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Determination of Shape Distribution of Metallic Nanostructures from the Absorption Spectra using Neural Networks

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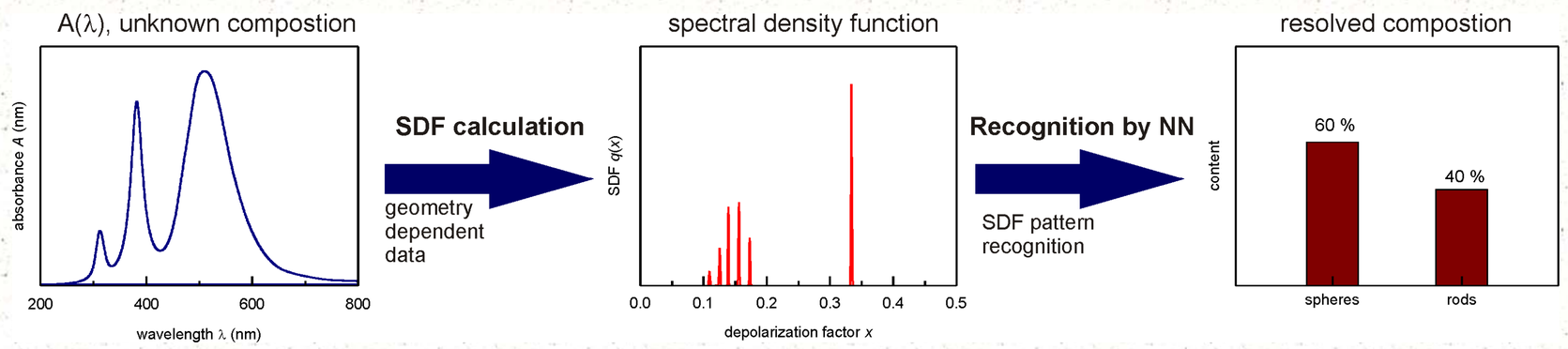
Summary

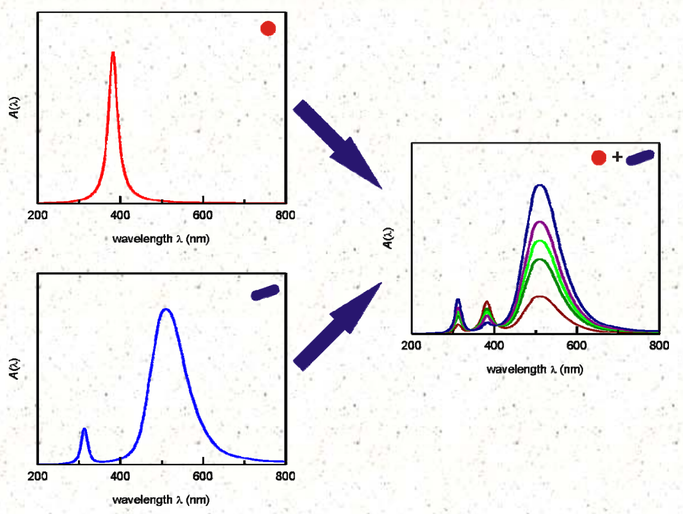
The shape composition of colloidal solutions of metallic nanostructures from the absorption spectra was resolved using multilayer perceptron neural networks (NN). The NN was trained using sets of theoretical absorption curves ($A(\lambda)$) of known composition obtained from Mie theory. Prior to training, the spectral density functions (SDF) were calculated from the absorption spectra in order to introduce the shape dependence directly into the method.



Theory

Theoretical absorption spectra

Theoretical absorption spectra $A(\lambda)$ for the mixture of Ag nanospheres and nanorods in aqueous solution were calculated form the relation $A(\lambda) = c_s\ Q^s_{ext}(\lambda) + c_r\ Q^r_{ext}(\lambda)$, where Q^s_{ext} and Q^r_{ext} are the size and shape dependent Mie theory extinction efficiencies of small metallic spheres and rods, respectively.



SDF calculation

Spectral density functions analysis of the $A(\lambda)$ curves was employed to investigate the contribution of the nanoparticles with particular shapes to the absorption spectrum. SDF $q(x)$, where x is the eccentricity related depolarization factor, were calculated from the relation

$$A(\lambda) = \frac{4}{3}\tilde{x}\int_0^1 q(x)\,\mathrm{Im}\left[\frac{1}{t(\lambda)-x}\right]dx$$

The function $t(\lambda)$ stands for

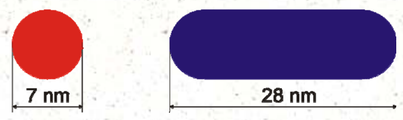
$$t(\lambda) = \frac{\varepsilon_m}{\varepsilon_m - \varepsilon(\lambda)}$$

where ε_m is the dielectric constant of the environment and $\varepsilon(\lambda)$ is the size corrected dielectric function of silver. Using known values of the functions $A(\lambda)$ and $t(\lambda)$ for a given λ, the spectral density functions $q(x)$ were calculated in the depolarization factor range from 0 to 0.5 using constrained least squares method.

Neural Network Training Set

Nanostructure:

In this study, for the testing of neural network approach for the estimation of the shape composition of nanostructured colloids we considered mixtures of silver nanospheres and nanorods. In the case of nanospheres, we assumed normal distribution of particles by size with an average diameter of 7 nm and standard deviation 1.5 nm. For the silver nanorods, smaller dimensions were also 7.0 ± 1.5 nm, while the average nanorod length used was 28 ± 3 nm.



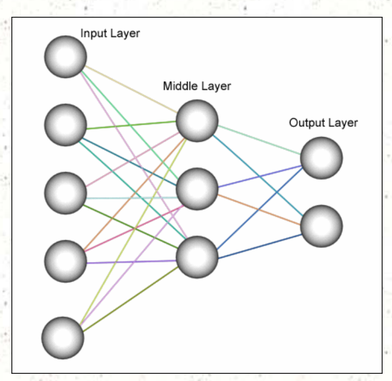
Training set:

The total of 100 absorption spectra of the colloidal mixtures were calculated with silver nanosphere fractions c_s ranging from 0 to 1. The corresponding spectral density functions were obtained and introduced into the multi layer perceptron neural network.

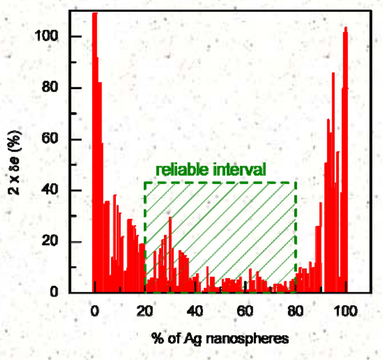
Using Multi Layer Perceptron Neural Network with Backpropagation for Nanoparticle Shape Recognition

Methodology

Neural networks are well known tools for treating the problems such as recognition, classification, prediction, and approximation. They have the ability to learn from sample data through the training process. In the training process, a sample data is presented to the NN, and its parameters (connection weights) are being adjusted in order for a network to achieve desired behavior. (provide desired recognition, approximation, etc.). If the training data sets are representative for the problem, it is possible to train the NN to successfully analyze the unknown data. The most commonly used type of NN are multi layer perceptron (MLP), with backpropagation learning rule used for training (shown on image).



Here we suggest the use of MLPs to recognize absorption spectra patterns transformed into SDF for the determination of the shape distribution of colloidal solutions of the nanostructures. To achieve that we have trained the MLP NN with the theoretical SDF sets and tested it with unknown data and observed the total relative recognition error. During training and testing we concluded that the most reliable interval for the recognition is between 20 and 80% of nanospheres.



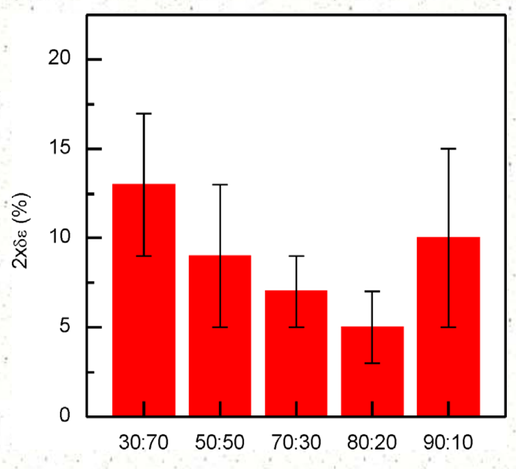
We used data set with 60 SDF samples in total to train and test our neural network. This data was divided into two non-overlapping sets: a training set, which was used to train the NN, and a test set, used to test the predictions of the trained network. The network was optimized with different training-to-test set ratios, namely: 30:70, 50:50, 70:30, 80:20, and 90:10 (all in percent). In all cases, the optimizations was performed 3 times and the total relative error $2\delta\varepsilon$ for the estimation of composition was determined.

To implement neural network and run all tests we have used the open source Java Neural Network Framework Neuroph (http://neuroph.sourceforge.net).

Results

Optimization of training

The results of NN training optimization in the reliable interval of c_s are presented in the figure. It can be seen that the total relative error $2\delta\varepsilon$ for the estimation of composition is the lowest in the 80:20 case. The decrease of relative error with the increase of training set length is expected, however in our case the increase of $2\delta\varepsilon$ to 10 % for 90:10 can be attributed to overtraining of the NN due to which it looses its ability of generalization. The total relative error of 5% in 80:20 case results in low average relative error per set of only 0.4%, which confirms the consistency of the procedure.



Determination of composition

The 80:20 trained neural network was used to resolve the composition of 3 samples with random values of c_s that was not previously used for training or testing. The comparison between the calculated spectra (circles) and those recognized by the NN (line) are shown in the figure. In all of presented cases the absorption curves were virtually the same indicating that the neural networks can be successfully used to determine the shape composition of colloidal mixtures of metallic nanostructures. Additional testing may be require prior to evolution of the procedure to more realistic nanostructured systems.