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Plasmon – plasmon interaction effect on effective medium electrical conductivity (an effective agent for photothermal therapy)

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ABSTRACT

This article presents an investigative study of the photothermal effect of various compound nanoparticles (attaching the several small nanoparticles to a large nanoparticle by linkers). Initially, some compound nanoparticles such as Au-Au nanoparticles were fabricated and the effective medium electrical conductivities, found to vary greatly in gradient with variations in temperature, were analyzed using a nano-lens – based approach. A nano-lens forms when Au-Au nanoparticles interact with electromagnetic waves. More precisely, the interaction of larger nanoparticles with an incident light generates a high intensity plasmonic field around it, and the dramatic effect of this near-field on small nanoparticles leads to the creation of a nano-lens. The modeled and experimental results obtained in this study showed that the Plasmon-plasmon interaction, which leads to the formation of a nano-lens with Au-Au nanoparticles, strongly influenced the medium electrical conductivity which is a vital key for detection of cancer cells. The gradient of electrical conductivity correlated directly with the amount of localized heat generation by Au-Au nanoparticles, offering means by which the temperature could be inferred. The amount of heat generated depended on both the number of nanoparticles present and the effectiveness with which they interacted, particularly in such a high intensity nano-lens.

1. Introduction

Heat can be generated with metal nanoparticles (NPs) as they contain mobile carriers that can be resonated at certain frequencies determined by the structure of NPs. Moreover, this effect becomes significantly enhanced under a plasmon resonance frequency. With plasmon frequency excitation, all of the mobile carriers on NPs resonate as a whole, creating an interesting case for heat generation by NPs. NPs have a very low optical quantum yield and there are several publications describing the calculation of generated heat through the estimation of total optical absorption rate [1–3,5]. With this knowledge, the increases in surface temperatures of NPs can thus be easily measured. Detection of surface temperature changes in NPs is important for nanomedical applications of NPs, such as photothermal therapy [4–6]. It should be noted that the cancer and healthy medium have different electrical conductivity features. In such cases, the relationship between temperature changes and electrical conductivity may be exploited to obtain data about NP photothermal behavior [7–10] and their effect on cancer cells [1–3]. Alterations in the electrical conductivity slope and its gradients can be translated as tangible and quantifiable effects of temperature increases. We speculated that the localized plasmonic heat generation resulting from the interaction of light with NPs will have a severe impact on electrical conductivity. To test this hypothesis we designed a new nanostructure to be used as an effective agent for heat generation. More specifically, we used different nanostructures formed by Au NPs capable of generating extra heat, such as the nano-lenses that are successfully used in photothermal therapies. The biomedical application of heated NPs for the treatment of various conditions is based broadly on simple principles. Functionalized NPs target tumor cells through selective antibody linkers. Once at the target site, these NPs are excited enough to generate sufficient heat for the targeted destruction of tumor cells. The key conditions affecting the success of this process include the surface temperatures of the NPs and the ability to obtain a collective response from the NPs. Due to the potential and significance of such applications; studies investigating the photothermal

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behaviors of NPs have garnered much interest. Inspired by the possibilities of such technologies, we synthesized Au-AU NPs to which small size gold NPs (SFGNPs) electrostatically attached to large size gold NPs (LSGNPs) to produce an efficient nano-lens. The high intensity plasmonic field produced by LSGNPs due to their interaction with electromagnetic waves, dramatically excites the SFGNPs. Stimulating SFGNPs with this near-field will significantly enhance the heat generation capacity of these particles. Moreover, the heat generated by NPs is affected by their interaction with each other, a synergistic NP accumulation effect [5–7,11–16]. It has been reported of late that the magnitude of the near-field intensity amplitude is at least 10 times larger than the incidence wave [13–16]. In the light of these recent findings, the primary aim of our work is to engineer the Plasmon-plasmon interaction in Au-Au NPs such that a sufficient localized heat can be generated using a low intensity incidence, a consequence of which will be the influence it will have on electrical conductivity. In this work we used Multiphysics COMSOL 4.4 to simulate the Au-Au NP interactions with the electromagnetic waves.

2. Mathematics and theory

In this section, we begin by exploring heat generation by NPs and the related temperature changes, by considering NP plasmonic fields and their ultimate impacts on electrical conductivity. When an electromagnetic wave interacts with any NP, the optically excited NP will create heat. In other words, NPs can effectively produce heat under light irradiance, when they are excited by the right wavelength. The mechanism of heat generation by NPs is very simple and can be easily understood; the electromagnetic field strongly drives the mobile carriers of NPs and the energy gained by these carriers is converted into heat. Then, the heat that diffuses away from the NPs leads to an increase in the local temperature in their surrounding environment. It should be mentioned that the heat released by NPs becomes quite strong in the case of plasmonic resonance in metal NPs. The plasmonic resonance depends on several factors such as electromagnetic wavelength incidence, NPs size, type of material, its shape, and the dielectric constant of the medium. In this paper, typical gold NPs with different inter-distance and incidence wavelengths were used. Hence, by manipulating some of the aforementioned parameters, the plasmonic resonance could be altered such that an increase local temperature could be achieved. Moreover, by changing the inter-distance between NPs, the plasmon-plasmon interactions could be improved. In other words, the plasmonics will interact with each other and this interaction can then manipulate the electric and current density in the structure. For this purpose, the magnitude of energy gained by mobile carriers is altered. It has been reported that the temperature distribution around NPs is given by the following heat transfer equation [5,6,16]:

$$\rho(r).c(r).\partial T(r,t)/\partial t = \nabla\kappa(r).\nabla T(r,t) + Q(r,t) \quad (1)$$

where r, t, $T(r,t)$, $p(r)$, $c(r)$, and $\kappa(r)$are the radial coordinate, time, local temperature, mass density, specific heat, and thermal conductivity, respectively. As well as $Q(r,t)$ represents an energy source from wave dissipation in NPs and is obtained through the following equation:

$$Q(r,t) = \langle j(r,t).E(r,t)\rangle_t \quad (2)$$

where $j(r,t)$ and $E(r,t)$ denote the current density and electric field in the system, respectively. To solve Eq. (1), either numerical or exact analytical methods can be utilized. This equation can be modified to suit the case of our study, by considering the high intensity nano-lens near-field effect. We mentioned that in the nano-lens, we exploit the near-field effect to influence SFGNPs, alongside the influence of the incidence wave. This addition causes a serious and effective interaction between NPs and electromagnetic waves. So, in Eq. (2), the energy source could be re-arranged based on summation of $E(r,t)$ and $E_{int}(r,t)$, with the latter denoting the nano-lens near-field. It has been reported that the square of the absolute value of this localized field surrounding NPs can be at least 100 times larger than the incidence field [2,13,16,19]. Hence, this case can have a severe effect on the heat generation capacity of the nano-lens. In the following, substituting Eq. (2) into Eq. (1) and solving it in the steady-state condition, the local temperature around any NPs can be described by Ref. [16]:

$$\Delta T(r) = V_{NPs}.Q(r)/4\pi.\kappa_0.r \quad (3)$$

where r, κ_0, and V_{NP} refer to the NP radius, the thermal conductivity of surrounding medium, and NPs volume, respectively. Here, $Q(r)$ represents an energy source from wave dissipation in NPs due to the incidence wave and plasmonic near-field generated by NPs. Moreover, based on the above-mentioned equations, it can be pointed out that the heat generation rate and temperature enhancement depend on the physical properties of the material. Furthermore, it is indicated that the heat generation efficiency by Au NPs is about 10^{-3} under the plasmonic resonance conditions [5]. This is based on the fact that the NP has a much small diameter than the laser spot-size. Nevertheless, this efficiency and the heat generation capacities of NPs can be optimized by plasmon-plasmon interactions between several NPs. This is attributable to the interaction mechanism between NPs, namely the accumulative effect and Coulomb interaction. The accumulative effect refers to the addition of heat fluxes produced by the NPs and its synergistic outcomes. Comparatively, in the case of Coulomb interaction, the heat generation by NPs is influenced by the interaction of neighboring NPs (nano-lens) so that the total amount of heat generated by the interaction of the two NPs will be different to the amount produced by two single, separate NPs. This is attributed to the partial screening of electric field inside the NPs. Thus, based on the discussion about temperature and its relation to the localized plasmonic generation of NPs, it is appropriate to consider next the relationship between temperature variations and the electrical conductivity of the material. It is a well-known fact that changes in the temperature will impact the mobility of the carriers inside the samples, offering an indirect means by which electrical conductivity can be altered. The basic principle here is that the localized plasmonic greatly affects the carrier's mobility thereby affecting the electrical conductivity. Hence, by easily measuring the sample's resistivity, with careful consideration of electrode positions and their physical dimensions, the electrical conductivity is calculated. With regards to the pervious statement, it should be noted that the main aim is to examine the nano-lens high intensity plasmonic field effect on carrier mobility, an agent for changing electrical conductivity. In fact, by manipulating the electrical field in Eq. (2), the heat generation by NPs can be controlled and this in turn will influence temperature and carrier mobility.

3. Materials and methods

Tetrachloroauric acid trihydrate ($HAuCl_4\cdot 3H_2O$) (99.9+%), Ascoric acid (90–100.5%), Tetrakis (Hydroxymethyl) phosphonium chloride (referred to here after as THPC), and trisodium citrate ($Na_3C_6H_5O_7$) were purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB) was supplied by Merck. Dithiolated-polyethylene glycol (SH-PEG-SH) was synthesized and kindly provided by co-workers in a Polymers Laboratory at Hacettepe University. All