Design of lumpy metallic nanoparticles for broadband and wide-angle light scattering

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Broadband and wide-angle light scattering media are highly desirable in photonic applications. In this paper, we theoretically investigate the light scattering properties of lumpy nanoparticles of silver, aluminum, and copper compared to those of smooth nanospheres with the same volume. The lumpy nanoparticles are found to provide broadband scattering enhancement over the smooth nanoparticles in a variety of dielectric environments. A maximum 18% enhancement in angular scattering for Al lumpy particles was found. More importantly, near-field scattering intensity mapping confirms that the enhanced scattering is achieved in all directions, making them more attractive in diverse photonic applications. © *2012 American Institute of Physics*.
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Scattering is one of the fundamental phenomena for light-matter interaction and can lead to important applications, for example, random lasers[1–3] and solar cells,[4–8] in which broadband and wide-angle scattering is highly desired. Metallic nanoparticles are well-known strong light scatterers because their scattering cross-sections can considerably exceed the geometrical cross-sections when the incident wavelength of light falls in the plasmonic resonant scattering region. However, dependent on the particle size, shape, and the surrounding environment, the resonant scattering has sharp peaks, which leads to a limited bandwidth. Furthermore, determined by the nanoparticle size, large scattering strength and scattering angle cannot be achieved simultaneously.[9,10] These limitations pose great challenge for metal nanoparticles to be used for practical applications, in particular, in random lasers and plasmonic solar cells where broadband scattering with large scattering strength and scattering angle are required.

There have been several proposals for broadband enhancement using nanoparticles,[11–13] but the majority of these involve a combination of different sized or shaped nanoparticles. Each type of nanoparticles has its own narrowband enhancement, and their sum together over a large area results in an overall broadband enhancement. However, there is a fundamental limit for this method, in which a single narrowband enhancement source can only occupy one location at a time, and ultimately any broadband enhancement is relatively small.

Designing special nanoparticles that provide large scattering across broadband spectra allows for strong broadband enhancement at each nanoparticle location on a sample. It has been revealed recently that the surface roughness of the nanoparticles can have unexpected strong impact on the nanoparticle scattering strength and angler distribution. Based on the different scattering properties of large and small nanoparticles from the Mie theory, we have recently proposed a unique nucleated (also called lumpy) nanoparticle geometry,[9] where a lumpy particle combines several smaller particles surrounding a larger core, which provides multiple scattering regions for each lumpy particle. Although this type of nanoparticles facilitates broadband absorption in thin-film solar cells,[9] the key parameters determining the optimized scattering strength, bandwidth, and angle have not been revealed. Furthermore, the effectiveness of this geometry for other low cost materials, for example, Al and Cu have yet to be investigated. Herein we theoretically study the scattering properties of the lumpy nanoparticles including the small surface nanoparticle sizes, the surface to core particle ratio, and the dielectric environment for Ag, Al, and Cu and compare the lumpy nanoparticles to their smooth counterparts of the same volume to achieve the optimized design. After optimization, a maximum 18% angular scattering enhancement has been achieved by using the lumpy Al nanoparticles compared to that of the spheres in free space. The near-field scattering enhancement maps suggest that the angular scattering of the lumpy nanoparticles are larger and in all directions than that of the smooth particles.

Investigations have been undertaken by using the finite difference time domain modeling software produced by Lumerical.[14] The model consists of a nanoparticle within a medium illuminated with a total-field-scatter-field (TFSF) plane wave source with a spectral range investigated from 300 to 1200 nm. Perfectly matched layers (PML) boundaries are used on all axes. The scattering and absorption cross-sections and the scattering intensity maps as a function of the scattering direction are calculated. Refractive index data for silver was obtained from Johnson and Christy[15] and copper and aluminum were obtained from Palik.[16] As shown in Fig. 1(a)), a large sphere is used as the scaffolding to anchor 26 smaller spheres half embedded surrounding the outside of the large core sphere, producing the "roughing" effect. The effects of the surface particle (roughness) size, the core size, and the surrounding medium have been all investigated.

Fig. 1 shows the normalized scattering cross-section, Q_{scat}, of lumpy nanoparticles with varying surface roughness. The surface morphology was investigated by adjusting the surface particle radius from 0 to 120 nm for materials (Cu (Fig. 1(b)), Al (Fig. 1(c)), and Ag (Fig. 1(d))) on a 100 nm radius core (selected based on our previous experience[9]).

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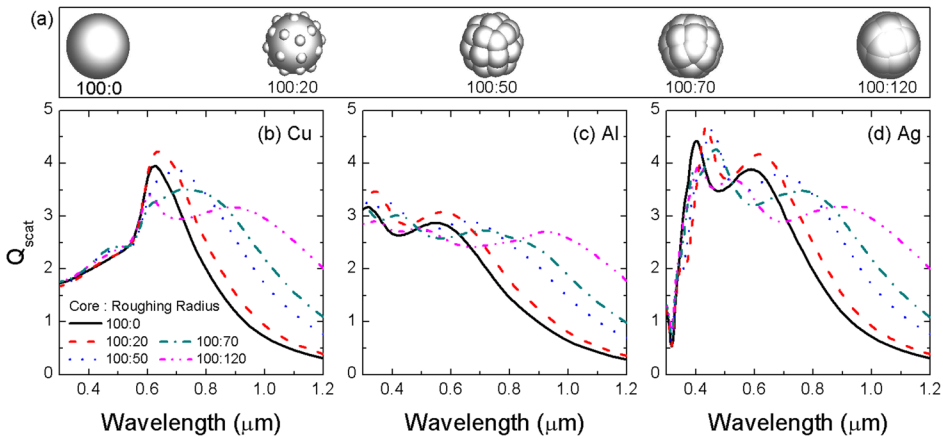

FIG. 1. (a) Schematics of five of the different surface morphologies investigated. Normalized scattering cross-sections of lumpy particles with core radius 100 nm and roughing radius from 0 to 120 nm radii surrounding a 100 nm radius core particle for materials (b) Cu, (c) Al, and (d) Ag in free space.

Fig. 1(a) identifies the five different morphologies consisting of a smooth case (100:0), small isolated particles around the core (100:20), medium particles completely covering the core and providing the greatest roughing amount (100:50), large particles with less total roughing (100:70) and finally very large particles with little roughing (100:120). It is expected that the addition of roughing particles to provide extra scattering and broaden the scattering angles over smooth spheres. In all cases (b), (c), and (d) the addition of the roughing particles increased the Q_{scat} amount at wavelengths longer that the surface plasmon resonances (SPRs). As such, for Cu, the improved Q_{scat} region is from 600 to 1200 nm and beyond whereas Al is improved across the entire investigated spectral region. Ag provides the highest Q_{scat} peak intensity and the largest scattering strength but does not correlate to the largest material scattering enhancement. The increase in roughing particle size provides red-shift and broadening of scattering resonances and introduces additional scattering resonances. This is due to a combination of two factors: (i) the increase in particle volume and (ii) surface morphology changes.

Another aspect to investigate of the lumpy particles is the effect of core size to the scattering efficiency. Fig. 2 illustrates the scattering enhancement of lumpy particles over smooth particles of the same volume for (a) Cu, (b) Al, and (c) Ag. A ratio of half the core radii is used as the roughing radii and the lumpy particles investigated are 50:25 (core radius: roughing radius), 100:50, and 200:100. The enhancement is the greatest for the 50 nm core cases for all the materials; however, the Q_{scat} is not the largest for this case. In particular, although there is significant enhancement observed at longer wavelengths the Q_{scat} in this region is small. Also, the small particles have larger respective contributions to the absorption cross-section, Q_{abs}, than the larger particles. The 100 and 200 nm core particles have a much larger Q_{scat} across the entire investigated spectral range. At wavelengths above the initial resonance peak, broadband enhancement of about 10% is achieved for all the materials and is solely due to the increase in surface roughing. The use of Al provides the greatest enhancement as the initial resonance peak is below the investigated spectral region, and as such there is no loss minima observed. The large enhancement minimum for silver lumpy particles is caused by the slight red-shifting of the resonances for the lumpy case allowing the sphere to be the best scatterer at 380 nm. To design the lumpy nanoparticles with maximum scattering, the larger the surface roughness, the greater the incident light interaction volume; however, if the roughing particles become too large (>1/2 the core radius) the surface morphology reduces, and the incident light interaction volume approaches that of a sphere of the same size. Increasing the volume of a particle allows more scattering resonances to be excited, and the previous resonances are red-shifted and broadened.

The dielectric environment of the surrounding medium is a key parameter influencing the scattering and absorption of a nanoparticle. To quantify the effect of the surrounding medium, the spectra of the scattering enhancement ratio of lumpy particles (100:50) to smooth particles of the same volume are investigated with refractive indices (RI) of surrounding media varied from 1 to 3. Fig. 3 shows the effect of surrounding media for (a) Cu, (b) Al, and (c) Ag nanoparticles. For all three materials investigated the enhancement factor decreased when the particles are embedded in higher index surrounding media. Increasing the RI causes a red-shift of the SPR peaks as well as additional resonances for both lumpy and smooth cases although there is a much stronger increase for the lumpy case. As a result the resonance for

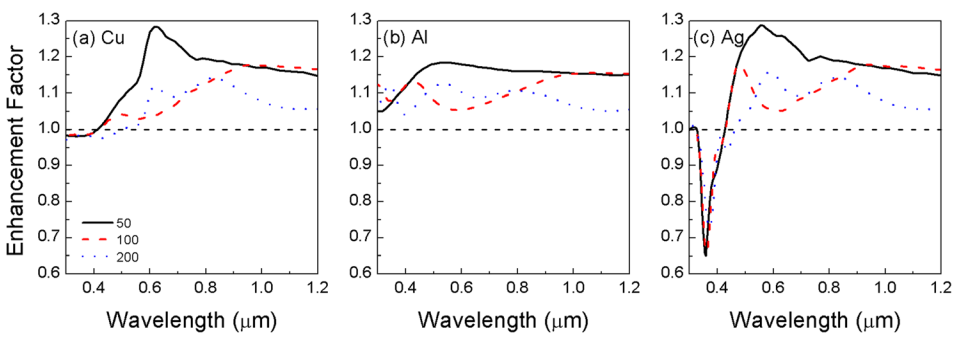

FIG. 2. Scattering enhancement factor for the Q_{scat} of lumpy nanoparticles over smooth particles of the same volume embedded in free space where the lumpy particles have a relative roughing radius of half of the core radius. The core radius in nm is listed in the legend.

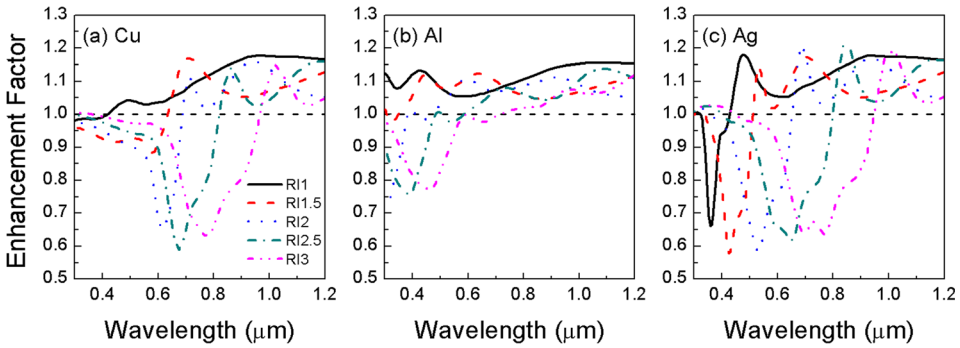

FIG. 3. Scattering enhancement factor for the Q_{scat} of lumpy nanoparticles (100:50) over smooth particles of the same volume embedded in surrounding media with refractive index (RI) of 1 to 3 for nanoparticles of (a) Cu, (b) Al, and (c) Ag.

the smooth case at the initial resonance frequency (650 nm for Cu, <300 nm for Al, and 400 nm for Ag in free space) produces a strong minimum in the scattering enhancement due to the stronger red-shifting of the lumpy particles. This effect results in stronger scattering factors for lower RI mediums within the investigated spectral range for the particle dimensions designed for free space. The scattering enhancement factor for lumpy particles is higher than for spheres of the same volume when the RI is below 2.5 for Cu, 3 for Al, and 2 for Ag.

The enhancement factor listed in Fig. 3 is calculated for the wavelength range from 300 to 1200 nm, as such when enhancement maxima are shifted beyond 1200 nm they are no longer included in the enhancement factor. This causes a significant drop in the enhancement for embedding materials with refractive index above 1.5. Precise control over the embedding medium allows for enhanced broadband scattering at a desired spectral region for lumpy particles compared to the smooth spheres.

Scattering strength is not the only parameter judging the scattering capability of a particle. In many applications, a large light-matter interaction path length is essential, which requires the scatterer to have large scattering angles.

The direction of scattering is investigated for the particle consisting of the highest amount of roughing, the 100:50 particles in free space. Fig. 4 shows the real part of the Poynting vector for the lumpy particle divided by that of the sphere of the same volume corresponding to the scattering enhancement factor for forward, backward, and sideway scatterings. Cu, Al, and Ag nanoparticles are illuminated by an unpolarized light

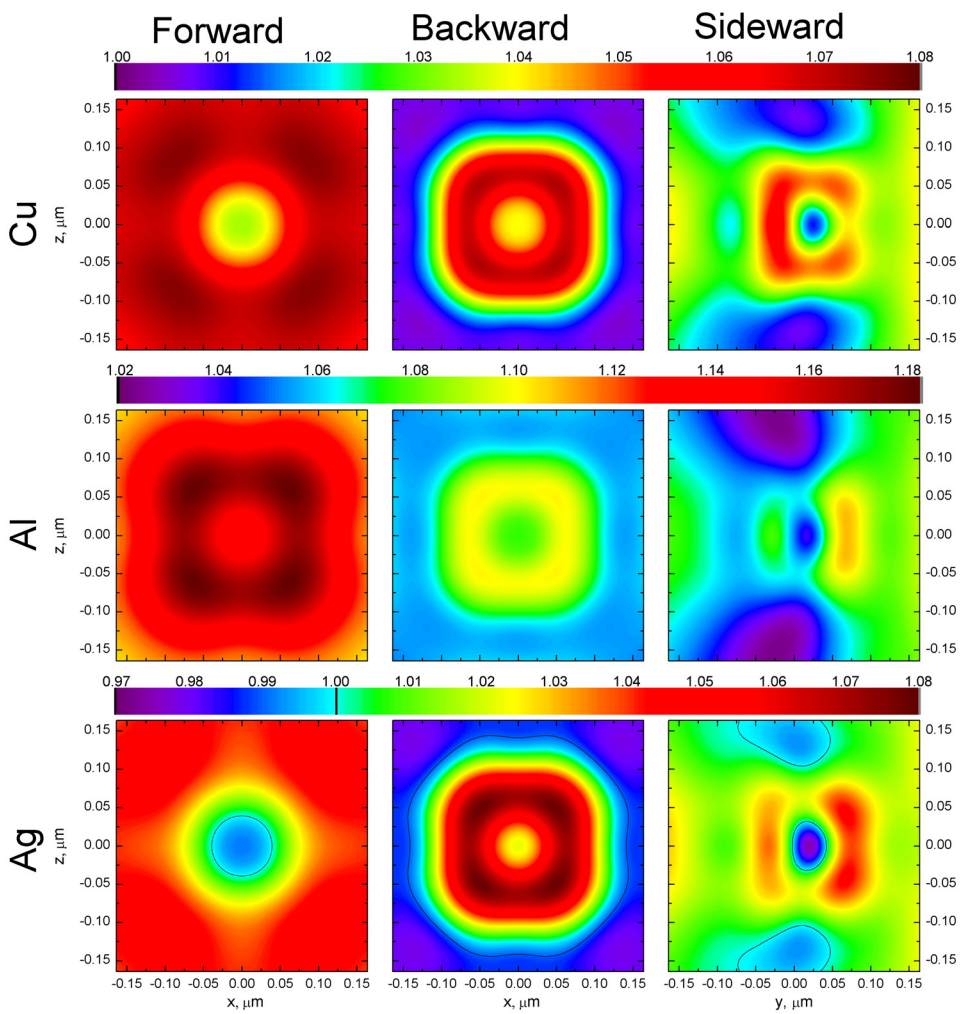

FIG. 4. Scattering enhancement maps of a 100:50 lumpy particle against a smooth particle of the same volume for Cu, Al and Ag in free space. Scattering enhancement is recorded as a function of forward, backward, and sideward directions at a distance of 165 nm from the particle center. Each material has its own enhancement scale.

source, where the incident light direction is +y. Each material has its own scattering enhancement color scale. The scattering enhancement was integrated across the entire spectral wavelength from 300 to 1200 nm, allowing the total scattering to be observed for each direction. The scattering of lumpy particles provides stronger scattering at wider angles (forward, backward, and sideways) than the corresponding smooth particle of the same volume. It should be noted that there are limited wavelengths where the scattering of the smooth particles is more effective than the lumpy particles, but overall the lumpy particles lead to strong enhancement for all materials investigated. Cu and Ag particles provide a maximum enhancement of 8% in all different directions, whereas Al particle showed an 18% improvement forward and 10% backwards and to the sides. The lumpy particles have larger scattering angular distribution in the forward direction. However, in the direct forward scattering direction (0°) the scattering is strongest for smooth particles, which leads to a circular center minimum in the forward scattering enhancement maps for all the materials. A similar process occurs for the backward scattering (180°). Although there is much broader backward scattering for lumpy particles than smooth particles, this enhancement is reduced as the scattering angle approaches the boundary at 135° from the particle. Sideways, the majority of scattering occurs directly sideways (90°) from the nanoparticle and reducing both in the incident light direction and back scattered direction. Ag particles are the only material where there exist some scattering regions for the smooth case that are better than the lumpy case.

In summary, the key parameters influencing the scattering efficiency of the lumpy nanoparticles of three different materials have been investigated. A larger core size provides stronger scattering strength, and Al was observed to provide the greatest broadband enhancement across the broad spectral range from 300 to 1200 nm. Control over the surrounding medium allows higher scattering enhancements within a desired spectral range. The scattering of lumpy particles is improved in all directions in free space, with the greatest enhancement of 18% for the forward scattering from Al particles. When the lumpy nanoparticles are in free space, strong enhanced scattering is achieved over most of the spectral region investigated. Our findings suggest tailoring particle roughness is another effective way to achieve desired scattering for various applications including solar cells and random lasers.

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[1]G. D. Dice, S. Mujumdar, and A. Y. Elezzabi, Appl. Phys. Lett. **86**, 131105 (2005).
[2]X. Meng, K. Fujita, Y. Zong, S. Murai, and K. Tanaka, Appl. Phys. Lett. **92**, 201112 (2008).
[3]O. Popov, A. Zilbershtein, and D. Davidov, Appl. Phys. Lett. **89**, 191116 (2006).
[4]D. Derkacs, S. H. Lim, P. Matheu, W. Mar, and E. T. Yu, Appl. Phys. Lett. **89**, 093103 (2006).
[5]S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, J. Appl. Phys. **101**, 093105 (2007).
[6]K. R. Catchpole and A. Polman, Appl. Phys. Lett. **93**, 191113 (2008).
[7]K. R. Catchpole and A. Polman, Opt. Express **16**, 21793 (2008).
[8]V. E. Ferry, L. A. Sweatlock, D. Pacifici, and H. A. Atwater, Nano Lett. **8**, 4391 (2008).
[9]X. Chen, B. Jia, J. K. Saha, B. Cai, N. Stokes, Q. Qiao, Y. Wang, Z. Shi, and M. Gu, Nano Lett. **12**, 2187 (2012).
[10]C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley-Interscience, New York, 1983).
[11]Z. Ouyang, X. Zhao, S. Varlamov, Y. Tao, J. Wong, and S. Pillai, Prog. Photovoltaics **19**, 917 (2011).
[12]T. L. Temple and D. M. Bagnall, "Broadband scattering of the solar spectrum by spherical metal nanoparticles," Prog. Photovoltaics (in press).
[13]T. L. Temple, G. D. K. Mahanama, H. S. Reehal, and D. M. Bagnall, Sol. Energy Mater. Sol. Cells **93**, 1978 (2009).
[14]FDTD solutions (Lumerical, Toronto, Canada).
[15]P. B. Johnson and R. W. Christy, Phys. Rev. B **6**, 4370 (1972).
[16]E. D. Palik, *Handbook of Optical Constants of Solids* (Elsevier, 1998), p. 3227.