Supporting Information

Aggregation Kinetics of Citrate and Polyvinylpyrrolidone Coated Silver Nanoparticles in Monovalent and Divalent Electrolyte Solutions

KHANH AN HUYNH AND KAI LOON CHEN*

Department of Geography and Environmental Engineering
Johns Hopkins University
Baltimore, MD 21218-2686
(*E-mail: kailoon.chen@jhu.edu)

Contents

Additional Details on Materials and Methods

Synthesis of Unmodified Silver Nanoparticles. Unmodified silver nanoparticles (AgNPs) were synthesized through the reduction of a Tollens' reagent using glucose (*1-3*). Stock solutions of 0.1 M $AgNO_3$ and 1.0 M glucose were prepared and filtered using 0.1-μm alumina syringe filters (Anotop 25, Whatman, Middlesex, UK). A Tollens' reagent comprising 0.1 mM $AgNO_3$ and 0.8 mM NH_4OH was prepared and the pH was adjusted to 11.5 by adding NaOH. The reagent (20 mL) was contained in a 50-mL polypropylene centrifugal tube (BD Biosciences, NJ) which was placed into a glass chamber filled with water. The chamber was connected to a refrigerated isotherm bath circulator (Fisher) in order to maintain the water temperature at 25˚C. The glass chamber was subsequently put into an ultrasonic bath (Branson 5510, power 180 W, frequency 40 kHz) to homogenize the reactants in the centrifugal tube and enhance their reactivity (*1*). The formation of AgNPs was initiated by introducing 40 μL of glucose stock solution into the Tollens' reagent while the reagent was ultrasonicated. After 45 min of ultrasonication, the color of the mixture changed from colorless to bright yellow, indicating that the formation of AgNPs had occurred. This suspension will be referred to as the *original AgNP stock suspension*.

Preparation of Citrate- and PVP-Coated AgNP Stock Suspensions. In order to prepare the citrate-coated AgNPs, the original AgNP stock suspension was centrifuged at 3,650*g* (Beckman Coulter, CA, 4,000 rpm) and 15˚C for 60 min. 90% volume of the supernatant was decanted and replaced with an equal amount of 1 μM trisodium citrate solution. This cleaning process was repeated two more times. The final suspension was ultrasonicated for 30 min to break up the AgNP aggregates that might have formed during the centrifugation process. The suspension was then contained in a tightly capped Pyrex glass bottle and stored in the dark at 4˚C. This suspension will be referred to as the *citrate-coated AgNP stock suspension*. The dissolved silver and AgNP concentrations of the citrate-coated AgNP stock suspension used for the aggregation experiments were 0.112 mg/L and 8.467 mg/L, respectively. Approximately 18% of AgNPs were lost during the cleaning process, calculated based on ICP-MS measurements before and after cleaning. The average hydrodynamic diameter of AgNPs in a sample prepared by washing the original AgNP stock suspension three times with deionized (DI) water and ultrasonicated for 30 min was also measured. It was found that the hydrodynamic diameter of these AgNPs was about 14 nm larger than that of the AgNPs washed with citrate solutions. This observation shows that the AgNPs are more easily dispersed when modified with citrate.

In order to prepare the PVP-coated AgNPs, a PVP stock solution was first prepared by adding 24.4 mg of PVP (MW 10 kDa, Sigma-Aldrich) into 50 mL of DI water and stirring the mixture overnight in the dark at room temperature. The total organic carbon (TOC) content of the PVP stock solution was determined to be 297.4 mg/L via UV-persulfate oxidation (Phoenix 800 TOC analyzer, Tekmar-Dohrmann, OH). The original AgNP stock suspension was centrifuged at 3,650*g* at 15˚C for 60 min. 90% volume of the supernatant was decanted and replaced with an equal amount of DI water. This cleaning process was repeated two more times. However, after the supernatant was decanted in the third cleaning process, the remaining highly concentrated AgNP suspension was re-suspended in a diluted PVP solution (instead of DI water) such that the final PVP concentration in the suspension is 6.6 mg/L TOC. The suspensions were then ultrasonicated for 30 min and stored in the dark at 4˚C. The dissolved silver and AgNP concentrations of the PVP-coated AgNP stock suspension used for the aggregation experiments were 0.222 mg/L and 8.247 mg/L, respectively.

Determination of Silver Nanoparticle and Dissolved Silver Concentrations. The total silver concentrations (including both AgNPs and dissolved silver) of the AgNP suspensions were determined by digesting the suspensions with 70% HNO_3 in a microwave at 150˚C for 10 min (*4*). The digested solutions were then diluted with DI water in order to reduce the HNO_3 concentration to ca. 3.5% before the silver concentrations of the diluted samples were measured by inductively coupled plasma mass spectroscopy (ICP-MS) (PerkinElmer Elan DRCII). In order to determine the dissolved silver concentration of a suspension, AgNPs were first removed by filtering the suspension using a 3-kDA centrifugal membrane filter (Nanosep, Pall Corp., NY) at 12,000*g* (Eppendorf, NY, 13,375 rpm) for 20 min. The filtrate was subsequently diluted with 3.5% HNO_3 and analyzed with ICP-MS. The concentration of silver nanoparticles in the suspension can then be calculated through mass balance.

Humic Acid Solution. The humic acid stock solution was prepared by introducing 22.9 mg of Suwannee River humic acid (Standard II, International Humic Substances Society) into 50 mL DI water. The mixture was stirred overnight in the dark at room temperature and then filtered through a 0.22-μm cellulose acetate filter (Millipore, MA). The pH of the filtrate was adjusted to 10.3 by adding NaOH and the filtrate was stored in the dark at 4˚C. The TOC of the humic stock solution was determined to be 174.9 mg/L through UV-persulfate oxidation. The chemical properties of the humic acid can be found elsewhere (*5*).

Procedure for Dynamic Light Scattering Measurements. For the aggregation experiments in the absence of humic acid, a predetermined volume of electrolyte stock solution was added into a vial containing a diluted AgNP suspension in order to induce nanoparticle aggregation. All vials used for DLS measurements were cleaned according to the method described elsewhere (*6, 7*). The suspension was briefly mixed for less than 3 s by using a vortex mixer (Vortex Genie 2, Fisher Scientific) operated at its maximum setting. The vial was then quickly inserted into the vat of the light scattering unit and the DLS measurements were started immediately. For the aggregation experiments in the presence of humic acid, a premeasured volume of humic acid stock solution was introduced into a vial which contained a dilute suspension of citrate-coated AgNPs or PVP-coated AgNPs such that the final humic acid concentration was 1 mg/L TOC. The mixture was vortexed briefly before an appropriate volume of electrolyte stock solution was added into the mixture to induce aggregation.

Detection of AgNP Dissolution. The citrate- and PVP-coated AgNP dissolution experiments were conducted in diffusion-limited regime of the AgNPs at the highest electrolyte concentrations used for the aggregation experiments (455 mM NaCl, 27 mM $CaCl_2$, and 27 mM $MgCl_2$). The citrate- and PVP-coated AgNP concentrations used for the dissolution experiments were 1.074 mg/L and 0.912 mg/L, respectively, (similar to the concentrations used for aggregation experiments) and the total volume for each AgNP suspension was either 550 or 1100 µL. The dissolved silver concentrations were determined 30 min after the addition of electrolyte stock solutions by filtering the samples with the 3-kDa centrifugal membranes and then measuring the filtrate with ICP-MS, as described earlier in the Supporting Information. Since each aggregation experiment in the diffusion-limited regime took only ca. 12 min, the dissolved silver concentrations at the end of the aggregation experiments were expected to be smaller than the dissolved silver concentrations measured in the dissolution experiments. Control experiments were performed by introducing DI water of the same volume as the electrolyte stock solutions, which were added into the other samples, into diluted AgNP suspensions and leaving the suspensions aside for 30 min. The dissolution experiments were performed 4–10 times for each solution chemistry.

Additional Details on Results and Discussion

DLVO Interactions. The function $\beta(h)$ is used to correct for the hydrodynamic interactions between two approaching particles (*6, 8*)

$$\beta(h)=\frac{6\left(\frac{h}{a}\right)^2+13\left(\frac{h}{a}\right)+2}{6\left(\frac{h}{a}\right)^2+4\left(\frac{h}{a}\right)} \tag{S1}$$

$V_A(h)$ is the van der Waals attractive interaction between two particles with the consideration of retardation effect (*9*)

$$V_A(h)=-\frac{Aa}{12h}\left[1-\frac{bh}{\lambda}\ln\left(1+\frac{\lambda}{bh}\right)\right] \tag{S2}$$

where A is the Hamaker constant of the particles in water, λ is the characteristic wavelength for the reaction (100 nm), and b is a constant with a value of 5.32.

Linear superposition approximation (LSA) was made in the calculation of electrical double layer interaction, $V_R(h)$ (*10*)

$$V_R(h)=32\pi a\varepsilon\left(\frac{kT}{Ze}\right)^2\gamma^2\exp(-\kappa h) \tag{S3}$$

where Z is the valence of ions and equal to 1 in NaCl solution, ε is the dielectric constant of water, e is the elementary charge, κ is the Debye-Hückel parameter, and γ is the reduced surface potential.

The reduced surface potential, γ, can be calculated using the equation

$$\gamma=\tanh\left(\frac{Ze\varphi}{4kT}\right) \tag{S4}$$

where φ is the surface potential.

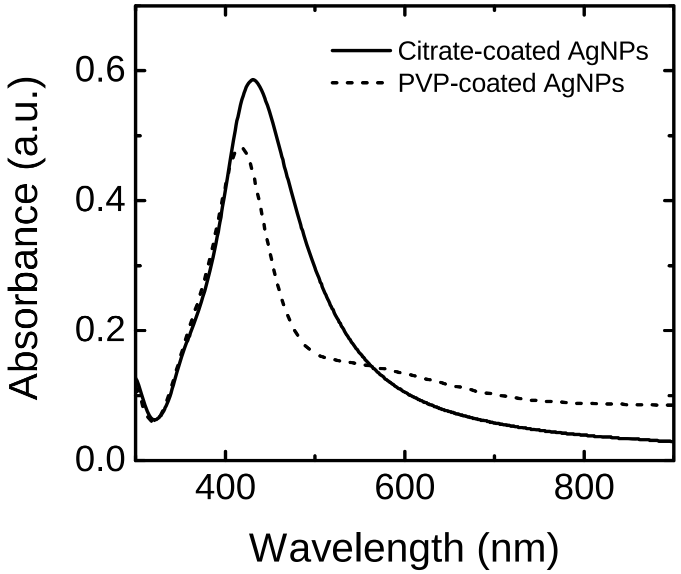


FIGURE S1. Absorbance spectra of citrate- and PVP-coated AgNP stock suspensions. The spectra are expressed in arbitrary units (a.u.). The maximum absorption peaks are at 431 nm and 418 nm for citrate- and PVP-coated AgNPs, respectively.

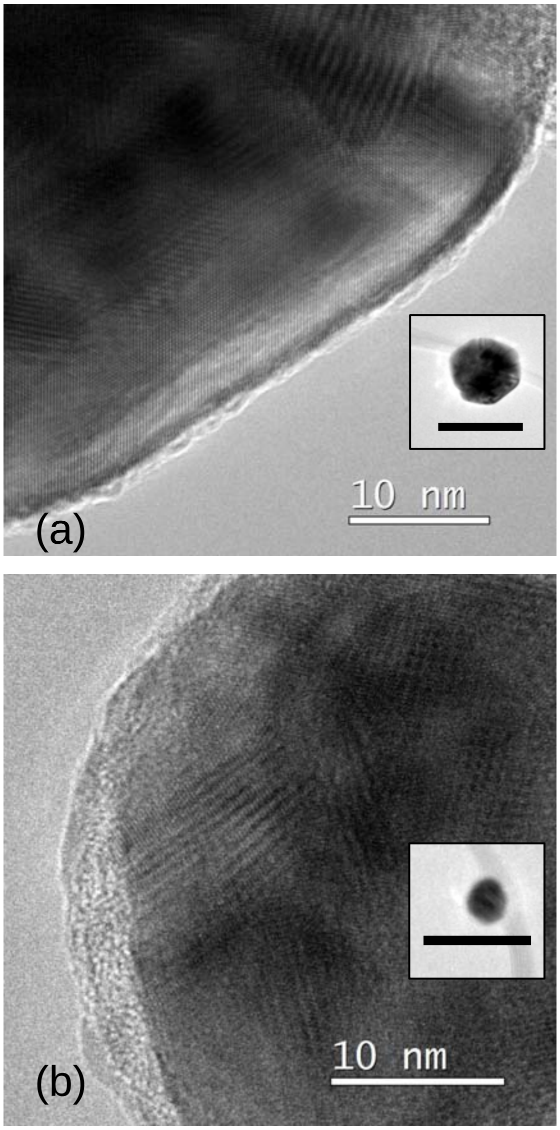


Figure S2. High-resolution TEM image of (a) citrate-coated AgNP and (b) PVP-coated AgNP. The inserts present TEM images of the entire nanoparticles and the scale bars in the inserts represent 100 nm.

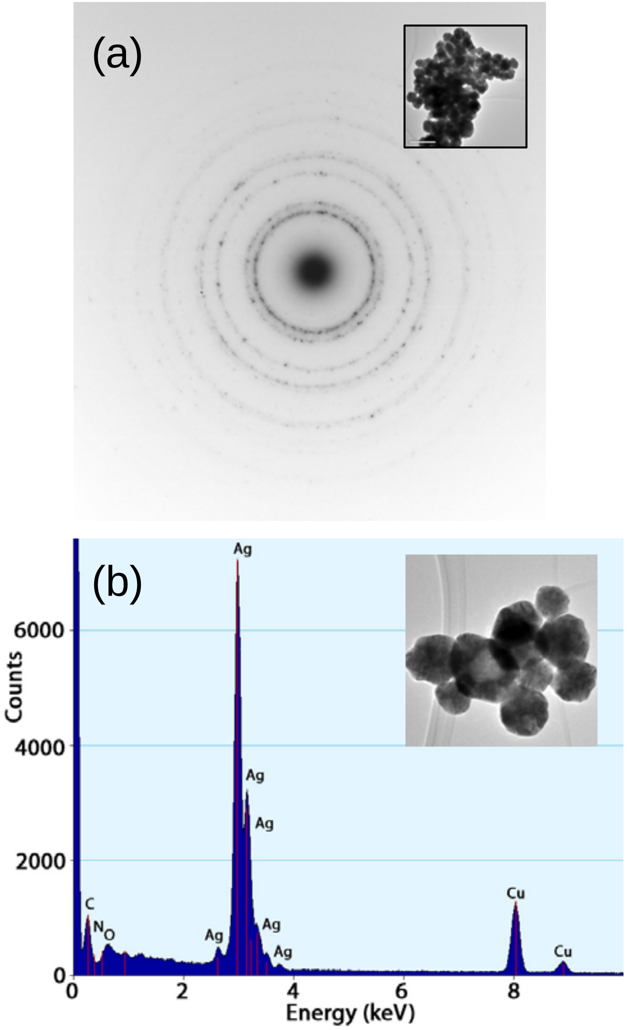


FIGURE S3. (a) TEM-SAED pattern of citrate-coated AgNPs. The insert presents a TEM image of the AgNP cluster used for the SAED analysis. (b) TEM-EDS spectrum of citrate-coated AgNPs. The insert presents a TEM image of the AgNP cluster used for the EDS analysis.

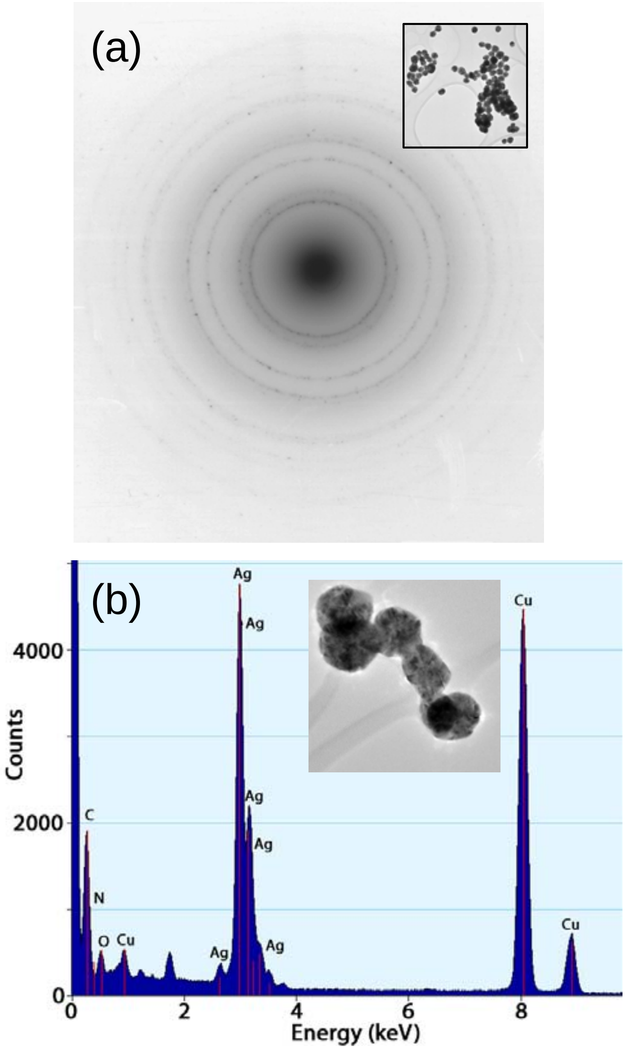
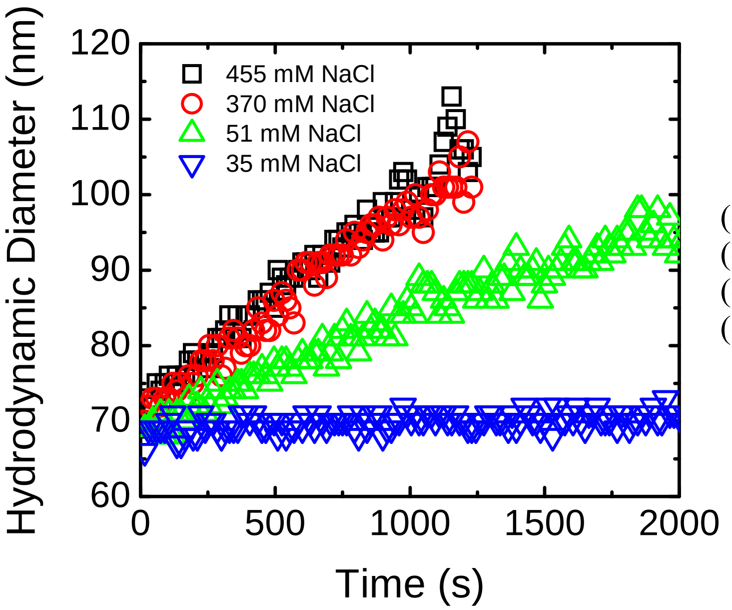


FIGURE S4. (a) TEM-SAED pattern of PVP-coated AgNPs. The insert presents a TEM image of the AgNP cluster used for the SAED analysis. (b) TEM-EDS spectrum of PVP-coated AgNPs. The insert presents a TEM image of the AgNP cluster used for the EDS analysis.



$(\mathrm{d}D_\mathrm{h}(t)/\mathrm{d}t)_{455\ \mathrm{mM}} = 0.0290$ nm/s
$(\mathrm{d}D_\mathrm{h}(t)/\mathrm{d}t)_{370\ \mathrm{mM}} = 0.0295$ nm/s
$(\mathrm{d}D_\mathrm{h}(t)/\mathrm{d}t)_{51\ \mathrm{mM}} = 0.0140$ nm/s
$(\mathrm{d}D_\mathrm{h}(t)/\mathrm{d}t)_{35\ \mathrm{mM}} = 0.0012$ nm/s

FIGURE S5. Representative aggregation profiles of citrate-coated AgNPs at four different NaCl concentrations.

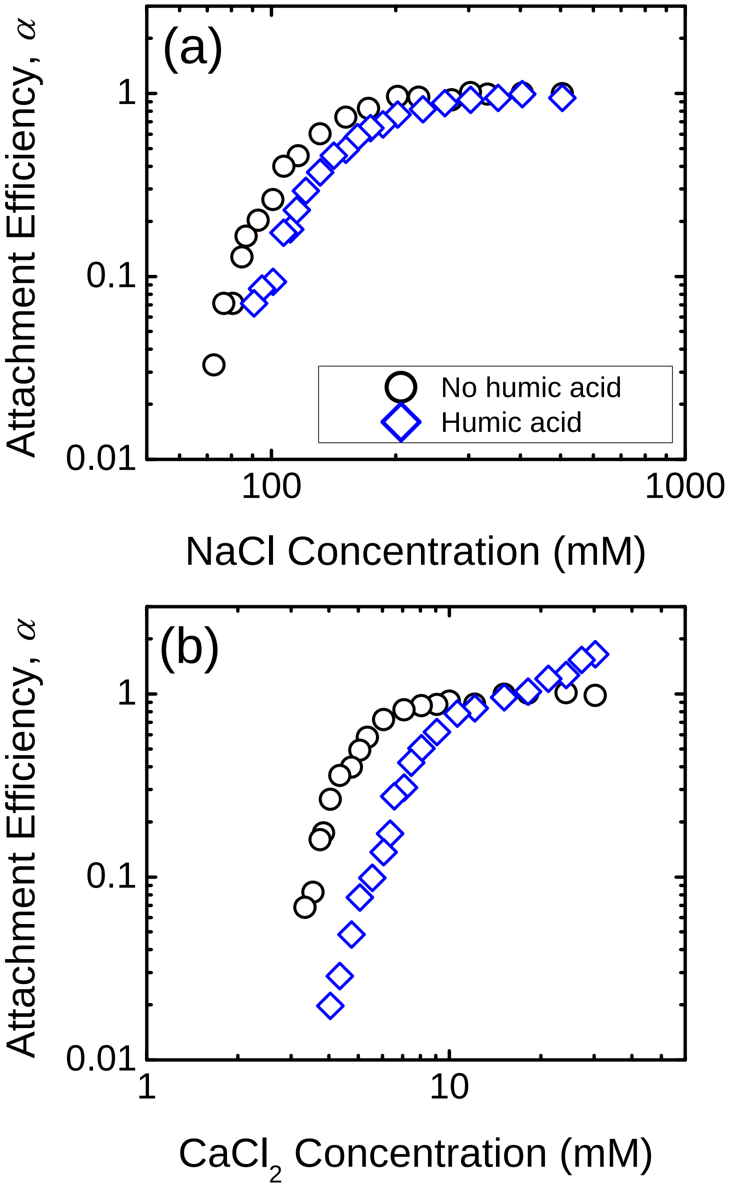


FIGURE S6. Attachment efficiencies of PVP-coated AgNPs in the absence and in the presence of humic acid (1 mg/L TOC) as functions of (a) NaCl and (b) $CaCl_2$ concentrations at pH 7.0. The attachment efficiencies of PVP-coated AgNPs in the absence of humic acid in a and b are reproduced from Figures 4a and b, respectively, in the manuscript. For all experiments, the PVP concentration in the suspension was 0.88 mg/L TOC.

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