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Determination of surface amine groups on amorphous carbon nitride thin films using a one step covalent grafting of a redox probe

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ABSTRACT

A fluorocarbonyl terminated ferrocene based redox probe was synthesized and characterized using infrared spectroscopy and nuclear magnetic resonance. It was then successfully grafted on various amorphous carbon nitride (a-CN$_x$) samples ($0.12 \leq x \leq 0.27$) via the formation of a -CO-NH- type linkage with surface amine groups, whose spontaneous formation on the surface of a-CN$_x$ materials was thus proved and exploited. Cyclic voltammetry experiments were carried out in an acidic aqueous solution in the presence of this freely diffusing redox probe, in order to identify its electrochemical behavior. By comparison, CV experiments carried out on the modified a-CN$_x$ electrodes in the same blank electrolytic solution undoubtedly confirmed the presence of electroactive sub-monolayers, in spite of distortions of the resulting voltammograms. These latter were shown to reflect the influence of bulk atomic nitrogen content on the electrochemical reactivity of a-CN$_x$ materials. The grafted surface amine percentage deduced from the charge passed during oxidation of grafted ferrocene moieties was found to decrease from 6.5% for a-CN$_{0.12}$ down to 1.1% for a-CN$_{0.27}$. This trend is expected to reflect the trend in surface concentration of reactive amine groups as a function of bulk atomic nitrogen content.

1. Introduction

Over the last few years and until now, carbon materials were the target of an intense and growing research activity. A major contribution to this latter is aimed at exploiting their surface as a starting platform for various molecular architectures in view of various applications such as electrochemical or bio-sensors, molecular electronics or coatings with special physical or chemical properties [1–3]. As an example and besides glassy carbon or raw carbon materials (such as graphite), thin films of boron doped diamond (BDD) have been widely investigated in this research field due to their remarkable physical properties: mechanical resistance, chemical stability, biocompatibility and electronic conductivity [4]. In electrochemistry, these materials show weak parasitic current densities and wide potential windows in aqueous media. On the other hand, their surface functionalisation requires an appropriate pretreatment depending on the initially existing surface functional groups of the as-grown materials produced from the plasma based deposition process. These functional groups may also result from the reactivity in the presence of atmospheric water and oxygen.

Though sustained activity was long-carried out on the investigation of electronic, structural or mechanical properties of amorphous carbon or carbon nitride materials [5–7], much less effort, and only since the end of the nineties, was put on their use as electrode materials: however both a-CN$_x$ or a-CN$_x$H$_y$ were purposely envisaged and their electrochemical activity assessed with respect to different redox couples [8–19]. a-CN$_x$ materials have been suggested for applications in liquid effluent treatment (nitrate reduction on the cathodic side, degradative oxidation of organic pollutants on the anodic side) but no achievement emerged so far. Conversely, applications in electroanalysis for heavy metals detection by stripping voltammetry [20–23] or biological analyte detection [24], in catalysis [25,26], for anti-corrosion coatings [27–29], humidity sensing [30], elaboration of a-CN$_x$ (or a-C)/metal composite materials [31,32] or new p-n junctions [33,34] have been proposed. Moreover, these materials possess a very smooth surface, as shown from AFM images on a-CN$_x$ films when deposited by cathodic sputtering on doped silicon [35].

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A development of a-CN_x based biosensors following the examples of graphite or BDD requires first to determine the amine surface groups naturally expected for this material at variance with the former two ones. The next question to come: is a further amination necessary? There is an abundant literature dealing with the characterization of chemical composition and C/N bond structures in a-CN_x or a-CN_xH_y materials depending upon the nature of precursors, N_2 partial pressure in the sputtering gas, or power imposed during the deposition process. Either vibrational (IR or Raman) spectroscopies or XPS technique allowed to prove the existence of sp^3 to sp^1 (C-N, C = N or C≡N) hybridizations [6,13,16,36–42]. In particular, infrared absorption spectra of a-CN_x thin films showed bands at 1220 cm^{-1} and 1650 cm^{-1} that can be reasonably assigned to sp^3 C-N and sp^2 C = N bonds respectively [6,13,43]. In addition, FTIR spectra of a-CN_x thin films were shown to exhibit a very high visible to infrared transmittance and to reveal surface amine groups (-NH_2) [44]. All these indications lead to the conclusion that the spontaneous formation of amine- and imine-type functional groups on a-CN_x materials is more than likely, as a result of the reactivity of a-CN_x materials towards atmospheric water and oxygen as soon as they are withdrawn from the deposition chamber [45]. Nevertheless, surface amine groups have never been exploited for the development of covalent grafting strategies on a-CN_x surfaces in literature.

Surface IR or FTIR spectroscopies do not provide a quantitative determination of the different C-N bonds coverage, and surface Raman on glassy carbon gives, even with a sophisticated treatment, overestimates of the coverage by an organic monolayer as compared to cyclic voltammetry (CV) [46]. In the case of a-CN_x materials, XPS is not appropriate to this end since the probed thickness of the material is about 10 nm, which brings a significant contribution of bulk nitrogen atoms with respect to the surface ones. The EDC/NHS technique [47] allows grafting of carboxyl-substituted redox compounds to amine surface groups for further electrochemical signature and evaluation of amine sites. As this technique, widely recognized, is specific of primary amines, we propose in this work an alternative grafting route. More precisely, the one-step grafting of a well-known reversible redox probe, *i.e.* a ferrocene moiety, is reported, probably for the first time on a-CN_x thin films, via the formation of an amide bond between the a-CN_x surfaces and the redox probe. It therefore confirms the reasonable abovementioned expectations predicting the presence of amine functional groups on the surface. In addition, cyclic voltammetry experiments carried out on the grafted surfaces allowed an approach of the determination of the number of amine groups per surface unit assumed uniformly distributed, for a-CN_x samples with different atomic nitrogen contents.

2. Experimental

2.1. Preparation of a-CN_x samples

a-CN_x thin films were deposited on boron doped (p-type) silicon substrates (doping level: 10^{20} cm^{-3}, resistivity: 1-5 mΩ.cm) with the help of DC magnetron cathodic sputtering technique using a graphite target and a reactive Ar/N_2 plasma. The reactor used was a MP 300 S model from Plassys (France). The substrates were first sonicated in successive distilled water, acetone and ethanol baths, then allowed to dry in air, and finally submitted to an RF (13.56 MHz) ionic etching (substrate + target) in the reactor. The films were produced using a 0.4 Pa total pressure, a 10 min deposition time and a 250 W target power for various gaseous nitrogen contents (3, 7, 15 and 30%) in the sputtering gas mixture. The target-to-substrate distance was *ca.* 7 cm.

2.2. Chemical synthesis of the grafted redox-active molecules

The ferrocene based redox probes intended for grafting experiments were prepared according to the synthetic route shown in Scheme 1 and resulting from a modified procedure reported in literature [48,49].

2.2.1. Synthesis of compound **2**

Ferrocenecarboxylic acid (2 mmol, compound **1**) was dissolved in dichloromethane (25 mL) and then stirred under argon atmosphere in an ice bath (0 °C) for 10 minutes. Pyridine (4 mmol) and cyanuric fluoride (4 mmol) were added in the solution and the argon flux was stopped and the resulting mixture contained in a closed glass vessel was kept under stirring for 2 hours. Ice cubes made from distilled water were then added to the mixture placed under stirring. The filtered solution resulted at rest in two immiscible phases. After separation, the orange-brown organic phase was washed twice using frozen water. The washed organic phase was then dried with the help of magnesium sulphate, carefully filtered and washed again using dichloromethane. The resulting solution was stored under vacuum until the solvent was completely evaporated, producing then a dark orange powder that was purified by re-crystallisation using hexane first and then dichloromethane so as to obtain an orange powder. It was characterized using ^{1}H NMR (300 MHz in $CDCl_3$) and ^{13}C NMR (75 MHz in DMSO-d_6) as well as IR spectroscopy in a KBr pellet loaded with the reaction product. Identification of the peaks confirmed the production of fluorocarbonylferrocene **2**. ^{1}H NMR δ (ppm): 4.37 (s, 5H, C_5H_5), 4.75 (d, 2H, ^1J= 1.6 Hz, C_5H_4), 4.91 (t, 2H, ^1J = 1.6 Hz, C_5H_4). ^{13}C NMR δ (ppm): 164.3 (C = O), 73.3 (C_5H_4), 70.6 (C_5H_4), 69.9 (C_5H_5). IR ν (cm^{-1}): 3092 ν(CH), 1801 ν(C = O), 1474 ν(CC), 1373 ν(CF), 1271 ν(CO), 1072 δ(CH), 1107 δ(CH), 895 π(CH), 756 π(CH), 698 π(CH), 480 ν(Fe-Cp).

2.2.2. Synthesis of compound **3**

Compound **2** (2 mmol) was dissolved in anhydrous tetrahydrofurane (THF) under constant argon atmosphere to avoid fluorhydric acid formation. β-alanine (2.33 mmol) was added and the reaction mixture was stirred for five days under argon bubbling at ambient temperature. After reactants in excess have been removed by washing, the solvent was removed under vacuum and the remaining powder was re-crystallised using hexane first and then dichloromethane so as to obtain an orange powder. The addition of the β-alanine moiety on fluorocarbonylferrocene **2** via formation of an amide type linkage and the subsequent synthesis of compound **3** were confirmed: ^{1}H NMR δ (ppm): 4.20 (s, 2H, $C_5\mathit{H}_5$), 4.33 (t, 2H, $C_5\mathit{H}_4$), 4.65 (t, $C_5\mathit{H}_4$), 3.36 (dt, 2H, $C\mathit{H}_2$NH), 2.35 (t, 2H, $C\mathit{H}_2$COOH); ^{13}C NMR δ (ppm): 175.37 (COOH), 169.46 (*C*ONH), 70.11 (*C*$_5H_5$), 68.96, 70.61, 77.68 (*C*$_5H_4$), 34.52 (*C*H_2COOH).

2.2.3. Synthesis of compound **4**

Compound **4** was obtained after compound **3** had undergone the synthetic route applied on ferrocenecarboxylic acid to get fluorocarbonylferrocene **2**, as the purpose of this last step is again to make the fluorinated compound from the carboxylic acid compound. Briefly, a suspension of 0.67 g of compound **3** (2 mmol) and pyridine (4 mmol) in dry dichloromethane (60 mL) was cooled to 0° C under argon atmosphere. To this solution cyanuric fluoride (10 mmol) was added and the mixture stirred for 3 h. A copper color was observed. Crushed ice/water (50 g) was then added, the suspension filtered, and the organic layer separated and washed with cold water. The organic layer was then dried over anhydrous $MgSO_4$ and filtered. Solvent removal was performed under vacuum and a dark crystalline orange solid was obtained.