

SUPPORTING INFORMATION

UV-VIS Spectra for Silver Nanoparticle Synthesis

To characterize the silver nanoparticle samples, UV-VIS spectra were taken with the aim of detecting the characteristic surface plasmon resonance band (SPR) at a wavelength of $\lambda_{\text{spr}} \approx 450$ nm. All UV-VIS spectra are reproduced below, however, spectra from the $R \geq 6$ -12 and $S \geq 3$ -12 range warrant special consideration as this represents the general range of nanoparticle stability as determined by TEM. We anticipate that the aggregated suspensions will “red-shift”; thus, the lack of “red-shifting” in spectra with $R=3$ or $S=1$ is in conflict with the skewed size distribution displayed in the TEM images in Fig. 6 in the manuscript, indicating that the larger aggregates settled out of suspension before data collection; with that in mind, the absorbance band at $\lambda_{\text{spr}} \approx 450$ nm in the spectra appearing as Figs. 1A-O below confirms the synthesis of small Ag nanoparticles within the region of particle uniformity at $R \geq 6$ -12 and $S \geq 3$ -12.

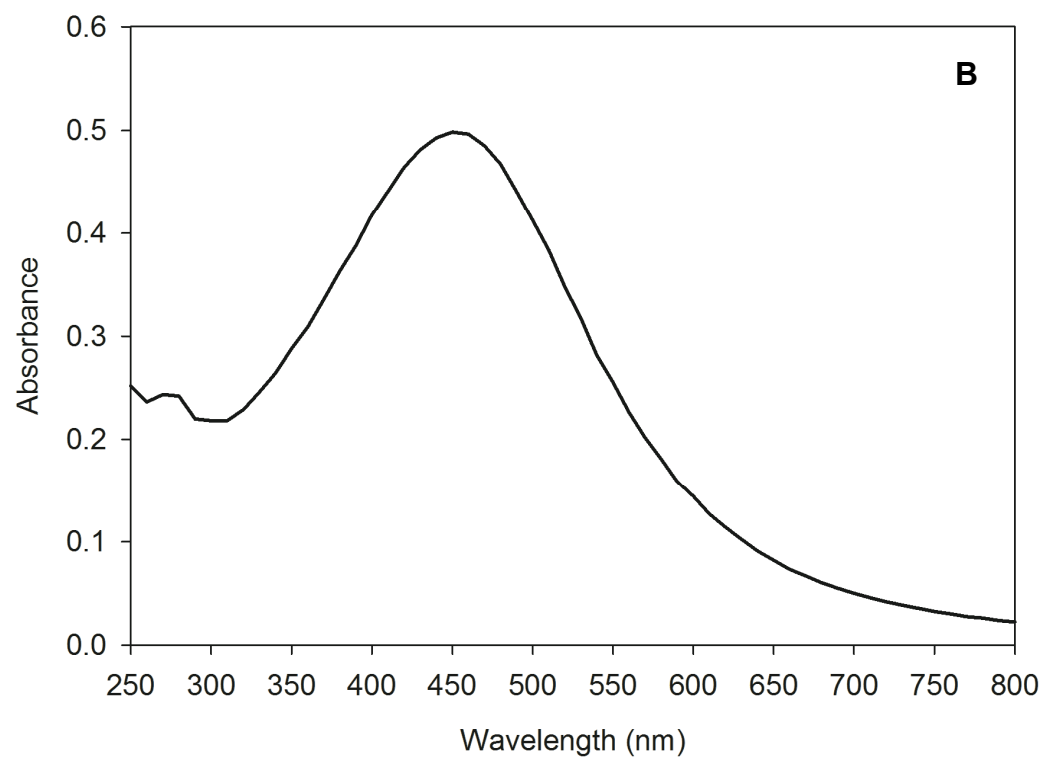
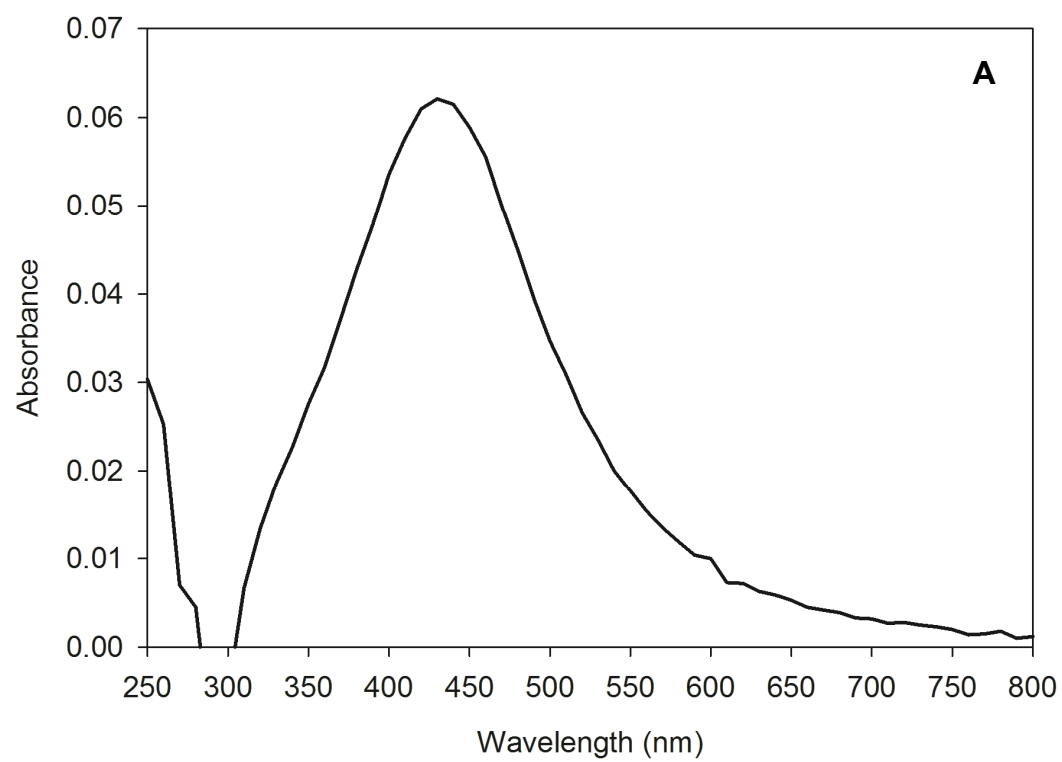


Figure 1A. UV Spectra of the alkanethiol-functionalized silver nanoparticles: A) $R=3:S=1$; and B) $R=3:S=3$.

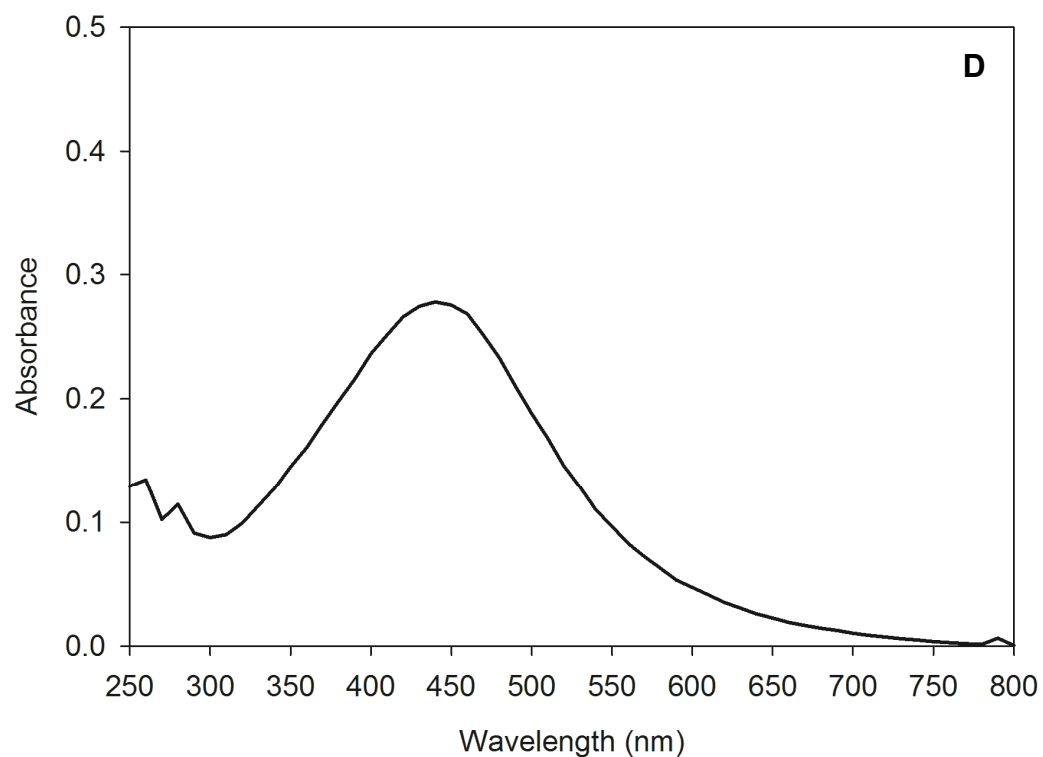
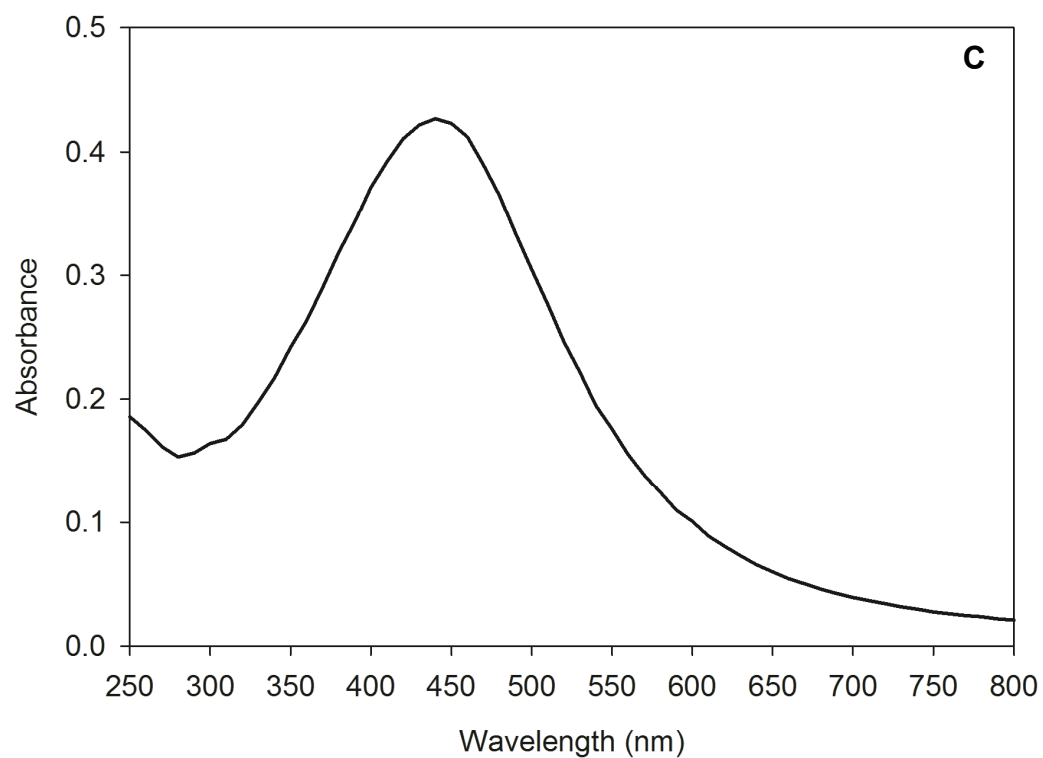


Figure 1B. UV Spectra of the alkanethiol-functionalized silver nanoparticles: C) $R=3:S=6$; and D) $R=3:S=12$.

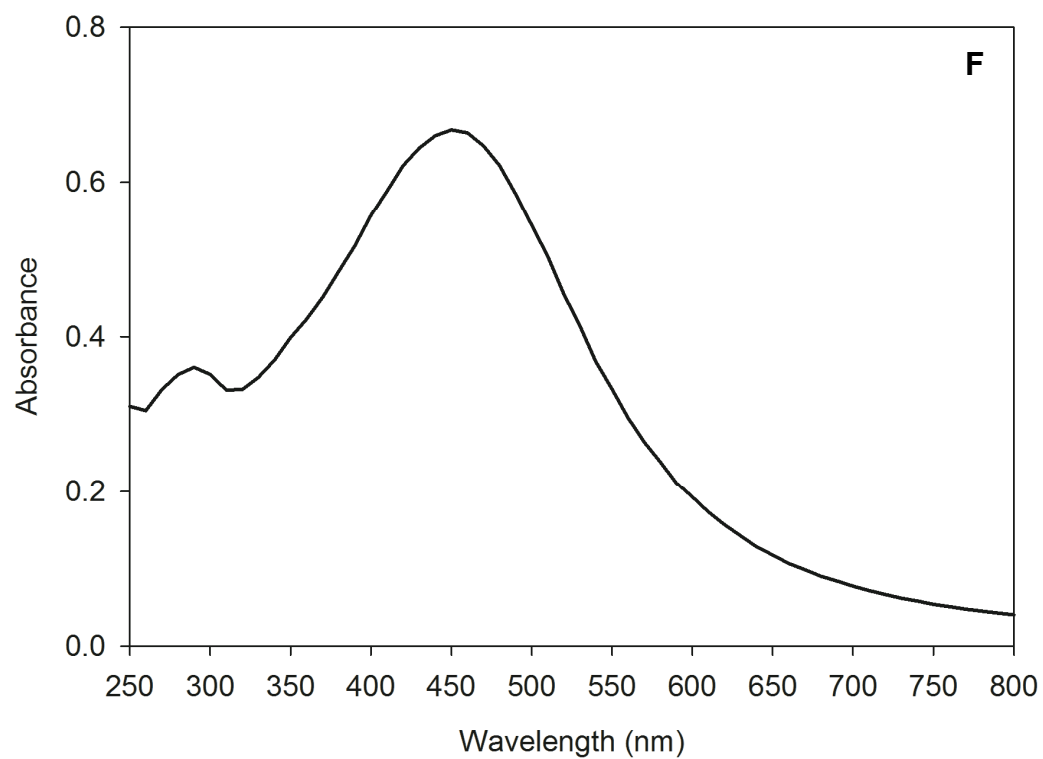
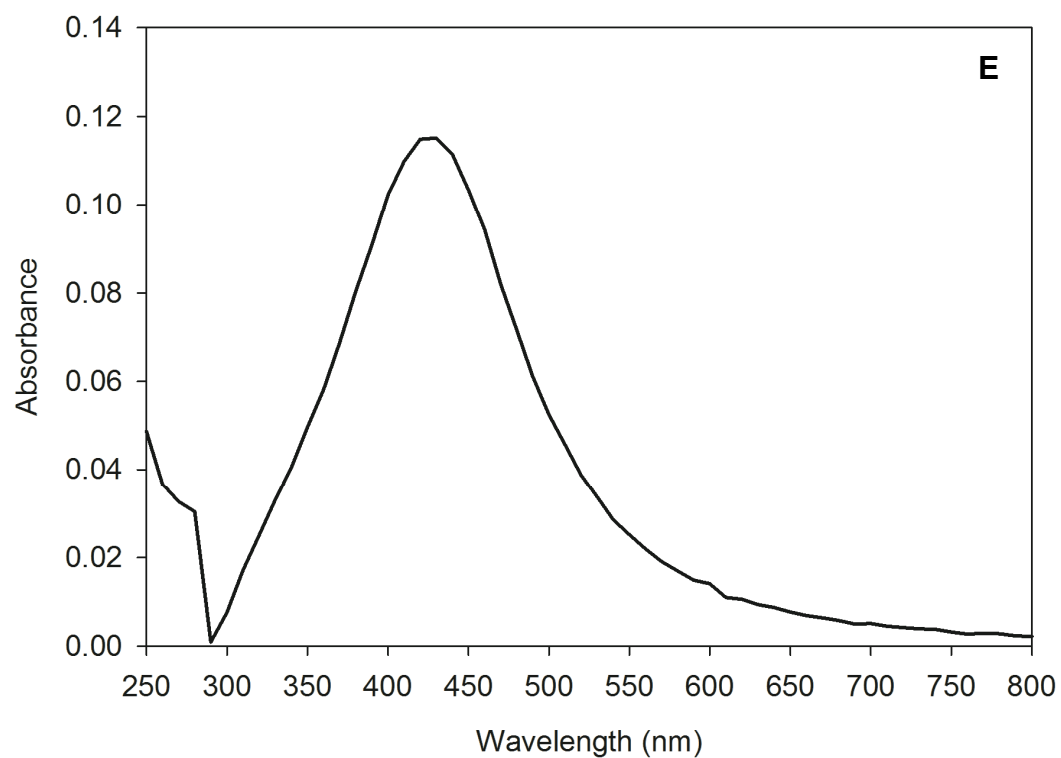


Figure 1C. UV Spectra of the alkanethiol-functionalized silver nanoparticles: E) $R=6:S=1$; and F) $R=6:S=3$.

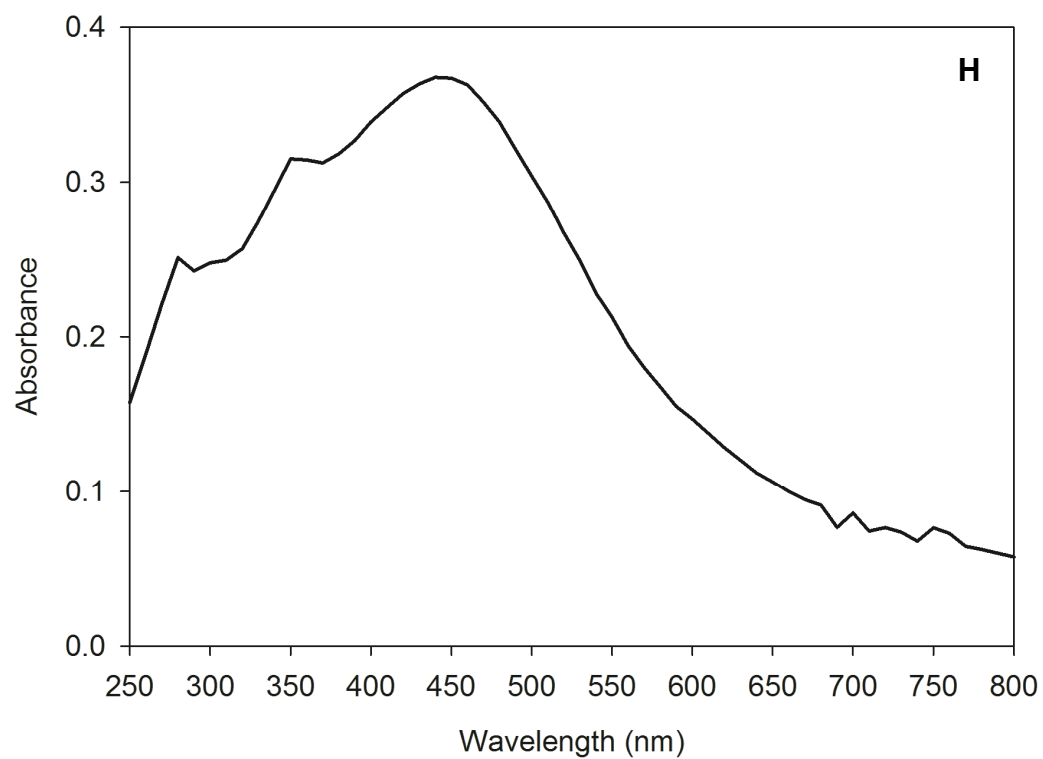
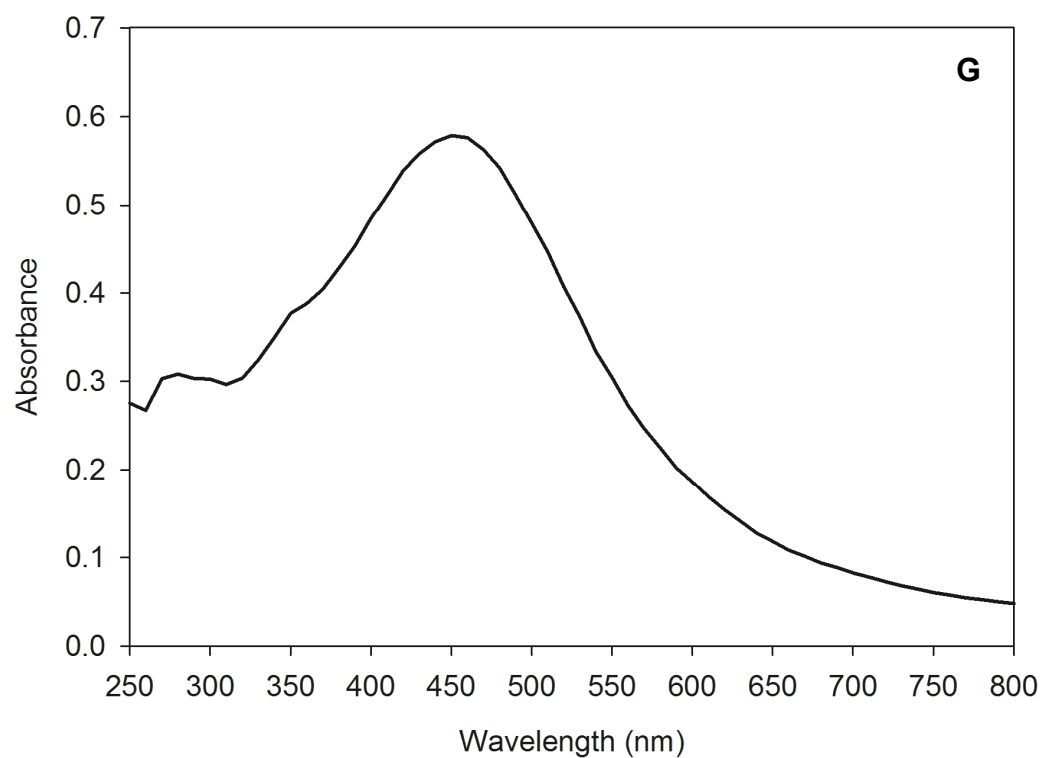


Figure 1D. UV Spectra of the alkanethiol-functionalized silver nanoparticles: G) $R=6:S=6$; and H) $R=6:S=12$.

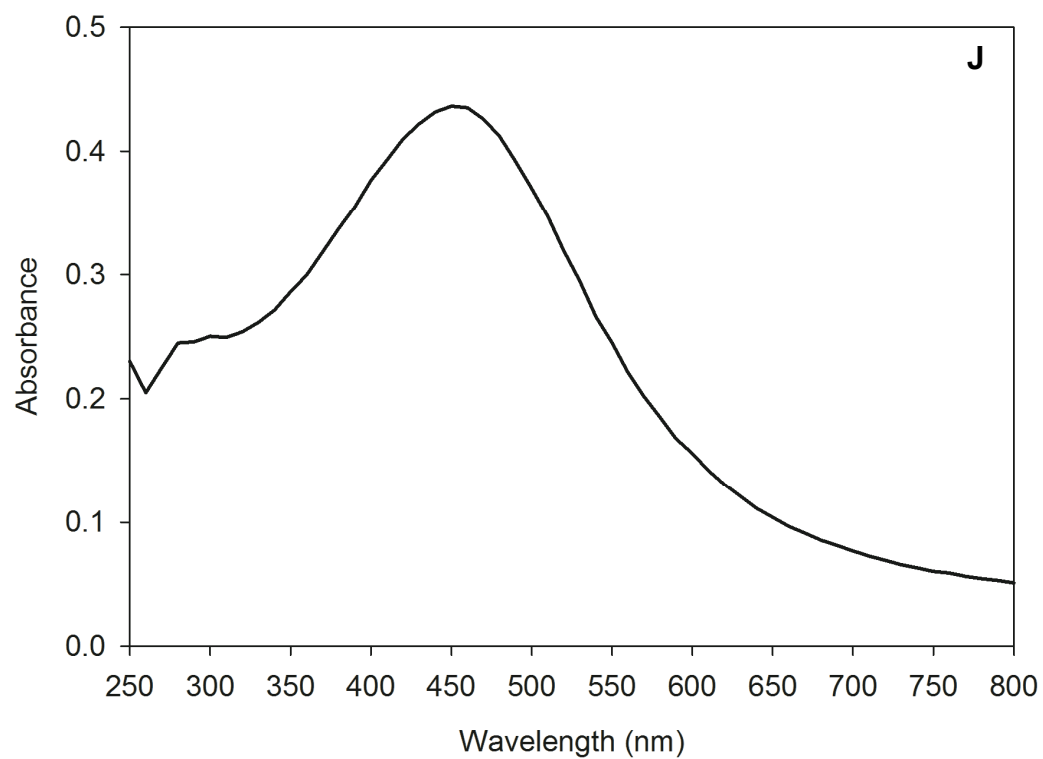
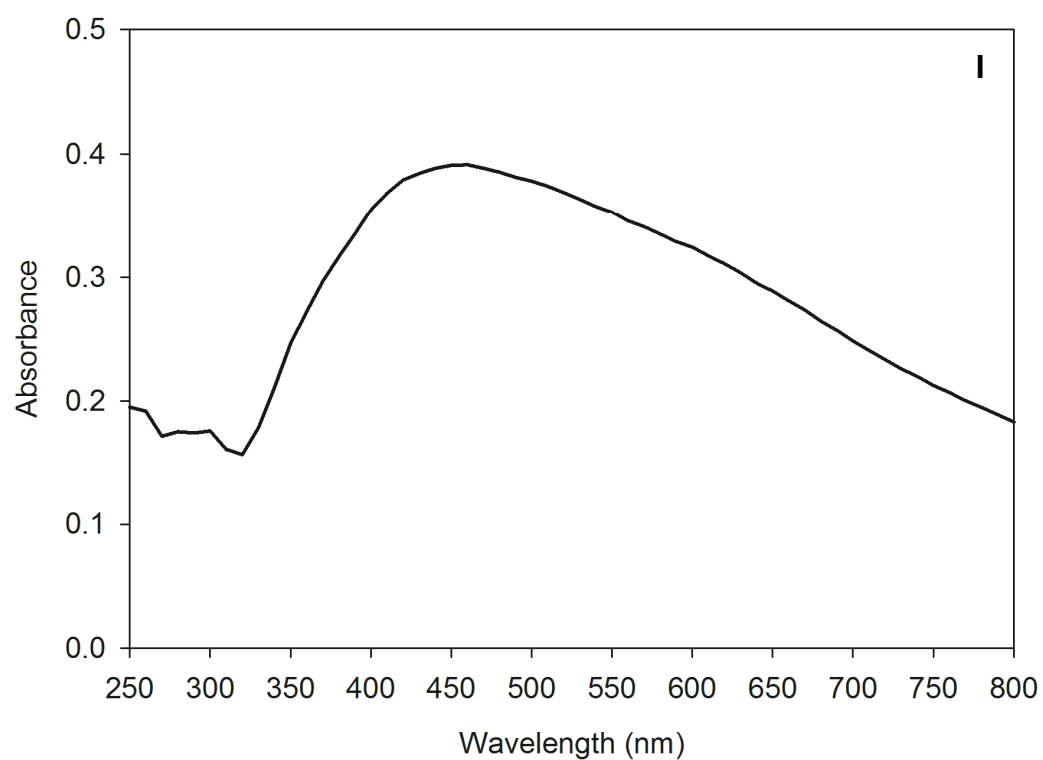


Figure 1E. UV Spectra of the alkanethiol-functionalized silver nanoparticles: I) $R=9:S=1$; and J) $R=9:S=3$.

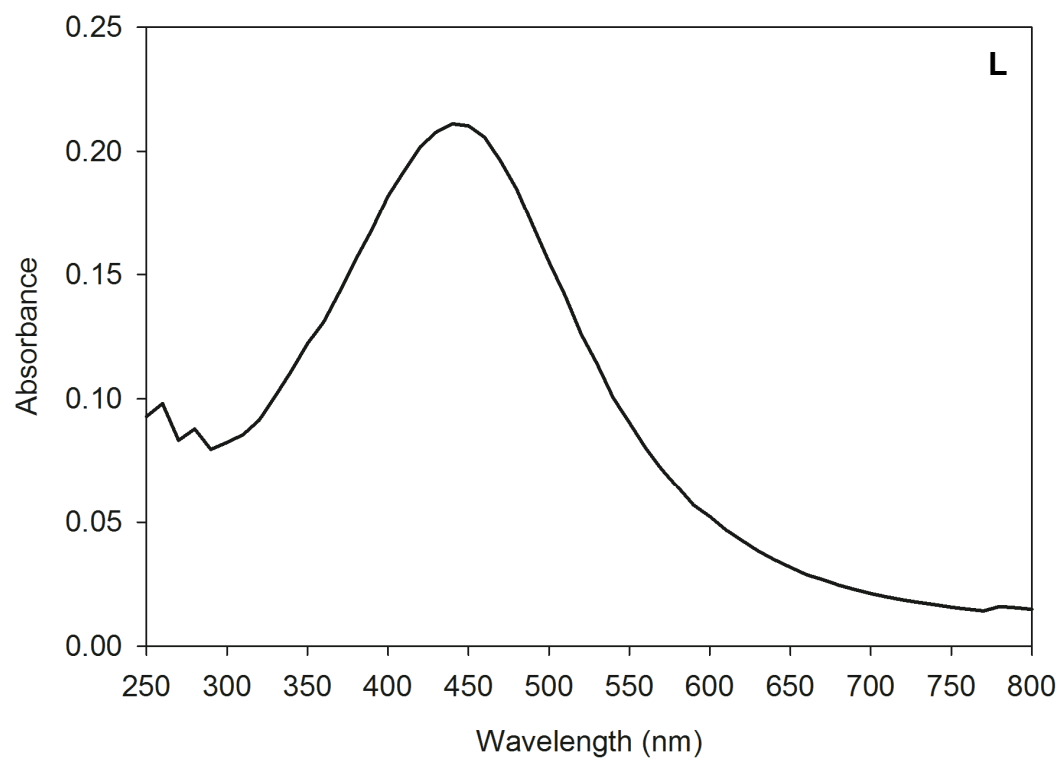
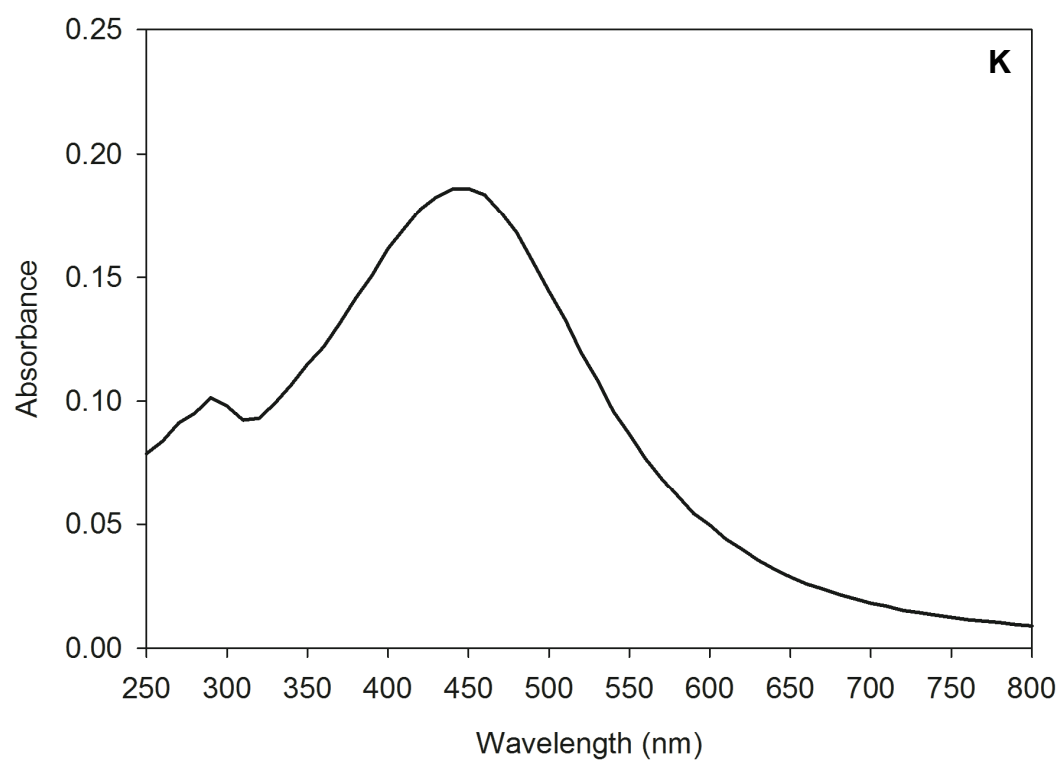


Figure 1F. UV Spectra of the alkanethiol-functionalized silver nanoparticles: K) $R=9:S=6$; and L) $R=9:S=12$.

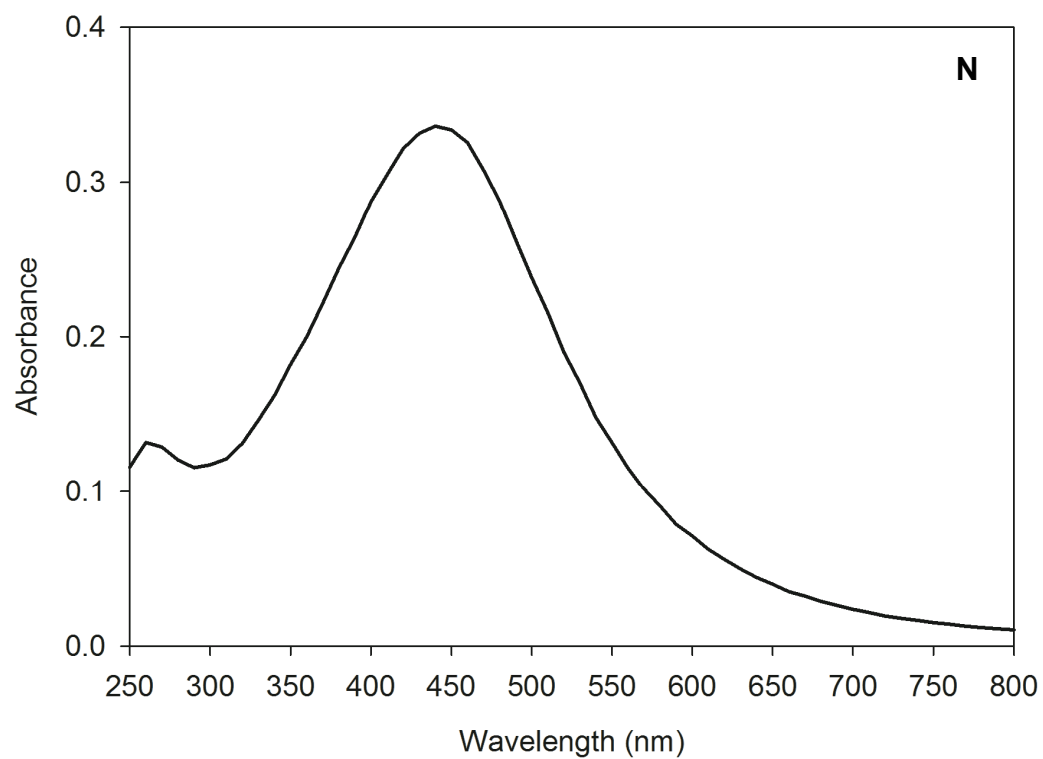
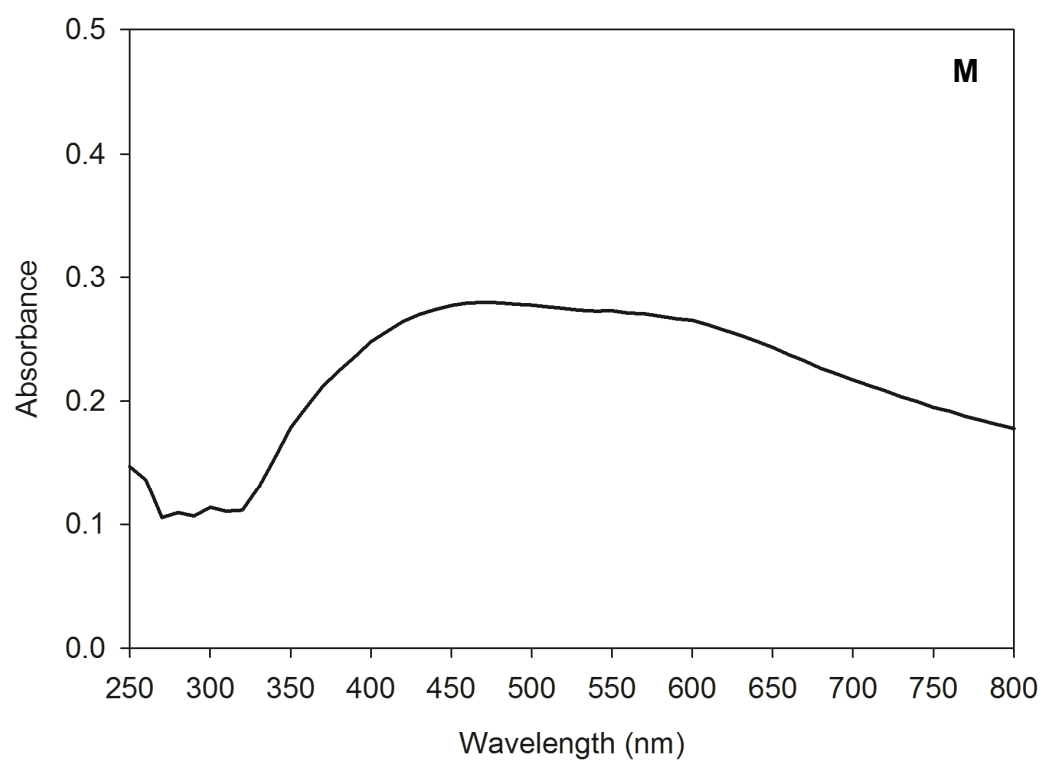


Figure 1G. UV Spectra of the alkanethiol-functionalized silver nanoparticles: M) $R=12:S=1$; and N) $R=12:S=3$.

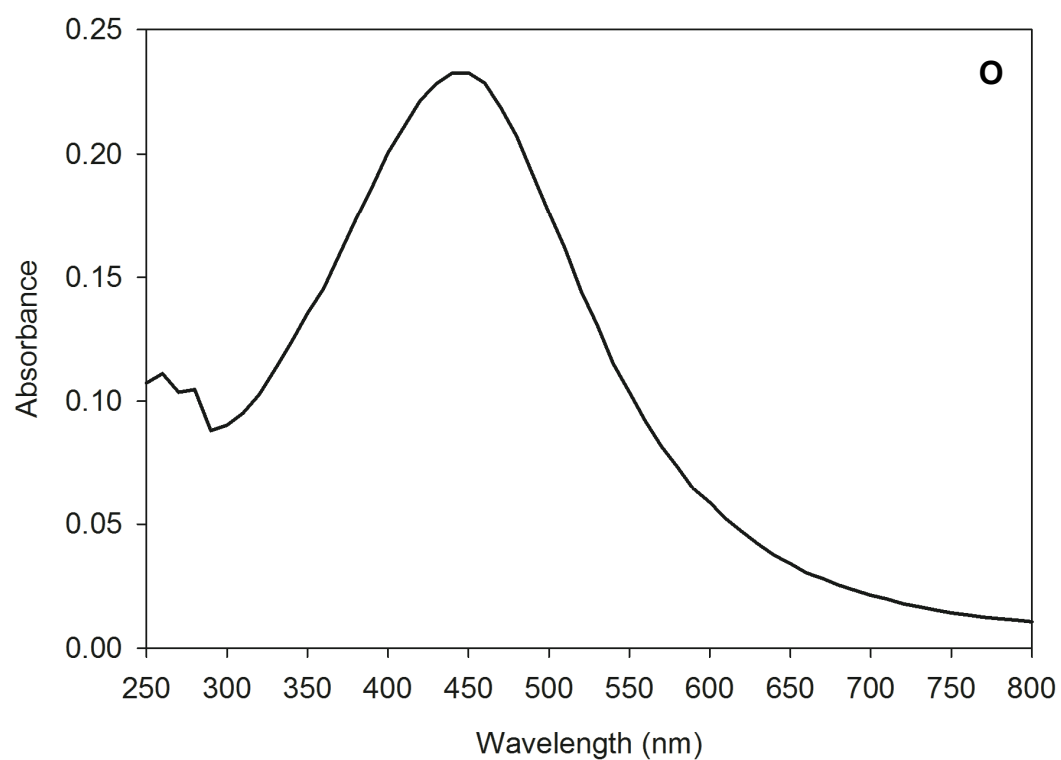


Figure 1E. UV Spectra of the alkanethiol-functionalized silver nanoparticles: O) $R=12:S=12$.

Effect of High Ionic Strength – R=72:S=12 Sample

In addition to the $R=108:S=12$ sample data presented in the manuscript, TEM images and UV-VIS spectra were collected for the $R=72:S=12$ silver nanoparticle sample. From the sample TEM image shown as Fig. 2A below, we observe the formation of small, uniform nanoparticles with an average diameter of 3.8 ± 1.7 nm. Further, the UV-VIS spectrum provided as Fig. 2B supports this conclusion, with the characteristic surface plasmon band for silver appearing at $\lambda_{\text{spr}} \approx 450$ nm.

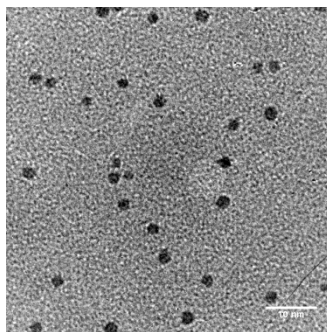


Figure 2A. TEM image of $R=72:S=12$ Ag NPs shows the presence of uniform spherical NPs in toluene with $D=3.8 \pm 1.7$ nm. A UV-VIS spectrum is shown in Fig. 2B which supports this conclusion.

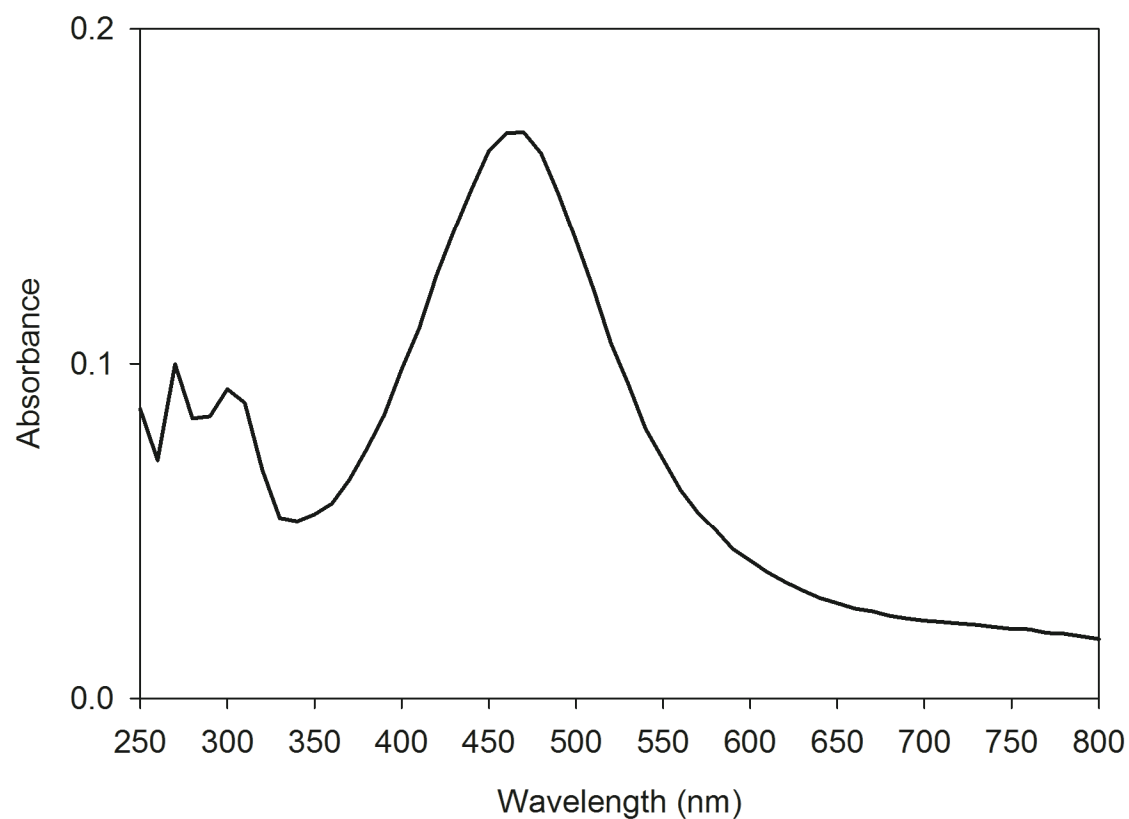


Figure 2B. UV-VIS spectrum of R=72:S=12 Ag NPs displays characteristic peak near 450 nm which is indicative of small silver nanoparticles. The small peak at 300 nm also points to the presence of small amounts of didodecyl disulfide in solution.

Resistance of Didodecyl Disulfide to Reduction by Sodium Borohydride

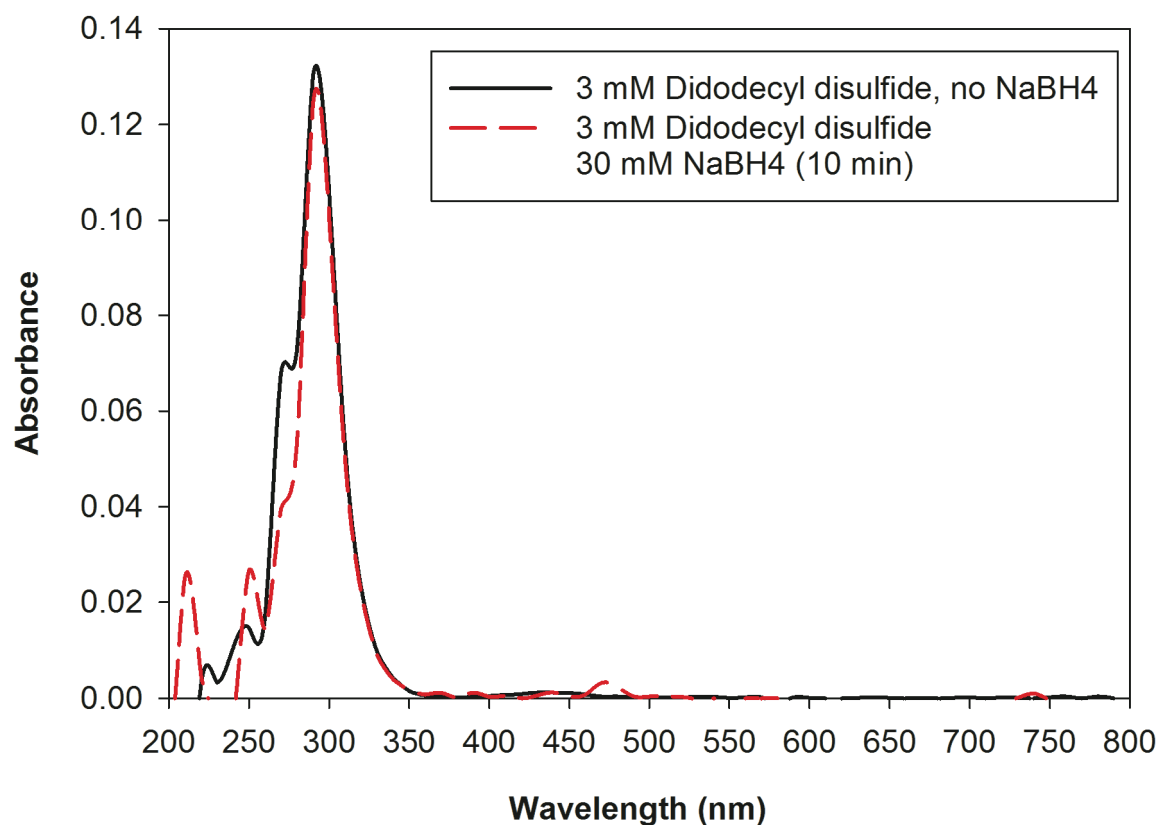


Figure 3A. UV-VIS spectra for 3 mM didodecyl disulfide in ethanol and for an identical 3 mM didodecyl disulfide solution in the presence of a 10-fold molar excess of sodium borohydride after 10 minutes. As the peak height at the maximum near $\lambda \approx 300$ nm is near unchanged, it is reasonable to conclude that didodecyl disulfide is not undergoing significant reduction by sodium borohydride.

Didodecyl Disulfide Capped Silver Nanoparticles

As mentioned in our manuscript, TEM images were taken of the nanoparticles synthesized with didodecyl disulfide present in place of dodecanethiol. The average nanoparticle diameter measured was $3.7 \pm 2.3 \text{ nm}$ which is comparable to the $4.0 \pm 2.0 \text{ nm}$ diameter measured for dodecanethiol functionalized nanoparticles. A representative image of didodecyl disulfide functionalized nanoparticles is reproduced below as Figure 4A.

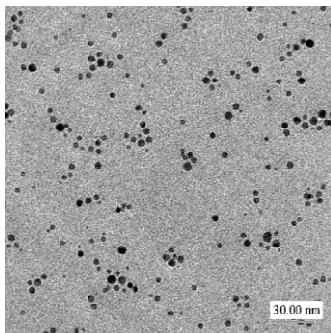


Figure 4A. TEM image of Ag nanoparticles synthesized with didodecyl disulfide as capping agent. The average nanoparticle diameter for this sample is $D = 3.7 \pm 2.3 \text{ nm}$. Thus, neither the average particle size nor the standard deviation change due to the substitution of didodecyl disulfide for 1-dodecanethiol.

Derivation of Generalized Smoluchowski Equation (GSE) and Primary Particle Growth Rate

In the manuscript we present a heuristic derivation of nucleation. In this section of the supplementary documents we give a detailed derivation of the GSE, which we use to derive the rate equation that characterizes early-stage Ag NP growth with respect to singlet-to-doublet formation. This is Eq. 5 in the manuscript, and as stated in the manuscript, our objective is to use this relation to elucidate the reaction conditions that facilitate the end-on adsorption of alkanethiol monolayers on primary particles, mitigating aggregation. Hence, subsequent to nucleation, we use Eq. 5 to capture the growth of primary particles, which on the basis of studies by Zukoski and Polte, growth occurs through controlled aggregation, or the aggregation of primary particles into doublets, triplets, etc., ultimately reaching a stable size based on particle

interactions.^{1,2} The starting point for the analysis of particle aggregation through Eq. 5 in the manuscript is the generalized Smoluchowski diffusion equation (GSE), characterizing the dynamics of a system of N colloidal objects (e.g, sphere, rods, cubes, etc.). We present the following derivation in real-space coordinates to correspond with our use of transmission electron microscopy, a direct visualization method to image the DDT-functionalized Ag NPs.

The starting points for the derivation of GSE are Eqs. A.1, A.2, and A.3. Eq. A.1 is the probability conservation equation for $P(\mathbf{x}_1, \mathbf{x}_2, t)$, or the pair, or two-particle probability distribution function (PDF), which characterizes the stochastic, time-dependent, spatial arrangement of nanoparticles at positions $\mathbf{x}_1$ and $\mathbf{x}_2$ relative to the average position of an assembly of the other $N-2$ spheres. For convenience, we represent $\mathbf{x}_1$ and $\mathbf{x}_2$ as the set of position coordinates, $\mathbf{X}$, and bold text represents vector quantities.

$$\frac{\partial P(\mathbf{X}, t)}{\partial t} + \sum_{i=1}^N \nabla \cdot (\mathbf{v}_i(\mathbf{X}) P(\mathbf{X}, t)) = 0 \quad (\text{A.1})$$

Eq. A.1 is a familiar mass balance equation to quantify the accumulation and flux of particles in and across an arbitrary control volume, where $\mathbf{v}_i$ is velocity of particle i . Eq. A.2 is Newton's equation of motion for particle i , otherwise called the Langevin equation as it accounts for particle diffusion through Brownian motion:

$$\frac{d\mathbf{p}_i}{dt} = \sum_i \mathbf{F}_i = \mathbf{F}_i^p + \mathbf{F}_i^{ex} + \mathbf{F}_i^H + \mathbf{F}_i^B + \mathbf{F}_i^c \quad (\text{A.2})$$

where $\mathbf{p}_i$ is the momentum of particle i which equals $\mathbf{p}_i = m\mathbf{v}_i$ where m is the particle mass. On the left hand side of Eq. A.2 is the summation of the forces acting on the particle where $\mathbf{F}_i^p$ is due to direct interparticle forces, $\mathbf{F}_i^{ex}$ to external forces (e.g., gravity), $\mathbf{F}_i^H$ to the hydrodynamic force by the surrounding fluid, $\mathbf{F}_i^B$ to Brownian motion, which drives particle diffusion, and

F_i^c fluid convection. By definition, the position coordinate, x_i , of the particle relates to the momentum coordinate in Eq. A.3 as:

$$\frac{dx_i}{dt} = \frac{p_i}{m} \quad (\text{A.3})$$

Eqs. A.1-3 provide the basis for addressing a variety of dynamic colloidal processes such as suspension rheology or aerosol transport. Russel, Saville, and Schowalter and Dhont provide a full treatment and application of these relations to colloidal processes.^{3,4}

Knowledge of the reaction conditions permits a number of simplifications to Eq. A.1-3 to model the early stage growth of a dilute suspension of hydrodynamically non-interacting Ag nanoparticles in an unbounded, quiescent solvent without the influence of external fields. Growth in a quiescent solution dictates a lack of fluid convection, or $F_i^c=0$, and that particle movement through Brownian motion occurs at low Reynolds number, i.e., the ratio of inertial to viscous forces, where viscous forces dominate inertial ones. Particle growth from a dilute suspension permits the assumption that particle motions and collisions occur on time scales much greater than the diffusive, or Brownian time scale of $\tau_b \approx 10^{-9}$ s.^{3,4} We anticipate that after nucleation, collisions between primary particles should occur on a time scale of $t > 10^{-3}$ s thus, $t \gg \tau_b$.²⁻⁴ The time scale τ_b corresponds to the translational momentum relaxation time; thus at $t \gg \tau_b$, the particles experience quasi-inertia free motion, reaching a constant velocity, which sets $dp_i/dt=0$ in Eq. A.2.^{3,4} This simplifies further analysis that depends only on position coordinates since velocities can be calculated from Eq. A.3. Moreover, setting $dp_i/dt=0$ yields a force balance between the hydrodynamic, Brownian, and direct particle interaction terms in Eq. A.4 as $F_i^{ex}=0$,

$$F_i^H = -(F_i^p + F_i^B) \quad (\text{A.4})$$

since we assume that particle sedimentation is negligible at the early stages.

Determination of the GSE requires calculation of the particle velocity from the hydrodynamic force, the latter of which depends on a phenomenological treatment of solvent motion where processes on the molecular level are not considered. Thus, only macroscopic properties such as the viscosity and mass density of the solvent enter into the analysis. The large difference in relevant length and time scales of momentum relaxation between the solvent and the ensemble of primary particles facilitates the phenomenological treatment of hydrodynamics in colloidal systems without losing the microstructure of the nanoparticle arrangements.^{4,5} To this end, the hydrodynamic force on particle i by the surrounding fluid is shown in Eq. A.5 and the generalized hydrodynamic Stokes-Einstein relation is given in Eq. A.6; both equations provide the starting point for incorporating hydrodynamics in early stage nanoparticle growth:

$$\mathbf{F}_i^H = -\sum_{j=1}^N \zeta_{ij}(\mathbf{X}) \cdot \mathbf{v}_j \quad (\text{A.5})$$

$$\sum_{j=1}^N \zeta_{ij}(\mathbf{X}) \cdot \mathbf{D}_{ij}(\mathbf{X}) = k_b T \delta_{ij} \mathbf{1} \text{ or } \zeta(\mathbf{X}) \cdot \mathbf{D}(\mathbf{X}) = k_b T \mathbf{1} \quad (\text{A.6})$$

where ζ_{ij} and D_{ij} are the friction and diffusion coefficients for the particle pairs. One adds the minus sign in Eq. A.5 to account for the force exerted by the fluid on the particle. For the case of interacting particles in a concentrated suspension, the friction coefficients form a real, symmetric, positive definite $3N \times 3N$ matrix that depend on particle position, resulting in a non-symmetric matrix of microscopic diffusion coefficients due to the inversion of the friction coefficients in Eq. A.6. For a dilute suspension of hydrodynamically non-interacting primary particles, the friction coefficient and diffusion matrices become diagonal in Eq. A.7 and factor to a scalar value D_o , in Eq. A.8, resulting in linear relationship between $\mathbf{v}_i$ and $\mathbf{F}_i^H$:

$$\mathbf{D}_{ij}(\mathbf{X}) = D_o \delta_{ij} \mathbf{1} \quad (7)$$

$$\mathbf{v}_i(\mathbf{X}) = -\sum_{j=1}^N \beta \mathbf{D}_{ij}(\mathbf{X}) \cdot \mathbf{F}_j^H = -\beta D_o \mathbf{F}_i^H = -\zeta^{-1} \mathbf{F}_i^H = -\mathbf{F}_i^H / 6\pi\eta_o R \quad (8)$$

where $\beta = (k_b T)^{-1}$ and ζ is the well known Stokes-Einstein friction factor for spheres equal to $6\pi\eta_o R$ where η_o is the solvent viscosity and R the particle radius.

Substituting Eqs. A.4 and A.7 into Eq. A.1 yield the GSE for the primary particles in Eq. A.9:

$$\frac{\partial P(\mathbf{X}, t)}{\partial t} + \beta D_o \sum_{i=1}^N \nabla_i \cdot [(\mathbf{F}_i^p + \mathbf{F}_i^B) P(\mathbf{X}, t)] = 0 \quad (A.9)$$

which can be further clarified by considering the direct interparticle and Brownian forces, or $\mathbf{F}_i^p$ and $\mathbf{F}_i^B$, respectively. Calculation of direct interparticle forces stems from the gradient of the total potential energy $\Phi_T(\mathbf{X})$ of the ensemble of primary particles which is a function of the position coordinates in Eq. A.10.

$$\mathbf{F}_i^p = -\nabla \Phi_T(\mathbf{X}) = -\sum_{j=1}^N \nabla_i \Phi_T(x_{ij}) \quad (A.10)$$

The basis for the Brownian force stems from the establishment of equilibrium at long times where the PDF is proportional to the exponential of the Boltzmann distribution:⁶

$$\lim_{t \rightarrow \infty} P(\mathbf{X}, t) \sim \exp(-\beta \Phi_T(\mathbf{X})) \quad (A.11)$$

and the terms in within the round brackets in Eq. A.9 becomes zero for the particular form of the PDF in Eq. A.11. From this requirement, one finds the form of the Brownian force in Eq. A.12.

$$\mathbf{F}_i^B = -k_B T \nabla_i \ln P(\mathbf{X}, t) \quad (A.12)$$

Substitution of Eqs. A.10 and A.12 into A.Eq. 9 yield the GSE in Eq. A.13 for the primary particles,

$$\frac{\partial P(\mathbf{X}, t)}{\partial t} = D_o \sum_{i=1}^N \nabla_i \cdot [(\nabla_i + \beta \nabla \Phi_T(\mathbf{X}))] P(\mathbf{X}, t) \quad (\text{A.13})$$

The GSE forms the basis of our analysis of the reaction conditions that control the early stage growth of the DDT-functionalized Ag nanoparticles. To quantify singlet-to-doublet formation, one derives the conservation equation for the primary particle concentration, C_1 , by multiplying Eq. A.1 by $1/(N-1)$ integrating over the position of $N-1$ spheres. The derivation requires the tracking of doublet formation upon primary particle overlap, corresponding to $P(\mathbf{X}, t)=0$ for the interparticle distance $r_{ij}=|\mathbf{x}_1-\mathbf{x}_2|<2R$ for $i \neq j$. The analysis of the integrals over the remaining volume is found in Russel, Saville, and Schowalter who use the transport and divergence theorems to determine the rate of change of C_1 ,

$$\frac{dC_1(t)}{dt} = - \int_{r=2R} P(\mathbf{X}, t) \cdot \mathbf{n} d\mathbf{r} \quad (\text{A.14})$$

where $C_1 = C_{1,0}$ at $t=0$.³ Hence, the disappearance rate of primary particles depends on $P(\mathbf{X}, t)$, which can be determined assuming pseudo-steady state and spherically-symmetric direct pair interactions, $\Phi(r)$, reducing Eq. A.13 to,

$$\frac{D_o}{r^2} \frac{d}{dr} r^2 \left(P \frac{d(\beta \Phi_T)}{dr} + \frac{dP}{dr} \right) = 0 \quad (\text{A.15})$$

subject to the following boundary conditions:

$$P(r) = \begin{cases} C_1^2 & r \rightarrow \infty \\ 0 & r = 2R \end{cases} \quad (\text{BC 1})$$

The former assumes a random, spatially homogenous particle arrangement, or microstructure, and the latter doublet formation. Integration and application of the boundary conditions yields:³⁰

$$P(r) = C_1^2 \frac{\exp(-\beta\Phi_T) \int_{2R}^r \exp(\beta\Phi_T) r^{-2} dr}{\int_{2R}^{\infty} \exp(\beta\Phi_T) r^{-2} dr} \quad (\text{A.16})$$

The primary particle disappearance rate follows from Eq. A.14 as,

$$\frac{dC_1(t)}{dt} = -\frac{4k_B T}{3\eta_o R} \frac{C_1^2}{\int_{2R}^{\infty} \exp(\beta\Phi_T) r^{-2} dr} = -k_s C_1^2 \quad (\text{A.17})$$

where k_s is the binary aggregation rate constant. Eq. A.17 in this section is Eq. 5 in the main text.

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