MULTILAYER PERCEPTRON NEURAL NETWORK TO PREDICT THE SURFACE PLASMON RESONANCE OF GOLD NANOSPHERES USING THEIR MORPHOLOGICAL CHARACTERISTICS

Lima Navarro G., Arzola Flores J.A., Maldonado García A., Guarneros Bejarano G., Vidal Robles E., Hernandez Santiago A.A.
Benemerita Universidad Autonoma de Puebla
Avenida San Claudio y 18 Sur, Colonia San Manuel, C.P. 72570, Puebla, Mexico; email: jesus.arzola@correo.buap.mx
Received: 07.08.2021

Abstract. The Surface Plasmon Resonance (SPR) is an interesting optical property of metallic nanoparticles, which is strongly influenced by the morphology of the nanoparticles, their surface chemistry, and of course, the medium in which the particles are dispersed; therefore, knowing the position of the SPR is of vital importance to define its possible field of application. Here, we present the prediction of the position of the dipolar SPR in gold nanospheres, employing a Multilayer Perceptron Neural Network (MLP). The data for the training, validation and testing of the MLP were obtained by calculating the extinction efficiencies of gold nanospheres with different diameters using the Mie Theory and the MiePlot software. 5-fold cross-validation was used as evaluation method and MSE, RMSE, MAE and R^2 as evaluation metrics. The MLP allows predicting the dipolar SPR of gold nanospheres with an accuracy close to 100%, knowing only its diameter, so our methodology can be extended to predict different physicochemical, optical, or morphological properties of metallic and non-metallic nanoparticles.
Key words: *Surface Plasmon Resonance, Artificial Intelligence, Machine Learning, Multilayer Perceptron Neural Network, Mie Theory, MiePlot.*

INTRODUCTION

Au nanoparticles have been widely used in different fields of application due to their interesting optical properties, specifically surface plasmon resonance (SPR) [1], so this optical property has been used in photocatalytic processes [2], elimination of bacteria and cancer cells [3,4], to improve the efficiency of solar cells [5], etc.

When an electric field whose frequency coincides with the natural oscillation frequency of the conduction electrons in metals a resonance phenomenon emerges, giving rise to a collective movement of the sea of conduction electrons. From the point of view of Quantum Mechanics, a quantum of this oscillation is called a plasmon. Plasmons, based on the Fermi electron sea model, can be described as a cloud of negatively charged electrons consistently displaced from their equilibrium position around a lattice made of positively charged ions [1,5].

Knowing the position of the dipolar SPR in Au nanoparticles is of vital importance because the possible field of application depends on this [1]. Nowadays, thanks to the development of nanoscience, it is possible to synthesize nanoparticles with a great variety of morphologies, which allows the position of the dipolar SPR to be tuned [1]. However, this process is usually expensive, so it is necessary to implement computational tools that allow us to predict the position of the dipolar SPR and thus optimize resources. Currently, thanks to the rise of Artificial Intelligence, specifically Machine Learning (ML), it is possible to implement computational models that have a certain learning capacity, which can be obtained from experience, that is, from the analysis of historical data of the phenomenon under study [6]. An example of these models are artificial neural networks [6].

Inspired by the human brain, the Artificial Neural Networks (ANN) were born of the necessity of automating prediction, identification, and control tasks. To create a functional model of the biological neuron, three elements are required. Firstly, the synapses are represented by a value called weight, which indicates the strength of the connection between an input and the neuron. The second component must be an adder that sums up all the inputs, and, finally, an activation function that controls the output of the neuron [6-8].

In the present work, an ANN known as multilayer feed-forward neural network or Multilayer Perceptron Neural Network (MLP) is proposed for predicting the dipolar SPR of Au nanospheres as a function of their diameter, using their extinction spectra, which were obtained using the MiePlot software.

METHODOLOGY

The rigorous method chosen to generate the data needed to train, validate, and test the neural network is the Mie theory [9,10], which is applied by means of MiePlot software (http://www.philiplaven.com/mieplot.htm) [11,12]. The required values are those of the wavelength of incident light at which extinction reaches its highest point for different diameter values. To obtain the desired results, one must input data as it is described below.

Firstly, method and graphic variables are selected as it is showed in Figure 1. In this case, the extinction efficiencies (Q_{ext}) were calculated for Au nanospheres with different diameters and dispersed in a medium with a refractive index of 1.33 (water).

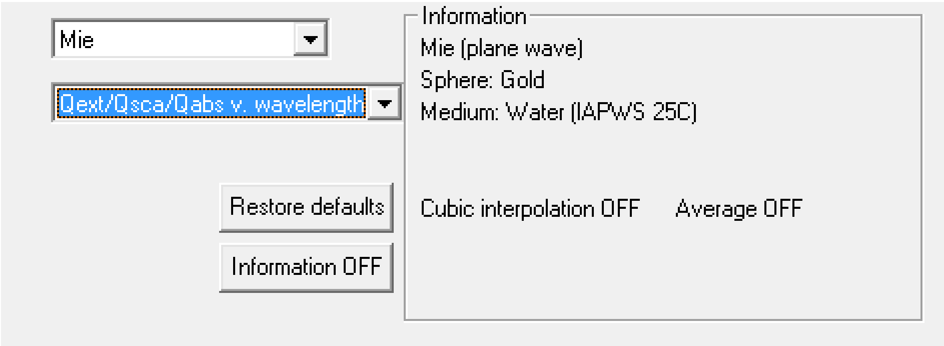

Figure 1. Method and variables selection in Mie Scattering's interface

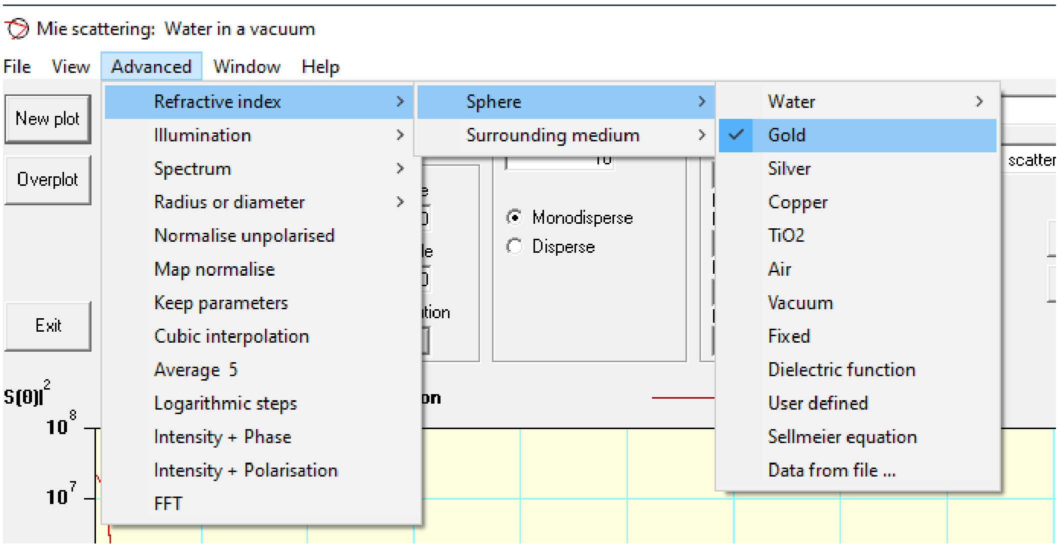

Figure 2. Procedure to select the type of material in MiePlot interface

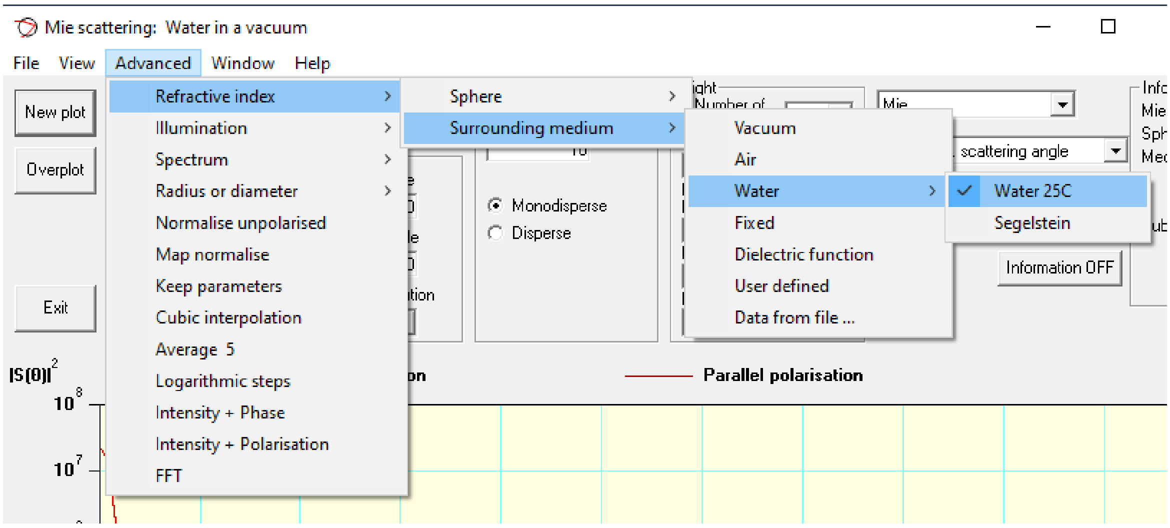

Figure 3. Procedure to select the surrounding medium in MiePlot interface

Later, the refractive index is selected; there, the pointer must be placed on the "Sphere" option to display the available materials, out of which gold is selected. Then, the surrounding medium chosen is water, and temperature is fixed at 25 °C (Figs. 2 and 3).

The particle size (spherical) was varied from 0.002 μm (2 nm) to 0.1 μm (100 nm), and the lower wavelength limit is fixed at 200 nm and the upper at 1000 nm. It is also important to select "linear" at intensity scale and horizontal scale (see Fig. 4). Fig. 5 shows the Q_{ext} for an Au nanosphere with a diameter equal to 20 nm. In this figure, it is possible to observe that the maximum of the Q_{ext} is around 520 nm. This maximum is related to the position of the dipolar SPR.

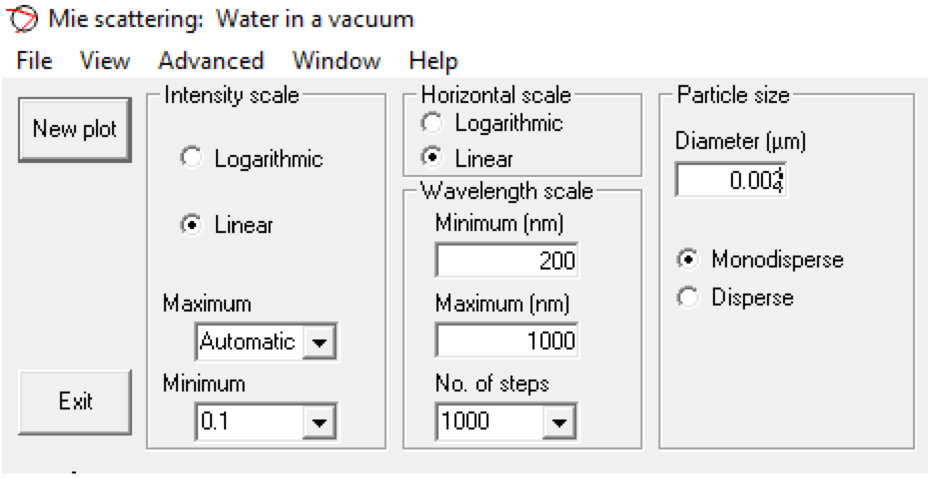

Figure 4. Selection of scale and particle size in MiePlot interface

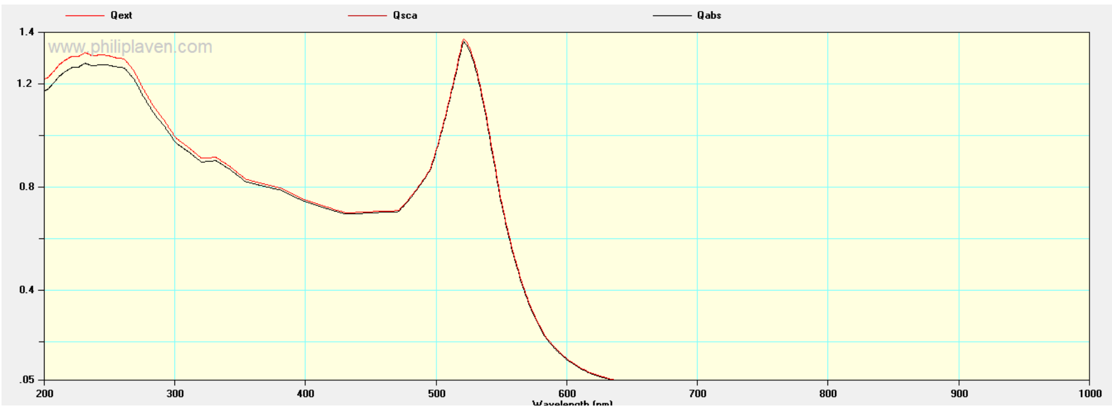

Figure 5. Q_{ext} for a 0.02 µm Au nanosphere dispersed in water at 25 °C (obtained using MiePlot). The maximum of the extinction spectrum is related to the position of the dipolar SPR

This procedure is repeated for several particle diameter values between 0.002 and 0.1 µm to obtain the corresponding wavelength results at which resonance phenomenon is reached.

Once the SPR was obtained for the Au nanospheres with different diameters, the training, validation, and testing of an MLP was carried out, using the 5-fold cross-validation evaluation method [6], and the Mean Square Error (MSE), the Root Mean Square Error (RMSE), the Mean Absolute Error (MAE), and the Determination Coefficient (R^2) were used as evaluation metrics [6,8]. The MLP consisted of one input layer (related to the diameter of the nanosphere as a predictor variable), a hidden layer formed by ten neurons with rectified lineal activation function (RELU) [6,8], and one output layer of a neuron (related to the target variable, in this case, the position of the dipolar SPR). In addition, the $L_2 = 0.001$ penalty was used as a regularization method, and as an optimizer of synaptic weights, the quasi-newton L-BFGS-B method was used [6,8]. For the implementation of this supervised learning model, Orange V2.28 software was employed (https://orangedatamining.com/) [13].

RESULTS AND DISCUSSION

In Figure 6 a) the Orange workflow for predicting dipolar SPR of Au nanospheres is shown. Figure 6 b) shows the dialog box to interact with the Neural Network widget. In this window it is possible to select the number of hidden layers and the number of neurons per hidden layer, the value of the L_2 regularization and the optimization method of the synaptic weights. On the other hand, in Figure 6 c) the dialog window of the “Test and Score” widget is observed, in which it is possible to select the 5-fold cross validation method as the model evaluation technique. In addition, in this widget the evaluation metrics for the prediction of the dipole SPR are appreciated, as can be seen, the following values of the evaluation metrics are obtained: MSE = 0.173, RMSE = 0.416, MAE = 0.309 and $R^2 = 0.999$, which implies an excellent prediction of the dipole SPR of Au nanospheres as a function of their diameter.

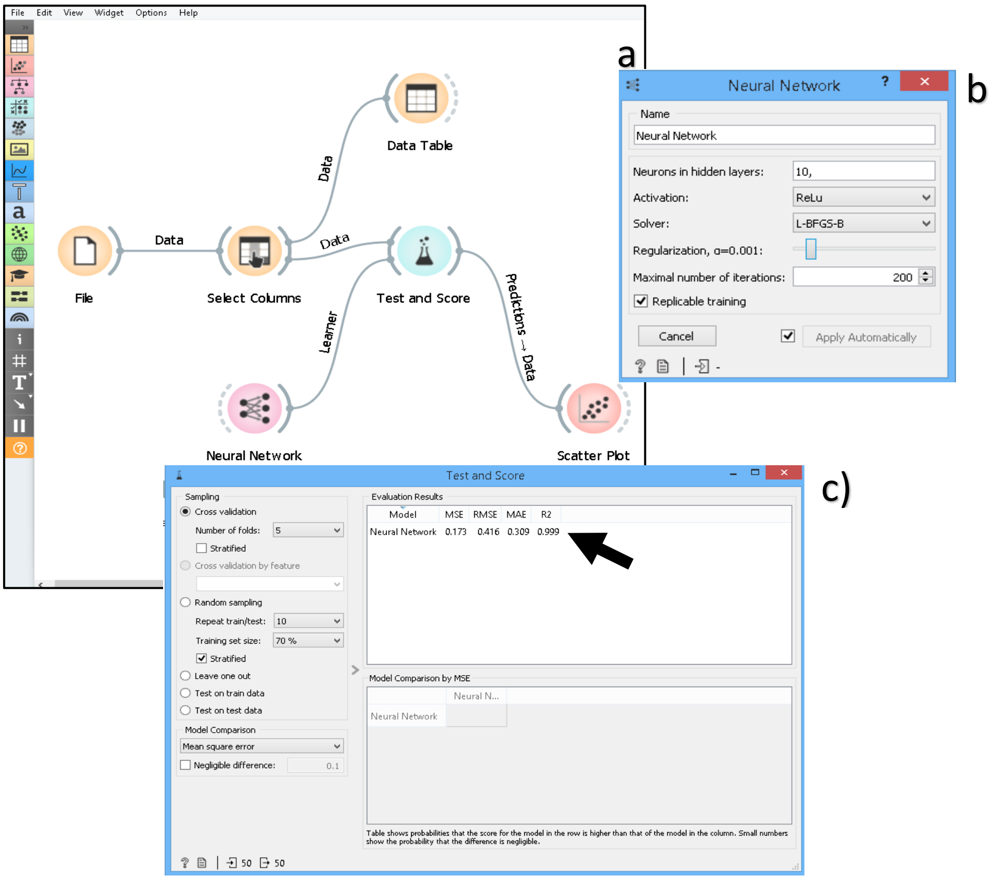

Figure 6. a) General workflow in Orange to predict the dipolar SPR of Au nanospheres, b) "Neural Network" widget dialog window, and c) "Test and Score" widget dialog window

On the other hand, Fig. 7 shows the dipole SPR prediction parity diagram. In this figure, the horizontal axis is related to the position value of the dipole SPR in nanometers obtained using MiePlot, while the vertical axis is related to the dipolar SPR values obtained from the MLP. As can be seen, by making a linear fit with those SPR values, it is possible to obtain both a Pearson correlation coefficient and a determination coefficient close to unity, which indicates that it is possible to predict the position of the dipole SPR with a precision close to 100%.

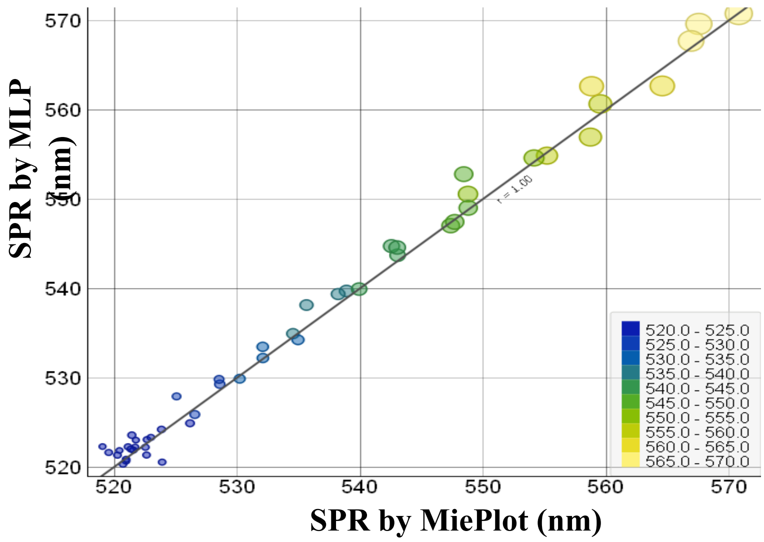

Figure 7. Parity Plot for the prediction of the dipolar SPR of Au nanospheres. The horizontal axis represents the SPR values obtained using MiePlot, while the vertical axis is related to the SPR values obtained from the MLP prediction. The color and size of the points is related to the position of the SPR in nanometers. On the other hand, the black line shows a good fit of the data

CONCLUSIONS

Today, thanks to the rise of Artificial Intelligence, it is possible to optimize resources in nanoscience, to the point that it is possible to predict the optical properties of different types of nanoparticles. Here we can conclude that it is possible to use an MLP to predict the position of the SPR dipole of Au nanospheres with an accuracy close to 100%, knowing only their diameter. This result opens the possibility of expanding our methodology to predict different physicochemical, optical, or morphological properties of metallic and non-metallic nanoparticles.

References:

1. Amendola V., Pilot R., Frasconi M., Marogo O. M., Iati M.A. Surface plasmon resonance in gold nanoparticles: a review. *Journal of physics: Condensed Matter*, 2017, vol. 29, no. 20, p. 203002.
2. Thompson D.T. Using gold nanoparticles for catalysis. *Nano Today*, 2007, vol. 2, no. 4, pp.40-43.
3. Giljohann D.A., Seferos D.S., Daniel W.L., Massich M.D., Patel P.C., Mirkin C.A. Gold nanoparticles for biology and medicine. *Spherical Nucleic Acids*, 2020, pp. 55-90.
4. Sperling R.A., Gil P.R., Zhang F., Zanella M., Parak W.J. Biological applications of gold nanoparticles. *Chemical Society Reviews*, 2008, vol. 37, no. 9, pp. 1896-1908.
5. Notarianni M., Vernon K., Chou A., Aljada M., Liu J., Motta N. Plasmonic effect of gold nanoparticles in organic solar cells. *Solar Energy*, 2014, vol. 106, pp. 23-37.
6. Berzal F. *Redes neuronales & deep learning: Volumen II*. Independently published, 2019.
7. Dongare A.D., Kharde R.R., Kachare A.D. () Introduction to Artificial Neural Network. *International Journal of Engineering an Innovative Technology*, 2012, vol. 2, no. 1, pp. 189-194.
8. Arzola-Flores J. A., Gonzaalez A.L. Machine Learning for Predicting the Surface Plasmon Resonance of Perfect and Concave Gold Nanocubes. *The Journal of Physical Chemistry C*, 2020, vol. 124, no. 46, pp. 25447-25454.
9. Wriedt T. Mie theory: a review. *The Mie Theory*, 2012, pp. 53-71.
10. Hergert W., Wriedt T. (Eds.). The Mie theory: basics and applications. Springer, 2012, vol. 169.
11. Laven P. Simulation of rainbows, coronas, and glories by use of Mie theory. *Applied optics*, 2003, vol. 42, no. 3, pp. 436-444.
12. Laven P. Simulation of rainbows, coronas and glories using Mie theory and the Debye series. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2004, vol. 89, no. 1-4, pp. 257-269.
13. Demsar J., Curk T., Erjavec A., Gorup C., Hocevar T., Milutinovic M., Zupan B. Orange: data mining toolbox in Python. *The Journal of machine Learning research*, 2013, vol. 14, no. 1, pp. 2349-2353.