_4BF_4 of a) 1.85 mM CH_3NO_2 on a GC electrode ($d = 3$ mm), b) $\text{GC-CH}_2\text{NO}_2$; grafting through 10 voltammetric cycles between 0.3 and -0.5 V/SCE. Normalized voltammograms, arbitrary current units. $v = 0.1$ V/s.

The presence of a film on $\text{GC-CH}_2\text{NO}_2$ and $\text{Au-CH}_2\text{NO}_2$ was tested with redox probes (Fig. S9 in SI). The complete absence of the ferricyanide system indicates, as above, that their surfaces are entirely blocked.

The thickness of $Au-CH_2NO_2$, measured by ellipsometry is 5.6 ± 1.8 nm that corresponds to ~ 36 monomeric units (length of 10 fully extended CH_2-NO_2 groups from molecular models: 1.5 nm). The water contact angle of the modified plate is $67.2 \pm 2.4^\circ$.

3.2.2. IRRAS

The IRRAS spectra of $Au-CH_2NO_2$ and $Cu-CH_2NO_2$ (Fig. 6) show the strong asymmetric and symmetric stretching bands of the NO_2 group at 1560 and 1370 cm^{-1} and the scissoring NO_2 band for $Cu-CH_2NO_2$ at 635 cm^{-1} (not shown) (by comparison 1558 , 1377 and 668 cm^{-1} for CH_3NO_2 [33,34]). A similar spectrum (not shown) is obtained on Fe (1560 , 1378 cm^{-1}). In the absence of 2,6-DMBD there is no signal of the NO_2 group (Fig. S10 in SI).

Fig. 6. IR spectra of a) CH_3NO_2 (ATR), b) $Cu-CH_2NO_2$ (IRRAS) and c) $Au-CH_2NO_2$ (IRRAS) obtained in a $CH_3NO_2 + 0.1\text{ M } NBu_4BF_4 + 20\text{ mM } 2,6\text{-DMBD}$ solution. Electrolysis time for Cu and Au plates ($s = 1\text{ cm}^2$): 1200 s at -0.5 V/SCE .

3.2.3. XPS

The XPS spectra of $Au-CH_2NO_2$, $Cu-CH_2NO_2$ and $Fe-CH_2NO_2$ confirm the grafting of the different substrates. The survey spectra are summarized in Table 2. The nitro group (406 eV) is present in the four analyzed samples, indicating the grafting of nitromethane.

Fig. 7 shows high resolution spectra of the $N1s$ region for Cu -, Fe -, and $Au-CH_2NO_2$. Large $N1s$ peaks are present at 406 (nitro group) and $400\text{--}402\text{ eV}$ (amines and protonated amines), but the $N1s(406\text{ eV}) / N1s(400\text{--}402\text{ eV})$ ratio is always very small. This low ratio is related to the reduction of the nitro into an amino group under the XPS beam: with $Au-CH_2NO_2$, the $N1s(406\text{ eV}) / N1s(400\text{--}402\text{ eV})$ ratio decreases by half after a second spectrum [35]. Such reduction of the nitro group is not observed by IRRAS: the spectrum of $Au-CH_2NO_2$ (Fig.

6) does not show the signal of an amine at $\sim 1600\text{ cm}^{-1}$. If the CH_3NO_2 solvent was reduced during electrografting the products should be either removed from the surface during rinsing or, if included in the film, they should be observed in the IRRAS spectrum.

Table 2. XPS spectra of $\text{Au-CH}_2\text{NO}_2$, $\text{Cu-CH}_2\text{NO}_2$ and $\text{Fe-CH}_2\text{NO}_2$.

Sample	Substrate %	C1s %	O1s %	N1s / %		
				400 eV	402 eV	406 eV
$\text{Au-CH}_2\text{NO}_2$	Au4f: 13.2	12.6	66.3	4.7	0.6	0.5
$\text{Cu-CH}_2\text{NO}_2$	Cu2p: 0	62.5	5.8	4.6	0.7	0.5
$\text{Fe-CH}_2\text{NO}_2$	Fe2p: 0	30.9	69.1	1.9	1.8	0.2
$\text{GC-CH}_2\text{NO}_2$		84.3	10.6	3.6	0.5	1.0

3.2.4. Surface concentration of nitro groups

The electrochemical reduction in ACN of the grafted nitro groups on a GC electrode at -1.73 V/SCE (Fig. 5) gives access, by integration of the voltammogram and assuming that all the nitrophenyl groups are electroactive [36], to a high surface concentration of nitro groups: $\Gamma = 77 \times 10^{-10}\text{ mol cm}^{-2}$. Assuming a 36-mer, as estimated above, there should be 2.1×10^{-10} chains per cm^2 . Assuming that the surface is entirely Au(111) it would contain $23.0 \times 10^{-10}\text{ mol cm}^{-2}$ of gold atoms [37], the surface is covered by a chain of $\sim 36\text{ CH}_2\text{-NO}_2$ units every gold atom out of 11.

3.2.5. Stability of the film. The bonding of the film on the surface was tested by rinsing under ultrasonication $\text{Au-CH}_2\text{NO}_2$ and then maintaining it for 2 h in boiling toluene; this resulted in a decrease of the IRRAS absorbance of the 1560 cm^{-1} band by less than 15 %, which indicates a strong bonding between the organic film and gold.

The AFM image of $\text{Au-CH}_2\text{NO}_2$ is shown in Fig. S6B (in SI). As with methylamine, the image permits to observe the grafted film.

Fig. 7. XPS high resolution N1s spectra of Cu, Fe, Au plates ($s = 1 \text{ cm}^2$) modified with CH_3NO_2 in the presence of 2,6-DMBD. 30 scans between -0.5 V and -0.8 V/SCE for Cu and Fe and 5 scans between 0.3 V and -0.8 V/SCE for Au. $v = 0.1 \text{ V/s.}$

3.2.6. Modelisation of the film.

Since all the carbon atoms of $\text{Au-CH}_2\text{NO}_2$ are substituted by a nitro group, including the first one, one could wonder if the steric hindrance could destabilize the structure. A DFT modelization of $\text{C-(CH}_2\text{NO}_2)$ and $\text{Au-(CH}_2\text{NO}_2)_4$ indicates that the grafting is possible; the surface-organic moiety bond lengths are, respectively, $d = 0.15 \text{ nm}$ and 0.24 nm . The latter value is similar to the 0.23 nm Au-C(alkyl) bond length [38], which means that the grafted structure is stable. The Bond Dissociation Energy (BDE) values for the grafted carbon surface ($\text{C}_{\text{surface}}\text{-C}_{\text{bond}}$) is -121.3 kcal/mol and for the grafted gold surface ($\text{Au}_{\text{surface}}\text{-C}_{\text{bond}}$) -34.3 kcal/mol - a value close to that obtained for the valeric acid moiety grafted on gold: $-36.9 \text{ kcal mol}^{-1}$. This means that the binding of the nitromethyl moiety to gold or carbon surface as evaluated by BDE provides a strong interface.

Fig. 8 Modelization of the $\text{C-(CH}_2\text{NO}_2)_4$ structure.

3.2.6. Reduction of the nitro groups to amino groups.

The reduction of the nitro to amino groups was performed by electrochemistry [39,40] (1200 s at $E = -0.5$ V/SCE) on $Au-CH_2NO_2$ in ACN + 0.1M HCl (24 :1) to give $Au-CH_2NH_2$. The NO_2 band located at 1560 cm^{-1} (Fig. 9a) decreases by 70% (Fig. 9b), meaning the reduction to be partial. A NH deformation band appears at 1590 cm^{-1} (by comparison 1590 cm^{-1} for butylamine and $Au-CH_2NH_2$ in Fig. 2). The appearance of NH deformation indicates the conversion of nitro to amino groups. After reduction the thickness of the film remains constant at $\sim 6\text{ nm}$.

Fig. 9. IRRAS spectra of a) $Au-CH_2-NO_2$; b) $Au-CH_2-NH_2$ obtained by partial reduction of $Au-CH_2-NO_2$ (five scans between 0.3 V and -0.8 V/SCE in the presence of 2,6-DMBD, $v = 0.1$ V/s). c) $Au-CH_2-NH-CO-C_6H_4-NO_2$ obtained by reaction of $Au-CH_2-NH_2$ with p- NO_2 -benzoyl chloride. (normalized spectra, arbitrary absorbance units). ($s = 1\text{ cm}^2$).

To ascertain the presence of the amino groups $Au-CH_2-NH_2$ was reacted with 4-nitro benzoylchloride to give $Au-CH_2-NH-CO-C_6H_4NO_2$; its IR spectrum (Fig. 9c) presents the expected nitroaromatic bands at 1528 and 1350 cm^{-1} that are easily distinguished from the starting unreduced aliphatic nitro bands.

The electrochemical transformation of NO_2 groups to amino groups is confirmed by XPS (Fig. 10): there is no signal at 406 eV for $Au-CH_2-NO_2$ (Fig. 10a). After post modification with nitrobenzoyl groups (Fig. 10b) the presence of the aromatic NO_2 group at 406 eV is observed.

Fig. 10. N1s high resolution XPS spectra of of a) $Au-CH_2NH_2$ obtained by reduction of $Au-CH_2NO_2$ (five scans between 0.3 V and -0.8 V/SCE in the presence of 2,6-DMBD, $v = 0.1$ V/s) and b) $Au-CH_2NH-CO-C_6H_4-NO_2$ obtained by reaction of $Au-CH_2NH_2$ with p- NO_2 -benzoyl chloride. ($s = 1$ cm²).

3.3. Surface modification by oxidation of CH_3NH_2

3.3.1. Cyclic voltammetry

The electrochemical oxidation of methylamine on GC (Fig. 11A) exhibits a broad irreversible wave at 1.5 V, which is attenuated during the successive scans due to the electrode surface passivation. The entire voltammogram of methylamine cannot be observed on an Au electrode due to the background at potentials higher than 1.15 V/SCE (Fig. 11 Ba and b).

Fig. 11. Cyclic voltammetry of 50 mM $CH_3NH_2 + 0.1$ M NBu_4BF_4 in ACN on A) a GC electrode ($d = 3$ mm). a) 1st; b) 2nd; c) 3rd; d) 4th and e) 10th scan. B) an Au electrode ($d = 1$ mm); voltammetric scan up to a) 1.15 V and b) 1.20 V; a, b) in the absence of CH_3NH_2 ; c, d, e) after the addition of 50 mM CH_3NH_2 1st; d) 2nd; e); 10th scan. $v = 0.1$ V/s.

The presence of a grafted film on the electrode surface was tested with redox probes under the same conditions as before. The voltammogram of the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple recorded on the GC-NHCH_3 electrode is only partially inhibited by the organic film (Fig. S11A in SI). The inhibition is more efficient, but not complete with the Au-NHCH_3 electrode (Fig. S11B).

A gold plate ($s = 1 \text{ cm}^2$) was grafted by cyclic voltammetry (100 scans) from 0.9 to 1.0 V/SCE in $\text{ACN} + 100 \text{ mM CH}_3\text{NH}_2 + 0.1 \text{ M NBu}_4\text{BF}_4$. The film thickness measured by ellipsometry is $8.7 \pm 1.7 \text{ nm}$ while its water contact angle is $57.2 \pm 4.5^\circ$. Therefore, the oxidation of methylamine provides a film that is thicker but less compact than that obtained by the indirect electrografting of methylamine and nitromethane

3.3.2. IRRAS

The spectrum of an Au-NHCH_3 plate presents a band at 1578 cm^{-1} (Fig. 12) that is attributed to the NH deformations of grafted amino groups ($1580\text{-}1490 \text{ cm}^{-1}$ for secondary amines [41]).

Fig. 12. IRRAS spectrum of an Au-NHCH_3 plate ($s = 1 \text{ cm}^2$) modified by electrochemical oxidation of methylamine (100mM) in $\text{ACN} + 0.1\text{M NBu}_4\text{BF}_4$. 100 scans from 0.9 to 1.0 V/SCE. $v = 0.1 \text{ V/s}$; spectrum recorded immediately after grafting.

3.3.3. XPS

The XPS survey spectrum of Au-NHCH_3 (Fig. 13) is similar to that of $\text{Au-CH}_2\text{NH}_2$ with a high value for $\text{Au}4f$ (32.7%) that indicates the presence of pinholes inside the film in agreement with the redox probe experiments, $\text{C}1s$ with three contributions at 284.7 eV (22.4%), 286.3 eV (12.1%) and 288.4 eV (7.0%), and a high value for $\text{N}1s$ at 399.8 eV (14.0%) that indicates a highly aminated surface.

Fig. 13. XPS of an $Au-NHCH_3$ plate ($s = 1 \text{ cm}^2$) obtained as in Fig. 11: A) Survey spectrum and B) High resolution N1s spectrum.

The mechanism for the oxidative electrografting of aliphatic amines [25] allows deducing that the species responsible for the reaction of methyl amine on surfaces is $\cdot NH-CH_3$.

4. Conclusion

Under electrochemical control, highly aminated surfaces are obtained from amino aliphatic moieties i) by C-H reductive activation (to give primary amines) or ii) direct oxidation (to give secondary amines). Such surfaces can also be obtained by C-H reductive activation of nitro aliphatic moieties followed by reduction. These simple electrochemical methods permit to obtain surfaces modified with either primary or secondary amines. Grafting is ascertained by electrochemistry, IRRAS, XPS and ellipsometry.

The reactions proceeding by C-H reductive activation follow Scheme 1A and B. For the sake of simplicity, Scheme 1 has been written with diazonium salt, but in the basic aqueous solution of methyl amine diazoates and/or triazenes can be formed. The involvement of the diazoate in the grafting process is more likely as triazenes are stable in basic media [42]. In any case the 2,6-DMBD is reduced to the corresponding aryl radical, which abstracts an hydrogen atom from CH_3NH_2 or CH_3NO_2 . The ensuing radicals react both on the surface and

the already grafted moieties. These reactions are very efficient as long oligomeric chains are obtained [16]. To our knowledge, the reduction of 2,6-DMBD in the presence of methylamine is the simplest way to obtain these highly aminated surfaces. The grafting of nitromethane under the same conditions is also efficient, but the reduction of the nitro group necessitates one more step and the reaction is not quantitative.

Although it is not possible to obtain a thorough description of such chains, the results of the different methods point to a gold surface modified by quite long oligomers (50 units for methylamine). These oligomers are well separated from each other (one oligomer out of 11 Au atoms for $Au-CH_2-NO_2$), which should facilitate the reaction of amino groups. The formation of these oligomers indicates that the abstraction of an H atom from the growing oligomer by the $\cdot CH_2NH_2$ or $\cdot CH_2NO_2$ radicals is faster than the reaction of the same radical on the surface [25].

The direct oxidation of methylamine provides secondary amines; previous studies have demonstrated the mechanism that involves the deprotonation of an initial radical cation to give finally a carbon radical that reacts with the surface.

The high surface concentration of the amino groups is an asset for applications of these surfaces in different fields. Amino groups can be easily reacted with different chemicals such as peptides. Cationic surfaces evidence antibacterial properties, protonation or methylation of the amino groups could impart such properties [43] to different materials including polymers. Preliminary experiments indicate that such surfaces react with atmospheric CO_2 and could be used as solid scrubbers [44,45] or for CO_2 reduction [46].

Declaration of competing interest

There are no conflicts to declare.

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