



Chemical characterization of fluorinated/hydrogenated mixed monolayers grafted on gold nanoparticles

Ilaria Tirota^a, Alberto Calloni^b, Claudia Pigliacelli^c, Alberto Brambilla^b, Gianlorenzo Bussetti^b, Lamberto Duò^b, Pierangelo Metrangolo^{a,c}, Francesca Baldelli Bombelli^{a,*}

^a Laboratory of Supramolecular and BioNano Materials (SupraBioNanoLab), Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Via Luigi Mancinelli 7, Milano I-20131, Italy

^b Department of Physics, Politecnico di Milano, Piazza Leonardo Da Vinci 32, Milano I-20133, Italy

^c Department of Applied Physics, Aalto University, Espoo FI-02150, Finland

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ABSTRACT

Perfluorocarbons are omniphobic compounds as a consequence of their unique properties such as, e.g., high electronegativity, low polarizability, high ionization energy, and low surface tension. The possibility of combining such properties with the features of nanoscale materials promoted a recent upsurge in the production of fluorinated nanoparticles for application in different fields. Attainment of mixed fluorinated/hydrogenated stabilizing layers is also desired in some cases, but often the composition of the ligand mixture used in the exchange reaction is not reflected in the resulting monolayer. Thus, methodologies for determining the resulting chemical composition of the final mixed fluorinated/hydrogenated monolayers grafted on the nanoparticle (NP) surface are needed. Here we propose a combined Fourier Transform Infrared (FTIR) and X-ray Photoemission Spectroscopy (XPS) investigation for assessing the final chemical composition of a mixed monolayer of hydrogenated and fluorinated alkanethiols grafted on the surface of gold NPs obtained through two different synthetic routes. This analysis allowed the evaluation of the exchange efficiency of the two synthetic routes, and also, coupled with UV–vis studies, highlighted that the colloidal stability of the final NPs was not only dependent on the fluorinated/hydrogenated ratio but also on the chosen exchange route, which seems to influence the ligand organization on the mixed monolayer.

1. Introduction

Gold nanoparticles (AuNPs) have gained increasing interest due to the peculiar optical properties of their core, biocompatibility and versatility, resulting in a large quest for methodologies to ensure an accurate functionalization of the organic layer, together with control of their shape and size [1–3].

Several protocols have been developed for the synthesis of functionalized AuNPs, bearing a wide range of different ligands linked to the gold surface *via* electrostatic interactions or covalent bonds. Among these ligands, thiols are a recurrent choice due to the strong bond formed between Au atoms and thiolates [4]. Generally, the resulting AuNPs are stabilized by a monolayer of a chosen ligand in a good solvent. Sometimes, it can be necessary to modify the obtained shell and introduce new chemical functionalities, and ligand-exchange is probably one of most common approaches for further altering the composition of the obtained monolayer after NP synthesis [1]. In fact, ligand-exchange reaction is a generally mild reaction that allows using a wide

range of molecules, particularly those that could not withstand the harsh reducing ambient of the *in-situ* AuNP nucleation reaction, at the same time ensuring control over the core size, which is not usually affected by the exchange reaction [5]. The final composition of the monolayer is largely dependent on the reaction conditions, in particular ratio between the new ligand (or mixture of) and the starting one, temperature, and reaction time [4,6]. Accurately tuning all these aspects, it is possible either to completely substitute the original ligand with the new one or only exchange a certain amount of the pre-existing shell with the new ligand or, using a ligand mixture for the exchange reaction, to obtain a completely new mixed-monolayer [7].

Mixed-monolayer AuNPs, where two or more ligands are attached to the Au core, have been widely investigated for their application in both materials science and biomedical fields [8,9]. Several research groups put a lot of efforts in trying to rationalize the mechanism of self-assembling of these monolayers, as well as in their synthetic routes [10–14]. However, the chemical composition and ligand organization of a mixed monolayers on AuNPs is still hard to accurately characterize,

* Corresponding author.

E-mail address: francesca.baldelli@polimi.it (F. Baldelli Bombelli).

due to the small amount of molecules on the surface of each NP and complexity of applying common analytic techniques to nano-objects [8,15]. To date the most promising results have been obtained detaching the ligands from the gold core, following iodine addition, and analyzing the residue *via* proton magnetic resonance (H^1 -NMR) or mass spectrometry [8,16,17]. In particular the latter technique has recently been shown to be a valuable tool to track the monolayer composition during the ligand exchange procedure [18]. Both NMR and mass spectrometry approaches suffer from the need of a relatively large amount of material to analyze, as well as the possibility of ligands loss or damage during I_2 destruction of the NPs. For these reasons methods like X-ray Photoemission Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) recently started to gain prominence, allowing accurate quantification of the elements present on the surface of the NPs, while only using a few drops of unaltered sample [19–22].

In the plethora of ligands used for functionalizing AuNPs, fluorinated ligands have increasingly been exploited as functional groups on NP surfaces for the production of materials characterized by different properties such as corrosion resistance, anti-fouling properties, catalytic activity, *etc.* [23,24]. More recently fluorinated AuNPs (*i.e.*, F-AuNPs) have also found large use as imaging tools [25–27] and as analytical probes for environmental, technological and chemical fields [28–30]. Thus, there is an increasing interest from different scientific communities to develop NPs coated with completely or partially fluorinated monolayers [17,31].

In this work we studied the chemical composition of perfluorinated/hydrogenated mixed monolayer AuNPs, obtained starting from completely hydrogenated NPs through ligand-exchange reaction, *via* XPS coupled with FT-IR analysis as a function of the ligand ratio. In fact, often the ligand ratio used during the conjugation does not reflect the real composition of the bound monolayer on the NP surface and further investigation is needed to determine it.

Fluorinated AuNPs were obtained following two different approaches: in a first set of samples, we followed a methodology used by Pasquato *et al.* [17], where 1H,1H,2H,2H-perfluorodecanethiol (PFDT) ligands were introduced on pre-formed dodecanethiol (DDT)-AuNPs. A second set of samples was prepared starting from NPs capped with oleylamine (OLEAM), which were treated with different ratios of DDT and PFDT mixtures (see Scheme 1). XPS coupled with Fourier Transformed Infrared Spectroscopy (FTIR) analysis were used for studying

the dependence of the exchange reaction yield on the amount of PFDT ligand used in the first case as well as determining the relationship between the initial DDT/PFDT ratio and the final monolayer composition in the second case.

2. Results and discussion

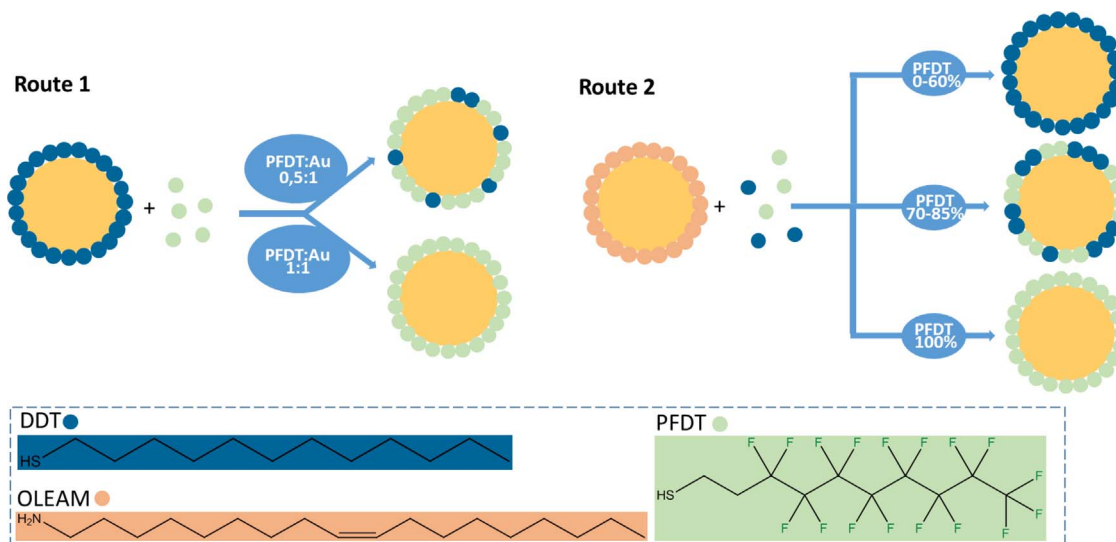
2.1. Physical-chemical characterization of the starting AuNPs

DDT-AuNPs, starting material for the first set of samples, were obtained *via* a modified Brust synthesis [32] in which the reduction of Au (III) was carried out before the addition of the capping agent, which allowed obtaining a stable dispersion of 4 nm NPs in toluene (Fig. 1b).

Oleylamine (OLEAM) was used as starting capping agent of the AuNPs chosen for the second set of samples allowing an easy substitution in the presence of thiols. In fact, amines tend to form weaker bonds with the gold core of NPs [33]. To understand how the starting ligand ratio used in the exchange reaction influences the DDT/PFDT ratio on the final monolayer, it was important to ensure a complete substitution of the initial oleylamine shell and work in large excess of exchanging ligand mixture. A stable dispersion of 7.5 nm size OLEAM-AuNPs (Fig. 1a) was obtained through a well-known monophasic procedure, using oleylamine both as a reducing and capping agent [34].

Finally, a reference sample of fully fluorinated NPs (F-AuNPs), functionalized with PFDT ligands and comparable in size, was needed in order to evaluate the FT-IR and XPS profile of the potentially mixed perfluorinated/hydrogenated NPs. Few examples of direct synthesis of F-AuNPs are reported in the literature, all comprising smaller NPs up to 3 nm of diameter [35–38]. A two steps procedure similar to that described for DDT-AuNPs was developed, which yielded slightly larger PFDT-AuNPs with an average size of about 4 nm (Fig. 1c) (See Methods in the ESI for details).

Table 1 summarizes the properties of the three samples used as starting and reference materials for the analyses. Both hydrogenated NPs were readily soluble in toluene, forming dark red homogeneous dispersions. On the other hand, PFDT-AuNPs synthesis was performed in trifluoro-toluene to avoid precipitation of the NPs during the reaction and, after purification, the F-AuNPs were only soluble in fluorinated solvents, such as perfluorooctane and 1,1,1,3,3-pentafluorobutane (SOLKANE 365°, concentration $\geq 99.5\%$), which was the fluorinated solvent of choice throughout this work. The gold content of the samples



Scheme 1. Schematic representation of ligand exchange synthetic routes to obtain fluorinated nanoparticles: Yellow sphere (Au core), blue sphere (DDT chains), orange sphere (OLEAM chains), and green sphere (PFDT chains). Route 1 (left): PFDT is added at increasing concentrations to preformed DDT-AuNPs resulting in either partially fluorinated or fully fluorinated NPs. Route 2 (right): PFDT/DDT mixtures at increasing concentration of PFDT are added to preformed OLEAM-AuNPs resulting in either DDT-AuNPs or partially fluorinated or fully fluorinated NPs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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