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Smoluchowski Formulation for Simulation of Nano Core-Shell Structure Creation in Nanoparticle Fabrication by Laser Ablation in Liquid Media Process

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The nano core-shell can be generated in a proper liquid medium under controlled laser ablation condition. In this work, the formation of core-shell structure by laser ablation of two different targets was modeled based on the Smoluchowski approach. In this model, the movement and aggregation of the ablated fragments ejected from the targets were investigated based on Brownian motion, hydrodynamics considerations and coulomb's interactions. The nano core-shell could be generated in the water under controlled exposure conditions using Q-SW Nd:YAG laser shots at 1064 nm. This work addresses a simple numerical modeling of the formation of core-shell nanoparticles in water by laser ablation. The late stage of nanoparticle formation by collisional aggregation was considered avoiding hydrodynamic calculations. Each collision is assumed to be effective in aggregate formation. The rate constants are simply expressed through the diffusion coefficient depending on the temperature and viscosity of the liquid and the aggregation time was estimated. Moreover, Smoluchowski approach was used to describe the step between laser ablation and nano core-shell creation. This proves to be a suitable method for modeling of nanoparticle formation in liquid by laser ablation. The model could be applied to both the nanoparticle and the core-shell formation; however the latter is emphasized here. At first, the gold target was irradiated in water to generate nano particles. Then, the silver target was immersed into water-gold suspension. It was irradiated by multiple laser shots subsequently. The nano core-shells (Ag-Au) are created in the water having 30-50 nm size. The formation of core-shell using laser ablation of metallic targets was modeled based on the Smoluchowski approach. The movement and aggregation of the ablated fragments ejected from the targets were investigated based on Brownian motion, hydrodynamics considerations and coulomb's interactions. For investigation of validation of the model, the results obtained by the model for the nano core – shell (Ag-Au) generation were comprised with reported experimental results.

Modeling was based on the irradiation on gold target in water to generate Au nano particles. Then, the silver target was immersed into water-gold suspension. It was irradiated by multiple laser shots subsequently in the liquid medium. The predicted sizes of the nano core-shells (Ag-Au) by the model were 30-50 nm which were in good agreement with experimental reported results.

Keywords: Aggregation, Nano core-shells, Smoluchowski approach, Brownian motion, Laser.

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1. INTRODUCTION

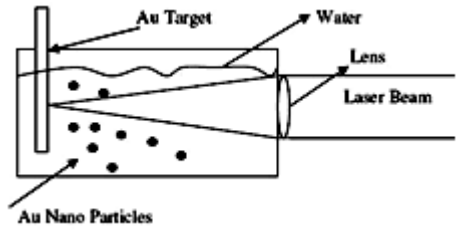
Because of their size dependent physical properties, nanoparticles are interesting for many of technologists and fundamental researchers. In the last decade, pulsed laser ablation becomes one of the nanoparticle generation approaches. Laser ablation process for nanosecond to femtosecond lasers has the three significant steps i.e. plasma generation, expansion and ejection. After the later irradiation, the nanoparticle generation occurs inside the plasma. Nanoparticles show special aggregation characteristics caused by their ultrafine sizes. At the nano-scale, attractive dispersion interactions, known as London- van der Waals forces [1], are significant and often equilibrate the inertia of the particles. Distortional electron density leads to a temporary fluctuating dipole character of the molecules [2]. London-van der Waals attractions are existed in ultrafine particles. As reported previously [2-5] such attractions are significant near the micron particle size range. As particle size decreases those attractions become stronger. Thus, for nanosparticles, those are usually very strong. When particle surfaces are close to each other, this effect results a generalized attractive interaction which is inversely proportional to the sixth power of the particle radius. Therefore, this force is very noticeable for nanoparticles and the aggregation is commonly observed [6]. Due to the natural tendency for nanoparticles to aggregate finding isolated primary nanosized particles in dry systems is difficult.

As nanoparticles aggregate, the balance between the cohesive and inertial forces in the particulate system becomes different. The unusual characteristic of the nanoparticle systems is due to the different levels of this force balance. Different arrangements of nanoparticles can be characterized as the size of these aggregates grows from only a few nanometers to several hundred of microns. By the primary particle size, shape and roughness as well as tendency of the particles to show other surface effects such as liquid bridging and electrostatic interactions this phenomenon can be controlled. Due to the negative charge on their surfaces, repulsions between particles may exist. The last type of inter-particle forces is the liquid bridging effect. This effect takes place when a liquid is absorbed on the surface of fine particles. The tendency is creation liquid bridges between the primary particles, forming aggregates [6]. One of the advantages of using liquids for nanoparticle creation by laser ablation is providing the near distances between ablated fragments. In this case, because of much slower movement of ablated fragments with respect to their initial condition, their movement can be considered as Brownian motion in liquids. When the fragments are close together, they could connect to each

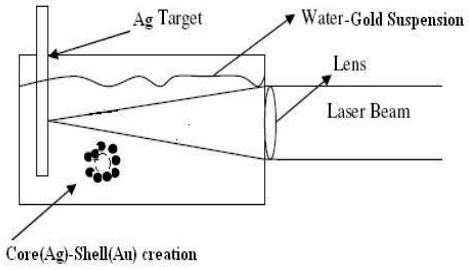
other and the Smoluchowski approach may be used to describe the aggregation and nanoparticles generation under the aqueous circumstances. In this work, Smoluchowski approach describes the final stage of the nanoparticles formation just at the onset of particle slowing down leading to nanoparticle clusters eventually. The model validity verification was studied by several researchers' empirical data [7-9].

2. THEORY

Figs. 1 (a) and (b) illustrate the schematic form of core (Ag)-shell (Au) generation. At first, Au target was suspended in water, then it was irradiated by fundamental harmonic of pulsed Nd:YAG laser at 1064 nm. Au nanoparticles were diffused into water. Subsequently, Ag target was inserted into suspension solution and it was irradiated by the laser. Eventually, core-shell creation took place. Fig. 2 depicts plasma formation and particle aggregation inside the created plume near the target surface.



a



b

Fig.1 – (a) Au target is situated in front of laser beam inside water and subsequent Au fragmentation. (b) Ag target was irradiated inside suspension solution (Au+ water) leading to core (Ag) - shell (Au) generation

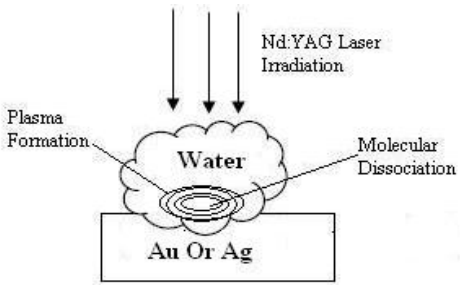


Fig. 2 – Schematic diagram of plasma formation at the vicinity of the target surface inside water

The aggregation rate can be described by Smoluchowski classic work. Considering a distribution of initial particles, which after a period of aggregation, contains aggregates of different sizes and variety of concentrations such as n_i particles of size i, n_j particles of size j etc., is more convenient. Considering the aggregation as a second order rate process is the main assumption. In fact, the rate of collision and the product of the concentrations of two colliding species are proportional. Thus, the collision number between i and j particles in unit time and unit volume, J_{ij} is [10]:

$$J_{ij} = k_{ij}\, n_i\, n_j \tag{1}$$

where k_{ij} is the second order rate constant, which depends on particle size and transport mechanisms.

Despite of theoretical difficulties, the assumption of independency of the collision rate from colloid interactions is usual; however, it is particle transport dependence strongly. This assumption could be justified based on short- range nature of inter-particle forces, which operates over a range which is usually much less than the particle size. For present condition, we assume that each collision is effective to form an aggregate, so that the aggregation rate constant is equal to the collision rate constant. We can write following expression for concentration of k-fold aggregates, where $k = i + j$, as bellow [10]:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i=1}^{i=k-1} k_{ij} n_i n_j - n_k \sum_{k=1}^{\infty} k_{ik} n_i \tag{2}$$

The first term on the right hand side shows the rate of formation of k-fold aggregates by collision of any pair of aggregates and the second term represents the loss of $k-$fold aggregates by collision, and aggregation, with any other aggregates.

When the particles have nearly the similar sizes, the rate constant, kij, would be [10]:

$$k_{ij} = \frac{8kT}{3\mu} \tag{3}$$

where, k, T and μ show Boltzmann constant, absolute temperature and viscosity of the suspending fluid respectively. As the interface of the bubble and water is as high as the water boiling point, using values appropriate to aqueous dispersions at 373 K gives $k_{ij} = 3 \cdot 10^{10}$ $cm^3\ s^{-1}$.

The loss of primary particles is almost entirely due to collisions with other primary particles. The result is [10]:

$$\frac{dn_T}{dt} = -k_a n_T^2 \tag{4}$$

Where $n_T = n_1 + n_2 + n_3 + \ldots$ and $k_a = 4kT/3\mu$. Considering initial condition as $n_T = n_0$ when $t = 0$ leads to:

$$n_T = \frac{n_0}{1 + t/\tau} \tag{5}$$

where $\tau = 1/k_a n_0$ is characteristic time in which the total particle concentration decreases to the half of initial value. The initial number density n_0 is equal to $1.6 \cdot 10^{-6}$ cm^{-3} [11].

A uniform laminar shear field is one in which the fluid velocity changes linearly in only one direction, perpendicular to the direction of flow. Smoluchowski assumed that according to their relative position, parti-

cles would follow straight fluid streamlines and collide with particles moving on different streamlines. The collision frequency has the velocity gradient or shear rate G dependence. Even in laminar shear, it is difficult to predict maximum aggregate size. The expression to model break-up of flocs in simple shear which is derived by balancing the van der Waals force between the hydrodynamic force acting to separate two aggregates is as follow [12]:

$$\frac{R}{a}=\left(\frac{A}{18\mu G a\delta^2}\right)^{1/2} \quad (6)$$

where R denotes limiting floc size, A is Hamaker constant ~ $5\cdot10^{-21}$ J [10], a shows the primary particle radius to be ~10 nm, G is shear rate ~ 50-100 s^{-1} and δ asserts the initial separation of particles ~ 10 nm [10]. The criterion for limiting floc size is based on the assumption that if the sum of their hydrodynamics radii does not exceed a certain critical value a collision between two aggregates can only lead to the attachment [10].

Aggregate size distribution as a function of time can be obtained by suggested equation as below [10]:

$$\frac{\partial n(i,t)}{\partial t}=\frac{1}{2}\int_0^t k(i-j,j)n(j,t)n(i-j,t)dj-\int_0^\infty k(i,j)n(j,t)dj \quad (7)$$

where the left-hand side shows the concentration rate change of particles of size i and the coefficients k *(i-j,j)* are equivalent to the collision rate constant k_{ij} in Eq. (2). In integral expressions, these are known as collision kernels. By the fact that the collision kernels depend on the size of colliding aggregates, and the dependence on size is not generally known, solution of these expressions is made very difficult except in very simple cases. The constant collision kernel is the simplest possible assumption. For the continuous particle size distributions, the aggregate size distribution using the constant collision kernel is given by [10]:

$$f(x)=\exp(-x) \quad (8)$$

where, x is dimensionless aggregate size, normalized by the aggregate average size.

3. RESULTS AND DISCUSSION

Fig. 3 shows the variation of n_T/n_0 versus time, by using of Eq. 5, as it is seen the relative concentration of particles decreases rapidly so that after ~ 200 μs it approaches to zero. It was estimated the time for the temperature of nanoparticles to reach the room temperature by the classical thermodynamics to be 70 μs [11]. Figs. 4 and 5 depict maximal size of aggregates in terms of primary particle radius and initial separation of particles respectively. Experimental results are in good agreements with the theory [7-9]. Particularly, by using of these graphs, for any final particle sizes, it may deduce probable primary particle size or the initial separation distance between them.

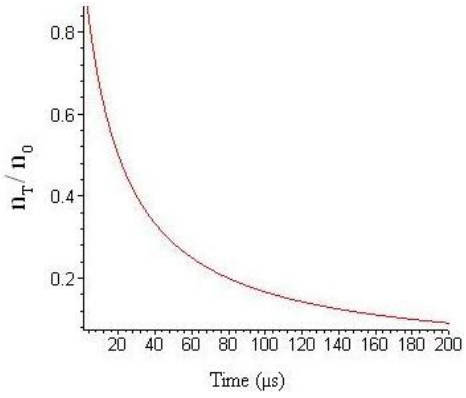


Fig. 3 – Variation of n_T/n_0 versus time

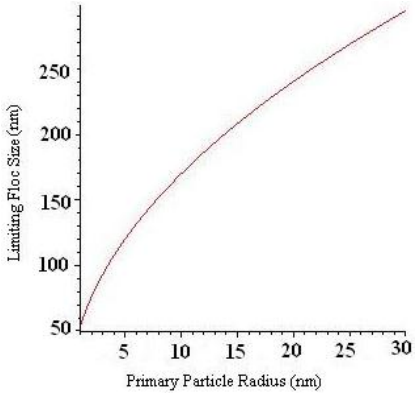


Fig. 4 – Maximal size of aggregates in terms of primary particle radius

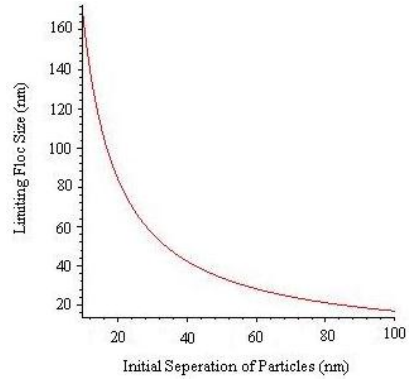


Fig. 5 – Maximal size of aggregates in terms of initial separation of particles

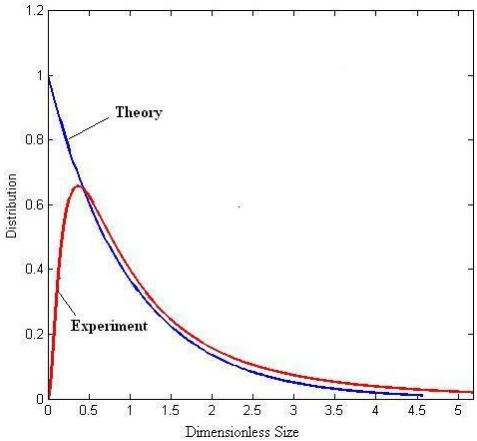


Fig. 6 – Size distribution functions versus dimensionless size of particles based on the theory and experiment

Fig. 6 displays size distribution functions versus dimensionless size of particles based on the theory and

experiment. In practice, the size distribution of particles suits to the fit a lognormal function [13, 14]. As shown in Eq. 8 the theory predicts size distribution function is a negative exponential function. For small size particles, the theoretical results do not agree with experiments likely due to the constant kernel assumption in the theory. Conversely, for larger size particles, lognormal is in good agreement with distribution function given in Eq. 8.

4. CONCLUSION

The model could be applied to both the nanoparticle and the core-shell formation; however the latter is emphasized here. By introducing some weight factors in Eq. 2, the core-shell and nanoparticle formation are taken into account. In case that the separate mixtures of Ag and Au nanoparticles are produced by laser ablation in water, the core-shell does not take place. In fact, δ in Eq. 6 becomes very large due to the diffusion of particles in water and therefore the maximal size of aggregate would be very small, leading to the condition where no core-shell finds a chance to be generated. The model succeeds to reproduce the characteristic half time and maximal core-shell size correctly.

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