In silico design of metal-dielectric nanocomposites for solar energy applications

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Recently, a homogenization procedure has been proposed, based on the tight lower bounds of the Bergman-Milton formulation, and successfully applied to dilute ternary nanocomposites to predict optical data without using any fitting parameters [Garcia et al. Phys. Rev. B, 75, 045439 (2007)]. The procedure has been extended and applied to predict the absorption coefficient of a quaternary nanocomposite consisting of Cu, Ag, and Au nanospheres embedded in a SiO\textsubscript{2} host matrix. Significant enhancement of the absorption coefficient is observed over the spectral range 350-800 nm. The magnitude of this enhancement can be controlled by varying the nanosphere diameter and the individual metal volume fraction with respect to the host matrix. We have determined the optimal composition resulting in enhanced broadband (350nm-800nm) absorption of the solar spectrum using a simulated annealing algorithm. Fabricating such composite materials with a desired optical absorption has potential applications in solar energy harvesting.

I. INTRODUCTION

Judicious selection of the materials used for a given photonic application is of paramount importance in tailoring the desired optical properties of a composite material [1]. Light waves, when directed to the interface between a metal and a dielectric are capable of a resonant interaction with the mobile electrons present at the surface of the metal, giving rise to surface plasmons, i.e. density waves of electrons that propagate along the interface [2]. Similarly, such nanocomposites offer much potential in designing materials with enhanced light absorption due to the local electromagnetic field enhancement from the surface plasmon resonances that occur at the metal-dielectric interface [3]. The wavelength-dependent absorption of such metal-dielectric nanocomposites can be tuned by varying parameters such as the shape, size and volume fraction of the nanoparticles as well as the dielectric constants of the host and metal [4, 5, 6]. The increasing emphasis on renewable energy sources has generated interest in finding cost-effective ways of enhancing the efficiency of solar energy harvesting systems. One promising route is the use of metal nanoparticles or nanocomposite coatings as an absorbing layer on silicon devices, thereby giving rise to photocurrent enhancement that correlates well with the plasmonic response of the applied coating [6, 7, 8].
While consideration of the effects of electromagnetic scattering due to the coating morphology on the device performance needs to be addressed [8], optimization of the absorption of incident solar energy though design of an absorption coating is a critical step in the development of improved solar absorbing materials. Recently, we have developed and validated against experimental data a hierarchical homogenization procedure capable of accurately predicting the absorption characteristics of multi-metal/dielectric nanocomposites [9]. Typically, optical analysis and experimentation in the literature are limited to nanocomposites with one or two differing species [5, 7, 8, 10, 11]. Here, we show that by employing the above homogenization procedure each metal added in the dielectric host introduces an added degree of freedom from which the optical response of a multi-metal nanocomposite material may be tailored. In particular, we demonstrate how a Cu:Ag:Au-SiO$_2$ nanocomposite might be used as an absorption coating optimized to the solar spectrum via the manipulation of parameters such as volume fraction and particle size. The ability to design such materials from first principles can guide future experimental efforts aimed at controlling particle size and spacing in techniques such as laser-induced dewetting [12, 13, 14], ion implantation [10, 11], and laser-assisted chemical vapor decomposition [15, 16].

II. HOMOGENIZATION PROCEDURE AND NANOCOMPOSITE SPECTRAL RESPONSE

The Bergman-Milton formula [17, 18] for the effective dielectric constant for a binary metal-dielectric composite is given by:

$$
eff(\gamma) = \left[ \frac{f_a}{\epsilon_a} + \frac{f_h}{\epsilon_h} - \frac{2 f_a f_h (\epsilon_a - \epsilon_h)^2}{3 \epsilon_a \epsilon_h \left[ \epsilon_h \gamma + \epsilon_a (1 - \gamma) \right]} \right]^{-1}$$

where $f$ corresponds to the component’s volume fraction, $\epsilon$ is the component’s dielectric constant with subscripts $a$ and $h$ referencing the metal and host matrix respectively. $\gamma$ is a geometrical factor taking into account the shape of the metal particles. For the purposes of this paper we are interested in spherical particles and accordingly choose $\gamma = \frac{2}{3}(1 - f_a)$. Equation (1) denotes the effective dielectric function for the two component case of a metal particle embedded in a host dielectric matrix. Note it is customary to let $f_h = 1 - \sum f_n$ where $f_n$ corresponds to the metal components. In Fig. 1 the effective absorption coefficient, $\alpha = \frac{2\pi}{k \sqrt{\epsilon_{eff}}}$, $\text{Im}(\epsilon_{eff})$ where $\lambda$ is the wavelength of incident electromagnetic energy, of a single metal species of either Ag, Au, or Cu embedded in a dielectric SiO$_2$ matrix is presented. The effective absorption coefficients of Ag and Au in SiO$_2$ have the desirable property of exhibiting strong absorption near their plasmonic resonances; although this response is localized at 414 nm and 529 nm for Ag and Au nanoparticles respectively. Cu embedded in SiO$_2$ exhibits a rather broad spectral response spanning
from 200 nm to 645 nm. However, the maximum obtainable magnitude of the effective absorption of
the Cu-SiO$_2$ system is clearly weaker than that of Ag-SiO$_2$ and Au-SiO$_2$. Quantitatively, over the range of
wavelengths spanning from 225 to 1200 nm, the Cu, Ag, and Au in SiO$_2$ systems in Fig. 1 have an integrated
absorption $I = \int_{225 \text{nm}}^{1200 \text{nm}} \alpha d\lambda$ of 0.229, 0.338, and 0.203 (unitless) respectively. Thus, Ag exhibits the
most enhancement over the spectral range, but this enhancement is localized and may not be the optimum
response for a given application.

For our proposed design, we limit the analysis to a dilute system (i.e. total volume fraction of metal
versus dielectric $\leq 10\%$) because it is desirable from a practical standpoint of cost and fabrication efficiency.
A second constraint we have placed is to set the minimum nanosphere diameter to be no less than 10 nm.
Above this size regime, quantum confinement effects may be neglected [19]. Moreover, nanoparticles of
size $> 10$ nm can be assembled on SiO$_2$ substrates using robust nanomanufacturing techniques such as laser-
induced dewetting [12, 13, 14], ion implantation [10, 11], and laser-assisted chemical vapor decomposition
[15, 16]. In Fig. 2, the homogenization procedure is presented for a dilute 3-metal mixture in a host
dielectric matrix. The top level represents the effective dielectric function for the target nanocomposite of
design interest. At each level, the total volume fraction is constrained so $f_h + \sum f_n = 1$. The schematic
for homogenization of a 2-metal mixture and alloys in a host dielectric matrix has been presented elsewhere
[9]. Here, the 2-metal mixing rule is extended to treat the quaternary system by viewing each component as
having an effective permittivity $\varepsilon_{a,h}^{\text{eff}}$, $\varepsilon_{b,h}^{\text{eff}}$, and $\varepsilon_{c,h}^{\text{eff}}$. During the mixing process, the average electric field
within the composite is held constant while the final effective permittivity is calculated using equal volumes
at each level of mixing. As described in Ref. [9], the effective permittivity of an N-component mixture
can be determined by mixing N-1 binary mixtures, each comprising of a host and a distinct metal, the host
being common to the N-1 pairs.

The nanoscale effect of change in the electron relaxation time due to scattering of electrons on the
metal-dielectric interface can be quantified via a modified Drude model [20] expressed by Eq. 2

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{\nu_F}{2d_n}$$

(2)

where $\tau_{\text{eff}}$ is the effective electron relaxation time, $\tau_{\text{bulk}}$ is the bulk electron relaxation time, $d_n$ corresponds
to the particle’s diameter and $\nu_F$ is the Fermi velocity of the electrons. The size effect may then be accounted
for by modifying the imaginary portion of the effective dielectric coefficient [9] as follows

$$Im(\varepsilon_a) = \frac{\omega^2}{\omega^2 \tau_{\text{eff}}} = Im(\varepsilon_{a}^{\text{bulk}}) \left( \frac{2d_n + \nu_F \tau_{\text{bulk}}}{2d_n} \right)$$

(3)
where $\omega_p$ is the plasmon frequency and $\omega$ is the angular frequency of the incident electromagnetic energy. By exploiting this nanosize effect, one is able to broaden the plasmonic peaks at the expense of their magnitude as demonstrated in Fig. 3.

Ag and Au embedded in SiO$_2$ exhibit very intense absorptions near their plasmonic resonance. On the other hand, the spectral response of Cu is broadband, extending into the range of green light. The net effect of mixing these particular materials allows one to achieve a wide degree of freedom in choosing the spectral response of the composite. Fig. 4 shows the nonlinear response of the composite system as a function of variations in the volume fraction. Here the volume fraction of each metal is permuted between 6%, 3%, and 1% while the size of the particles is fixed at 15 nm. Changing volume fraction results in a nonlinear change in the wavelength dependence absorption. Further, decreasing the diameter of a given metal broadens the spectral behavior of the metal’s plasmon resonance at the expense of absorption magnitude. Fig. 5 shows the trade-off between spectral broadening and plasmon resonance magnitude. To demonstrate the wide degree of control of this particular quaternary system, Fig. 5 presents examples of manipulating magnitude over the spectral range as a designer might do for a given application. Our mixing approach predicts the intrinsic spectral behavior of the nanocomposite with certain volume fraction ratios and particle diameters. Extrinsic parameters, such as the actual composite volume and area exposed to solar irradiation, determine the magnitude of solar energy absorbed.

III. OPTIMIZATION

Towards designing the initial framework of an solar-harvesting device, we have used a simulated annealing algorithm [21, 22, 23] to determine the optimum composite configuration. We define the “energy” to be minimized as $E(f, d) = \sum \abs{(s_i - \alpha_i(f, d))}$ with composite parameters $f = f_1, f_2, \ldots, f_n$ and $d = d_1, d_2, \ldots, d_n$. $s_i$ and $\alpha_i$ represent the normalized solar spectrum data [24] and effective nanocomposite absorption at a given wavelength $i$ respectively. Since the majority of the solar energy is concentrated in the visible band (see Fig. 6), we only define this “energy” for $i$ spanning from 350 to 800 nm. This choice of $E$ allows for the absorption profile that most closely resembles the shape of the solar spectrum to be determined. The algorithm begins by initializing the system to some initial state $E^s(f, d)$. A neighboring state $E^n$ is called by using the condition

$$E^n(f^n, d^n) = E^s(f + \Delta f, d + \Delta d)$$

where $\Delta f = f_{\text{max}} \times x$ with $x$ being a vector of dimension $n = 3$ with each component taking a random value between $\{-1, 1\}$. $f_{\text{max}}$ represents the maximum magnitude the volume fraction of a particular species
may step. Similarly, $\Delta d = d_{\text{max}} \cdot x$ with $d_{\text{max}}$ representing the maximum magnitude the diameter of the particles corresponding to a particular species may step. Here, values of $f_{\text{max}} = 0.1\%$ and $d_{\text{max}} = 0.1$ nm provided sufficient finesse in moving through the search space. Next, the neighboring state is compared with the best state encountered thus far $E^b$ (where $E^b$ was originally initialized to the same state as $E^s$). If $E^n < E^b$ then $E^b$ is set equal to $E^n$. Then, the algorithm must decide if this neighbor state will become the preferred state for the system. To accomplish this, a Boltzmann-type probability $P$ analogous to classical statistical physics is calculated– namely

$$P = \exp\left(-\frac{(E^n - E^s)}{kT}\right)$$

where $T$ is the annealing parameter analogous to temperature and $k$ is a constant used to refine the annealing schedule. Note that if $P > 1$ then $P$ is simply reassigned to 1. $P$ is then compared to a random number $x$ between $\{0, 1\}$. If $x < P$ then $E^n$ is accepted as the new system state and $E^s(f, d) = E^n(p^n, d^n)$. Notice from Eq. 5 that if $E^n < E^s$, then the neighboring state is always accepted as the new system state. The process of calling neighbor states and deciding whether or not to accept them as system state is repeated over $C$ cycles. This represents a random walk of $C$-steps through the $\{f, d\}$ parameter space. For optimization calculations performed here, $C$ was chosen to be 500 as for values greater than this no appreciable difference in the results was observed. At each iteration of the algorithm, only values in the dilute regime and outside the realm of quantum effects were accepted (i.e. $\sum f_n \leq 0.1$ and $d_n \geq 10$ nm were enforced at each step). In addition, the maximum particle size was constrained to $d_n \leq 30$ nm as mentioned above and only physically realizable values of volume fractions were permitted ($f_n \geq 0$). If the algorithm suggested a neighbor state outside the allowable domain, a large value was assigned to the energy ($E^n \sim 10^8$). This, by virtue of Eq. 5 gives a very low probability for such states to be accepted. Finally, $T$ is reduced and the entire process repeated again. $T$ is reduced according to a prescribed schedule until it is nearly equal to zero after $N$ iterations. Notice that as $T$ is slowly reduced the system begins to accept lower and lower energy configurations until the it is forced to into a (global) minimum. For calculations conducted here, the annealing schedule prescribed was $T_N = (1-\mu)T_{N-1}$ where $\mu = 0.99$ using $N = 1000$ iterations. The initial value of $T$ was chosen so that the probability of the algorithm proceeding from a lower state to a higher state and vice versa was approximately the same. This ensured that the search space was relatively large during the initial stages of the anneal. A value of $T = 100$ with $k = 0.1$ was used for simulations here. Typically, $f = < 3.0\%, 3.0\%, 3.0\%>$ and $d = < 15.0nm, 15.0nm, 15.0nm>$ was taken as an initial guess. When numerical parameters were determined such that different simulation runs yielded the same answer (within a tolerance of $\Delta E \sim 10^{-7}$), different initial states where chosen and simulations ran again. This was done to verify that the algorithm had, in fact, determined the system configuration
yielding the global minimum. The optimized configuration is presented in Fig. 6 with material parameters 1.80%Cu:0.35%Ag:6.4%Au with respective particle diameters of 10.1 nm, 29.6 nm and 10.0 nm.

IV. CONCLUSION

In summary, we have extended our homogenization procedure to quaternary nanocomposites. This procedure yields an analytic expression that acts as a constraint for tuning the spectral characteristics of the nanocomposite system. Via manipulation of metal volume fraction and nanoparticle diameter, one is able to tune the spectral response over the degree of freedom allowed by the nanocomposites’ constituents. We note the selection of Ag, Au, and Cu in SiO$_2$ allows for a controllable broadband filter with a wide degree of freedom over a spectral range of 350-800nm. Furthermore, we have shown how a nanocomposite of this type maybe optimized to offer a promising potential application as an absorption coating on solar devices.

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Figure 1: The wavelength-dependent response of single species of 30 nm diameter nanoparticles embedded in SiO$_2$. Ag and Au exhibit strong optical absorption at 414 nm and 529 nm respectively. Cu in SiO$_2$ yields a fairly broad resonance spanning from 200 nm to 645 nm.

Figure 2: Schematic of nanocomposite mixing rule to find effective dielectric constant for the case of dilute quaternary metal-dielectric system.
Figure 3: Dependence of composite absorption on particle size calculated from homogenization procedure. The volume fractions of the metal species are held fixed at 3%. The size of the nanoparticle diameters are permuted between 10 nm, 15 nm, and 20 nm. Decreasing the diameter of a given metal broadens the spectral behavior of the metal’s plasmon resonance at the expense of absorption magnitude.

Figure 4: Dependence of absorption on volume fraction calculated from homogenization procedure. The nanoparticles for all metal species are held fixed at 15 nm. The volume fraction of each metal species is permuted between 6%, 3%, and 1%. The ensuing nonlinear response of the effective medium’s absorption coefficient is shown.
Figure 5: Manipulation of broad-band absorption for a dilute Cu:Ag:Au-SiO$_2$ mixture. The only constraint is that the nanoparticle diameter lie between 10 nm and 30 nm. The spectral response can be tailored to a given application fairly precisely over the spectral range of 350-800nm.

Figure 6: Optimized absorption of the solar spectrum for a Cu:Ag:Au-SiO$_2$ nanocomposite. The optimal composition of the system was found to be 1.80%Cu:0.35%Ag:6.40%Au with respective particle diameters of 10.1 nm, 29.6 nm and 10.0 nm. Spectral data curve fit is plotted in arbitrary units for visualization.