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Kinetics of gold nanoparticle aggregation: Experiments and modeling

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Abstract

We investigate the aggregation kinetics of gold nanoparticles using both experimental techniques (i.e., quasi-elastic light scattering, UV–visible spectroscopy, and transmission electron microscopy) and mathematical modeling (i.e., constant-number Monte Carlo). Aggregation of gold nanoparticles is induced by replacing the surface citrate groups with benzyl mercaptan. We show that the experimental results can be well described by the model in which interparticle interactions are described by the classical DLVO theory. We find that final gold nanoparticle aggregates have a fractal structure with a mass fractal dimension of 2.1–2.2. Aggregation of approximately 11 initial gold nanoparticles appears to be responsible for the initial color change of suspension. This kinetic study can be used to predict the time required for the initial color change of a gold nanoparticle suspension and should provide insights into the design and optimization of colorimetric sensors that utilize aggregation of gold nanoparticles.

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1. Introduction

Gold nanoparticles have attracted much attention due to their uniformity and optical properties since the report by Faraday [1,2]. The introduction of the citrate-reduction method by Turkevich and co-workers enabled quick and easy preparation of gold nanoparticles with sizes on the order of tens of nanometers [3]. Gold nanoparticles find applications in various fields, including chemical, medical, and biological sciences [4–6].

One of the most promising applications of gold nanoparticles is in colorimetric sensors for specific target detection. Aggregation of gold nanoparticles leads to a change in their optical properties (i.e., a red shift in surface plasmons, or a red-to-blue color change as detected by the naked eye), which can be used in the colorimetric detection of target agents [7–9]. The localized surface plasmon resonance of metal nanoparticles that is responsible for the change in optical properties results from collective oscillation of conduction electrons upon interaction with electromagnetic radiation [10,11]. Mirkin and co-workers showed that the change in the localized surface plasmon band should be related to the aggregated size [8]. For practical applications of gold nanoparticles as colorimetric sensors, though, there still remain issues such as the response time control and miniaturization. To resolve these issues, it is essential to understand the kinetics of the aggregation process [12–15]. We have recently investigated the aggregation of gold nanoparticles in real time and analyzed colloidal stability with theoretical interpretations [16]. These results were rationalized by calculating the interparticle interaction energy and the stability ratio of nanoparticle aggregates.

In this paper, we examine the aggregation kinetics of gold nanoparticles using both experiments and mathematical modeling. The colloidal dispersions of gold nanoparticles are induced to aggregate by replacing the surface citrate groups with benzyl mercaptan, which acts as a well-defined, simple, and robust monolayer adsorbate [16]. The stability ratios calculated from classical DLVO theory are used to rationalize the experimental results [17,18], and the constant-number Monte Carlo method [19] is used to model the aggregation kinetics.

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This work is, to the best of our knowledge, the first comprehensive kinetic study of gold nanoparticle aggregation that can be used to predict the time required for the initial color change of a suspension. Since the response time of biological sensors is a crucial factor in the detection of target agents, this work will be useful in the design and optimization of sensors based on gold nanoparticle aggregation.

2. Materials and methods

2.1. Preparation and characterization of gold nanoparticle aggregates

Stable suspensions of gold nanoparticles were prepared by the citrate-reduction method [3]. A 0.01% potassium tetrachloroaurate (III) solution ($KAuCl_4$, Aldrich) in water was brought to boiling with trisodium citrate dihydrate. The sizes of gold nanoparticles in this reductive synthesis were controlled by changing the amount of citrate added. The concentration of trisodium citrate was set to 13.0×10^{-4} M for samples A1–A3 and 5.5×10^{-4} M for samples B1–B3. After stable suspension of gold nanoparticles was formed, we added a concentrated ethanolic solution of benzyl mercaptan in suspension to induce aggregation. The concentration of benzyl mercaptan was set to 5.0×10^{-5} M (samples A1 and B1), 7.5×10^{-5} M (samples A2 and B2), and 10.0×10^{-5} M (A3 and B3).

The diameter and zeta potential of particles were monitored by quasi-elastic light scattering (QELS) and zeta potential measurements (Nano-ZS from Malvern Instrument Co). To monitor the change in the optical properties of gold nanoparticle suspension, UV–visible absorption spectroscopy (Shimadzu UV–1650PC spectrophotometer) was used. Transmission electron microscopy (TEM, JEOL JEM-4010) was also used to observe the morphology of gold nanoparticle aggregates.

2.2. Constant-number Monte Carlo with the DLVO interactions

The constant-number Monte Carlo method developed by Smith and Matsoukas [19] was used to model aggregation of gold nanoparticles. In this method, we start with a simulation box containing 30,000 initial particles. First, a pair of particles (i and j) is randomly picked from the initial particle matrix. To determine whether they aggregate, we pick a random number, r, and calculate the aggregation probability, P_{ij}, which is defined as

$$P_{ij} = \frac{K_{ij}}{K_{ij,\max}}. \tag{1}$$

In Eq. (1), K_{ij} is the aggregation rate between particles i and j, and $K_{ij,\max}$ is the maximum aggregation rate among all particle pairs in the simulation box. If r is smaller than P_{ij}, the two particles are allowed to aggregate. If not, a new particle pair is selected and this step is repeated until two particles aggregate. After each aggregation event, the simulation time is increased and a particle is randomly selected from the simulation box and copied onto the empty array to keep the total number of particles constant.

2.3. Calculation of the aggregation probabilities

To calculate the aggregation probability in the Monte Carlo, the aggregation rate, $K(r, r')$ of particles of radius r and r' is defined as follows [16–18]:

$$K(r, r') = K_B(r, r')/W(r, r'). \tag{2}$$

In Eq. (2), $K_B(r, r')$ and $W(r, r')$ are the Brownian aggregation rate and the stability ratio, respectively. The Brownian aggregation rate can be expressed as [17,18]

$$K_B(r, r') = \frac{2kT}{3\mu}(r + r')\left(\frac{1}{r} + \frac{1}{r'}\right). \tag{3}$$

The stability ratio accounts for the effect of interparticle interaction on the aggregation rate [17,18],

$$W(r, r') = 2\int_0^\infty \frac{\exp[V_T/kT]}{s^2}\,ds. \tag{4}$$

Total interaction potential in Eq. (4), V_T, can be expressed as the sum of the electrostatic repulsion (V_{elec}) and the van der Waals attraction (V_{vdw}) according to the classical DLVO theory [17,18]:

$$V_T = V_{\mathrm{elec}} + V_{\mathrm{vdw}}. \tag{5}$$

To calculate the electrostatic repulsion potential, V_{elec}, the following two different forms were used depending on the value of κa [16]:

$$V_{\mathrm{elec}} = 4\pi\varepsilon\psi_0^2\frac{a_1a_2}{a_1 + a_2}\ln\left[1 + \exp(-\kappa x)\right] \quad \text{(in the case of } \kappa a > 5\text{)}, \tag{6}$$

$$V_{\mathrm{elec}} = 4\pi\varepsilon a_1a_2Y_1Y_2\left(\frac{kT}{e}\right)^2\frac{\exp(-\kappa x)}{x + a_1 + a_2} \quad \text{(in the case of } \kappa a < 5\text{)}. \tag{7}$$

Inverse Debye length (κ) and Y_i are defined as

$$\kappa = \left[\frac{1000e^2N_A(2I)}{\varepsilon kT}\right]^{1/2}, \tag{8}$$

$$Y_i = \frac{8\tanh(\varepsilon\psi_0/4kT)}{1 + [1 - 2\kappa a_i/(\kappa a_i + 1)^2\tanh^2(\varepsilon\psi_0/4kT)]^{1/2}}. \tag{9}$$

Assuming that gold nanoparticle aggregates were spherical, we used the following form to calculate the van der Waals attraction potential between the two particles:

$$V_{\mathrm{vdw}} = -\frac{A_H}{6}\left[\frac{2a_1a_2}{R^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{R^2 - (a_1 - a_2)^2} + \ln\frac{R^2 - (a_1 + a_2)^2}{R^2 - (a_1 - a_2)^2}\right]. \tag{10}$$

In the above equations, the surface potential was estimated from the zeta potential measurement, and 2.5×10^{-19} J was used for the Hamaker constant (A_H) [16].

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