

Effect of surfactant concentration to aggregations of nanogold particles

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Abstract. This research presents a study of aggregation of colloidal gold nanoparticles using 400 nm diameter gold nanoparticles mixed with a surfactant (Plantacare 2000) at various concentrations. When observed under a microscope, we found that the nanoparticles aggregated to form nearly spherical clusters at the beginning of the formation, and then sedimented to the bottom of the container. These clusters moved with Brownian's motion and collided with each other in the horizontal plane, forming branch-like clusters in 2D. The appearance and size of the clusters were different depending on the concentration of surfactant. The clusters' size and appearance were rarely changed after mixing with surfactant for 90 minutes, and we found that the cluster's shapes were nearly spherical at low surfactant concentration ($c = 0.25\%$). At surfactant concentration between $0.50\% - 5.00\%$, the aggregates formed branch-like clusters with skinnier branches and smaller sizes at higher surfactant concentration. Moreover, we also found that, at surfactant concentrations between $2.50\% - 5.00\%$, nanoparticles and aggregates stuck to the bottom of the glass container quickly and rarely moved after 10 minutes. At $c = 0.25\%$, the 2D fractal dimension of the aggregates was measured to be $D = 1.88 \pm 0.04$, since the aggregates were nearly spherical. The fractal dimension decreased to the minimum of $D = 1.50 \pm 0.12$ at $c = 1.50\%$, similar to $D \sim 1.45$ found in diffusion-limited cluster aggregation (DLCA). At surfactant concentration above 1.50% , the fractal dimension increased until it reached the value of $D \sim 1.66$ at $c = 5.00\%$.

1. Introduction

Researches on aggregations of nanoparticles have received much attention from scientists in the past 3 decades [1-9] because of their widely usages in mining and cleaning industries [10] and their applications in sensor technology, such as melamine detection [11] or cocaine detection [12]. Typically, nanoparticles, made of various types of materials such as polystyrene, gold, or silica, attract each other via Van Der-Waal force. To prevent aggregation, nanoparticles are coated with charges on the surfaces. However if electrolytes [1,2] or surfactants [3-5] or other chemicals [6-8] are added to the solution, opposite-charges from those chemicals move to the surfaces of nanoparticles, shielding the Coulomb repulsion force, and induce aggregation. The net attractive force between nanoparticles increases with the concentration of chemicals in the solution and reaches its maximum when the opposite-charges in the solution completely shield the Coulomb repulsion force between nanoparticles.

The shapes and sizes of aggregates depend on the strength of the inter-particle force and can be simplified into 2 limits: the diffusion-limited cluster aggregation (DLCA) and the reaction-limited cluster aggregation (RLCA). In DLCA limit, the inter-particle force is strong and the probability of sticking after particle-collision is close to one. The aggregates formed in this limit take branch-like shapes and are loosely packed. In RLCA limit, the inter-particle force is very weak and the probability of sticking after particle-collision is close to zero. Nanoparticles in the aggregates are allowed more time to relax to equilibrium and hence take more dense structures. The shapes of the aggregates in both limits can be characterized by fractal dimensions.

Fractal dimension [13] provides a solid framework for analysis of natural phenomena in various scientific domains. Studies of fractal dimensions can be used to characterize the structure of a disordered system, such as a random aggregate that is formed under nonequilibrium condition. A mass m of an aggregate is related to its radius of gyration r through a relation $m \sim r^D$, where D is the fractal dimension and the mass m is equal to an area and volume of the aggregate in 2D and 3D respectively. Various methods have been used to calculate fractal dimensions. In 2D, images of aggregates obtained from Transmission Electron Microscope (TEM) [2,3,5,8], Atomic Force Microscope (AFM) [8], and optical microscope [1,9] are analyzed to find fractal dimensions using various techniques such as Box counting[1], Radius of gyration[3], or Sandbox method [14]. In 3D, the fractal dimensions are usually extracted from light-scattering experiments [2]. For DLCA, the fractal dimensions are found to be $D \cong 1.45$ in 2D and $D \cong 1.80$ in 3D, and for RLCA, the fractal dimensions are found to be $D \cong 1.60$ in 2D and $D \cong 2.10$ in 3D [1]. M. Y. Lin et al. [2] have found that the fractal dimensions in both DLCA and RLCA limits are universal; they are independent of nanoparticles' materials nor chemicals used to induce aggregations. However, Wan Y. Shih et al. [3] found that the 3D fractal dimensions in DLCA can vary greatly when a surfactant is used to induce aggregation.

This research presents a study of aggregation of colloidal gold nanoparticles using 400 nm diameter gold nanoparticles mixed with a surfactant (Plantacare 2000) at various concentrations. We observe the structures and sizes of the clusters as well as their 2D fractal dimensions using an optical microscope and report their dependence on the concentration of surfactant.

2. Experimental Section

Nonionic Surfactant, Plantacare 2000 (decyl glucoside, $(C_{16}H_{32}O_6)$), was obtained from a local distributor. Various amount of surfactant was mixed with distilled deionized water to get to a surfactant concentration of 0.5 % (v/v), 1.0 % (v/v), 2.0 % (v/v), 3.0 % (v/v), 4.0 % (v/v), 5.0 % (v/v) and 10.0 % (v/v) in water solution.

A colloidal suspension of spherical gold particles, stabilized in citrated buffer, was obtained from Sigma Aldrich. The diameters of the particle are 400 nm. A 40- μ l of surfactant-water solution at the concentration indicated above was dropped into a 40- μ l of colloidal suspension contained in a transparent container made of a cover glass slide and an O-ring, glued together. As a result the final surfactant concentration (c) in the nanogold suspension was 0.25 % (v/v), 0.5 % (v/v), 1.0 % (v/v), 1.5 % (v/v), 2.0 % (v/v), 2.5 % (v/v) and 5.0 % (v/v).

The aggregations of nanogold particles were observed from the bottom of the cover-glass container using an inverting microscope (Nikon's Eclipse TE300) and an oil-immersion objective lens (Nikon LU Plan Flour 100x / 1.30 oil WD 0.20). The dynamics of the aggregation above the cover-glass surface were video-recorded for the first 2 minutes and imaged for every 1-minute interval for the total of 90 minutes using a DSLR camera (Canon EOS Kiss X5). The images of nanoparticles' clusters were analyzed for sizes and fractal dimensions using free image analysis softwares (imageJ [15] and fractalyse [16]).

3. Results and Discussion

Figure 1 shows an aggregation of nanoparticles at $c = 0.5$ % (v/v) at different time (t) after the surfactant was released. At $t = 1$ minute (figure 1 a), the nanoparticles were still well dispersed. At

$t = 7$ minutes (figure 1 b), the nanoparticles aggregated to form nearly spherical clusters, and then sedimented to the bottom of the glass container. These clusters moved with Brownian's motion and collided with other clusters in the horizontal plane just above the glass container, forming branch-like clusters in 2D (figure 1 c, d). As time has passed, the clusters grown bigger but at slower rate and moved slower and finally were rarely changed after $t = 90$ minutes. At higher c , spherical aggregates formed at earlier time and were smaller in sizes before they collided with other aggregates to form branch-like clusters, producing skinner branches.

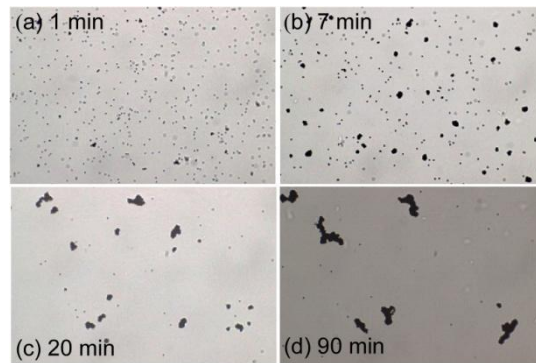


Figure 1. Aggregation of nanoparticles at $c = 0.5\%$ (v/v) at different time (t) after the surfactant was released.

Figure 2 shows comparison of 10 biggest clusters at time $t = 90$ minutes at various surfactant concentrations (c). The appearances and sizes of the clusters were different depending on the concentration of surfactant. At $c = 0.25\%$, the equilibrium cluster's shapes were nearly spherical. At c between $0.50\% - 5.00\%$, the aggregates formed branch-like structures with skinnier branches and smaller sizes at higher surfactant concentration. Moreover, we also found that, at c between $2.5\% - 5.0\%$, nanoparticles and aggregates stuck to the bottom of the glass container quickly and rarely moved after 10 minutes.

The areas of all clusters in figure 2 were calculated with imageJ software and their average values for various concentrations are shown in figure 3. We can see that the average cluster area increases when the cluster shapes change from being nearly spherical at $c = 0.25\%$ to being branch-like at $c = 0.5\%$. It is largest at $c = 0.5\%$ and decreases when the concentration is increased. When $c \geq 2.5\%$, the average cluster areas are smallest and almost unchanged with concentrations.

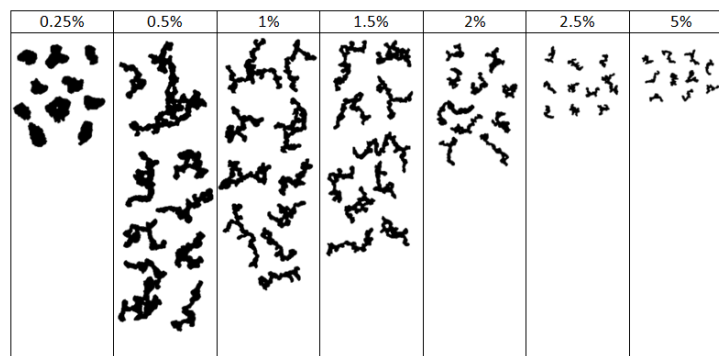


Figure 2. Comparison of 10 biggest nanogold clusters at $t = 90$ minutes and surfactant concentrations between $0.25\% - 5.00\%$.

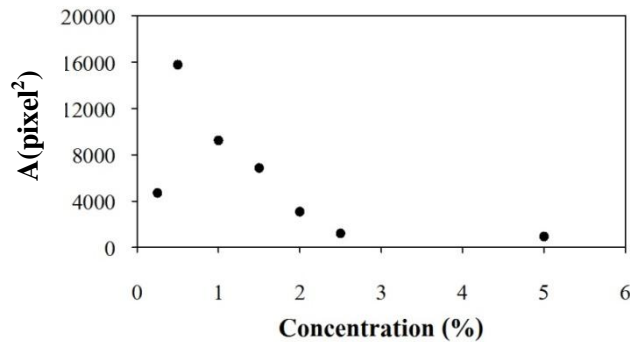


Figure 3. Average area A (in a unit of pixel^2) of the clusters shown in figure 2 as a function of concentration.

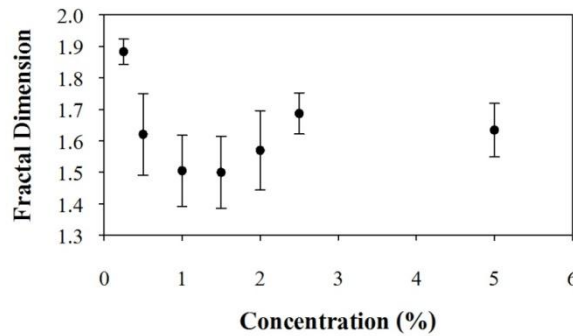


Figure 4. Average fractal dimension of the clusters shown in figure 2 as a function of concentration.

At $c = 0.25\%$, the surfactant concentration is very low so that system is in RLCA limit all the time and the shapes of the clusters remain nearly spherical. At $c \geq 0.50\%$, the surfactant concentration is high enough but it takes a while for the surfactant molecules to diffuse to the surface of the nanoparticles. Therefore, the aggregation is only in the RLCA limit only at early time, while at longer time, the aggregation is in DLCA limit, forming branch-like clusters.

The fractal dimensions (D) of all clusters in figure 2 were calculated with fractalyse software and their average values for various concentrations are shown in figure 4. When $c = 0.25\%$, the cluster shapes look nearly spherical and therefore D is close to 2. Video recording revealed that nanogolds moved around easily in the clusters, allowing more time to relax to equilibrium configurations, suggesting RLCA limit. As c increases from 0.25% to 5.0% , the fractal dimension decreases and reaches a minimum value of $D = 1.50 \pm 0.11$ at $c \approx 1.5\%$. This value is slightly greater than the theoretical value of $D = 1.45$ in 2D DLCA limit [1]. When c is further increased, D increases and reaches a stable value of $D = 1.66$ at $c \geq 2.5\%$.

The change in fractal dimension can be explained from the shapes and sizes of the aggregates. If we draw a rectangular box that just barely fits each aggregate, the ratio of aggregate area to the box area represents the aggregate's density (σ). The fractal dimension is related to the aggregate's density. As c increases from 0.5% to 1.5% , σ decreases due to the skinnier branches of the clusters at higher c , resulting in lower D . As c increases from 1.5% to 2.5% , the thicknesses of the branches of the clusters are roughly the same, but σ increases because of the smaller sizes of the clusters. The smaller the cluster size the more spherical the cluster shape is, and σ will be larger and closer to the value of 1, causing D to be larger and closer to the value of 2. The aggregate's sizes and shapes at $c = 2.5\%$ and $c = 5.0\%$ in figure 2 are indistinguishable and therefore their fractal dimensions are indifferent.

4. Conclusion

We have observed aggregations of 400-nm colloidal gold nanoparticles under the influence of surfactant concentrations, using optical microscope. The use of optical microscope allows real-time dynamical study of aggregations. At early time the aggregation is in the RLCA limit and the aggregates are nearly spherical. At longer time, the aggregation is in DLCA limit, forming branch-like clusters (except for $c = 0.25\%$, where the aggregation is in RLCA limit all the time). The shapes and sizes of the clusters vary with the surfactant concentrations, and the fractal dimensions also change accordingly.

References and Notes

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- [15] This freeware program has been developed by Frankhauser, Vuidel and Tannier and may be downloaded on the website (<http://www.fractalyse.org/>). The original version of this software has been developed in the frame of the French research program “Ville é’mergente” financed by the PUCA (Plan Urbanisme–Construction–Architecture).
- [16] ImageJ is being developed at the National Institutes of Health by an employee of the Federal Government in the course of his official duties. Pursuant to Title 17, Section 105 of the United States Code, and may be downloaded on the website (<https://imagej.nih.gov/ij/>).