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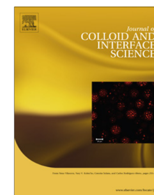

Amino acid induced fractal aggregation of gold nanoparticles: Why and how

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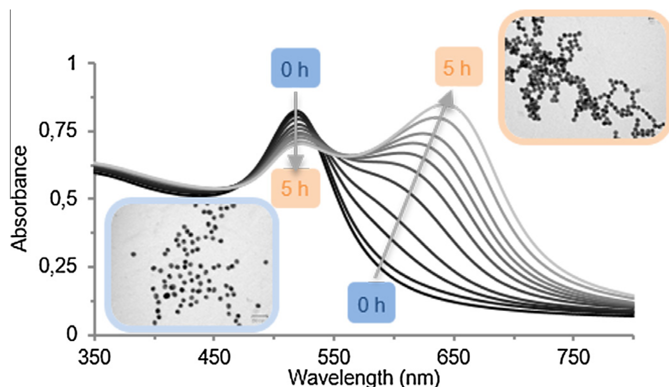
GRAPHICAL ABSTRACT



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ABSTRACT

Gold colloids are the object of many studies as they are reported to have potential biological sensing, imaging and drug delivery applications. In the presence of certain amino acids the aggregation of the gold nanoparticles into linear structures is observed, as highlighted by the appearance of a second plasmon band in the UV–Vis spectra of the colloid. The mechanism behind this phenomenon is still under debate. In order to help elucidate this issue, the interaction between gold colloids and different amino acids, modified amino acids and molecules mimicking their side-chain was monitored by UV–Vis absorption, DLS and TEM. The results show that phenomenon can be rationalized in terms of the Diffusion Limited Colloid Aggregation (DLCA) model which gives rise to the fractal aggregation colloids. The global charge of the compound, which influences the ionic strength of the solution, and the ease with which the compound can interact with the GNPs and affect their surface potential, are, the two parameters which control the DLCA regime. Calculations based on the Derjaguin, Landau, Verwey and Overbeek (DLVO) theory confirm all the experimental observations.

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1. Introduction

The unique and tailorable physical, optical, electrical and chemical properties of noble metal nanoparticles are the source of much inspiration for the development of novel devices with varied applications in the biological and biomedical fields [1–4]. Gold nanopar-

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ticles (GNPs) are in this context of particular interest due to their remarkable optical properties [5,6], presumed biocompatibility [7] and ease of surface functionalization.

With a Localized Surface Plasmon Resonance (LSPR) band in the visible range (around 520 nm for GNPs with a diameter of 15 nm) [5,6], GNPs are particularly good candidates for the development of colorimetric sensors [1,2]. The detection of an analyte is based on a change in the LSPR band following the analyte adsorption or recognition at the GNP surface. Studies have been reported with proteins [8–11], DNA [12–16], amino acids [17–19] and metal ions [20–23]. Most often, the adsorption of the analyte is designed to lead to GNPs aggregation as this leads to a drastic change in colour due to the coupling between the surface plasmons of neighbouring nanoparticles [24,25]. In order to develop reliable analytical applications, it is important to understand the origin of the GNP–biomolecule interactions and to control the aggregation step.

For drug delivery [3] or imaging applications [4], GNPs must be stable in biological fluids, a complex environment composed of a dense mixture of molecules such as proteins, lipids, carbohydrates and amino acids. It is known that when nanoparticles come into contact with biological fluids, the biomolecules present can cover their surface forming what is usually called a "*corona*" which defines the "*biological identity*" of the nanoparticle [26–29]. The corona is what the cell "*sees*" and interacts with, and it controls the distribution and fate of the nanoparticles in the organism. It is consequently of also of great importance for *in vivo* applications to know how to control the interaction between GNPs and biomolecules so as to improve their efficiency and safety.

Several studies devoted to the monitoring of the interaction between citrate stabilized GNPs and biological molecules are described in the literature. It has for example been observed, that the interaction between GNPs and some of the natural amino acids, more particularly arginine [30–34], lysine [33–36], histidine [34], cysteine [34,37], homocysteine [38] and methionine [33,39], leads to an aggregation mode which gives rise to a second LSPR band at higher wavelengths. This phenomenon has been described as the consequence of the formation of linear chains of GNPs, leading to the formation of "*rod-like*" structures, as observed by TEM [31,32,37,39]. It is indeed known that nanorods present two bands in their UV–Visible spectrum, one in the 520 nm range, associated to their transverse dimension, and a second, bathochromically shifted, associated to their longitudinal axis [40].

Two models are proposed to explain the appearance of this second band. The first model hypothesises that the amino acids partially replace the citrate ions adsorbed at the surface of the GNPs, and that favourable interactions between the zwitterionic heads of adjacent amino acids lead to the formation of amino-acid dense clusters on the surface. This patchy distribution on the surface induces an electronic dipole through the nanoparticle and the alignment of theses dipoles leads to the formation of branched linear structures of GNPs [31,32]. The second proposed model hypothesises that certain amino acids interact with the gold surface specifically via their side chains and that hydrogen bonds between the zwitterionic heads of amino acids adsorbed at the surface of neighbouring GNPs, leads to their aggregation in a linear structures [33,35,37–39].

As the explanations put forward to explain changes in the UV–Visible spectra of GNPs when brought in contact with different amino-acids is currently still controversial, we have decided to investigate these interactions more closely. A better understanding of the mechanism of interaction between GNPs and amino acid would indeed be very helpful for the development of reliable biosensors and could also contribute to the understanding of the fate of gold nanoparticles in biological fluids.

2. Materials and methods

2.1. Synthesis of gold nanoparticles (GNPs)

GNPs were synthesized according to a modified Turkevich method [41,42]. All solutions were prepared with HPLC grade water. Glassware was soaked prior to use with aqua regia (25% HNO_3, 75% HCl) and thoroughly rinsed with milli-Q water. 1 mL of trisodium citrate solution ($Na_3C_6H_5O_7$, Alfa Aesar) was injected into 50 mL of boiling aqueous tetrachloroauric solution ($KAuCl_4$, Sigma Aldrich), both adjusted to pH 7 using concentrated HCl or NaOH. After mixing, the solution was refluxed for five minutes and then allowed to cool to room temperature. Concentrations were chosen so as to achieve a final concentration of 3 mM in $AuCl_4^-$ with a citrate to gold ratio of 1. GNPs were analysed by transmission electron microscope (TEM), Philips CM20-UltraTWIN equipped with a lanthanum hexaboride (LaB6) crystal at 200 kV accelerating voltage.

2.2. Study of the interactions between GNPs and amino acids

GNPs were dialyzed during 24 h in a 1 mM citrate solution (HPLC grade water) using dialysis membrane with a 1 kDa Molecular Weight cut-off (purchased from Orange Scientific) to remove unreduced chloroaurate and oxidation products of citrate present in solution while controlling precisely the citrate concentration. GNPs were diluted using a 1 mM citrate solution to obtain an absorbance of around 0.75. GNP suspension at different concentrations of the following molecules (L configuration), but keeping the citrate concentration constant, were prepared (HPLC grade water): arginine, aspartic acid, glutamine and N-acetyl-arginine (purchased from Sigma Aldrich), asparagine, glutamic acid and arginine methyl ester (purchased from Alfa Aesar), cysteine, glycine, histidine, lysine, threonine and guanidinium (purchased from Merck).

UV–Vis spectra were recorded between 330 and 800 nm at a 480 nm/min scan rate on a Lambda-35 Perkin-Elmer spectrophotometer. Dynamic light scattering (DLS) and zeta potential measurements were recorded with a Malvern Zetasizer Nano ZS equipped with a He–Ne laser (633 nm). GNPs were dispersed in water at 25 °C. A PMMA cuvette for DLS measurements and Zetasizer nanoseries cells for Zeta potential measurements were used as sample container.

2.3. Functionalization of GNPs with mercaptoundecanoic acid

The pH of the GNP suspensions was adjusted to 11 and an ethanolic solution of mercaptoundecanoic acid (Sigma Aldrich, MUA) was added progressively to obtain a final MUA concentration of 1 mM. The solution was then incubated during 60 h at room temperature. The excess of MUA was removed from the GNPs suspension by five rounds of: centrifugation, removal the supernatant and resuspension of the GNPs in water.

3. Results and discussion

The interaction between GNPs and amino acids was studied by time-resolved UV–Vis absorption spectroscopy by following the LSPR band of the colloidal suspension in the presence of different concentrations of amino acids. GNPs used for these studies show a LSPR band at 520 nm and present a size, determined by electron microscopy (TEM), of 14 nm with a standard deviation of 1 nm (see SI – Fig. S1).

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