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How to Accurately Predict Solution-phase Gold Nanostar Stability

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Abstract

Unwanted nanoparticle aggregation and/or agglomeration may occur when anisotropic nanoparticles are dispersed in various solvents and matrices. While (extended) Derjaguin, Landau, Verwey, Overbeek (DLVO) theory has been successfully applied to predict nanoparticle stability, the model fails at accurately predicting the physical stability of anisotropic nanostructures thus limiting its applicability in practice. Herein, DLVO theory accurately predicts gold nanostar stability by considering how nanostar dimension influences attractive and repulsive interactions between nanostructures. The model predicts that using the average radius of curvature of the nanostar tips instead of average radius increases the accuracy of experimentally observed nanoparticle behavior. The aforementioned predictions are validated by measuring time dependent localized surface plasmon resonance (LSPR) spectra of gold nanostars suspended in various ionic strength solutions. Minimum energy barriers calculated from collision theory as a function of nanoparticle concentration are utilized for introducing kinetic predictions. All in all, these studies suggest that gold nanostar dimensions are crucial for understanding and predicting the tendency of anisotropic nanostructures such as gold nanostars either to remain stable and be used reproducibly or aggregate and exhibit inconsistent results. Thus, a deeper understanding of inter-nanoparticle interactions in solution is provided and expected to lead to more consistent and efficient analytical and bioanalytical applications of these important materials in the future.

Graphical abstract

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Author Contributions

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

Keywords

Gold nanostars; size; stability; DLVO theory

Introduction

Anisotropic gold nanoparticles synthesized via seed [1, 2] and seedless [3] as well as surfactant [4, 5] and surfactant-free [6, 7] synthetic methods yield shape and size tunable optical properties [8, 9] that are widely used for chemical [10], biological [11, 12], and medical sensing [13] applications. Gold nanostars exhibit large surface energies and small positive and negative curvature features relative to spheres and larger structures, thus flocculation and restructuring over time are likely. Restructuring, for example, most likely occurs at regions of high surface free energy such as at the end of the nanostar branches (i.e., tips) because of their small, positive radius of curvature relative to other surface sites on these materials [14]. This was demonstrated previously when the tips of gold nanostars were shown to dissolve more quickly than other portions of the structures in an acidic medium [15, 16]. Additionally, gold nanostar branches were shown to blunt upon irradiation by a near-infrared (NIR) laser [17]. These dynamic structural changes complicate elucidation of structure-function relationships for these materials and can limit shelf-life.

Reproducible use of these materials in analytical and bioanalytical applications is also limited by particle homogeneity [18], aging [19], and physical stability [20]. For instance, the ionic strength [21] and pH [22] of a solution were shown to induce nanostar aggregation while temperature during synthesis greatly influenced the reproducibility of the resulting plasmonic properties of the materials [23]. Previously, localized surface plasmon resonance (LSPR) spectroscopy revealed that the morphology of gold nanostars changed during storage [19]. Furthermore, both supporting electrolyte composition and concentration as well as surface functionalization with molecules such as PEG [24], PVP [25], PSS-PDD multilayers [26], and hyperbranched polymers [27] improved nanostar stability. These functionalized nanostructures provide excellent examples as to why nanostructure stability is important in analytical applications. For instance, fluorophore-labeled PSS-PDD multilayers were shown to stabilize gold nanostars [26] for more reproducible fluorescence imaging. This was attributed, in part, to the elimination of fluorophore quenching, which depended on

interparticle interactions. Consequently, there are many important parameters that need to be considered for attaining reproducible functionality and adequate shelf-lives of nanostars for desired applications.

Shelf-life and functionality of nanostructures also depend on the inherently high surface energy of these materials as flocculation is a surface energy-driven process [28]. Nanoparticle flocculation occurs when short-range attractive potentials exceed longer range repulsive interactions both of which can be modeled using DLVO theory [29–31]. This model assumes that the interaction potential between a pair of nanostructures can be estimated using the dielectric properties of the objects and medium as well as the shape and size of the objects. Of note, the van der Waals potential between two nanoparticles depends on their dielectric constant. As a result [32], the attractive potential between two metallic nanoparticles increases at a fixed separation distance as particle size decreases [28]. This causes smaller nanoparticles to more readily flocculate (i.e., exhibit worsening physical stability) than larger objects.

Because gold nanostars exhibit complex geometries with positive, negative, and neutral curvature features, the physical stability of gold nanostars likely depends on the chemical potential of each of these regions with the part of the particles with the largest chemical potential (i.e., surface free energy) likely being the most important parameter for facilitating flocculation or promoting stability, and as a result, shelf-life. Herein, we investigate how ionic strength from the supporting electrolyte NaNO_3 impacts the optical and physical stability of gold nanostars before and after functionalization with 6-mercaptopentanoic acid (6-MHA) as a function of average particle size or radius of curvature of nanostar tips. These experimental results are understood using collision theory and (extended) DLVO theory. It is demonstrated that experimentally observed solution-phase nanostar stability as indicated from LSPR spectroscopy can be predicted when the radius of curvature of the nanostar tips are considered and not average particle dimensions. This suggests that small changes in these areas of high chemical potential likely impact the shelf-lives and use of these increasingly popular nanostructures.

Materials and Methods

Chemical Reagents

Gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), 4-(2-hydroxyethyl)-1-piperazine propanesulfonic acid (EPPS), and 6-mercaptopentanoic acid (6-MHA) were purchased from Sigma Aldrich. Sodium hydroxide (NaOH), sodium nitrate (NaNO_3), and ethanol were purchased from Fisher Scientific. Ultrapure water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$) was obtained from a Barnstead Nanopure System (Dubuque, IA) and used throughout this study. All glassware were cleaned using aqua regia (3:1 HCl/HNO_3) and rinsed with water before drying in the oven.

Gold Nanostar Synthesis and Functionalization

Gold nanostars were synthesized according to slightly modified literature protocols [33, 34]. Briefly, the pH of a 50 mM EPPS solution was adjusted to 7.45 using 1 M NaOH . HAuCl_4

(200 μL , 20 mM) was then added to 20 mL EPPS and incubated for 2 hours. Next, an additional 50 μL of 20 mM HAuCl_4 was added to the solution to promote nanostar growth. This solution was stirred for 60 minutes at 35°C , centrifuged (40 minutes, 2000 $\times g$) three times, and dispersed in 1 mM EPPS until use. The stock Au nanostar concentration was 0.48 nM as estimated using a previously published extinction coefficient (ϵ) = $2.08 \times 10^9 \text{ M}^{-1} \text{ cm}^{-1}$) [35]. Gold nanostars functionalization with 6-MHA was performed exactly according to our previously published protocol [34].

Transmission Electron Microscopy (TEM)

Gold nanostars were characterized using TEM (JEOL JEM-1230) equipped with a Gatan CCD camera and 120 keV accelerating voltage. Samples were prepared by first diluting the nanoparticle solution by 50% using ethanol. This solution was pipetted onto 400 mesh copper grids coated with a thin film of Formvar and carbon (Ted Pella). TEM images were analyzed (Image Pro Analyzer or Image J) to estimate the average overall (ferret) radius before ($33.0 \pm 8.6 \text{ nm}$, $N = 163$) and after functionalization ($24.8 \pm 5.0 \text{ nm}$, $N = 149$) as well as the tip radius of curvature (before $4.4 \pm 0.8 \text{ nm}$, $N = 213$ and after $4.5 \pm 0.5 \text{ nm}$, $N = 205$ functionalization) where N = the total number of measurements collected, and the average $\pm$ standard deviation of these are reported.

Extinction Spectroscopy

LSPR spectra were collected using disposable methacrylate cuvettes (pathlength = 1 cm) and an ultraviolet-visible (UV-vis) spectrometer (i-trometer, B&W Tek). Samples were prepared by diluting the stock gold nanostars in water to a final nanostar concentration of $\sim 0.3 \text{ nM}$. Next, 1 M NaNO_3 was added slowly to the nanostar solutions so that the final electrolyte concentration ranged from 0–50 mM. The final EPPS concentration in all samples was 0.6 mM. For each sample, LSPR spectra (integration time = 36 msec, average = 50 scans) were collected every 15 seconds continuously for 1 hour with a lag time of 25 seconds. Spectral changes were evaluated by integrating spectral areas from 950–1050 nm to 520–570 nm and reporting relative changes in these values (in %) vs. initial measurements. This allows for assessment of gold nanostar stability before and after 6-MHA functionalization in terms of aggregation. Finally, the extinction maximum wavelength (λ_{max}) was estimated from the zero point crossing of the first derivative of each LSPR spectrum.

Zeta Potential

Nanoparticle surface potentials were quantified from their electrophoretic mobilities at 25°C using a Malvern Zetasizer (Worcestershire, UK). Mobilities were measured after incubation in 0–50 mM NaNO_3 (calculated ionic strengths = 0.15–50.15 mM, respectively). Both residual EPPS and added electrolyte concentrations were assumed to contribute to these ionic strengths. All solutions were vortexed for 10 seconds then incubated at room temperature for 1 hour prior to electrophoretic mobility measurements. Zeta potential was calculated using Henry's equation, measured mobilities, and calculated ionic strengths [36]. EPPS stabilized and 6-MHA functionalized nanostars exhibited zeta potentials of -41.6 ± 2.9 and $-32.0 \pm 1.9 \text{ mV}$, respectively. These values represent averaged measurements at all ionic strengths used in this study.

DLVO and Collision Theory Calculations

Nanoparticle stability depends on the concentration of as well as the number of collisions between nanostructures in a given period of time. Here, we use collision theory, which assumes that the minimum required energy for particles to remain physically stable and suspended in solution must exceed their kinetic energy from Brownian motion [37], to estimate stability. As such, the total number of collisions (z) between two particles was estimated as follows:

$$z = 4\pi r^2 \langle \nu \rangle N \cdot t \quad (\text{eq. 1})$$

where r is the radius of nanoparticles (ferret radius or radius of curvature of the tips), N is the number of nanoparticles, and t is the duration time. The collision rate is equal to $4\pi r^2 \langle \nu \rangle N$, and the root mean square speed ($\langle \nu \rangle$) of Brownian motion is calculated as follows:

$$\langle \nu \rangle = \left(\frac{8kT}{\pi\mu} \right)^{0.5} \quad (\text{eq. 2})$$

where k is the Boltzmann constant, T is the temperature, and μ is the reduced mass of the two objects.

DLVO theory assumes that all objects exhibit both attractive and repulsive interactions via van der Waals and electrostatic forces, respectively. For two objects with identical sizes (r), the van der Waals interaction potential (Φ_{VDW}) is calculated as follows:

$$\Phi_{VDW} = \frac{V_{vdw}}{k_B T} = -\frac{A}{6} \left[\frac{2r^2}{s^2 + 4rs} + \frac{2r^2}{s^2 + 4rs + 4r^2} + \ln \left(\frac{s^2 + 4rs^2}{s^2 + 4rs + 4r^2} \right) \right] \quad (\text{eq. 3})$$

where A is the size-dependent Hamaker constant and s is the separation distances [37, 38]. The electrostatic interaction potential (Φ_{EL}) between two objects depends on the inverse Debye length (κ) and exhibits two limits [39] first understood by Derjaguin in 1937 [30] including when $\kappa r > 5$ (double layer thickness is small vs. particle radius),

$$\Phi_{EL} = \frac{V_{ele}}{k_B T} = \frac{2\pi\epsilon_0\epsilon\psi_0^2 r}{k_B T} \ln(1 + e^{-\kappa s}) \quad (\text{eq. 4})$$

and when $\kappa r < 5$, the double layer thickness is large vs. particle radius and

$$\Phi_R = \frac{V_{ele}}{k_B T} = \frac{4\pi\epsilon_0\epsilon Y^2 r^2 k_B T}{e^2} \frac{e^{-\kappa s}}{s + 2r} \quad (\text{eq. 5})$$

$$\text{where } Y = \frac{8 \tanh\left(\frac{e\psi_0}{4k_B T}\right)}{1 + \left[1 - \frac{2\kappa r + 1}{(\kappa r + 1)^2} + \tanh^2\left(\frac{e\psi_0}{4k_B T}\right)\right]^{1/2}}; \psi_0 = \xi \left(1 + \frac{1}{\kappa r}\right) \cdot \exp(1), \kappa^{-1} = \left(\frac{2e^2 N_A I}{\epsilon \epsilon_0 k_B T}\right)^{-1}, \psi_0 \text{ is}$$

the surface potential, ξ is zeta potential, e is elementary charge, ϵ is the relative permittivity of water (78.54), ϵ_0 is the electric permittivity of free space, R is the gas constant, I is ionic strength (0.15–50.15 mM), and N_A is Avogadro's number.

Stability calculations for nanostructures functionalized with 6-MHA also include osmotic (Φ_{osm}) and elastic (Φ_{elas}) interaction potentials (i.e., extended DLVO). These short range repulsive contributions depend on monolayer thickness (t) and separation distance [37, 40]. When the separation distance is larger than twice the effective monolayer thickness ($s > 2t$), $\Phi_{osm}(s) = 0$. When $t < s < 2t$,

$$\frac{\Phi_{osm}(s)}{k_B T} = \frac{4\pi a N_A}{v_1} \phi_P^2 \left(\frac{1}{2} - \chi\right) \left(t - \frac{s}{2}\right)^2 \quad (\text{eq. 6})$$

can be used where v_1 is the molar volume of the solvent, χ is the Flory-Huggins interaction parameter (0.45 for a well-ordered monolayer) [41], and ϕ_P is the volume fraction of the ligand. When the separation distance is less than the effective monolayer thickness ($s < t$), ligand interactions between the nanoparticle pair causes elastic deformations and compression of ligand tails [40, 41]. As a result, $\Phi_{osm}(s)$ and $\Phi_{elas}(s)$ contribute to the total interaction potential between a pair of objects and are calculated as follows:

$$\frac{\Phi_{osm}(s)}{k_B T} = \frac{4\pi a N_A}{v_1} \phi_P^2 \left(\frac{1}{2} - \chi\right) \left[t^2 \left(\frac{s}{2t} - \frac{1}{4} - \ln\left(\frac{s}{t}\right)\right)\right] \quad (\text{eq. 7})$$

$$\frac{\Phi_{elas}(s)}{k_B T} = \left(\frac{2\pi a N_A}{M_W} \phi_P t^2 \rho_d\right) \left[\left(\frac{s}{t}\right) \ln\left(\frac{s}{t} \left(\frac{3 - \frac{s}{t}}{2}\right)^2\right)\right] - \ln\left(\frac{3 - \frac{s}{t}}{2}\right) + 3\left(1 - \frac{s}{t}\right) \quad (\text{eq. 8})$$

where M_W (148.22 g/mol) and ρ_d (4.581×10^{14}) are the molecular weight and density of the (pure) ligand, respectively.

The total interaction potential between a pair of nanostructures is the sum of all relevant contributions ($\Phi_{total}(s) = \Phi_{vdw}(s) + \Phi_{EL}(s) + \Phi_{osm}(s) + \Phi_{EL}(s)$). Maximum energy barriers (V_{max}) required for solution-phase nanoparticle stability were estimated from the total interaction potential (Φ_{total}) then plotted as a function of ionic strength. Nanostructures were considered to be stably suspended in solution when V_{max} was greater than the kinetic energy calculated using collision theory.

Results and Discussion

Gold Nanostar Functionalization and Characterization

To use nanoparticles such as gold nanostars in applications, the materials are typically functionalized and/or dispersed in buffer [42]. Thus, understanding how functionalization and buffer composition influence the physical stability of gold nanostars is important. For instance, nanostructure size governs resulting electro-optical properties, stability in solution, as well as how these nanomaterials interact with/influence matter [28, 43]. Here, gold nanostars synthesized via reduction of EPPS [33] are used to explore how functionalization and ionic strength impact the size, structure, surface potential, and optical stability (and hence the physical stability) of gold nanostars. 6-MHA is selected for functionalization as it forms self-assembled monolayers (SAMs) on gold [34] and contains a carboxylic acid terminal group that is deprotonated in solutions with $\text{pH} > 5.4\text{--}6.3$ [44]. As a result, a repulsive steric barrier (i.e., from elastic and osmotic potentials) is present on the nanostructure surface of functionalized nanostars in physiologically relevant (pH) solutions.

Representative TEM images of gold nanostars before and after functionalization are shown in Figures 1A and 1B. These seedless and surfactantlessly prepared nanostructures contain a core and three to seven extruding branches, which mimic a star shape. Because of the complex structure of the nanostars, size of these structures can be quantified in multiple ways including the ferret radius, branch length, core size, and radius of curvature of the branch tips. The two extreme dimensions are also the most straight forward and accurate dimensions to quantify and are the ferret radius and radius of curvature of the tips. A summary of these dimensions are compared for gold nanostars before and after functionalization with 6-MHA as shown in Figures 1C and 1D. Before functionalization, the ferret radius of the nanostars is 33.0 ± 8.6 nm. Upon functionalization with 6-MHA, this value decreases to 24.8 ± 5.0 nm. This decrease in size is similar to small dimensionality changes in gold nanostructures upon thiolation [45]. The radius of curvature of the tips, however, do not significantly change (4.4 ± 0.8 nm vs. 4.5 ± 0.5 nm, respectively).

Along with slight structural changes, the surface potentials of these nanostructures vary from -41.6 to -32.0 mV at $\sim\text{pH } 7$, respectively. Surface potential depends on double layer effects at the nanoparticle surface as well as the charge of terminal functional groups from the SAM. These data suggest that the electrostatic double layer from ions in solution are larger on unfunctionalized vs. functionalized nanostructures. This change in surface chemistry is also reflected in LSPR analysis. Before functionalization, the nanostars exhibit a λ_{max} centered at 714.4 nm (Figure 2A-1), which is consistent with previously reported gold nanostar optical properties [33]. Upon functionalization, this value red shifts 11.9 nm to 726.3 nm (Figure 2A-2). In addition, the LSPR band shape broadens, which is consistent with slight electromagnetic coupling between nanostructures. Despite this, these nanostructures remain suspended in solution and thus can be used to estimate the effective refractive index and effective thickness of the 6-MHA monolayer.

Changes in the λ_{max} before and after functionalization can be used to estimate the effective monolayer thickness (t) and refractive index of the monolayer because the LSPR is sensitive

to local refractive index [46]. The SAM thickness and refractive index sensitivity (m) of the gold nanostars is calculated using the following equation [47, 48]:

$$\Delta\lambda_{\max} = m\Delta n \left(1 - e^{-\frac{2t}{l_d}} \right) \quad (\text{eq. 9})$$

where n is the refractive index difference between the SAM and water (1.33), and l_d is the $1/e$ electromagnetic field decay length. The refractive index sensitivity of the gold nanostars is estimated by systematically changing the bulk refractive index of unfunctionalized gold nanostars in H_2O solution using 0–80% (w/v) sucrose [49]. In so doing, a refractive index sensitivity of 416 nm/refractive index unit (RIU) is estimated for nanostars stabilized electrostatically (Figure 2B-1). After functionalization, this value decreases to 369 nm/RIU as shown in Figure 2B-2. The $1/e$ decay length is approximated as ~ 4 nm, which is reasonable assuming each branch can be treated as a nanorod [34]. The effective refractive index of the SAM can be estimated from where these lines cross [50]. As a result, the effective refractive index of the SAM is 1.437. From these values and eq. 9, an effective SAM thickness of 0.6 nm is estimated.

Experimental Evaluation of Gold Nanostar Stability

Now that the structure, surface potential, and surface chemistry of the nanostars have been evaluated, the physical stability of the nanostars is assessed using LSPR spectroscopy. Most ions in solution exhibit weak to no affinity for gold thus impact the physical stability of gold nanostars by contributing to solution ionic strength and double layer composition and thickness [51, 52]. Nitrate is a “good” electrolyte for this purpose as it exhibits minimal affinity to gold so is used here to adjust the ionic strength of the solution from 0.15 – 50.5 mM. Gold nanostar concentration is maintained at ~ 0.3 nM so that the number of collisions between nanostructures is approximately constant on average as estimated using collision theory (equations 1–2). While ionic strength may slightly impact Brownian motion, these effects are assumed to be minimal. LSPR spectra are collected continuously for 1 hour for gold nanostars before and after functionalization in otherwise identical solution conditions.

Figures 2C and 2D show representative, time dependent LSPR spectra for gold nanostars incubated in 50 mM NaNO_3 before and after 6-MHA functionalization, respectively. Similar trends are noted for both samples. First, $\lambda_{\max}$ values red-shift with increasing time, trends that are consistent with an increase in local refractive index induced from a decrease in interparticle distances and/or cluster formation [53]. Second, the extinction magnitude at the $\lambda_{\max}$ decreases with time. This occurs because of plasmon dampening, which occurs upon nanostar aggregation. Finally, the LSPR spectra broaden significantly at longer wavelengths for unfunctionalized gold nanostars. This spectral change is once again consistent with increased short-range interparticle interactions associated with cluster formation. All of these trends are time dependent and suggest that gold nanostars with and without SAM functionalization undergo significant nanoparticle-nanoparticle interactions with increasing time in this ionic strength solution.

To quantify these time-dependent variations, the λ_{max} and integrated spectral area near 1000 nm are plotted in Figure 3. To quantify differences in flocculation (i.e., both agglomeration and aggregation), relative changes in integrated area $((t_1 - t_0)/t_0, \%)$ are calculated from LSPR spectra [54]. Once again, interesting trends are noted. First, the λ_{max} increases three times faster when nanostars are functionalized vs. electrostatically stabilized structures. Second, relative changes in the integrated area for gold nanostars stabilized by the SAM reveal similar time dependent changes as observed with changes in λ_{max} . Electrostatically stabilized structures, however, show more complex behavior where this value increases rapidly (~2 times more quickly than SAM-stabilized nanostars) suggestive of a rapid electromagnetic coupling between nanostructures followed by a slow decay. This result is consistent with irreversible formation of clusters that subsequently settle out of solution via sedimentation. In contrast, the SAM stabilized structures are electromagnetically coupling but not forming stable or large aggregates.

To closely investigate the temporal responses of these interactions, time dependent LSPR spectra of gold nanostars with and without SAM functionalization incubated in 0–50 mM NaNO_3 are evaluated for 1 hour. Trends in the λ_{max} and changes in relative integrated spectral area near 1000 nm are plotted in Figure 3. As shown in Figures 3A and 3C, the of electrostatically and 6-MHA stabilized gold nanostars do not change significantly during this time period in 0–30 mM NaNO_3 . Above 30 mM NaNO_3 , evidence of electromagnetic instability (i.e., from agglomeration and/or aggregation) is evident for both samples through shifts in λ_{max} and relative integrated area analysis. Evaluation of relative integrated areas near 1000 nm is more sensitive to flocculation than changes in λ_{max} . As shown in Figure 3B, evidence of gold nanostar flocculation caused by increasing ionic strength is observed at NaNO_3 concentrations greater than 20 mM. From 25–30 mM NaNO_3 , these values increase by ~35% over the course of an hour whereas a rapid increase to ~75 and 115% were observed within 5 minutes for 40 and 50 mM NaNO_3 , respectively. After 5 minutes, this area decreases slightly, which is consistent with sedimentation of clusters and/or plasmon dampening.

In contrast, SAM functionalized nanostructures did not exhibit evidence of large changes in electromagnetic coupling due to aggregation and/or sedimentation until the nanostars were immersed in 50 mM NaNO_3 (Figure 3D). Instead, evidence of slight changes in electromagnetic coupling between nanostars is observed when NaNO_3 concentration were less than 40 mM (<2 nm red shift in the LSPR maximum wavelength and < 5% change in the relative integrated area regions of the spectra). As the ionic strength is increased further, the increases by ~30 nm and the relative integrated area near 1000 nm increases rapidly by ~20% (similar to unfunctionalized nanostructures) accordingly. These trends at the highest ionic strength are consistent with previously observed trends in the plasmonic changes of solution-phase gold nanostructures that arise from electromagnetic coupling and nanoparticle instabilities that arise from cluster formation. Importantly, overall size [55], branch length [35], number of branches [46], and radius of curvature of nanostar tips [14] were shown to impact the resulting optical properties of similar nanostructures yet little to no insight was provided in these studies.

Predictions of Gold Nanostar Stability as a Function of Dimension

Gold nanostar stability depends on both the energetics associated with collisions as well as the number of collisions that occur between nanostructures over a period of time. In an effort to develop a model that predicts the experimentally observed nanostar stability, we employ both collision theory and DLVO modeling. Collision theory estimates collision frequency between objects and kinetic energy of objects from Brownian motion [37]. In this study, duration times of 24 hours and 1 week were selected to mimic sample handling and storage conditions [56]. For example, 2.2×10^7 collisions between primary nanoparticles will occur in a ~ 0.3 nM gold nanostar solution at 298 K in 1 week. Assuming a Boltzmann distribution, the probability $\left(e^{-V_{max}/k_B T} \right)$ of two colliding nanoparticle overcoming this energy barrier and aggregating is less than $1/(\text{number of collisions per week})$. Importantly, collision theory overestimates collision frequencies once clusters have formed thereby providing a worst-case scenario for stability predictions. Thus, gold nanostars must possess a minimum energy of $\sim 16\text{--}17/k_B T$ to remain stable in solution for 1 week. This value is independent of nanoparticle functionalization.

(Extended) DLVO theory is used in conjunction with results from collision theory as DLVO modeling is widely applied to predict nanomaterial stability as a function of interaction pair potential [28, 37, 57, 58]. Here, we consider impacts of both nanoparticle dimensionality (size) and functionalization. Dimensionality is an important parameter in applying this model as both van der Waals and electrostatic interactions exhibit size dependence whereas extended DLVO incorporates both elastic and osmotic interaction potentials for SAM functionalized nanostructures (these potentials are zero for unfunctionalized materials [37] as the volume fractions of the ligands are zero in equations 8 and 7, respectively, reducing these potentials to zero). To apply DLVO modeling to the nanostars used in this study, surface potential and surface ligand densities/thicknesses are assumed to be uniform, and experimental values for these can be estimated using zeta potential and LSPR spectroscopy, respectively (*vide supra*).

To evaluate how nanostar size impacts solution-phase stability of nanostars, dimensionality can be characterized in terms of ferret radius, branch length, core size, and tip size (i.e., radius of curvature). Here, we compare how the largest (ferret radius) and smallest (radius of curvature of the tips) dimensions of the experimentally used nanostars in this study to evaluate the impacts of “size” on experimentally observed and predicted nanostructure stability. Interaction pair potentials for gold nanostars before (Figure 4A) and after (Figure 4B) 6-MHA functionalization are compared using equations 3–8. First, the gold nanostar “size” that is used in DLVO modeling is the ferret radius. Because the ferret radius decreases from 33.0 to 24.8 nm upon functionalization, previously determined size-dependent Hamaker constants of 2.98 and 3.10×10^{-19} J are used, respectively [37]. These differences influence the predicted van der Waals potentials between two nanostructures. Repulsive interactions are influenced by variations in electrostatic potential (-41.6 and -32.0 mV, respectively) and by the presence/absence of the SAM.

As shown in Figures 4A and 4B, the individual contributions and total interaction potential between a pair of two nanostars in a 20 mM ionic strength solution without and with 6-

MHA functionalization are shown, respectively. While differences are noted in the individual contributions, the shapes of the total interaction pair potential curves are significantly different but consistent with previous modeling for DLVO and extended DLVO calculations for spherical particles [37]. In addition, differences in the maximum energy barrier ($V_{\max}$) are noted in the total interaction potential. These values are ~ 100 and $\sim 60/k_B T$, for electrostatically and SAM-stabilized nanostructures, respectively. Similar calculations for total interaction pair potentials were also calculated for ionic strengths ranging from 0.5–50.5 mM so that theoretical $V_{\max}$ can be evaluated. These are summarized as a function of ionic strength in Figure 4C. These values decrease for the nanostructures as ionic strength increases because the electrostatic double layer becomes more compressed thus lowering the electrostatic pair potential. In addition, the SAM provides additional stability when ionic strengths exceed ~ 38 mM. While these general predictions are reasonable, the values are inconsistent with our experimental observations of solution-phase stability from LSPR measurements. In addition, collision theory suggests that any energy barrier in excess of $\sim 17/k_B T$ should result in both thermodynamically stable nanostructures for one week. This suggests that ferret radius is not the “size” dimension that governs the solution-phase stability of the gold nanostars.

To improve DLVO predictions, similar modeling is performed using the radius of curvature of the nanostar tips as shown in Figures 5A and 5B for nanostars before and after functionalization, respectively. In contrast to the ferret radius, the radius of curvature of the nanostar tips do not change significantly upon 6-MHA functionalization (4.4 and 4.5 nm, respectively) so a Hamaker constants of 3.85×10^{-19} J can be used to model both samples. Total interaction pair potentials and maximum potential barriers as a function of ionic strength vary systematically as shown in Figure 5C. Several notable differences are observed in comparison to the calculated behavior using the ferret radius. First, the overall $V_{\max}$ is smaller for these nanostructures ($< \sim 40/k_B T$ vs. $< \sim 100/k_B T$) at all ionic strengths when considering the radius of curvature vs. ferret radius, respectively. Second, functionalized gold nanostars exhibit larger energy barriers at all ionic strengths than electrostatically stabilized nanostars. This is reasonable given the large steric potentials that arise from the SAM. Finally, ionic strengths of ~ 20 and ~ 32 mM are predicted to lead to unstable nanostars without and with SAM functionalization, respectively. These predictions are consistent with the experimentally measured results from LSPR. This result suggests that the smallest dimensions of solution-phase nanostructures dictate stability and if used, can predict whether or not nanostructures will remain suspended in solution for the desired period of time.

All in all, DLVO modeling and collision theory provide a strong platform for understanding how the experimentally observed optical stability of gold nanostars vary in solution as a function of time and ionic strength. Because of this, the stability of these nanostructures in solution can be predicted in advance of any analytical or bioanalytical application – a merit previously unachieved for anisotropic nanostructures. This is important because nanostructures in solution will collide. The probability as to whether or not clusters will form upon a collision depends on the kinetic energy of the particles as well as potential energy landscape at the particle surface. These depend on nanostructure dimension and can be predicted using collision theory and DLVO modeling, respectively. Use of average

nanoparticle size overestimated nanostar stability relative to experimental measurements. Instead, comparisons of the theoretical results and LSPR spectral data for gold nanostars as a function of ionic strength revealed that the smallest nanostructure dimension, in this case, the tips of the nanostar branches, dictated solution-phase nanostructure stability. Knowing this could be empowering for researchers who use these materials in subsequent analytical and bioanalytical measurements.

Conclusions

In summary, experimentally observed solution-phase gold nanostar stability before and after functionalization with 6-mercaptopentanoic acid can be predicted accurately using (extended) DLVO theory and collision theory if radius of curvature of nanostar tips is considered. This was achieved using experimentally estimated size (ferret radius and radius of curvature of nanostar tips), surface potential, and/or SAM thickness. LSPR spectra of nanostars with and without functionalization provided experimental evidence of nanostar instability by revealing time-dependent changes in extinction maximum wavelength and relative integrated areas near 1000 nm. Experimental results were consistent with modeling predictions by comparing the calculated minimum required kinetic energy of the nanostructures from collision theory with the maximum energy barrier of the nanostructures from DLVO theory as a function of ionic strength. In so doing, accurate predictions of experimental behavior were achieved when the smallest nanostructure dimensions were considered. These results suggest that small changes in these small nanostructure dimensions, which also possess high chemical potentials likely govern material shelf-lives in solution and use of these and other increasingly popular anisotropic nanostructures in various applications.

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Biographies

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Fig. 1.

TEM analysis of gold nanostars (A) before and (B) after functionalization with 6-MHA. Size distribution of nanostars as a function of (C) ferret radius and (D) radius of curvature of nanostar tips, respectively, (1) before (33.0 ± 8.6 nm, $N = 163$ and 4.4 ± 0.8 nm, $N = 213$) and (2) after 6-MHA functionalized gold nanostars (24.8 ± 5.0 nm, $N = 149$ and 4.5 ± 0.5 nm, $N = 205$)

Fig. 2.

Plasmonic characterization of gold nanostars. (A) LSPR spectra ($\lambda_{\max,1} = 714.4$ nm, $\lambda_{\max,2} = 726.3$ nm, $\lambda_{\max} = 11.9$ nm) and (B) refractive index sensitivity of gold nanostars to 0–80% (w/v) sucrose (1) before and (2) after functionalization with 6-MHA. The linear refractive index sensitivities before and after 6-MHA functionalization are 461 and 369 nm/RIU, respectively. The intersection of these lines indicate the refractive index of 6-MHA on the nanostars and is 1.437. Representative LSPR spectra of nanostars (C) before and (D) after 6-MHA functionalization immersed in 50 mM NaNO₃ after (1) 10, (2) 20, (3) 30, (4) 40, (5) 50, and (6) 60 minutes

Fig. 3.

Time dependent plasmonic responses of gold nanostars (A and B) before and (C and D) after 6-MHA functionalization in the presence of (1) 0, (2) 5, (3) 10, (4) 15, (5) 20, (6) 25, (7) 30, (8) 35, (9) 40, and/or (10) 50 mM NaNO₃. Changes in (A and C) $\lambda_{\max}$ and (B and D) change in relative integrated area (%) from 950–1050 nm and 520–570 nm for gold nanostars before and after 6-MHA functionalization, respectively

Fig. 4.

Predictions of interaction potential as a function of size defined using the ferret radii between a pair of gold nanostars (A) before and (B) after functionalization with 6-MHA using DLVO and xDLVO theory, respectively. Interaction potentials as a function of (1) van der Waals, (2) electrostatic, (3) total, (4) elastic, and (5) osmotic potentials. Experimental inputs were used for modeling as follows: Ionic strength = 20 mM, (A) radius = 33.0 nm, Hamaker constant = 2.98×10^{-19} J, zeta potential = -41.6 mV and (B) radius = 24.8 nm, Hamaker constant = 3.10×10^{-19} J, zeta potential = -32.0 mV, molecular weight of ligand = 148.22 g/mol, density of pure ligand = 1.087 g/cm³, SAM packing density = 4.58×10^{14} , and SAM thickness = 0.6 nm. (C) Maximum potential barrier ($V_{\max}$) as a function of ionic strength for nanostars (1) before and (2) after functionalization. The dashed gray lines represents the interaction potential that must be overcome to prevent aggregation for one week using 0.3 nM nanostars at room temperature (estimated using collision theory)

Fig. 5.

Predictions of interaction potential using size defined using the radius of curvature of the tips between a pair of gold nanostars (A) before and (B) after functionalization with 6-MHA using DLVO and xDLVO theory, respectively. Interaction potentials as a function of (1) van der Waals, (2) electrostatic, (3) total, (4) elastic, and (5) osmotic potentials. Experimental inputs were used for modeling as follows: Ionic strength = 20 mM, (A) radius = 4.4 nm, Hamaker constant = 3.85×10^{-19} J, zeta potential = -41.6 mV and (B) radius = 4.5 nm, Hamaker constant = 3.85×10^{-19} J, zeta potential = -32.0 mV, molecular weight of ligand = 148.22 g/mol, density of pure ligand = 1.087 g/cm³, SAM packing density = 4.58×10^{14} , and SAM thickness = 0.6 nm. (C) Maximum potential barrier (V_{max}) as a function of ionic strength for nanostars (1) before and (2) after functionalization. The dashed gray lines represents the interaction potential that must be overcome to prevent aggregation for one week using 0.3 nM nanostars at room temperature (estimated using collision theory)