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Novel Design of Quantum Dot Arrays to Enhance Near-Fields Excitation Resonances

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***Abstract*—**Semiconductor crystals smaller than about 10 nm, known as quantum dots, have properties that differ from large samples, including a band gap that becomes larger for smaller particles. These properties create several applications for quantum dots. In this paper new shapes of quantum dot arrays are used to enhance the photo physical properties of gold nano-particles. This paper presents a study of the effect of nano-particles shape, array, and size on their absorption characteristics.

***Keywords*—**Quantum Dots, Nano-Particles, LSPR.

I. Introduction

QUANTUM DOTS (QDs) were first characterized in 1983 by Brus [1], [2] as small semiconductor spheres in a colloidal suspension. When the radius of a semiconductor sphere becomes small, on the order of a few nanometers, the Bohr radius of the charge carriers become larger than the sphere, and their confinement to the sphere causes their energy to increase.

QDs have vast applications across many industries. Their small size (~2-10 nanometers or ~10-50 atoms in diameter) gives QDs unique tuning property. Like that of traditional semiconductors, the importance of QDs is originated from the fact that their electrical conductivity can be altered by an external stimulus such as voltage or photon flux. One of the main differences between QDs and traditional Semiconductor is that the peak emission frequencies of QDs are very sensitive to both the dot's size and composition. [3], [4].

Electronic characteristics of a QD are closely related to its size and shape. For example, the band gap in a QD which determines the frequency range of emitted light is inversely related to its size. In fluorescent dye applications the frequency of emitted light increases as the size of the QD decreases. Consequently, the color of emitted light shifts from red to blue when the size of the QD is made smaller this allows the excitation and emission of QDs to be highly tunable. Since the size of a QD may be set when it is made, its conductive properties may be carefully controlled. QD assemblies consisting of different sizes, such as gradient multi-layer nano-films, can be made to exhibit a range of desirable emission properties [6].

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II. Enhanced Photo Physical Properties of Gold Nano-Particles

When matter is exposed to light, a number of processes can occur:

- The light can be absorbed.
- The light can be scattered at the same frequency as the incoming light (Mie or Rayleigh scattering).
- The absorbed light can be re-emitted (i.e., fluorescence).
- The local electromagnetic field of the incoming light can be enhanced.

In the case of gold nanoparticles (NPs), all these process are enhanced strongly owing to the unique interaction of light with the free electrons in the metal particles.

When gold NPs are exposed to light radiation, the electric field of the light causes the collective oscillation of the conduction-band electrons at the surface of the particle, with respect to the ions of the NPs. In metals, the coherent oscillations of the free electrons in resonance with the electromagnetic field are called the surface Plasmon resonance (SPR). SPR in nanometer-sized structures is called localized surface Plasmon resonance (LSPR) [5].

III. Light Scattering Imaging

The Rayleigh (Mie) scattering by gold NPs enhanced greatly owing to the excitation of the SPR. The SPR scattering frequency and intensity are sensitive to the size, shape, composition and environment of the nanoparticles and can be quantified using the Mie theory for spherical gold NPs. Typically, NPs of 30-100 nm diameter scatter intensity can be detected easily by a commercial microscope under dark field illumination conditions. Likewise, the scattering from 60 nm gold NPs is 10^5stronger than the emission of a fluorescent molecule.

The light scattering of gold nanorods is dependent strongly on the aspect ratio (length/width) of the nanorods. The wavelength shift of the longitudinal band depends linearly on the rod aspect ratio [9]. The high-scattering cross-section of gold NPs, together with their superior photo-stability makes them powerful for imaging based medical application [8], [9].

In addition to the strong Mie scattering, gold NPs absorb light strongly as a result of the SPR. This SPR absorption depends on the particle size and shape, the dielectric constant of the metal and that of the surrounding medium. For particles smaller than 25 nm, the absorption cross-section is linearly dependent on the volume of the particle and can be quantified by Mie theory. When the shape of NPs is changed from nanospheres to nanorods, the SPR absorption splits into two bands: a stronger long-wavelength band in the near-infrared

region owing to the longitudinal oscillation of electrons and a weak short-wavelength band in the visible region at approximately 520 nm owing to the transverse electronic oscillation. The position of the longitudinal absorption band of the gold nanorods is very sensitive to the aspect ratio, whereas that of the short wave length is not.

In addition, the absorbed light is converted to heat efficiently on a picoseconds time scale by rapid electron-phonon and phonon-phonon interaction. This strong SPR absorption followed by fast energy conversion and dissipation can be used readily for the heating of the local environment by using light radiation with a frequency strongly overlapping with the NPs SPR absorption band. The high efficient and localized light to heat conversion by gold NPs makes them very useful for the photo-thermal therapy of different diseases [5].

IV. Generating Heat with Metal Nanoparticles

The optical properties of NPs, including both semiconductor and metal nanocrystals, have been studied intensively. Recently, another related physical property heat generation by NPs under optical illumination has also attracted much interest. The heat generation process involves not only absorption of incident photons, but also heat transfer from the NP to the surrounding matter. The heating effect is especially strong for metal NPs since they have many mobile electrons. It becomes strongly enhanced under SPR or when the light signal hits the collective resonance of an NP. Since metal NPs have a very low optical quantum yield (i.e. they are very poor light emitters), the total amount of heat generated can be estimated in a relatively simple way as the total optical absorption rate. At the same time, it is more challenging to measure the temperature increase at the surface of the NPs. The temperature increase is the most important parameter for current applications of heated NPs in nanomedicine. An attempt to measure the temperature on the surface of Au NPs directly has recently been performed. It was achieved by embedding Au NPs in ice and driving them optically. Then, by observing the power threshold for the melting process, one can determine the NP surface temperature. Crystalline NPs composed of various materials can efficiently release heat under optical excitation. The mechanism of heat release is very simple – the light electric field strongly drives mobile carriers inside the nanocrystals, and the energy gained by carriers turns into heat. Then the heat diffuses away from the nanocrystal and leads to an elevated temperature of the surrounding medium. Heat generation becomes especially strong in the case of metal NPs in the regime of SPR. In the case of semiconductor NPs, the heat generation rate is much weaker since heat dissipation occurs through an inter-band absorption process with the creation of a single mobile electron and hole (exciton).In the absence of phase transformations, temperature distribution around optically-stimulated NPs is described by the usual heat transfer equation [7]:

$$\rho(r)c(r)\frac{\partial T(r,t)}{\partial t} = \nabla K(r)\nabla T(r,t) + Q(r,t) \quad (1)$$

where r and t are the coordinate and time, $T(\mathbf{r}, t)$ is the local temperature, and the material parameters$\rho(r)c(r)$, and $K(r)$ are the mass density, specific heat, and thermal conductivity, respectively.The function $Q(r,t)$represents an energy source coming from light dissipation in NPs:

$$Q(r,t) = (\mathbf{j}(r,t).\mathbf{E}(r,t))_t \quad (2)$$

where $\mathbf{j}(\mathbf{r}, t)$ is the current density and $\mathbf{E}(\mathbf{r}, t)$ is the stimulating electric field in the system. This field should be calculated from a system of Maxwell's equations. For a single, spherical NP this equation can be easily solved analytically (see the model in Fig. 1). In the steady-state regime, the local temperature around a single NP is described by a simple equation:

$$\Delta T(r) = \frac{V_{NP}Q}{4\pi K_o r} \quad (3)$$

where r is the distance from the center of an NP, K_o is the thermal conductivity of the surrounding medium, and V_{NP} is the NP volume. Equation (3) is valid outside the NP, i.e. $r > R_{NP}$, where R_{NP} is the NP radius.The surrounding medium can be water, a chemical solution, or a polymer. We can also calculate analytically the heat generation Q, assuming that the wavelength of the incident light is much longer than the NP radius ($\lambda >> R_{NP}$):

$$Q = \frac{\omega}{8\pi}E_o^2\left|\frac{3\varepsilon_m}{2\varepsilon_m+\varepsilon_{NP}}\right|^2 IM(\varepsilon_{NP)} \quad (4)$$

where$E_o$is the amplitude of the incident radiation, and ε_{NP} and ε_m are the dielectric constants of the NP and surrounding medium, respectively.

The maximum temperature increase occurs at $r = R_{NP}$ and is given by [8]:

$$\Delta T_{max}(I_o) = \frac{R_{NP}^2}{3K_o}\frac{\omega}{8\pi}\left|\frac{3\varepsilon_o}{2\varepsilon_o+\varepsilon_{NP}}\right|^2 IM\varepsilon_{NP}\frac{8\pi I_o}{c\sqrt{\varepsilon_o}} \quad (5)$$

where I_o is the light intensity inside the material. This equation includes the important dependence of temperature on the NP size:

$$\Delta T_{max} \propto R_{NP}^2 \quad (6)$$

The temperature increase is proportional to the second power of the NP radius.

V. Simulation and Discussion of the Results

We used the High Frequency Structure Simulator (HFSS) software to compare the performance of different shapes of NPs: nanosphere, nanorod, nanosandwich, nanocircle (loop), nanoring, nanodesk and nanorectangular shape. Each of these shapes has been put in two different forms: Single element and array. The reflection coefficient S_{11} is taken as a measure for

the back scattering of the different structures. The effect of arraying result in:

a- Shifting of the resonance frequency from that of the single element
b- Decreasing the reflection coefficient comparing to different structures.

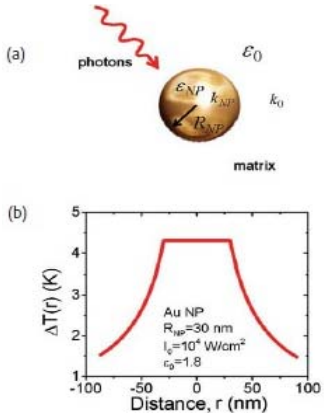


Fig. 1 (a) Schematic of an optically driven spherical NP (b) Calculated temperature increase for a single Au NP as a function of the distance from the NP center. The surrounding medium is water

From Table I, we show the different shapes with compare between each other. It is clear from the table that in case of nano-sphere element gives higher absorption spectra (reflection coefficient) at $S_{11} = -42.5\ dB$ at resonance frequency=1035.7 THz.

Also Fig. 2 shows the S_{11} of all single element and it is clear that nano-sphere single element gives higher absorption spectra at $S_{11} = -42.5\ dB$ at resonance frequency=1035.7 THz.

Also Fig. 3 shows the S_{11} of all array element and it is clear that nano-rectangular array elements gives higher absorption spectra at $S_{11} = -31.9\ dB$ at resonance frequency=1239.8 THz.

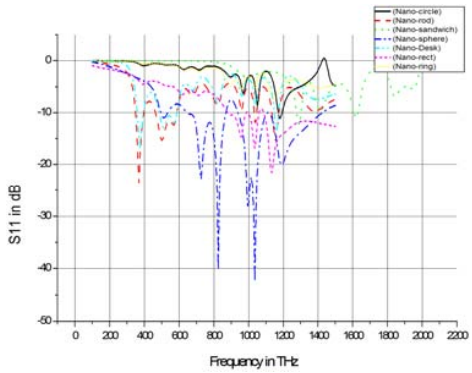


Fig. 2 The S_{11} versus frequency for all single elements shapes

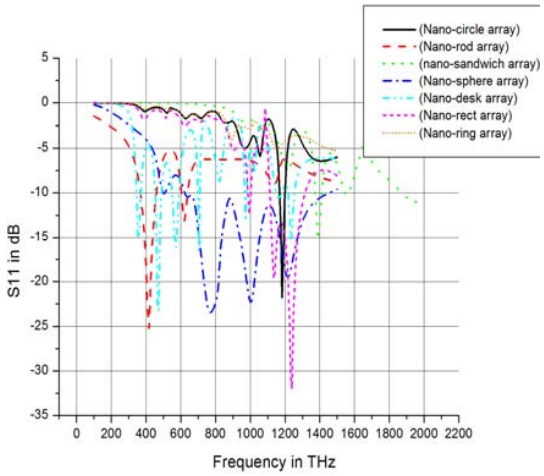
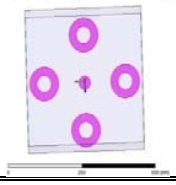
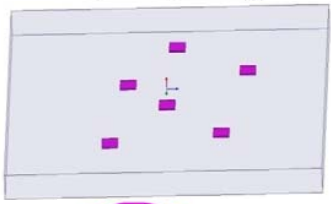
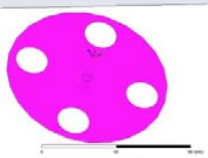
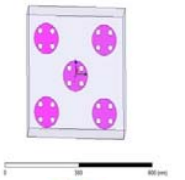
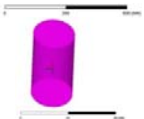
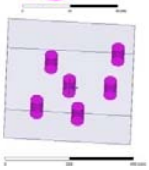
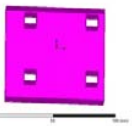
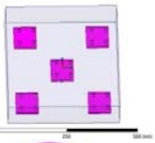
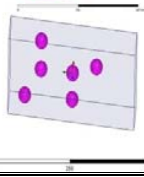


Fig. 3 The S_{11} versus frequency for all array elements shapes

TABLE I
COMPARE BETWEEN 14 DIFFERENT ELEMENTS IN NANO SCALE

Shape	Design	Dimension	$S_{11}\ dB$	Resonance frequency	Shifted frequency
Nanoring element		Gold nanoring (outer radius=50 nm and inner radius=25 nm) Excited by circular patch has 25 nm inside dielectric substrate (has the dimensions 400 × 400 × 100 nm and $\varepsilon_r = 58$).	$-7.3\ dB$	1141.2 THz	14.1 THz
nanoring array elements			$-4.9\ dB$	1155.3 THz	

Shape	Design	Dimension	$S_{11}\ dB$	Resonance frequency	Shifted frequency
nanosandwich element		the nano-sandwich which consists of two layers of gold sandwiched (each one has the dimensions $20 \times 20 \times 0.5\ nm$)in-between by glass as the dielectric material(which has dimension $20 \times 20 \times 1\ nm$and $\varepsilon_r = 5.5$) and with dielectric substrate (which has dimension $400 \times 400 \times 30\ and \varepsilon_r = 58$)	$-12.3\ dB$	$1293.5\ THz$	$95.5\ THz$
nanosandwich array elements			$-15.1\ dB$	$1389\ THz$	
nanocircle element		structure of the nano-circle element which consist of gold nano-circle has $radius = 50\ nm$ and has 4 holes each one has $radius = 5\ nm$ (to improve reflection coefficient) inside dielectric substrate (has the dimensions $400 \times 400 \times 100\ nm\ and \varepsilon_r = 58$)	$-11.04\ dB$	$1183.4\ THz$	$0.1\ THz$
nanocircle array elements			$-21.8\ dB$	$1183.5\ THz$	
nanodesk element		structure of the nano-Desk element which consists of gold nano-Desk(outer radius= $20\ nm\ and\ inner\ radius = 10\ nm$) inside dielectric substrate (has the dimensions $400 \times 400 \times 100\ nm\ and \varepsilon_r = 58$)	$-16.7\ dB$	$374.4\ THz$	$98.5\ THz$
nanodesk array elements			$-23.2\ dB$	$472.9\ THz$	
nanorod element		structure of the nano-rod element which consists of gold nano-rod (height= $50\ nm\ and\ radius = 20\ nm$) inside dielectric substrate (has the dimensions $400 \times 400 \times 100\ nm\ and \varepsilon_r = 58$).	$-23.4\ dB$	$367.4\ THz$	
nanorod array elements			$-25.2\ dB$	$416.6\ THz$	$49.2\ THz$
Nanorectangular element with 4 waveguide holes		Structure of the nano-rectangular element which consists of gold nano-rectangular (has the dimensions $80 \times 80 \times 10\ nm$) with 4 wave guide hole (each one has the dimension $10 \times 10 \times 10\ nm$) inside dielectric substrate (has the dimensions $400 \times 400 \times 100\ nm\ and \varepsilon_r = 58$).	$-21.5\ dB$	$1134.1\ THz$	
nanorectangular array elements			$-31.9\ dB$	$1239.8 THz$	$105.7\ THz$
nanosphere element		structure of the nano-sphere element which consists of gold nano-sphere ($radius = 20\ nm$) inside dielectric substrate (has the dimensions $400 \times 400 \times 60\ nm\ and \varepsilon_r = 58$)	$-42.5\ dB$	$1035.7\ THz$	
nanosphere array elements			$-23.4\ dB$	$768.4\ THz$	$267.3\ THz$

VI. Conclusion

The success of new applications of NPs depends on improvement in the understanding of the properties of LSPR and the environment around them. Different shapes of NPs, nanosphere, nanorod, nano-sandwich, nanocircle, nanoring, nanodesk and nanorectangular have been studied. It is found that array them in random manner aiming to reach the optimum absorption spectrum. A comparison between the results of [4], (the nano-rod elements in wave length range scale between 500-1100 nm) and this work that in case of nano-rod single element that absorption spectra at $S_{11} = -23.4\ dB$ at resonance frequency =$367.4\ THz$ shows that they are close to each other . It is found that array of rod elements given$S_{11} = -25.2\ dB$. Also, it is found that the nano-sphere element gives the best result compared to the other shapes in different configurations. It is observed that nano-sphere element gives the best result at $S_{11} = -42.5dB$ and frequency = 1035 THz.

Future work may introduce new shapes, and also may introduce new nano-array structures giving higher absorption better than our work.

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