Rapid material identification via low-resolution Raman spectroscopy and deep convolutional neural network

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Abstract. Raman spectroscopy is a vital technique being able to detect and identify molecular information with advantages of being fast and non-invasive. This technique also enables numbers of potential applications, including forensic drugs detector, explosive detection, and biomedical analysis. In this work, we investigated the identification performance of a custom-made low-resolution Raman system equipped with machine learning capability to classify various types of materials. Here, a relatively broadband laser diode with center wavelength of 808 nm was used for Raman excitation. An off-axis parabolic mirror with through hole was used in place of a beamsplitter for sample excitation, as well as collection, and collimation of scattered light from long working distance of 50 mm. The signal was filtered and delivered to a cooled spectrometer via an optical fiber for spectra measurements. Raman spectra of test samples were on the range of 100-2000 cm\(^{-1}\) with 7.65 cm\(^{-1}\) data steps. For spectral analysis, a convolutional neural network (CNN) was implemented as classification algorithm with feature extraction from multiple layers together with error-back propagation, which displayed the performance in term of accuracy. It was found that with only three sets of convolution layers up to 96.7\% testing performance can be achieved even with low spectral resolution input.

1. Introduction
Raman spectroscopy uses a laser to excite molecules in a targeted material and generate output light containing a tiny fraction of wavelength-shifted components from inelastic scattering. This so-called Raman spectrum is specific to chemical bonding, which provides information useful to identify the chemical composition of the sample. This technique enables numbers of potential applications, including forensic drugs detector [1], explosive detection device [2], identification for mineral mixtures [3] and biomedical analysis [4].

However, Raman spectroscopy is a weak process susceptible to noises, especially fluorescence background. This noise could be removed by using various types of filters, or through a curve fitting baseline removal via a computer algorithm by using the asymmetric least squares (AsLS) method [5] to estimate the smoothness function to remove the baseline from the raw spectrum. Essentially, for the intense fluorescence case, a method of shifting the excitation Raman can improve the extraction of the pure spectrum by comparing two different spectra from a multi-wavelength excitation, and reconstruct the spectrum for all wavenumber positions along the spectral axis [6].
In fact, the performance of a Raman system is affected by several factors; for instance, spectral linewidth of the laser source, spectral purity, optical components, and the resolution of the spectrometer. Particularly, a high-performance Raman grade laser should have a very narrow linewidth of 0.00001-0.06 nm [7] and exceptional thermal stability to provide clear spectrum measurements for molecular identification; this comes at relatively high costs. Trading the system performance with lower system cost will compromise the Raman spectral resolution and its resolvability for small differences in the Raman shift, thus making spectrum identification via database lookup less specific.

Matching a Raman spectrum with a chemical structure is also a challenging task particularly for poor spectral resolutions and those that share similar characteristics. Conventional search algorithms for Raman spectra together with available databases could be effectively used to identify materials [8]. However, this requires intensive data preprocessing that can be time consuming for poor Raman spectra, thus not applicable for real-time operations. Machine learning provides a potential identification tool by learning features and creating a model for rapid classification of unknown materials. In addition, convolution neural network (CNN) has been developed from machine learning combined with feature extractions from multi-layer filters with error-back propagation in classification layers to drastically improve the performance of the algorithms [9,10]. Here, we demonstrate that by applying CNN as a classification technique to a low-resolution Raman system an accurate real-time identification for unknown materials can be achieved.

2. Materials and methods

2.1. Custom-made Raman spectroscopy system

A low-resolution Raman spectroscopy system was custom-built using a low-cost continuous wave (CW) laser diode (LSR808NL-2W) with emitting center wavelength of 808 nm, a spectral linewidth of 10 nm, and with an operating power as high as 1.59 W. Therefore, no tight focus is required, which increases spot size on sample surface. A narrow bandpass filter at the center wavelength 808 nm with a FWHM of 3 nm was applied to reduce the laser bandwidth and to eliminate undesirable wavelength components. The laser beam was weakly focused using a 100 mm plano-convex lens through a small hole of an off-axis parabolic mirror. The laser beam was then directed on a sample placed 50 mm under the parabolic mirror as shown in figure 1. The produced Raman scattering was collected and collimated by the off-axis parabolic mirror, which showed a better performance compared to a dichroic beam splitter when used with a relatively high-power laser. The reflected light was then filtered to suppress the incident wavelength by using dual notch filters. Subsequently, the beam was coupled to an optical fiber via a 20 mm plano-covex lens and delivered to a thermoelectrically cooled spectrometer (Exemplar Plus: BWTEK) for spectral measurements. The spectral resolution of the spectrometer is 1.5 nm. Here, six different materials with similar physical appearance and spectral characteristics, namely, NaNO₃, BaSO₄, Ba(NO₃)₂, KNO₃, Pb(NO₃)₂, and CH₃N₂O were used for the test of the Raman identification. The integration time was set to 20 seconds and the measurements were done on ten different spots randomly chosen for each sample.
2.2. Implementation of CNN
Six sets of Raman spectra obtained from six types of material were exported to MATLAB. Each spectrum was considered as 1D data containing 313×1 data points. It is a general precaution that a large number of input data can cause overfitting. Therefore, data augmentation was applied to prevent this problem by including white Gaussian noise to the raw data with different signal to noise ratios, 15, 25, and 35 by using functions in MATLAB. This augmentation procedure can increase the data numbers from 51 to 204 spectra, and all spectra were normalized to 1. The dataset was then divided into three parts as follow: training, validation, and testing set. The training dataset was randomly selected from 70% of all datasets, leaving 30% for validation (15%) and testing (15%). The CNN structure (figure 2) consists of four sets of convolution layers for feature extraction. Each of them contains convolutional filters, ReLU and max pooling function to downsize the feature output. The output layer has six neurons connected to softmax function to estimate the probability.
3. Result and discussion

3.1. Resolution of Raman system
The Raman spectral resolution of the custom-made system was mainly controlled by the relatively broadband laser linewidth of 3 nm, which is equivalent to a Raman bandwidth of 46 cm\(^{-1}\). In practice, from the Raman measurements of Ba(NO\(_3\))\(_2\) it was found that the FWHM of the characteristic peak was around 65 cm\(^{-1}\), compared with 3 cm\(^{-1}\) obtained from a high-resolution equipment (RAMANforce, Nanophoton) as shown in figure 3. In fact, the resolving power of the customize Raman system shows a nearly 22 times lower than that of the standard Raman equipment; some level of fluorescence background observed was also observed. This significant deviation from the pure spectrum obtained from a high-performance Raman system necessitates the implementation of CNN for spectrum identification.

![Figure 3. Raman spectra of Ba(NO\(_3\))\(_2\) from a custom system (a) and RAMANforce system (b).](image3)

3.2. Raman spectra of test materials
The Raman spectra collected from all test materials shows the major characteristic peak located at around 1,000 cm\(^{-1}\), corresponding to the nitrate and sulfate groups that make small differences in Raman shift, as shown in figure 4. Minor peaks play a role in providing more distinguishable features to the spectrum data. Moreover, the fluorescence background is still substantially observable even excited by a near infrared laser. In particular, BaSO\(_4\) shows the highest fluorescence baseline compared to other materials.

![Figure 4. Raman spectra of all test materials collected from a custom system.](image4)
3.3. Visualized features of a convolutional neural network

After 1D spectral data was fed into the neural network, the convolution filters operated and automatically extracted features from the input data as shown in figure 5. Here, features of the test data from the first four convolution layers are presented as light and dark areas representing values ranging from 0 to 1, indicating good and bad features, respectively. These features were selected by max pooling function before entering the next layer. Therefore, feature results from the last convolution layer contain useful features; for instance, it shows the feature of same the test data from the fifth 32 number of convolution layers. It is noted that all images in figure 5 were expanded to ease visualization.

![Diagram](image)

**Figure 5.** 1D plot of a raw spectrum of test data (a). Data features from convolution layer 1 (b) and layer 5 (c).

3.4. Performance of the network

Classification results from the CNN are represented in term of confusion matrix plot as shown in figure 6. It shows the results from the testing progress of the network with a learning rate of 0.01. Every epoch during the progress shuffled the data to avoid overfitting. The prediction performance shows an accuracy of 96.7%, as a few of the miss-predicts were from Ba(NO\textsubscript{3})\textsubscript{2} and Pb(NO\textsubscript{3})\textsubscript{2} due to the similarity of these two Raman spectra. However, the performance of the network can be further improved by collecting more experimental data to train the network.
4. Conclusion
We demonstrated that a low-cost and low-resolution Raman spectroscopy system can also achieve high performance in material identification when using with CNN. Here, a custom-made Raman system afforded spectral resolution of around 65 cm\(^{-1}\), over 20 time lower in resolving power when compared to a standard Raman system. Six materials with similar Raman peak features were used for spectrum measurements, CNN training, and finally classification. It was found that the trained CNN resulted in good classification performance of 96.7\%, even with low spectral resolution and relatively high fluorescence background.

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