

## Effect of Particles Diameters on the Theoretical and Experimental Surface Plasmon Absorption (SPA) of Gold Nanoparticles Prepared by Laser Ablation Method

Kahtan A. Mohammed <sup>1,\*</sup>, Azhar A. Habieb <sup>2</sup>, Ahmed O. Soary <sup>2</sup>

<sup>1</sup> College of Science, Department of Physics, University of Basrah, Basrah, Iraq

<sup>2</sup> College of Science, Department of Physics, University of Kufa, Kufa, Iraq

\* Correspondence: [kahtan444@gmail.com](mailto:kahtan444@gmail.com); Scopus ID: 57210814038

**Abstract:** Gold nanoparticles were synthesized by laser ablation method and investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM), and UV–vis spectrum. It was found out that the number of lasers shots is an essential factor in determining the morphology and average diameter of prepared nanoparticles. Optical measurements show absorption bands of varying strengths around 526 and 518 nm. The surface Plasmon absorption maxima for gold nanoparticles changes linearly with increasing shoots number. Scanning electron micrograph (SEM) and atomic force micrograph AFM showed the presence of spherical particles in the range of 10–30 nm size, and the size of these particles decreases with increasing laser shoots number.

**Keywords:** laser ablation; noble metals; gold nanoparticles; surface Plasmon absorption.

© 2020 by the authors. This article is an open-access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

### 1. Introduction

Nanotechnology can be defined as new emerging technology and science that includes manufacturing, synthesizing, and studying materials that fall within the nanoscale. Nanoparticles that fall within the range of 1 to 100 nanometers can display unique physical and chemical properties compared to the same materials when they are in their standard form owing to their large surface area volume ratio and quantum size effect [1][2][3]. A dramatic and significant change in the properties of these materials can occur due to their large surface-to-volume ratio. Reducing the dimensions and size of

a particle leads to a change and development in the electronic properties of this substance because the density of states and the spatial length scale of the electronic motion are reduced with decreasing size [4].

Recently, considerable attention has been paid and directed towards preparing and synthesizing metallic nanoparticles for their exceptional, unique properties. The most important of these materials are noble metals such as gold, silver, and platinum, as they possess important size-dependent optical properties and required in many electronic,



industrial, and medical applications [5]. Gold is a noble and essential metal as it possesses some important specifications as its resistance to chemical scratching as well as its resistance to oxidation in influencing surrounding conditions such as high temperatures [6].

The collective oscillations of conduction electrons stimulated by the electromagnetic field (EM) of incident light are identified as surface Plasmon resonance (SPR). The phenomenon is only observed in nanoscale metallic particles in which the electrons are confined in three dimensions. Due to this effect, an electric field is induced around nanoparticles (NPs), which could be larger than that of the incident light by orders of magnitude. SPR is a nanoscale-size effect; that is, the bulk metal particles do not possess such properties. In the case of MNPs, the electrons are confined in three dimensions, which results in LSPR. Nanowires, nanotubes, and nanofilms could also exhibit SPs. In consequence of their large dimensions compared to the light wavelength, however, the induced EM field propagates along with the interface of the metal and dielectric medium instead of being localized [7].

Plasmonics is a recent research line of Nanophotonics based on the properties of surface plasmons, which are collective excitations of the free electrons at the interface between a metallic structure and a dielectric. This phenomenon can be optically observed in thin metal films like a surface plasmon resonance (SPR) and in metal nanostructures and NPs, like the so-called Localized Surface Plasmon Resonance (LSPR). Optical excitations remain localized in space, given the nanostructure/ nanoparticle size with respect to the light wavelength [8].

The morphology and optical properties and particle size distribution of nanomaterials are entirely dependent on the method used to manufacture and prepare them. A large number of synthetic procedures have been employed in order to synthesize gold nanoparticles like one-pot reaction [9] photochemical methods [10] green methods [11] laser ablation [12]. The laser ablation method is suitable for generating metal particles,

particularly gold, in solution [13]. Pulsed Laser Ablation in Liquid media (PLAL) is an optimistic routine for the controlled nanomaterials assembly by means of quick quenching of reactive of ablated pieces at the boundary between the plasma and liquids.

"PLAL" is a beneficial method for making many categories of nanoparticles, such as noble metal NPs. PLAL has many benefits compared with other conventional chemical and physical methods like stability, purity of the fabricated nanoparticle colloids, and do not need a vacuum chamber. It is the most promising and flexible technique because of its ability to control NPs size by adjusting the laser parameters; this technique provides the possibility of producing a large variety of NPs that are free of both surface-active substances and counter ions [14]. Moreover, PLAL is a chemically "clean and simple" synthesis due to the process with reduced product formation, more straightforward starting materials, no need for catalyst [15].

When a laser with high power exposes on a surface of the material, an amount of the energy of the laser is absorbed and conducted into the inside of the material. If the energy that absorbed is suitable, the material surface will liquefy and evaporate. The ablation process, and thus the features created, depends on the properties of the material used and the laser pulse. Experiments have indicated that incubation effects have a significant impact on multishot laser ablation. It has been seen that in irradiating with several laser pulses, each being below the single-shot threshold for ablation, at the substrate, that after a few shots ablation does take place, even though the individual pulses do not have sufficient energy to ablate the material in a single pulse [16]. The control of particle size is commonly achieved by choice of proper laser shoots.

Here, we propose the fabrication of Au nanoparticles obtained by the single-step laser ablation of the gold target in water and study the effect of laser shoots number on the properties of gold nanoparticles, especially the average diameters and the surface Plasmon absorption.

## 2. Materials and Methods

### 2.1. Synthesis of gold nanoparticles.

The laser ablation method was used to prepare the gold nanoparticles as a high-purity gold foil was used. The gold foil was prepared and cleaned by washing it more than once with distilled water and

ethanol to remove any unwanted materials after cutting it to the appropriate area. The "Nd-YAG" laser (shown in figure 1) with a wavelength equal to 1.064  $\mu\text{m}$  had been operated as a source for ablation. The energy of pulse at the gold foil

## Effect of Particles Diameters on The Theoretical and Experimental Surface Plasmon Absorption (SPA) of Gold Nanoparticles Prepared by Laser Ablation Method

• • •

superficial was 700 mJ. The metal foil was putted in a quartz cell occupied with 1ml DDW; thus, the smoke like colloids overhead the gold foil has been observed. The foil was placed at 9 mm from the surface of a liquid. The number of laser shots is an additional parameter owing to a significant influence on the creation of noble metals NPs. Gold samples are organized at different shoots of the laser. Colloidal nanoparticles were deposited on silicon wafer by the drop-casting method to test by SEM and AFM.

### 2.2 Characterization of gold nanoparticles.

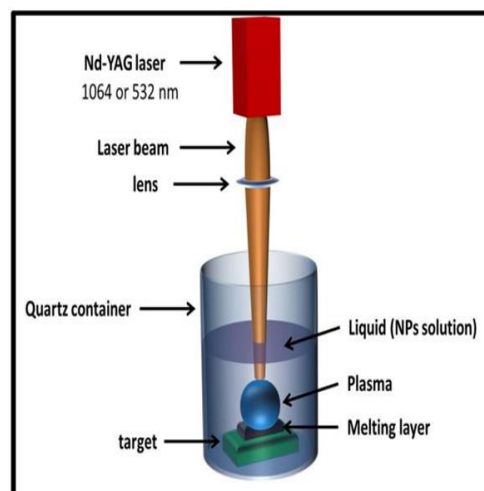
The optical properties (surface Plasmon absorbance) of colloidal Nanogold were estimated with T90+ UV-VIS double beam scanning spectrometer from PG instrument company in a 1 cm optical path quartz cuvette at a wavelength range of 300–700 nm. SEM (INSPECT-550) Scanning Electron Microscope (SEM) is generally performed at 10 kV to measure the surface morphology of the samples. In most cases, the highest magnification achievable by this microscope is 300,000. CSPM

## 3. Results and Discussion

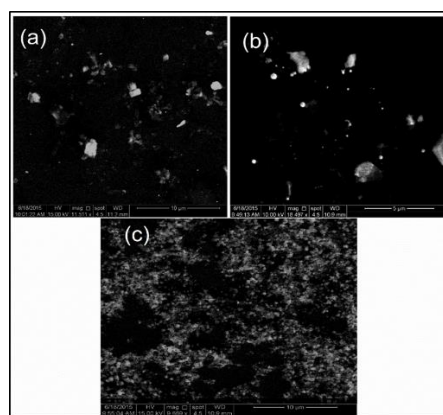
Colloidal of gold nanoparticles were produced by pulsed laser ablation, focused energy 700mJ, and the number of applied pulses ranged from 25 to 90 pulses and 1064 nm Nd: YAG laser. When the pulse of laser hits the surface of the gold plate dipped in liquid, it forms a flash plume with a strong shockwave that spreads in the liquid. The flash radiated light and cracking sound, following by a visible cloud of gold particles emission out of the surface of the metal and dispersed slowly in all directions floating in liquid, easily noticed by the naked eye. It was seen that the solution color was varied from soft pink color, to then finally dark. The darker color indicates a higher concentration of gold nanoparticles.

Figure 2 illustrates the (SEM) images, which indicate the mean diameter of the synthesized nanoparticles by laser ablation at 25, 50, and 90 pulses, respectively. The Nd-YAG laser with an energy of 700 mJ is used. As it was noticed the impact of the number of shoots clearly on the diameters and morphologies of nanoparticles and their density. The increase in the number of laser strokes made reduces the diameter of the nanoparticle and becomes more spherical.

model AA33000 AFM Atomic Force Microscopy supply by Angstrom Company was used to determine the particle's dimensions range of the prepared Au nanoparticles and their statistical distribution.



**Figure 1.** Experimental arrangement for nanoparticles production by laser ablation method.

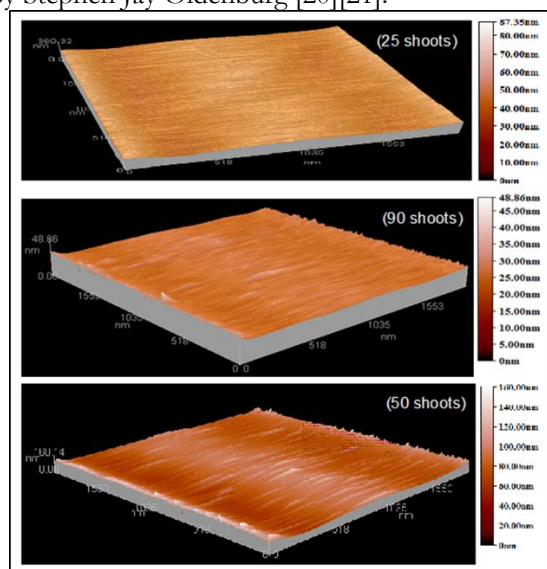


**Figure 2.** SEM images of gold nanoparticles at different laser shoots: 25 (a), 50 (b) and 90 (c).

Figure 3 and figure 4 display the AFM images and the size distributions of gold nanoparticles formed by laser ablation at 25, 50, and 90 pulses. Hence the formed gold nanoparticles have a mean diameter of 15 nm, 24 nm, and 34 nm at 90, 50, and 25 pulses, respectively. The result has shown that the mean diameter of formed nanoparticles and size distribution decrease with the increasing number of pulses. This result agrees with previous studies in ref. [17]. We have expected that the reason for reducing particle size is the repeated laser shot cause fragmentation of the large particles and produces smaller particles. Interactions

between NPs under laser irradiation lead to the fusion of gold colloids [18]. UV-visible spectroscopy is one of the general characterization methods to determine particle formation and its properties. Furthermore, it is known that the spectrum surface Plasmon resonance of nanoparticles is influenced by the size, shape, interparticle interactions, free electron density, and the surrounding medium, which indicates that it is an efficient tool for monitoring the electron injection and aggregation of NPs. [19][nnl-12].

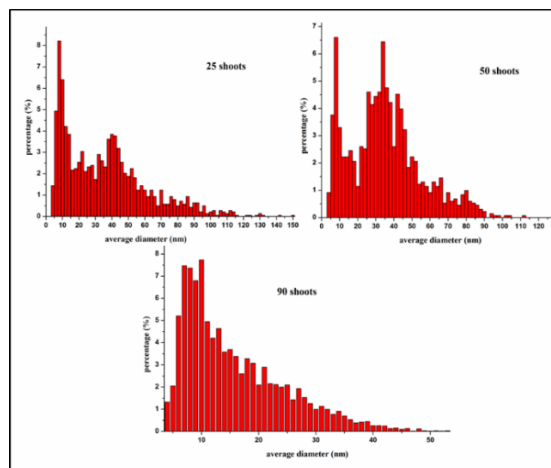
We can use the diameters of gold nanoparticles obtained from the SEM and AFM tests in calculating the surface Plasmon absorption and determining the absorption region in the visible spectrum by using a theoretical program developed by Stephen Jay Oldenburg [20][21].



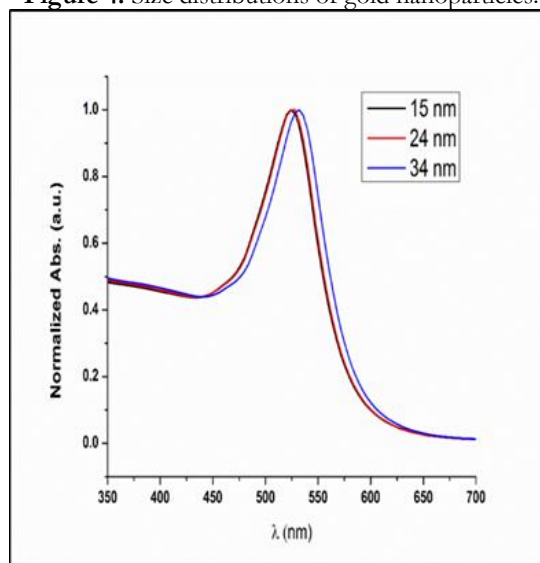
**Figure 3.** AFM topographical 3D images of gold nanoparticles at different laser shoots.

Where the following figure 5 shows the absorption spectra obtained from the theoretical program after entering the particle sizes that were equal to 34 nm at 25 laser shoots, 24 nm at 50 laser shoots, and 15 nm at 90 laser shoots.

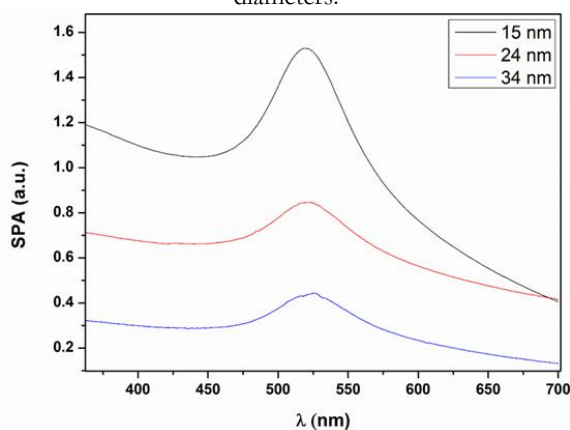
From figure 5 it can be noted that the peak absorption shifted to shorter wavelengths with a decrease of the diameter of the nanoparticle. Figure 6 displays that the spectrum of absorption in a solution of gold nanoparticles quasi-symmetrically is around 518-526 nm and the particle size is 20-50 nm in a spherical shape that agreement with former stud in ref.[17][22]. The intensity of absorption is increases when the laser shots increase.



**Figure 4.** Size distributions of gold nanoparticles.



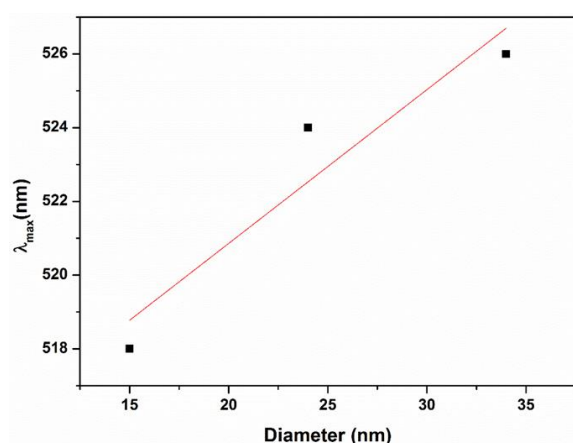
**Figure 5.** The theoretical SPA spectra of the Plasmon band of Au NPs, obtained different mean diameters.



**Figure 6.** The experimental SPA spectra of the Plasmon band of Au NPs, obtained different mean diameters.



## Effect of Particles Diameters on The Theoretical and Experimental Surface Plasmon Absorption (SPA) of Gold Nanoparticles Prepared by Laser Ablation Method



**Figure 7.** Position of the surface Plasmon resonance peak ( $\lambda_{max}$ ) as a function of the particle diameter for Au NPs.

It can be seen from figure 6 that the increase of the number of pulses leads to an increase in absorbance intensity, which is evidence of an increase in the density of nanoparticles inside the liquid. The increase in the number of nanoparticles is due to the fact that the laser beam works to uproot the number of nanoparticles in each pulse. Figure 7. Position of the surface Plasmon resonance peak ( $\lambda_{max}$ ) as a function of the particle diameter for Au NPs.

### 4. Conclusions

In the current study, gold nano colloid solutions were prepared physically by laser ablation in liquid. The effect of laser shoot on the optical absorption and size of particles have been tested. Optical measurements show absorption bands of varying strengths around 526 and 518 nm. The surface Plasmon absorption maxima for gold nanoparticles

### Funding

This research received no external funding.

### Acknowledgments

The authors declare no acknowledgments.

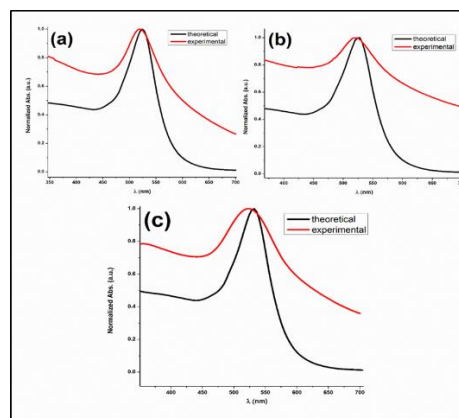
### Conflicts of Interest

The authors declare no conflict of interest.

### References

1. Steinigeweg, D.; Schlücker, S. Monodispersity and size control in the synthesis of 20–100 nm quasi-spherical silver nanoparticles by citrate and ascorbic acid reduction in glycerol–water mixtures. *Chemical Communications* **2012**,

We can compare the theoretical results with the practical results of the absorption of the surface Plasmon of gold nanoparticles of various sizes. Where the figure shows theoretical and practical surface Plasmon absorption of various diameters. Figure 8 shows the theoretical and experimental spectra of the surface Plasmon absorption for gold nanoparticles with different.



**Figure 8.** Theoretical and experimental spectra of the surface Plasmon absorption for gold nanoparticles with different diameters (a) 15 nm, (b) 24 nm, and (c) 34 nm.

changes linearly with increasing shoots number. Scanning electron micrograph (SEM) and atomic force micrograph AFM showed the presence of spherical particles in the range of 10–30 nm size, and the size of these particles decreases with increasing of laser shoots number.

- Nano Science and Engineering* **2016**, *6*, 29–37, <https://doi.org/10.4236/wjnse.2016.61003>.
3. Muniz-Miranda, M.; Muniz-Miranda, F.; Giorgetti, E. Spectroscopic and Microscopic Analyses of Fe<sub>3</sub>O<sub>4</sub>/Au Nanoparticles Obtained by Laser Ablation in Water. *Nanomaterials* **2020**, *10*, <https://doi.org/10.3390/nano10010132>.
  4. [Pal, A.; Shah, S.; Devi, S. Synthesis of Au, Ag and Au–Ag alloy nanoparticles in aqueous polymer solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2007**, *302*, 51–57, <https://doi.org/10.1016/j.colsurfa.2007.01.054>.
  5. A. N. Krklješ, M. T. Marinović-Cincović, Z. M. Krklješ, A.N.; Marinović-Cincović, M.T.; Kačarević-Popović, Z.M.; Nedeljković, J.M. Dynamic thermogravimetric degradation of gamma radiolytically synthesized Ag–PVA nanocomposites. *Thermochimica Acta* **2007**, *460*, 28–34, <https://doi.org/10.1016/j.tca.2007.05.015>.
  6. Amendola, V.; Meneghetti, M. Laser ablation synthesis in solution and size manipulation of noble metal nanoparticles. *Physical Chemistry Chemical Physics* **2009**, *11*, 3805–3821, <https://doi.org/10.1039/B900654K>.
  7. Tabor, C. *Some optical and catalytic properties of metallic nanoparticles*. Georgia Institute of Technology, 2010.
  8. Gradess, R.; Abargues, R.; Habbou, A.; Canet-Ferrer, J.; Pedrueza, E.; Russell, A.; Valdés, J.L.; Martínez-Pastor, J.P. Localized surface plasmon resonance sensor based on Ag-PVA nanocomposite thin films. *Journal of Materials Chemistry* **2009**, *19*, 9233–9240, <https://doi.org/10.1039/B910020B>.
  9. Giesen, B.; Nickel, A.-C.; Garzón Manjón, A.; Vargas Toscano, A.; Scheu, C.; Kahlert, U.D.; Janiak, C. Influence of synthesis methods on the internalization of fluorescent gold nanoparticles into glioblastoma stem-like cells. *Journal of Inorganic Biochemistry* **2020**, *203*, <https://doi.org/10.1016/j.jinorgbio.2019.110952>.
  10. Surendra, B.; Raju, B.M.; Onesimus, K.N.S.; Choudhary, G.L.; Paul, P.F.; Vangalapati, M. Synthesis and characterization of Ni doped TiO<sub>2</sub> nanoparticles and its application for the degradation of malathion. *Materials Today: Proceedings* **2020**, <https://doi.org/10.1016/j.matpr.2020.02.216>.
  11. Divakaran, D.; Lakkakula, J.R.; Thakur, M.; Kumawat, M.K.; Srivastava, R. Dragon fruit extract capped gold nanoparticles: Synthesis and their differential cytotoxicity effect on breast cancer cells. *Materials Letters* **2019**, *236*, 498–502, <https://doi.org/10.1016/j.matlet.2018.10.156>.
  12. Hu, X.; Takada, N.; Machmudah, S.; Wahyudiono; Kanda, H.; Goto, M. Ultrasonic-Enhanced Fabrication of Metal Nanoparticles by Laser Ablation in Liquid. *Industrial & Engineering Chemistry Research* **2020**, *59*, 7512–7519, 2020. <https://doi.org/10.1021/acs.iecr.9b06384>.
  13. Lin, Z.; Yue, J.; Liang, L.; Tang, B.; Liu, B.; Ren, L.; Li, Y.; Jiang, L. Rapid synthesis of metallic and alloy micro/nanoparticles by laser ablation towards water. *Applied Surface Science* **2020**, *504*, 144461, <https://doi.org/10.1016/j.apsusc.2019.144461>.
  14. Muto, H.; Miyajima, K.; Mafuné, F. Mechanism of Laser-Induced Size Reduction of Gold Nanoparticles As Studied by Single and Double Laser Pulse Excitation. *The Journal of Physical Chemistry C* **2008**, *112*, 5810–5815, <https://doi.org/10.1021/jp711353m/>.
  15. Zamora-Romero, N.; Camacho-Lopez, M.A.; Vilchis-Nestor, A.R.; Castrejon-Sanchez, V.H.; Aguilar, G.; Camacho-Lopez, S.; Camacho-Lopez, M. Synthesis of molybdenum oxide nanoparticles by nanosecond laser ablation. *Materials Chemistry and Physics* **2020**, *240*, <https://doi.org/10.1016/j.matchemphys.2019.122163>.
  16. Bonse, J.; Baudach, S.; Krüger, J.; Kautek, W.; Lenzner, M. Femtosecond laser ablation of silicon—modification thresholds and morphology. *Applied Physics A* **2002**, *74*, 19–25, <https://doi.org/10.1007/s003390100893>.
  17. Herrera, M.G.; Padilla, C.A.; Hernandez-Rivera, P.S. Surface Enhanced Raman Scattering (SERS) Studies of Gold and Silver Nanoparticles Prepared by Laser Ablation. *Nanomaterials* **2013**, *3*, 158–172, <https://doi.org/10.3390/nano3010158>.
  18. Mortazavi, S.Z.; Parvin, P.; Reyhani, A.; Golikand, A.N.; Mirershadi, S. Effect of Laser Wavelength at IR (1064 nm) and UV (193 nm) on the Structural Formation of Palladium Nanoparticles in Deionized Water. *The Journal of Physical Chemistry C* **2011**, *115*, 5049–5057, <https://doi.org/10.1021/jp1091224>.
  19. Desai, R.; Mankad, V.; Gupta, S.K.; Jha, P.K. Size Distribution of Silver Nanoparticles: UV-Visible Spectroscopic Assessment. *Nanoscience and Nanotechnology Letters* **2012**, *4*, 30–34, <https://doi.org/10.1166/nnl.2012.1278>.
  20. Oldenburg, S.J. *Light Scattering from Gold Nanoshells*. Rice University, 2000.
  21. <https://nanocomposix.eu/pages/mic-theory-calculator>.
  22. Sadrollhosseini, A.R.; Noor, A.S.M.; Faraji, N.; Kharazmi, A.; Mahdi, M.A. Optical Nonlinear Refractive Index of Laser-Ablated Gold Nanoparticles Graphene Oxide Composite. *Journal of Nanomaterials* **2014**, *2014*, 8, <https://doi.org/10.1155/2014/962917>.