Simulation Effects on the Optical Response of Gold Nanoparticles

Tanaporn Leelawattananon[1] and Suphamit Chittayasothorn[2]

[1]*Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand*

[2]*Department of Computer Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand*

Keywords: Localized Surface Plasmon Resonances, Gold Nanoparticles, Optical Properties, Finite Element Method.

Abstract: In this research work, we use simulation models for the investigation of the sizes and shapes of gold nanoparticles on BK-7 substrate base, which affect the optical characteristics in a large spectral range of the gold nanoparticles. Linearly polarized light with wavelengths of 300 – 800 nm are specified as the impact light on gold nanostructures. We try to find the suitable wavelength of the impact light when localized surface plasmon resonance takes place. The gold nanoparticles are spherical, elliptical oval, and 10nm x 40 nm block-shape and have their aspect ratio similar to the nanorod shape nanoparticles used in other experiments. The results are useful for the development of plasmonic complex nanostructure with tunable surface plasmon resonances which generate heat and have potential applications in medical thermal therapy.

1 INTRODUCTION

According to technological advancement, metals which have structures at the nanometer level can be manufactured. This advancement attracts attention of physicists, chemists, material scientists, and biologists which are interested in the surface plasmon phenomenon. Surface Plasmon Resonance (SPR) is the phenomenon which takes place when there are excitations of free electrons at the interface between an electrical conductor and a dielectric layer thus create evanescent electromagnetic waves. The excitation of Surface Plasmon waves leads to the occurrence of other phenomena, including the optical responses of materials. Plasmonics in the material structures at the nanometer level find applications in the surface-enhanced sensing and the measuring of intra molecular distances in molecules.

The optical response of metallic nanoparticles (NPs) can be adjusted by the controlling of the size and shape of the particles and also the environment. This knowledge initiates research areas such as Surface Plasmon based Photonics or Plasmonics (G. Alexandre Brolo, 2012). There have also been new techniques in the synthesis of nano particles which aim at the creation of nanoparticles, which have adequate size and shape for excitation of the Surface Plasmon waves (Z. Ying et.al., 2018). These surface plasmon waves can be employed in magneto-optic applications. They also help improve the efficiency of surface-enhanced sensing and spectroscopy, which find applications in bio detection and chemical therapy (Z. Zhang et.al., 2014).

It has been recently found that the shape of the nanoparticles affects the optical response of the particles. Researches have been conducted to study optical characteristics of nanoparticles and to find out the effects of sizes and shapes of these nanoparticles. Shapes include spherical, cube, and other polyhedrons (Y. Wang et. Al., 2013) (M. Chen et.al., 2017). The more nanoparticle becomes sphere-like, the more the main surface plasmon resonance is red-shifted where the dependence of the position of the resonances is analytically explained in terms of their aspect ratio (Cecilia Noguez, 2007). The development of plasmonic complex nanostructure with tunable surface plasmon resonances results in a higher heat generation which finds applications in medical thermal therapy (H. Vahid et.al., 2018) (K. Jiang et.al., 2013).

In this project, we simulate the Surface Plasmon Resonance phenomenon of gold nanoparticles which have different shapes and sizes and have been employed to align 1D structures. The finite element method (FEM) is used in the analysis and simulations. The simulation results show plasmon wave electric fields when using these gold

Leelawattananon, T. and Chittayasothorn, S.
Simulation Effects on the Optical Response of Gold Nanoparticles.
DOI: 10.5220/0007959603600367
In *Proceedings of the 9th International Conference on Simulation and Modeling Methodologies, Technologies and Applications (SIMULTECH 2019)*, pages 360-367
ISBN: 978-989-758-381-0

nanoparticles which are excited by the visible light sorce. The goal of the project is to find suitable sizes and shapes of gold nanoparticles for plasmonics which can be applied in medical thermal therapy including the killing of cancer cells. There has been successful experiments in using such thermal therapy using heats from the localized surface plasmon resonances (LSPR) of gold nano particles (Z. Qin et al., 2016). The simulation results will also lead to the development of plasmonics complex nanostructures with tunable surface plasmon resonances and to compare heating between increasing complex plasmonic nanostructures.

2 THEORY AND PRINCIPLES

2.1 Surface Plasmon Resonance (SPR) Phenomenon

Surface plasmon waves take place at the surface of the metal. The highest amplitude of the electric field which is called the evanescent field is at the interface between the metal surface and the dielectric layer. The amplitude drops exponentially when the distance from the metal surface increases.

The excitation of the SP waves is typically done by using the Kretchmann configuration (T.A. Leskova et. Al., 2000) which uses light from a light source to impact a prism and the metal thin film on the prism surface. The reflected light from the prism is then detected and measured using a light detector. Metal thin films which have the suitable characteristics for the excitement of the SP waves are noble metals such as gold, silver, and copper. The typical thickness of the metal layer is 50 nanometers.

The evanescent field of the reflected light at the dielectric-metal interface penetrates into the metal. With the appropriate thickness of the metal layer, the evanescent wave reaches the metal-dielectric interface (or metal-air interface). In the case that the phase of the incoming light matches the phase of the surface plasmon waves, the surface plasmon resonance is generated and surface plasmon waves propagate along this metal-dielectric interface. They are generated according to a certain condition which depends on the incident angle and the incident wavelength: (H. Bateman, 1915)

$$k_{sp} = k_x = k_0 n_p \sin\theta \tag{1}$$

k_{sp} is the wave vector of surface plasmon waves
k_x is the wave vector of the incoming light
n_p is the refractive index of the prism
θ is the resonance angle

According to the equation, the energy and momentum of the incoming light which impact the prism is transferred to the electrons group of the metal thus excite surface plasma wave. The dispersion relation of surface plasmon wave is shown in the following equation: (H. Bateman, 1915)

$$k_{sp} = k_x = \frac{\omega}{c}\sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \tag{2}$$

ε_m is the relative permittivity of the metal
ε_d is the relative permittivity of the dielectric layer

The necessary condition for the surface plasmon resonance to take place is the wave vector (k_x) of the incoming light must be the same as the wave vector of the surface plasmon waves (k_{sp}). Surface plasmon waves propagate along the metal-dielectric interface as shown in Fig. 1a.

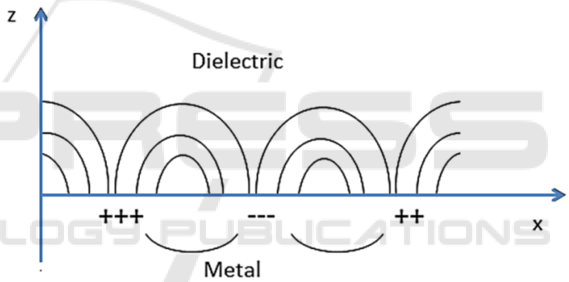


Figure 1a: Surface plasmon resonance at the interface between the metal thin film layer and dielectric layer.

From Fig. 1b, when light impacts structure at the nano level of the metal, electrons are excited to the conduction band and oscillate with the impact light thus creates plasmon polaritron which can be transferred at the interface between metal and dielectric layers. This phenomenon takes place at the external shell of the metallic nanoparticle since the external light cannot penetrate into the nanoparticle. This phenomenon is therefore called the localized surface plasmon resonance (LSPR) phenomenon.

The impact light on the surface of the particle has two kinds of interactions: absorption, and scattering. The strong optical absorption and scattering of noble metal nanoparticles is due to an effect called localized surface plasmon resonance, which enables the development of novel biomedical applications. When plasmon resonance takes place, the absorbed light generates enough heat which can kill cancer cells. This phenomenon also find applications in biosensing (R. M. Cabral et.al., 2014) (X. Cao et.al., 2011).

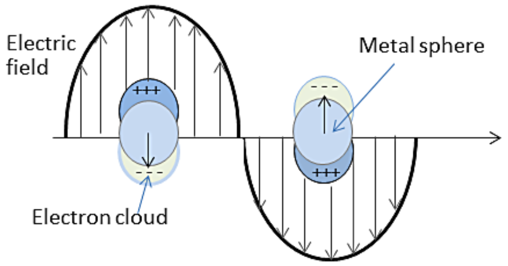


Figure 1b: The excitation of localized surface plasmon resonance of spherical nanoparticles.

2.2 Localized Surface Plasmon Resonance (LSPR)

We can use the result of the Mie theory to explain the scattering and absorption of impact light on spherical particles (G. Mie, 1908). The extinction cross section (σ_{ext}) can be obtained from the summation of the absorption cross section (σ_{abs}) and the scattering cross section (σ_{sca}) of metal nanoparticles: ($\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$)

For very small particles, ($d << \lambda$) the Mie equation for explaining σ_{ext} for spherical nanoparticles is:

$$\sigma_{ext} = 9(\frac{\omega}{c})\varepsilon_{3/2}V_0 \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2} \quad (3)$$

where $V_0 = (4\pi/3)\ R^3$

ω is angular frequency

ε_m is dielectric function of metal nanoparticles

ε_1 is real value of dielectric functions of metal nanoparticle.

ε_2 is imaginary value of dielectric functions of metal nanoparticle.

From equation (3) the absorption of plasmon takes place when $\varepsilon_1(\omega) \approx -2\varepsilon_m$ and from the detection of LSPR signals, it has been found that the shape of the nanoparticles influences the LSPR signals. These nanoparticals have several possible shapes such as nanospheres, nanodiscs, nanopyramids, and nanorods.

3 THE SIMULATED EXPERIMENTS

In this research project we simulate the optical excitation of the localized surface plasmon resonance (LSPR). We specify that linearly polarized light impacts on metal nanoparticles and substrate base. The nanoparticles are gold in spherical, block, and oval shapes. For each shape, the size, height, width, and distance between particles are varied. The substrate base is BK7 Cover glass. Both the gold nanoparticles and the substrate base are contained in a spherical PML surface as shown in Fig. 2.

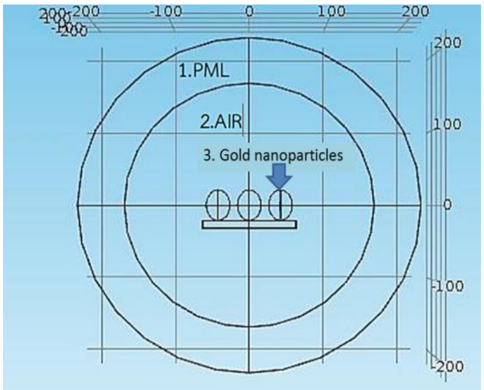


Figure 2: The simulation model of gold nanoparticles and BK-7 substrate in the internal PML surface.

Fig 3 is a simulation model of the optical excitation. The gold nano particles are in block shape with the size 10x40 nm. The distance between adjacent particles is 10 nm. The impact light is specified to be the linearly polarized plane wave and the light impact angle is $\pi/4$ rad. The finite element method (FEM) is used to analyze the resultant electric field at the interface between the gold nanoparticles and dielectric (air) layer. Parameters used in the simulation are shown in Table 1.

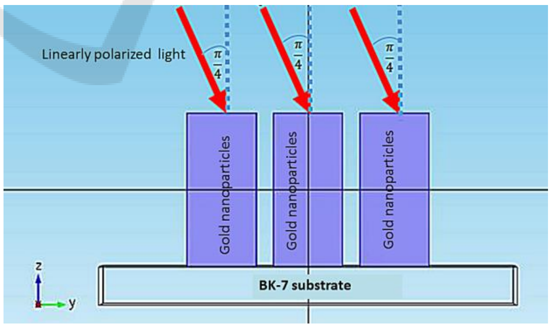


Figure 3: The simulation model of the optical excitation of 10x40 nm block-shape gold nanoparticles.

We change the wavelength of the impact light from 300 nm to 800 nm by 50 nm increment to observe the wavelengths which are suitable for the excitation of the localized surface resonance waves. The light source is the linearly polarized plane wave and the gold nanoparticles are as shown in Fig. 4.

Table 1: Parameters used in the simulation.

Parameter name	Value
Refractive index of Air	1
Refractive index of substrate BK-7	1.5151
Relative permitivity of gold nanoparticle (real part)	-4.6810
Relative permitivity of gold nanoparticle (imaginary part)	2.4266
r_pml	11*radius
t_pml	3*radius
radius	20 nm

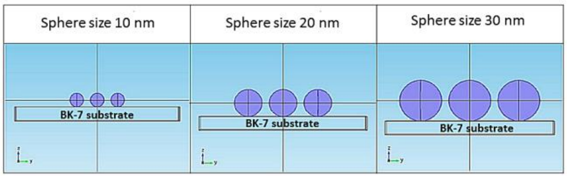
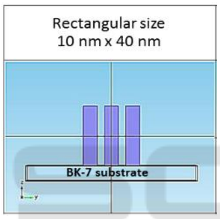


Figure 4a: Sphere shape.



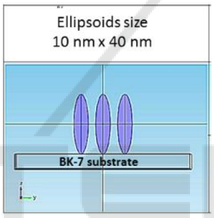


Figure 4b: Rectangular shape. Figure 4c: Ellipsoid shape.

Electromagnetic wave propagation as explained by Maxwell's wave equation in the frequency domain is as follows:

$$\nabla \times \frac{1}{\mu_r}(\nabla \times \mathrm{E}) - k_0^2\left(\varepsilon_r - \frac{j\sigma}{\omega\varepsilon_0}\right)\mathrm{E} = 0 \qquad (4)$$

where ε_r is the relative permittivity of material
E is the electric field equation
k_0 is the wave vector in free space

This is an equation in differential form for the analysis of the size of electric field at the interface between gold nanoparticles and air dielectric. We also specify the scattering boundary condition so that the scattering of the light is within the PML surface only. We partition subdomain in triangular mesh elements with extrafine details.

4 SIMULATION RESULTS

In the first simulation experiment using the finite element method (FEM), we use linearly polarized incident light which has wavelength range from 300 to 800 nm and increment by 50 nm impact on spherical gold nanoparticles with BK-7 substrate base. The results surface plasmon resonance at the interface between the nanoparticles and air dielectric differ when the size of the nanoparticles varies.

When the size of the spherical gold nano particle is 10 nm, the electric field at the interface between the gold nanoparticles layer and the air has maximum amplitude is equal to 4.6x10^5 V/m when the wavelength is 550 nm as shown in Fig. 5. The graph which shows relationships between the wavelength of the impact light and the electric field at the interface is shown in Fig. 6.

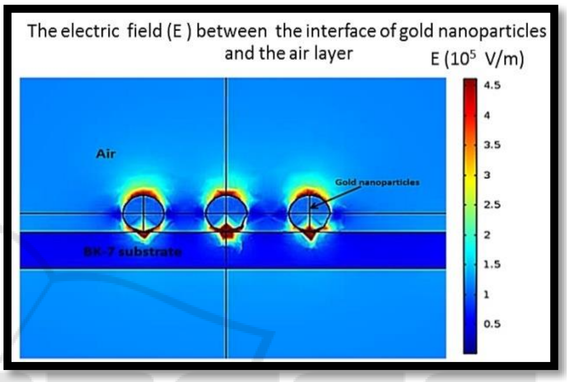


Figure 5: Electric field at the interface between 10 nm spherical gold nanoparticles and air dielectric.

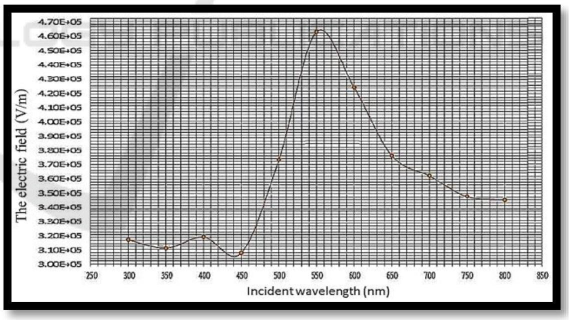


Figure 6: Graph which shows relationships between wavelength of the impact light and electric field at the interface between 10 nm gold nanoparticles and ir dielectric.

When the size of the spherical gold nano particle is 20 nm, the electric field at the interface between the gold nanoparticles layer and the air has maximum amplitude equal to 4.4x10^5 V/m when the wavelength is 550 nm as shown in Fig. 7. The graph which shows the relationships between the wavelength of the impact light and the electric field at the interface is shown in Fig. 8.

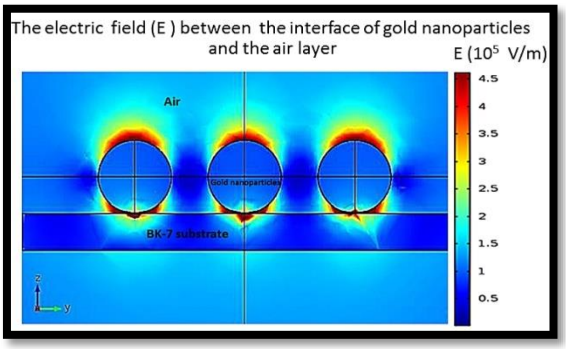


Figure 7: Electric field at the interface between 20 nm spherical gold nanoparticles and air dielectric.

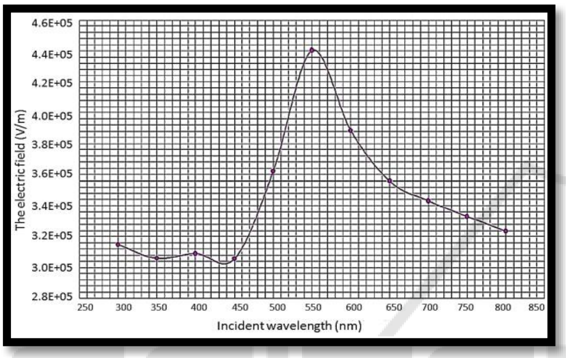


Figure 8: Graph which shows relationships between wavelength of the impact light and electric field at the interface between 20 nm gold nanoparticles and air dielectric.

When the size of the spherical gold nano particle is 30 nm, the electric field at the interface between the gold nanoparticles layer and the air has maximum amplitude equal to $6.3x10^5$ V/m when the wavelength is 550 nm as shown in Fig. 9. The graph which shows relationships between the wavelength of the impact light and the electric field at the interface is shown in Fig. 10.

From the results of the first set of simulation experiments, when the nanoparticles have spherical shape, it has been noticed that the localized surface plasmon resonance (LSPR) phenomenon takes place with highest electric field magnitude when the impact wavelength is 550 nm, for all the size of the gold nanoparticles tested. These results correspond with the results of the physical experiments. (Z. Qin et al., 2016)

The second set of simulation experiments are then conducted using the same light source with the wavelength range from 300 nm to 800 nm, increment by 50 nm on oval-shape gold nanoparticles with the aspect ratio (b/a) >1. The a axis is 10 nm and the b axis is 40 nm, the localized

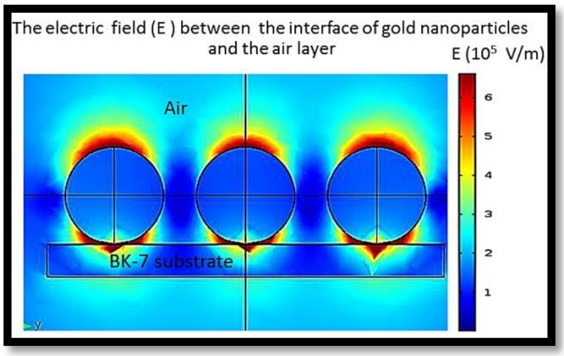


Figure 9: Electric field at the interface between 30 nm spherical gold nanoparticles and air dielectric.

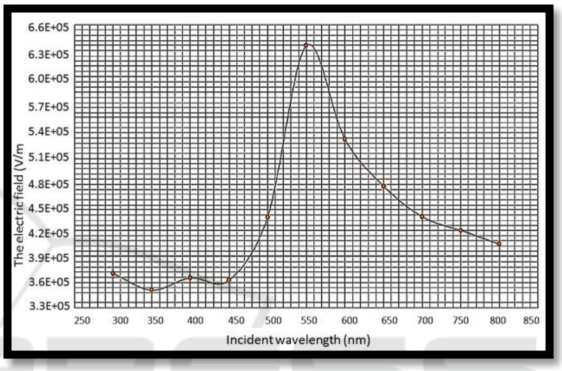


Figure 10: Graph which shows relationships between wavelength of the impact light and electric field at the interface between 30 nm gold nanoparticles and air dielectric.

surface plasmon resonance electric field at the interface between the gold nanoparticles layer and the air has maximum amplitude is equal to $8.5x10^6$ V/m when the wavelength is 650 nm as shown in Fig. 11. The graph which shows the relationships between the wavelength of the impact light and the electric field at the interface is shown in Fig. 12.

The third set of simulation experiments are then conducted using the same light source with the wavelength range from 300 nm to 800 nm, increment by 50 nm on 10 nm x 40 nm block-shape gold nanoparticles. The localized surface plasmon resonance electric field at the interface between the gold nanoparticles layer and the air has maximum amplitude is equal to $1.8x10^6$ V/m when the wavelength is 700 nm as shown in Fig. 13. The graph which shows the relationships between the wavelength of the impact light and the electric field at the interface is shown in Fig. 14.

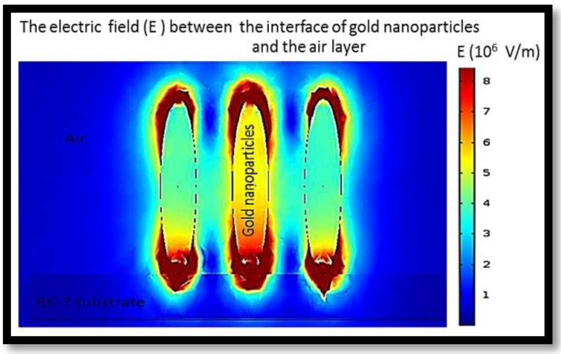


Figure 11: Electric field at the interface between elliptical oval gold nanoparticles and air dielectric with the 10 nm distance between particles.

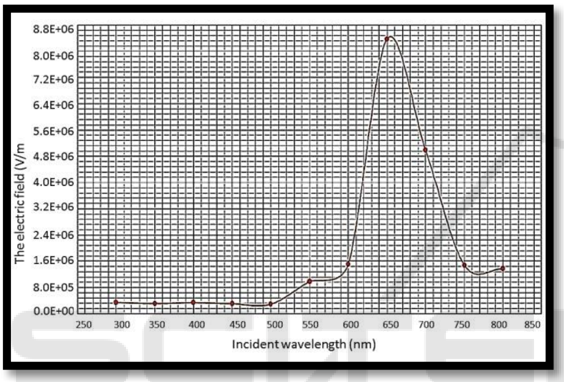


Figure 12: Graph which shows relationships between wavelength of the impact light and electric field at the interface between elliptical oval gold nanoparticles and air dielectric with the 10 nm distance between particles.

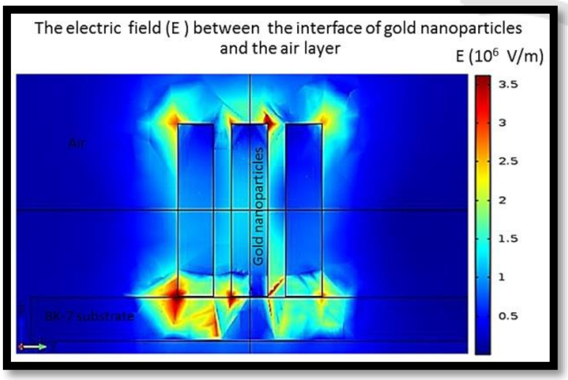


Figure 13: Electric field at the interface between block-shape gold nanoparticles and air dielectric with the 10 nm distance between particles.

We then try the fourth set of experiments using the finite element method on the same software. The impact light is the linearly polarized light with the wavelength range from 300 nm to 800 nm and increase the wavelength 50 nm at a time.

Figure 14: Graph which shows relationships between wavelength of the impact light and electric field at the interface between block-shape gold nanoparticles and air dielectric with the 10 nm distance between particles.

The nanoparticle is the elliptical oval shape with a axis = 10 nm and b axis = 40 nm. The distance between nanoparticles is now reduced to 5 nm. The simulation result shows that when the localized surface plasmon resonance takes place at the interface between the air dielectric and the elliptical oval nanoparticles, the highest amplitude of the electric field is 6.3×10^6 V/m. The wavelength of the impact light is 650 nm as shown in Fig. 15. The graph which show relationships between wavelength of the impact light and the electric field at the interface is shown in Fig 16.

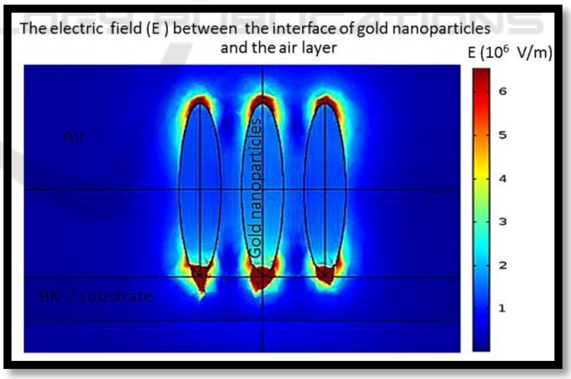


Figure 15: Electric field at the interface between elliptical oval gold nanoparticles and air dielectric with the 5 nm distance between particles.

We then try the fifth set of experiments using the finite element method on the same software. The impact light is the linearly polarized light with the wavelength range from 300 nm to 800 nm and increase the wavelength 50 nm at a time. The nanoparticle is the block shape with the size 10 nm x 40 nm. The distance between nanoparticles is now reduced to 5 nm. The simulation result shows that

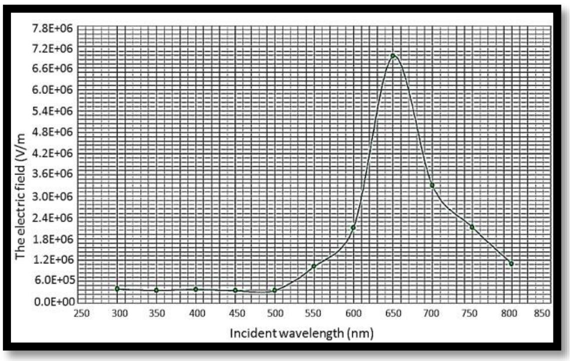


Figure 16: Graph which shows relationships between wavelength of the impact light and electric field at the interface between elliptical oval gold nanoparticles and air dielectric with the 5 nm distance between particles.

when the localized surface plasmon resonance takes place at the interface between the air dielectric and the elliptical oval nanoparticles, the highest amplitude of the electric field is 1.15×10^6 V/m. The wavelength of the impact light is 700 nm as shown in Fig. 17. The graph which show relationships between wavelength of the impact light and the electric field at the interface is shown in Fig 18.

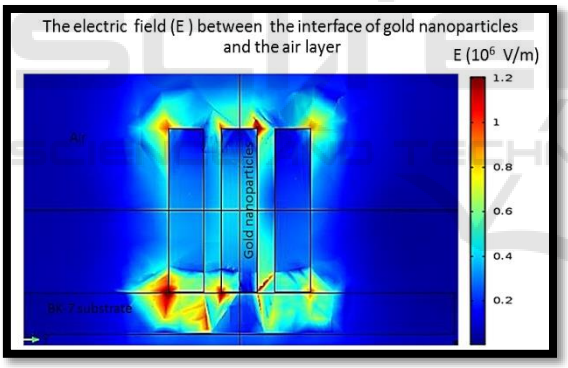


Figure 17: Electric field at the interface between block-shape gold nanoparticles and air dielectric with the 5 nm distance between particles.

From the second and the third set of simulation experiments, it is noticed that the wavelengths of the impact light which produce the LSPR phenomenon on non-symmetrical nanoparticles such as elliptical oval and block shape are higher red-shifted than the ones on spherical nanoparticles. These correspond with the physical experimental results as described in [9]. From the fourth and fifth simulation results, it has been noticed that the amplitude of the electric field is higher when the distance between nanoparticles is 10 nm than when the distance is 5 nm when the LSPR phenomenon takes place.

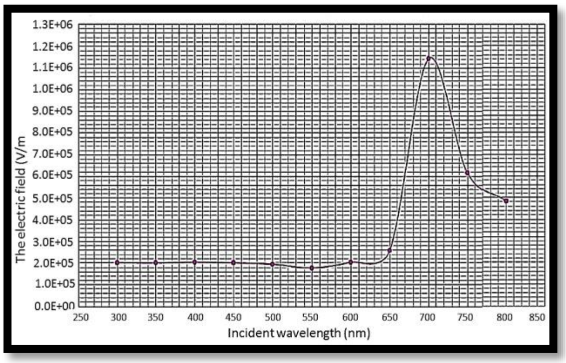


Figure 18: Graph which shows relationships between wavelength of the impact light and electric field at the interface between block-shape gold nanoparticles and air dielectric with the 5 nm distance between particles.

5 CONCLUSIONS

According to the advances in material synthesis, nanostructures for medical applications are available. They can be applied in useful biomedical applications such as thermal therapy, drug nano-carriers, photothermal agents for tumor ablation. The understanding of the effects of nanoparticles sizes and shapes will lead to the wider and more precise applications. This is due to the fact that the size and the shape of nanoparticles can determine the optical properties and interactions with biological systems. In the case of gold spherical nanoparticle, which is symmetric, the change in the size of the nanoparticle results in color changes. Color can be tuned within the visible spectrum to dark red when plasmon resonances occur. In the case that the shape of the gold nanoparticles are not symmetrical such as gold nanorod the change of their aspect ratio causes plasmon resonance to be tunable in the visible to near-infrared spectrum range. Heat generations from plasmonic nanostructure when plasmon resonances can be used in thermal therapy.

In this research work, we analyze by simulation, gold nanostructures which have a block-shaped aspect ratio (b/a) = 4 which is similar to the aspect ratio of gold nanorod to find electric fields at the interface between the gold nanoparticles and the air dielectric. With the applications of linearly polarized light to gold nanoparticles on BK-7 base substrate, we simulate and measure the electric fields at the interface between the nanoparticles, with different shapes and sizes, and the air dielectric. Linearly polarized light with the wavelengths between 300 nm – 800 nm are employed for excitation. From the simulation results, it has been found that gold nanoparticles with elliptical oval shapes with a axis 10 nm and b axis 40 nm, and block-shape gold nanoparticles 10nm x40 nm, which have the same aspect ratio, are suitable for producing plasmon resonance which can be tuned in the visible to near-infrared spectrum. The elliptical oval shape gold nanoparticle with a axis 10 nm and b axis 40 nm gives higher electrical field amplitude than the 10nm x40 nm block-shape nanoparticle which has the same aspect ratio. The amplitude of the electric field is higher when the distance between nanoparticle is 10 nm than when the distance is 5 nm when the LSPR phenomenon takes place.

REFERENCES

G. Alexandre Brolo, 2012. Plasmonics for future biosensors. In *Nature Photonics, 6(11), pp. 709-713*.

Z. Ying et.al., 2018. Terahertz spoof surface-plasmon-polariton subwavelength waveguide. In *Photonics Research , 6(1), pp. 18-23.*

Z. Zhang et.al., 2014. Near infrared laser-induced targeted cancer therapy using thermoresponsive polymer encapsulated gold nanorods. In *J. Am. Chem. Soc.,136, pp. 7317–7326*.

Y. Wang et. Al., 2013. Synthesis of Silver Octahedra with Controlled Sizes and Optical Properties via Seed-Mediated Growth. In *ACS Nano ,pp. 754586-4594.*

M. Chen et.al., 2017. Synthesis and optical properties of size-controlled gold nanoparticles. In *Powder Technology, 311(15), pp. 25-33*.

Cecilia Noguez, 2007. Surface Plasmons on Metal Nanoparticles: The Influence of Shape and Physical Environment. In *J. Phys. Chem. C, 111, pp. 3806-3819.*

H. Vahid et.al., 2018. Multimodal cancer cell therapy using Au@Fe2O3 core–shell nanoparticles in combination with photo-thermo-radiotherapy. In *Photodiagnosis and Photodynamic Therapy, vol.24, pp. 129-135.*

K. Jiang et.al., 2013. Size-Dependent Photothermal Conversion Efficiencies of Plasmonically Heated Gold Nanoparticles. *In J. Phys. Chem. C 117, pp. 27073–27080.*

Z. Qin et al., 2016. Quantitative Comparison of Photothermal Heat Generation between Gold Nanospheres and Nanorods. In *Sci. Rep. 6, pp. 1–13.*

T.A. Leskova et. Al., 2000. The surface enhanced second harmonic generation of light from a randomly rough metal surface in the Kretschmann geometry. In *Optics Communications(183), 529-545.*

H. Bateman, 1915. The mathematical analysis of electrical and optical wave motion on the basis of Maxwell’s equations. In *Cambridge: Cambridge University Press, pp.159.*

R. M. Cabral et.al., 2014. Anti-cancer precision theranostics : a focus on multifunctional gold nanoparticles. In *Expert Rev. Mol. Diagn. 14, pp.1–12.*

X. Cao et.al., 2011. Gold nanoparticle-based signal amplification for biosensing. In *Anal. Biochem., vol. 417, pp. 1-16.*

G. Mie, 1908. Beitrge zur optik tr¨uber medien, speziell kolloidaler metall¨osungen. In *Annalen Der Physik, vol. 330, no. 3, pp. 377–445.*