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Detection of Beverage Aspartame Bysurface-Enhanced Raman Scattering Spectroscopy Based on Deep Learning

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ABSTRACT

In this paper, a self-developed surface-enhanced Raman scattering (SERS) substrate was used to detect aspartame (APM) in beverages by combining Raman spectroscopy with deep learning. A composite film of titanium dioxide nanocones and precious metals (gold, silver) nanoparticles was prepared on a titanium substrate by hydrothermal method and magnetron sputtering. The detection limit of Rhodamine 6G on the substrate was 10-7 M. A convolutional neural network deep learning algorithm model was compiled based on Python language to identify and analyze aspartame detected on SERS basis. The model could quickly identify whether the beverage contained aspartame with an accuracy of 99.11%, providing a rapid detection method for protecting public food safety.

KEYWORDS

Surface-enhanced Raman scattering; Deep learning aspartame

1. EXPERIMENTAL PROCEDURE

1.1. Substrate Preparation and Characterization

1.1.1. Substrate preparation

Materials required for the experiment include industrial titanium foil, urea, sodium hydroxide, hydrochloric acid, ethanol, acetone, isopropyl alcohol, Rhodamine 6G(R6G) and aspartame. All the materials were purchased from Sinophosphoric Group, and the purity of the drugs except titanium foil was analytically pure. The purity of the titanium foil is 99.97% and the thickness is 125μm. The typical process for preparing the nanocone base by [6] hydrothermal method is to cut the titanium foil [6] to 4cm*4cm and sand it to remove the surface oxide layer, and fold it into an "A" shape for effective contact with the reaction liquid. The titanium sheets were then placed in a 1:1 mixture of acetone and isopropyl alcohol for ultrasonic treatment for 10 minutes. Then, 1.6g sodium hydroxide and 2.4g urea were weighed in a beaker according to mol ratio 1:1, and purified water was added to 40ml and stirred to dissolve. The titanium sheet was put into the reaction kettle, heated to 220℃ and kept for 48 hours. The removed titanium foil was soaked in 0.6mol/L hydrochloric acid solution for 1 hour, and then cleaned with pure water and alcohol to remove residual hydrochloric acid. Finally, the titanium foil was dried in a tube furnace and calcined at 400℃ for 2 hours. A magnetron sputtering instrument is used to deposit silver particles (35 seconds of sputtering) and gold particles (6 minutes of spraying) on the surface of the titanium foil, respectively.

1.1.2. Material characterization

S4800 field emission scanning electron microscope was used to test the surface morphology of the sample, and XD-3 X-ray diffractometer was used to test the sample structure. The test Angle was

20 °-80 °, the voltage was set to 36KV, the current was set to 20mA, the power was set to 1.5KW, and the scanning speed was 4 °/min. Figure 1 and Figure 2 are XRD of silver nanocone substrate and gold-sprayed nanocone substrate (Figure 1, Figure 2), where the diffraction peaks of Ag, Au and Ti indicate the Ag/TiO_2 and Au/TiO_2 structures on the surface of the Ti sheet.

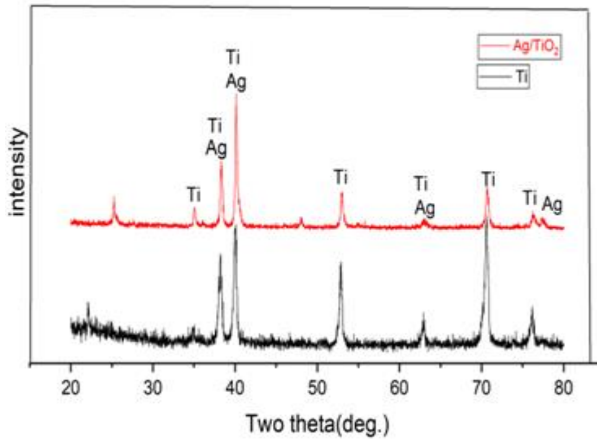

Figure 1. XRD pattern of SERS substrate for silver nanocones

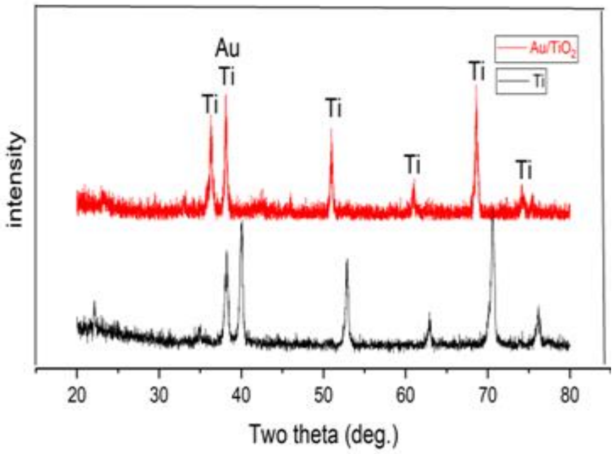

Figure 2. XRD pattern of SERS substrate for gold nanocones

Figure 3 and Figure 4 are the SEM images of the silver nanocone substrate and gold-sprayed nanocone substrate (Figure 3, Figure 4). Octahedral cones and other regular dense crystals grow on the surface of the titanium foil, and many metal particles are deposited on the crystal surface, with a diameter of about 10nm.

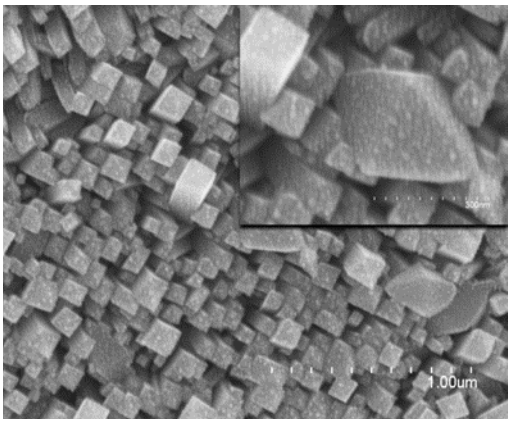

Figure 3. Electron microscopic images of the nanocone substrate after 35s silver spraying

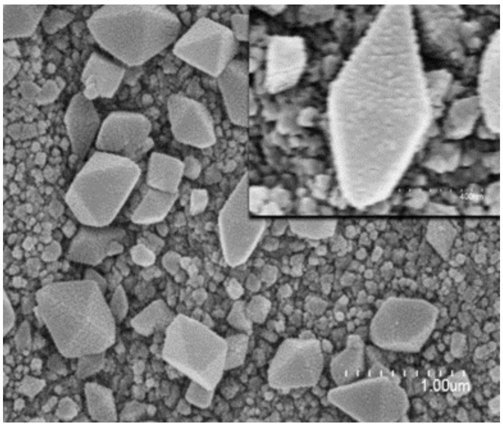

Figure 4. Electron microscopic images of the nanocone substrate after 6min gold spraying

1.2. Acquisition of Spectral Data

The HR800 microconfocal Raman spectrometer produced by HORIBA company was used in this experiment. The laser wavelength was 632.8nm and the full laser power was 10mW. Firstly, pure water and aspartame powder were used to continuously dilute aspartame aqueous solution and R6G aqueous solution of different concentrations, and the enhanced substrate was pasted on the slide, the tested solution was added and dried by heat source. The instrument was calibrated for mapping measurement, in which the sampling range of R6G aqueous solution was 600-1800cm^{-1}, and the sampling range of aspartame aqueous solution was 500-1500cm^{-1}.

1.3. Build a Deep Learning Model

Compared with traditional method s [11-13], a trained convolutional neural network model is used, which can directly process the original Raman spectral data collected by the device (Figure 5). This paper mainly discusses and studies the qualitative classification model of aspartame Raman spectrum. According to the characteristics of Raman spectrum data, one-dimensional convolutional neural network structure is used. Three problems are studied and solved: First, a one-dimensional convolutional neural network structure suitable for Raman spectrum classification is established. The number and size of convolutional nuclei in the model are determined, as well as the activation function and the fully connected layer structure. Second. In the training process, the main parameters of the model are constantly optimized. The main parameters that need to be optimized are learning rate, batch sample number, convolution sum size and size, etc. Thirdly, compared with other classification methods, the performance and effect of the classification model established in this paper are evaluated.

According to the classification requirements of the experiment, the three substances are expected to be classified, and the convolutional neural network model is constructed by referring to the design ideas of the existing literature [14, 15]. The training and optimization of the convolutional neural network rely on the Loss Function, which calculates the error between the predicted value and the true value. The error is backpropagated from the last layer to all layers of the network through the backpropagation algorithm and the weight is updated. The updated parameters continue to participate in the training, repeating the cycle until the loss function value reaches a minimum. The training process can be represented by Figure 5.

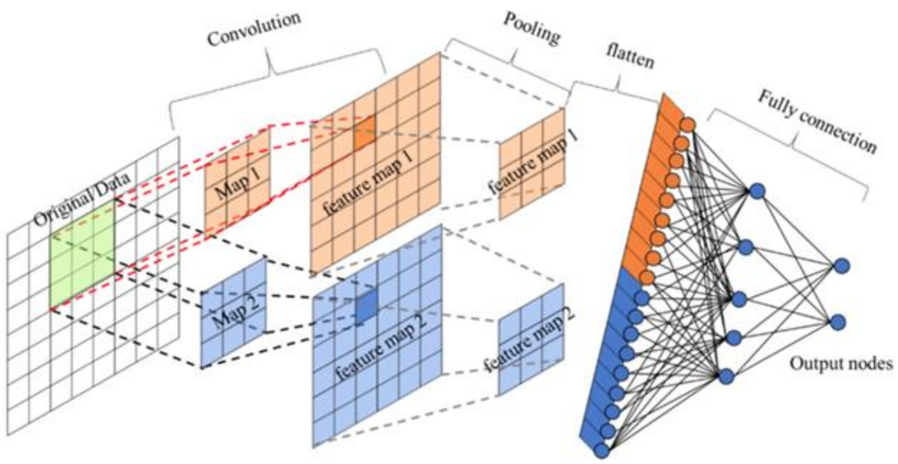

Figure 5. Schematic diagram of convolutional neural network

2. SPECTRAL DATA PREPROCESSING AND ANALYSIS

2.1. Raman Spectral Data Preprocessing

Raman spectroscopy is a commonly used spectral analysis method that can provide information about the structure and composition of substances. After the equipment has collected the Raman spectrum, it can be directly input into the convolutional neural network model as the original data in theory. However, the original Raman spectrum data is often affected by noise, baseline drift, insufficient spectral resolution and other factors, which makes the data analysis difficult. Therefore, the pre-processing of the spectral signal is an essential step. We can improve the stability of qualitative and quantitative analysis results and improve the quality of spectral data by preprocessing. In this paper, the methods of baseline correction and smooth de-noising are used. The original data of three kinds of spectra are first corrected by baseline, and then smooth de-noising is carried out. After that, the obtained spectral data are all processed by peak normalization, and the processed data is input into the convolutional neural network for training [10].

Raman spectral baseline correction:

Taking Eastern leaves (drinks) as an example, it can be seen that there is significant noise in the raw data and baseline deduction needs to be made first. The following picture shows the baseline correction process for eastern leaves, with reference to the original data. Similarly, we performed baseline correction on the spectral data of Oriental leaves plus APM and sugar-free Sprite, and obtained the results as shown in the figure below (Figure 6).

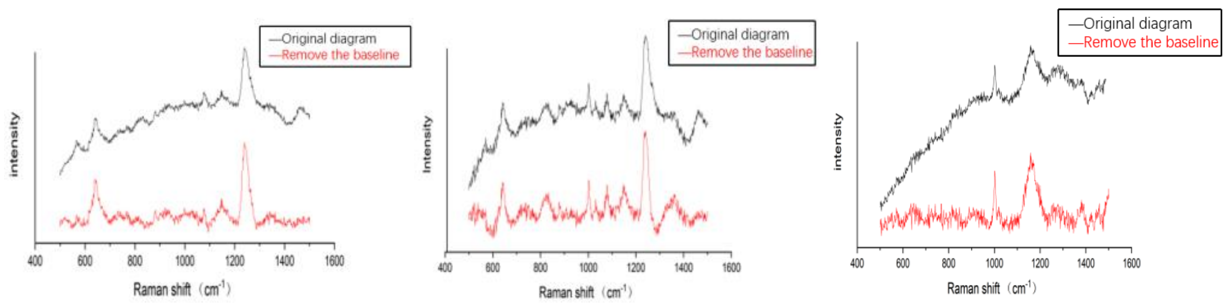

Figure 6. Baseline correction of three Raman spectra Raman spectrum smoothing and denoising

In this paper, the Savitzky-Golay smoothing filter algorithm is used to de-noise the Raman spectral signal, so as to ensure that the noise in the signal is filtered out as much as possible while maintaining the original shape of the signal without distortion. Three kinds of Raman spectra processed by baseline correction and smoothing denoising are shown as follows (Figure 7).

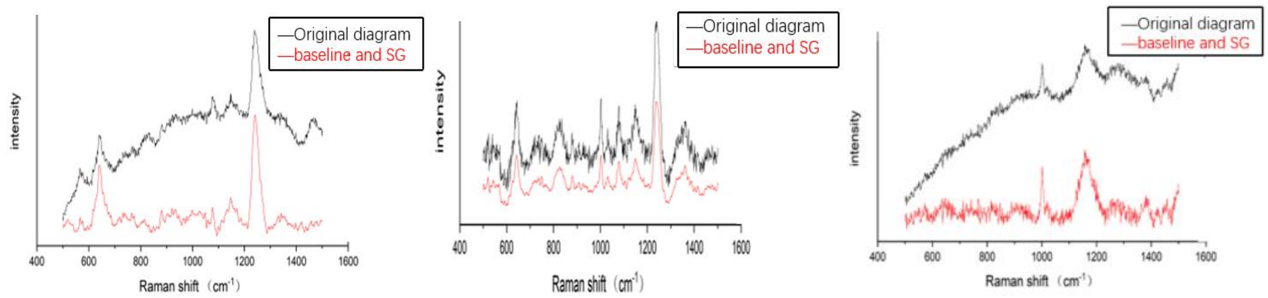

Figure7. Three Raman spectrum smoothing denoising image

2.2. Analysis of Spectral Data

After the surface enhanced substrate was made, the prepared substrate was put into practical application. In order to ensure that a variety of prepared substrates had practical application value, Raman spectra of r6g solution with a concentration of 10-6mg/L were measured using different substrates. After observation, it was found that multiple obvious fingerprint peaks could be seen on the spectral diagram displayed by the system (Figure 7). Subsequently, different concentrations of aspartame aqueous solutions and several different beverages were detected by spectroscopic measurements. It is known from literature that aspartame has an obvious fingerprint peak [7]. In order to avoid the interference [8] of water molecules on the measurement results, dry measurement method is used to bake the substrate with the solution to be tested under a heat source. The results show that there is an obvious fingerprint peak at 1004cm-1. The fingerprint peak can be detected for various concentrations of aspartame (Figure 8), and the detection limit can reach 0.39mg /L (Figure 9), which is far lower than the national monitoring requirements for aspartame.

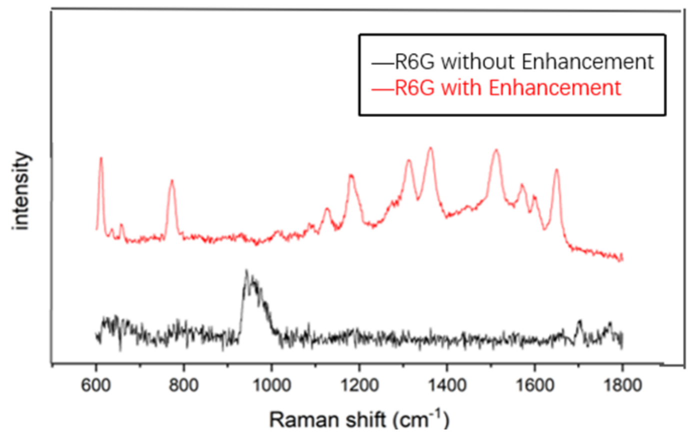

Figure 8. Comparison of Raman spectra of R6G surface

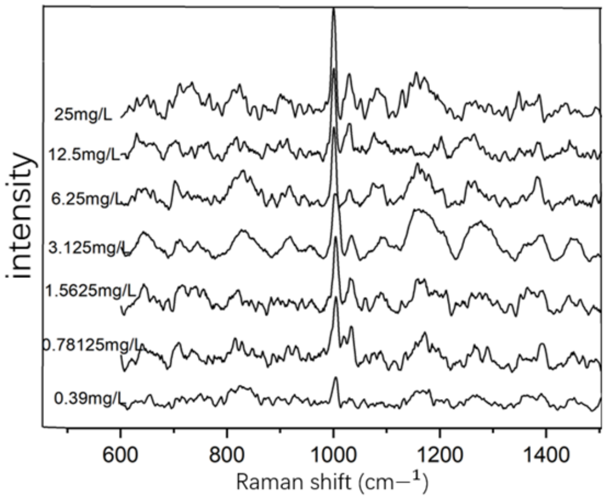

Figure 9. Raman spectra of aspartame in multiple concentrations

In this paper, three kinds of beverages were selected as the samples to be tested, namely Oriental leaf tea beverage, Jasmine tea and sugar-free Sprite. Among them, only the ingredients list of sugar- free Sprite contained aspartame. In order to make a contrast between the ingredients with aspartame and those without aspartame, an Oriental leaf sample was added with a concentration of 50 mg/Laspartame solution at a ratio of 1:1, so that the content of aspartame reached 25 mg/L. After the spectral measurement, the results are as follows (Figure 10):

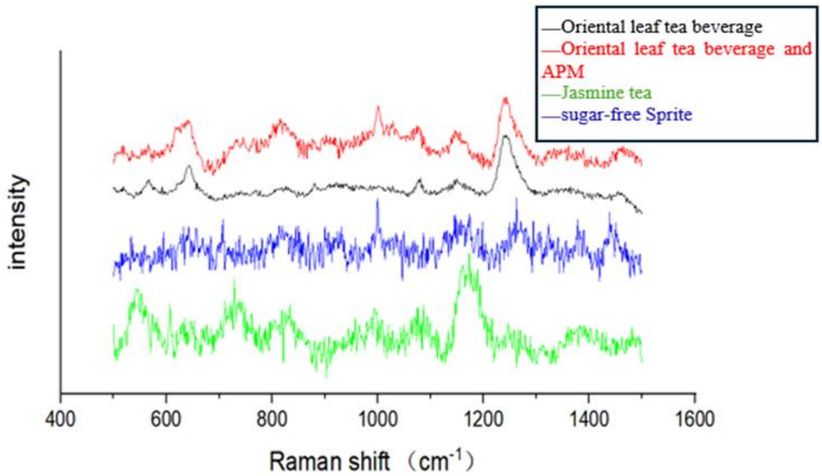

Figure 10. Raman spectra of the four samples

Through the spectrogram, it was found that aspartame was added to sugar-free Sprite, jasmine tea and Oriental leaves did not contain aspartame, and the Oriental leaves samples with aspartame added showed an obvious peak at 1004 cm^{-1}, and aspartame was detected [9]. At the same time, we also carried out a large number of experiments to obtain more Raman spectra of the three types of drinks. As a dataset used for deep learning training.

3. ANALYSIS OF DEEP LEARNING RESULTS

3.1. Correction and Optimization of Hyperparameters

3.1.1. Convolutional kernel configuration

The setting of the number of convolutional cores is very important for convolutional neural networks, and it needs to be reasonably configured to ensure that the neural networks can fully learn the local and global features of training samples. In this paper, the training sample used is one-dimensional signal, which has low dimension and is easy to learn. Therefore, setting too many convolutional layers will lead to overfitting problem. The setting of 2 convolutional layers is determined by experiments. At the same time, convolution kernels with dimensions of 3×1 and 5×1 are set for peak width and local features in Raman spectral characteristics, so that the neural network can fully learn spectral features. In addition, the influence of the number of convolution kernels on the training, test accuracy and convergence effect is also investigated through simulation experiments.

Table 1. Effects of different convolutional kernel configurations on classification accuracy

Convolution kernel configuration	Training set accuracy	Test set accuracy	Number of iterations to reach convergence	Training time (s)
(16, 32)	96.94	97.34	4	98.42
(32, 64)	98.11	98.56	10	141.96
(64, 128)	98.65	98.69	12	167.23
(128, 256)	99.03	98.88	22	208.11
(16, 64)	98.28	97.96	8	112.07
(32, 128)	98.49	99.08	16	155.59
(64, 256)	99.16	98.74	33	224.98

Table 1 records the change rule of classification accuracy of training and test sets when the neural network is configured with different number of convolutional nuclei, and records the epoch convergence and the training time. According to the experimental data, with the increase of the number of convolutional nuclei, the parameters of neural network training will also increase, resulting in a longer training time for each epoch, a significant increase [16] in the total training time, and the training becomes inefficient. This is in line with the theoretical situation. For Raman spectral data, in order to balance accuracy and efficiency, we believe that when the convolutional kernel number is configured in the way of (32, 64), the best classification accuracy can be obtained, and the training time is relatively short.

3.1.2. Optimization and adjustment of learning rate

According to the different neural network structure and training tasks, the use of appropriate optimization algorithms and learning rates can improve the training speed and classification accuracy of the model. Deep convolutional neural networks usually employ stochastic gradient descent type optimization algorithms for model training and parameter optimization. In machine learning, Adam is an efficient optimization algorithm whose purpose is to adjust the learning rat e [17] of each parameter. The calculation flow of the Adam optimizer algorithm is as follows: Set the initial value 2. Calculate gradient 3. First order matrix estimation 4. Second order Matrix estimation 5. Correcting moment deviation 6. Updating parameters

$$m_0 = 0 \tag{1}$$

$$v_0 = 0 \tag{2}$$

$$t=0 \tag{3}$$

$$g_t = \nabla_\theta f_t(\theta_{t-1}) \tag{4}$$

$$m_t = \beta_1 \cdot m_{t-1} + (1-\beta_1) \cdot g_t \tag{5}$$

$$v_t = \beta_2 \cdot v_{t-1} + (1-\beta_2) \cdot {g_t}^2 \tag{6}$$

$$\widehat{m_t} = \frac{m_t}{1-\beta_1^t} \tag{7}$$

$$\widehat{v_t} = \frac{v_t}{1-\beta_2^t} \tag{8}$$

$$\theta_{t+1} = \theta_t - \frac{\alpha \cdot \widehat{m_t}}{\sqrt{\widehat{v_t}+\epsilon}} \tag{9}$$

Through the simulation experiment, different learning rates were set, each group of training was repeated 5 times, and the average classification accuracy rate of the training set and the test set after the training was completed was recorded, as shown in Table 2.

Table 2. Performance of classification accuracy rate at different learning rates (%)

Optimizer	**Learning Rate**			
	0.01	0.001	0.0001	0.00001
Adam	33.26	Trainig set accuracy 34.92	98.32	88.43
Adam	34.88	Trainig set accuracy 33.47	97.98	89.26

Through the simulation experiment, different learning rates were set, each group of training was repeated 5 times, and the average classification accuracy rate of the training set and the test set after the training was completed was recorded, as shown in Table 2.

For Adam optimizer, when different values of learning rate are taken, according to the experimental results of Adam optimizer, the change trend of learning rate 0.01 and 0.001 is similar, and the classification accuracy is not high. This is because if the learning rate is set too large, the step size of gradient descent will be very large, which may cause the value of loss function to skip all the time. Cannot converge to the local best point, or even convergence. In addition, setting too large learning rate may cause instability of the model, causing gradient explosion or gradient disappearance, affecting the training and effect of the model. In general, based on the Adam optimizer, setting the basic learning rate to 0.0001 can be well adapted to the training task of Raman spectroscopy. The initial setting of the learning rate is too large or too small will have a bad effect on the training.

3.1.3. Batch the number of samples

In order to train deep neural networks, we usually need to process large amounts of data. Since it can be difficult to load all the data at once, a single sample iterative approach can be difficult to converge and easily fall into local optimality. Therefore, we usually divide the data into multiple batches and set a suitable batch size to achieve orderly parameter update and fast convergence. In this paper, the effects of different batch sample numbers on the classification accuracy and training time of the training set and the test set are studied through simulation experiments. 2n In the experiment, since the number of batch samples is generally set as a numerical value, we selected 16-512 representative batch samples and carried out 5 tests for each group. The evaluation accuracy of the training set and test set obtained from 5 tests was taken as our final result for reference and evaluation. The average correct rate and average training time of 5 simulations were recorded.

Table 3. Influence of the number of batch samples on the classification accuracy

Number of batch samples	Average accuracy (%)		Training time (s)
	training set	test set	
16	98.14	97.69	169.82
32	99.26	98.89	141.96
64	99.56	99.19	116.12
128	99.67	98.52	98.26
264	96.23	96.55	84.69
512	95.84	95.81	77.14

The simulation experiment results are shown in Table 3.In deep learning, batch size has a great influence on the training process. Theoretically, on the one hand smaller batch sizes may cause problems with noise gradients. Since each lot contains only a small part of the data, the gradient estimates for each lot can be wildly off, leading to problems with noise gradients. This can cause the training process to be unstable, the accuracy rate to drop, and even affect the convergence rate of the training. On the other hand, large batch sizes may make the model unable to adapt to new data. When the batch size increases, the memory and computational resources required to update the gradient increase accordingly, which can lead to training time growth and overfitting problems. At the same time, larger batch sizes may constrain the model around a wider range of best merits, making it difficult to adjust the parameters to accommodate the new data. According to the experimental results, with the increase of the number of batch samples, the time of data passing through the neural network decreases, and the training time decreases, but the accuracy will decrease. When the number of batches is set to 64, the convolutional neural network model can achieve the best classification accuracy of training set and test set, and the training time is short, which can take into account the learning efficiency of neural network and classification effect.

3.2. Comparison of Effect of Different Classification Methods

In order to test the performance of convolutional neural networks in Raman spectral classification, we compared them with other classification methods. For other classification methods, pre-processing of baseline correction and smoothing filtering is usually required. Therefore, we selected 2 datasets of original spectral data and pre-processed data (including baseline correction and Savitzky-Golay smoothing filter) for research, compared the classification accuracy of different classification methods, and explored the influence of pre- processing on the effect of various classification methods. We adopted K-nearest neighbor (KNN), Random forest, support vector machine (SVM) Decision tree and Gradient lift boosting) a total of 5 traditional classification methods and the Convolutional neural network (CNN) used in this paper a total of 6 classification methods to classify Raman spectral datas [18, 19] ets.

In order to reduce the experimental error, we conducted 10 experiments on each data set and counted the classification accuracy of their training set and test set. The experimental results were recorded in Table 4.

Table 4. Comparison of evaluation classification accuracy rates of different classification algorithms

	Training set average accuracy		**Test set average accuracy**	
sorting algorithms	original data	preprocessing data	original data	preprocessing data
KNN	67.41	88.13	68.44	90.56
Random forest	58.65	80.48	60.11	81.33
SVM (linear)	88.13	93.78	85.97	93.68
Decision tree	70.59	89	69.25	87.46
Gradientboosting	80.56	94	81.11	96.43
CNN	9.86	98.61	99.24	99.11

It can be seen from the experimental results that for the original data, the classification accuracy of other 5 algorithms is low, and there is a big gap between the classification accuracy and that of the convolutional neural network model used. In the training after the pre-processing of the original spectral data set (including baseline correction and smoothing and denoising), the traditional algorithm has been greatly improved. However, the classification accuracy of our one- dimensional convolutional neural network model is still the highest. On the original spectral data set, the one-dimensional convolutional neural network model can achieve the best classification effect, and the accuracy rate can reach 99.11% (Figure 11).

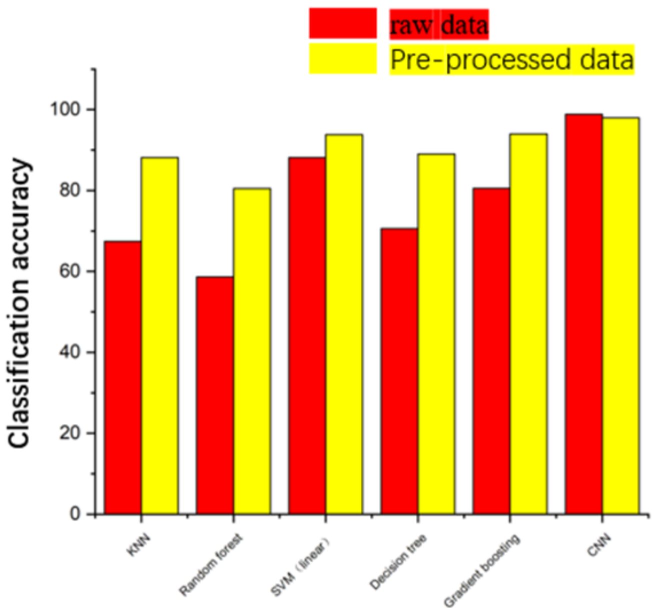

Figure 11. Comparison of average classification accuracy of pre- processed data of different algorithms for original data

From the results of Figure 11, it can be intuitively concluded that other Raman spectrum analysis methods are limited by the baseline and noise of the original Raman spectrum. If the original data is directly input for training and testing, the classification accuracy is not high, and it is more dependent on the pre-processing of Raman spectrum. There is a strong dependence on the spectrum preprocessing steps. However, the pre-processing of Raman spectral data will inevitably exclude some effective information of the original spectrum, so some features of the original spectrum may be lost when using CNN for qualitative classification, resulting in a small decrease in classification accuracy. In general, the classification accuracy of convolutional neural networks is still very high. Moreover, convolutional neural networks can directly use the original Raman spectral data for model training and classification without complicated pre-processing steps such as baseline correction and smoothing filtering, which can greatly save our computing costs and improve our classification speed. It can also carry out accurate qualitative classification.

4. SUMMARY

This paper mainly studies the preparation of surface-enhanced Raman substrate, the recognition and classification method of Raman spectrum, the preparation of high-quality nano-cone substrate enhanced Raman signal, after obtaining Raman spectrum data, the convolutional neural network is used to establish Raman spectrum classification and recognition model, and realize the rapid identification of aspartame added in three different beverages. The accuracy rate of successfully identifying whether the beverage contains aspartame can reach 99.11%, which proves that convolutional neural network can be used for classification and recognition of Raman spectra, and the classification accuracy and efficiency are superior to other classification methods, providing support for rapid detection of aspartame.

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