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Feasibility Investigation of Near Infrared Spectrometry for Particle Size Estimation of Nano Structures

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***Abstract*—**Determination of nano particle size is substantial since the nano particle size exerts a significant effect on various properties of nano materials. Accordingly, proposing non-destructive, accurate and rapid techniques for this aim is of high interest. There are some conventional techniques to investigate the morphology and grain size of nano particles such as scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffractometry (XRD). Vibrational spectroscopy is utilized to characterize different compounds and applied for evaluation of the average particle size based on relationship between particle size and near infrared spectra [1,4] , but it has never been applied in quantitative morphological analysis of nano materials. So far, the potential application of near-infrared (NIR) spectroscopy with its ability in rapid analysis of powdered materials with minimal sample preparation, has been suggested for particle size determination of powdered pharmaceuticals. The relationship between particle size and diffuse reflectance (DR) spectra in near infrared region has been applied to introduce a method for estimation of particle size. Back propagation artificial neural network (BP-ANN) as a nonlinear model was applied to estimate average particle size based on near infrared diffuse reflectance spectra. Thirty five different nano TiO2 samples with different particle size were analyzed by DR-FTNIR spectrometry and the obtained data were processed by BP- ANN.

***Keywords*—**near infrared, particle size, chemometrics, neural network, nano structure.

I. Introduction

THERE are some conventional techniques to investigate the morphology and grain size of nano particles such as scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffractometry (XRD) [1-3]. Vibrational spectroscopy is utilized to characterize different compounds and applied for evaluation of the average particle size based on relationship between particle size and near infrared spectra [1,4], but it has never been applied in quantitative morphological analysis of nano materials. In this paper we introduce a novel technique based on diffuse reflectance Fourier transform near infrared spectrometry (DR-FT-NIR) and back propagation artificial neural network (BP-ANN) has been proposed to estimate the average particle size of nano materials. Nowadays, due to development of optical devices such as optical fibers and reflectance spheres, this situation has been completely changed and this technique yields good precision and selectivity [5]. Some evidences of utilizing DR have been reported in literature which show the appropriate application of DR spectroscopy could yield reliable results for quantitative analysis of ions [6,7]. The application of ANN systems in different fields of spectroscopy, e.g. infrared [8,9] or mass [10] spectroscopy has become an efficient tool for structure identification. In this research BP-ANN has been applied to propose a rapid and reliable approach for estimation the average size of TiO_2 nano particles.

II. Experimental

Titanium isopropoxide (TTIP), acetic acid and double distilled water were used as the starting materials for preparation of TiO_2 sols. In the first step, acetic acid was added to TTIP, drop by drop, while the mixture was being stirred. After gelation, the samples were dried to be aged at different temperatures and different time processes. In the next step, the calcination procedure was followed. Since the size of nano particles strongly depends on synthesis parameters such as molar ratios of precursor, catalyst, and water; aging times; aging temperatures and calcination times; by changing this parameters different samples were synthesized. Totally, 75 nano TiO_2 samples were prepared to be analyzed. All prepared TiO_2 nano particles were finely powdered to acquire homogenous samples. Considering the heterogeneity of nano powder samples, in order to perform the replicated analysis for each sample, the sample was rotated to achieve a higher analyzed sample volume.

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III. Results and Discussions

All the samples were studied by SEM to determine the minimum, maximum and range of their particle size. All recorded NIR spectra were modified by multipoint baseline technique and smoothed by quadratic method. According to the form of DR-FTNIR spectra (figure 1) it was concluded that the spectral pattern is similar for all of the samples and they would demonstrate the same bands and the differences refer to the signal intensities.

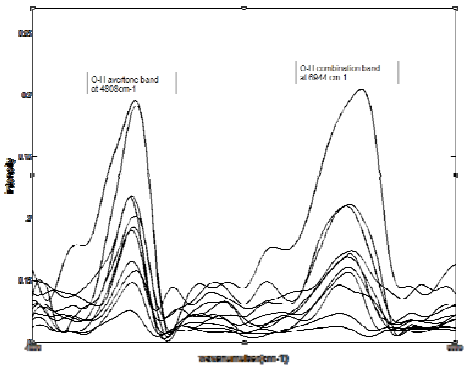

Fig. 2 Diffuse reflectance FT-NIR spectra of 11 different nano TiO_2 samples in 4000-8000 cm^{-1} spectral region.

Nano TiO_2 spectra demonstrate signals at 1440 nm (6944 cm^{-1}) and 2080 nm (4808 cm^{-1}), indicating the presence of O-H functional group. These two different bands refer to combination and overtone of O-H group adsorbed on surface of TiO_2 nano particles and the intensity of these signals is in accordance with size of nano particles, closely. Among the multiple developed artificial neural network structures a feed forward with the error back-propagation learning rule was selected. A two layer feed-forward neural network with tansig- purelin function in hidden neurons was used. Five different classes were defined based on average particle size and particle size ranges obtained by SEM characterization tests (Table 1).

TABLE I
PARTICLE SIZE CLASSES OF NANO TIO_2 SAMPLES FOR CLASSIFICATION APPROACH IN BP-ANN

Class	Particle size range (nm)
1	20-45
2	45-60
3	60-90
4	90-130
5	Above 130

Since it is difficult to choose the optimal value of these three parameters, it is necessary to train networks in different situations and choose the best configuration in practice. An important step in development of calibration model was to split the spectroscopic data were into 3 main subsets: A training set (used to estimate the network model parameters), a validation set (used to check the generalization ability of the network) and test set. In ANNs, the problem is more complex because they fit to an arbitrary precision in the training data, confirming that the number of provided hidden nodes is sufficient and the training time is long enough. Therefore, an additional monitoring set is necessary to stop the training before the ANN learns idiosyncrasies present in the training data. The monitoring set must be representative of the studied population in order to avoid any probable overtraining. Thus, in the study 30 spectra were used to train the BP-ANN model, 5 samples were used to validate the optimized model and 44 spectra were applied in model testing step. The prediction results, obtained by the proposed BP-ANN are detailed in Table II.

TABLE II
ACCURACY RESULTS OF PREDICTING THE TEST SAMPLES BY BP-ANN .

	Class	Samples	misclassified
Training set	1	6	0
	2	4	0
	3	7	1
	4	6	1
	5	7	0
	Total	30	2
Test set	1	9	0
	2	6	0
	3	12	2
	4	7	1
	5	10	0
	Total	44	3

Among the multiple developed artificial neural network structures a feed forward with the error back-propagation learning rule was selected. The input vector consisting of spectral data provides useful information to obtain the desired output vector. Optimization process of ANN involves selection of the parameters related to each function (known as the bias and weight values of the transfer-function of each neuron) in order to minimize the mean square error (MSE) values of a monitoring dataset.

A two layer feed-forward neural network with tansig-purelin function in hidden neurons was used. The neurons were arranged as input layer, hidden layer and output layer, in which the hidden layer consisted of 5 neurons. The network was trained by offering typical data to the input layer and adopting the weights of each interconnection in such a way that the desired output could be obtained. In this work, gradient descent with momentum was applied and the performance function was the mean square error (MSE), the average squared error between the network outputs and the actual output. The proposed network was trained with Levenberg-Marquardt back propagation algorithm. The number of outputs was set equal to the number of class identities to be recognized by the network. Five different classes were defined based on average particle size and particle size ranges obtained by SEM characterization tests.

The learning rate (α) and the momentum (μ) are of high importance and must be fixed after optimization. Momentum can also help the network to overcome a shallow local minimum in the error surface and settle down at or near the global minimum. Since it is difficult to choose the optimal value of these three parameters, it is necessary to train networks in different situations and choose the best configuration in practice. The optimal learning rate and the momentum term were selected as 0.1 and 0.4, respectively. Random Learning cycle (epoch) during all of the training patterns was used.

An important step in development of calibration model was to split the spectroscopic data were into 3 main subsets: A training set (used to estimate the network model parameters), a validation set (used to check the generalization ability of the network) and test set. In ANNs, the problem is more complex because they fit to an arbitrary precision in the training data, confirming that the number of provided hidden nodes is sufficient and the training time is long enough. Therefore, an additional monitoring set is necessary to stop the training before the ANN learns idiosyncrasies present in the training data. The monitoring set must be representative of the studied population in order to avoid any probable overtraining.

IV. Conclusions

The findings suggest analysis of nano particle samples by DRIFT-NIR and data processing by BP-ANN would provide a novel method for average nano particle size estimation. The abundance of adsorbed O-H groups on surface of nano TiO2 particles are different and depend on size of nano particles, strongly. We detected these changes by DRIFT-NIR spectroscopy and applied for estimation of the particle size range by BP-ANN analysis.

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