Modeling the Impact of Silver Particle Size and Morphology on the Covering Power of Photothermographic Media

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Abstract

Photothermographic images generated from silver carboxylates consist of silver particles with two distinct morphologies, dendritic and filamentary. The dendritic silver particle has the appearance of a spherical aggregate of smaller spheres. The filamentary particle is a solid strand of silver. Of particular interest for such a silver image is the covering power, i.e., the image density achieved per unit coverage of silver. Therefore, it would be useful to have the capability of calculating the covering power given the concentration, size, and morphology of the silver particles. However, to perform such a calculation on the complex Ag particle morphologies seen in the film is not a trivial matter. Some initial work was carried out to determine the utility of modeling the silver particles with simple morphologies and to provide a basis for modeling more complex geometries. A discussion of these calculations and a comparison to experimental measurements of covering power will be the focus of this talk.

Introduction

Images from conventional black-and-white photography are generated by small silver particles, which are typically in the form of filaments [1]. Photothermographic images generated from silver carboxylates might be filamentary or round. The round particles are typically an agglomeration of spherical 5-30 nm diameter nanoparticles of silver and have been called dendrites in the literature [2]. The size and morphology of the silver have an impact on the absorption spectrum and thus impact the tone and covering power of the image.

The simplest approximation for covering power is based on the Nutting model, which uses the projection area of the silver particles [3,4]. However, this does not give correct results because the actual extinction cross section for small particles is not equal to the geometric cross section. In order to correct for this, Farnell and Solman introduce a correction factor [5]. In order to quantify this correction factor, the absorption cross section of the silver particles needs to be calculated. The absorption cross sections of isolated silver spheres can be calculated directly from Mie theory [6]. The calculation for a cluster of noncontacting silver spheres is much more difficult, especially for cluster sizes that are typically observed for photothermographic materials [2]. Recently, code from Mackowski et al. has been used to calculate the extinction and scattering cross sections for infinite silver cylinders, linear chains of up to three silver spheres, and a small cubic cluster that consists of eight silver spheres [7]. These results show the importance of the distance between the silver nanoparticles.

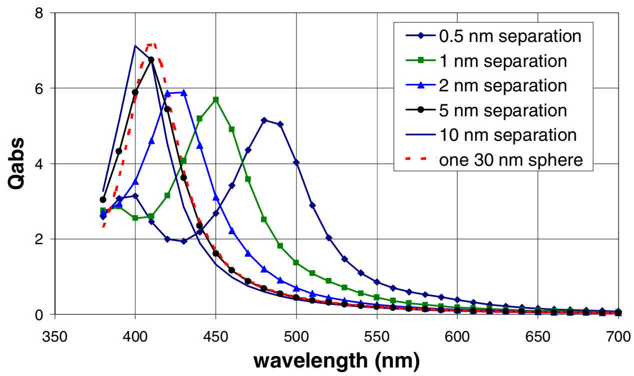
With the extinction cross section of the silver particles that make up an image, the covering power can be calculated using the Nutting model for the geometry of specular transmission. The Nutting model does not address the diffuse transmission of light. However, in practical situations, the total transmission is much more relevant. Obtaining the total transmission for a random distribution of particles given the extinction and scattering cross sections for these particles is not a trivial task. Assuming the particles are far enough apart to be treated independently, one can use a geometric optical approach to follow the path of the light between the scattering or absorption events. In this case, an accurate solution can be obtained using Monte Carlo Simulation [8]. However, this approach is time-consuming and more practical approaches have typically been used. The most widely used approximation is the Kubelka Munk Theory [9]. However, this is not very applicable to media with high absorption. More recently, the topic of photon transmission in a turbid media has become of great interest in both soft condensed matter physics and medical diagnostics [10]. In this paper, we adopt the approach based on the telegrapher's equation [10]. Details of this approach and the general topic of photon transmission in a turbid media will be addressed more extensively in the companion paper [11]. Here, we extend the work in Reference [7] to include larger clusters of silver spheres and use these results and the solution obtained from the telegrapher's equation to perform calculations for covering power.

Results and Discussion

Cross Sections

The calculations for extinction, scattering, and absorption cross sections were carried out in a manner similar to Reference [7]. In these calculations, no corrections were made to the refractive index for particle size, and code from Xu [12] was used in addition to the code from Mackowski et al. [13]. The code from Xu converges more rapidly for large separation distances. Both codes give the same results except at very short distances where Xu's code does not converge as well. Therefore, the Mackowski et al. code was used in the short to mid range separation distances, and the Xu code was used in the mid to longer separation distances.

The results for randomly oriented $3 \times 3 \times 3$ cubic arrays of twenty-seven 10-nm-diameter silver spheres at various separation distances are shown in Fig. 1. The separation distance is the distance between surfaces for the nearest-neighbor spheres in a cluster. It is clear that these clusters are still too small to give a neutral tone. However, they do absorb at longer wavelengths and with less scattering than does a solid sphere of equivalent volume. Calculations for a dendrite of a more desirable size, such as a cluster of several hundred 10-nm-diameter spheres, would require very extensive computing power, which is beyond the scope of this study.



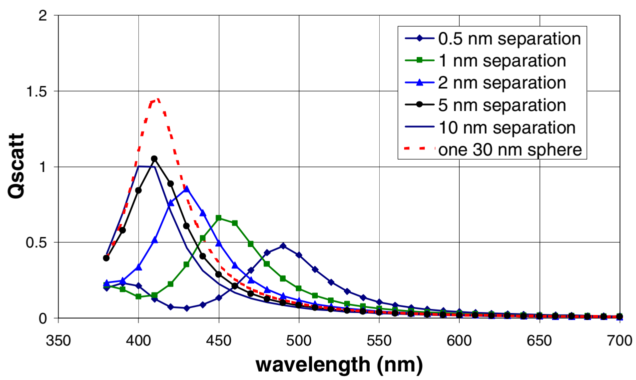


***Figure 1**. (solid lines) Calculated Q_{abs} and Q_{scatt} spectra for randomly oriented $3 \times 3 \times 3$ cubic arrays of twenty-seven 10-nm-diameter silver spheres at various separation distances. Q_{abs} and Q_{scatt} are the calculated absorption and scattering cross sections normalized by the geometric cross section of a single sphere of equivalent volume, i.e., 30 nm in diameter. (dotted line) Calculated Q_{abs} and Q_{scatt} spectra for a single 30-nm-diameter silver sphere.*

Covering Power Calculations

Of particular interest for a silver image is its covering power, which is the image density achieved per unit coverage of silver. In a photothermographic media based on silver carboxylate, the latent image catalyzes the chemical reduction of silver carboxylate to neutral silver atoms (Ag^0). The covering power (CP) will be defined as follows:

$$CP = (D - D_0) / Ag^0 \text{ Wt},$$

where Ag^0 Wt is the amount of Ag^0 per unit area of the imaged film. $D - D_0$ is the image density contribution by the Ag^0 particles. D is the image density of the processed film. D_0 is the contribution to the density by components other than Ag^0 such as the base, silver halide, silver carboxylates, and dyes. This can be taken as the unprocessed density assuming there are no heat-bleachable dyes or thermally generated dyes, or it can be taken as the processed D_{min}, assuming there is negligible contribution from fog centers.

The covering power was obtained by using the calculated spectra for the absorption and scattering cross sections as input to the following relationship for total transmission [11]:

$$T = \frac{\eta q s \exp[-\varepsilon d]\left((a\varepsilon + \eta q^2)(\exp[\varepsilon d] - \cosh[qd]) - q(\eta\varepsilon + a)\sinh[qd]\right)}{(\varepsilon^2 - q^2)\left(2\eta q a \cosh[qd] + (\eta^2 q^2 + a^2)\sinh[qd]\right)} + \exp[-\varepsilon d] \quad (1)$$

where,

$a = \sigma_A n$

$s = \sigma_S n$

$\varepsilon = a+s$

$q^2 = 3a(a+\beta s)$

a, s, and ε are the absorption, scattering, and extinction coefficients. σ_A and σ_S are the absorption and scattering cross sections, d is the layer thickness, and n is the number of silver particles per unit volume. η is the average z-component magnitude of the unit velocity vectors for the diffusely reflected and transmitted photons. For the calculations in this paper, η and the constant β are set to 1/2.

Equation (1) was derived using the telegrapher's differential equation to model the photon diffusion in a turbid media [10]. Reflections at the interfaces were ignored in this calculation. Details of the calculation can be found in Reference [11]. The resulting total transmission spectra was used to calculate a visual density, which is taken to be –Log (Y/Y_n), where Y is the CIE Y tristimulus value for the transmitted light, and Y_n is the CIE Y tristimulus value for the incident beam [14]. The D65 illuminant was used for these calculations.

Figure 2 shows the calculated covering power for a 20-µm-thick layer containing randomly dispersed silver spheres as a function of the sphere diameter at a constant total Ag loading of 1.9 g/m^2. The covering power in the case of specular transmission was calculated by using the extinction cross section in the Nutting formula. The covering power in the case of total transmission was calculated by using Eq.1.The cross sections for the spheres were calculated using Mie theory with no size correction in the Ag refractive index values of Hagemann et al. [7] and a refractive index of n = 1.481 assumed for the medium. Figure 2 shows that the optimal diameter for a silver sphere is between 100 and 120 nm.

The typical covering power for photothermographic media is between 2 and 3. Because the covering power reached for total transmission in Fig. 2 is not this high for any diameter, these results suggest that solid silver spheres are not the optimal morphology for covering power.

The covering power for the cubic array of twenty-seven 10-nm silver spheres was calculated for several separation distances (Fig. 3). In this case, there is minimal diffuse transmission. The covering power increases as the distance between the spheres in the array decreases. The covering power increases dramatically as the separation distance decreases below the radius of the spheres. In this regime, the covering power is greater than that for the sphere of equivalent volume

(30-nm diameter), which has a covering power of about 0.4 (Fig. 2). The results suggest that a cluster of spheres with sufficiently small separation distance has a better morphology than do solid spheres. Ideally, larger clusters where light scattering plays a larger role should be studied to verify this conclusion.

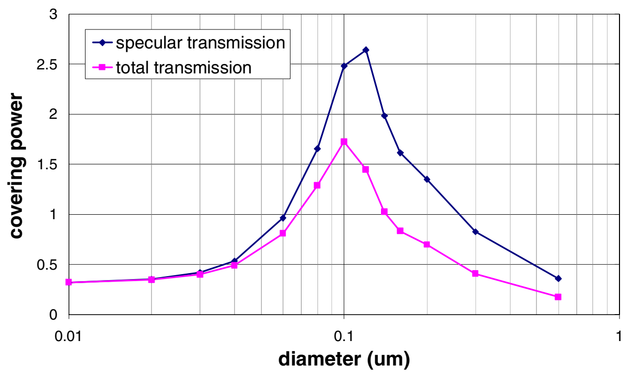


***Figure 2**. Calculated covering power for solid silver spheres dispersed randomly in a 20 μm layer with a silver loading of 1.9 g/m^2.*

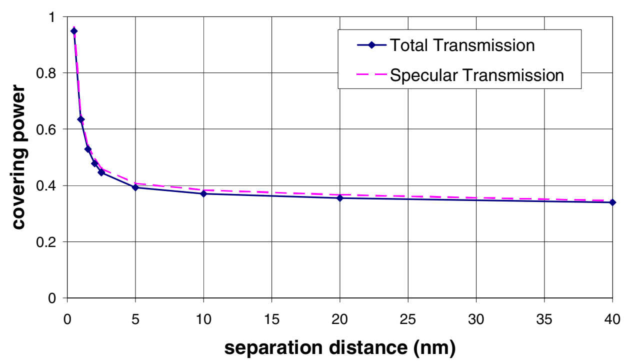


***Figure 3**. Calculated covering power for randomly oriented 3 × 3 × 3 cubic clusters of twenty-seven 10-nm-diameter silver spheres in a 20-μm layer with a silver loading of 1.9 g/m^2.*

Summary

The covering power was calculated for solid spheres and cubic arrays of twenty-seven 10-nm silver spheres. The calculations were performed using theoretical cross sections and a relationship for total transmission derived from the telegrapher's equation. The absorption and scattering cross sections were calculated using Mie theory, code from Mackowski et al., and code from Xu. The total transmission was estimated using Eq. (1) for a silver loading of 1.9 g/m^2. The CIE Y tristimulus values were calculated from the transmission spectra, which are used to derive the visual density. The results suggest that a cluster of small silver spheres can result in a higher covering power than can a single silver sphere of equivalent volume. Therefore, these results give some indication why the dendritic silver particles in photothermographic materials are ideal.

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Author Biography

Steven Kong is a Research Physicist with Eastman Kodak Company. He received his B.S. in applied physics and applied mathematics from the California Institute of Technology and a Ph.D. in physics from the University of Illinois at Urbana-Champaign. He began working in the field of photothermography at 3M in 1995. He is a member of IS&T and ANSI I3A. He also serves in an ISO task group that addresses the image permanence of digital hard copies for medical imaging.