

Fine structure of gold nanoparticles stabilized by buthlydithiol: Species identified by Mössbauer spectroscopy



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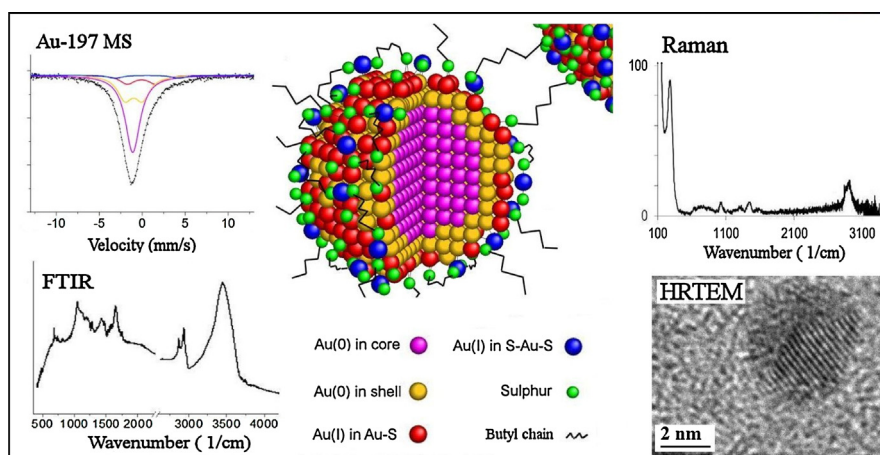
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HIGHLIGHTS

- Various gold species are identified in stabilized 1.3–4 nm nanoparticles.
- Partial coverage of particles with thiol is suggested.
- Partly irregular crystal structure of nanoparticles is evidenced.

GRAPHICAL ABSTRACT



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ABSTRACT

Stabilized gold nanoparticles (Au NPs) were prepared with 4:2.6 Au to buthlydithiol stoichiometry using modified Brust synthesis. The size of the particles falls into the 1.3–4 nm range in which the molecular cluster – metallic particle transition takes place. Stabilized particles were characterized by transmission electron microscopy (TEM/HRTEM). Moreover, numerous spectroscopic techniques like UV–vis, infrared (FTIR), X-ray diffraction (XRD), Raman, photoacoustic and Mössbauer spectroscopies were also used for detailed structural identification of the functionalized Au NPs. The presence of Au–S bonds was proven by FTIR and Raman spectra. It was found that the distribution of covering thiol layer is uneven, therefore the presence of uncovered surface gold atoms can be assumed at the applied stoichiometry. In good coincidence, four types of gold species could be identified in the corresponding Mössbauer spectrum.

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They can be attributed to metallic gold in the core, to bare gold in the surface layer, to surface gold atoms attached to thiol, and finally, to gold atoms pulled out from the particle, located in S–Au–S bridges.

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1. Introduction

Gold nanoparticles (Au NPs) have attracted attention since their first preparation as stabilized sols by Michael Faraday in 1857. Their studies have been enhanced in the last 30–40 years since new fields for applications have been opened recently [1]. Au NPs can be synthesized in a wide size range starting from the assembly of few atoms to stabilized particles with several hundred nanometer size. Stabilization of particles by protecting them with an insulating layer is essential otherwise they easily aggregate. In the low size range there are certain x values for Au_x clusters at which their stabilization is preferred (25, 38, 55, 144, etc.) [2–5]. Transition from these large molecular complexes (exhibiting separate valence bands) to metallic particles is around at Au_{55} , i.e. at ca. 1.4 nm particle diameter where onset of formation of collective bands can be observed [6]. An important proof of the metallic character is the presence of the characteristic plasmon excitation in the UV–vis spectra at ca. $\lambda = 520$ nm which can be observed on particles with diameters exceeding 2–3 nm [7,8]. The 1.4–4 nm size region is specific from another structural point of view, too. Namely, the fcc structure is not prevailing in the Au NPs, instead, multiple twinned particles (MTPs) are composed from aggregation of decahedral, icosahedral and fcc morphologies as XRD and HRTEM studies revealed [9]. Further, the disorder may induce strains in MTPs, up to 4% decrease in the nearest neighbour distance can even be deduced [10].

One of the most rapidly developing fields for applications of Au NPs is their utilization in therapeutics [11]. Small particles with diameters below 2 nm exhibit intense photoluminescence [8,12,13], e.g. cytotoxic singlet oxygen can be generated on them by using appropriate photosensitisers [14]. On larger particles, instead of photoluminescence, plasmonic excitation is utilized [15]. As applications, heat can be generated on the particles, selected drug molecules can be released, or they can be used as tracer particles for imaging methods [16–18].

The Au NPs should be stabilized by covering them with a protecting layer. In most cases the particles are prepared by reduction of Au^{3+} salt in a solution with simultaneous covering. Various complex forming ligands (phosphines, amino acids, citrates etc.) have been applied for protection so far. Most commonly used is the thiol group (-SH) combined with optional functionalizing groups on the other side of the capping molecules. Interaction of metallic gold with sulphur is the strongest among the optional donor (P, N, O) atoms [19]. The size of Au NPs can be controlled by varying the Au/thiol ratio [20]. Depending on the size various types of gold-sulphur bonds can be formed. Beside the Au–S linear bonds additional monomeric ($Au_{metal}-SR-Au(I)-SR-Au_{metal}$) and dimeric ($Au_{metal}-SR-Au(I)-SR-Au(I)-SR-Au_{metal}$) “staples” can be formed in large molecular complexes, containing only a few dozens of core gold atoms. These structures are dominant at small thiolate capped Au_m ($10 < m < 45$) molecular clusters [2,4,21,22] and they can be observed on the surface of larger particles as well [3,23]. On well-developed crystal faces of larger particles thiol molecules may form self-assembled monolayers [24]. In the transient size range (1–3 nm) the encapsulated particles may easily aggregate and sinter, by preserving simultaneously their protecting layers in part [25]. Dithiols exhibit a particular feature, namely their terminal thiol groups on the same molecule may be linked

to different Au NPs stabilizing thereby large clusters of them. As a possible application, different vapour sensors can be constructed from these assemblies [26,27].

Besides the commonly used spectroscopic techniques, the ^{197}Au Mössbauer spectroscopy is also a suitable tool to study gold, but substantially less articles have been published for structural characterization of gold nano-objects using this method. In this technique all the gold atoms (either present inside metallic particles or located in top surface layers) contribute to the detected signals, occasionally in different extents. A particular advantage is that oxidation state of gold can also be derived from spectra [28]. Glutathione encapsulated various Au_m ($10 < m < 45$) molecular clusters have already been characterized by the method, existence of different types of Au–S bonds were revealed [21,29]. Studies were also performed starting from the other, metallic side of the transition region. Namely, neutral metallic particles were obtained by evaporation onto Mylar foil in various diameters (1.5–8 nm) and contributions emerging from core and surface atoms in different extents depending on the size of particles were separated [30].

Study of stabilization of buthlydithiol encapsulated Au NPs is reported in the present work with regard for perspective sensoric applications. Emphasis was also laid on the distinction of various gold-thiol interactions. The size of particles falls into the range of 1.3–3.9 nm, i.e. spans over the interval from the molecular cluster to evolving small metallic particle size range. The portion of surface Au atoms compared to entirely core ones is still significant in this range (may extend to ca. 50% of the total amount). Thus, detection of surface Au–S bonds can also be envisaged. Distribution of particle sizes is obtained from TEM images, thicknesses of the protecting layers are estimated from thermogravimetry. The protecting thiolate layers are characterized with optical spectroscopies (FTIR and Raman). Metallic cores are characterized with HRTEM and XRD, while the appearance of characteristic surface plasmon is confirmed by UV–vis. Moreover, Mössbauer spectroscopy is also applied with the presumption that signals originated from the core metallic part and from the surface Au–S bonds can be distinguished.

2. Materials and methods

2.1. Materials

The following starting materials were used in the experiments: Gold(III) chloride trihydrate ($HAuCl_4 \times 3H_2O$; $\geq 99.9\%$ Sigma-Aldrich); tetraoctylammonium bromide (TOABr, 98% Aldrich), 1,4-Butanedithiol ($HS(CH_2)_4SH$, 97%, Aldrich), sodium borohydride ($NaBH_4$, $\geq 99\%$ Fluka). The toluene and the ethanol solvents were purchased from Molar. All the materials were used without any further purification.

2.2. Preparation of buthlydithiol functionalized Au NPs

Samples were prepared by modified Brust's synthesis [31]. Namely, 8.88 g (16.24 mmol) tetraoctylammonium bromide (TOABr) was dissolved in 300 ml toluene with continuous stirring. Next, after complete dissolution of the TOABr tenside, 16 ml solution of 4 mmol $HAuCl_4 \times 3H_2O$ was added dropwise. The two phases were firmly stirred for 15 min, when Au(III) ions were transferred to the organic phase by TOABr. 300 μ l (2.58 mmol)

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