Imaging through plasmonic nanoparticles

Mehbuba Tanzid*, Ali Sobhani†, Christopher J. DeSantis†, Yao Cui†, Nathaniel J. Hogan†, Adam Samaniego†, Ashok Veeraraghavan‡, and Naomi J. Halas*‡,‡,†

*Department of Electrical and Computer Engineering, Rice University, Houston, TX 77005; †Department of Chemistry, Rice University, Houston, TX 77005; and ‡Department of Physics and Astronomy, Rice University, Houston, TX 77005

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The optical properties of metallic nanoparticles with plasmon resonances have been studied extensively, typically by measuring the transmission of light, as a function of wavelength, through a nanoparticle suspension. One question that has not yet been addressed, however, is how an image is transmitted through such a suspension of absorber-scatterers, in other words, how the various spatial frequencies are attenuated as they pass through the nanoparticle host medium. Here, we examine how the optical properties of a suspension of plasmonic nanoparticles affect the transmitted image. We use two distinct ways to assess transmitted image quality: the structural similarity index (SSIM), a perceptual distortion metric based on the human visual system, and the modulation transfer function (MTF), which assesses the resolvable spatial frequencies. We show that perceived image quality, as well as spatial resolution, are both dependent on the scattering and absorption cross-sections of the constituent nanoparticles. Surprisingly, we observe a nonlinear dependence of image quality on optical density by varying optical path length and nanoparticle concentration. This work is a first step toward understanding the requirements for visualizing and resolving objects through media consisting of subwavelength absorber-scatterer structures, an approach that should also prove useful in the assessment of metamaterial or metasurface-based optical imaging systems.

Significance

How is an image transmitted through a material consisting of subwavelength structures? We use two distinct methods to obtain quantitative answers to that question. The first, structural similarity index, is a method related to human perception, initially developed to quantify transmitted image quality following image compression in digital image transmission systems. The second method treats the medium as an optical component itself, where we determine the spatial frequency content of the image transmitted by the medium. This study opens the door to analyzing images transmitted through particulate media that absorb and/or scatter light, which applies generally to imaging systems whose components are composed of subwavelength structures, such as those composed of random particulates or nanoengineered flat-optics metasurface lenses.
The experiment consisted of a bright field Köhler illumination setup for imaging an object through plasmonic nanoparticle suspensions (details shown in SI Appendix, Fig. 1). A fiber optic white light illumination source (MI-150; Edmund Optics) with a series of wavelength-selective bandpass filters (FWHM, ±10 nm; FB series; Thorlabs) spanning the wavelength range of 450–900 nm were used. For imaging, a CCD camera (PIXIS 400; Princeton Instruments) sensitive in the 400 to 1,100 nm wavelength range was used. The object was a 1951 US Air Force (USAF) resolution target conforming to the military standard (MIL-STD-150A) (SI Appendix, Fig. 1). Nanoparticle suspension in a quartz cuvette was placed directly in front of the camera so that the suspension influenced only the target image and not the illumination source.

A suspension of plasmonic nanoparticles was designed and prepared with spectrally distinct transmission maxima and minima (Fig. 2). The suspension consisted of a mixture of Au nanorods of two different sizes and aspect ratios corresponding to two spectrally distinct dipolar plasmon modes (Fig. 2A). One type of Au nanorods were 20 nm × 45 nm in size with a dipolar...
resonance wavelength of 637 nm (Fig. 2B). The second type of Au nanorods were 30 nm × 120 nm in size with a dipolar resonance wavelength of 877 nm (Fig. 2C). Finite-difference time domain (FDTD) calculations of Au nanorods with these dimensions indicate that absorption dominates the cross-section of the smaller nanorods (Fig. 2D), whereas for the larger nanorods, scattering and absorption contribute equally (Fig. 2E). Mixing the nanorod solutions results in an extinction minimum at 770 nm and two maxima at 637 and 877 nm, which frame the transmission window. Normalized monochromatic images of a set of vertical bars [12.7 line pairs/mm (lp/mm)] on the USAF resolution target were obtained after transmission through the mixed-nanorod suspension (Fig. 3). The extinction spectrum of the suspension and the specific illumination wavelengths used for imaging, which ranged from 450 to 900 nm at 50 nm wavelength intervals, are shown (Fig. 3A). The image is transmitted clearly within the transmission window near 750 nm and becomes increasingly distorted for illumination wavelengths detuned from the 750 nm transmission window (Fig. 3B). Imaging through the aqueous solution (Fig. 3C) shows that the observed image distortion is attributable to transmission through the mixed nanoparticle suspension. To quantitatively analyze and assess the quality of the transmitted image, we apply a quality metric known as the SSIM. Unlike traditional methods for evaluating image quality, such as mean squared error (MSE) or peak signal-to-noise ratio (PSNR) (SI Appendix, Fig. 3), SSIM is not biased toward oversmoothed or blurry results but has been proven to be consistent with human visual perception (19). The human visual system is highly adaptive for extracting structural information from a scene: this is taken into account in the definition of the SSIM metric [computational details are given in the SI Appendix, and we refer the reader to the original publication (17) for details regarding the SSIM metric]. In practice, an SSIM of 0 indicates no similarity between the transmitted and the original image, and an SSIM of 1 indicates no detectable difference between the original and the transmitted image. Additionally, multiscale (MS)-SSIM (20) can be calculated to take into account image details, such as the sampling density of the image signal, the distance from the image plane to the observer, and the perceptual capability of the observer’s visual system at different resolutions (more details are provided in the SI Appendix). For the transmitted images displayed in Fig. 3B and using the images shown in Fig. 3C as the original images, we calculated the SSIM (red) and MS-SSIM (blue) values for each transmitted image, as shown in Fig. 3D. We can see that these values correlate well with the quality of the images as perceived by the human eye. The SSIM and MS-SSIM follow the transmission spectrum of the solution to some extent. MS-SSIM shows a slightly more uniform spectral distribution compared with SSIM. However, both deviate from the spectrum at certain wavelengths. For example, even though the extinction maxima near 650 and 850 nm have comparable optical densities, the image obtained at 850 nm wavelength (with SSIM 0.094 and MS-SSIM 0) has substantially greater image distortion than the image obtained at 650 nm wavelength (with SSIM 0.285 and MS-SSIM 0.131). The difference between the change in image distortion at 650 and 850 nm can be attributed to the difference in the ratio of scattering to absorption cross-sections for the two nanorod sizes in the mixed-nanorod suspension: for the 20 nm × 45 nm nanorods, this ratio is 0.11, and for the 30 nm × 120 nm nanorods, this ratio is 1.04. Because the smaller nanorods with their dipolar plasmon near 650 nm scatter less light than those with their resonance near 850 nm and because absorbed light merely reduces the brightness of the image and not the contrast, there is less
perceived image distortion at the 650 nm illumination wavelength. Conversely, the larger nanorods with their dipolar resonance near 850 nm have a larger relative scattering cross-section, which distorts the image, because scattering results in redirected photons that, although detectable, have lost information regarding the object, resulting in a distorted image. This result indicates that the absorption and scattering properties of the constituent nanoparticles of a plasmonic medium directly affect the quality of a transmitted image.

Another method to assess the quality of an image transmitted through a plasmonic medium is to consider the medium to be an additional component of the imaging system and determine the MTF of that component (Fig. 4). The MTF describes the maximum resolution of an imaging system as a function of transmittable spatial frequencies (lp/mm), indicating the minimum-sized feature of an object resolvable in a transmitted image (18, 21) (details are provided in the SI Appendix). MTF is also a normalized metric, whose amplitudes range from 0 to 1, where 0.05 is the threshold for resolvability for average human observers (22). To determine the MTF of the mixed-nanorod suspension, we imaged a specific portion (17.96 to 228.1 lp/mm) of the USAF resolution target through the suspension. Normalized images through the mixed-nanorod suspension, along with images transmitted through an aqueous medium as a control, at the wavelength of maximum transmission (750 nm) and at the two resonance peaks (650 and 850 nm) are shown in Fig. 4A. The MTF from each transmitted image is shown in Fig. 4B–D. At 750 nm, the MTF through the mixed-nanorod suspension is almost equal to the MTF through H2O. However, at the resonance peaks (650 and 850 nm), the MTF through the mixed-nanorod suspensions is substantially reduced (Fig. 4B and D). Although the optical density of the mixture is similar at both resonance peaks, the absorption and scattering cross-sections are substantially different. The MTF determined at 850 nm, where scattering is more dominant, is reduced more than the MTF at 650 nm. The MTF cutoff for the average human visual system, 0.05, is shown by the black dashed lines in Fig. 4B–D. In Fig. 4E, we see that at the transmission maximum, the cutoff spatial frequency is the same for the mixed-nanorod suspension as it is in H2O, meaning that the maximum resolvable spatial frequency through the nanoparticle suspension is unaltered at this wavelength. The cutoff resolution is much lower at the longer wavelength resonance, where scattering is stronger (850 nm), than for the shorter wavelength, predominantly absorptive resonance (650 nm). This finding clearly indicates that scattering, rather than absorption, is the dominant light interaction mechanism that limits the size of the smallest resolvable feature when imaging through plasmonic media.

The total optical density of a plasmonic nanoparticle suspension also affects the quality of the transmitted image. One can vary the optical density of a plasmonic nanoparticle suspension by varying either the optical path length or the concentration of nanoparticles in suspension. First, we varied the
within the same 600 to 650 nm wavelength window but possess for this study, because they both have similar extinction maxima 100 nm diameter Au nanospheres and 20 nm × 45 nm Au nanorods at a 600 nm illumination wavelength as a function of optical density. optical path length of the nanorod-mixture suspension through which objects were imaged (Fig. 5). The normalized images of 17.96–228.1 lp/mm in the USAF resolution target that were obtained for optical path lengths of 10, 5, and 2.5 mm (Fig. 5A, Lower, top three rows) and through H₂O (Fig. 5A, Lower, bottom row) are shown in Fig. 5. The SSIM and cutoff spatial frequencies across the spectrum as a function of optical path length are shown in Fig. 5B and C. As optical path length is increased from 2.5 to 5 mm, high image quality as well as spatial resolution persist within a broad spectral window centered at the wavelength of maximal transmission. As we increase optical path length further (from 5 to 10 mm), image quality and maximum spatial resolution drop off dramatically. This result likely indicates a threshold optical density where optical densities larger than this value will distort all images beyond recognition and below this value, there will be minimal image distortion.

To further examine this imaging threshold, we determined the SSIM obtained through two different suspensions of individual nanoparticles, this time changing optical density by varying the concentration of nanoparticles in each suspension. We chose 100 nm diameter Au nanospheres and 20 mm × 45 nm Au nanorods for this study, because they both have similar extinction maxima within the same 600 to 650 nm wavelength window but possess different absorption and scattering properties (SI Appendix, Fig. 4). Specifically, the ratio of scattering and absorption cross-sections for the nanosphere solution is 40 times larger than the nanorod solution at the 600 nm imaging wavelength. We varied the optical densities of these two plasmonic nanoparticle solutions by varying their concentrations (SI Appendix, Fig. 5). The concentration of 100 nm diameter Au nanosphere solutions was varied from 1.9 × 10⁹ to 2.6 × 10¹⁰ particles/cm³ and for the 20 nm × 45 nm Au nanorod solutions, the concentration was varied from 7.7 × 10¹⁰ to 4.6 × 10¹² particles/cm³. We performed imaging at 600 nm wavelength, avoiding the interband transition of gold at 520 nm wavelength (23). We calculated the SSIMs for the images obtained through these nanorod and nanosphere solutions at different concentrations, which are plotted against the corresponding optical densities in Fig. 6. The imaging threshold observable in Fig. 5 can also be observed here as a nonlinear dependence of the SSIM on the optical density of the solution. Below a threshold optical density (<1.5), the image transmits clearly through the nanoparticle solutions with minimum distortion, regardless of the absorption or scattering properties of the plasmonic nanoparticles. However, above a threshold optical density (shown by the gray area in Fig. 6), there is a rapid decrease in image quality, according to the SSIM metric. Additionally, the threshold optical densities, or concentrations, are different for the two nanoparticle solutions. The SSIM drops below 0.2 at a concentration of 1.3 × 10¹⁰ particles/cm³ (optical density 2.3) for the nanosphere solution with larger scattering cross-sections and at a concentration of 2.7 × 10¹¹ particles/cm³ (optical density 2.8) for the nanorod solution, which is more absorbing. Although the value of the threshold optical density is also dependent upon the specifics of the imaging system, this threshold behavior should be generally observable in any imaging system.

Our quantitative study on the influence of plasmonic nanoparticles on the visual quality of images transmitted passing through such nanoparticle-laden media may open a new area of research to use engineered plasmonic nanoparticles not only for reshaping the light spectrum but also to selectively preserve or distort a transmitted image for visual or machine detection. Among various image quality metrics, SSIM provides realistic information regarding the clarity or distortion of an image when transmitted through plasmonic nanoparticles that is directly related to human perception. On the other hand, MTF evaluates the performance of plasmonic nanoparticles by considering them as a part of the imaging system and provides the maximum spatial resolution visible through the particular plasmonic nanoparticle-based medium. We showed that for equal extinction values, plasmonic nanoparticles with higher scattering cross-sections more effectively distort transmitted images compared with nanoparticles with more predominant absorption cross-sections. Furthermore, we showed that image distortion and optical density of the nanoparticle solution have a strongly nonlinear relation, where below a threshold optical density, there is virtually no image distortion, whereas above this threshold, the image distortion drops dramatically with increasing optical density. We believe that this initial study will facilitate the assessment of image visualization through other types of media composed of subwavelength nanostructures with light-scattering properties, such as metasurface lenses (24, 25), which can be combined into flat optics-based imaging systems.

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