

Synthesis of gold nanoparticles in solid state by thermal decomposition of an organometallic precursor

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Gold nanoparticles were obtained directly in solid polymer films by thermal decomposition of the $[\text{O}(\text{Au}(\text{PPh}_3)_3)_3][\text{BF}_4]$ precursor molecularly dispersed in the polymer and by decomposition of microcrystals on different supports. The nanoparticles were characterized with transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-Vis spectroscopy, and wide-angle X-ray scattering (WAXS). In spite of high precursor concentration, the size of the obtained nanoparticles was similar to those prepared in diluted solutions.

Key words: *metal nanoparticles; polymer nanocomposites; organometallic precursor; TEM; WAXS*

1. Introduction

The synthesis as well as chemical and physical properties of metal and semiconductor nanoparticles (NPs) and nanocomposites are presently of considerable interest due to their potential application in materials science, including molecular electronics. Obtaining polymeric materials containing nanoparticles has been the subject of several studies (e.g. [1–4]). The nanoparticles are usually obtained in a separate process and dispersed in polymers using various methods. The surfaces of nanoparticles are covered by stabilizers screening interactions between the metal and polymer. It is also difficult to obtain a uniform dispersion of NPs in the matrix. The decomposition of organometallic precursors directly in the polymer film should lead to a “clean” metal surface (no strongly bound stabilizer layer between the metal and polymer) and good dispersion without using additional stabilizers.

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There are only a few reports on the preparation of metal particles *in situ* in solid polymer films. Tannenbaum et al. [1] obtained Fe particles by thermolysis and photolysis of carbonyl complexes. Polymer composites with several transition metal nanoclusters were also obtained by decomposing organometallic precursors in phase-separated block copolymers [2, 3].

We have found [5] that different organometallic precursors, e.g. Ru(COD)(COT) (COD – 1,5-cyclooctadiene, COT – 1,3,5-cyclooctatriene), Co(η^3 -C₈H₁₃)(η^4 -C₈H₁₂), Ni(COD)₂, and Rh(allyl)₃ can be decomposed under dihydrogen yielding small metal nanoparticles also in the solid state. The nanoparticles obtained are only a few nanometers in size, not much more than when the decomposition is carried out in dilute solution.

In this paper, we report the preparation of gold nanoparticles by decomposition of an organometallic precursor dispersed in solid polymer films or as microcrystals. The organometallic complex, μ_3 -oxo[tris(triphenylphosphine)gold](1+)tetrafluoroborate(1-) [O-(Au(PPh₃))₃][BF₄], was chosen as the Au atom precursor, because it has been shown to be a good source of Au for NP synthesis in solution, well soluble in many organic solvents, and sufficiently stable to handle in an ambient atmosphere [6].

2. Experimental

[O(Au(PPh₃))₃][BF₄], was synthesized according to [7]. The starting materials used to obtain nanocomposites with gold nanoparticles were polymer films with a dispersed organometallic complex. Poly(methyl methacrylate) (PMMA) ($T_g = 115^\circ\text{C}$) was used as the stabilizing matrix. The films were prepared by casting toluene (for PMMA) solutions and slowly evaporating the solvent. Initial solutions (4% of the polymer with respect to the solvent) contained the precursor (0.25–15 wt. % of the precursor with respect to the polymer). Two kinds of films were studied: standard free-standing films cast on glass plates (ca. 20 μm thick), which were used for UV-Vis and XRD measurements, and thin films (below 200 nm) prepared by placing a drop of the solution directly on a TEM copper support grid covered with a carbon layer. The decompositions of precursor crystals or thin layers obtained from solution, without the polymer, on TEM grids or on a solid support were also carried out. Samples for SEM were prepared by depositing a drop of the precursor solution or gold NPs in a suitable solvent on a freshly cleaved mica or Si support covered with a 100 nm SiO₂ layer.

Thermal decompositions of the gold precursor were performed in air at 130 $^\circ\text{C}$ (above T_g of the polymer). The initially transparent film turns red during the reaction due to absorption by surface plasmons. For comparison, the decomposition was also carried out in a mesitylene solution. The reaction was carried out in air (20 min. at 130 $^\circ\text{C}$). Hexadecylamine was used as the stabilizing agent. Transmission electron microscopy (TEM) and scanning electron microscopy with a field emission gun (SEM-FEG) were used to determine the morphology, particle size, and size distribution. TEM measure-

ments were performed on a JEOL 200 CX (200 kV), SEM measurements on a JEOL JSM 6700F – both at the TEMSCAN facility, Université Paul Sabatier, Toulouse. More than 200 particles were measured in order to draw a size histogram. UV-Vis transmission measurements of standard films with Au NPs were carried out using a Perkin-Elmer Lambda 35 spectrophotometer. Structural characterizations of NPs by wide angle X-ray scattering (WAXS) were performed in the solid state. The polymer film was rolled and measured in air. Measurements of the X-ray intensity scattered by the samples irradiated with graphite-monochromatised molybdenum K_{α} radiation (0.071069 nm) were performed using a dedicated two-axis diffractometer. Fluorescence of gold was removed in the measurement step by filtering. The data collection time was typically 30 hours for a set of 457 measurements collected at room temperature, in the range of $0^{\circ} < \theta < 65^{\circ}$ for equidistant s values [$s = 4\pi(\sin\theta/\lambda)$].

3. Results

Figure 1 shows TEM images of gold NPs obtained by the thermal decomposition of $[\text{O}(\text{Au}(\text{PPh}_3)_3)]\text{BF}_4$ in a thin PMMA film for various concentrations of the precursor. It can be seen that for precursor concentrations of 1–2 wt. %, the obtained NPs are small (ca. 5 nm) and uniformly distributed. For higher concentrations, the average size increases and the size distribution is much broader. This is probably caused by the coalescence of small NPs rather than by their continuous growth. At high concentrations, NPs have some tendency to agglomerate in the film and their distribution is not so uniform. The formation of gold nanoparticles gives rise to surface plasmon absorption in the visible range. In Figure 2, we show UV-Vis spectra of nanocomposites prepared by annealing PMMA standard films containing oxonium salt. Increasing the concentration above 2 wt. % of the precursor leads to a red shift of the surface plasmon resonance peak, caused by a change in the distances between NPs (agglomeration) and to some extent by an increase in their size.

Figure 3 shows the reduced radial distribution function (RDF) of Au NPs in a PMMA film (5 wt. % of the metal). The pattern observed is typical of Au NPs of fcc structure, and no distances above 4 nm are observed. The instrument used for WAXS measurements, however, introduces a significant peak broadening. Since the size observed by TEM (ca. 9 nm) is much larger than the related instrumental size limit (ca. 4.5 nm) and no evidence of polycrystallinity has been observed for the NPs, the former is retained as the actual size.

Figures 4 and 5 show SEM micrographs of Au NPs obtained by decomposition of precursor crystals and its layers deposited on a support. In spite of a very high, 100% concentration of the precursor, the size of the nanoparticles is only ca. 10 nm. The kind of support used (mica or Si) does not significantly influence the NP size. Non-uniform distribution of NPs seems to be caused by an inhomogeneous thickness of the initial precursor layer in some places.

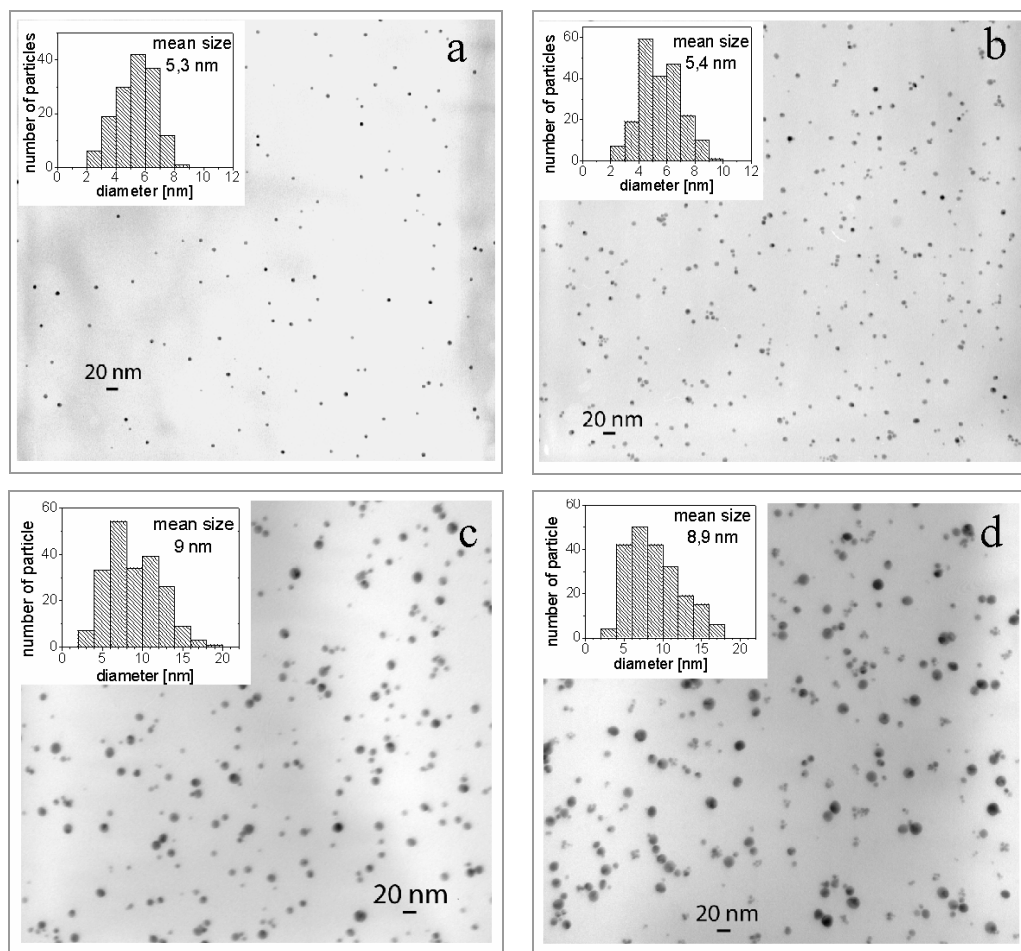


Fig. 1. TEM images of gold NPs obtained by the thermal decomposition of $[\text{O}(\text{Au}(\text{PPh}_3)_3)][\text{BF}_4]$ dispersed in a thin PMMA film: a) 1%, b) 2%, c) 4%, d) 8wt. % of the precursor. The insets show size distributions

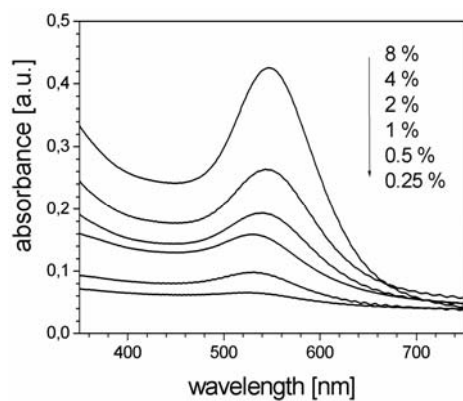


Fig. 2. UV-Vis spectra of gold nanoparticles prepared by annealing of $[\text{O}(\text{Au}(\text{PPh}_3)_3)][\text{BF}_4]$ dispersed at different concentrations (from 0.25 to 8 wt. %) in PMMA standard films

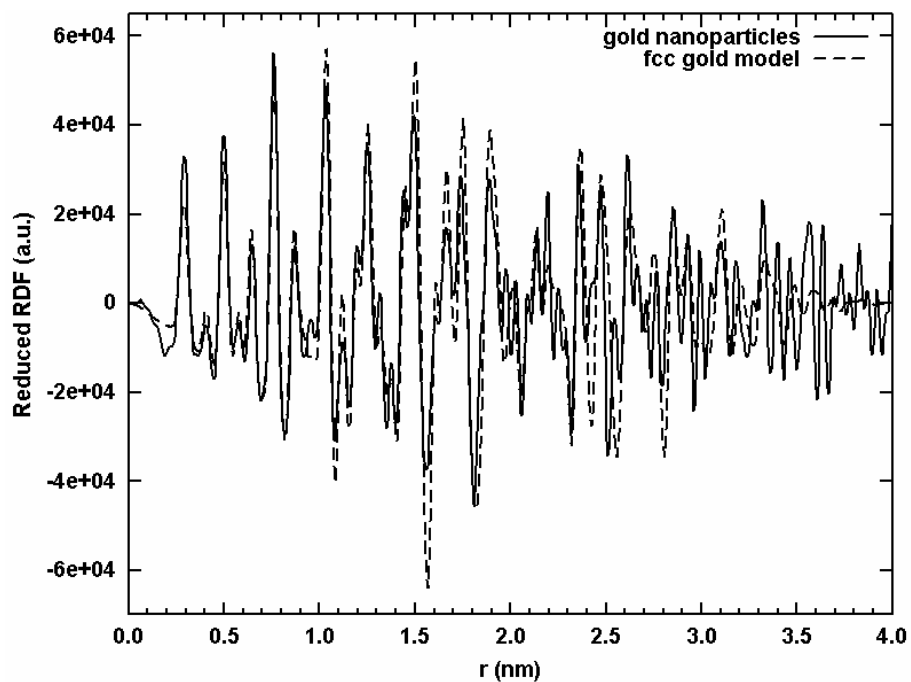


Fig. 3. RDF of Au NPs in PMMA films (5 wt. %), compared to a computed RDF for a 4 nm fcc structure

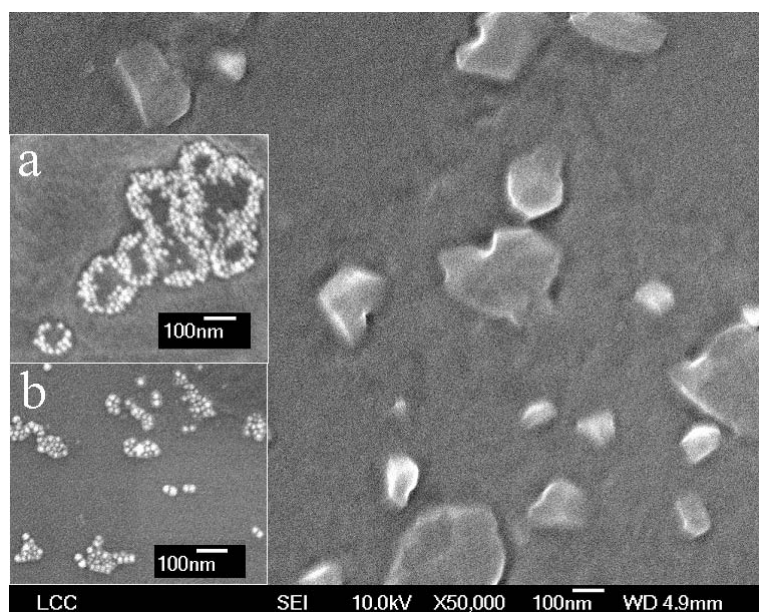


Fig. 4. SEM-FEG images of $[\text{O}(\text{Au}(\text{PPh}_3)_3)][\text{BF}_4]$ microcrystals deposited on a Si support. Insets show Au NPs obtained after the decomposition of the crystals (5 min. at 130°C)

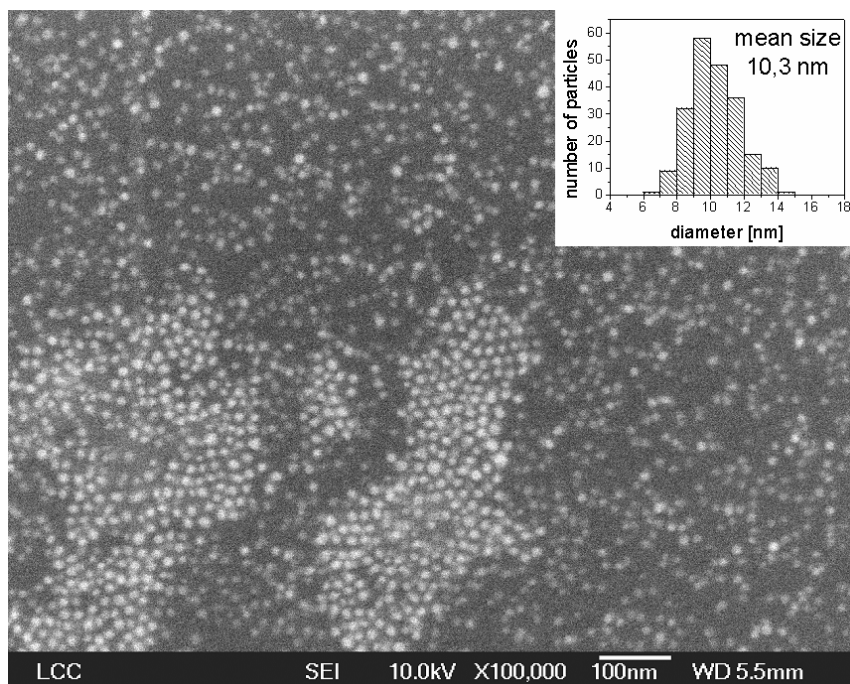


Fig. 5. SEM-FEG images of gold NPs obtained by decomposing (10 min. at 130 °C) a thin layer of $[\text{O}(\text{Au}(\text{PPh}_3)_3)][\text{BF}_4]$ crystals deposited on a Si support

4. Discussion

Our results show that small metal nanoparticles can be obtained in the solid state not only by hydrogen reduction (described by us in detail elsewhere [5]), but also by thermal decomposition of the $[\text{O}(\text{Au}(\text{PPh}_3)_3)][\text{BF}_4]$ precursor. The obtained Au NPs are much bigger than those of Ru, Co, and Rh obtained by us previously (ca. 2 nm, obtained, however, below T_g), but they are still only 5 nm in size, even when precursor concentration is very high, up to 100% in the case of precursor crystal or thin layer decomposition. This is interesting in view of the efforts of various groups that use diluted solutions, different stabilizing agents, or “nanoreactors”. It is not surprising that after the decomposition of the precursor in a polymer matrix, metal nanoparticles are formed (in agreement with results obtained by other groups [1–3]) but one could expect the formation of bigger particles by solid precursor decomposition. This result means that the products of precursor decomposition act as stabilizers, preventing the growth of NPs. These results also show that this effect is quite common, as we have observed it for several different precursors and for different metals.

From the point of view of polymer composite preparation, the relatively strong interaction of NPs with the products of precursor decomposition can be a disadvantage, since it means that the decomposition products are difficult to remove from the system

and that the polymer may not be in direct contact with the metal. Comparing with the results for the carbonyl precursor decomposition presented in [1], our nanoparticles are several times smaller and more homogeneously dispersed. This can be related to a more homogeneous, probably molecular, distribution of the precursor in the matrix in our case.

5. Conclusions

We have shown that polymer nanocomposites with small metal nanoparticles can be prepared by the decomposition of organometallic precursors dispersed in solid polymer films and even precursor crystals or layers. The obtained NPs have fcc structure, that of bulk gold, with a coherence length of ca. 4 nm. Also, the decomposition of precursor microcrystals and thin layers yields small metal nanoparticles. The obtained nanoparticles were in all cases only a few nanometers big, not much larger than when the decomposition was carried out in dilute solution. The presented method can probably also be used to obtain semiconductor nanoparticles, and it offers new possibilities of preparing materials for molecular electronics.

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