Adsorbate-Induced Silver Nanoparticle Aggregation Kinetics

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Metal sols are often stabilized in solution by the presence of a charged double layer surrounding each colloidal nanoparticle that produces a coulomb barrier to aggregation. The nanoparticles can be induced to aggregate by replacing the charged surface species by uncharged adsorbate. We present a simple analysis that produces an expression for the initial rate constant describing the aggregation process, which is shown to depend nontrivially on the adsorbate concentration. The expression is tested experimentally by following and analyzing the time rate of decrease of the surface plasmon resonance absorption of isolated Ag nanoparticles in aqueous solution. The experimental result accords well with theory, producing a rough estimate of the (adsorbate-concentration dependent) barrier to aggregation that in the absence of added adsorbate is approximately equal to 0.08 eV.

Introduction

Sols consisting of metal nanoparticles stabilized against aggregation have been known for at least two centuries. A sample of the gold colloid prepared by Michael Faraday in the late 18th century is still on display in the Royal Institution.[1] Its purple/violet color is immediate visual proof of the reluctance of the gold colloidal particles to aggregate into a more massive gold sample despite the strong thermodynamic impulse to do so, driven both by the exoergicity of the bulk reactions as well as by the ensuing reduction in surface free energy. (There are some thermodynamic terms that go the other way, such as the entropic contribution to the structure of water in the neighborhood of the nanoparticles that is increased upon aggregation; but these effects are smaller in magnitude.) The stability of most metal sols against aggregation is largely a kinetic effect due to the large Coulombic repulsive barrier resulting from the localization of charged particles on or near the nanoparticle's surface,[2,3] making the effective charge on the nanoparticle nonzero. It has been known for some time, moreover, that the addition of ionic or neutral species to a stable sol can result in the destabilization of the colloid through one of a number of mechanisms, which may vary according to the concentration of the added material. Specifically, the mechanism for replacing a charged adsorbate with a neutral species at the surface of the colloid particle has been proposed before.[2,3] (There are several other ways of stabilizing colloidal particles, such as steric stabilization. These have been the subject of numerous publications,[2,4] but are not pertinent here.)

A simple treatment of the potential governing two charged colloidal metal particles proceeds as follows. At very small distances one would have a short-range repulsive potential of the approximate form $V_1 = B/r^n$, where r is the center-to-center distance between the two particles, each assumed to be spherical, and n is an exponent that normally lies in the range 9−13. The potential term arising from the van der Waals attractive force between the two particles has the form $V_2 = -C/r^6$. Finally, if one assumes that there are N species each carrying an electronic charge e at the surface of the colloid particle, there will be a Coulomb repulsion term of the form $V_3 = N^2e^2/\epsilon r$, in which ϵ is the dielectric constant of the ambient. The overall potential,

$$V = B/r^n - C/r^6 + N^2e^2/\epsilon r \tag{1}$$

has the form shown in Figure 1. The stability of the colloid results from the potential barrier that develops as a result of the competition between van der Waals attraction and Coulomb repulsion. The height of the barrier, V_{max}, depends approximately on the (average) number, N, of surface charges residing on a nanoparticle as:

$$V_{max} = 0.5823C^{-1/5}(N^2e^2/\epsilon)^{6/5} \tag{2}$$

(The expression was obtained by ignoring the V_1 term, since it contributes negligibly in the neighborhood of the potential maximum, and determining the maximum value of V_2+V_3 using simple calculus.)

Aggregation occurs rapidly when V_{max} is not too great with respect to k_BT. One way to reduce V_{max}, thereby encouraging aggregation, is to replace charged species on the surface with uncharged species. Such a displacement will occur if the binding energy of the (uncharged) adsorbate is greater than that of the charged surface species.[3,5,6] This effect is often seen in SERS experiments[5,7] with, say, silver nanoparticles when an adsorbate

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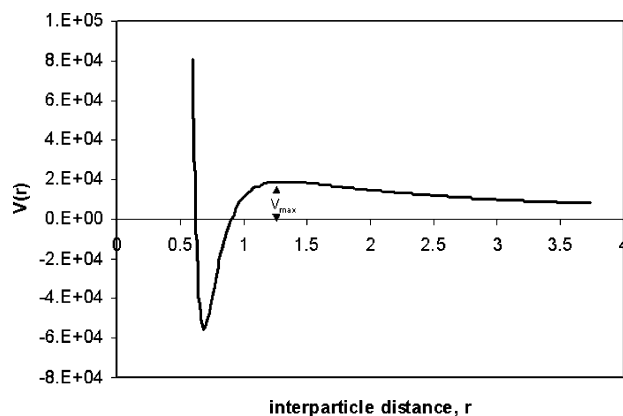* Corresponding author. E-mail mmoskovits@ltsc.ucsb.edu.

Figure 1. Potential between two charged nanoparticles as a function of the interparticle distance. Both ordinate and abscissa are in arbitrary units.
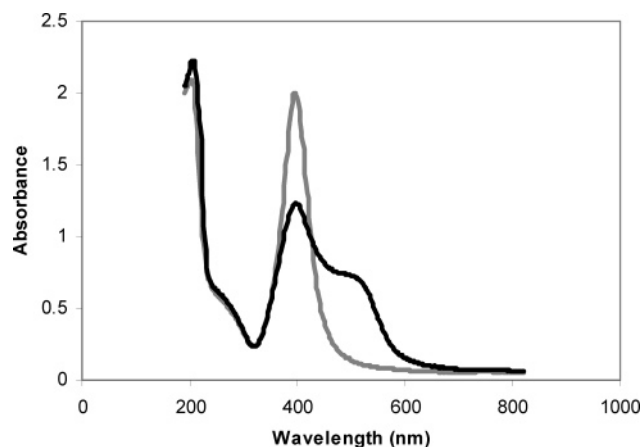

Figure 2. Surface plasmon extinction spectra of the parent (gray curve) and the aggregated (black curve) Ag colloid. The second absorbance maximum observed at ~500 nm is due to silver nanoparticle aggregates.

that has an affinity for silver is introduced into the colloid solution. In that case, a limited degree of aggregation is a desirable effect since SERS intensities tend to be very much greater for systems consisting of interacting nanoparticles as opposed to isolated single particles.[2,8]

The number of charges remaining on the nanoparticle surface will be the difference between the number of charges originally residing on the nanoparticle's surface less the number of charges displaced by the (uncharged) adsorbate molecules actually adsorbed at the nanoparticle's surface. Since at equilibrium the surface coverage by adsorbate will depend on the concentration of adsorbate molecules in solution through some isotherm, the charge on the nanoparticle's surface will be a function of the concentration of adsorbate in solution. We shall illustrate the process by assuming the isotherm to be a Langmuir isotherm and assume that each adsorbate molecule displaces one charge from the surface. (This choice of isotherm is arbitrary, although not unreasonable, and chosen entirely for heuristic reasons. The approach can be easily modified for other isotherms and other assumptions regarding the charge reduction that accompanies adsorption.)

The number of adsorbed molecules, N_{ads}, at a given equilibrium concentration, m, of adsorbate in solution is given by

$$N_{ads} = \frac{N_{max}\beta m}{1 + \beta m} \tag{3}$$

in which β is a temperature-dependent constant. N, which is equal to $N_{max}-N_{ads}$, is therefore given by

$$N = \frac{N_{max}}{1 + \beta m} \tag{4}$$

Substitution into eq 2 produces the equation

$$V_{max} = \frac{V_o}{(1 + \beta m)^{12/5}} \tag{5}$$

where $V_o = 0.5823C^{-1/5}N_{max}{}^{12/5}e^{12/5}\epsilon^{-6/5}$. The barrier to dimerization of the particles will therefore be a function of the concentration, m, of adsorbate molecules in solution.

Aggregation processes in colloids have been the subject of numerous experimental, theoretical, and computational studies.[2,3,9-11] Metal sols normally aggregate through two global (nanoparticle-concentration-dependent) mechanisms called cluster−particle aggregation and cluster−cluster aggregation.[3,10] In the former, aggregates form primarily through the addition of

single nanoparticles to a growing cluster. In the latter, clusters of all sizes can assimilate into larger clusters. An aggregating colloid can switch from one mechanism to the other as the number of nanoparticles becomes depleted. Whatever the overall process governing aggregation, all aggregation processes begin with the formation of a nanoparticle dimer from two isolated nanoparticles. The rate constant, k, describing that process will be related to the aggregation barrier height, V_{max}, as

$$k = k_o e^{-V_{max}/k_B T} = k_o e^{-V_o/(k_B T(1+\beta m)^{12/5})} \tag{6}$$

(The last term of eq 6 was obtained by substituting the value of V_{max} from eq 5.) Equation 6 predicts a very specific adsorbate-concentration dependence for the initial rate of aggregation of a metal sol brought about by replacing the charged surface species stabilizing the sol with uncharged adsorbate. Testing this simple conclusion is the subject of this communication.

Experimental Section

Aqueous silver sols were prepared by reducing silver nitrate in solution with sodium borohydride according to the procedure reported previously.[12] Aqueous phthalazine was used to induce aggregation of the silver nanoparticles. Samples for kinetic measurements were prepared by injecting 20 μL of the aqueous phthalazine solution into precisely 2 mL of the silver sol solution contained in a quartz cuvette, vigorously shaking the cuvette then following the decrease of the near-UV surface plasmon feature centered at 394 nm with time using a Hewlett-Packard HP 8952 diode array UV−vis spectrometer. Several runs were carried out varying the concentration of the injected phthalazine solution such that the overall phthalazine concentration in the cuvette varied from 2 × 10^{-5} to 5 × 10^{-3} M. (Lower concentrations of adsorbate were also used, but they resulted in impractically slow rates of aggregation.)

Results and Discussion

Isolated pseudospherical silver nanoparticles in aqueous solution are characterized by a single intense near-UV band centered at ~394 nm (Figure 2), which is generally understood to result from the excitation of the dipolar surface plasmon (sp) of the nanoparticle.[13] As the nanoparticles aggregate, electromagnetic interactions between the particles produce new sp resonances that are in essence normal sp modes. These lie to the red of the 394 nm peak but can have absorbance contributions overlapping the sp band of the isolated nanoparticle (Figure
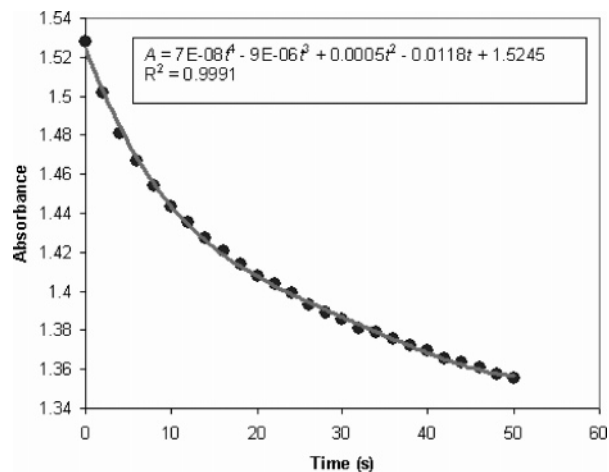
Letters

J. Phys. Chem. B, Vol. 109, No. 31, 2005 **14757**

Figure 3. Measured time-evolution of the absorbance (at 394 nm) of a silver nanoparticle sol after the addition of phthalazine to induce aggregation (black circles). The gray curve is the best fit fourth-order polynomial.

Figure 4. Rate constants of Ag nanoparticle dimerization as a function of adsorbate (phthalazine) concentration determined from the initial time-rate of change of the absorbance at 394 nm (gray points). The black curve is the function $k_A = 0.0632 \, e^{-2.658/(1+1796m)^{12/5}}$ obtained by fitting the experimental points using a nonlinear regression routine.

2). One might hope to be able to follow the kinetics of formation of nanoparticle dimers by following the rate of growth of its red-shifted sp band. In practice, this is not possible. The nanoparticles rapidly aggregate into clusters of differing sizes and shapes, which produce greatly overlapping sp bands to the red of, and overlapping the 394 nm band. It is, therefore, essentially impossible to extract an sp feature that confidently belongs to the dimer. Accordingly, we have opted to follow a different strategy. The rate of decrease of the intensity of the band at 394 nm was observed as a function of time and a polynomial time function fitted to it. The time evolution of the absorbance at 394 nm could be fitted at an accuracy limited only by experimental error, with a fourth-order polynomial for every concentration of adsorbate used (Figure 3). To compare our results to the simple theory presented in the Introduction, one needs to extract from these kinetics the rate of nanoparticle dimerization, which we assume will be the very first step in the aggregation process. That rate of decrease in the absorbance of the sp band belonging to the isolated silver sol particles at time $t = 0$ is given by the equation

$$-\left.\frac{dA}{dt}\right|_{t=0} = k_A c_{Ag}{}^2 \tag{7}$$

where A is the absorbance at 394 nm (which at early values of t is uniquely a measure of the concentration of the isolated monomers) and c_{Ag} is the initial concentration of the silver sol, which was the same value in all of the runs. The rate constant k_A is proportional to k (as given by eq 6). The constant of proportionality linking the two (which is the product of the absorption coefficient and the cuvette path length) only affects the value of the preexponential factor of eq 6, and is therefore, unimportant since the key elements of the model are contained in the argument of the exponential. That is, only relative values of the rate constant are needed as a function of adsorbate concentration, m, to illustrate the validity of the analysis outlined in the Introduction. A value proportional to the rate constant, k, can therefore be determined from the *initial* time-rate-of-change of the absorbance at 394 nm.

Because the time evolution of the absorbance was fitted to a polynomial, the first derivative required in this analysis can be determined analytically. However, the very initial value of dA/dt could not be determined directly from the measured data because the solution was shaken for a given time for proper
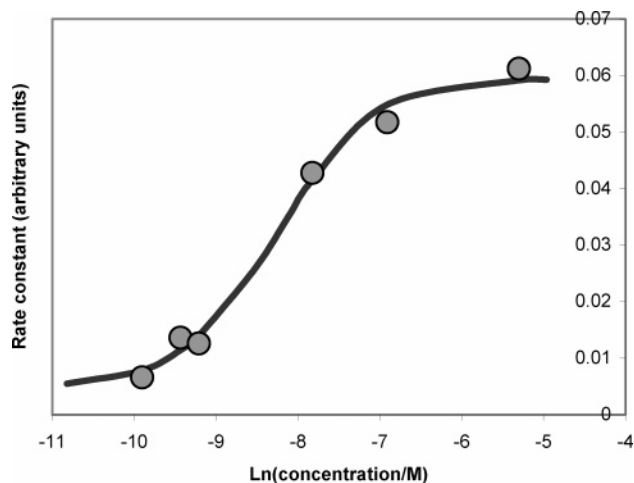
mixing before the time evolution of the spectra were recorded. The values of these "mixing times" could be determined with some confidence by extrapolating the time-varying absorbance values backward to the initial value of absorbance (which was measured for each run) then determining dA/dt at that actual initial point, rather than at the (arbitrary) first absorbance value actually recorded. This extrapolation was carried out individually for each run. In all cases the initial absorbance value was recovered by extrapolating the polynomial fit backward by approximately 20 s, corresponding to the "effective time" that it took to mix the reagents, place the cuvette in the spectrometer, and begin the measurements. The fact that this value came out equal within three or four seconds for each of the runs provides some confidence in the consistency of the approach.

A summary of the rate constants determined in the above manner is given in Figure 4 as a function of adsorbate concentration. The dependence of the measured rate constants on m follows the form given by eq 6 very well. The solid line in Figure 4 is calculated from the expression

$$k_A = 0.0632 e^{-2.658/(1+1796m)^{12/5}} \tag{8}$$

which suggests that $V_o/k_B T \cong 2.7$, for $T \sim 295$ K, the approximate temperature at which all of the runs were carried out. This expression was obtained by fitting eq 6 to the measured data using a nonlinear least-squares fitting program. Equation 5 states that, in the absence of added adsorbate (i.e., when $m = 0$), $V_o = V_{max}$. Hence, the initial barrier to aggregation is only $\sim 3k_B T \cong 0.08$ eV, and the quantity β is ~ 2000 M^{-1}. This barrier, although sufficient to slow the aggregation of the sol to a very low rate, is rather small. The purpose of this presentation is not to elicit robust numbers, however, but to present a very simple approach to colloid aggregation kinetics which, when combined with other known factors such as the precise nature of the isotherm and a detailed understanding of the surface species being replaced, can lead to robust results. Hence, the uncertainty of the value determined for V_{max} should be considered to be high. Nevertheless, the underlying physicochemical approach must be valid for it to produce the observed level of agreement with experiment.

Summary

Metal sol nanoparticles can be induced to aggregate by replacing the charged surface species by uncharged adsorbate.

We present a simple analysis that produces an expression for the initial rate constant, k, describing the aggregation process, which is shown to depend on the adsorbate concentration, m, as $k = k_o e^{-V_o/(k_B T(1+\beta m)^{12/5})}$. The expression is tested experimentally by analyzing the time-rate of decrease of the surface plasmon resonance absorption of isolated Ag nanoparticles in aqueous solution. The experimental result accords well with theory, producing a rough estimate of the (adsorbate-concentration dependent) barrier to aggregation that in the absence of added adsorbate ~0.08 eV.

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