Optimized plasmonic nanoparticle distributions for solar spectrum harvesting

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The large optical cross sections of metallic nanoparticles at wavelengths corresponding to their plasmon resonance make them highly attractive for harvesting solar energy for a variety of applications. Here the authors determine ideal distributions of spherical metallic nanoparticles, both nanospheres and nanoshells, that match the AM 1.5 solar spectrum in a mixed component, submonolayer geometry. Both absorbing and scattering distributions are determined and their properties compared to conventional broad spectrum absorbing and scattering media. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2360918]

The advent of nanoscale control of metallic nanoparticle geometries enables scientists and engineers to exploit their intense interaction with light in a wide range of applications, from medicine,[1] to sensing,[2] to light harvesting and energy conversion.[3,4] Since the Sun is our most plentiful source of energy it is of significant technological interest to determine the most effective methods that could be used to harvest that energy. Here we determine optimized distributions of plasmonic nanoparticles for absorbing or scattering the solar spectrum that may be relevant for a variety of energy harvesting or conserving applications.

Spherical nanoparticles such as solid nanospheres and nanoshells are plasmonic nanoparticles of particular interest for solar light harvesting applications, since their spherical geometry allows for interaction with incident light of any polarization. Solid nanospheres have fixed frequency plasmon resonances in the dipole, or quasistatic, limit where the nanoparticle geometry is much smaller than the wavelength of light. For metals such as Au or Ag, these resonances occur in the visible and near UV regions of the optical spectrum, shifting to longer wavelengths with increasing particle size. Nanoshells, consisting of a Au or Ag spherical shell layer surrounding a dielectric (SiO_2) core, have plasmon resonances whose wavelengths are a sensitive function of the relative size of their core and shell layers (Fig. 1).[5] This sensitive dependence arises from the hybridization interaction between the plasmons of the inner and outer metallic interfaces of the nanoshell.[6] The resonance frequencies of nanoshells can be extended from the visible well into the infrared domain.[7] In the quasistatic limit, plasmonic nanoparticles are purely absorptive in character, becoming scatterers with increasing particle size. Therefore it should be possible to determine optimal combinations of nanospheres and nanoshells of various sizes and internal geometries whose absorption or scattering characteristics fit the solar spectrum at the earth's surface.[8]

In order to determine a distribution of nanoparticle absorbers that best approximates the solar spectrum, all unique combinations of two, three, or four nanoshell species were examined. For each combination the downhill simplex method[9] was used to minimize the difference between the spectrum of light that interacts with the nanoparticles and the AM 1.5 solar spectrum. Brent's method[9] was used to independently confirm results for two-component mixtures. The function to be minimized is

$$\int I\left(1-\sum_{R} c_i q_i\right) d\lambda, \qquad (1)$$

where I is the solar irradiance, c_i is the cross sectional area of a two-dimensional projection of particle species i onto a supporting substrate, q_i is the absorption or scattering efficiency of the particle, R is the number of particle species in the mixture, and the integral is taken over wavelength. This equation is minimized using the c_i's as the optimization parameters. The user specifies the total coverage of the particles on the surface as a constant ($\Sigma_R c_i = c_{\text{tot}}$), so there are $R-1$ degrees of freedom in the problem. The total absorption

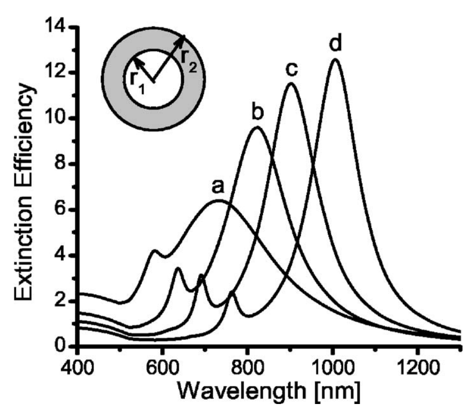

FIG. 1. Plasmon resonances of silica/Au nanoshell structures in water with r_1=60 nm and r_2 = (a) 80 nm, (b) 70 nm, (c) 67 nm, and (d) 65 nm, respectively.

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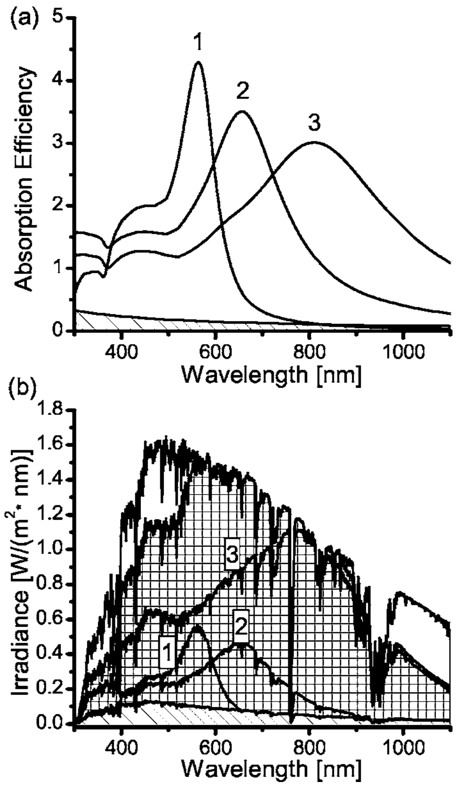

FIG. 2. Optimal nanoparticle mixture for absorbing solar energy. (a) Absorption efficiency of three selected nanoparticle geometries. (1) Au nanosphere, $r=32$ nm. (2) Au nanoshell, $[r_1,r_2]=[28,42]$ nm. (3) Au nanoshell, $[r_1,r_2]=[47,58]$ nm. Diagonal filled curve: absorption efficiency of carbonaceous soot. (b) Predicted optimal absorption of the AM 1.5 solar spectrum for mixture of nanoparticle species from (a) on a silicon substrate in air with surface coverage of 50%. Square cross-hatched curve: total absorbed irradiance of mixture. Diagonal filled curve: absorbed irradiance for carbonaceous soot.

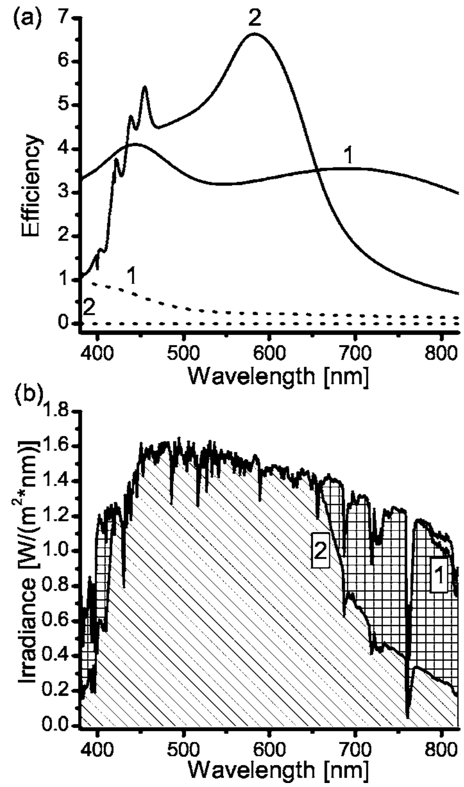

FIG. 3. Optimal nanoparticle mixture for scattering solar energy. (a) Scattering (solid) and absorption (dotted) efficiencies. (1) Solid Ag nanosphere, $r=105$ nm. (2) TiO_2 nanospheres. (b) Optimal scattering of the AM 1.5 solar spectrum for nanoparticles from (a) on glass in air. Surface coverage is capped at 30%. Labels (1) and (2) correspond to the particles from (a).

or scattering cross section for all the particles on the surface is restricted by the inequality,

$$1-\sum_{R} c_i q_i > 0, \tag{2}$$

to ensure that a unit area of the surface does not absorb or scatter more light than is incident upon it. If the inequality is false for a given wavelength, the absorbed or scattered light is capped by whatever is available in the AM 1.5 spectrum.

Mie theory[10] was used to calculate the absorption or scattering efficiency of each particle species assuming dilute suspensions in a homogenous effective medium that partially corrects for the presence of a supporting substrate.[11] The effective medium was an average of the dielectric function of the substrate and air, weighted by their respective volumes within one particle radius.[12] We also neglect the possibility that scattered light is subsequently absorbed by adjacent nanoparticles.[13]

The first scenario we examined was the absorption of AM 1.5 sunlight using a nanoparticle sensitized silicon surface with air ambient, a geometry relevant for solar cell applications.[4] Surface coverage of 50% was required to absorb most of the light. Both Au and Ag particles were tested, and the dielectric functions for Au, Ag, and Si were obtained from standard literature sources.[14]

The optimal solar spectrum absorber determined in our analysis is a mixture of plasmonic nanoparticles composed of three species: (1) Au nanospheres of $r=32$ nm at 35.9%, (2) Au nanoshells of $[r_1,r_2]=[28,42]$ nm at 22.8%, and (3) Au nanoshells of $[r_1,r_2]=[47,58]$ nm at 41.3%. For this distribution, we find that 678 W/m^2 out of 805 W/m^2 available is absorbed [Fig. 2(b)]. The 127 W/m^2 not absorbed in the model is predominantly at the low energy side of the spectrum, where nanoparticle aggregates would likely provide additional absorption due to interparticle coupling effects.[15] The percentages of surface coverage due to this distribution are (1) 8.5%, (2) 9.3%, and (3) 32.2%, respectively.

We examined how such an optimized solar spectrum absorber compares to a conventional absorber coating, such as black paint. For an equitable comparison we considered a submonolayer of "paint" particles with total surface coverage equal to 50%. Black pigment is typically composed of carbon,[16] and Mie scattering theory is commonly used to describe clusters of soot.[17] For our comparative analysis we modeled black paint as a layer of dispersed, small (20 nm), spherical soot particles.[18]

Figure 2(a) shows the absorption efficiency of carbon soot from 300 to 1100 nm. The optical behavior is relatively flat across the wavelength region of interest. The black color of soot originates from this even and smooth absorption spectrum. However, the optical efficiency is extremely low: at 50% surface coverage, only 48 W of 805 W available per square meter is absorbed [Fig. 2(b)]. While a realistically thick coat of black paint may have absorptivity greater than 90%,[19] for the case of broadband solar energy absorption with sparse surface coverage, the plasmonic nanoparticle distribution determined here is far more absorptive than a layer of black carbon particles.

The optimal nanoparticle distribution for solar spectrum visible light scattering was also determined. Here we addressed the specific case of nanoparticles on a glass substrate in air, optimized for wavelengths between 380 and 820 nm. Initially, we permitted total surface coverage to be 40%, but we found that 30% coverage is sufficient to scatter almost all of the incident irradiation. Our analysis determined that optimal solar scattering could be achieved with a single species of silver colloid with a radius of 105 nm, scattering 571.5 W/m^2 out of an available 578 W/m^2 (Fig. 3).

Here also we compare the scattering properties of our optimal plasmonic nanoparticle distribution with the scattering properties of TiO_2 nanoparticles, the primary scattering component in white paint.[16] The scattering spectrum of TiO_2 (rutile phase)[20] is shown in Fig. 3(a). Titanium dioxide does not scatter the low energy light well, and with 30% surface coverage it scatters 458 W/m^2, as shown in Fig. 3(b). However, TiO_2 will still appear more brilliantly white than silver colloid because its absorption spectrum is nearly zero for all visible wavelengths [Fig. 3(a)].

In conclusion, we have applied a straightforward optimization model to determine the most effective nanoparticle component distributions for single layer films of plasmonic nanoparticles that would either absorb or scatter the AM 1.5 solar spectrum. These studies demonstrate the potential for the nanoengineering of light harvesting for solar energy applications using plasmonic nanoparticles, for particle sizes, geometries, and substrates that may be relevant for a range of devices and applications.

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