2DCOS-XII

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*All pre-recoded presentations are avariable to pre-registration person from August 14 to 25, 2023 on shared folder 2DCOS-12 (enter password: 2dcosXII2023).

**All participants are welcome to discuss at ZOOM meeting at August 17-18, 2023 (22:00-24:00; Korean time) as below URLs.

1. Day1 (August 17, 2023 22:00-24:00)

   https://kangwon-ac-kr.zoom.us/j/81130046588
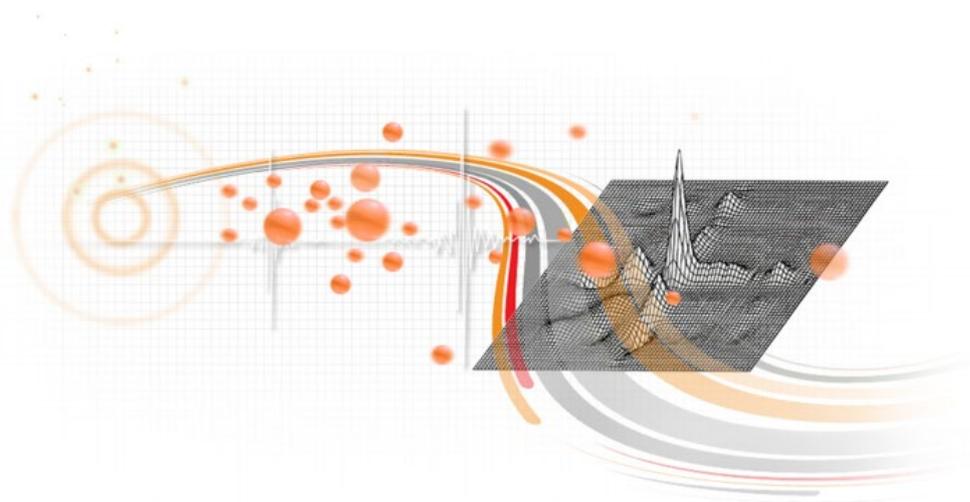2. Day2 (August 18, 2023 22:00-24:00)

   https://kangwon-ac-kr.zoom.us/j/81300917782

***The detailed information is available on the 2DCOS-XII homepage. (https://2dcos.org).

Abstracts of
Keynote
and Oral Talks

Keynote

PROGRESS IN TWO-DIMESNIONAL CORRELATION SPECTROSCOPY (2D-COS)

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Recent progress and noteworthy developments in the field of two-dimensional correlation spectroscopy 2D-COS are briefly surveyed first. 2D-COS can be applied using many different types of probes analyzing various systems of interest under diverse perturbation parameters. A number of important theoretical developments and useful techniques have also emerged, extending the utility of the technique. In addition to the status review of the field, two specific topics of recent interest are also reported: refining the spectral resolution enhancement provided by 2D-COS, and a new concept of component group evolution.

The apparent spectral resolution is enhanced in 2D-COS by spreading the overlapped peaks along the second spectral dimension. This feature is especially prominent in asynchronous spectra, where bands originating from different moieties are vividly differentiated. However, asynchronous spectra are not always well-suited for classifying signals originating from the common or shared origins. Combined use of synchronous spectra and appropriate scaling adjustment, sometimes with the help of band narrowing techniques, can provide a useful tool to effectively sort out and classify signals originating from various contributing moieties.

2D-COS is also well suited for the analysis of sequential spectral evolution of a system under the influence of an external perturbation. However, examination of a coarsely distributed heterogeneous system, where signal sampling variations occur for each measurement stage during the evolving process, poses an extra challenge. Time-dependent change in hyperspectral images of an aging biological tissue is a good example. A simple average spectrum of the entire sampling space for each evolving stage may not be suitable for representing the dynamics of individual components heterogeneously distributed within the sample, and a new approach addressing this common issue must be developed.

Multivariate curve resolution (MCR) is usually applied to decompose mixture spectra into those of pure molecular component spectra. It turns out that MCR can also be used to classify complex mixtures into a finite set of component groups consisting of similar but different compounds. The loading vector in this case is no longer an estimate of a pure molecular component spectrum but represents a collective mixture of similar compounds, e.g., proteins and lipids. Such component group loadings obtained at different stages of an evolving system are no longer constant but vary along the perturbation variable. 2D-COS analysis can be readily applied to such evolving MCR loading vectors. This concept actually can be further extended to the analysis of a seemingly homogeneous evolving system. A moving window of evolving dataset is then subjected to a localized MCR analysis, and the potential existence of the variations in MCR loadings with the shift of the window may be examined.

Oral talk-01

THE FOOTPRINT OF LINEAR DICHROISM IN INFRARED 2D-CORRELATION SPECTRA

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At the Bouguer-Beer-Lambert level, classic linear dichroism theory can be used to simulate the effects of linear dichroism on absorbance spectra.[1] For this low-level theory, it is only the angle between polarization direction and transition moment that is relevant. Accordingly, this angle can be used as perturbation to calculate corresponding infrared 2D correlation spectra. On a higher level of theory, if wave optics and dispersion theory are used, linear dichroism can be modeled with a 4x4 matrix formalism. On this level, spectra are influenced not only by the angle between polarization direction and transition moment, but also by the angle between the normal of the surface of the sample and the transition moment. While this increases complexity, it also predicts that orientations and orientation distributions can be determined to a much higher degree than according to linear dichroism theory.[2]

In this contribution, we compare the different footprints of linear dichroism according to both, low-level and higher-level theories in infrared 2D correlation spectra and show that only those footprints based on wave optics and dispersion theory match experimental results. As a result we also find that asynchronous spectra can detect orientation with a sensitivity that is much higher than if conventional spectra are employed for this task.

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Oral talk-02

ELUDIATING THE SELF-ASSEMBLING MECHANISMS OF ULTRA-SHORT AMYLOIDOGENIC PEPETIDES BY VIBRATIONAL SPECTROSCOPY

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Ultra-short peptides could form a variety of peptide-based nanostructures and these nanostructures have attracted great interests in recent years among materials scientists (1-3). In this work, the self-assembly behaviors of several ultra-short amyloidogenic peptides were investigated by FTIR spectroscopy. Our aim is to obtain the vibrational spectroscopic signatures for the different steps of the self-assembly processes of these peptides. In addition, the effect of side chain modification on the self-assembly processes of the ultra-short peptides was also explored. We found that different intermediates during the self-assembling process could display different FTIR signatures in the amide I region. We also discovered that the side chain modification could lead to different self-assembly behaviors for the ultra-short peptides. This work not only demonstrated that FTIR spectroscopy is a useful and convenient tool to tackle the self-assembly mechanisms of ultra-short peptides.

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INVESTIGATION ON THE INTERMOLECULAR INTERACTION BETWEEN QUERCETIN AND HYDROCYPROPYL β– CYCLODEXTRIN

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Quercetin is a flavonoid compound extracted from rutin, and exhibits a variety of beneficial therapeutic effects. However, the solubility of quercetin in aqueous solution is low, which limits the application of quercetin in medical practice. Hydroxypropyl β-cyclodextrin turns out to be a useful excipient to enhance the solubility of quercetin. Herein, we adopt two-dimensional correlation spectroscopic method to investigate the intermolecular interaction between quercetin and hydroxypropyl β-cyclodextrin. From the pattern of cross-peaks, we found evidences of the mechanism of the enhancement of solubility of quercetin by hydroxypropyl β- cyclodextrin.

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PROTEIN DYNAMICS IN A PHOTOSYNTHETIC REACTION CENTERS ANALYZED BY TIME-RESOLVED FTIR DIFFERENCE SPECTROSCOPY AND 2D-COS ANALYSIS

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Photosynthesis is the process that basically sustains all life on Earth. The initial event is a light-induced charge separation that takes place in special proteins called reaction centers. Recently, a large number of studies have focused on the protein response to this initial charge separation state DA $\rightarrow$ D+ A- [1,2]

Time-resolved FTIR difference spectroscopy is an excellent tool to investigate photobiological reactions at an atomic level[3]. Fast sample preparation and relatively cheap instrumentation can indeed make it possible to follow in time the evolution of almost all the components, provided that they undergo some kind of change (chemical, physical, conformational….) during the reaction.

We have investigated the charge separation event – under different conditions - in reaction centers from *R. sphaeroides,* a system that has been largely studied by IR since the late 80's and for which several IR marker bands for key player (pigments, cofactors, protein backbone, later chain of specific amino acids….) are available[3-5].

We have found that under continuous illumination conditions, a "light-adapted" state is built. After stopping the illumination, the starting neutral state is recovered on a much longer timescale compared to the situation where the charge separate state has been formed using a saturating laser flash.

We have examined the building-up of the "light-adapted" charge separate state under continuous illumination by 2D-COS spectroscopy. Interestingly, we have found that spectral contribution from pigments and cofactors (on one hand) and protein response (on the other hand) are not synchronous.

Even more interesting is the "relaxation" behavior after illumination (with continuous light) and after a saturating laser flash, that suggest two completely different scenarios in term of protein response.

The results are discussed in the framework of current research on protein response to biochemical redox reactions and on the still-too-limited application of 2D-COS to time-resolved FTIR difference spectroscopy in photobiology and biochemistry.
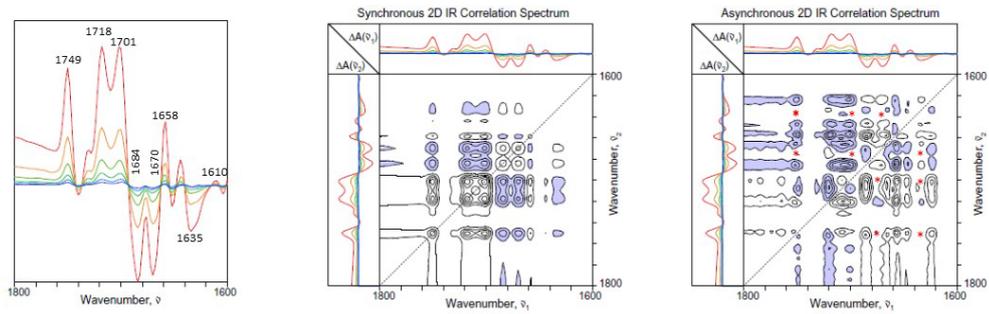
Figure 1. Time-resolved FTIR difference spectra after a saturating laser flash and their 2D-COS analysis

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CAN 2D-COS INDICATE BIOCOMPATIBLE MATERIAL?

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Carbon nanofibers are the novel type of materials that are of interest in many fields also in medicine. The carbonization of the polymer precursor is one of the perspective method of producing carbon nanofibers. Carbon nanofibers are a material which properties can be modified in a wide range [1]. Type of fiber nanoprecursor and the parameters of the carbonization process, induce formation of materials with designed structure and surface parameters. Biomimetic materials are of interest to medicine, especially regenerative medicine. Two types of CNFs obtained by PAN precursor carbonizaton at 1000ºC were studied, one was cytotoxic, while the other after functionalization was biocompatible. 2D COS with the use of laser wavelengths of 442 nm, 514.5 nm and 785 nm, treated as an external disturbance, allowed to distinguish both structures [2]. The first sample showed autopeak at position 1650 cm^{-1} while the other at position 1585 cm^{-1}(Fig. 1).

Figure 1. 2D synchronous spectra of genotoxic (left) and biocompatible (right) CNFs.

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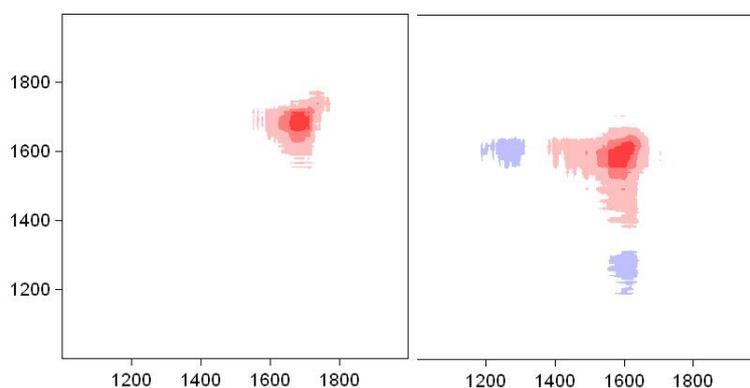2. Noda, I.; Dowrey, A. E.; Marcott, C.; Story, G. M.; Ozaki, Y. Applied Spectroscopy; 2000. 52; 236A-248A.

Oral talk-06

A SPECIFIC FLUORESCENCE-ENHANCED METHOD FOR FURFURAL DETECTION IN *CHINSES BAIJIU* BASED ON CARBON DOTS

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We have prepared a kind of carbon dots (o-CDs, λ_{em} = 570 nm) with orange emission by using o-phenylenediamine as a carbon source [1]. Under the strong oxidation of ammonium persulfate (APS) and the catalytic action of tetramethylethylenediamine (TEMED), the o-CDs can specifically interact with furfural and produce a new fluorescence emission peak at 520 nm. In the presence of other aldehydes and furfural analogs, there was no such specific response, indicating that this method has good recognition selectivity and anti-interference ability toward furfural. When we plot the furfural concentration using the new emission peak intensity, it showed a good linear response in the range of 0-200 μM. Then the present method was applied to determine furfural content in actual liquor samples, which showed good recovery, indicating high practical application potential [2]. Further study indicated that the specific response was attributed to the oxidation reaction between the two adjacent amino groups on the benzene ring of o-phenylenediamine and the aldehyde group of furfural to form furanyl benzimidazole [3]. And the new structure increased the density of the electron cloud on the surface of the carbon dots, which induced the blue shift of the fluorescence emission peak at the o-CDs and generated a new fluorescence emission peak at 520 nm.

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Oral talk-07

TWO-DIMENSIONAL CORRELATION ANALYSIS OF MICRO AND MACROSCOPIC STRUCTURE EVOLUTION IN ANNEALED CARBON NANOTUBES

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Complex micro- and macroscopic structures of materials are widely characterized by microscopy, spectroscopy, in-situ measurements, and their combinations [1-3]. However, such multifaceted data are difficult to comprehend due to complex relationships. In this study, two-dimensional correlation (2DCOS) analysis is applied to a tabular data set of multifaceted characterization data to reveal the complex relationships of micro- and macroscopic structures. This study focused on carbon nanotubes [4], potential materials for electrical wiring and energy devices. The synchronous matrix clearly revealed the highly correlated structural parameters, while the asynchronous matrix showed the delay of structural parameters during high-temperature annealing. The 2DCOS results strongly supported our proposed mechanism of graphitization during annealing of carbon nanotubes [5].
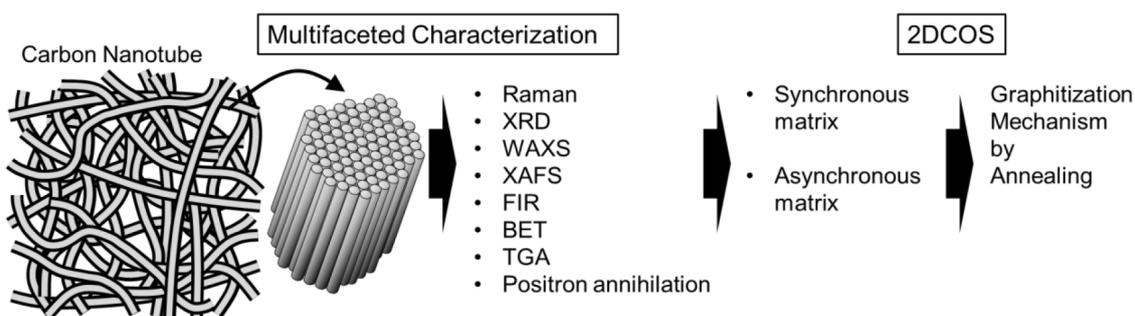
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Oral talk-08

USE OF 2D-COS TO UNRAVEL THE CRYSTALLIZATION MECHANSIM OF PHA FROM POLARIZED RAMAN MEASUREMENTS OF SPHERULITES

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Polarized Raman spectra of spherulites of PHA (polyhydroxyalkonate) in thin PHA films were acquired along spherulite axis lines. The laser and Raman polarizations were defined along the line and normal to it. In some samples, under some conditions, band intensities varied as a function of distance from the spherulite center, which is consistent with the known rotation of the crystallite along that axis. For a vertical scan (defining vertical in the spherulite image) polarizations were either along that axis (called vertical) or normal to that axis (called horizontal). VV, HH, HV, and VH spectra were acquired. Band intensities varied greatly for the different polarization conditions, reflecting the group theoretical characteristics of the vibrations. Because it is known that rapid growth is along the a axis, and the spherulite radius will be along a, it is possible to understand the intensity behavior. Combining this observation with the spectral characteristics known to be associated with the crystallization phenomenon (especially the behavior of the carbonyl band and the high frequency CH bands), provides information on the formation of the spherulite. The use of 2D-COS simplifies the determination of important spectral effects.

SPECIES ANALYSIS IN THE MODEL ELECTROLYTE OF LITHIUM ION BATTERIS CONTAINING LITFSI AND PROPYLENE CARBONATE

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Electrolytes, like the "blood" in human bodies, are the media for the transportation of ions in batteries. Identifying the existing forms of ions in electrolytes, referred as species, is of particular importance to understand/improve the transport efficiency of the ions, which affects the battery performance. In this work, we studied the solution structure in a model electrolyte consisting of a lithium salt, lithium bis(trifluoromethane sulfone)imide (LiTFSI), and an organic solvent propylene carbonate (PC). By employing excess spectroscopy and two-dimensional correlation spectroscopy (2D-COS), assisted by quantum chemical calculations, 12 species were identified, namely $Li^+(PC)_4$, $TFSI^-$, $TFSI^-(PC)$, $TFSI^-(PC)_2$, $Li(TFSI)_2^-$, LiTFSI, $LiTFSI(PC)_3$, $LiTFSI(PC)_2$, LiTFSI(PC), as well as PC monomer, PC dimer, and PC multimer. Their relative quantities were also analyzed. In addition, the order of interaction strength is determined as follows: cation-solvent >> anion-solvent > solvent-solvent. Thus we concluded that the dominate ion transport mechanism of Li^+ in the LiTFSI-PC electrolyte is solvation carriage and that of $TFSI^-$ is hopping. These results provide physical insights into the structural and interactive properties of the electrolyte of lithium ion batteries.
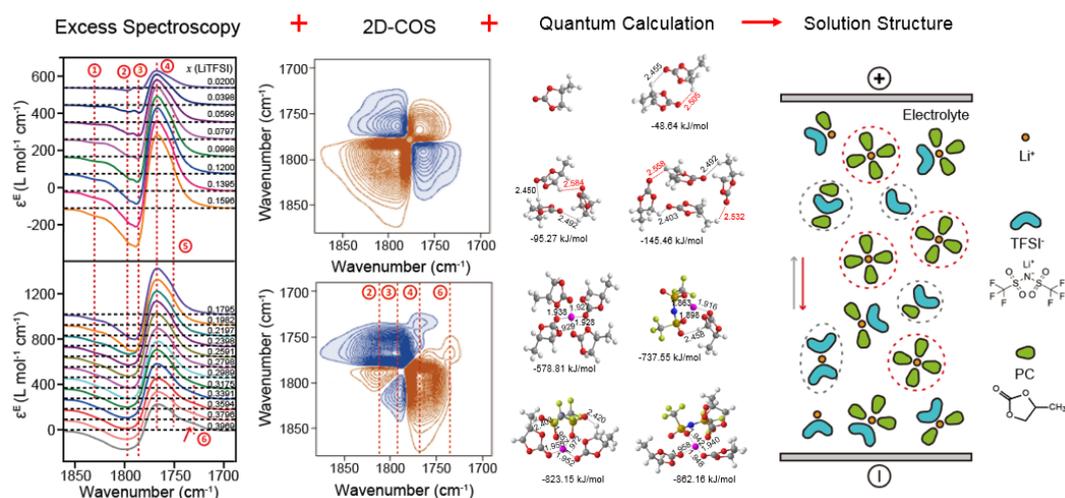

Figure 1. Experimental excess spectra and 2D-COS spectra, theoretical predicted complexes, and the schematic of possible species in the electrolyte.

Oral talk-10

DETERMINATION OF STRUCTURAL CHANGES TAKING PLACE IN SPRUCE WOOD FOLLOWING (HYDRO)THERMAL TREATMENT

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Wood, a natural composite material, is used in many applications (from construction to furniture and/or different domestic or art objects and tools), but due to its structural features and depending on the environmental conditions can be easily degraded by different factors. In this study spruce (*Picea sitchensis*) wood samples were subjected to different conditions of (hydro)thermal treatment at 140ºC by varying the relative humidity (0, 60, 75 and 100%RH) and period of exposure (up to 47, 7, 4 and 1 days). After the treatment, the samples were weighted to asses the weight percent loss and then the wood pieces were inserted into water in order to eliminate the water soluble compounds formed during the treatment and trapped into the wood structure.

To identify the structural changes taking place in the wood structures during the applied treatment conditions and to quantify the differences between non-extracted and water-extracted wood specimens after the treatment, the infrared (FT-IR) spectroscopy, principal component analysis (PCA) and two dimensional correlation spectroscopy (2D-COS) were employed. Following this, the changes were reflected in shifting of the bands position, modifications in bands intensities and width. Larger variations were observed for the samples exposed at higher relative humidity values and for longer period. At the same time, it has been also observed that during the hydro-thermal treatment a high amount of extractives remain in the wood structure, extractives which vary in quantity and composition.

PCA and 2D-COS analysis made possible to discriminate the changes in the wood structure according to treatment time, amount of relative humidity, and also between non-extracted and water-extracted samples, as well as to identify the sequential order of the bands' modification.

2D CORRELATION TECHNIQUE FOR PERIODICITY DETECTION

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Generalized 2D correlation spectroscopy (2DCOS) is based on the phase relationship among Fourier components comprising the time series. Capitalizing on the fundamental 2DCOS properties, we developed 2D correlation technique using wavelet transform for periodicity detection in time series (comprising the red noise) of the most powerful compact objects in the Universe called quasars [1, 2, 3]. As fundamental premises of 2D correlation and wavelet transform are generally applicable, we demonstrated our technique on ionospheric signals[4]. With this talk we would like to outline that there is an intriguing opportunity to explore a new possibility of correlation analysis and its application.

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QUANTITATIVE 2D-CORRELATION ANALYSIS

<u>Thomas G. Mayerhöfer</u>,[1,2] Susanne Pahlow,[1,2] Isao Noda,[3] Reiner Heintzmann,[1,2] Juergen Popp[1,2]

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2D-COS is usually assumed to be a semiquantitative method at best. In fact, it is possible to compare different synchronous spectra by using the Minkowski distance (or, as special case, the Euclidian distance) in a quantitative way.[1] The same seems to be impossible for asynchronous spectra. To derive such a quantitative measure, also for asynchronous spectra, one can use the symmetry properties of the 2D spectra, according to which synchronous spectra are always symmetric and asynchronous spectra are always antisymmetric to the diagonal from low to high wavenumbers. For hetero- or hybrid 2D-COS, corresponding points in the synchronous/asynchronous spectra are no longer symmetric/antisymmetric. If one calculates the sum of squared residuals for corresponding points above and below the diagonal, the Euclidian distance is rederived for synchronous spectra and a related measure is introduced for the asynchronous spectra.[2] For 2T2D-COS, a corresponding measure can also be introduced for the asynchronous spectra, but with an altered condition according to which each point of the asynchronous spectrum should become zero.[3] Based on these measures and a generalization of 2D-Correlation Analysis it is possible to quantitatively correlate any two series of function values or any two functions. Accordingly, these 2D correlation-based similarity measures can be used, e.g., for nonlinear fitting procedures that allow to compensate for systematic errors.

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Acknowledgements

AG(I) IONS CONCENTRATION-DEPENDENT DYNAMIC MECHANISM OF THE THIOLACTIC ACID CAPPED GOLD NANOCLUSTERS AS REVEALED BY FLUORESCENCE SPECTRA AND 2D CORRELATION ANALYSIS

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We have applied in situ fluorescence spectroscopy, in combining with two dimensional correlation spectroscopy (2DCOS), to investigate the dynamic fluorescence changes of the thiolactic acid capped gold nanoclusters (AuNCs@TLA) induced by Ag(I) ions, which induced the generation of two new emission peaks at 610 and 670 nm in sequence and quenching the original emission at 800 nm. Several spectral components, around (785, 654) nm, (677, 587) nm and (741, 673) nm, are revealed by 2DCOS analysis, suggesting that new luminescent substances or groups are generated with the addition of Ag(I) ions. The interaction between AuNCs@TLA and Ag(I) are discussed in detail and the emission change is ascribed to the AGR and size growth. The present study will facilitate and promote more interests in focusing on the application of NIR emitted metal nanoclusters.

Keywords: gold nanoclusters, Ag(I) ions, fluorescence spectroscopy, 2DCOS
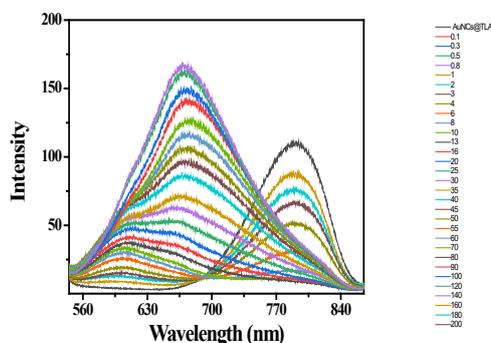
Fig. 1. Fluorescence spectra of AuNCs@TLA (50 μg·mL^{-1}) in the presence of different amounts of AgNO$_3$ (0, 1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10, 13, 16, 20, 25, 30, 35, 40, 45, 50, 60, 70, 90, 100, 120, 140 μM)
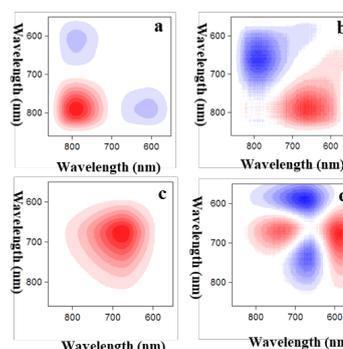
Fig. 2. Two-dimensional correlation contour maps of the fluorescence spectra of AuNCs@TLA based on spectral data from Fig. 1: (a) and (c) for the synchronous at range of 0-10 and 10-140 μM Ag (I) ions, respectively; (b) and (d) for the asynchronous, correspondingly.

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INFRARED TWO DIMENSIONAL CORRELATION SPECTRUM UNDER THERMAL AND MAGNETIC PERTURBATIONS

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Tungsten oxygen cluster compounds have a broad potential for applications[1-3], but the mechanism of action for these applications is unknown due to their complex structures. Two-dimensional infrared spectroscopy can characterize functional groups such as hydrogen bonds at the molecular level and resolve the application mechanism, and our group has investigated the relationship between the structure of tungsten polyacid compounds and two-dimensional infrared spectroscopy. A novel Antimonotungstate $[La(H_2O)_5]_4\{H_6[Fe_2(H_2O)_5(B-\beta-SbW_9O_{33})]_6\}\cdot12H_2O$ **1**) was synthesized by hydrothermal synthesis. The compound **1** cluster anion is linked into a three-dimensional chain by La-O bonds and hydrogen bonds (Ow2-Hw2A…O_c2, Ow2-Hw2B…O_c15. Ow1-Hw1A…Ow_d9, Ow1-Hw1B…O_b26)(Fig.1(a)).
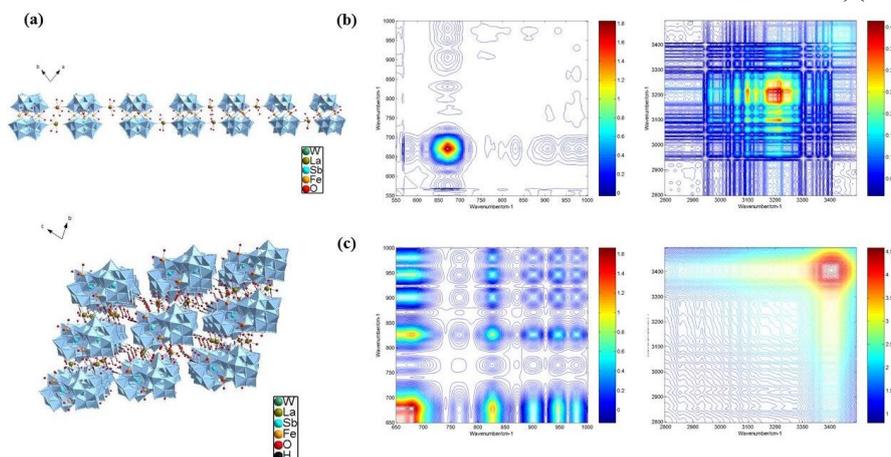
Fig.1(a) 1D structure and 3D structure of compound **1**; (b) 2D IR spectra of compound **1** under temperature variation from 30-110 °C; (c) 2D IR spectra of compound **1** under the magnetic field variation from 5-50 mT.

Two-dimensional infrared correlation spectroscopy of compound **1** under magnetic perturbation and thermal perturbation was performed. The data showed that the strong peak around 670 cm^{-1} is the response of v_{as}(W-O_c-W) to magnetic perturbation, probably due to the bridging oxygen on the tungsten-oxygen cluster skeleton connected to the trivalent magnetic ion, resulting in its stretching vibrational dipole moment with the magnetic field(Fig.1(b)). The thermal response of the v_{as}(W-O_c-W)(680cm^{-1}), v_{as}(W-O_b-W)(820cm^{-1}) and v_{as}(W=O_d)(945cm^{-1}) is relatively strong. The reason may be due to the formation of relatively strong hydrogen bonds between the oxygen on the cluster cage and free water molecules(Fig.1(c)).

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Oral talk-15

APPLYING 2D CORRELATION SPECTROSCOPY AND PRINCIPAL COMPONENT ANALYSIS TO UNDERSTAND HOW TEMPERATURE AFFECTS THE NEPTUNIUM(V) ABSORPTION SPECTRUM

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Numerous f–f electronic transitions occur in the visible–near infrared electronic absorption spectrum of neptunium(V) (NpO_2^+), with recently documented temperature dependencies. The effect of temperature on the absorption spectra of actinide species is an important factor to consider but has often been overlooked. Optical visible–near infrared absorption spectra (400–1,700 nm) of neptunium(V) (0.017–0.89 M) in 1 M HNO_3 with varying temperatures (T = 10–80°C) were studied using principal component analysis and 2D correlation spectroscopy. Principal component analysis described the intensity, position, and overall shape of the bands and their sensitivity to interactions with the solvent and coordination environment. 2D correlation spectroscopy revealed that the absorption band near 1,095 nm likely consists of two bands centered near 1,087 and 1,096 nm, helped reveal the location of numerous isosbestic points and provided an unambiguous assignment of unresolved peaks in the visible region. These unique results will be useful to validate computations in future work.

Oral talk-16

SIMULTANEOUS MEASUREMENT OF NEAR-INFRARED (NIR) ABSORPTION AND SMALL ANGLE X-RAY SCATTERING (SAXS) FOR CHARACTERIZING THERMALLY AGED POLYPROPYLENE (PP)

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Aging of PP polymer was examined by simultaneous measurement of NIR spectrum and SAXS profile. Sets of NIR spectra and SAXS profile of the initial and thermally aged PP samples were collected by a SAXS sample chamber equipped with a NIR fiber probe as shown in Fig. 1. Change in SAXS scattering peak was readily captured by applying the thermal aging treatment, indicating the development of a specific structure having much longer period (Fig. 2).

NIR spectra of the initial and aged PP, on the other hand, resulted in seemingly similar feature. The pair of the NIR spectra was thus effectively compared by calculating two-trace two-dimensional (2T2D) correlation spectra. The asynchronous correlation spectra indicated the predominant decrease in the amorphous component in the aging-treated PP (Fig. 3). All put together, it was revealed that thermal aging of the PP substantially induces the additional development of periodic crystalline lamellar structures by the consumption of the rubbery amorphous component.
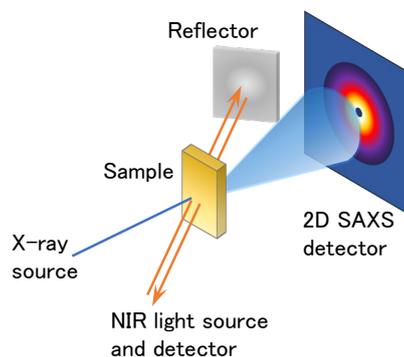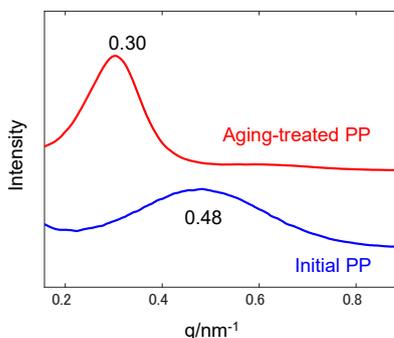

Fig. 1 Schematic illutration of NIR-SAXS system
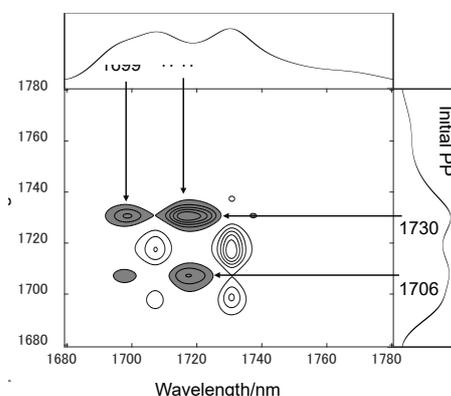

Fig.2 Change in SAXS profile feature by aging treatment

Fig.3 Asynchrnous correaltion spectra calucrated with a pair of NIR spectra of intial and aging-treated PP samples

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SPECTROSCOPIC STUDY OF MICRO/NANO-HYDROXYAPATITE POLYMER COMPOSITES MODIFIED WITH CARBON NANOFIBERS.

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In the presented study the composite membranes of polycaprolactone (PCL) and nano- / micro-hydroxyapatie (nano-HA /micro-HA) of different HA concentration (5%, 15%, 30%, 50% w/w) were prepared. In the next step the PCL/nano15%-HA membrane was modified with carbon nanofibers (CNF). The presented materials are a proposal of potential biomaterial with applications in bone tissue engineering strategies.

Microscopic images showed that the size of the PCL spherulites of PCL/nano5%-HA and PCL/micro5%-HA increased in comparison to the reference PCL membrane. However, the diameter of PCL spherulites decreased with increasing amount of HA addition, and it seems that the micro-HA disturbed the crystallization process of the PCL more prominently than the nano-HA. The modification of material by the CNF leaded to the most significant change of topography since the size of spherulites decreased to the point that they cannot be distinguished. The water contact angle indicated a general increase of hydrophobicity of polymeric membrane after introduction of the HA, that was even higher with modification by the CNF. In the Raman spectra of studied materials bands of the components: PCL, HA and CNF were observed. Along with the increase of the HA amount in membranes the intensity of 960 cm^{-1} band was increasing as well as the $I_{960(HA)}/I_{913(PCL)}$ ratio that confirmed the expected composition of fabricated samples. The spectroscopic crystallinity parameters, such as I_{913}/I_{867} ratio, indicated increasing prevalence of polymer amorphous domains in the material structure with the increase of the HA concentration. Two-dimensional correlation spectroscopy (2D-COS) was employed for further analysis of the HA addition influence on the polymeric matrix (the concentration of the HA was regarded as perturbation). Asynchronous map of PCL/nano-HA membranes shows cross-peaks of correlation between 2880, 2898, 2928, 2943 cm^{-1} bands and the 960 cm^{-1} band of the HA (Fig. 1), that indicates the interaction of the hydroxyapatite with aliphatic chain of the PCL while it builds into the composite structure. Moreover, all remain cross-peaks come from the coupling between the HA band and polymeric bands from crystalline domains, while no effect of amorphous domains was observed.
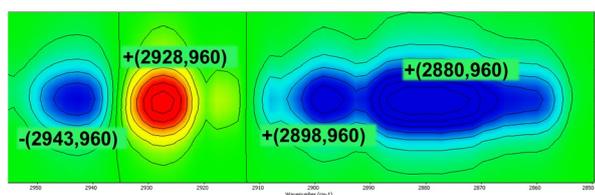

Figure 1. 2D asynchronous map of PCL/HA membrane (2955–2850 vs 975–945 cm^{-1} range).

TWO-DIMENSIONAL CORRELATION SPECTROSCOPY ANALYSIS FOR CORE BROWNING OF 'YALI' PEARS

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The core browning is one of the common non-infectious physiological diseases of 'Yali' pear. At present, it mainly relies on manual identification after cutting along the equator of 'Yali' pear . The manual sampling detection method is random and slow, which is difficult to ensure the quality. Some researchers have proposed spectral methods, but the detection accuracy needs to be improved. In this paper, the core browning was detected online by near infrared spectroscopy, and the spectral characteristics under different storage time (from 0 days to 210 days) and different storage environment (rapidly reduce to 0 degrees, slowly reduce to 0 degrees) were observed dynamically. NIR diffuse reflectance spectra of 90 samples were collected in the range from 900 to 25000 nm and their synchronous two-dimensional correlation spectroscopy (2D-COS) were calculated.

The 'Yali' pear and the average core browning index at different storage times are showed in Figure 1 and Figure 2, respectively. It can be observed that with the increase of storage time, the browning index shows an upward trend. When stored for 60 days, the browning index of 'Yali' pear is lower than 0.05, and there is no significant browning. However, during the storage period from 60 to 90 days, browning shows a significant upward trend. During this period, the pears began to brown. And as the storage time increases, the browning index of 'Yali' pear also continues to increase, and the degree of browning worsens. Especially after the storage time reaches 150 days, the browning index is greater than 0.3, presenting a more severe browning. Figure 3 shows NIR diffuse reflectance spectra and the characteristic peaks. Figure 4 shows the synchronous 2D NIR correlation spectra with the storage time as disturbance. It shows that the spectrograms of 'Yali' pear with different storage times are basically consistent, but with the increase of storage time, the absorbance increases. At the same time, there are three absorption peaks in the spectra of 'Yali' pear at wavelengths of 1455 nm, 1950 nm, and 2336nm. The absorption peak at 1455 nm is mainly due to the combined frequency vibration of the C-H (CH_3, CH_2) group, the absorption peak at 1950 nm is due to the second harmonic vibration of the C=O group, and the absorption peak at 2336 nm is due to the stretching and twisting vibration of the C-H (CH_3, CH_2) group[1].

According to the browning index of 'Yali' samples, the samples are divided into normal 'Yali' and browning 'Yali' (the threshold was 0.2). The discriminant model of core browning was built combining these spectra with the multi-way partial least squares discriminant analysis (NPLS-DA) (Table 1). The results show that, the prediction accuracy could be 100% by the synchronous 2D-COS. The proposed method may provide an rapid non-destructive detection method for core browning of 'Yali' pears.

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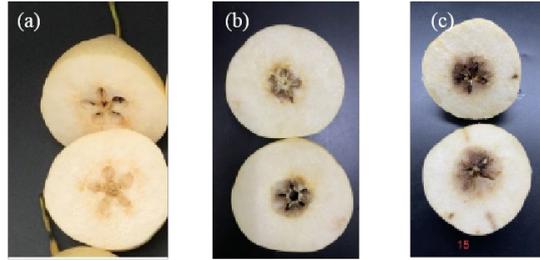
Figure 1. Core Browning of 'Yali' pear: (a) stored for 0 days; (b) Storage for 90 days; (c) Storage for 210 days.
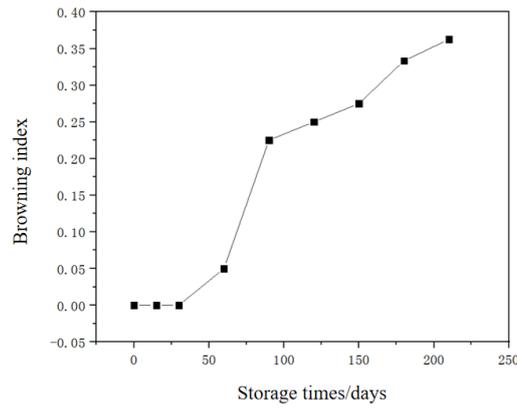
Figure 2. Browning index of 'Yali' pear at different storage times.
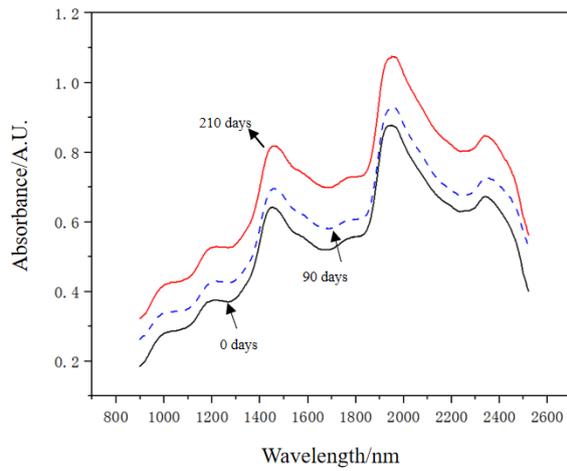
Figure 3. NIR diffuse reflectance spectra of 'Yali' pears at different storage times.
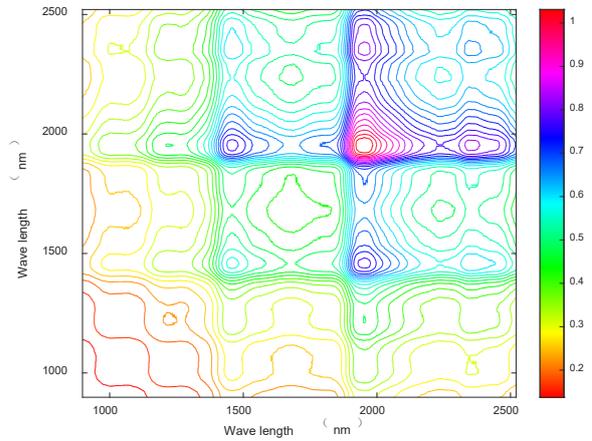
Figure 4. Synchronous 2D NIR correlation spectra.

Table 1. The rate of correct discriminate for validation set

Sample processing method	NIR	2D-COS
RR[a]	92.5%	100%
SR[b]	97.5	100%

[a]RR represents rapidly reduce to 0 degrees; [b]SR representsslowly reduce to 0 degrees.

SILICONE RUBBER STRUCTURAL CHANGES UNDER THERMAL STRESS AND SALT EXPOSURE

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Composite polymer insulators are next-generation devices for global power distribution networks, replacing aging glass and ceramic components on the electrical grid.[1] Silicone materials are particularly attractive for high voltage applications as the insulator surfaces have prolonged hydrophobicity, especially under harsh environmental conditions such as contamination by de-icing salts and algae.[2,3] To date, measurements of the water contact angle has been used as an indicator of insulator performance and lifetime, as loss of hydrophobicity is associated with eventual component failure.[4] It is therefore of significant interest to have a more quantitative, reliable, and chemically-specific marker of insulator performance to provide better correlation with predicted service life. Here we explore the use of vibrational spectroscopy, specifically ATR-IR spectroscopy, in order to achieve this objective. A tracking wheel is used to expose 15 kV rating composite polymer insulators to concentrated salt solutions while 12 kV at 60 Hz is applied across the insulators, alternating chemical and electrical stress for tens of thousands of cycles.[5] Subsequently, the heating-cooling hysteresis of the polymer vibrational bands is investigated with ATR-IR. Two-dimensional correlation analysis (2D-COS) is then used to reveal patterns accompanying density changes that can be traced to material degradation due to aging.

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2T2D CORRELATION ENABLED DEAMIDATION SCREENING OF AN ARRAY OF THERAPEUTIC PROTEINS

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The pipeline of therapeutic proteins has exceeded small molecules as drugs designed for the treatment of autoimmune, inflammatory, Cancer or neurodegenerative diseases among others.1 These drugs are increasingly complex and as such need to be evaluated to ensure their safety and efficacy for patients worldwide. These proteins can undergo degradation in the form of deamidation, a non-enzymatic process; that may occur at low pH, high pH, during thermal stress or a combination thereof.2 A negative charge is introduced in the amino acid sequence due to the loss of asparagine or glutamine residues with the production of aspartate or glutamate, respectively. Typically, these proteins are evaluated using chromatographic methods, as well as LC-MS peptide mapping to determine the % of deamidation and the sites of deamidation. We have developed a novel simplified workflow using a Quantum Cascade Laser Microscope (QCLM) for the evaluation of an array of therapeutic proteins against a reference standard. The spectral data is then subject to 2T2D correlation analysis3,4 for comparability assessment. The asynchronous plot provides the cross peaks used to identify the major and minor components in the mixture due to the deamidation process. Specifically, non-deamidated sample from the deamidated state. Also, the weighted difference spectra associated with the sample and reference are generated, the results of which are orthogonal to the HPLC cation exchange.

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Abstracts of
Posters
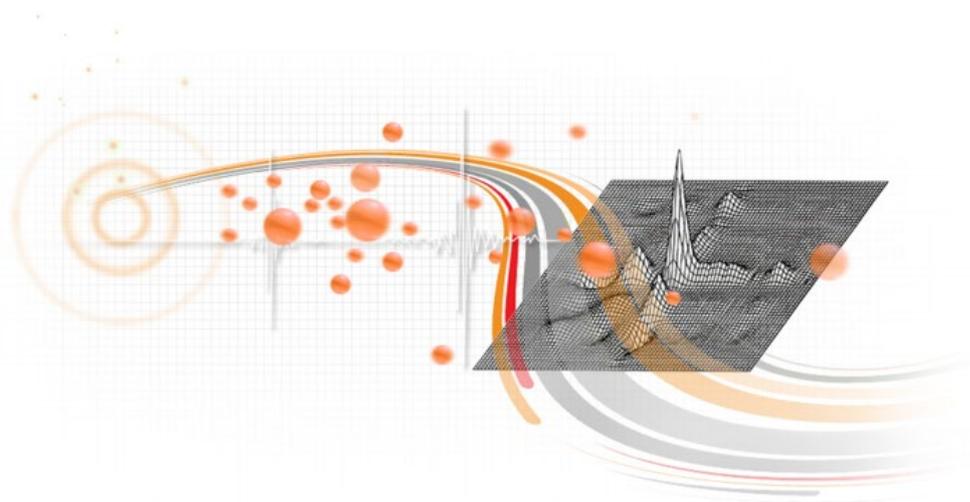
CHANGES IN INTERNAL STRUCTYRE OF AGE-RELATED CURVED HAIR CAUSED BY CYCLICAL EXTENSION STUDIED BY 2D IR CORRELATION SPECTROSCOPY

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As aging progresses, our hair becomes curly, frizzy, or splayed attribute. Everyday grooming has been reported to significantly increase the curvature of age-related curved hair [1]. This study aimed to find structure changes inside of hair by cyclical extension using IR spectroscopy coupled with two-dimensional correlation spectroscopy (2D–COS). In age-related curved hair, extension of 500 cycles at 0.3 N strain levels were seen to significantly increase the signal of SO_3H at 225 cycles, while no architectural modifications were discernible in straight hair. 2D–COS was performed to probe the genesis pathway of SO_3H in the range of 1000–1200 cm^{-1}. Cyclical extension prompted two distinct patterns of disulfide bond cleavages, namely C–S and S–S fissions. It was found that initially a C-S cleavage occurred, succeeded by an S-S cleavage. Additionally, 2D–COS performed in the range of 1600–1700 cm^{-1} exhibited an elevation in the secondary structural motif, β-sheet structure, subsequent to the formation of SO_3H. These findings allude to the hypothesis that the amplification in the curvature of age-related curved hair is a consequence of the structural change by cyclical extension.
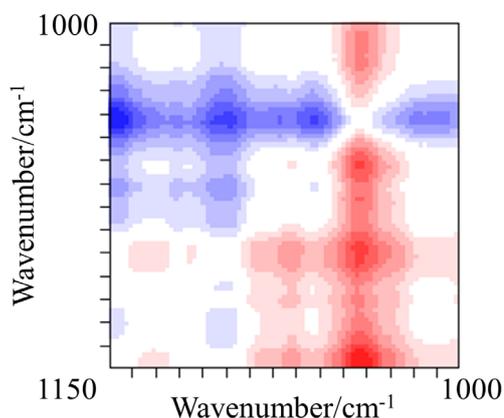
Figure 1 Asynchronous 2D correlation spectra constructed using the IR spectra up to 500 extension cycles of age-related curved hair in the 1000–1150 cm^{-1} region. Red and blue areas in the 2D map represent positive and negative correlations, respectively.

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MONITORING THE SYNTHESIS OF METAL COMPOUNDS WITH CINCHONIDINE USING 2D-COS METHOD

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2D correlation spectroscopy was used to monitor the process of crystallisation of the complex compounds – cinchonidine with cadmium(II) and copper(II). The UV-Vis data were collected and then the 2D-COS method followed. It helped compare spectral intensity variations measured at different spectral variables[1].

Both synchronous and asynchronous 2D spectra present an interaction between a quinoline ring and metal ions.

Synchronous spectrum of the cinchonidine complex with cadmium(II) shows an autopeak at 205 nm. As for the complex with copper(II) an autopeak is shown at 370 nm and a positive cross peak is at the coordinates 800 and 370 nm. These results are shown in Figure 1.

Asynchronous spectrum of the cinchonidine complex with cadmium(II) shows positive cross peaks at the coordinates: 190 and 204 nm, 198 and 204 nm. The most distinguished cross peaks for complex with copper(II) are at the coordinates: 357 and 375 nm, 245 and 375 nm – representing the positive peaks; 342 and 375 nm – representing the negative peaks.

These results interestingly correlate with the 2D analysis of Raman spectra, which also track the course of the synthesis. Emerging dependencies are discussed.
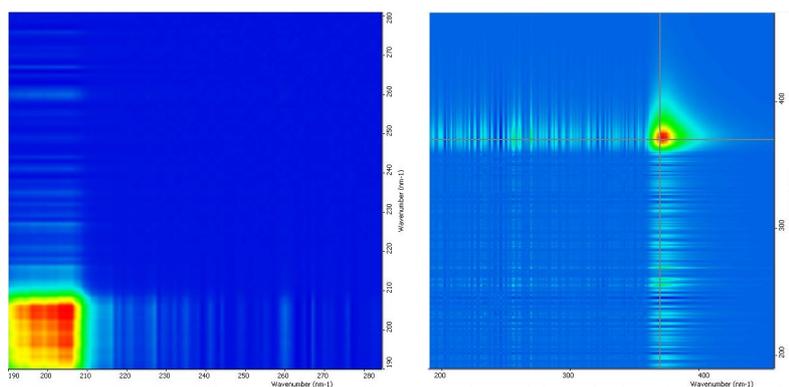
Figure 1. The synchronous spectra of the cinchinodine complex with cadmium(II) on the left and copper(II) on the right

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CLARIFICATION OF ETHANOL-WATER CLUSTERS IN ALCOHOLIC BEVERAGES BY TWO-DIMENSIONAL CORRELATION SPECTROSCOPY

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Several studies have conducted on alcoholic beverages which suggested that the tastes and quality of them were determined not only by the type and content of ingredients but also influenced by the supramolecular clusters between ethanol and water (E-Wc). However, the supramolecular clusters in alcoholic beverages, especially the intrinsic relationship of the hydrogen-bonding (HB) strength to the organoleptic sensing and quality assessment, have not been elucidated in detail up to now. This study will summary the supramolecular E-Wc in several kinds of alcoholic beverages revealed by several kind of spectroscopy as fluorescence emission, Raman scattering, and near-infrared absorption spectrum. Besides, the use of two-dimensional correlation analysis (2D-COS) as a powerful tool in unrevealing the important structural information of clusters has also been performed. Beyond identifying a number of important supramolecular E-Wc, the prospects and challenges in this field will also be briefly discussed in the hope that it would be of interesting and help to more researchers in the fields of food and agriculture.

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HETEROSPECTRAL TWO-DIMENSIONAL CORRELATION OF RAMAN AND NEAR-INFRARED (NIR) SPECTROSCOPY FOR DISCRIMINATION OF GEOGRAPHICAL ORIGIN OF RED PEPPER

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Both Raman and near-infrared (NIR) spectroscopy are fast and non-destructive analytical methods with providing rich information on molecular composition of a sample. Moreover, the spectral information provided by Raman and NIR spectroscopy is complementary to each other, so the combination of both spectral information would be synergetic to improve accuracy in discriminant analysis.

With this potential, the discrimination of red pepper powder samples according to geographical origin was attempted using Raman and NIR spectroscopy, and heterospectral two-dimensional correlation analysis (H2DCOS) [1] was chosen as a tool to accommodate the complementary two spectral features for the discriminant analysis. Figure 1 shows the average H2DCOS synchronous maps of the imported (a) and domestic samples (b), and the aynchronous maps of the imported (c) and domestic samples (d). As seen, the patterns of aynchronous maps between the imported and domestic samples are considerably different. It means that the differences in the compositions between the two sample groups are highlighted using H2DCOS.

To quantitatively assess the discrimination accuracy, *k*-NN was used as a classifier. Initially, when the principal component (PC) scores obtained from the Raman and NIR spectra of samples were separately employed as the inputs for *k*-NN, the accuracies were 91.0 and 93.0%, respectively. Next, when the merged PC scores of Raman and NIR spectra were adopted, the accuracy was elevated to 94.9%. Finally, the use of PC scores of the H2DCOS slice spectra for *k*-NN made the discrimination most accurate (97.4%). This observation confirms the usefulness of H2DCOS in recognizing the dissimilar spectral features in the Raman and NIR sample spectra.

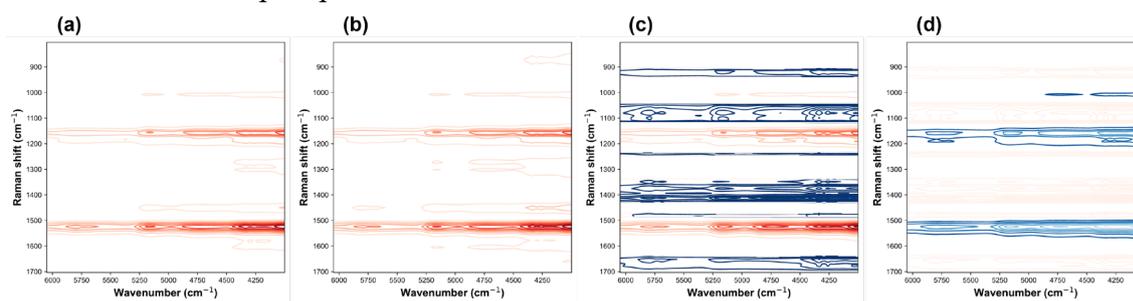Figure 1. Average H2DCOS maps constructed using the Raman and NIR spectra of red pepper powder samples: synchronous maps of imported (a) and domestic samples (b), and asynchronous maps of imported (c) and domestic samples (d).

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IDENTIFICATION OF METHANOL ADULTERATED FAKE LIQUOR BASED ON TWO-DIMENSIONAL CORRELATION SPECTROSCOPY

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In this paper, a method based on two-dimensional (2D) correlation spectroscopy combined with pattern recognition is proposed to discriminate adulterant methanol in liquor. 50 pure ethanol (52% v/v) solutions and 50 methanol-adulterated ethanol solutions (the concentrations were 0.1% ~ 1% v/v for methanol and 52% v/v for ethanol) were prepared. One-dimensional (1D) Raman spectra of all samples were collected, but when methanol traces, it was difficult to extract characteristics information. Therefore, under the concentration perturbation, 2D correlation spectrum of all samples were constructed, and the N-way partial least squares (N-PLS) discrimination model of the adulterant methanol in ethanol solutions was established. For comparison, a discrimination model of the 1D spectroscopy was established. The result shows that 2D correlation spectroscopy can extract more characteristics information, and improve the accuracy and stability of the model.

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USE OF 2D-COS CORRELATION SPECTROSCOPY IN MONITORING THE SYNTHESIS OF METAL COMPOUNDS WITH QUINOLINE ALKALOIDS

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The aim of this work was to study the emerging interactions in cinchonine complexes with copper(II) and cadmium(II)[1]. The analysis was carried out using UV-Vis spectroscopy in the 190-1100 nm range, followed by 2D-COS correlation analysis in OmnicTM v.9.3 software, in order to observe the shifts of individual bands, characteristic of structural elements in the resulting compounds (Fig.1).
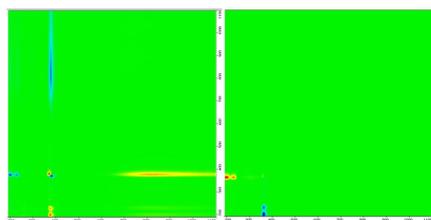
Figure 1. 2D asynchronous spectra of Cu(II)-Cin (left) and Cd(II)-Cin (right)

Changes marked by the synchronous auto-peaks at 199, 230, 378 nm for Cu(II)-Cin, and 199, 231, 361 nm for Cd(II)-Cin, were observed. The synchronous cross-peaks were observed at +(230, 202) nm for Cu(II)-Cin and +(231, 200), –(364, 202), –(364, 228) nm for Cd(II)-Cin. Changes marked by the asynchronous cross-peaks at +(375, 199), +(376, 229), –(381, 371) nm for Cu(II)-Cin and –(361, 199), –(361, 230) nm for Cd(II)-Cin, were also observed.
The peaks present, both in the synchronous and asynchronous parts, indicate the formation of interactions between the quinoline ring and the metal ion[2].
The synthesis was also monitored by Raman spectroscopy. 2D correlation was also performed for the obtained spectra. The obtained results for both spectroscopic methods were compared.

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SORPTION PROPERITES OF PHENANTHRENE ON POLYPROPYLENE MICROPLASTICS: KINETIC, ISOTHERM AND A TWO-DIMENSIONAL CORRELATION SPECTROSCOPIC STUDY

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Microplastics (MPs), as a pollutant commonly found in the environment, can interact with polycyclic aromatic hydrocarbons (PAHs), and form bound state further affect the environment. Therefore, it is necessary to study the interaction mechanism between MPs and PAHs. Integrating molecular spectroscopy with model fitting, this work explored the chemical and microstructural changes of polypropylene (PP) microplastics complex induced by phenanthrene (Ph) to reveal the mechanism of MPs -Ph interaction at a molecular level. FTIR spectroscopy show that the MPs did not exhibit new functional group peaks after the adsorption of Ph, indicating that the adsorption of Ph by MPs was mainly a physical process. 2D-COS analysis show that different functional groups play an important role in the adsorption process of Ph onto PP MPs. The results suggest that the 2D-FTIR-COS technique is a very effective means to study the interaction between MPs and other substances.

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PREDICTION OF WATER AND PROTEIN CONTENT IN DIFFERENT CORN FEEDS USING NEAR-INFRARED SPECTROSCOPY AND DEEP LEARNING METHODS

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Corn is one of the most important crops with great production potential and high economic benefits, serving as both a food and feed crop. The nutritional quality of corn feed directly impacts the development of the feed industry. Therefore, accurate determination of the nutritional composition of corn feed is crucial. Near-infrared spectroscopy (NIRS) has been widely applied due to its rapid, accurate, and non-destructive nature. However, it has limitations in analyzing nutrient content such as moisture and protein in feeds. To extract useful information from complex spectral data, it is necessary to establish a mathematical model? between spectra and the types and quantities of substances. Improving the capabilities of spectral preprocessing, feature selection, and modeling methods are essential for enhancing the predictive power of models.

This study aimed to investigate six different types of corn feed, comprising a total of 731 samples. The water content and crude protein content of the samples were determined using chemometric methods, along with the collection of near-infrared spectral data in the wavelength range of 1750nm to 2150nm. Different preprocessing methods were applied., including baseline correction, scatter correction, smoothing, and normalization. Feature extraction methods such as partial least squares (PLS), competitive adaptive reweighted sampling (CARS), and two-dimensional correlation spectroscopy (2DCOS) were employed to establish the mathematical model between the spectra and the nutritional components of corn feed for predicting water and protein content. The results demonstrated that 2DCOS, as an effective feature extraction method, significantly improved the accuracy of the prediction model. Furthermore, by incorporating deep learning methods, different neural network models were established to analyze the original spectral data and 2DCOS data separately for compositional analysis. The findings indicated that 2DCOS provided more information in situations with limited sample features, effectively enhancing the predictive accuracy of neural network models.

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IMPROBED RESNET NETWORK COMBINED WITH 2D CORRELATION SPECTROSCOPY FOR COD SPECIES CLASSIFICATION

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The cod family of fish is an important commercial fishery resource, with high economic value. However, it is challenging to accurately and automatically differentiate specific cod species using traditional detection methods during transportation. To address this problem, we propose a classification method that combines two-dimensional correlation spectroscopy with an improved ResNet network to achieve accurate classification of four cod species.

In this study, the experimental samples consist of four cod species. A handheld 1750-2150nm spectrometer is used to collect spectral data from a total of 400 samples. Near-infrared spectra are recorded, and each sample is sampled three times with the average spectrum calculated. Due to potential issues such as baseline drift and background noise in the raw data, we apply preprocessing techniques including baseline fitting, Whittaker-Eilers smoothing, first derivative, Savitzky-Golay smoothing, multiplicative scatter correction (MSC), and standard normal variate (SNV) transformation. We compare the classification performance of these preprocessing methods and select the most suitable one. In order to perform classification tasks, we use the average spectral method to obtain synchronized two-dimensional spectra from preprocessed spectral data. We use the average spectrum of each type to perform two-dimensional correlation calculations on each sample

ResNet is a deep neural network architecture widely used in image recognition and computer vision tasks. In this study, we compared the classification performance of resnet networks with different structures. To enhance the classification performance of ResNet, we propose an improved ResNet method based on attention mechanisms, which achieves superior classification results.

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APPLICATION OF 2T2D CORRELATION SPECTROSCOPY IN THE ANALYSIS OF HERBAL PRODUCTS

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The relatively new concept of two-trace two-dimensional correlation spectroscopy (2T2D-COS), introduced by Isao Noda in 2018 [1], already has wide applications [2, 3, 4]. 2T2D-COS can use only a pair of spectra to generate synchronous and asynchronous correlation spectra, and their analysis can provide helpful information, especially in the case of very similar spectra. This approach helps distinguish the weak signals of two spectra of different origins and find the difference in overlapped peaks between the reference and sample spectra. Two-dimensional spectra can be applied as input data in chemometric techniques, which are crucial for mining the most valuable data and building efficient models.

This work aimed to explore the application of the 2T2D-COS technique to the analysis spectra of plant material combined with the different chemometric methods. Much lower requirements for the manufacturing of plant products with the status of dietary supplements than drugs, such as the lack of the obligation to standardize plant materials and the complex composition of the raw materials and extracts, may cause problems with maintaining their high quality and potential risk of adulteration. To verify the usefulness of various variants of 2T2D spectroscopy in analyzing herbal products (with complex compositions), we selected drugs and dietary supplements with ginkgo biloba leaf extract. The analysis was performed for ATR-FTIR and UV-VIS spectra. The study utilized different reference spectra and used synchronous and asynchronous spectra, their combination (syn-asyn), and slices from asynchronous maps for further chemometric analysis. Effectiveness of MPCA and PLS-DA in differentiating dietary supplements with an undeclared amount of rutin, quercetin, and kaempferol and samples with lower than the declared amount of ginkgo leaf extract were tested.

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CORRECTION OF THE EFFECT OF HUMIC ACID ON THE FLUORESCENCE DETECTION OF PAHS BY COMBINATION SPECTROSCOPY

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Polycyclic aromatic hydrocarbons (PAHs) are widely distributed in soil and water, but fluorescence spectrometry for PAHs is often interfered by organic matter in the environment. The purpose of this paper is to study the correction method based on combined spectral technology in the environment where humic acid and PAHs coexist. The fluorescence, ultraviolet (UV) and near-infrared spectra (NIR) of single and mixed samples of humic acid and benzo [ghi] perylene were analyzed at different concentrations. The NIR prediction model of humic acid in mixed samples was established based on SiPLS, and the standard fluorescence spectrum curve of humic acid was established. The fluorescence intensity of humic acid at 478 nm (characteristic wavelength of benzo [ghi] perylene) in the mixed sample was predicted, which was subtracted by the fluorescence intensity of the mixed sample at the same wavelength to correct. The corrected fluorescence intensity was linearly correlated with the concentration of benzo [ghi] perylene with $R^2 = 0.8362$, while $R^2 = 0.3538$ before correction. Similarly, the UV spectral characteristics of humic acid in mixed samples were established by the same method to predict the fluorescence intensity, and the result showed $R^2 = 0.8781$. Furthermore, the effectiveness was verified, which provides a new idea for the calibration modeling of the combined spectral method.

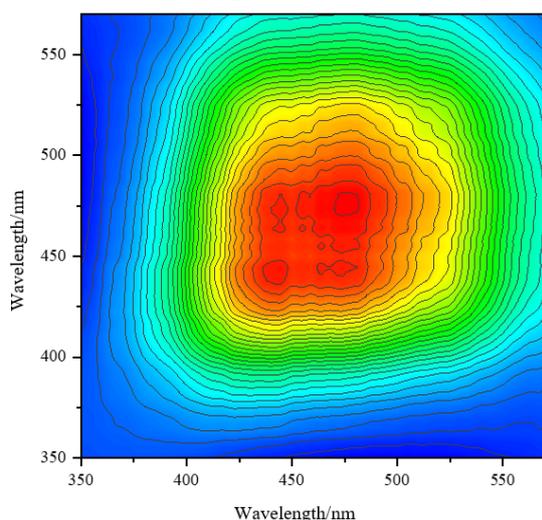

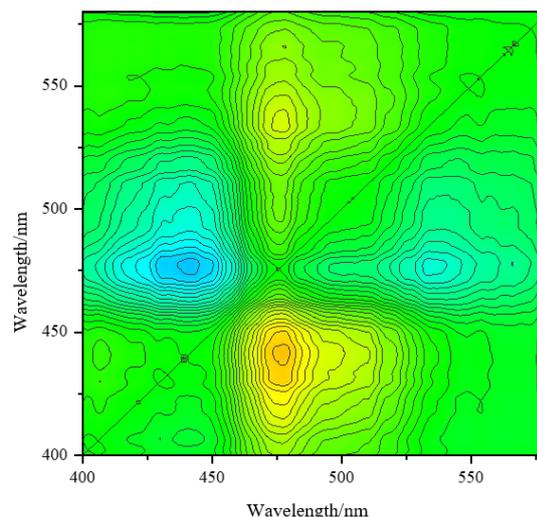Fig.1 2D synchronous correlation spectra of mixed samples

Fig.2 2D asynchronous correlation spectra of mixed samples

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2D-COS RAMAN STUDY OF NIO NANOPARTICLES

Jin Qiu [a], Thi Huyen Nguyen [a], Seung Kim [a], Young Jin Lee [a], Meng-Ting Song [b], Wen-Juan Huang [b], Xiang-Bai Chen [b], Thi Minh Hien Nguyen [c], In-Sang Yang [a,*]

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We report two-dimensional correlation spectroscopy (2D-COS) analyses of the Raman spectra of NiO nanoparticles over a temperature range from 100 to 300 K. 2D-Raman correlation spectra suggest a strong correlation of the spectral intensity variation of the phonon modes with the spin excitations in NiO nanoparticles. It is revealed that the antiferromagnetic ordering affects the TO phonon anisotropy in NiO nanoparticles. We elucidate the complex spectral features of two-magnon (2 M) bands by performing appropriate 2D-COS model simulations. Significant spin-phonon coupling in NiO nanoparticles is supported by our results. High-energy magnon-magnon interaction tails are also found to be involved in spin-phonon coupling. 2D-COS analyses provide rich information regarding the nature of the phonon and magnon excitations of NiO nanoparticles.

EFFECT OF DISSOLVED ORGANIC MATTER ON ADSORPTION OF PAHS BY MICROPLASTICS

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Microplastic pollution is an increasingly serious problem, which has been widely concerned. The strong sorption of microplastics on organic pollutants, which in turn affects the migration and transformation of pollutants in the environment, poses a threat to both ecological environment and human health. This paper focuses on the influence and interaction of dissolved organic matter (humic acid) on the adsorption of typical organic pollutants by microplastics. PAHs (phenanthrene) and polypropylene (PP) were selected as the research objects, and the adsorption behavior of PP on PAHs was investigated by adsorption kinetics experiments in the background of aqueous solution based on fluorescence spectroscopy, while humic acid were conducted to explore the effects on the adsorption of PAHs by microplastics. The results showed that humic acid could inhibit the adsorption of PAHs by microplastics, and the inhibition ability increased with the increase of humic acid concentration. Furthermore, 2D-COS were applied to reveal that the interaction between humic acid and PAHs is the main reason that humic acid inhibits the adsorption of PAHs by microplastics, which provides a basis for further research on the behavior and migration of organic pollutants adsorbed by microplastics in the environment.
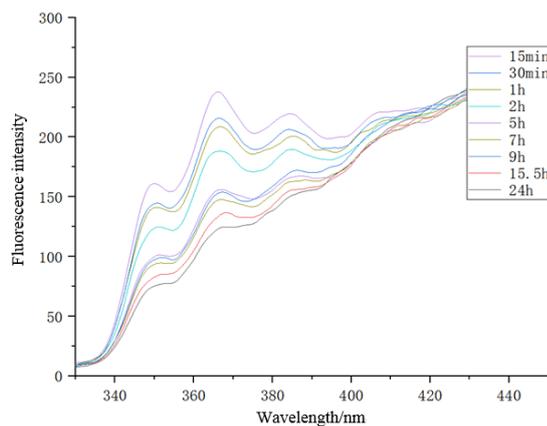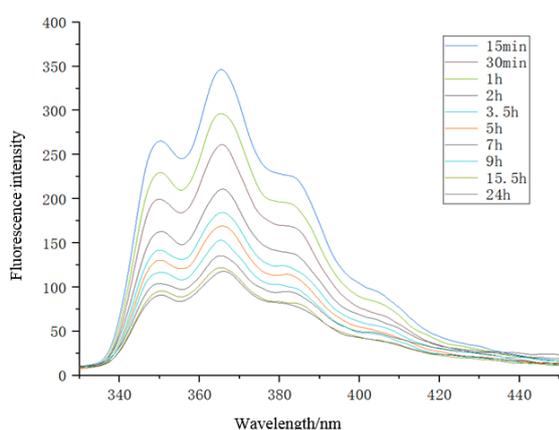
Fig.1 Fluorescence spectra for adsorption kinetics of ph   Fig.2 Fluorescence spectra for adsorption kinetics with HA added

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A METHOD OFPREDICTION OF THREE INDEXES OF SUGAR CONTENT HARDNESS AND PH IN PEAR BASED ON INTER-INDEX CORRECTION

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This paper aims to establish the relationship between the near-infrared spectral data in the wavelength range of 590−1100 nm and the corresponding three index of sugar, hardness and pH. However, with modeling method of partial least squares regression, there are large errors in the prediction results of the three index. And although the MSC and SNV preprocessing methods and Wavelength screening have certain correction capabilities for the results of prediction, the results are still not accurate enough, and the best correlation coefficient is only 0.82. Near infrared spectral image shows that while the prediction index is the same, the spectral curve is still significantly different under the influence of the other two indexes. In this paper, the accurate hardness and pH data were used for quadratic fitting through multiple linear regression to predict the sugar content data, which significantly improved the accuracy. Then a quadratic fitting model based on the three predictors is designed, and the experimental results are improved and satisfactory.

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EXPLORING THE APPLICATION OF TWO-DIMENSIONAL CORRELATION SPECTROSCOPY TO PREDICT PROTEIN CONTENT IN FLOUR BASED ON ENSEMBLE LEARING

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To predict protein content in flour, the effectiveness of the two-dimensional correlation spectrum(2DCOS) characteristic wavelength selection method and synchronous spectral grayscale image on the modeling efficiency and quantitative analysis prediction accuracy of near-infrared spectroscopy (NIRS) based on Ensemble Learning was studied. Taking the protein content in flour as the research object, using the Stacking Heterogeneous Ensemble Learning with four base learners and a meta-learner, adding regularization and cross-validation, to analyze and compare the quantitative regression prediction accuracy of single base learner and Ensemble Learning for flour NIRS. A 2DCOS of protein content difference was constructed, and it was found that the correlation intensity of flour protein content is relatively high at the four wavelengths, which could be used as feature points of protein content difference, selected by using 2DCOS characteristic wavelength and other feature extraction algorithms, the 2DCOS-L2Stacking model for protein content had the best prediction results. Then, using the synchronous spectral grayscale image to predict the protein content after extracting features, the root mean square error (RMSE) of the L2Stacking model decreased by 0.305. The results show that using the 2DCOS synchronization spectrum for prediction, the coefficient of determination (R^2) of the prediction results increased by 0.237. This experiment provides relevant methods for in-depth research on the application of the 2DCOS method in spectral quantitative analysis.
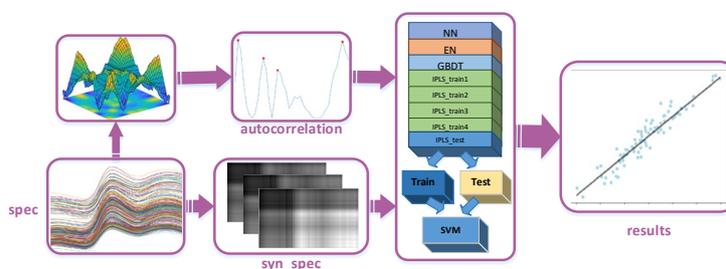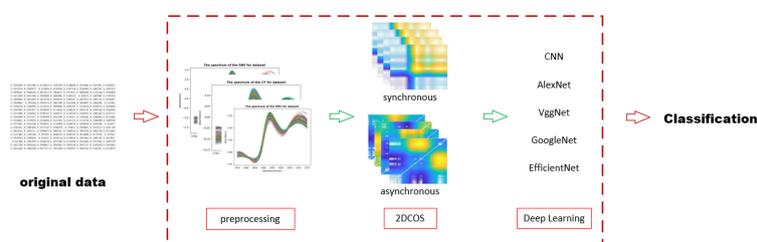
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AN EFFICIENT DEEP LEARNING NETWORK COMBINED WITH TWO-DIMENSIONAL CORRELATION SPECTRUM FOR SPECIES CLASSIFICATION OF FLOUR

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Flour is a widely used food ingredient, but distinguishing between different types can be difficult. One of the effective methods for flour type detection is the analysis of one-dimensional (1D) near-infrared spectroscopy (NIRS) data of flour. This paper presents a novel method for flour species recognition that utilizes deep learning in conjunction with Two-dimensional correlation spectrum (2DCOS). In this study, we collected 232 samples of 5 different kinds of flour using a spectrometer, and the raw spectra of each sample were preprocessed using different pretreatment methods. We apply the discrete generalized 2DCOS algorithm to generate 464 2DCOS images from the preprocessed 1D spectral data. These images were trained using various deep learning models commonly used in computer vision, including CNN, AlexNet, GoogleNet, and VggNet. Our analysis revealed that the combination of multiply-scatter correction (MSC) preprocessing and the VggNet model resulted in the highest accuracy, achieving 95%. We further improved the network model by introducing a more efficient network model (EfficientNet) specifically tailored for 2DCOS, which ultimately led to a correct recognition rate of 98.5%. The results show that it is feasible to directly use 2DCOS to transform 1D spectra into two-dimensional images for species recognition by deep learning. And by comparing with the 1DCNN network model used for 1D spectral data, the accuracy of our method is relatively improved by about 10%. This study provides a new idea for flour type identification. It successfully combines the latest results in deep learning with 2DCOS for spectral type identification, and it can be extended to the spectral identification of other products.

References
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RHEO-OPTICAL NEAR-INFRARED (NIR) ANALYSIS OF STYRENE-BUTADIENE RUBBER (SBR)

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A rheo-optical characterization technique of rubber based on the combination of a near-infrared (NIR) spectrometer and a tensile testing machine is presented. In the rheo-optical analysis of rubber sample, tensile deformation is applied to styrene-butadiene rubber (SBR) polymer to induce displacement of polystyrene and polybutadiene domains. The molecular-level variation of the sample occurring on short time scales is readily captured as a form of strain-dependent NIR spectra.
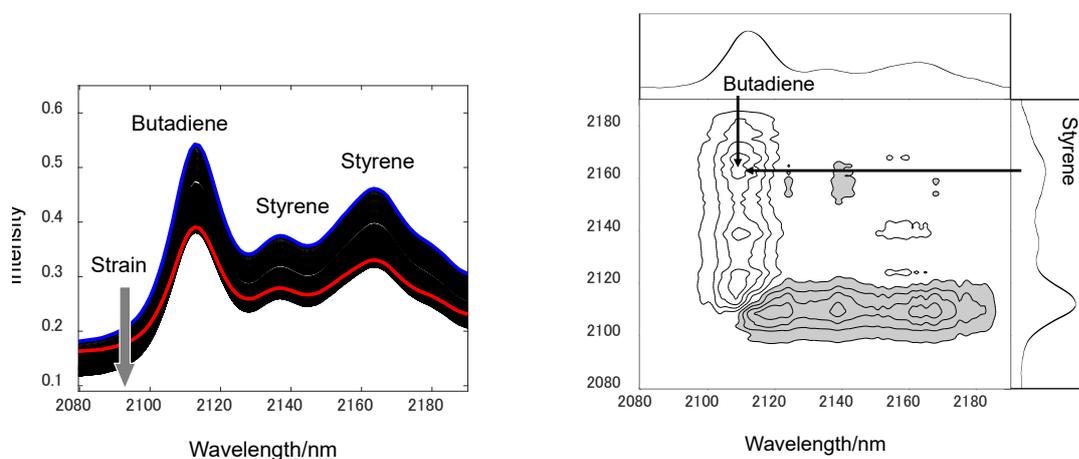
Fig. 1 Strain-dependent NIR spectra of BR sample (left) and 2D asynchronous correlation spectra derived from the NIR spectra

Sets of NIR spectra of the SBR sample were collected by using an acousto-optic tunable filter NIR spectrometer coupled with a tensile testing machine as an excitation device. The sequential order of NIR peaks determined with two-dimensional (2D) correlation spectra revealed that predominant deformation of polybutadiene phase in the early stage of elastic deformation.

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2T2D-COS STUDY OF SELECTIVE ENHANCEMENT MECHANISM IN SERS TAGS ON SINGLE GOLD NANOSPHERE AND NANOROD

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  To perform robust and sensitive surface-enhanced Raman scattering (SERS) measurements in a wide range of applications, from chemical and biological sensing to surface analysis, it is essential to understand the selective enhancement mechanisms of SERS and to carefully select SERS active substrates and probe molecules. The choice of a SERS active substrate depends on its ability to generate a strong electromagnetic field and provide a surface suitable for molecular adsorption. In this study, to elucidate the role of localized surface plasmon resonance (LSPR) in the SERS spectra and the mechanism of selective enhancement of SERS, two-trace two-dimensional correlation spectroscopy (2T2D-COS) applied to the SERS spectra of two SERS tags, 4-mercaptobenzoic acid (4-MBA) and 4-aminothiophenol (4-ATP), adsorbed on single Au nanospheres or Au nanorods. The 2T2D-COS spectra showed two distinct populations in the a_1 and b_2 modes of the C-S stretching coupled with the C-C stretching bands observed in the SERS tags, which demonstrates the presence of LSPR in the SERS spectra and its selective enhancement mechanism.

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