



Thermogravimetry and evolved gas analysis for the investigation of ligand-exchange reaction in thiol-functionalized gold nanoparticles

Federico Locardi^{a,b,*}, Ester Canepa^a, Silvia Villa^a, Ilaria Nelli^{a,b}, Chiara Lambruschini^a, Maurizio Ferretti^{a,c}, Fabio Canepa^{a,c}

^a Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy

^b Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163, Genoa, Italy

^c CNR-SPIN, Corso F.M. Perrone 24, 16152 Genoa, Italy

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ABSTRACT

The increasing use of gold nanoparticles (AuNPs), especially in biomedical applications, requires strict chemical-physical characteristics achievable by organic functionalization via ligand-exchange process. Nowadays, one of the most common synthetic procedures to obtain small and hydrophilic AuNPs consists on the synthesis of 1-Dodecanethiol (1-D) coated AuNPs, afterwards functionalized by a partial substitution of the previous alkyl hydrophobic moiety with carboxylic species, such as the 11-Mercaptoundecanoic acid (11-MUA). It is evident that the characterization of the organic coating and the quantification of the ligand-exchange reaction become crucial for the nanoparticles real applicability. We report the use of thermogravimetry (TG) and evolved gas analysis, performed through gas chromatography-mass spectrometry (GC-MS), for the investigation of 1-D and mixed 1-D/11-MUA functionalized AuNPs. The two samples present different thermal behaviours, discernible through the GC-MS use, thus allowing the quantification of the 1-D/11-MUA ratio. The insertion of GC before the MS analysis provides an accurate identification of the gaseous products and supplies additional information on the ligand-surface interaction. The results demonstrate that TG is a rapid and satisfactory method for the quantification of the ligands amount on the nanoparticles surface; moreover, the coupling with GC-MS provides additional information (more discernible respect to the only use of MS) on the decomposition products.

1. Introduction

Functionalized nanoparticles (NPs) are nowadays a fundamental research field, presenting different applicative and technological possibilities, ranging from energy (fuel cell catalysts, hydrogen steam reforming) [1] to environment (wastewater treatment) [2,3], biology and medicine (drug delivery, antibacterial agents, biomarkers) [4–6]. Among these nanomaterials, functionalized gold nanoparticles (AuNPs) present a continuous increasing interest for biomedical applications thanks to their remarkable optical, electronic and thermal properties [7–9]. For this specific use a functionalization with suitable organic moieties, preventing aggregation and ensuring a hydrophilic behaviour, is required [10].

In 1994 Brust et al. [11] proposed a convenient synthesis of thiol-functionalized gold nanoparticles (Au@S-R NPs), which is still one of the most adopted preparation methods to obtain small (2–5 nm), stable and homogenous functionalized AuNPs. In this reaction, AuNPs are

prepared in the presence of an alkyl thiol (e.g. 1-Dodecanethiol, 1-Octanethiol, 1-Decanethiol) as capping agent. The surface passivation occurs during the gold nucleation and growth and the reaction is carried out in a two-phase liquid-liquid system. Due to the nature of alkyl species, thiol-functionalized AuNPs synthesized with this procedure are soluble only in non-polar solvents (e.g. toluene, pentane, dichloromethane), not usable for biological systems. Therefore, the ligand-exchange process [12], during which the hydrophobic coating is partially or totally replaced by a hydrophilic one, is a fundamental and necessary further step to allow the use of these NPs in biomedicine [6]. In most cases, hydrophilic thiol-functionalized AuNPs are prepared replacing the hydrophobic alkyl thiol moiety with new anionic or cationic ligands, through place-exchange reactions [13]. This functionalization leads only to a partial substitution of the original organic coating, but sufficient to radically change the chemical behaviour of the final product [13,14]. In this work, we synthesized 1-Dodecanthiol-protected AuNPs (Au@SC₁₂ NPs) and, subsequently, carboxylic acid-

* Corresponding author at: Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146 Genoa, Italy.
E-mail address: federico.locardi@unige.it (F. Locardi).

functionalized $[(\text{HOCC}_{10}\text{H}_{20}\text{S})_x(\text{C}_{12}\text{H}_{25}\text{S})_{n-x}]\text{Au}$ NPs (hereafter called $\text{Au}@SC_{10}\text{COOH}$ NPs) by partially exchanging the 1-Dodecanethiol (1 – D) with an ω -thiolated carboxylic acid, *i.e.* the 11-Mercaptoundecanoic acid (11 – MUA) [15,16]. This final product can be solubilized in aqueous basic solution thanks to the carboxylic moiety deprotonation.

In addition to a suitable hydrophilic functionalization, the characterization of these ligand-protected nanosystems constitutes a crucial point for their applications and improvements. Firstly, the quantification of the organic moiety is strictly necessary. Furthermore, also the investigation of surface properties, especially in the presence of a functionalization with secondary coatings, furnishes additional information. Thermogravimetry (TG), for its operative simplicity and requiring no or minimal specimen preparation, represents a straightforward characterization method, [17–20] able to quantify residual solvents [21], organic moieties [22] and impurities in traces [23]. Moreover, TG coupled with the evolved gas analysis (EGA) increases the power of this technique allowing a better identification of molecules released during heating and, consequently, supplying a more accurate explanation of the TG curve behaviour [24–33]. However, the discrimination of a mixture formed by different molecules arising from a single thermal decomposition is still missing [23,25,28]. Indeed, only if a single substance is released by the specimen, an accurate identification is possible. In other cases, the use of a set-up able to separate evolved species (*i.e.* a gas chromatograph) is mandatory [24,34]; moreover, different chemometric approaches have been developed for the analysis of multicomponent systems [35].

In this paper, the use of Differential Thermal Analysis/Thermogravimetry (DTA/TG) coupled with Gas Chromatography and Mass Spectrometry (GC – MS) has been used to detect qualitatively and quantitatively the amount of different thiolated ligands (1 – D and 11 – MUA) used to synthesize functionalized AuNPs. From our knowledge, no data on the thermal degradation of ligand-protected AuNPs using the aforementioned equipment are available in literature. GC allows the separation of evolved molecules improving as a result their identification through MS and furnishing additional information on the organic moiety decomposition products.

2. Materials and methods

2.1. Materials

Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.999%),

tetraoctylammonium bromide (TOAB, 90%), toluene, 1-Dodecanethiol (1 – D, $\geq 98\%$), sodium borohydride, ethanol absolute ($> 99.8\%$), 11-Mercaptoundecanoic acid (11 – MUA, 98%), tetrahydrofuran anhydrous (THF, $> 99.9\%$), dichloromethane ($\geq 99.8\%$), trisodium citrate dihydrate ($\geq 99\%$), sodium hydroxide (NaOH, pellets) were purchased from Sigma Aldrich and used without further purification. All aqueous solutions were prepared using water purified with a MilliQ ultrapure water system (MilliPore). Each samples were prepared and analysed twice.

2.1.1. Dodecanethiol-protected AuNPs: $\text{Au}@SC_{12}$ NPs

Thiolated gold nanoparticles ($\text{Au}@SC_{12}$ NPs) were prepared following the known procedure reported by Brust et al. [11]. Few adjustments were adopted in order to obtain the best results in morphology and dimension. All the additions and the reaction itself were carried out under vigorous stirring and controlled temperature (283 K). A HAuCl_4 aqueous solution (7.5 ml, 30 mM) was mixed with a solution of TOAB in toluene (20 ml, 50 mM). After ten minutes, 50.3 μl of 1 – D (molar ratio 1:1 with Au^{3+} ions) were added to the two-phase mixture. A cold freshly prepared aqueous solution of the reducing agent NaBH_4 (6.25 ml, 0.4 M) was then slowly added to the mixture. The reduction proceeded for 1 h. The organic phase was then separated and evaporated by rotary evaporation. The dark-brown product was finally dispersed in 100 ml ethanol to remove the excess thiol. This mixture was kept for 15 h at 247 K and the precipitate was further purified by several washings in ethanol at room temperature. Waxy nanoparticles were obtained after one day under vacuum.

2.1.2. Carboxylic acid functionalization: $\text{Au}@SC_{10}\text{COOH}$ NPs post- $\text{Au}@SC_{12}$ NPs

Carboxylic acid-functionalized AuNPs were prepared *via* Murray place – displacement reaction (Fig. 1A) of the precursor $\text{Au}@SC_{12}$ NPs previously described [15]. As specified before, this functionalization leads only to a partial substitution of the 1 – D original coating. In particular, we synthesized $\text{Au}@SC_{10}\text{COOH}$ NPs using the 11 – MUA. In this reaction 100 mg of 11 – MUA were added to 20 mg of $\text{Au}@SC_{12}$ NPs in 1 ml of anhydrous tetrahydrofuran. The dispersion was stirred for two days under argon at 293 K. The product was washed by repeated suspension, centrifugation and decantation in dichloromethane in order to remove the 1 – D and 11 – MUA excess and finally stored under vacuum. $\text{Au}@SC_{10}\text{COOH}$ NPs can be solubilized in NaOH aqueous solution at pH 12.

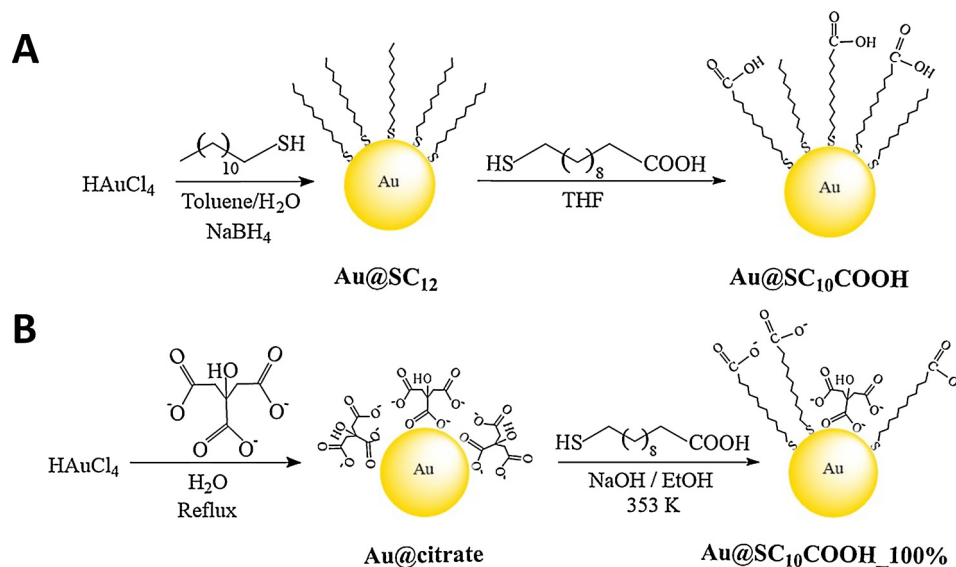


Fig. 1. Schematic drawing illustrating (A) followed to obtain the two-step synthesis followed to obtain $\text{Au}@SC_{10}\text{COOH}$ NPs (precursor $\text{Au}@SC_{12}$ NPs) and (B) $\text{Au}@SC_{10}\text{COOH}_{100\%}$ NPs (precursor $\text{Au}@citrate$ NPs).

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