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Optical absorption of carbon-gold core-shell nanoparticles

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ABSTRACT

In order to enhance the solar thermal energy conversion efficiency, we propose to use carbon-gold core-shell nanoparticles dispersed in liquid water. This work demonstrates theoretically that an absorbing carbon (C) core enclosed in a plasmonic gold (Au) nanoshell can enhance the absorption peak while broadening the absorption band; giving rise to a much higher solar absorption than most previously studied core-shell combinations. The exact Mie solution is used to evaluate the absorption efficiency factor of spherical nanoparticles in the wavelength region from 300 nm to 1100 nm as well as the electric field and power dissipation profiles inside the nanoparticles at specified wavelengths (mostly at the localized surface plasmon resonance wavelength). The field enhancement by the localized plasmons at the gold surfaces boosts the absorption of the carbon particle, resulting in a redshift of the absorption peak with increased peak height and bandwidth. In addition to spherical nanoparticles, we use the finite-difference time-domain method to calculate the absorption of cubic core-shell nanoparticles. Even stronger enhancement can be achieved with cubic C-Au core-shell structures due to the localized plasmonic resonances at the sharp edges of the Au shell. The solar absorption efficiency factor can exceed 1.5 in the spherical case and reach 2.3 in the cubic case with a shell thickness of 10 nm. Such broadband absorption enhancement is in great demand for solar thermal applications including steam generation.

1. Introduction

Small particles can strongly interact with electromagnetic waves, resulting in enhanced absorption and scattering, especially when plasmonic resonances are excited. It is well known that metallic nanoparticles exhibit localized surface plasmon resonance (LSPR), enabling applications for biochemical imaging, medical diagnostics, and photothermal therapy [1–6]. Effects of composition, size and shape of metal nanoparticles on the resonance wavelength and absorption (or scattering) spectrum have been extensively investigated [5–8]. The enhancement in optical scattering and absorption by dielectric-metal core-shell nanoparticles over metal spheres has been modeled theoretically and demonstrated experimentally [9–13]. The scattering enhancement by exciting LSPR at the surface of metallic nanoparticles can also boost the efficiency of photocurrent generation in photodetectors and solar photovoltaic cells [14–17].

Another important application of nanoparticles dispersed in liquids is for solar thermal energy conversion by creating a highly absorbing "black" liquid, which absorbs solar radiation volumetrically for flat-panel or concentrated solar collectors [18–22]. Photothermal effects can enable steam generation using solar radiation or a laser source [23–29]. For solar thermal applications, increasing the resonance absorption peak and broadening the absorption band are equally important. Otanicar et al. [19] experimentally tested nanofluids with water as the base fluid and three types of fillers made of graphite nanospheres, carbon nanotubes, and silver nanospheres. Subsequently, they demonstrated an enhancement in solar collector efficiency. Lee et al. [30] predicted the absorption coefficient of nanofluids embedded with SiO_2-Au core-shell nanoparticles and showed a strong improvement over nanofluids made of metal spheres. Lv et al. [31] used the dipole approximation to study radiative properties of Si-Au core-shell structures and demonstrated that a redshift of the absorption peak can enhance the overall solar absorption. The redshift due to the increased refractive index of the dielectric core has also been shown for Si and Ge cores based on Mie theory [32]. Xuan et al. [33] experimentally demonstrated an absorption enhancement, at wavelengths from 200 nm to about 800 nm, in nanofluids with TiO_2-Ag core-shell nanoparticles. The influence of asymmetric core-shell nanoparticles (i.e., when the dielectric core is not fully wrapped by

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the metallic shell) on the plasmonic resonance absorption of TiO_2-Ag nanoparticles has also been studied theoretically [34].

It is well known that carbon-related materials, such as soot particles, graphite flakes, carbon nanotubes, and graphene nanoplatelets have broadband absorption properties. Due to the electronic transitions between $\pi-\pi^*$ bands, these materials exhibit a strong absorption from the ultraviolet to the infrared and appear black to human eyes [35–38]. Sani et al. [39] showed that carbon nanohorns in aqueous suspensions can improve both the thermal conductivity and light absorption of nanofluids. Han et al. [40] demonstrated enhanced solar absorption with carbon black aqueous nanofluids. Luo et al. [22] experimentally tested several different nanofluids including oxides and observed that graphite nanoparticles are the most effective in terms of boosting the photothermal efficiency. Vakili et al. [41] showed that nanofluids with graphene nanoplatelets can increase both thermal conductivity and optical absorptivity. Lim et al. [42] observed an enhanced photothermal effect for metallic nanoparticles coated with reduced graphene oxide.

In order to increase both the absorption peak height and bandwidth, it is natural to consider the combination of a broadband absorbing material (e.g., carbon) with a plasmonic resonance material (e.g., noble metal). While there have been some activities in fabricating carbon-metal or metal-carbon core-shell nanoparticles [43,44], little has been done to analyze the absorption enhancement by C-Au core-shell nanoparticles. The objective of the present study is to calculate the absorption enhancement in the visible and near-infrared from 300 nm–1100 nm for C-Au core-shell nanoparticles for solar photothermal applications. Both spherical and cubic nanoparticles are considered. We use Mie theory to calculate the spectral absorption efficiency factor (AEF) for the spheres and spherical core-shell nanoparticles. For cubic nanoparticles, we employ a finite-difference time-domain (FDTD) method. The electric fields are also calculated at the resonance wavelengths to illustrate the LSPR and its effect on the absorbed energy distribution. Furthermore, the solar absorption efficiency factor (SAEF) is defined to characterize the effective solar energy absorption efficiency of a single particle based on the integration of the spectral AEF using the solar spectral irradiance as a weighting function. The SAEF can be used as a figure of merit for solar absorption enhancement by nanoparticles.

2. Model description

For spherical particles, Mie theory can be used to calculate electric field distributions as well as absorption and scattering efficiency factors [45]. Aden and Kerker [46] first derived an analytical solution of the electromagnetic fields and scattering parameters of a coated sphere. Exact solutions for multilayered or stratified spherical particles have also been derived [47,48]. The AEF of a spherical core-shell nanoparticle with radii r_1 and r_2 at a given vacuum wavelength λ can be expressed by an infinite series:

$$Q_{\text{abs}} = \frac{2}{x_2^2}\sum_{n=1}^{\infty}(2n+1)\left[\text{Re}(a_n+b_n)-|a_n|^2-|b_n|^2\right] \tag{1}$$

Here, the geometric parameter $x_2 = 2\pi r_2 n_m/\lambda$ where n_m is the refractive index of the incident medium (i.e., water in this work), and the scattering coefficients a_n and b_n depend on optical constants of the materials and reduced radii as expressed in Ref. [45]. In practice, the number of terms that is sufficient for convergence is given by $N = x_2 + 4.3x_2^{1/3} + 1$ [45]. Note that AEF is the ratio of the absorption cross-section to the geometric cross-section. For small particles, the AEF Q_{abs} can exceed one, which is the far-field blackbody limit according to geometric optics. The calculation of the electric field distribution is more involved. Detailed expressions for the electric field inside the core and shell of a spherical particle and the Mie coefficients can be found in Refs. [45–49]. We developed an algorithm in MATLAB based on the formulas given by Pluchino [49] to calculate the electric field distribution as well as absorption, scattering, and extinction efficiency factors. Note that absorption cross-sections of individual regions or layers of a stratified spherical particle can also be defined [47]. In the present study, only the overall AEF of the core-shell is used to characterize the absorption enhancement of the nanoparticles. For a solid nanosphere, one can set the inner radius to zero and the outer radius to the sphere radius r to calculate the AEF and the electric field distribution. It is assumed that all the surfaces and interfaces are smooth enough without any corrugations.

The magnitude and the direction of the rate of electromagnetic energy propagation at any point in space can be described by the Poynting vector $\mathbf{S} = \mathbf{E}\times\mathbf{H}$, where the electric field $\mathbf{E}$ and magnetic field $\mathbf{H}$ are related via Maxwell's equations. For a harmonic field, the time-averaged Poynting vector can be expressed as $\langle\mathbf{S}\rangle = \frac{1}{2}\text{Re}(\mathbf{E}\times\mathbf{H}^*)$ where the * denotes the complex conjugate [45,50]. The Poynting theorem describes the energy conservation for electromagnetic field inside a material. For a nonmagnetic material, it can be expressed as follows [50]:

$$-\nabla\cdot\mathbf{S} = \frac{\partial}{\partial t}\left(\frac{1}{2}\varepsilon_0\varepsilon\mathbf{E}\cdot\mathbf{E}+\frac{1}{2}\mu_0\mathbf{H}\cdot\mathbf{H}\right)+\mathbf{E}\cdot\mathbf{J} \tag{2}$$

where ε_0 and μ_0 are the vacuum permittivity and permeability, respectively, and $\varepsilon = (n+ik)^2$ is the dielectric function of the material with n and k being the real and imaginary parts of the refractive index (also known as the optical constants). In Eq. (2), the left side represents the energy flow into the differential small control volume, the first term on the right (time derivative) denotes the change in the stored energy, and the second term on the right is the power dissipation that generates Joule heating, which is related to the photothermal conversion process. Because the time average of the time derivative terms on the right is zero under steady-state conditions, one can integrate the Poynting vector along the enclosure boundaries of a finite control volume or integrate the dissipation density $\mathbf{E}\cdot\mathbf{J}$ over the control volume to determine the heat generation. It can be shown that the time-averaged power dissipation density takes the following form [51,52],

$$w = \frac{1}{2}\varepsilon_0\omega\varepsilon''(\omega)|\mathbf{E}|^2 \tag{3}$$

where ω is the angular frequency and ε'' is the imaginary part of the dielectric function of the material. The power dissipation density distribution can help explain the resonance or non-resonance local absorption [52]. Furthermore, integration of the power dissipation density allows the distinction of the contribution to the AEF by the core from that by the shell.

One of the most commonly used methods for numerically solving Maxwell's equations is the FDTD method, originally introduced by Yee [53]. The basic idea is to use the Yee cell to transform Maxwell's equations into a set of linear algebraic equations that can be solved numerically. With the introduction of the perfect matching layer (PML) boundary conditions [54] and other algorithmic developments, FDTD has become a well-accepted method for solving electromagnetic wave interactions with nanostructures and near-field thermal radiation due to its flexibility and accuracy [55,56], especially for nanostructures with arbitrary shapes. Since the Yee cell method is based on fixed mesh size, for curved boundaries one has to use either a staircase discretization or a conformal mesh technique [57]. In the present study, commercial software (Lumerial FDTD Solutions) is employed to calculate the absorption properties and field distributions mainly for cubic nanoparticles [58]. For nanostructures with strong plasmonic interactions between metal and a dielectric, care must be taken to