

Optical interactions of silver nanoparticle decorated cellulose nanocrystals created from a one-pot reduction method

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Modified cellulose nanocrystals were decorated with silver nanoparticles using a one-pot reduction method. In contrast to a quasi-uniform distribution of silver nanoparticles, we report on the interactions of non-contact nanoparticle clusters with significant line broadening and red shifts in the extinction spectra. The particle size and cluster distributions were examined using a transmission electron microscope. Monte Carlo random walk (MCRW) simulations of the extinction spectrum show that the interacting silver nanospheres are organized in small, non-contact clusters. We observed that the MCRW optimization using the first-order iterative approximation to the self-consistent dipole field equations quickly approaches the observed localized clusters. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4977872>]

I. INTRODUCTION

Interest in nanoscience has erupted over the last decade with new fabrication techniques and interdisciplinary advances. Several applications of metal nanoparticles have been discovered and improved upon including catalysis,¹ drug delivery,² biomedical imaging,³ and light manipulating devices.^{4,5} The electron density of a noble metal can couple to electromagnetic waves resulting in plasma oscillations. Metal nanoparticles are confined to a small volume, where the geometry and plasmonic response of the material affect light-particle interactions.

Metal atom clusters form nanoparticles, and some work has been performed on nanoparticle arrays and randomly distributed nanoparticle clusters.⁶ Nanoparticles in close proximity interact via radiative energy transfer;^{7–9} however, the high concentrations required for near-field interactions cause the particles to aggregate.¹⁰ Some methods have been developed to fix the particle locations so that they are in close proximity to each other. Nanoimprint¹¹ and electron-beam lithography^{12–15} have been used to fabricate one- and two-dimensional arrays of large nanoparticles on a rigid surface. Three-dimensional arrays of large nanoparticles have also been achieved by sol-gel imprint lithography.¹⁶ Nanoparticles can also be attached to organic scaffolds to create periodic, two-¹⁷ and three-dimensional structures.^{18,19}

Metallic nanoparticles tend to form large particles as a result of Ostwald ripening.²⁰ Polymeric surfactants such as polyvinyl alcohol and polyvinylpyrrolidone have been used to prevent nanoparticle aggregation.²¹ A wide variety of polymers and monomers including poly[(2-ethyl dimethylammonioethyl methacrylate ethyl sulfate)-co-(1-vinylpyrrolidone)],²² polypyrrole,²³ poly(propyleneimine) dendrimers,²⁴ and *p*-phenylenediamine²⁵ have been used to produce silver nanoparticles without the use of an external reducing agent. Cellulose nanocrystals (CNCs) have been used as the

templating agent to replace polymeric surfactants and produce organic-inorganic nanohybrid materials with silver, usually in the presence of external reducing agents such as sodium borohydride²⁶ or dopamine.²⁷ Yu *et al.* showed that CNCs with appendant formate groups can act as reducing agents for Ag(I), while simultaneously acting as a surfactant for nanosilver.²⁸ The aforementioned methods did not show an interaction between Ag nanoparticles and CNCs. In other words, a direct evidence of interaction was not observed.

Despite the progress in producing advanced organic-inorganic nanohybrid materials, these methods suffer from the use of a two-pot method. We report here on the optical interactions of silver nanoparticles grown on modified CNCs using a one-pot reduction method. This organic-inorganic hybrid material was manufactured using a citrate modified CNC bio-templating agent,²⁹ which provides an economical and simple approach to prepare highly functionalized nanohybrid materials. Pendant citrate groups were used both as reducing agents for silver (I) and dispersing groups, without the use of external reducing agents or surfactants.

CNCs provide an easily functionalizable bio-based template on which to form metal nanoparticles with a quasi-random spatial distribution over the modified attachment sites on the crystal surface. The proximity of nanoparticles fixed to the surface of the crystals provides for many-body electromagnetic interactions when in the presence of an exciting field. The decorated crystals could be used as components for enhancing absorption and emission, where we show that the distribution of particles provides for strong scattering over a broad frequency range. The presence of metal particles and the inhomogeneous nature of the spatial distribution result in plasmonic structures with site specific, local field enhancements. These structures may lead to environmentally friendly additives to enhance the performance of solar cells or broad light-emitting sources.

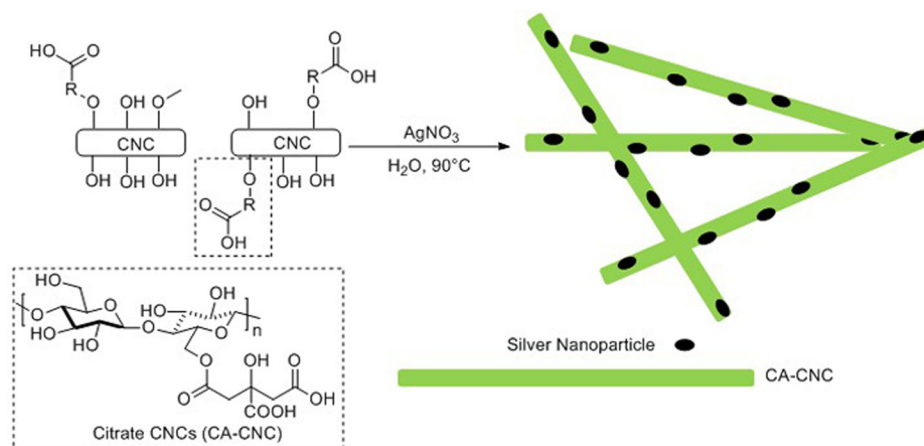


FIG. 1. One pot bio-templation of silver nanoparticles onto a citrate CNC scaffold.

In the present work, we report on the optical interactions of nanoparticle-on-nanoparticle structures, where a CNC scaffold has been used to attach silver nanoparticles. Aggregates of CNCs provide scaffolds for complicated three-dimensional plasmonic materials that are unlike traditional nanoparticle clusters. We present an experimental evidence of small, non-contact, silver nanoparticle clusters attached to aggregated CNC scaffolds, which have strong short-range interactions. These clusters have a red-shifted and significantly broadened extinction spectrum in contrast to a uniform spatial distribution of similar density. The presence of discrete silver nanoparticles on the surface of CNCs was confirmed by transmission electron microscopy (TEM), and successful reduction was confirmed by wide angle X-ray powder diffraction (WAXS) and thermogravimetric analysis (TGA). The optical extinction spectra were recorded for the nanohybrid materials. We model the effects of dipole field interactions between nanospheres, where Monte Carlo random walk (MCRW) optimizations result in spatial distributions which correlate with the observed extinction spectrum.

II. MATERIALS AND CHARACTERIZATION

Citrate modified CNCs were used both as a reducing agent and nanoparticle stabilizer for silver nanoparticles through a bio-templation approach as shown below in Fig. 1. The CNCs were dispersed in basic water (pH = 9.1), and silver nitrate was introduced at 90 °C. The color turned bright yellow immediately, indicating the presence of silver nanoparticles. Following the addition of silver nitrate, the reaction proceeded for 30 minutes and allowed to cool to room temperature. Free (i.e., non-attached) silver nanoparticles were removed by centrifugation, and the resulting dark black powder was purified by centrifugation.

The presence of crystalline silver nanoparticles and the amount of silver nanoparticles attached to CNC surfaces was provided by XRD and TGA respectively. The XRD diffractogram in Fig. 2(a) shows the presence of typical CNC crystalline peaks at 22°³⁰ corresponding to the (002) face and silver nanoparticles related to the (111) diffraction of face-center cubic silver nanoparticles at 38°^{31,32}. These results confirm the presence of both discrete silver nanoparticles and CNCs, thus producing a nanoparticle-on-nanoparticle hybrid material. The amount of silver nanoparticles was

calculated using TGA, and the results are shown in Fig. 2(b). The calculated T50 values, or the temperature when 50% of the material degrades, for citrate-CNCs and Ag-CNCs were respectively 345 °C and 368 °C. Control of the size of nanoparticles may be possible by controlling the CNC degree of substitution; however, we cannot yet report on this procedure. The control of silver in the final composite was done by adjusting the molar ratio between cellulose and silver.

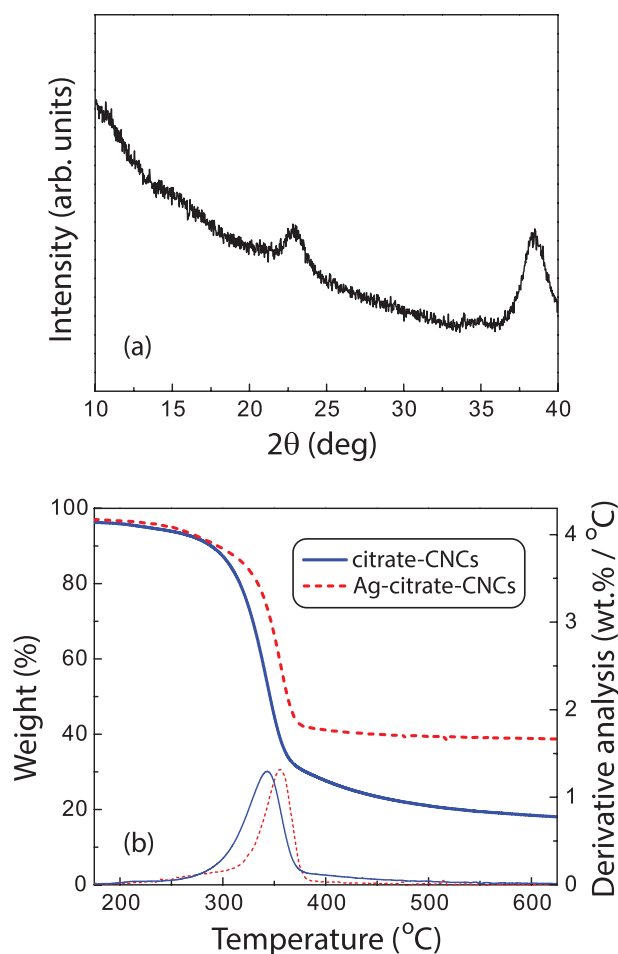


FIG. 2. (a) Wide angle X-Ray spectroscopy (WAXS) of citrate CNC/Ag nanoparticle nanohybrid materials. (b) The thermogravimetric analysis under N₂ (g) with a heating rate of 20 °C/min (thick lines) and the derivative curves (thin lines).

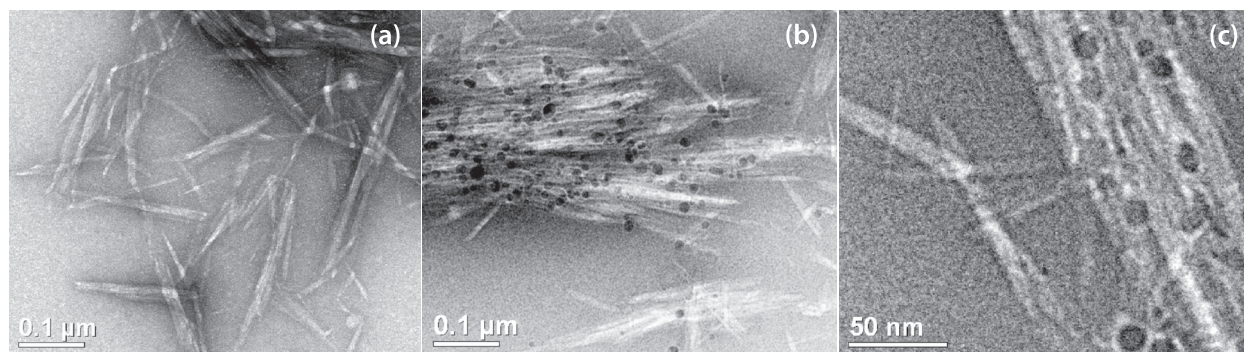


FIG. 3. (a) TEM image of neat CNCs. (b) TEM image of Ag-CNCs showing a nonuniform distribution of silver nanospheres. (c) Higher magnification TEM image of Ag-CNCs.

It was previously shown that heating citrate CNCs results in 20% char due to cross-linking occurring at high temperatures.²⁹ The amount of silver was calculated by subtracting the weight percentage of the citrate-CNCs from the weight percentage of the Ag-citrate-CNCs (Ag-CNCs) at 550 °C, assuming that the residual mass difference is due to the presence of silver nanoparticles. Thus, the amount of silver present on the surface of the citrate-CNCs is 20%. By using a unique biotemplating strategy, we have shown that silver nanoparticles can be reduced and dispersed without aggregation.

A Zeiss Libra 200EF transmission electron microscope (TEM) was used to take bright field images of the Ag-CNCs. We used a 400 mesh, copper grids with carbon (3–4 nm) and formvar (25–50 nm) coatings purchased from Electron Microscopy Sciences. We cleaned the TEM grids by placing them in a Novascan PSDP-UV8T UV-ozone system for 30 minutes at room temperature.

A suspension of Ag-CNCs was prepared at a concentration of 0.4 mg/ml in deionized (DI) water. The Ag-CNC aqueous suspension was sonicated in a bath at room temperature for two hours. Aggregates were allowed to form a precipitate at the bottom of a vial over several hours. A drop of the aqueous suspension of Ag-CNCs was placed on Parafilm[®] followed by two separate drops of uranyl acetate/DI water solution (2 wt. %). The grids were floated on the first drop with suspended Ag-CNCs for 60 s. The grid was removed, and the solution was wicked away by placing filter paper at the edge of the grid. The drying step was immediately followed by a washing step, where we floated the grid on the first drop of uranyl acetate solution for 5 s. The residual solution from the wash was removed with the filter paper. We stained the grid by floating it on the second drop of the uranyl acetate solution for 60 s again dried with filter paper.

The prepared grids were placed in the TEM, and images were taken with a CCD camera. A TEM image of neat CNCs is shown in Fig. 3(a) next to a typical TEM image of Ag-CNCs shown in Fig. 3(b). A higher magnification TEM image of Ag-CNCs is shown in Fig. 3(c). No aggregation was observed in the samples, indicating that citrate CNCs act as reducing agents and nanoparticle dispersants. The silver nanospheres are unevenly distributed on the formvar substrate due to the presence of the CNC scaffolds. Energy-dispersive X-ray spectroscopy was also performed while taking images using scanning transmission electron microscopy

(STEM) mode with the high-angle annular dark-field (HAADF) detector to confirm the composition of these nanoparticle-on-nanoparticle structures.³³

The Ag nanoparticles are approximately spherical in shape. The size distribution of nanoparticles follows a log-normal distribution

$$P_r(D) = \exp[-(\log D - \mu)^2 / (2\sigma^2)] / (\sqrt{2\pi}\sigma D). \quad (1)$$

The diameter of the nanoparticles was taken from TEM images for Ag-CNCs synthesized at a pH of 9.3, and the size distribution is shown in Fig. 4. The black curve in Fig. 4 is the log-normal distribution with fit parameters of $\mu = 2.461$ and $\sigma = 0.236$. A trust-region method was used to fit the two-parameter log-normal distribution, where the median of the boxes' horizontal components was used for the size estimates of the silver nanosphere simulations.

Optical extinction spectra were taken with a Cary UV-VIS spectrophotometer. Ag-CNC and CNC suspensions were created using the method described above at a concentration of 0.4 mg/ml in DI water. Extinction spectra were taken for CNCs, Ag-CNCs, and 10 nm, citrate capped, Ag nanospheres purchased from nanoComposix.

III. MODEL

Scattering and absorption of light by a nanoparticle is well-described by the Mie theory³⁴ when the particle's

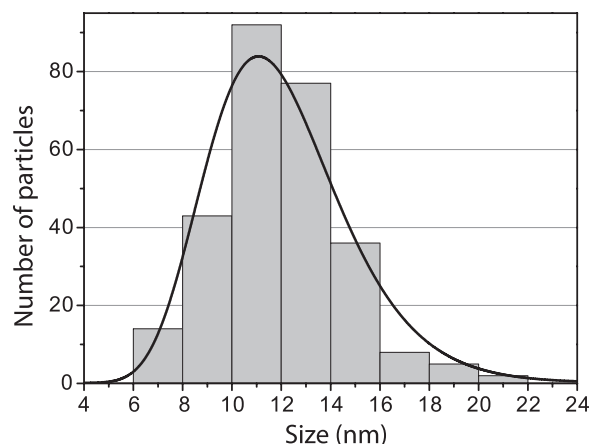


FIG. 4. The size distribution of silver nanospheres grown at a pH of 9.3 on CNC scaffolds.

diameter is greater than a few nanometers.³⁵ The extinction spectrum of a nanosphere with a diameter of >5 nm is given by

$$\sigma = \frac{2\pi}{k^2} \sum_j (2j+1) \text{Re}(A_j + B_j), \quad (2)$$

where j is an integer, and k is the wavenumber. The coefficients are given by

$$A_j = \frac{n_p S_j \left(\frac{n_p}{n_m} kR \right) S'_j(kR) - n_m S'_j \left(\frac{n_p}{n_m} kR \right) S_j(kR)}{n_p S_j \left(\frac{n_p}{n_m} kR \right) \zeta'_j(kR) - n_m S'_j \left(\frac{n_p}{n_m} kR \right) \zeta_j(kR)} \quad (3)$$

and

$$B_j = \frac{n_m S_j \left(\frac{n_p}{n_m} kR \right) S'_j(kR) - n_p S'_j \left(\frac{n_p}{n_m} kR \right) S_j(kR)}{n_m S_j \left(\frac{n_p}{n_m} kR \right) \zeta'_j(kR) - n_p S'_j \left(\frac{n_p}{n_m} kR \right) \zeta_j(kR)}, \quad (4)$$

where R is the radius of a nanosphere, n_p is the refractive index of the particle, and n_m is the refractive index of the medium.

The Riccati-Bessel functions in Eqs. (3) and (4), for an arbitrary argument x , are given by

$$S_j(x) = \sqrt{\frac{\pi x}{2}} J_{j+\frac{1}{2}}(x) \quad (5)$$

and

$$\zeta_j(x) = \sqrt{\frac{\pi x}{2}} H_{j+\frac{1}{2}}^{(1)}(x), \quad (6)$$

where J is the Bessel function of the first kind, and $H^{(1)}$ is the Hankel function of the first kind.

The optical constants of a noble metal may be approximated by the Lorentz-Drude model³⁷ over a broad energy band. For silver nanospheres, we first fit the Lorentz-Drude

model with five poles (LD5) to the optical constants as a function of frequency for bulk silver. The relative permittivity from the LD5 model is given by

$$\epsilon_r^{\text{LD5}} = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma_D \omega} + \sum_{n=1}^5 \frac{f_n \omega_p^2}{\omega_n^2 - \omega^2 - i\Gamma_n \omega}, \quad (7)$$

with $i = \sqrt{-1}$. We used an unconstrained trust-region method³⁸ to fit the Lorentz parameters given in Fig. 5. The parameters used in the Drude model for bulk silver were obtained from the Fermi velocity $v_F = 1.38 \times 10^6$ m/s, the mean free path of an electron $\ell = 4.38 \times 10^{-8}$ m, the effective mass $m = 8.75 \times 10^{-31}$ kg, and the electron number density $\rho = 5.86 \times 10^{28}$ m⁻³. The fitting results of the (a) real and (b) imaginary components of the refractive index of silver are shown in Fig. 5.

Using the LD5 fit parameters and Eq. (2), the resulting peak extinction for a 10 nm silver sphere is at 391 nm. The peak extinction of the 10 nm, nanoComposix nanospheres was observed to be approximately 392 nm, which is close to the value predicted using the LD5 parameters.

The field from the surrounding particles affects the magnitude and frequency of the optical response when there are multiple nanospheres in close proximity. The equation of motion for a single transition resonance, ω_n , of the i th nanosphere in a system of interacting nanospheres is given by

$$\begin{aligned} \frac{N_i e^2}{m} f_n E_{\alpha,i}(\omega) = & -\omega^2 p_{\alpha,i}(\omega) - i\Gamma_n \omega p_{\alpha,i}(\omega) \\ & + \omega_n^2 p_{\alpha,i}(\omega) - \sum_{j \neq i} \Omega_{ij}^2 \\ & \times \left[(1 - ikr_{ij}) g_{\alpha\beta,ij} - k^2 r_{ij}^2 h_{\alpha\beta,ij} \right] \\ & \times \mathcal{P}_{\beta,ij} p_{\beta,i}(\omega), \end{aligned} \quad (8)$$

where $E_{\alpha,i}$ is the electric field in the α direction felt by the nanospheres when excluding the fields from the other nanospheres. Here, N_i is the number of charges displaced in the i th nanosphere, e is the magnitude of an electron's charge, m is the effective mass of an electron, f_n is the dimensionless

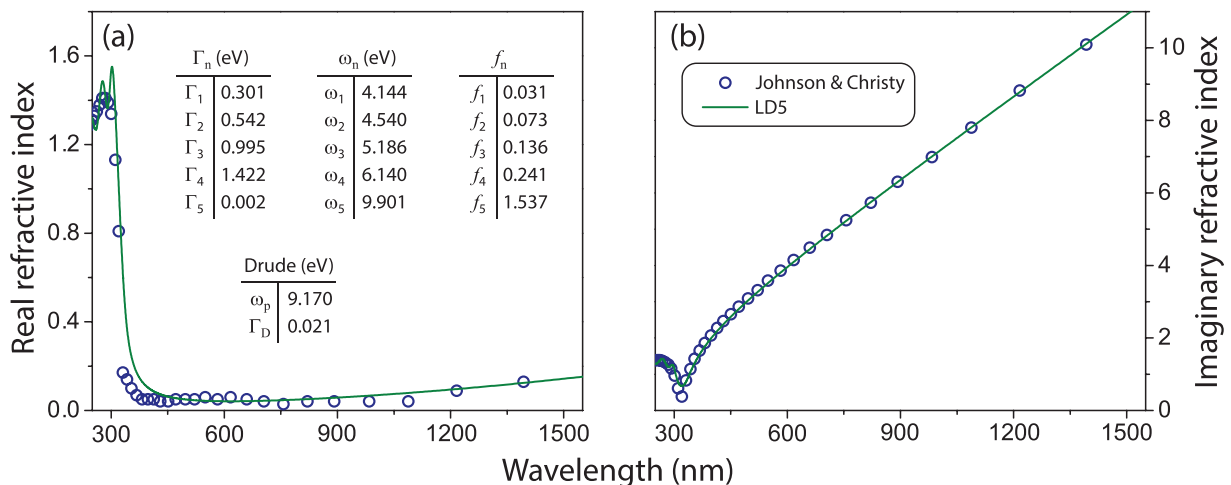


FIG. 5. The (a) real and (b) imaginary components of the refractive index of silver. The circles are experimental values given by Johnson and Christy,³⁶ and the lines are the LD5 model fits. The fitted parameters to the Lorentz terms are given in (a) along with the estimated values of the Drude parameters.

parameter for n th resonant state's strength of interaction with the field, $p_{\alpha,i}$ is the dipole moment of the i th particle along the α direction, ω is the angular frequency of the field, Γ_n is the damping parameter for the n th transition, and $r_{ij} = |\vec{r}_i - \vec{r}_j|$ is the separation distance between the center-of-masses of the i th and j th nanoparticles.

The last term in Eq. (8) describes the field interaction between nanoparticles, where the field from the j th particle measured at the i th particle is given by

$$E_{\alpha,ij} = \frac{\exp(i\mathbf{k}r_{ij})}{4\pi\epsilon_m\epsilon_0 r_{ij}^3} \left[(1 - i\mathbf{k}r_{ij})g_{\alpha\beta,ij} - k^2 r_{ij}^2 h_{\alpha\beta,ij} \right] p_{\beta,j}. \quad (9)$$

The tensors in Eq. (8) are given by

$$g_{\alpha\beta,ij} = 3[(\hat{r}_i - \hat{r}_j) \cdot \hat{\alpha}][(\hat{r}_i - \hat{r}_j) \cdot \hat{\beta}] - \delta_{\alpha\beta} \quad (10)$$

and

$$h_{\alpha\beta,ij} = [(\hat{r}_i - \hat{r}_j) \cdot \hat{\alpha}][(\hat{r}_i - \hat{r}_j) \cdot \hat{\beta}] - \delta_{\alpha\beta}. \quad (11)$$

In addition to the dimensionless tensors, $g_{\alpha\beta,ij}$ and $h_{\alpha\beta,ij}$, the magnitude of the shift in the resonant frequencies in the i th nanoparticle caused by the j th nanoparticle in Eq. (8) also depends on

$$\Omega_{ij} = \exp\left(\frac{i}{2}kr_{ij}\right) \sqrt{\frac{N_i e^2}{4\pi m \epsilon_m \epsilon_0 r_{ij}^3}} \quad (12)$$

multiplied by the factor $\mathcal{P}_{\alpha,ij}$.

The factor $\mathcal{P}_{\alpha,ij} = p_{\alpha,j}/p_{\alpha,i}$ in the last term of Eq. (8) allows for an iterative approximation to the dipole moment of the i th nanoparticle via a self-consistent solution.³⁹ In most cases, the first-order iterative approximation to the self-consistent dipole equation is sufficient, and we will use this approximation for the remainder of the paper. Because the particles have a near spherical symmetry, the only contribution to the off-diagonal elements of the susceptibility tensor is due to the interactions between nanospheres. Typically, these off-diagonal elements make small contributions to the dipole moment,³⁹ where the contributions from small dipole moments orthogonal to the orientation of the incident light's polarization induced by neighboring nanospheres are negligible.

To first order, it is only necessary to know $\mathcal{P}_{\alpha,ij}$ to zeroth-order, where the nanospheres are assumed to be non-interacting. With these assumptions, $\mathcal{P}_{\alpha,ij} \approx \kappa_j E_{\alpha,j}/\kappa_i E_{\alpha,i}$. Here, κ denotes the polarizability of a non-interacting nanosphere along the direction of the plane wave's polarization. For a zeroth-order approximation to $\mathcal{P}$, the magnitude of the electric field is equal at all locations for a continuous exciting plane wave in the medium, and therefore, $\mathcal{P}_{\alpha,ij} \approx \kappa_j/\kappa_i = R_j^3/R_i^3$. Assuming that the nanospheres have a uniform density, this ratio may be rewritten as

$$\mathcal{P}_{\alpha,ij} \approx \frac{N_j}{N_i}. \quad (13)$$

The n th bound state contribution to the first-order corrected, undressed microscopic susceptibility follows from Eq. (8).

Prior to correcting the magnitude of the response self-consistently, the contribution to the undressed microscopic susceptibility follows as

$$\chi_{b,i}^{\text{un}}(\omega; \omega_n) = \frac{N_i e^2}{m V_i} \frac{f_n}{\omega_n^2 - \omega^2 - i\Gamma_n \omega - \Upsilon_{\alpha\alpha,i}}, \quad (14)$$

where V_i is the volume of the i th nanosphere and

$$\Upsilon_{\alpha\beta,i} = \sum_{j \neq i} \Omega_{ij}^2 \left[g_{\alpha\beta,ij}(1 - i\mathbf{k}r_{ij}) - k^2 r_{ij}^2 h_{\alpha\beta,ij} \right] \mathcal{P}_{\beta,ij}. \quad (15)$$

The Drude model gives the free electron contribution to the microscopic susceptibility. The equation of motion is similar to that of the bound state contribution except that the free electrons have no resonant bound state. The free electron contribution to the undressed microscopic susceptibility to first-order approximation is

$$\chi_{f,i}^{\text{un}}(\omega) = -\frac{N_i e^2}{m V_i} \frac{1}{\omega^2 + i\Gamma_{D,i} \omega + \Upsilon_{\alpha\alpha,i}}, \quad (16)$$

where

$$\Gamma_{D,i} = \Gamma_0 + \frac{v_F}{R_i} \quad (17)$$

with $\Gamma_0 = v_F/\ell$. The total undressed microscopic susceptibility from the free and bound state contributions follows as:

$$\chi_i^{\text{un}} = \chi_{f,i}^{\text{un}}(\omega) + \sum_n \chi_{b,i}^{\text{un}}(\omega; \omega_n), \quad (18)$$

which is proportional to the plasma frequency squared

$$\omega_p^2 = \frac{\rho e^2}{\epsilon_0 m}. \quad (19)$$

The dressed microscopic susceptibility due to the electric field contributions of the surrounding nanospheres may be determined self-consistently from the polarization density of the i th nanosphere. This method is also iterative and similar to the self-consistent solution for the Hertzian dipole moment equation. To first-order iterative correction

$$\chi_i = \frac{\chi_i^{\text{un}}}{1 - v_{\alpha\alpha,i} \chi_i^{\text{un}}}, \quad (20)$$

with

$$v_{\alpha\beta,i} = \frac{1}{3} \sum_{j \neq i} \frac{R_j^3}{r_{ij}^3} \exp(i\mathbf{k}r_{ij}) \times \left[g_{\alpha\beta,ij}(1 - i\mathbf{k}r_{ij}) - k^2 r_{ij}^2 h_{\alpha\beta,ij} \right] \quad (21)$$

after the iterative approximation to first-order where we introduced $\mathcal{P}_{\alpha,ij} \approx R_j^3/R_i^3$ in Eq. (21).

The effective relative permittivity of the i th nanosphere in a system of interacting nanospheres may be expressed as

$$\epsilon_{r,i} = 1 + \chi_i. \quad (22)$$

The i th nanosphere's contribution to the extinction coefficient in the medium is found by substituting Eq. (22) into

Eqs. (3) and (4), and calculating the extinction coefficient given by Eq. (2). Note that higher-order approximations to the many-body interacting dipole approximation can be obtained by following the method given in Ref. 39; however, that work only describes the method at zero-frequency limit. For higher-order approximations to the interactions near resonance, both the local field correction and the corrections to the Hertzian dipole motion must be updated.

The extinction spectra shown in Fig. 6 correspond to three, 10 nm, spherical Ag nanoparticles distributed along a straight line in an aqueous solution and excited by the linearly polarized light. The upper graphs 6(a)–6(c) correspond to nanoparticles with an edge-to-edge separation of 10 nm. The lower graphs 6(d)–6(f) correspond to nanoparticles with an edge-to-edge separation of 5 nm. Figures 6(a) and 6(d) show the calculated extinction spectra for nanoparticles in a line oriented perpendicular to the polarization, Figs. 6(b) and 6(e) show the calculated extinction spectra for the line of nanoparticles oriented parallel to the polarization, and Figs. 6(c) and 6(f) show the calculated extinction spectra for the line of nanoparticles orientationally averaged over the three Euler angles. The thin black line represents the non-interacting approximation, the thick gray line represents the first-order approximation of the self-consistent equation for interacting nanoparticles, and the black dashed line represents the second-order iterative approximation to the self-consistent equation for interacting nanoparticles. The first-order correction provides a good qualitative description of the extinction spectrum for an isotropic medium as shown in Figs. 6(c) and 6(f); however, higher-order iterative approximations to the self-consistent dipole equation are necessary for closely spaced particles with fixed orientations relative to a linear polarization as shown in Fig. 6(b). Also, for extremely fine-tuned calculations or calculations

involving nonspherical symmetry, additional multipole moments and nonlinear optical coefficients may also be necessary for a more accurate description of some systems.

IV. DISCUSSION

The plasmonic resonant frequency of a system of two coupled metal nanospheres can be blue or red shifted. The direction of the frequency shift depends on the direction of the dipole field of a nanosphere at the adjacent nanosphere with respect to the direction of the exciting field. Thus, the separation distance and orientation of the displacement vector both contribute to the direction of the resonant frequency shift. The amount that a nanosphere's resonance is shifted depends on the separation distance, the relative position with respect to the exciting field's polarization, and the relative size of the adjacent nanosphere. The local field from other nanoparticles affects the magnitude of the response, where blue shifts are suppressed and red shifts are enhanced.

We observed a red shifted and broadened extinction spectrum when Ag-CNCs were suspended in an aqueous solution with a path length of 1 mm along the propagation direction. The Ag-CNC suspension is isotropic with no long-range order, where the extinction spectra for samples probed with unpolarized and linear polarized light were indistinguishable. The CNCs form clusters with smaller embedded clusters of nanoparticles as observed in the TEM images. These smaller anisotropic clusters cause the extinction spectrum to shift and broaden significantly.

To simulate the observed extinction of light due to the presence of Ag-CNCs suspended in an aqueous solution, we first generated a uniform distribution of particles on a three dimensional grid. Initially, the grid contains possible site filling locations separated by 1 nm along the cartesian directions. A random number between 0 and 1 was given to each

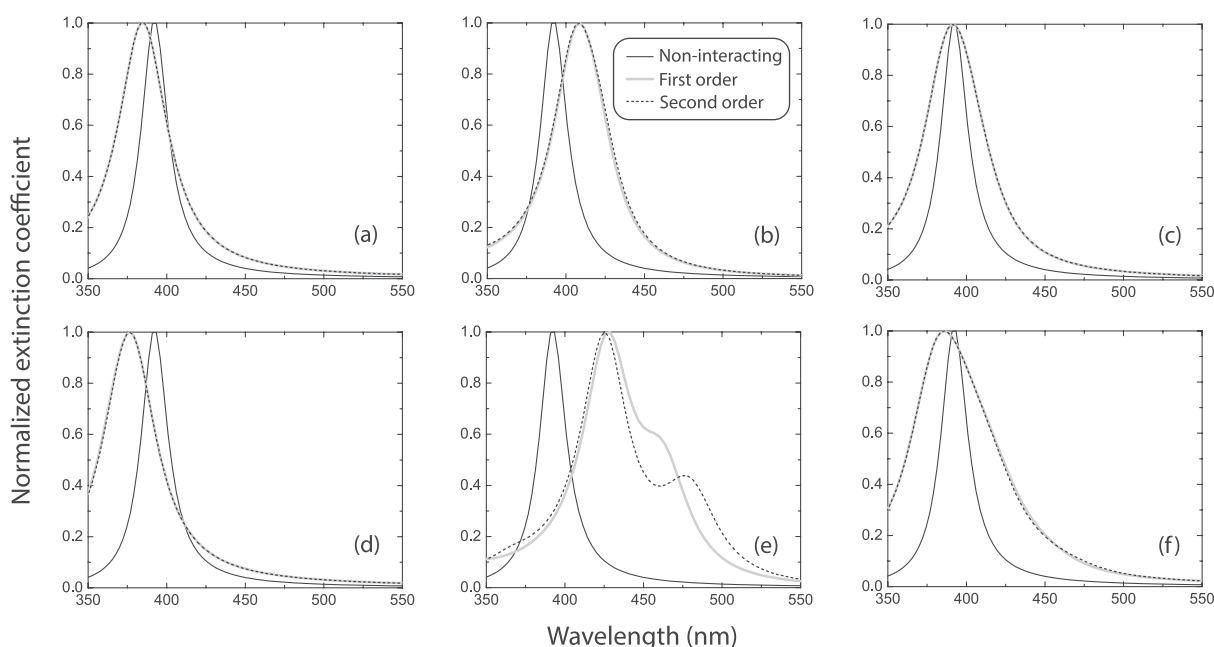


FIG. 6. Extinction spectra for a line of three 10 nm Ag nanoparticles in an aqueous solution. The upper row corresponds to a 10 nm edge-to-edge separation with the orientation (a) perpendicular and (b) parallel to the polarization direction, and (c) the orientationally averaged spectra. The lower row corresponds to a 5 nm separation with the orientation (d) perpendicular and (e) parallel to the polarization direction, and (f) the orientationally averaged spectra.

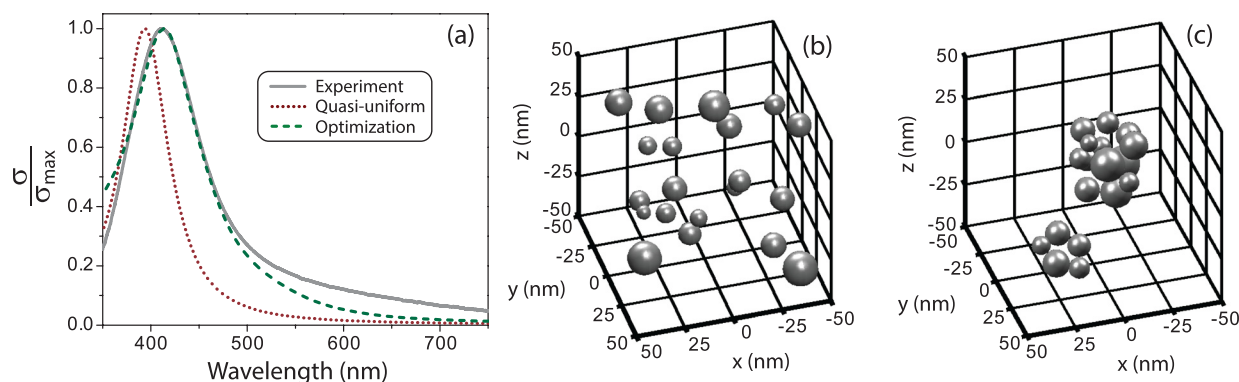


FIG. 7. The results of a position optimization for a 20 particle distribution. (a) The measured UV-VIS extinction spectrum and the calculated extinction spectra. (b) Quasi-uniform particle distribution and (c) optimized particle distribution.

site location. If the number is below a specified threshold, which controls the density, then a particle is generated at that location with the constraint that it does not overlap another particle on the grid. At every filled site, another random number is assigned from a log-normal distribution determined by the TEM measurement to assign the diameter of the nanosphere.

After the particles are generated, the spatial coordinates are varied along the cartesian directions by random numbers over a Gaussian distribution. This MCRW optimization algorithm was used to fit the calculated extinction spectrum with respect to the experimental data. The relative permittivities were calculated using Eq. (22) and substituted into Eqs. (3) and (4) which were used in conjunction with Eq. (2). We then averaged the system's orientation over the three Euler angles (θ, ϕ, ψ) , where the value of an arbitrary function f averaged over the three Euler angles is given by

$$\langle f \rangle = \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} f(\theta, \phi, \psi) \sin \theta d\theta d\phi d\psi. \quad (23)$$

The sum-of-squares between the calculated and experimental extinction spectra was used as the figure-of-merit (FOM). If the new positions of the nanospheres give a lower FOM, then the new coordinates are saved; otherwise, the nanospheres are moved back to their original positions. If two particles overlap during the random walk movement, those nanospheres are penalized and moved back to their original positions, where any new particles overlapping those particles are also moved to their original locations until a non-overlapping particle distribution is achieved.

The normalized extinction spectra from a quasi-uniform distribution, optimization calculation, and the experimental data are shown in Fig. 7(a). Note that the experimental extinction spectrum from an aqueous suspension of CNCs is subtracted from the experimental Ag-CNC extinction spectrum. The corresponding coordinates and sizes of the optimized nanospheres are shown in Fig. 7(c). Likewise, the particle coordinates and sizes of the quasi-uniform distribution are shown in Fig. 7(b). The normalized extinction spectrum of the optimized nanospheres fits well near the resonance of the measured extinction spectrum for only 20 nanospheres. Quasi-uniform distributions were also

generated at several nominal densities in various macroscopic geometries to test the influence of long-range interactions, which showed that long-range interactions had a minimal effect on the extinction spectrum.

The red shifted tail did not fit well, but we suspect that this heavy tail is caused by some larger sets of interacting metal nanoparticles not formed in our 20 particle optimizations; however, the many-body optimization becomes significantly more time consuming per additional particle. Higher-order multipole moments, defects in spherical symmetry, and higher-order iterative updates to the many-body self-consistent solution of the polarization density equation were neglected from the simulations. These computational and experimental results show untouched nanoclusters that cause the observed red shift and broadening at low concentration. The red shift and broadening, in this low concentration material, are primarily due to local particle interactions as observed for large cluster aggregates of surfactant coated metal nanoparticles formed at high concentration.⁴⁰ Thus, these results show that this nanohybrid material with fixed relative positions of non-contact silver nanoparticles has an excellent morphology for broadening the extinction spectrum for applications requiring a broad absorption in the visible spectrum.

V. CONCLUSIONS

We have shown that citrate-modified CNCs can be used in a bio-templation method to introduce silver nanoparticles onto CNC surfaces, which results in an organic-inorganic nanohybrid material. CNCs effectively act as dispersing agents for silver nanoparticles that deter Ostwald ripening. Confirmation of the presence of silver nanoparticles was provided using XRD and TGA. TGA experiments showed that hybrid nanoparticles consist of 20% silver content. TEM images illustrated the localized distribution of nanoparticles on the CNC fibers.

A discrete-dipole approximation was used to model the effects of nanosphere interactions near the optical resonance. The dipolar field interactions of small silver nanoparticle clusters are embedded within the larger nanoparticle-on-nanoparticle structure, as observed in the TEM images, significantly broadens and red shifts the extinction spectrum.

This extreme broadening was shown to be in contrast to simulations of Ag nanospheres with quasi-uniform distributions of similar macroscopic densities. Thus, these results explain the observations of large distributions of nanoparticles on three-dimensional scaffolds that have a long-range disorder. This is in contrast to much of the previous work performed on structured arrays of nanoparticles with homogeneous size and shape.^{11–15,17–19}

The broad and red-shifted spectrum of Ag-CNC could be useful where the broadband enhancement of absorption or emission of a device is desired, such as in photovoltaic devices. Ag-CNCs provide an easily functionalized bio-based substrate on which to attach metal nanoparticles with short-range interactions that have no long-range order. The possibility of aligning highly elongated, anisotropic, single CNCs that are individually decorated with Ag nanoparticles using an easy one-pot method could also provide a new avenue to easily-fabricate green materials with an anisotropic plasmonic response.

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