

# Synthesis of gold nano-plates by mercaptide thermolysis in poly(vinyl acetate)

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**Abstract.** Triangular gold nano-plates have been synthesized by thermal decomposition of Au(I) dodecyl-mercaptide (i. e., AuSC<sub>12</sub>H<sub>25</sub>) dissolved in poly(vinyl acetate). Such special shape was achieved because of the ability of polymer side-groups (i. e., the acetate groups) to be selectively absorbed on the most acid faces of the growing gold nanocrystals, thus inhibiting crystal development along these crystallographic directions. Nano-plates had an average edge length of ca. 30 nm and a thickness of a few nanometers.

**Keywords:** *nanomaterials, triangular nano-plates, mercaptides, thermolysis, shape-control*

## 1. Introduction

Physical properties of nano-sized metals, like surface plasmon resonance, luminescence, superparamagnetism, etc., are strictly related to the microstructure [1]. Consequently, the characteristics of nanoscopic metals can be simply tuned by modifying their morphology (i. e., the particle size and shape). Size-control has represented the first approach to achieve specific physical characteristics, but also shape-control can be used for the same purpose [2]. The dependence of physical properties on particle shape makes this second approach as the most convenient to tailor specific nanostructure properties. In the last decades, shape-control has represented a great challenge for researchers working in the nanoscience area, but it is quite difficult to obtain and it has been achieved only in few cases by solution-chemistry routes based on adequate capping agents [2].

Recently, a novel *in situ* chemical route for the synthesis of metal nanoparticles confined in polymeric matrices has been developed [3]. Such approach is based on the thermal decomposition of special metal precursors (namely homoleptic mercaptides) dissolved into a polymeric medium. In this paper, the isothermal decomposition of gold dodecyl-mercaptide in poly(vinyl acetate) at a temperature of 160°C has been investigated. This polymeric growth medium for the metal phase has shown a certain ability to influence crystal development, originating a differential growth in the crystallographic directions. In particular, the polymer side-groups are selectively adsorbed on specific crystal faces (the most acid one) [4], thus inhibiting the development of these crystal faces, while the less-acid faces may grow by progressive deposition of gold atoms. However, such selective 'poisoning-effect' produced by the poly(vinyl acetate) side-groups can be well evidenced only after that a significant growth of gold crystals has occurred. Con-

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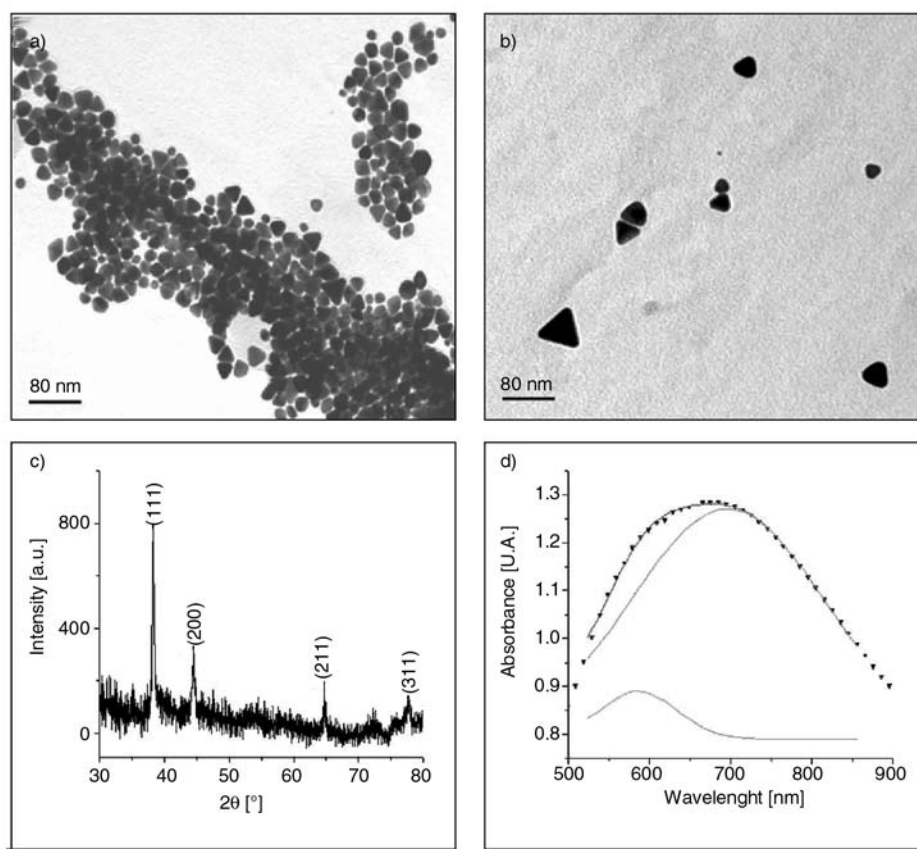
sequently, the formation of simple polyhedral structures (nano-prisms) is observed in the system when gold nanocrystals have reached a size of several tens of nanometers. To the best of our knowledge, it is the first time that a solid-state approach for the shape-controlled synthesis of triangular gold nanoplatelets has been described.

## 2. Experimental

The thermolytic organic precursor used to generate gold atoms inside the polymeric phase was Au(I) dodecyl-mercaptide (i. e., AuSC<sub>12</sub>H<sub>25</sub>) [5]. This chemical compound was synthesized by treating an ethanol solution of gold tetrachloroauric acid (HAuCl<sub>4</sub>, Aldrich) with an ethanol solution of 1-dodecane-thiol (C<sub>12</sub>H<sub>25</sub>SH, Aldrich) at room temperature under stirring. The obtained light-yellow solid precipitate was separated by vacuum-filtration, purified by washing with acetone, and then dissolved/dispersed in a chloroform solution of poly(vinyl acetate) ( $M_w = 245\,000\text{ g}\cdot\text{mol}^{-1}$ , Aldrich). Thin films of dry poly(vinyl acetate)/

gold-mercaptide blends, containing 10% by weight of mercaptide, were obtained by solution casting from chloroform: it is worth to mention that the chloroform evaporation rate is a parameter to be set as well in order to achieve an homogeneous spatial distribution of the mercaptide inside the polymeric matrix. Gold nano-crystals were generated in the polymer phase by thermal decomposition of gold mercaptide under isothermal conditions. In particular, the heat treatment was performed at a temperature of 160°C. To avoid temperature gradients in the thermally annealed blends, the specimens were shaped in form of films which were placed between two preheated metallic plates (at ca. 160°C) to have the same temperature value on both specimen surfaces.

The obtained polymer-embedded nano-crystals were characterized by Transmission Electron Microscopy (TEM, Philips EM2085), Atomic Force Microscopy (AFM, Nanoscope IIIA, Digital Instruments), X-Ray Diffraction (XRD, Rigaku DMAX-III C), and Optical Spectroscopy (UV-Vis-NIR Spectrophotometer, HP 8453).



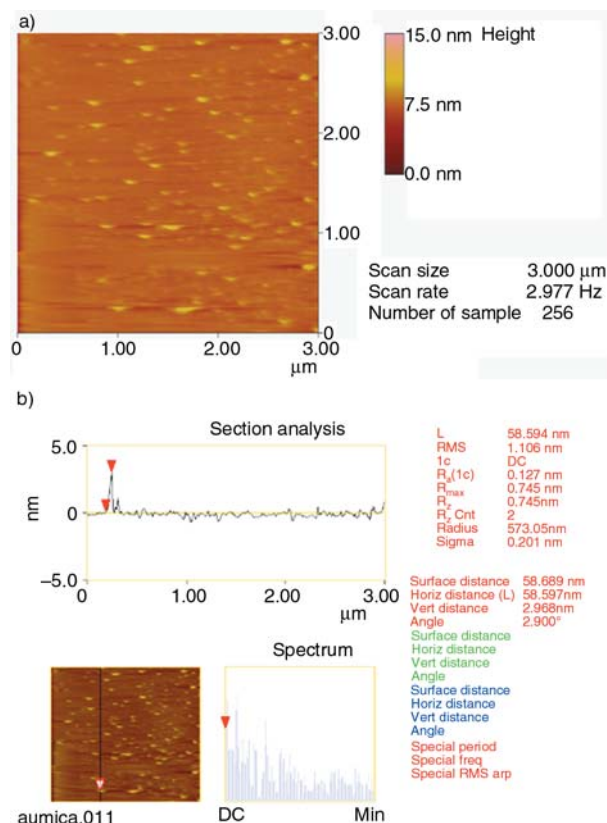
**Figure 1.** Gold nano-crystals characterization data: TEM-micrograph of variously shaped nano-crystals after separation/fractionation by centrifugation (a), TEM-micrograph of some isolated triangular nano-plates (b), XRD-diffraction pattern (c), and UV-Visible spectrum (d) (experimental data (▲); experimental Gaussian fit (solid black line); deconvolution of experimental data (grey lines))

### 3. Results

Figure 1 shows the microstructure of triangular gold nano-plates which resulted after isothermal annealing of 30 minutes at 160°C. As visible, the particles had a regular shape, consisting of simple polyhedrons, mainly made of triangular and square nano-platelets (prismatic crystals with triangular and square basal-planes). Since an uniform contrast characterized the crystal image, the presence of pyramidal geometry should be excluded. Both isolated and aggregated nanocrystals were present in the films. The average edge length of triangular nano-plates was of ca. 30 nm but a broad size-distribution characterized all samples. The thickness of nano-platelets cannot be estimated from TEM pictures but it was established by Atomic Force Microscopy (AFM). In particular, polymer-embedded gold nano-crystals were dissolved in chloroform and separated by centrifugation (6,000 rpm). Nanocrystals were dispersed in chloroform and a suspension drop was placed on a mica film for AFM observation. A thickness of ca. 2 nm can be measured by AFM investigation of the aggregated triangular nano-crystals, as the Figure 2 shows. In addition to the large nano-crystals, a low percentage of spherical gold clusters with a size inferior to 10 nm was also present in the samples.

Figure 1c shows the XRD-spectrum of polymer-embedded nano-plates. Owing to the amorphous nature of poly(vinyl acetate), only the diffraction pattern of gold phase was visible. The spectrum included tight peaks since the metallic phase had an average size of several nanometer tens. The most intensive peak was corresponding to the  $[111]$  plane, which is therefore the most developed crystallographic direction of triangular nano-plates [6]; such structural feature is quite common for metallic nano-plates, in fact similar structures have been found in the cases of silver, nickel, and copper nano-plates [7].

Optical properties of gold nano-crystals have been studied after their extraction from the polymeric matrix. To limit light-scattering phenomena produced by the large crystals, which significantly decreased the signal to noise ratio, optical spectra were recorded from quite dilute suspensions in chloroform. Figure 1d shows the typical optical spectrum of a gold nano-plate sample. The spectrum included a quite broad and intensive absorption band located at about 600 nm, which is



**Figure 2.** AFM image of gold nano-plates (a) and section analysis (b)

produced by the surface plasmon resonance of the nano-sized metallic phase. The convolution of this broad signal gives two distinct absorption bands. The band located at 580 nm can be attributed to the surface plasmon absorption of the low percentage of spherical nanoparticles present in the sample, whereas the absorption peak located at ca. 700 nm should be assigned to the in-plane quadrupole mode of gold triangular nano-plates [8].

### 4. Discussion

In general, an aspect of a fundamental importance to achieve nano-sized metal phases is to prevent aggregation in the produced solid. Particle aggregation can be avoided by generating the metal in a high viscous medium. Molten thermoplastic polymers have a very high viscosity and therefore they are ideal matrices for the nucleation/growth of nanometric metals. The polymeric medium should have a glass transition temperature ( $T_g$ ) lower than the decomposition temperature of the metal precursor. In addition to the high viscosity also a certain ability to be absorbed on the metal surface is required for the polymer, in order to avoid metal

segregation and therefore its aggregation. When the metal phase is generated by thermal decomposition of homoleptic mercaptides, amorphous polystyrene represents a quite good material for cluster formation/growth since the glass transition temperature is not too far below the mercaptide decomposition temperature and the ability for the polymer side-groups to be lightly absorbed on the electrophilic metal surface (probably by  $\pi$ -electron density donation from phenyl groups to the metal). However, the faces of a metal crystal have a different ability to bond nucleophilic species, because the acidity of absorption sites depends on the metal coordination number. The quite low ability of polystyrene side-groups to be absorbed on the crystal faces is not enough to discriminate between them. Owing to the ester functions in the poly(vinyl acetate) side-groups, these molecules are preferentially absorbed on the most acid faces of the metallic crystals. Polymer absorption creates a diffusion barrier on these crystal faces, thus inhibiting their development and simplifying the polyhedral geometry. To observe such a differential growth of the crystal faces a significant crystal development is required. For such a reason, mercaptide should be slowly decomposed to generate the metal atoms required to grow nuclei by surface deposition. In the growth of triangular gold plates, thermal decomposition was performed at 160°C and the annealing treatment required more than 30 minutes to allow significant growth of metal crystals with a differential development of crystal faces. Finally, according to the LaMer model for monodispersed particle formation, a single nucleation stage must take place during the process, and then the generated nuclei should grow by addition of gold atoms to the crystal surface. During the growth stage the most acid faces do not significantly develop because of polymer absorption, leaving to a simple geometrical figure.

## 5. Conclusions

The possibility to obtain triangular gold nanoplates by an *in situ* synthesis based on mercaptide thermal decomposition in polymer medium has been investigated. The selection of polymer with adequately capping side-groups allows to simplify the shape of polyhedral crystals by inhibiting the development of most acid crystallographic faces. As a result, the poly(vinyl acetate) with has shown to be a good growth medium to achieve triangular nanoplates.

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