Contents lists available at ScienceDirect

Applied Surface Science

Structural studies on drop-cast film based on functionalized gold nanoparticles network: The effect of thermal treatment

Laura Fontana [a], Ilaria Fratoddi [a,*], Iole Venditti [a], Dmitriy Ksenzov [b], Maria Vittoria Russo [a], Souren Grigorian [b]

[a] Department of Chemistry, Sapienza University of Rome, P. le A. Moro 5, 00185 Rome, Italy
[b] Department of Physics, University of Siegen, Walter-Flex-Straße 3, D-57072 Siegen, Germany

ARTICLE INFO

ABSTRACT

In the present work the role of the thermal treatment on the reorganization of gold nanoparticles (AuNPs) functionalized with a π-conjugated dithiol ligand, namely 9,9-didodecyl-2,7-bis-thiofluorene, is studied by grazing incidence X-ray diffraction technique. For a detailed investigation of the structural changes and reorganization occurring in the AuNPs network and of the monitoring of complex interactions between nanoparticles, the line profiles are analyzed in out-of-plane and in-plane directions. The obtained data support the idea of the formation of a uniform network of nanoparticles that after annealing are extended from hexagonal to cubic arrangement.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The control of the organization of nanostructures into well-defined network patterns offers a versatile approach for the development of solid state devices [1,2]. Among other nanomaterials, gold nanoparticles (AuNPs) exhibit a wide range of desiderable optical and electronic properties [3,4] and thanks to a variety of surface functionalizations they can be deposited in complex arrays. For example, self-assembled molecular (SAMs) networks with different architectures have been recently developed [5–7] and opened perspectives in technological applications of noble metal nanoparticles ranging from catalysis [8,9], sensors [10–14], electronics [15,16], biotechnology [17,18] and nanomedicine from diagnosis to therapeutics [19–22], also considering their possible toxicity [23,24].

One of the main challenges in current nanotechnology is the precise control of the size, composition and self-assembly of AuNPs that can be easily achieved by a proper choice of the stabilizing layer [25,26]. Among others, thiol based ligands offer the opportunity of a covalent, stable and chemically tunable layer [27] and in this context the research of our group has been recently devoted. In particular the choice of bifunctional organic or organometallic ligands [28–31] has attracted our attention for the preparation of metal nanoparticles, which lead to the achievement of interconnected network. Moreover, fluorene based bifunctional linkers have been used and by varying the Au/S molar ratio it was possible to tailor the optical and electronic properties of AuNPs and to improve their stability and potential applications [32,33].

Despite the impressive amount of the literature reports on synthesis and characterizations of AuNPs, some points still need further investigation. For example, the role of nanoparticles organization on their optical properties and the effects of interparticle interactions, are noteworthy. AuNPs based networks give rise to broad, red-shifted surface plasmon resonance (LSPR) feature and the morphology of the plasmonic particle assemblies and interparticle distance has a strong impact on their optical response [34]. Considering their potential technological applications it is strongly recommended to follow a controlled growth process to avoid plasmonic field coupling decay [35] and achieve conveniently spaced networks [36,37].

In the present work gold nanoparticles, with diameters of 3–5 nm, functionalized with the π-conjugated dithiol, 9,9-didodecyl-2,7-bis-thiofluorene (FL) have been prepared (namely Au-FL) and studied by means of the grazing incidence X-ray diffraction measurements (GIXD). The GIXD technique is particularly sensitive for the probing of the thin films and low dimensional nanostructures [38,39]. A special advantage of GIXD analysis is to probe orientational distribution within thin films by large-area detectors. In order to characterize the AuNPs network reorganization in particular directions, and to monitor a complex interaction between nanoparticles, the line profiles were analyzed. Assembly

* Corresponding author.
E-mail address: ilaria.fratoddi@uniroma1.it (I. Fratoddi).

and organization processes have been studied for the AuNPs [40] where the higher temperature leads to formation of the ordered crystals of the DNA-functionalized gold nanoparticles [41]. Therefore, the thermal treatment of AuNPs is carried out for detailed investigation the structural changes and reorganization occurring in the AuNPs network.

2. Experimental

2.1. Materials and methods

FTIR and FIR spectra have been recorded on films cast deposited from CH_2Cl_2 solutions using KRS-5 cells, with a Bruker Vertex 70 spectrophotometer. UV–vis spectra were run in CH_2Cl_2 solution by using quartz cells with a Varian Cary 100 Scan UV-vis spectrophotometer. Deionized water, obtained from Zeener Power I Scholar-UV (18.2 MΩ), was degassed for 30 min with Argon, before use.

9,9-Didodecyl-2,7-bis(acetylthio)fluorene was prepared according to previously reported method [42], tetrachloroauric(III) acid triidrate ($HAuCl_4·3H_2O$) tetraoctylammonium bromide (TOAB), sodium borohydride ($NaBH_4$), have been used as received (Aldrich reagent grade). Anhydrous solvents: toluene, CH_2Cl_2, EtOH, $CHCl_3$ (Aldrich reagent grade) have been used as received.

2.2. Gold nanoparticles synthesis

Functionalized gold nanoparticles stabilized with the fluorene derivative (Au-FL) herein used were prepared with Au/S molar ratio 1/2. The synthesis was carried out following literature procedure [43,44], starting from $HAuCl_4·3H_2O$ (0.183 g, 0.466 mmol) dissolved in deionized water (5 mL). The solution was mixed with a phase transfer (tetraoctylammonium bromide, TOAB, 0.310 g, 0.568 mmol) in toluene (10 mL). The mixture was vigorously stirred and the tetrachloroauric acid solution was transferred into the organic layer. At this point, a solution of 9,9-didodecyl-2,7-bis(acetylthio)fluorene (0.3035 g, 0.466 mmol) in toluene (10 mL) was added, allowed to deprotect into thio-ending groups and the mixture was kept under N_2. An aqueous solution of sodium borohydride (0.176 g, 4.66 mmol) in deionized water (5 mL) was added under vigorous stirring and allowed to react for 3 h. At the end, the organic phase was separated with a separator funnel, and washed with water. The organic phase was reduced to 2 mL in a rotary evaporator, and 40 mL of ethanol were added. After one night at −18 °C, the product was isolated by centrifugation at 5000 rpm for 15 min to remove the unreacted thiol and excess of TOAB. The surnatant was eliminated and the precipitate was further washed by centrifugation at 13,400 rpt for 10 min, with ethanol for 10 times. After the removal of the surnatant, a red-violet solution of Au-FL nanoparticles was obtained.

Main spectroscopic characterizations Au-FL sample: UV–vis (CH_2Cl_2): λ_{max} = 525 nm; FTIR and FIR (film): ν = 2992, 2921, 2872, 2851 (νCH_2 and νCH_3), 1712 (w), 1593, 1467, 1457, 1377, 1262, 1028, 973, 722, 226 ($\nu Au−S$) cm^{-1}. These spectra are reported in "Supporting Information" section (Supporting Information, Fig. 1: UV–vis absorption spectrum; Fig. 2: FTIR spectra of pure FL and AuNPs stabilized FL ligand).

2.3. Au-FL sample preparation

The AuNPs films have been prepared by drop casting from a 32.5 mg/mL chloroform solution onto a glass substrate at room temperature. The glass substrate was previously cleaned in an ultrasonic bath in three steps: with a hellmanex solution, isopropanol and acetone for 25 min at 40 °C, rinsing the substrate thoroughly with distilled water between each of the steps. During

the in situ annealing several temperature values starting from initial room temperature till 100 °C have been acquired. In the current paper the data measured at room temperature before the heating and after the cooling will be presented.

Annealing conditions have been set as follows: the sample has been heated up to 100 °C with a rate of 10 °C/min and maintained for 15 min, then the sample has been cooled to room temperature without an active cooling. The measurements have been acquired during 15 min.

2.4. X-ray diffraction experiment

The in situ X-ray diffraction measurements were conducted in grazing-incidence geometry at beamline BL9 the DELTA synchrotron. The experiment was performed at the photon energy of 12.38 keV corresponding to a wavelength λ of 1.0015 Å (with an energy resolution $\Delta E/E$ of 10^{-4}) and with the beam size of 0.5 mm × 0.2 mm in the horizontal and vertical direction, respectively. For the in situ studies, an incident angle α_i = 0.05° has been chosen. The scattering curves were recorded with a large-area MAR345 detector with a sample to detector distance of 0.4 m, covering a range of momentum transfer q to 2.5 Å^{-1}.

The calibration measurements using silver behenate standard were performed to refine the geometrical parameters of the setup. As far the measuring time depends on the intensity of the incident beam the typical exposure time was 10 s. However, for some diffraction patterns longer exposure times (i.e. 20 s and 25 s) have been acquired. Therefore, a normalization in respect to the exposure time has been taken into account for comparison of the line profiles. Temperature measurements under vacuum were conducted using Anton Paar Domed Hot Stage: DHS 1100. The time for thermal equilibration before each measurement was set to 15 min. Initial and final diffraction patterns were taken under ambient conditions. Corresponding GIXD line profiles before and after thermal
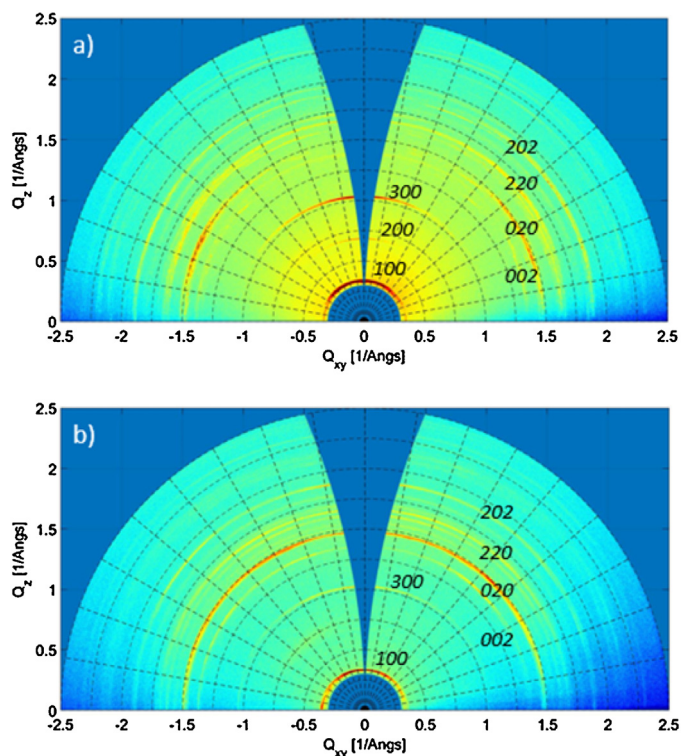

Fig. 1. The AuNPs 2D diffraction pattern in the Cartesian coordinate system (Q_{xy}, Q_z) acquired at room temperature before (a) and after (b) the thermal treatment.