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Phase transition induced by localized surface plasmon resonance of nanoparticle assemblies

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ABSTRACT

A numerical model concerning the phase transition and temperature distribution of matrix media around plasmonic nanoparticle assemblies under illumination of monochromatic light is investigated. The critical intensity of incident light for isolated nanosphere, nanodisk, and nanorod to melting the surrounding ice is obtained. For nanospheres and nanodisk dimers, enhancement of photothermal conversion (PTC) is observed. Besides, the phase transition of matrix media is not only influenced by PTC, but also the configuration of nanoparticle assemblies. In particular, we demonstrate that for nanorod dimers arranged end-to-end and side-to-side, the dissipation of light for two nanorods are the same in every polarization angles. The change of polarization angle only influence the overall light-to-heat conversion of the dimer. However, for L geometry nanorod dimer, the dissipation of light are different for the two nanorods. This present a way to manipulate and precisely control of temperature distribution and phase transition in nanoscale by tuning the light polarization angles.

1. Introduction

The photothermal conversion of nanostructures in different morphologies and components have been studied extensively due to their potential application in solar energy harvesting and storage [1–3], photothermal therapy [4–7], nanosurgery [8,9], nanochemistry [10,11], and optofluidics [12]. In these applications, the common basis is to take advantage of the enhanced light absorption induced by the localized surface plasmon resonance (LSPR) of nanostructures, which means when illuminated by light at LSPR wavelength, the nanostructures can absorb more light and convert it into heat. The accompanying thermal accumulation even can lead to phase transition (melting or evaporation) [1,13–15] of the matrix media around nanostructures besides temperature rise. The precisely control of light absorption and temperature distribution in nanoscale is of great importance in those applications.

For the early studies, most scholars focused on the optical properties of nanoparticles. Hunter and Fendler [16] summarized the applications of metal nanoparticles as waveguides, optical transmission, nanophotonic devices and so on. Jain and coworkers [17] did some pioneer works on the optical properties of different kinds of nanoparticles (nanorod, nanosphere, nanoshell, et al.), which are very important and fundamental to the deeper understanding of localized surface plasmon by nanoparticles. Rechberger [18] and Tian [19] investigated the optical interaction between nanosphere and nanorod dimers, respectively. They showed that the configuration of nanoparticle dimers make significant contribution to their spectral optical properties. Funston and coworkers [20] studied the plasmon coupling effect of nanorod dimers with different gap distances and configurations. They found that configurations has significant influence on the optical properties of nanorod dimers duo to the excitation of different coupling modes. However, the photothermal conversion and heat transfer process are not considered in the above mentioned works.

Without considering phase transition, Baffou et al. [21–25] investigated the photothermal effect of single nanoparticles and their assemblies with different morphologies and lattice geometries. In order to obtain the heat generation in a nanoparticle assemblies system, the Maxwell equation needs to be solved. However, when the particles become very close proximity, it will be too memory-consuming to discrete the entire system to get an accurate solution. To solve this problem, they developed a theoretical approach to estimate the temperature distribution for nanoparticles assemblies under illumination. The accuracy of the approach is verified by experiments. Govorov et al. [15,26,27] studied the localized surface plasmon resonance induced phase transformation

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when gold nanospheres are embedded in polymer or ice theoretically for the first time. They developed a theoretical model to solve this multi-physics problem. Based on the proposed model, the collective effect is discussed through analyzing the electric field enhancement and dissipation of light in the nanoparticles trimers, in which a nanosphere dimer is treated as an amplifier to create a hot spot. On this basis, they performed the experiment that shows the temperature and phase change in an ice matrix containing gold nanoparticles when illuminated by laser. For the heat transfer between nanostructures, Ben-Abdallah et al. [28,29] developed the radiative heat exchange theory between an *N*-body system. They derived a Meir-Wingreen-Landauer-type formula for the radiative heat flux through *N*-body interacting photon regions. A detailed study of three-body systems has allowed to identify a many-body exaltation mechanism of heat flux due to configurational resonances.

Beside the above mentioned heat transfer and phase transition problems, the simulation of spectral optical properties of plasmonic nanoparticles is also one of the essential problems that need to be investigated thoroughly. Considering the outstanding characteristics of nanorods in photothermal conversion, Funston et al. [20] studied the coupling effect of nanorod dimers. The anisotropy nature of nanorods leads to different configuration of nanorod dimers. The interaction between two close nanoparticles will affect the LSPR (enhancement or shift of resonance wavelength) [20], which can be exploited in many applications, such as surface-enhanced Raman spectroscopy [30,31], universal plasmon ruler [32], nearfield image [33,34], and subwavelength optoelectronic devices [35–37].

Despite the intensity of the mentioned efforts, the precise prediction and spatially control of phase transition induced by LSPR of nanoparticles assemblies remains challenging. The influence of particle shape and size on the phase transition of matrix media is still unclear. The mechanism of how to adjust and control the temperature distribution and phase transition in nanoparticles assembly system also needs further investigation. In our present work, we focus on the photothermal conversion and asymmetric temperature distribution of different nanoparticle assemblies. The influence of cluster effect on optical and heat transfer is taken into consideration. To start with, the phase transition induced by isolated nanoparticles (gold nanosphere, nanodisk, and nanorod) embedded in ice matrix is studied. The theoretical model for heat transfer and phase change of nanoparticles embedded ice or polymer matrix developed by Govotov and coworkers [15] are applied. Also, their theoretical results are applied to verify our numerical model. The critical intensity required to trigger this phase transition is obtained. On this basis, the temperature distribution and phase transition control of nanoparticle dimer is investigated. We demonstrate that for nanorod dimers arranged end-to-end and side-to-side, the dissipation of light for two nanorods are the same in any polarization angles. However, for L geometry nanorod dimer, the dissipation of light are different for the two nanorods, which indicates that the temperature distribution and phase transition in nanoscale can be manipulated by tuning the light polarization angles.

2. Theory and methods

In the problem under consideration, the gold nanostructure can be regarded as a heat source surrounded by ice. In the present work, we consider the photothermal conversion and phase change process around a gold nanostructure under continuous illumination. Therefore, the Fourier's law is still applicable. The transient heat transfer equation can be expressed as:

$$\rho_{\text{eff}}(\mathbf{r})C_{\text{eff}}(\mathbf{r})\frac{\partial T(\mathbf{r})}{\partial t} = \nabla\cdot[k_{\text{eff}}(\mathbf{r})\nabla T(\mathbf{r})] + Q(\mathbf{r}) \tag{1}$$

where ρ_{eff}, C_{eff}, and k_{eff} are the effective density, heat capacity, and thermal conductivity, respectively. For a steady state problem, heat transfer equation can be simplified as:

$$\nabla\cdot[k_{\text{eff}}(\mathbf{r})\nabla T(\mathbf{r})] = -Q(\mathbf{r}) \tag{2}$$

For a single nanoparticle, the time needed to achieve a steady state is in millisecond or even nanosecond level [15]. And for most of its applications, the total operating time will be a few seconds or minutes. In the present work, we focus on the photothermal conversion and asymmetric temperature distribution of nanoparticle assemblies. How to realize spatial control of temperature distribution in nanoscale is our primary purpose. Therefore, the steady state heat transfer process is investigated.

The heat source $Q(\mathbf{r})$ can be expressed as [38]:

$$\begin{cases} Q(\mathbf{r}) = \dfrac{\omega}{2}\text{Im}\{\varepsilon_{\text{Au}}(\omega)\}|\mathbf{E}(\mathbf{r})|^2, \text{inside the gold nanostructure} \\ Q(\mathbf{r}) = 0, \quad \text{outside the gold nanostructure} \end{cases} \tag{3}$$

where ω is the frequency of laser and ε_{Au} is the dielectric constant of gold. $\mathbf{E}(\mathbf{r})$ is the local electric field intensity, which can be obtained by solving the following equation [39]:

$$\nabla\times\mu_{\text{r}}^{-1}[\nabla\times\mathbf{E}(\mathbf{r})] - k_0^2\left(\varepsilon_{\text{r}} - j\frac{\sigma}{\omega\varepsilon_0}\right)\mathbf{E}(\mathbf{r}) = 0 \tag{4}$$

where μ_{r}, ε_{r}, and σ are the relative permeability, permittivity, and conductivity, respectively. k_0 is denotes the wave number.

According to effective heat capacity method [40], the effective density, heat capacity, and thermal conductivity can be expressed as:

$$\rho_{\text{eff}} = \theta\rho_{\text{l}} + (1-\theta)\rho_{\text{s}} \tag{5}$$

$$C_{\text{eff}} = \frac{1}{\rho_{\text{eff}}}[\theta\rho_{\text{l}}C_{\text{l}} + (1-\theta)\rho_{\text{s}}C_{\text{s}}] + L\frac{\partial\alpha_{\text{m}}}{\alpha T} \tag{6}$$

$$\alpha_{\text{m}} = \frac{1}{2}\frac{(1-\theta)\rho_{\text{s}} - \theta\rho_{\text{l}}}{(1-\theta)\rho_{\text{s}} + \theta\rho_{\text{l}}} \tag{7}$$

$$k_{\text{eff}} = \theta k_{\text{l}} + (1-\theta)k_{\text{s}} \tag{8}$$

where ρ, C, and k stand for density, heat capacity, and thermal conductivity, respectively. The subscript l and s represent 'liquid' and 'solid', respectively. L is the latent heat of liquefaction. θ is the liquid fraction. θ = 1 means the matrix media is in liquid state. θ = 0 means the matrix media is in solid state.

The above effective heat capacity method has an assumption that the phase change is not happened in a specific temperature. Instead, it happens in a certain temperature range, which is not coincident with the melting process of ice. The ice melts at a fixed temperature, which is 273.15 K at pressure of 101 kPa. In the present work, to make this method applicable for this situation, the phase change temperature interval is set as a small value, 0.1 K. To verify the present model, the results using effective heat capacity method are compared with the analytical solutions.

The analytical solution for temperature rise of a nanosphere embedded in ice under the illumination of laser can be expressed as follows [15]:

$$\Delta T(r) = \begin{cases} A - \dfrac{Q\cdot r^2}{6k_{\text{Au}}}, & r \leqslant R_{\text{Au}} \\ B + \dfrac{C}{r}, & R_{\text{Au}} < r \leqslant R_{\text{b}} \\ \dfrac{D}{r}, & r > R_{\text{b}} \end{cases} \tag{9}$$

where k_{Au} is the thermal conductivity of gold. R_{b} is the radius of the interface location of solid–liquid boundary. ΔT is temperature rise.