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ENGINEERING THERMOPLASMONIC RESPONSE OF LIQUID AND NOBLE METAL NANOPARTICLES FOR TEMPERATURE ELEVATION AND HEAT GENERATION

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Abstract: In recent years of research, it has been discovered that noble metal nanoparticles, due to their exceptional optical properties, have unique applications in nanoscience. Scientists believe that plasmonic nanoparticles can be utilized as nano heaters, opening new avenues of research at the nanoscale. Plasmonic nanoparticles act as nano heaters that can be controlled remotely by light, resulting in the emergence of an evolving field known as Thermoplasmonic. The goal of all Thermoplasmonic applications is to significantly improve the photothermal conversion of plasmonic nanoparticles, but different sizes of nanoparticles present challenges. The present paper describes the photothermal effect induced by plasmonic nanoparticles of different nano geometry that act as nano sources of heat. Further, basic understanding and some simulation techniques for measuring the heat unleashed by plasmonic nanoparticles at the nanoscale order, as well as recent advances summarized for the application of Thermoplasmonic, specifically to biomedical applications using the photothermal effect, particularly for photothermal cancer therapy, drug and gene delivery, photothermal imaging, and nano-surgery.

***Index Terms* -** Nanoparticles, Plasmonic, Thermoplasmonic, Heat generation.

1. INTRODUCTION

At the nanoscale large surface-area-to-volume ratio is the key feature, so materials compared to their bulk counterpart exhibit different properties be it electric, magnetic, physical or chemical, this change leads to the use of materials in many new ways for practical applications. Enhance optical fields that can be used for bio-imaging, solar cells with high efficiency, and extremely sensitive devices are created by the resonant interaction of electromagnetic light with conducting electrons excitation near metallic surfaces. Michael Faraday published a study in 1857 detailing the first detection of gold nanoparticles for the "ruby fluid" [1]. Plasma is made up of charged carriers, much as free electrons oscillate with regard to the stationary positive charge near the metal surface when exposed to light. The oscillation of free electrons near the metallic surface is quantized by a quasi-particle called a plasmon, like that of photon quantizing light and phonon quantizing mechanical vibration. This collective excitation of free electrons near the surface is supported by materials that exhibit a large negative real and small positive imaginary dielectric constant simultaneously. This excitation is known as Surface Plasmon excitation. Therefore, Figure 1 shows the LSP excited in a plasmonic metal nanoparticle.

The interaction of light and metallic surface involves two fundamental plasmonic excitations Surface Plasmon Polaritons (SPPs) and Localized Surface Plasmons (LSPs). Sekhon et al. determined the plasmonic properties based on LSPR peaks for Au, Ag and Cu nanoparticles in different shapes under various surrounding medium and found LSPR to be highly sensitive even for a minute change in above said parameters. This sensitivity scopes for biosensors and optical sensors devices [2]. Further, LSPR peaks depends on particle size, and it arises due to dipolar plasmon resonance mode in quasi-static approximation. As particle size increased, resonance peaks shifted, and a higher multipole mode appeared. When involving the surrounding medium effect, the resonant requirement for the LSPR to occur according to Mie Theory shows that the real component of the dielectric constant of metal NP decreases with increasing wavelength, and an increase in the dielectric of the surrounding medium leads to a red shift in the LSPR wavelength [3]. The resonance occurs strongly when noble metals are coated with other metals such as Gold (Au) and silver (Ag) which enhances the plasmonic applications due to their ability to support large LSPR over the broad region of EM spectrum. The LSPR based optical properties of noble metal NPs have many potential applications viz., optical imaging, biosensing, solar cells etc. Thus, some pictorial view to different strategies with potential applications is shown in Figure 2 (a, b).

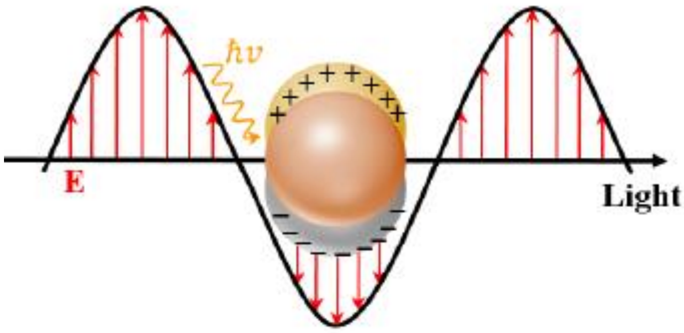

Figure 1. LSP excited in metal nanoparticles.

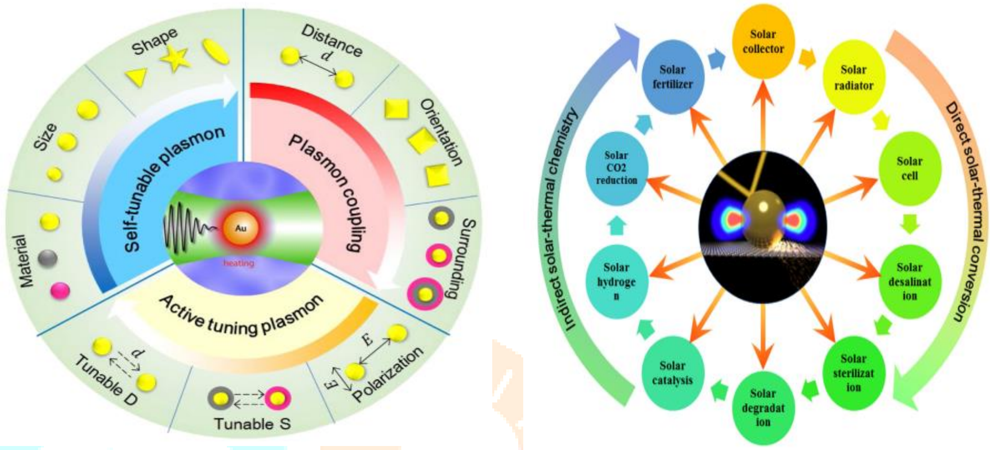

Figure 2. Graphical representation of different strategies with potential applications.

Recent advancements in research and technology demand for devices that can be folded into any shape, this calls for flexibility, portability and reform ability of devices. This research is to find new plasmonic materials that open new applications for tunable and reconfigurable plasmonic devices. Liquid phase NPS exhibits higher surface plasmonic efficiency than solid phase. Liquid metal-based plasmonics has many applications such as cost-effective liquid solar cells, active plasmonics, stretchable electronics 3D printing etc. Plasmonic properties of liquid metals Gallium (melting point 300C) and cesium (melting point 28.50C) have wide practical applications. Gallium is a critical element and shows immense use of liquid gallium to produce high resolution of X-ray scans of organs in Surface Enhanced Raman spectroscopy (SERS), phase change memory devices. Other than Ga compounds, gallium nitrides (GaN) and gallium arsenide (GaAs) are widely used in high-speed switching circuits and solar cells due to their higher efficiency [4]. Cesium (Cs) ions act as an efficient electron-transporting layer in photovoltaics and gas sensing, while Cs compounds are extensively utilised as optical glass and catalytic promoters in vacuum tubes and radiation monitoring systems. The cesium clock (atomic clock) plays a key role in the internet and Global positioning system (GPS) satellites. The absorption LSPR peak intensities are in the UV and visible NIR region of the EM spectrum for base gallium and cesium nanospheres. These peaks can be further tuned or enhanced by coating liquid MNPS with silver into the UV-visible-NIR region of the EM spectrum with varying core size and shell thickness.

2. PROGRESS IN RESEARCH FIELD

The last twenty years' literature has been carried out to highlight the progress in the field of plasmonic and thermoplasmonic with a further scope of research. Link S. et al., 1999 [5] reported that gold-silver alloy nanoparticles were synthesized by a co-reduction of chloroauric acid (HAuCl4) and silver nitrate (AgNO3) with sodium citrate at different mole fractions. They discovered that the maxima of the plasmon band blue shifts linearly with increasing silver content. On the other hand, the extinction coefficient was found to decrease exponentially rather than linearly with increasing gold mole fraction.

Liu et al., 2004 [6] chemically deposited silver on the surface of gold nanorods with varying shell thicknesses in an aqueous solution to create the Au/Ag core/shell nanorods. They conclude that the silver coating, the longitudinal plasmon mode of the nanorods was blue-shifted and enhanced. The line width of core/shell nanorods is about 40-50% broader than the simulation that used bulk dielectric constants, while that of Au nanorods is less than ~10% broader.

Jain P.K. et al., 2006 [7] employed Mie theory and the DDA technique were used to compute the absorption and scattering parameters of gold nanoparticles with varying sizes, shapes, and compositions. When gold nanospheres are sized from 20 to 80 nm, both the extinction's magnitude and the proportional contribution of scattering to it grow quickly. They discovered that the difference in the nanosphere's maximum plasmon wavelength, which is between 520 and 550 nm, will be helpful for in vivo applications.

Amendola V. et al., 2010 [8] investigated, using the discrete dipole approximation, the surface plasmon resonance (SPR) of silver nanoparticles (AgNPs) of various sizes, dielectric environments, and types (spherical, cubic, flat, cylindrical). AgNPs are discovered to be tunable in the 350–700 nm wavelength range. Their findings provided helpful guidance for the engineering of AgNPs with novel plasmonic features as well as for the in-situ characterisation and monitoring of AgNP production.

Bansal A. et al., 2015 [9] demonstrated, using discrete dipole approximation (DDA) simulations, the impact of form, size, and metal type on the optical response of alloy nanoparticles. Research has revealed that nanostructures with sharp corners exhibit better plasmonic characteristics than those with rounder corners. They took into account three different particle shapes: nanocubes, rectangular, and nanobar particles. They also took into account redshifts of the longitudinal plasmon resonance, improvements in the scattering yield, and relative efficiency metrics, with the exception of nanocubes with an edge length of 120 nm and longer. The effect of size on full width at half maxima (FWHM) has also been studied and found to be maximal for nanocubes in comparison to other considered nanostructures.

Bansal A et al., 2016 [10] studied the plasmonic response of Ag-Cu alloy coated with noble metals has been studied using extended Mie theory. Considering the impact of shell thickness on plasmonic peak position, scattering efficiency, and FWHM, it was discovered that in all of the bimetallic core-noble metal shell nanoparticles under consideration, the plasmonic peak shifts towards the longer wavelength region in combination with an increase in scattering efficiency.

Mann D. et al., 2017 [11] elucidated the effect of particle size distribution and imperfections in the metal shell on the plasmon resonance of Au and Ag nanoshells. To investigate their impact on the plasmon resonance, the thickness of the Au and Ag shells and the size of the polystyrene core are systematically adjusted. Their results are then compared to values determined by optical simulations using the finite element approach and extended Mie theory.

Bhardwaj, A. et al., 2019 [12] employed Mie theory-based theoretical model simulation of Gallium (Ga) and Cesium (Cs) liquid metals with their core-shell nanospheres coated with Silver (Ag) of different size spectra used to investigate their localized surface plasmon resonance (LSPR) wavelength and sensitivity of the peak position to the particle size and shell thickness. The resonance peaks are found in UV-Visible-NIR region for bare NPs and UV-Visible region for core-shell NPs. It was observed that the absorption efficiency increases with increasing the core size as well as shell thickness.

Bhardwaj, A. et al., 2022 [13] examined the plasmonic characteristics and absorption efficiencies of Ga alloys (GaAg, GaAl, GaHg, and GaIn) theoretically in order to find substitutes for the commonly used gallium-indium alloy. The precise computations of the plasmon-induced optical characteristics of nanoparticles (NPs) were obtained by applying the Mie theory. Potential applications of these intricate nanostructures and their optimum size have been discussed. The broad band absorption is shown between 100 to 400 nm, and the peak values are tuned by size and shell thickness factor. The maximum absorption efficiency of 4.57 is observed for GaAg alloy.

2.1 FUTURE SCOPE

Research findings from both theoretical and experimental in the thermoplasmonic field have been reported by number of researchers. There are various points to study optical and thermoplasmonic properties of plasmonic nanoparticles with their parameters like materials and their compositions, shapes, size, core-shell ratio, aspect ratio, surrounding mediums etc. Therefore, research can be carried out by choosing liquid and its alloys nanoparticles at room temperature with noble metals in stable structures like nanospheres and core-shell nanostructures. Further, this idea may reveal various applications like photothermal, heat generation, cancer therapy, solar cells etc. which are made from these combined flexible nanostructures.

3. THEORY AND COMPUTATIONAL TECHNIQUES

The Maxwell's curl equations in materials are given as:

$$\nabla \times \mathrm{E} = -\frac{\partial \mathrm{B}}{\partial \mathrm{t}} \text{ and} \quad (1)$$

$$\nabla \times \mathrm{H} = \frac{\partial \mathrm{D}}{\partial \mathrm{t}} \quad (2)$$

Where $\mathrm{D} = \varepsilon \mathrm{E}$ and $\mathrm{H} = \frac{\mathrm{B}}{\mu}$

Hence, Maxwell's equations reduces to $\nabla \times \mathrm{E} = -\frac{\partial \mathrm{B}}{\partial \mathrm{t}}$ and $\nabla \times \mathrm{B} = \mu\varepsilon \frac{\partial \mathrm{E}}{\partial \mathrm{t}}$

Evidently, electromagnetic waves propagate through medium at a speed v=c/n where $n \equiv \sqrt{\frac{\mu\varepsilon}{\mu_0 \varepsilon_0}}$ is the index of refraction of the materials. The refractive index (n) defines how matter affects light speed through electric permittivity (ε) and magnetic permeability (μ). The reference values for permittivity and permeability in free space are ε_0 and μ_0. These parameters explain how well a medium can handle electric and magnetic fields, respectively. During the interaction, the energy from the electric field is transiently present in the medium because the electrons in the material are temporally aligned with it. The stored energy is re-radiated, but the beam moves slowly due to the interaction of light with the substance. The earlier wave equation demonstrates that the refractive index (n) is also the ratio of the speed of light in a vacuum to the speed of light in the substance, i.e. n=c/v. Therefore, optical properties are often described by two sets of quantities:

(i) real and imaginary parts of the complex dielectric function;

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 \quad (3)$$

(ii) real and imaginary parts of complex refractive index;

$$\tilde{n} = n + ik \quad (4)$$

The relations between the two are:

$$\tilde{n} = \sqrt{\varepsilon} \quad (5)$$

$$\varepsilon_1 = n^2 - k^2 \quad (6)$$

$$\varepsilon_2 = 2nk \quad (7)$$

3.1 OPTICAL PROPERTIES WITH MIE THEORY

The particle-light interaction is formulated by Mie theory [14], firstly developed by Gustav Mie in 1908. Mie theory provides the optical properties for any particle size and optical constant of homogeneous spherical particles made of arbitrary materials. The approach is based on the solution of Maxwell equations with boundary conditions and multipole expansion of electromagnetic fields. The incident and internal fields are expanded in multipole fields that are regular inside the particle, while the scattered external field behaves as outgoing spherical waves at infinity. By applying the boundary conditions across the surface of the particle, i.e., the requirement of continuity of the tangential components of the electric and magnetic fields, the unknown coefficients in the expansions of the internal and scattered fields are determined from the known expansion coefficients of the incident plane wave. This solution for spherical particles is sometimes referred to as the Lorenz-Mie theory, since Lorenz also derived, independently, the solution in 1890. Mie theory takes less time, is cost effective and gives the same results as compared to other methods. Over the years, the theory was extended to core-shell spheres and radially inhomogeneous spheres. In the scope of nanoparticle optical properties, the real and imaginary components of the metal-dielectric constant are crucial in determining the LSPR peak position as well as the relative contribution of absorption and scattering in response to extinction. For a homogenous sphere, the total extinction and scattering efficiency is expressed as:

$$Q_{ext} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)Re[a_n + b_n] \qquad (8)$$

$$Q_{sca} = \frac{2}{x^2}\sum_{n=1}^{\infty}(2n+1)[a_n^2 + b_n^2] \qquad (9)$$

$$a_n = \frac{m\varphi_n(mx)\varphi'_n(x) - \varphi_n(x)y'_n(mx)}{m\varphi_n(mx)\varepsilon'_n(x) - m\varepsilon_n(x)\varphi'_n(mx)} \qquad (10)$$

$$b_n = \frac{\varphi_n(mx)\varphi'_n(x) - m\varphi_n(x)\varphi'_n(mx)}{\varphi_n(mx)\varepsilon'_n(x) - m\varepsilon_n(x)\varphi'_n(mx)} \qquad (11)$$

Once the extinction and scattering coefficients are obtained, it is possible to derive the absorption efficiency factor (Q_{abs})

$$Q_{abs} = Q_{ext} - Q_{sca} \qquad (12)$$

Where x is the size parameter given as $2\pi n_m R/\lambda$, λ is the wavelength of incident wave and R is the radius, φ_n and ε_n are the Riccati-Bessel functions, and the prime denotes first differentiation with respect to the argument in parentheses, m is the ratio of refractive index of the sphere (n) to that of the surrounding medium (n_m). There are various methods such as FEM, BEM, DDA, and FDTD [15-20], which solve the Maxwell equations and give solutions to optical properties for any particle size, arbitrary shape, and optical constant.

3.2 HEAT GENERATION IN METAL NANOPARTICLES

The ability of a metal nanoparticle to absorb light is measured by its absorption cross-section. When an electromagnetic (EM) wave interacts with a metal nanoparticle, some of it scatters in the environment, while the remainder is absorbed and subsequently converted to heat. As we are examining the heating process of nanomaterials, our first concern is the light absorbed by the metal nanoparticle. The process by which heat is released is relatively simple: a strong laser electric field drives mobile carriers into nanocrystals, and the energy received by the carrier is converted to heat. The medium around the nanocrystals then becomes warmer as the heat diffuses away from the nanocrystals. In the plasmon resonance regime, heat generation becomes especially strong in the case of metal NPs. Since metal nanoparticles have significant number of free conduction electrons, so the movement of these electrons has constant collisions with lattice atoms resulting the heat generation in metal nanoparticles arises from Joule effect, which is the major mechanism that causes thermoplasmonics to work. In order to examine the heating of plasmonic nanoparticles and their subsequent effects on the surrounding medium, the heat transfer equation is solved [21].

The heat generation in metal nanoparticle can be obtained from the heat power density q(r) which is the function of the electric field complex amplitude E(r) given as [22]

$$q(r) = \frac{1}{2}Re[J^*(r).E(r)] \qquad (13)$$

Where $J^*(r)$ represents the complex amplitude of J(r) and $J(r) = -i\omega P$ and $P = \varepsilon_o \varepsilon(\omega)E$. It has been observed that the heat source density is related to the square of the electric field inside the metal nanoparticle expressed as

$$q(r) = \frac{\omega}{2}Im(\varepsilon(\omega)\varepsilon_o\left|E(r)\right|^2 \qquad (14)$$

3.3 TEMPERATURE PROFILE UNDER CONTINUOUS ILLUMINATION

The temperature distribution and their influence in surrounding media by metal nanoparticles under illumination is governed by steady state heat equation, [23-24] and expressed as

$$\rho c\frac{\partial T}{\partial t} = \nabla.(K\nabla T) + Q \qquad (15)$$

where ρ, c, the mass density, the specific heat of the material, and T, K are the local temperature and thermal conductivity of the surrounding medium respectively. In the steady state, the heat transfer Eq. (15) reduces $K\nabla^2 T = -Q$ and the temperature rising outside the particle is given by a simple equation

$$\Delta T = \frac{Q}{4\pi K_{med} r} r > R \qquad (16)$$

where Q is the power of heat generation, r is the distance from the centre of a nanoparticle, K_{med} is the thermal conductivity of the surrounding environment, and R is NP radius. In the present work, R is defined as the sum of the core size and shell thickness. The temperature inside a spherically isolated nanoparticle is nearly uniform and the maximum temperature increase inside the particle is as given:

$$\Delta T_{max} = \frac{Q}{4\pi K_{med} R} \approx \frac{C_{abs*} I}{4\pi K_{med} R} \tag{17}$$

where C_{abs} and I is the calculated absorption cross-section and intensity of light of the incident source, respectively. At the surface of the nanoparticle, the maximum temperature rise occurs (i.e. r = R).

4. Conclusions

This review aims to provide insight into significant advances made in the field of thermoplasmonic. Thermodynamics and optics play a role in the science underlying photothermal phenomena produced by nanomaterials. The linkage of thermodynamics and optics is necessary for simulation setup in theoretical investigations of heat generation because of the dynamics of light absorption and heat transportation in the surrounding medium of the nanomaterial. The maximum amount of electromagnetic energy is converted into heat by the localized surface plasmon resonance (LSPR). By serving as nano-heaters, plasmonic nanoparticles provide new opportunities for studying at the nanoscale. For photothermal cancer treatment, magnetic and oxide-based nanostructures seem to be the best options; however, the ideal material with strong near-infrared absorption remains to be discovered. As a result, research into thermoplasmonic should continue in order to discover and develop new applications.

Declarations

Competing Interests

The authors declare no conflict of interest.

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