MACHINE LEARNING FOR PREDICTING THE SURFACE PLASMON RESONANCE OF SILVER NANOSPHERES

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Abstract. Today it is known that silver nanoparticles have interesting optical properties, especially surface plasmon resonance (SPR). This property has opened a sea of possible applications for silver nanoparticles, so knowing the effect of the size and morphology of the nanoparticles on the SPR is a very important task in synthesis processes. In this work, we present the prediction of the dipole SPR of spherical silver nanoparticles using their diameter as a predictor variable. To carry out the prediction, two Machine Learning algorithms were used, the Lasso regression with L_1 regularization and the Ridge regression with L_2 regularization. For the evaluation of the models, data obtained from the extinction spectra of silver nanospheres with different diameters calculated with the MiePlot software were used. For the evaluation of the models, the 5-fold cross-validation was used and MSE, RMSE, MAE, and R^2 were used as evaluation metrics. Both regression models allow the dipole SPR to be predicted with an accuracy above 95%. However, performing the Bayesian t-student test shows that the Ridge regression is slightly better than the Lasso regression for making the prediction.
Key words: *Machine Learning, Mie Theory, MiePlot, Surface Plasmon Resonance, Ridge Regression, Lasso Regression.*

INTRODUCTION

Noble metals are chemical elements of metallic type characterized by their high resistance to corrosion, air humidity and oxidation, so they are chemically unreactive; therefore, they have diverse applications. Noble metals are widely used in the petroleum, chemical, electronics, electrical, marine and aviation industries, known as the "industrial vitamin" [1]. Noble metal nanoparticles, especially gold (Au) and silver (Ag) exhibit unique and tunable optical properties due to their surface plasmon resonance (SPR) [2].

As first pointed out by Gustav Mie in 1908, the interaction of light with metal nanoparticles results in the collective oscillation of the metal free electrons with respect to the nanoparticle lattice in resonance with the electric field [3]. This phenomenon is known as SPR [2]. For gold (Au), silver (Ag), and copper (Cu), the resonance condition is fulfilled at visible frequencies, making them the plasmonic metals of choice for optical applications [2].

The SPR depends on parameters such as the morphology of the nanoparticle, its concentration, the refractive index of the solvent, the surface charge, and the temperature [2], so tuning this optical property is not usually so trivial from the experimental point of view; therefore, that it is vitally important to use computational methods to make the synthesis process more efficient and with this, minimize the expenditure of resources.

Nowadays, thanks to the development of artificial intelligence, specifically machine learning (ML), the development of materials science has accelerated since it is possible to optimize processes and minimize the use of resources [4], using a wide variety of computational algorithms that are capable of acquiring a certain level of learning from the analysis of previous data on the process or phenomenon under study [5,6], so in this work, we intend to study the effect of the morphology of silver nanoparticles (AgNPs), specifically, their diameters, on SPR, using Mie theory and MiePlot software (http://www.philiplaven.com/mieplot.htm) [7,8], in order to generate a data set for the training, validation, and testing of two machine learning algorithms.

In this work, we employed two ML algorithms, Lasso regression [9,10], and Ridge regression [9,11], to predict the position of the SPR of AgNPs as a function of their diameter, using the extinction spectra of spherical nanoparticles obtained through MiePlot.

METHODOLOGY

For the training, validation, and testing of the ML algorithms, the extinction spectra or extinction efficiencies of spherical AgNPs obtained using the MiePlot software were used. The extinction spectra were calculated for nanoparticles with diameters from 0.002 μm (2 nm) to 0.1 μm (100 nm), dispersed in a medium with a refractive index of 1.33 (water), at a temperature of 25° C. Figure 1 shows the extinction efficiency of an AgNP with a diameter of 50 nm.

Once the extinction efficiencies of the AgNPs were obtained, the position in nanometers of the maximum of each of the spectra was located, since this position corresponds to the position of the SPR, to build a data set where the target variable corresponds to the position in nanometers of the SPR and their diameter as a predictor variable.

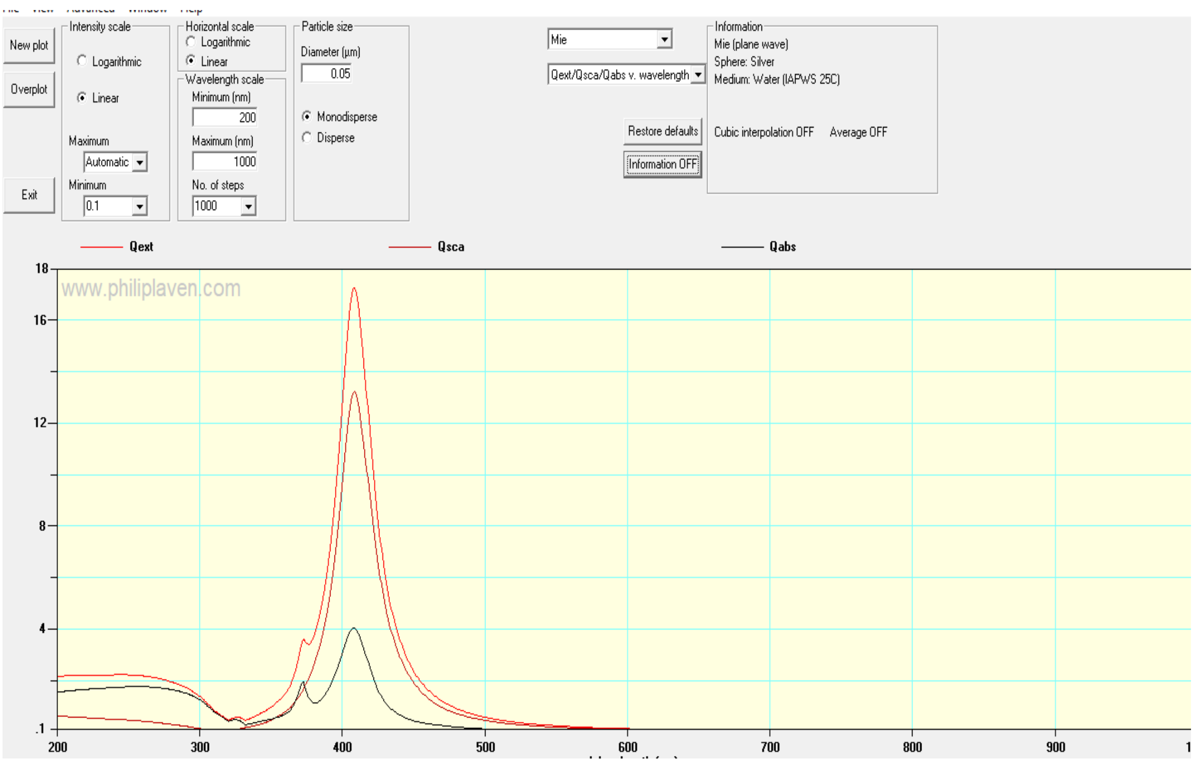

Figure 1. Extinction, dispersion, and absorption efficiency for an Ag nanosphere dispersed in water at 25°C

The training, validation, and testing of the two regression models were carried out using Orange software (https://orangedatamining.com/) [12]. For the Lasso regression, a regularization L1 = 1 was used, while for the Ridge regression, a regularization $L_2 = 2$ was used. As an evaluation technique, a 5-fold cross-validation was employed, and the mean square error (MSE), the Root Mean Square Error (RMSE), the Mean Absolute Error (MAE), and the Coefficient of Determination (R^2) were used as evaluation metrics [5].

RESULTS AND DISCUSSION

In Figure 2 a) the Orange workflow for the prediction of the dipolar SPR of AgNPs is observed. In Figure 2 b) we can see the dialog window to interact with the Ridge regression widget. In this widget, it is possible to select the value of the L_2 regularization. On the other hand, in Figure 2 c) we can see the dialog window to interact with the Lasso regression widget, where the value of the L_1 regularization can be selected. Finally, in Figure 2 d) the dialog box of the Test and Score widget is observed, in this window the evaluation method is selected, which in this case corresponds to 5-fold cross-validation. In addition, it is possible to observe the value of the evaluation metrics and the result of performing a Bayesian t-student test to identify which of the two algorithms is better to predict the dipolar SPR. Table 1 shows the evaluation metrics obtained by the two regression algorithms for predicting the dipolar SPR of AgNPs.

As can be seen in Table 1, it is possible to use both algorithms to predict the position of the dipole SPR, since excellent evaluation metrics are obtained. However, in the dialog window of the Test and Score widget, it is observed that the Bayesian t-student test[13] shows that the probability that the Ridge regression is better than the Lasso regression is slightly higher (P = 0.527) than the probability that the Lasso regression is a better model than the Ridge regression (0.473), so the Ridge regression could be a better model to predict the position of the dipole SPR of AgNPs.

Figure 3 shows the parity diagram for the prediction of the dipole SPR of AgNPs using the Ridge regression. While in Figure 4 the parity diagram is distinguished for the same prediction but using the Lasso regression. In both figures, the horizontal axis explains the dipolar SPR values in nanometers obtained from the extinction spectra calculated with the MiePlot software, while the vertical axis shows the dipolar SPR values in nanometers predicted by the ML models. Furthermore, in both figures the black line shows the existence of a linear relationship between both SPR values, since it is possible to obtain excellent values of the Pearson linear correlation coefficient and the coefficient of determination.

Table 1. Evaluation metrics for ML models

Model	MSE	RMSE	MAE	R2
Ridge Regression	23.534	4.851	4.168	0.955
Lasso Regression	23.521	4.850	4.170	0.955

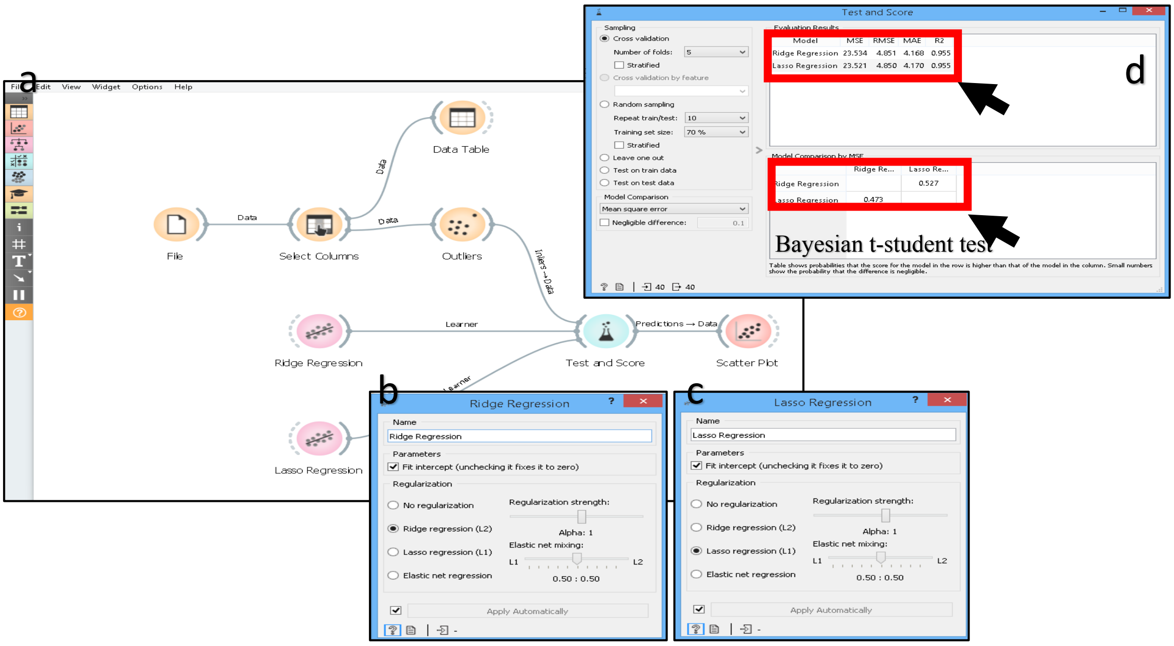

Figure 2. a) Orange workflow for predicting dipolar SPR, b) Ridge Regression widget dialog box, c) Lasso Regression widget dialog box, and d) Box thrown by Test and Score widget

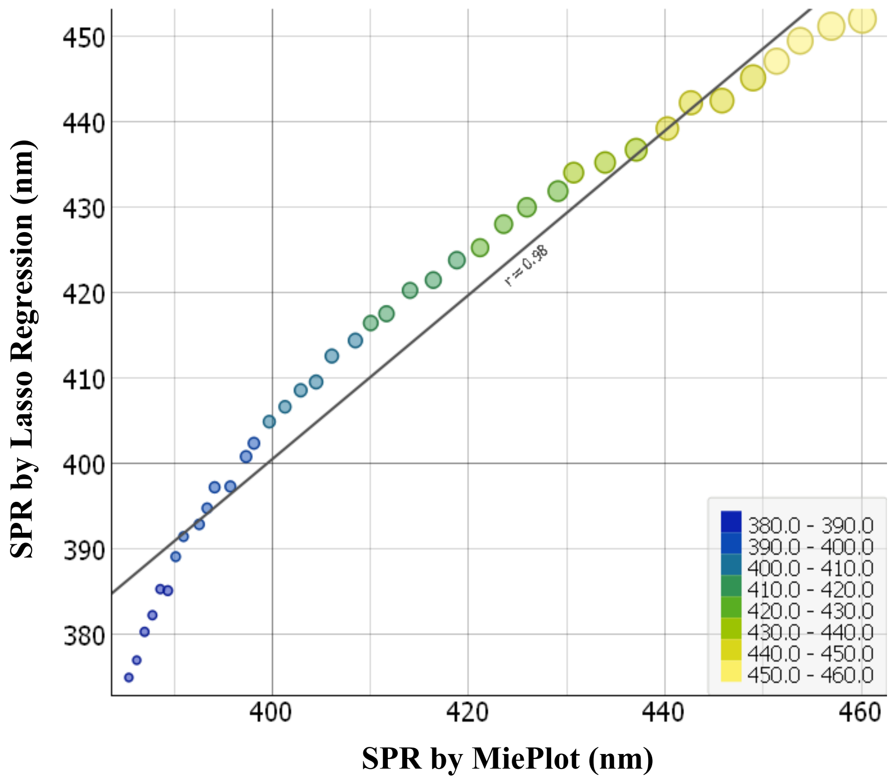

Figure 3. Scatter or parity diagram for predicting the dipole SPR of Ag nanospheres obtained using Lasso regression

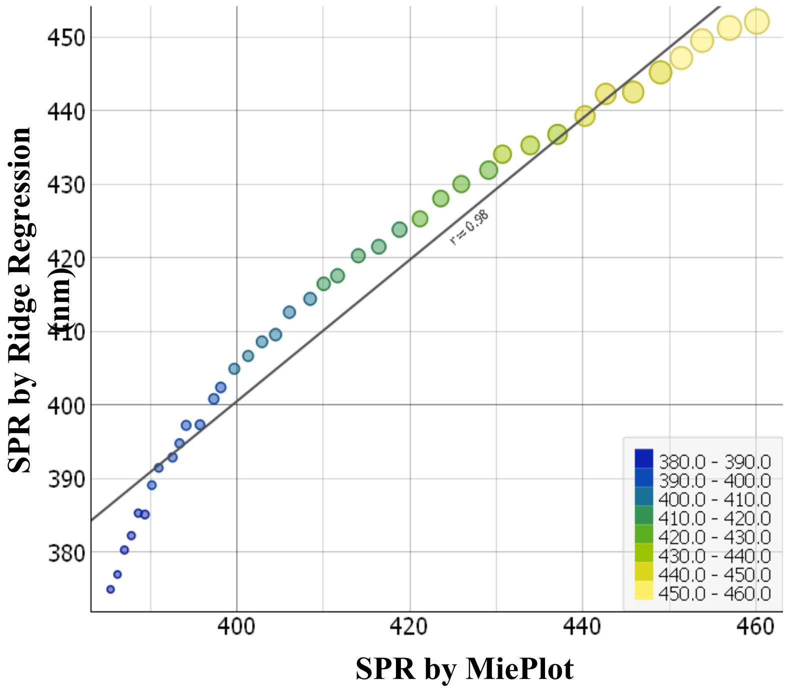

Figure 4. Scatter or parity diagram for predicting the dipole SPR of Ag nanospheres obtained using Ridge regression

CONCLUSIONS

Knowing the effect of size and morphology on the dipolar SPR of metallic nanoparticles is of vital importance to define its possible application. Currently, the tuning of the SPR of metallic nanoparticles is usually done experimentally or using computationally expensive theoretical methods, so the implementation of machine learning algorithms can help to streamline the processes of synthesis of metallic nanoparticles. Here we conclude that it is possible to use both a Ridge regression model and a Lasso regression to predict the dipole SPR of AgNPs with an accuracy above 95% for both cases. However, when using the Bayesian t-student test to compare both models, Ridge regression tends to be a better method for making the prediction.

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