



## Fractal analysis of inter-particle interaction forces in gold nanoparticle aggregates



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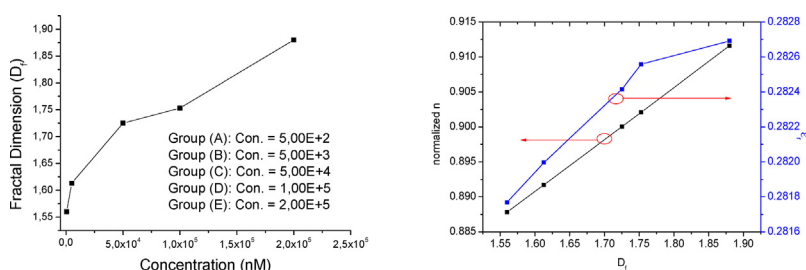
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### HIGHLIGHTS

- Gold nanoparticles drop-cast on glass form aggregates with fractal dimension.
- The higher the solution concentration, the higher the fractal dimension.
- Fractal dimension can describe the plasmonic shift due to different aggregation density.
- We infer a connection between the forces driving aggregation and the fractal dimension.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Self-assembly of gold nanoparticles (AuNPs) can be used for several applications including sensors, lab on chips, and surface enhanced Raman scattering sensitive substrates. The architecture of the AuNPs aggregates is driven by the nanoparticle size, surface charge, and dielectric constant, and by the surface functionality of the substrate, which determine the mutual interaction forces among the AuNPs. These forces were indirectly investigated by means of fractal analysis of the resulting patterns of aggregates. We drop-cast AuNPs dispersions with five different values of concentration onto glass substrates, which resulted in self-assembled thin films with different aggregation density. We imaged the AuNPs aggregates with scanning electron microscope and studied their topological properties. We observed an increase in the fractal dimension of the aggregates with the AuNPs concentration, reaching a fractal dimension value of  $1.56 \pm 0.01$  for the low-density samples and  $1.88 \pm 0.01$  for the high-density samples. Concurrently, the photoluminescence peak showed only a weak red-shift with increasing concentration, while the X-ray photoelectron spectroscopy showed higher binding energy than in the bulk gold, due to the different structural arrangement of the AuNPs. Thus, a correlation was established between the fractal dimension and the inter-particle interaction forces that control the aggregation.

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## 1. Introduction

Self-assembly of nanoparticles on a substrate is an adventitious process, in which the nanoparticles are spontaneously accumulated through correlative interaction [1,2]. The correlative behavior is affected by several factors, including the particle size, morphology [3], particle surface functionality, substrate nature, and finally

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the deposition technique [3]. All these factors together determine the electrostatic forces that are responsible for aggregation of the nanoparticles in the resulting pattern [4,5]. Hence, by knowing the surface chemistry and manipulating the solvent evaporation during the process, several architectural structures can be produced [3,6,7]. Various self-assembly patterns were reported up to date, including one-dimensional arrays [6] and spherical structures [7], which serve in distinct applications such as sensors [8], antennas [8], and nano-motors [9].

On the other hand, surface aggregates of nanoparticles may present a statistical self-similarity. Metal nanoparticle aggregates formed under different conditions show a symmetry that can be described by fractal analysis [10]. The fractal dimension is a crucial parameter for understanding numerous physical properties of the compositional structural materials. For example, fractal analysis was recently employed for characterizing the membrane protein aggregation using fluorescence resonance energy transfer [4]. Furthermore, fractal analysis was also successfully applied to illustrate various behaviors of biological molecules by using data extracted from plentiful techniques, such as light scattering, small angle X-ray scattering, and conductivity measurements [11–13].

Different from the spectroscopic characterization techniques, which were used to analyze the aggregation of the nanoparticles in a dispersive medium, scanning electron microscopy (SEM) provides an insight into the morphology of the areas covered by thin films of nanoparticles coated onto the supporting surfaces. By implementing the fractal analysis of SEM images of surface aggregates of nanoparticles, it is expected to deduce more cognition about the accumulating behavior of the nanoparticles during the formation, and a better understanding of the interaction forces that form the aggregates [4,5]. This is based on the assumption that a correlation may exist between the resulting aggregates patterns and the physical properties driving the self-assembly of the starting nanoparticles. Clarifying this possible correlation can probably pave the way for fabricating cheap metal contacts and self-assembled optoelectronics.

In principle, the coordination number of particle aggregates, i.e. the number of primary particles close to a given particle, can also be qualitatively determined from the fractal character: smaller fractal dimension implies a lower coordination number, which in turn implies lower tensile strength and low-density aggregation. Accordingly, the fractal dimension has different values for different scattering cross section of the aggregates [14,15].

To the best of our knowledge, there is no study in the literature that correlates the fractal dimension of the aggregates to their concentration and/or inter-particle interactions forces. We characterized the fractal nature of our aggregates of AuNPs from SEM images. Five concentrations of AuNPs dispersed in water were prepared, and deposited by drop-casting, with all the other parameters kept constant during preparation. The particle size was confirmed using X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the photoluminescence (PL) of the starting nanoparticle solutions was measured. The binding energy of the prepared high concentration group sample was also measured by using X-ray photoelectron spectroscopy (XPS). The study shows the direct connection of the fractal dimension of the aggregates, which describes their hidden symmetry, as a function of the inter-particle forces.

## 2. Experimental

### 2.1. Materials

Ultrapure (99.99%) Hydrogentetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) (Alfa Aesar, Germany) and trisodium citrate (TSC)

(Sigma Aldrich, Italy) were used as received. Milli-Q water with high purity and resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  was used during all the nanoparticles synthesis, cleaning and samples preparation. For deposition of the AuNPs films, we used glass substrates of  $\sim 4 \text{ cm}^2$ . The substrates were manually cut with a diamond scribe off of optical microscope glass slides (1 inch  $\times$  3 inches,  $\sim 1 \text{ mm}$  thickness) from Menzel-Gläser (Germany). After cutting, the substrates were cleaned by successive sonication (5 min at each step) in warm acetone, then isopropanol, then water, and finally blown dry under a nitrogen stream. As the last step, the substrates were treated for 20 min inside an UV-Ozone cleaner Procleaner (BioForce Nanosciences, USA).

### 2.2. Synthesis of the AuNPs

AuNPs were synthesized according to Turkevich-Frens method using TSC as reducing as well as capping agent [16]. Briefly, 250 mL of solution (pH 3.7) was prepared in an Erlenmeyer flask with 100 mL of 1 mM aqueous  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , brought to boiling with vigorous stirring. Thereafter, 10 mL of 70 mM aqueous TSC were added quickly, and then the reaction solution was continuously stirred until its color turned dark red. After that, the temperature was decreased and the nanoparticles were collected and cleaned by three cycles of centrifugation at 10,000 rpm for 20 min each, in which the supernatant was replaced every time by water. Finally, the nanoparticles precipitate was collected and dispersed in water for characterization and thin film preparation. AuNPs dispersions with five different concentrations were prepared, namely 0.5, 5, 50, 100 and 200  $\mu\text{M}$ , denoted A, B, C, D, and E, respectively. These solutions were used for thin film deposition, where 1 mL of each sample was drop-cast on a glass substrate, and allowed to dry at room conditions.

### 2.3. Characterization

The size of the primary AuNPs was measured using a TEM instrument JEM1011 (Jeol, Japan) at 100 kV, and the surface plasmon resonance was examined using a spectrophotometer Cary 6000i (Varian, Italy).

The  $\zeta$  potential of the AuNPs in the solutions used to prepare the films of aggregates was also measured, using a dynamic light scattering instrument Zetasizer Nano ZS (Malvern Instruments, UK). For each concentration,  $\sim 0.8 \text{ mL}$  of solution was added to a polystyrene disposable capillary cell DTS1070, and four runs of five measurements each were carried out, and finally averaged.

On the films of AuNPs aggregates, the samples prepared from the five differently concentrated solutions were investigated by field emission SEM with an instrument JSM 7500F (Jeol, Japan). The shift in binding energy from bulk value of Au for the core level  $4f_{7/2}$  and  $4f_{5/2}$  was characterized using XPS, in order to assess the possible changes of  $\text{Au}4f_{7/2}$  and  $\text{Au}4f_{5/2}$  peaks as compared to the same peaks arising from bulk Au.

XPS measurements were made using an electron spectrometer Lab2 equipped with a monochromatic X-ray source set at 1253 eV and with an hemispherical energy analyzer Phoibos HSA3500 (all from SPECS, Germany). The applied voltage of the Mg K alpha X-ray source was set at 10 kV and the applied current at 15 mA. The pressure in the analysis chamber was about  $2 \times 10^{-9} \text{ mbar}$ . Large area lens mode was used for both wide and narrow scans. For the wide scan, the energy pass was 90 eV, the energy step was 0.5 eV, and the scan number was 2. For the narrow high-resolution scan, the energy pass was 30 eV, the energy step was 0.1 eV, and the scan number was 20. Flood gun was used to neutralize the surface charge, with an energy of 7 eV and a filament current of 2.6 A. The C1s was charge corrected to 285.0 eV and used as a reference [17,18], and the spectra were then analyzed using CasaXPS software.

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