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Optical properties of hybrid plasmonic nanofluid based on core/shell nanoparticles

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ABSTRACT

The plasmonic effect is used in nanofluid to help capture and absorb sunlight. The optical absorption is significantly enhanced as plasmonic effect excited. To obtain an enhanced absorption in a broad band, the hybrid plasmonic nanofluid is developed. It is composed of core/shell nanoparticles of different sizes. The overall absorption of hybrid nanofluid is examined. Compared to the nanofluid of single particle size, the hybrid nanofluid exhibits a broadband absorption. As particle size increases, the plasmon resonance peak is shifted to longer wavelength. The variation in the sizes of core/shell nanoparticles can broaden the absorption spectrum. In the near-infrared region, the proportion of different size particles has an obvious influence. With the increase of proportion of larger particles, the absorption band is broadened. Since the suspended nanoparticles have different sizes, the particle distribution in base fluid also has an effect on absorption of light. The large particle in upper has a broadband absorption, however, less energy can be transmitted to lower after the absorption of upper particles. The contribution from the particles in lower is relatively weak.

1. Introduction

Metal nanoparticles which have unique optical properties, especially when electrons are collectively oscillated, have been widely studied. The collective resonance effect of electrons is excited when the frequency of incident light is consistent with that of electrons. This resonance effect around nanoparticles is called localized surface plasmon resonance (LSPR) [1,2], and the nanoparticles are called plasmonic nanoparticles. As LSPR effect is excited, light is confined to the plasmonic nanoparticles. Electric field around the nanoparticles is significantly enhanced, leading to a considerable amount of heat generated in particles [3]. LSPR effect is usually employed in solar harvesting applications, such as solar thermal collectors. The volumetric solar thermal collectors, using nanofluid as working fluid directly absorb sunlight to avoid indirect thermal loss by solar thermal collectors based on surface absorption. In Tyagi and co-workers' study [4], the efficiency of volumetric solar thermal collector based on aluminum nanofluid is found to be up to 10% higher than that of a flat-plate collector. The photo-thermal conversion efficiency is strongly dependent on the absorption properties of nanofluids. Nanofluid supporting LSPR effect (plasmonic nanofluid) as working fluid provides an alternative way to enhance light absorption. The solar energy absorbed by the plasmonic nanoparticles is converted to heat and transfer to the surrounding medium, resulting in an increased temperature of nanofluid. For plasmonic nanofluid based on Au nanoparticles, the study [5] shows that the photo-thermal conversion efficiency of base fluid can be increased by 20% just at low particle concentration (i.e., 0.15 ppm).

The absorption peak induced by LSPR effect is sensitive to particle shape, size and concentration [6]. By tuning these factors, the photo-thermal conversion efficiency can be improved. Wen et al. investigate the photo-thermal efficiency of Ag nanofluid with different particle shape and concentration. The light absorption by nanorods is stronger than spherical nanoparticles, and the photo-thermal efficiency is increased from 43% to 61% just at lowest particle concentration (0.0028%) [7]. LSPR effect can induce strong light absorption, but, unfortunately, the absorption peak is just located at resonance frequency with a narrow region. Solar spectrum spans from ultraviolet to near-infrared. In order to enhance light absorption at a broad band, it is desirable to tune the plasmon resonance peak in a wide waveband. Some studies reveal that plasmonic metasurfaces can extend the absorption bandwidths [8]. The variation in the sizes of particles can broaden the absorption spectrum [9]. However, the tune by particle size is limited for bare metal nanoparticles. For Au nanoparticle with size of 5 nm, the LSPR effect is excited at 530 nm. As the size increases to 100 nm, the resonance wavelength is just tuned by 25 nm [10]. However, for core/shell nanoparticles, a broad absorption can be obtained since LSPR excitation can be tuned in a wide waveband by

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adjusting core and shell sizes [11–15]. Correspondingly, the photothermal effect can also be enhanced. The temperature is increased by 45.1 K for a bare 30 nm Au nanoparticle. While for the 30 nm Au nanoparticle coated with a 10 nm SiO_2 shell, the temperature rise is 71.4 K, increased by 58% [10].

Consequently, the hybrid nanofluid composed by core/shell nanoparticles of different sizes has potential in enhancing light absorption in a wide wave band. A number of studies have been conducted on hybrid nanofluid, but, most of them are mainly on the thermodynamic properties [16]. While the studies of hybrid nanofluid on optical properties are still insufficient. Therefore, in this paper, we focus on the optical properties of hybrid nanofluid. The hybrid nanofluid is composed by SiO_2/Ag core/shell nanoparticles of different core and shell sizes. The particles of three different sizes are randomly suspended in water. As particle size increases, the absorption peak is broadened and shifted to longer wavelength. Therefore, the hybrid plasmonic nanofluid is helpful to obtain a broadband absorption from visible to near-infrared region. In this paper, the overall absorption of hybrid nanofluid as well as the absorption properties of suspended nanoparticle are discussed. The discussion on suspended nanoparticles at different position is helpful to understand the influence of depth on overall absorption of hybrid nanofluid.

2. Simulation

2.1. Structural model

SiO_2 core coated with Ag shell forms a composite plasmonic nanostructure. These nanoparticles of different sizes are randomly suspended in water. The core radius is R_1, and the shell thickness is t. In the simulation, the positions of different nanoparticles are generated by random numbers. The distance between adjacent nanoparticles can be adjusted to ensure the particles not overlap. Schematic structural model of this hybrid nanofluid based on core/shell nanoparticles of different sizes is shown in Fig. 1. In order to be convenient for simulation and discussion, the nanoparticles suspended in water have three typical sizes. The nanoparticles of different size have a certain proportion, and the total concentration of hybrid nanofluid is f. As shown in Fig. 1, light irradiates into the nanofluid from the top, and then absorbed or scattered by nanoparticles. Due to the suspended nanoparticles, the light undergoes multiple scattering within the nanofluid.

2.2. Optical simulation

The simulation of optical properties is based on finite difference time domain (FDTD) method, which is an explicit time marching algorithm used to solve Maxwell's curl equations on discretized spatial grids. The hybrid nanofluid is illuminated by a plane wave with a y-polarized electric field propagating along negative z direction. The periodic boundary conditions are imposed at the four surfaces along x and y directions. The period is set to 0.1 μm along x and y directions. When the period varied from 0.1 μm to 0.3 μm, the simulation results are almost the same. Therefore, the value set is reasonable in the simulation. Since particles are randomly suspended, the value of period has little effect on simulation results. At the surfaces along z direction, perfectly matched layers (PML) boundary conditions are imposed to absorb nearly all the incident waves. Based on this FDTD model, the simulation of photon propagation in hybrid nanofluid is performed, and the amount of light reflected and transmitted can be calculated (Fig. 2).

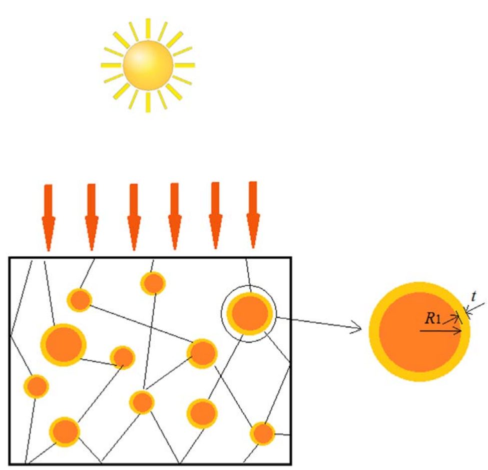

Fig. 1. Schematic structural model of hybrid nanofluid based on core/shell nanoparticles with different sizes.

In FDTD simulation, the discrete dielectric constants from experiment need to be fitted to function. For some materials, just Lorentz model or Drude model cannot describe the materials well. In order to make experimental data and fitted model in good agreement, the models (Lorentz model or Drude model) have to be necessarily corrected. A simple phenomenological model (Lorentz-Drude model) interpreting both the free-electron and the interband parts of the dielectric response is frequently used in FDTD simulation [17]. It can be expressed in the following form:

$$\varepsilon(\omega) = \varepsilon_\infty + \sum_{m=0}^{M} \frac{f_m \omega_p^2}{\omega_m^2 - \omega^2 + i\gamma_m \omega} \tag{1}$$

where ε_∞ is the relative permittivity in the infinity frequency, ω_p is the plasma frequency, M is the number of oscillators with frequency ω_m, strength f_m, and damping factor γ_m. The optical constants of SiO_2 and Ag from Ref. [18] are fitted by Lorentz-Drude model.

The energy density in the nanoparticle can be calculated using Eq. (2), which is proportional to the square of electric field.

$$P_{abs} = \frac{1}{2}\varepsilon_0 \omega \mathrm{Im}(\varepsilon_r)|E|^2 \tag{2}$$

where ε_0 is vacuum permittivity, ω is frequency of incident light, ε_r is the dielectric constant of nanoparticle, E is electric field in nanoparticle. The energy absorbed by the nanoparticle can be calculated by the integral of energy density in particle volume, as shown in Eq. (3):

$$P = \int_V \frac{1}{2}\varepsilon_0 \omega \mathrm{Im}(\varepsilon_r)|E|^2 dV \tag{3}$$

Accordingly, the absorptance α of the suspended nanoparticle can be expressed as Eq. (4). It is a ratio of energy absorbed to energy incident.

$$\alpha = \frac{P}{P_{inc}} \tag{4}$$

where P is energy absorbed by nanoparticle, P_{inc} is the incident energy.

3. Results and discussion

3.1. Optical properties of plasmonic nanofluid of single particle size

It is known that as particle size increases, the plasmon resonance frequency is red shifted. In order to facilitate the analysis, the core/shell nanofluid of three typical sizes (small size, medium size and large size) are studied under the same concentration. The volume concentration of plasmonic nanofluid f is set to 0.01. The optical absorption of plasmonic nanofluid as well as that of a certain suspended nanoparticle in the nanofluid are examined in this paper. The influence factors, like particles size, proportion of different particles, are discussed as well.

Fig. 3 shows the optical absorption of plasmonic nanofluid based on SiO_2/Ag core/shell nanoparticles of single size. They have the same volume concentration. The previous study shown that the optical