Ciencia Latina Revista Científica Multidisciplinar, Ciudad de México, México.
ISSN 2707-2207 / ISSN 2707-2215 (en línea), enero-febrero 2025,
Volumen 9, Número 1.

https://doi.org/10.37811/cl_rcm.v9i1

BIOSENSING AT THE NANOSCALE: GOLD FRACTAL NANOANTENNAS FOR NON-INVASIVE PLASMONIC RESONANCE FREQUENCY ANALYSIS

BIOSENSADO A NANOESCALA: NANOANTENAS FRACTALES DE ORO PARA ANÁLISIS DE FRECUENCIA DE RESONANCIA PLASMÓNICA NO INVASIVE

Alondra Hernandez Cedillo
Department of Applied Physics and Materials Science, Northern Arizona University, Flagstaff, Arizona

Fernando Sebastián Chiwo González
Universidad Marista de San Luis Potosí

Rosa Angélica Lara-Ojeda
Universidad Marista de San Luis Potosí

María Selene Ordaz Rodriguez
Universidad Marista de San Luis Potosí

Javier Mendez Lozoya
Universidad Marista de San Luis Potosí

DOI: https://doi.org/10.37811/cl_rcm.v9i1.16906

Biosensing at the Nanoscale: Gold Fractal Nanoantennas for Non-Invasive Plasmonic Resonance Frequency Analysis

Alondra Hernandez Cedillo[1]
ah3526@nau.edu
https://orcid.org/0000-0001-7518-2644
Department of Applied Physics and Materials Science, Northern Arizona University, Flagstaff, Arizona

Fernando Sebastián Chiwo González
1958@umaslp.maristas.edu.mx
http://orcid.org/0000-0002-1990-163X
Universidad Marista de San Luis Potosí

Rosa Angélica Lara-Ojeda
2004@umaslp.maristas.edu.mx
https://orcid.org/0000-0003-0892-7890
Universidad Marista de San Luis Potosí

María Selene Ordaz Rodriguez
mordaz@umaslp.maristas.edu.mx
http://orcid.org/0009-0004-6166-7148
Universidad Marista de San Luis Potosí

Javier Mendez Lozoya
1974@umaslp.maristas.edu.mx
https://orcid.org/0000-0002-4218-2231
Universidad Marista de San Luis Potosí

ABSTRACT

The biotechnology sector is focusing on developing biosensors that allow us to detect and monitor substances in vivo using non-invasive methods. For example, in substances detection using the label-less method, radiation in the mid-infrared (mid-IR) has been used to obtain the vibrational fingerprint. In this work, we propose to use plasmonic nanoantennas called spaceship to develop a SEIRA substrate that can be used in disease detection. The spaceship nanoantennas were fabricated using electron beam lithography. A potential SEIRA device was fabricated with Au spaceship nanoantennas based on gold fractal nanoantennas with dimensions of 5.5 µm long and 5 µm high, inner structure with 970 nm, 950 nm in length and height respectively. Arm width of 400 nm and 50 nm of thickness. The resonance frequency (ν_{res}) was analyzed using gold nanoantennas absorbance as a function of frequency where one peak was found at 33THz. Additionally, these results were corroborated with a simulation where the magnitude of the electric field E=7.79 V/m at 34.98 THz was found. These results allow us to propose spaceship nanoantennas as good candidates for the design of a SEIRA substrate.

Keywords: electron beam lithography, fractal nanoantenna, SEIRA substrate, resonance frequency, Fourier transformation infrared spectroscopy

[1] Autor principal
Correspondencia: ah3526@nau.edu

Biosensado a nanoescala: Nanoantenas fractales de oro para análisis de frecuencia de resonancia plasmónica no invasiva

RESUMEN

El sector de la biotecnología se está centrandzo en el desarrollo de biosensores que permitan detectar y controlar sustancias in vivo mediante métodos no invasivos. Por ejemplo, en la detección de sustancias mediante el método sin etiquetas se ha utilizado radiación en el infrarrojo medio (medio-IR) para obtener la huella vibracional. En este trabajo, proponemos utilizar nanoantenas plasmónicas denominadas spaceship para desarrollar un sustrato SEIRA que pueda utilizarse en la detección de enfermedades. Las nanoantenas spaceship se fabricaron mediante litografía por haz de electrones. Se fabricó un posible dispositivo SEIRA con nanoantenas spaceship de Au basadas en nanoantenas fractales de oro con unas dimensiones de 5.5 µm de longitud y 5 µm de altura, estructura interna con 970 nm, 950 nm de longitud y altura respectivamente. La anchura del brazo es de 400 nm y el grosor de 50 nm. La frecuencia de resonancia (ν_{res}) se analizó utilizando la absorbancia de las nanoantenas de oro en función de la frecuencia, donde se encontró un pico a 33THz. Además, estos resultados se corroboraron con una simulación donde se encontró la magnitud del campo eléctrico E=7.79 V/m a 34.98 THz. Estos resultados nos permiten proponer a las nanoantenas espaciales como buenas candidatas para el diseño de un sustrato SEIRA.

***Palabras clave**:* litografía por haz de electrones, nanoantena fractal, sustrato SEIRA, frecuencia de resonancia, espectroscopia infrarroja por transformación de Fourier

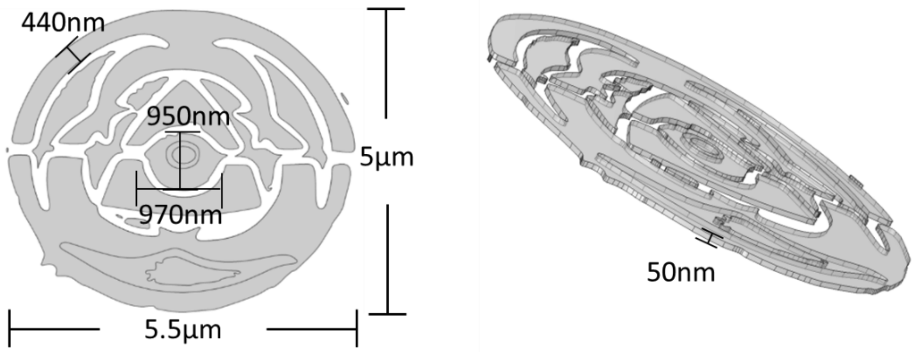
Artículo recibido 13 enero 2025
Aceptado para publicación: 19 febrero 2025

INTRODUCTION

The biotechnology sector is focusing on developing biosensors that allow us to detect and monitor substances in vivo using non-invasive methods. For example, in substances detection using the label-less method, radiation in the mid-infrared (mid-IR) [1] has been used to obtain the vibrational fingerprint. In fact, it has provided an identifying method for molecular capacity using the characteristic vibrational spectrum, which is directly related to its molecular constituents and chemical bonds. This allows us to obtain information from biosamples [2], such as lipids or proteins, for detection, identification, and diagnosis [3]. Therefore, it has been widely proposed that plasmonic nanostructures (patterned as nanoantennas) seem like candidates to take on a key role in detection using enhanced surfaces to overcome the problem of limited molecular absorption. Surface Enhanced Infrared Absorption (SEIRA) spectroscopy [4] [5] of substrates was successfully implemented and shown to have an advantage in the specific and selective detection of low and ultra-low concentrations of analytes in the (µM-pM) range [6]. These plasmonic devices based on nanoantenna arrays can be used for gas sensing, disease detection, and optical imaging [7]. Fractals, on the other hand, are geometric shapes that exhibit self-similarity at different scales. They are characterized by a repeating pattern that appears similar at all levels of magnification. Fractals can be found in nature, such as in snowflakes and ferns, and can also be created artificially using mathematical algorithms. Fractals have many interesting properties, including infinite complexity, non-integer dimensionality, and the ability to fill space without repeating. These properties make them useful for a variety of applications, including antenna design, data compression, and image processing. The combination of nanoantennas and fractals has led to the development of fractal nanoantennas, which combine the enhanced electromagnetic response of nanoantennas with the self-similarity and complex geometries of fractals. Fractal nanoantennas can exhibit a wide range of optical responses, including enhanced absorption, scattering, and fluorescence. They can also be used for sensing applications, such as detecting small molecules and biomolecules. Additionally, fractal nanoantennas have been used in the development of metamaterials, which are engineered materials with properties not found in natural materials.

In the present work, for the fabrication of spaceship nanoantennas, a morphology based on a fractal nanoantenna that refer to intricate patterns that appear in fields of crops, typically wheat, barley, or other cereal grains. These patterns often involve flattened crops in a circular or geometrically complex arrangement (see Fig. 1). This morphology was studied by analyzing the electric field generated due to the interaction between infrared radiation and the nanoantenna as a function of frequency. We analyze the feasibility of use in a SEIRA substrate based on the obtained results.

Figure 1. *Morphology and dimensions used as fractal nanoantenna in numerical simulations.*



Materials and Methods

We fabricate plasmonic devices based on Au nanoantenna arrays using electron beam lithography (EBL) on silicon (Si) substrates with 300nm silicon dioxide (SiO2), and their resonance frequency was investigated using infrared spectroscopy (FTIR). In addition, the frequency was studied using simulations by the finite element method to analyze the dependence of the electric field on frequency.

Numerical Simulations

COMSOL Multiphysics is a commercial software package that is widely used for simulating physical phenomena. It is based on the FEM and can be used to model a variety of engineering systems, including plasmonic devices [8].

In the simulations described plane waves that are linearly polarized to the z-axis are used to interact with a plasmonic device based on arrays of gold (Au) nanoantennas [9]. The purpose of the simulations is to evaluate the absorbance of the plasmonic device as a function of the frequency of the incident wave.

The range of frequencies considered in the simulations is (20 – 90) THz [10], [11], which is in the terahertz (THz) range. This is an important range for many applications, including imaging, sensing, and communication.

Overall, the simulations using COMSOL Multiphysics, and the FEM are a powerful tool for studying the behavior of plasmonic devices and can provide valuable insights into their performance and potential applications.

The software solves equation 1 in the frequency domain

$$\nabla \, x \, \mu_r^{-1}(\nabla \, x \, \boldsymbol{E}) - k_0^2 \left(\varepsilon_r - \frac{j\sigma}{\omega \epsilon_0} \right) \boldsymbol{E} = 0 \quad (1)$$

where ω is the frequency, E is the electric field, ε_0 is vacuum permittivity, ε_r is relative permittivity, σ is material conductivity, μ_r corresponds to relative permeability, and k0 is the wavelength vector, see Table 1 [12], [13].When using the COMSOL RF module to simulate the absorbance of a material, meshing is an important factor to consider in order to obtain accurate results. The mesh should be fine enough to capture the details of the electromagnetic waves at the highest frequency of interest. This means that the mesh density should be proportional to the wavelength, with smaller mesh elements for shorter wavelengths.

***Table 1**. Gold value used to analyze a resonant frequency of fractal nanoantennas at 10.3µm.*

Variable	Name	Value
ε_r	Relative permittivity	1975.6

To explain the resonance phenomenon in the far-field plots using the near-field contours, one can analyze the spatial distribution of the electric field around the structure at different frequencies. At frequencies far from the resonance frequency, the near-field contours show weak or spatially uniform field distributions, indicating weak interactions between the structure and the incident light. This will lead to far-field plots that show weak or isotropic radiation patterns.

As the frequency approaches the resonance frequency, however, the near-field contours will show strong and spatially non-uniform field distributions, indicating strong interactions between the structure and the incident light. This will lead to far-field plots that show enhanced and directional radiation patterns, with higher intensity in certain directions or polarizations.

By analyzing the near-field contours, one can also gain insight into the physical mechanisms underlying the resonance phenomenon. Near-field contours may reveal the formation of plasmonic hotspots, where the electric field is highly concentrated and leads to enhanced absorption. Near-field contours also show the formation of standing waves or interference patterns, which can lead to directional scattering of light [14].

Fabrication

The nanoantennas were fabricated using electron beam lithography on Si wafers with 300 nm SiO_2 as a thermal and electric insulator. The manufacturing procedure used was as follows: 300 nm of polymethylmethacrylate (PMMA) were deposited on the Si/SiO_2 substrates by spin coating, the pattern was made with a Raith ELPHY Quantum lithography system. Nanoantenna patterns were recorded using a 30 keV and an area dose of 250 $\mu C/cm^2$. The development was performed by immersing the Si/SiO_2 substrate in a MIBK: IPA solution for 80 seconds. Subsequently, 50 nm gold layer was deposited by RF sputtering. Finally, the devices were left two hours in acetone to remove excess resin and metal [15].

Results and discussion

FEM is a numerical technique used to solve partial differential equations (PDEs) by discretizing the problem domain into finite elements. It is commonly used in engineering and physics simulations to analyze complex physical systems. Here, FEM simulations were employed to study the behavior of an electromagnetic system. Figure 1 shows a 3D image of electric field enhancement E=7.79V/m at νres=34.98THz. The resonance frequency of 34.98 THz indicates the specific frequency at which the system under simulation exhibits resonance behavior. Resonance occurs when the system's response to the incident electromagnetic wave is maximized, leading to enhanced effects such as increased electric field strength.

Figure 2. *shows the magnitude of the electric field E=7.79 V/m at 34.98 THz.*

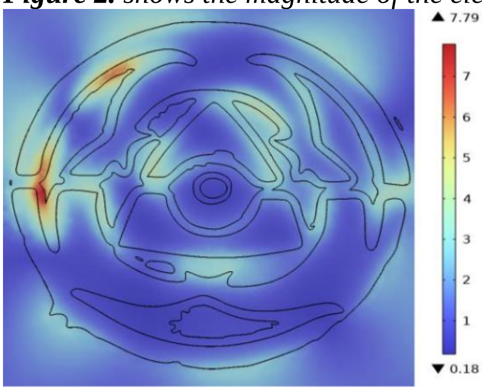


Figure 2 *shows the results obtained from the finite method simulation using COMSOL where absorbance was analyzed as a function of frequency. One peak corresponding to the resonance frequencies located at 34.98 THz was found [17].*

__Figure 3.__ Graph of the results of the finite element method simulation where absorbance was analyzed as a function of frequency; One peak corresponding to the resonance frequency located at 34.98 THz was found.

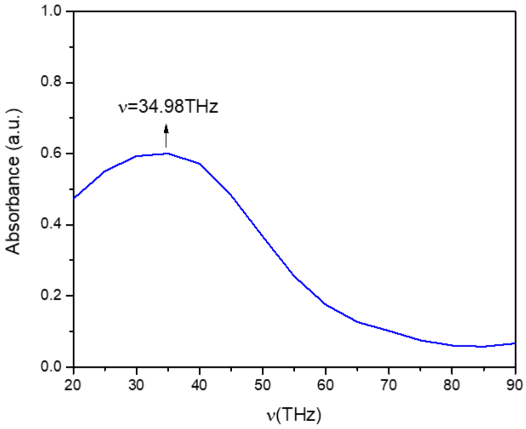
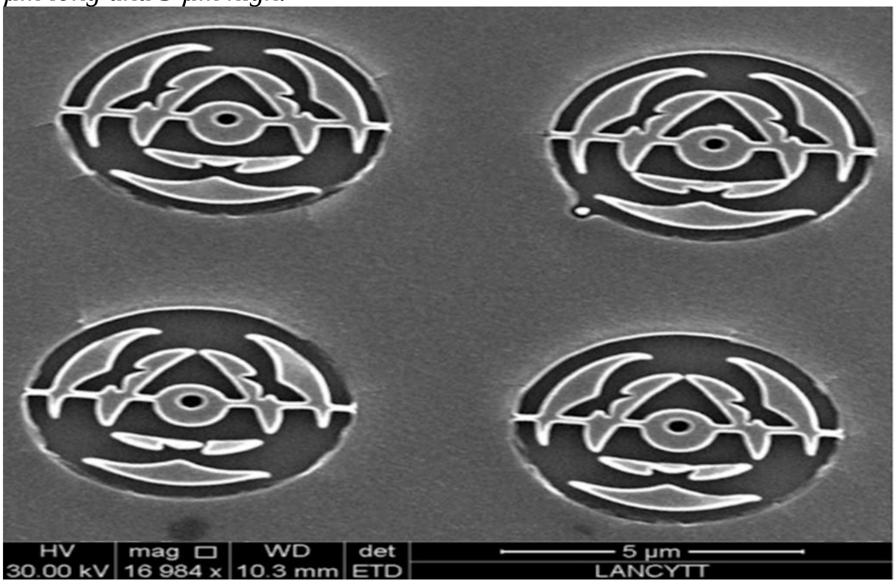


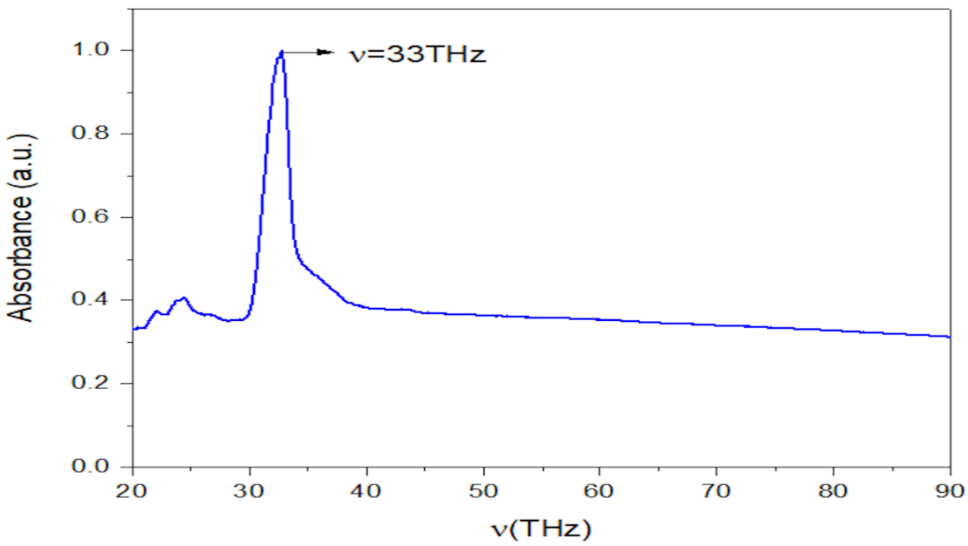
Figure 3 shows the results obtained from analyzing the fabricated morphology by electron beam using the FEI Inspect F50 field emission scanning electron microscope. We can see that each spaceship nanoantenna measures 5.5 µm in length, 5 µm in height, inner structure with 970 nm, 950 nm in length and height respectively. Arm width of 400 nm and 50 nm of thickness.

__Figure 4.__ Micrograph of spaceship nanoantennas based on gold fractal nanoantennas which are 5.5 µm long and 5 µm high.



Hence, the optical properties of plasmonic devices based on nanoantenna arrays were studied using infrared spectroscopy (FTIR) with Bruker Vertex 70 equipment, analyzing the absorbance as a function of frequency (THz), which allows us to define the resonance frequency of the device. Figure 4 shows that the resonance frequency (v_{res}) for the nanoantenna named spaceship presents one peak 33 THz [16].

Figure 5. *Graph of the infrared spectroscopy results where absorbance was analyzed as a function of frequency; it is seen that the resonance frequency (ν_{res}) for the nanoantenna called spaceship based on the fractal nanoantenna presents one peak at 33 THz.*



Comparing resonance frequency obtained from experimental and simulations results of the device, a shift was observed. This shift can due to different factors, such as material composition or environmental conditions. The experimental results are based on measurements taken from a physical system, whereas the simulation results are based on a model created within the finite element method. Discrepancies can arise due to simplifications or assumptions made in the simulation model that may not perfectly represent the real-world system.

Nanoantennas themselves are not typically used as biosensors or biodetectors in the same way that specific biomolecules, enzymes, or antibodies are used. However, nanoantennas can enhance the performance of biosensors and biodetectors by improving their sensitivity, signal-to-noise ratio, and detection limits. Nanoantennas can concentrate and enhance the interaction between electromagnetic waves (e.g., light) and the target molecules in the biosensor. This results in stronger and more detectable signals, making it easier to identify and quantify biological or chemical analytes. Moreover, plasmonic nanoantennas made of noble metals like gold or silver, can exhibit surface plasmon resonance (SPR). SPR is sensitive to changes in the refractive index of the surrounding medium, making it a valuable tool for label-free biosensing. When target molecules bind to the sensor surface, it causes a shift in the SPR wavelength, which can be measured and correlated with analyte concentration. Plasmonic nanoantennas, are often used in immunoassays. Functionalized nanoantennas can serve as labels for antibodies or antigens, and their plasmonic properties enable sensitive detection through changes in scattering or absorption when binding events occur. In summary, while nanoantennas themselves do not directly act as biosensors or biodetectors, they are valuable components in enhancing the performance of these devices. Their ability to manipulate light at the nanoscale and create localized electromagnetic fields makes them essential for improving the sensitivity and specificity of detection in various applications, including biosensing and biodetection.

CONCLUSIONS

A potential SEIRA device was fabricated with Au spaceship nanoantennas based on fractal nanoantennas with dimensions of 5.5 µm long and 5 µm high, inner structure with 970 nm, 950 nm in length and height respectively. Arm width of 400 nm and 50 nm of thickness. Using infrared spectroscopy (FTIR), the gold nanoantennas absorbance was analyzed as a function of frequency, where one peak was found that correspond to the resonance frequency located at 33 THz. These results were corroborated with finite method simulations, where it was found that the magnitude of the electric field was E=7.79 V/m when υ_{res}=34.98 THz. These results allow us to propose fractal nanoantennas as good candidates for the design of a SEIRA substrate. In summary, while nanoantennas themselves do not directly act as biosensors or biodetectors, they are valuable components in enhancing the performance of these devices. Their ability to manipulate light at the nanoscale and create localized electromagnetic fields makes them essential for improving the sensitivity and specificity of detection in various applications, including biosensing and biodetection.

ACKNOWLEDGMENTS

This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACyT) – Mexico, through Grants CEMIE-Sol 105, by the National Laboratory program from CONACYT through the Terahertz Science and Technology National Lab (LANCYTT) and by the Tecnológico Nacional de México/I.T. San Luis Potosí.

E. Garduño gratefully acknowledge support from the "Investigadoras e Investigadores por México" CONACYT program through project No. 674.

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability

The datasets generated and/or analyzed during the current study are available from the corresponding author on reasonable request.

REFERENCES

[1] Adrianna N. Masterson, Thakshila Liyanage, Hristos Kaimakliotis, Hamed Gholami Derami, Frédérique Deiss, and Rajesh Sardar, Analytical Chemistry 2020 92 (13), 9295-9304, DOI: 10.1021/acs.analchem.0c01639

[2] Altug, H., Oh, SH., Maier, S.A. et al. Advances and applications of nanophotonic biosensors. Nat. Nanotechnol. 17, 5–16 (2022). https://doi.org/10.1038/s41565-021-01045-5

[3] López-Lorente ÁI, Mizaikoff B. Mid-infrared spectroscopy for protein analysis: potential and challenges. Anal Bioanal Chem. 2016 Apr;408(11):2875-89. doi: 10.1007/s00216-016-9375-5. Epub 2016 Feb 16. PMID: 26879650.

[4] Odeta Limaj, Dordaneh Etezadi, Nathan J. Wittenberg, Daniel Rodrigo, Daehan Yoo, Sang-Hyun Oh, and Hatice Altug, Infrared Plasmonic Biosensor for Real-Time and Label-Free Monitoring of Lipid Membranes, Nano Letters 2016 16 (2), 1502-1508, DOI: 10.1021/acs.nanolett.5b05316

[5] Shabnam Andalibi Miandoab, Robabeh Talebzadeh, Ultra-sensitive and selective 2D hybrid highly doped semiconductor-graphene biosensor based on SPR and SEIRA effects in the wide range of infrared spectral, Optical Materials, Volume 129, 2022, 112572,

[6] Brown LV, Yang X, Zhao K, Zheng BY, Nordlander P, Halas NJ. Fan-shaped gold nanoantennas above reflective substrates for surface-enhanced infrared absorption (SEIRA). Nano Lett. 2015 Feb 11;15(2):1272-80. doi: 10.1021/nl504455s. Epub 2015 Jan 12. PMID: 25565006.

[7] Brolo, Alexandre G., "Plasmonics for future biosensors." Nature Photonics 6 (2012): 709-713.

[8] A. M. A. Sabaawi, C. C. Tsimenidis, and B. S. Sharif, "Infra-red nano-antennas for solar energy collection," *2011 Loughborough Antennas & Propagation Conference*, 2011, pp. 1-4, doi: 10.1109/LAPC.2011.6114082.

[9] Taflove A, Hagness S C and Piket-May M 2005 Computational Electromagnetics: The Finite-Difference Time-Domain Method The Electrical Engineering Handbook. (Cambridge: Academic) 629–70

[10] Johannes Hoffmann, Christian Hafner, Patrick Leidenberger, Jan Hesselbarth, and Sven Burger "Comparison of electromagnetic field solvers for the 3D analysis of plasmonic nanoantennas", Proc. SPIE 7390, Modeling Aspects in Optical Metrology II, 73900J (17 June 2009); https://doi.org/10.1117/12.828036

[11] Hao Hu, Wei Tao, Florian Laible, Thomas Maurer, Pierre-Michel Adam, Anke Horneber, Monika Fleischer, Spectral exploration of asymmetric bowtie nanoantennas, Micro and Nano Engineering, Volume 17, 2022, 100166, ISSN 2590-0072, https://doi.org/10.1016/j.mne.2022.100166.

[12] Baokuan Li, Fang Wang, and Fumitaka Tsukihashi, “Current, Magnetic Field and Joule Heating in Electroslag Remelting Processes”, ISIJ International, Vol. 52 (2012), No. 7, pp. 1289–1295.

[13] Elena E. Antonova and David C. Looman, “Finite Elements for Thermoelectric Device Analysis in ANSYS”, International Conference on Thermoelectrics, 2005.

[14] Hassani Gangaraj, Seyyed Ali and Monticone, Francesco. "Molding light with metasurfaces: from far-field to near-field interactions" Nanophotonics, vol. 7, no. 6, 2018, pp. 1025-1040. https://doi.org/10.1515/nanoph-2017-0126

[15] Javier Mendez-Lozoya, Ramón Díaz de León-Zapata, Edgar Guevara, Gabriel González, and Francisco J. González "Thermoelectric efficiency optimization of nanoantennas for solar energy harvesting," Journal of Nanophotonics 13(2), 026005 (2 May 2019). https://doi.org/10.1117/1.JNP.13.026005

[16] S Kuznetsov et al 2022 J. Phys.: Conf. Ser. 2316 012016

[17] Francisco Javier González, Javier Alda, Jorge Simón, James Ginn, Glenn Boreman, The effect of metal dispersion on the resonance of antennas at infrared frequencies, Infrared Physics &

Technology, Volume 52, Issue 1, 2009, Pages 48-51, ISSN 1350-4495, https://doi.org/10.1016/j.infrared.2008.12.002.