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Specific interactions of functionalised gold surfaces with ammonium perchlorate or starch; towards a chemical cartography of their mixture

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ABSTRACT

By functionalising gold samples, planar wafers or AFM tips, with an acid- or an amino acid-terminated thiols, mercaptoundecanoic acid (MUA) and homocystein (H-Cyst) respectively, we were able to differentiate the interactions with ammonium perchlorate (AP) and starch (S), two components of a nanocomposition mixture.

To do so, the interaction between gold functionalized surfaces and the two targeted compounds have been characterized and quantified by several complementary techniques. Polarisation modulation-infrared spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS), providing chemical analyses of gold surfaces after contacting S or AP, proved that both compounds were retained on MUA or H-Cyst-modified surfaces, but to various extents. Quartz crystal microbalance on-line measurements enabled to monitor the kinetics of interaction and showed distinct differences in the behaviour of MUA and H-Cyst-surfaces towards the two compounds.

Having observed that only H-Cyst-modified surfaces enables to get a contrast on the chemical force microscopy (CFM) images, this new result could be well explained by examining the data obtained by combining the above-mentioned surface characterisation techniques.

1. Introduction

With the emergence of nanotechnology in the domains of microelectronics or biology, new nanostructured complex materials are synthesized. Advanced tools were developed to characterize these materials at the nanometer scale, among which atomic force microscopy (AFM) appearing in 1986 [1]; then came up the possibility to modify AFM tips by chemicals having specific affinity towards the elements to be analysed, and thus making it possible to make a surface mapping with high spatial and chemical resolution. Classical methods used to functionalize AFM tips and using them for this application, called chemical force microscopy, or CFM, have been reviewed by Smith et al. [2]. Adhesion and friction forces were measured by coating AFM tips with COOH— or CH_3-terminated self-assembled monolayers, thus demonstrating the possibility to quantitatively measure adhesion and friction forces between functional groups on a tip and on a sample; by reducing the tip size to ca 10 nm, interactions between single molecular pairs could be measured [3]. CFM has also been successfully used to measure interaction forces between antibodies and protein arrays at the nanometer scale, and the force results brought the proof of the selective immobilisation of proteins on gold dot arrays [4]. For bi, or even multicomponent nanomaterials, the goal of the characterization is to determine the distribution of the various components and link it to the properties of this complex material. In the domain of explosive compounds, the nanocomposition is optimized in order to obtain new explosives with improved energy yield and safety. These explosive nanocompositions are synthesized by mixing a reducing and an oxidizing compound. The “nano” mixing is expected to increase the material energy and decrease the sensitivity of explosive compositions, because of the better exchange rate between the two components (by increasing their proximity to each other).

For the present study, a nanomixture of ammonium perchlorate (oxidant) and starch (reductant compound), described in a previous paper [5], was selected; its composition was investigated applying the AFM technique, using chemically modified gold probes modified by ω-functionalized alkylthiols following a now classical procedure [6]. Several strategies have indeed been used, with varying success, to bind ligands such as antibodies, drugs or nucleic acids to AFM tips for recognition studies [7]. Gold-covered tips are favoured, because gold is reasonably inert [8], and easy

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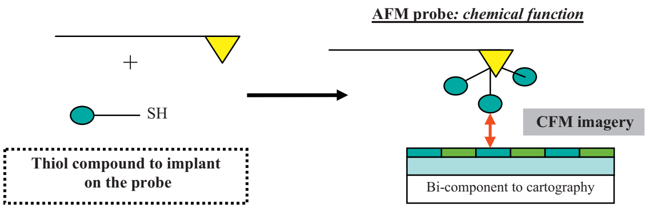

Fig. 1. Principle of chemically modified AFM probes for chemical force microscopy.

to functionalise with thiolate compounds. The gold functionalization procedures have already been optimized for the elaboration of chemical sensors [9], electrochemical applications [10–12], or to develop surface plasmon resonance (SPR)-based sensors [13].

Note that for such an ammonium perchlorate/starch mixture, essentially based on organic chemicals, despite the presence of chlorine in ammonium perchlorate, the contrast in scanning electron microscopy (SEM) or transmission electron microscopy (TEM) is not sufficient to provide a satisfying mapping. Conventional AFM analysis, with non-modified tips, has not given resolved images either. In this context, the development of adapted CFM appears to be a necessary and promising alternative to explore.

The CFM technique relies on the fact that the AFM tips exhibit specific chemical interactions, and thus chemical forces (with the organic surface species), giving rise to a chemical cartography of organic materials at the nanometer scale. As a simple example, a patterned mixed self-assembled monolayer with COOH and CH_3 rich regions was successfully imaged by adhesive force and mapping friction measurements, using AFM tip functionalized either with COOH or CH_3-terminated thiols [14]. The following figure illustrates the principle of tip functionalization and CFM measurement (Fig. 1).

CFM measurements have already been used, for biological applications, e.g. identifying affinities between a target and a given antibody [15–18].

The final challenge of this work was to prove that the selective mapping of an ammonium perchlorate and starch organic nanomixture is feasible by using chemically modified AFM probes. A prerequisite was to characterise the interaction of gold surfaces modified with each of the two components, ammonium perchlorate and starch, and identify some specific and preferential interactions; several functional groups have been grafted to gold, using various functionalized thiols, terminated by amine, acid, or amino-acid functions in order to look for possible differences in their interactions with the two above cited components. Planar gold surfaces were used first to test these interactions, and benefit from the possible use of three powerful surface characterisation techniques, polarisation modulation-infrared reflection absorption spectroscopy (PM-IRRAS), photoelectron spectroscopy (XPS), and quartz crystal microbalance (QCM). AFM gold tips were then functionalised and used to map a mixture of ammonium perchlorate (AP) and starch (S). This manuscript presents the results obtained with mercaptoundecanoic acid (MUA) and homocystein (H-Cyst) used to modify the gold sensing surfaces, as well as the AFM tips.

2. Experimental

2.1. Preparation of the sensing gold surfaces

The 11 mm × 11 mm glass substrates, coated with a 5 nm-thick chromium layer and a 200 nm-thick gold layer, were purchased from Arrandee (Werther, Germany). The gold-coated substrates were annealed in a flame to obtain a predominant (1 1 1) faceting of the surface.

To functionalise these planar gold surfaces, the latter were immerged in a 10 mM solution of Mercaptoundecanoic Acid (MUA, 97%, from Aldrich) in absolute ethanol (NormaPure, VWR) during 3 h, or in a 10 mM solution of DL-Homocysteine (Hcyst >95%, from Fluka) in absolute ethanol during 20 h. The substrates were then rinsed in a bath of absolute ethanol during 15 min, and in a bath of ultrapure water (18 MΩ) during 15 min, and finally dried under nitrogen flow.

2.2. AFM tips were modified following the same procedure

2.2.1. Preparation of the energetic nanocomposition of starch and NH_4ClO_4

The inorganic matrix (composition A) to be mapped is composed of a mixture of ammonium perchlorate (AP) and corn starch (S). The samples were obtained by lyophilisation of an aqueous solution of corn starch (Provider Fisher Scientific) and ammonium perchlorate 400 μm (Class 1, purity > 99.5%) (Provider: SNPE Matériaux Energétiques) by a method developed by the CEA [19]

2.2.2. Preparation of solutions and sample immersion

In order to test the interactions of each component with adequate solutions of known composition, of AP and S, had to be prepared, enabling immersion of the thiolate-modified gold samples and in situ QCM measurements. Knowing that corn starch is a polysaccharide consisting of a large number of glucose units linked together by glycosidic bonds, and starch is mainly composed of amylose and amylopectin molecules (Fig. 2a and b), the following procedures have been setup.

A 0.1 mol L^{-1} solution of AP (400 μm Class 1, purity > 99.5%, Provider SNPE Matériaux Energétiques)) was prepared in ultrapure water; a 10 g L^{-1} solution of corn starch (Provider Fisher Scientific) was prepared by pre-gelatination of corn starch (solution of 5 g in 500 mL of an ultrapure water almost boiling during 45 min). Then a dilution was carried out to obtain a 1 g L^{-1} solution of corn starch. All solutions were prepared right before each PM-IRRAS, XPS or QCM experiment.

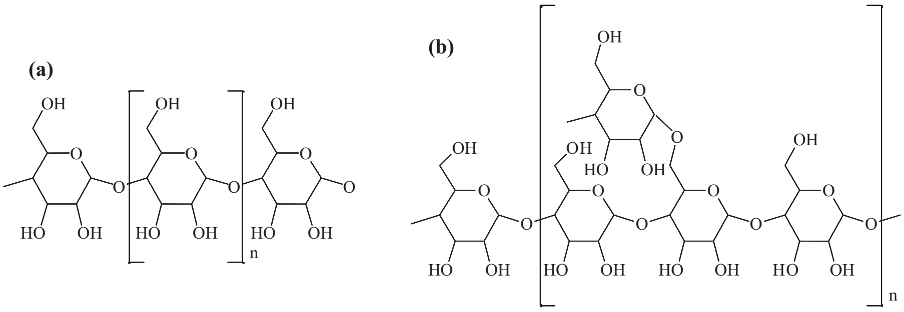

Fig. 2. Structure of the amylose (a) and amylopectin (b) molecules.