

(Physical Chemistry & Analytical and Environmental Chemistry)

Oral Abstract

Single particle ICP-MS combined with internal standardization for accurate characterization of polydisperse nanoparticles in complex matrices

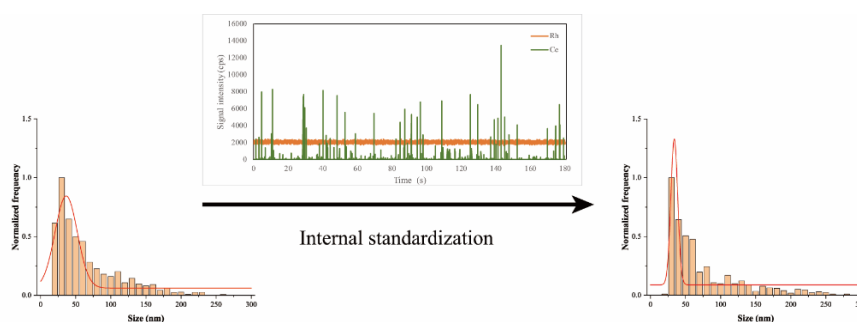
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Abstract

Single particle inductively coupled plasma-mass spectrometry (sp-ICP-MS) is a promising technique for nanoparticles (NPs) detection. It is convenient to analyze NPs in liquid medium, requiring simple sample dilution prior to analysis while providing chemical composition, mass concentration, particle number concentration and size distribution simultaneously. However, the complex matrices where NPs dispersed hamper the accuracy of sp-ICP-MS. Here, CeO₂ NPs, a typical kind of polydisperse NPs, were used to mimic the polydisperse NPs commonly appeared in real environmental and biological samples¹ in this study. The matrix effect of three types of biological samples, namely enzyme-digested matrix, urine and plasma was addressed by comparing mass concentrations determined by sp-ICP-MS and conventional ICP-MS. We then applied internal standardization accompany with dual mass mode² to correct for the matrix effect in sp-ICP-MS analysis. Through these experiments, we demonstrated that internal standardization is effective and practical in correcting for the matrix effect of NPs in real samples.



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(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Field observations of hydroxy diacids and insights into their formation
from aliphatic diacids through heterogeneous oxidation**

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Abstract

Recent chamber studies have suggested that oxygenated organic aerosol might be further oxidized within aerosol atmospheric lifetime. The oxidation transformation of the oxygenated organic compounds would change the composition of the aerosol and thus alter the hygroscopicity to affect the radiation balance of the Earth. This influence both the climate and the air quality. Laboratory studies indicated that the major heterogeneous oxidation functionalization product of aerosol-phase aliphatic DCAs was the corresponding hydroxy DCAs (hDCAs). We therefore focused our field investigation on hydroxyl DCAs and report in this work their abundance, correlations with aliphatic DCAs, SOA tracers, oxidant ($Ox=NO_2+O_3$), ions and estimated liquid water content by E-AIM to give insight on the formation of hDCAs. Spatial differences in correlations between two urban sites in Hong Kong and Shanghai suggested different formation mechanisms or dominant precursors for hDCAs. In Hong Kong, good correlations were observed between DCAs and hDCAs, supporting that DCAs might be one of the major precursors for hDCAs ($R\sim 0.5-0.9$) when their correlation in Shanghai were generally lower. Nevertheless, hDCAs in both Hong Kong and Shanghai have good correlation with α -pinene SOA tracers and also toluene SOA tracer, DHOPA. The correlation with oxidant and ions have shown that the formation of hDCAs in Hong Kong were oxidant driven while that of in Shanghai was ions driven. The stronger correlation with oxidant in Hong Kong might imply the possibility of gas phase oxidation, especially for C5 and C6 series hDCAs under the warmer climate. The heterogeneous aqueous phase formation could have increased importance at Shanghai site. The diurnal correlation with estimated liquid water content also revealed the dominant aqueous formation of hDCAs in different time period between the two sites under the combined effect of RH, ions and oxidant.

Zoom to ask the author: <https://hkust.zoom.us/j/8936093932> (Meeting ID: 893 609 3932)

(Physical Chemistry & Analytical and Environmental Chemistry)

Oral Abstract

From benchmarking *ab-initio* DMRG investigations to theoretical modelling of new singlet fission systems

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Singlet fission (SF), an ultrafast process, holds a 'two for one' potential by down-converting the higher energy solar photons and thus allowing the single-junction photonic devices to potentially break the Shockley-Queisser limit. The inherent complexity of SF candidates such as strong correlation & their multireference characters, involvement of 'dark electronic states' and the existing similarities between SF and intersystem crossing (ISC) posed severe experimental as well as theoretical challenges, limiting the ability of SF to increase solar cell efficiencies in real applications. We adopt Density Matrix Renormalization Group (DMRG) – a powerful multiconfigurational wavefunction ansatz, to treat a dominant part of static correlation in these systems and provide an accurate picture of electronic states in these molecules involving $\pi \rightarrow \pi^*$ transitions, which has been intractable due to the restrictions associated with traditional electronic structure methods.

We have implemented an extensive wavefunction analysis tools based on DMRG and investigated the low-lying singlet and triplet electronic states of pentacene dimer – a well-established SF system. This particle & state-density matrix based analysis provides an adequate notion of the nature of the di-radical character of the molecules, population density distribution during electronic transitions and the extent of SF charge transfer (CT) between excited states and within the fragments. The 'triplet-triplet pair' singlet adiabatic is not directly coupled with other 'local' and 'multi-excitonic' states through strong electronic couplings, which drops rapidly with large inter-molecular separations. However, an emphasis on vibronic coupling pathways in pentacene based chromophores reveals that these states interact strongly through several vibrational degrees of freedom, particularly at low frequencies (the temperature dependence of SF) and in C=C stretching regions. We quantify the direct evidences of triplet formation and CT in fission process with a concise projected local spin distribution for specific fragments, calculated at equilibrium as well as along the vibrational modulation associated with electronic and vibronic couplings. Furthermore, we employ these computational tools to look beyond the traditional 'parent acenes' based chromophores and tailor the electronic properties of new novel intermolecular and intra-molecular SF systems stabilized by various linkers and the captodative & carbene substituent effects.

(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

A hydrogel based artificial cell and applications

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Abstract

In this paper we report a new hydrogel based artificial cell which is a competent and versatile platform for cell-free biomanufacturing and cell-free synthetic biology. The artificial cells were prepared by covalently immobilizing the proteins in the *E. coli* cell extract, including the enzymes in the transcription and translation (TX-TL) system, onto the polymer backbone of the functionalized hydrogel particles. The artificial cells showed a high synthesis efficiency and supported continuous protein synthesis for at least 28 days. Both colicin E1, an antimicrobial protein, and urokinase, a protease containing multiple disulfide bonds, were successfully synthesized in the artificial cells. Furthermore, a genetic oscillator was demonstrated in the artificial cells. The artificial cells not only provide a powerful platform for continuous protein synthesis and convenient design and testing of genetic networks, but also hold great promise for the development of metabolic engineering, drug delivery, and biosensors.

(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Automated miniaturized digital microfluidic antimicrobial susceptibility
test using a chip-integrated optical oxygen sensor**

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Abstract

Rapidly antimicrobial resistance expansion worldwide has become one of the biggest global health problems as suggested by The World Health Organization. Effective invitro antimicrobial susceptibility test (AST) is essential for dosage advise before routine clinical treatment. We present the first automated digital microfluidic (DMF) AST using an optical oxygen sensor film for direct microbial metabolic respiration measurements. The platform allows monitoring of the extracellular oxygen depletion across the entire culture area that indicates the microbial metabolic activity in real-time.

The oxygen-sensitive probe Platinum (II)-5,10,15,20-tetrakis-(2,3,4,5,6pentafluorophenyl)-porphyrin was embedded in highly gas permeable perfluorinated polymer Hyflon AD 60 and spin coat onto an ITO glass serving as the transparent top plate of DMF. The fabricated oxygen sensor integrated into DMF was found to be able to perform multiple droplets manipulation and no negative effect to the cell growth on chip was observed. Sterile mineral oil was employed to prevent evaporation during long-term culture and cross-contamination between each virtual micro culture chamber. A rapid and reliable two-fold dilution procedure of the antibiotic solution was achieved via a pre-programmed coding sequence and mix with microbial inoculum solutions to perform phenotypic AST by recording dissolved oxygen decrease caused by cell proliferation. The oxygen depletion rate was delayed at subinhibitory concentration caused by antimicrobial stress. As a proof-of-concept, automated AST of three commercial antibiotics, ampicillin, chloramphenicol and tetracycline at different concentrations against *E. coli* ATCC 25922 as model organism was performed on DMF and the minimum inhibitory concentrations were determined.

(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Mass spectrometry-based untargeted metabolomics approach for
differentiation of beef of different geographic origins**

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Abstract

Beef is a common staple food in many countries, and there is a growing concern over misinformation of beef products, such as false claims of origin, species and production methods. In this study, we used a mass spectrometry-based metabolomics approach to study the metabolite profiles of beef samples purchased from local retailers in Hong Kong. Using multivariate analysis, beef samples from different a) geographical origins, namely the United States (US), Japan and Australia, and b) feeding regimes could be differentiated. We identified twenty-four metabolites to distinguish beef samples from different countries, ten metabolites to identify Angus beef samples from others and seven metabolites to discriminate Australian beef produced by the organic farming from that produced using other farming modes. Based on results of this study, it is concluded that metabolomics provides an efficient strategy for tracing and authenticating beef products to ensure their quality and to protect consumer rights.

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**Catalytic Activity of Gallium Selenide for Hydrogen Evolution Reaction via
Strain and Oxygen Doping**

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Abstract

Two-dimensional GaSe has garnered intensive attention for their potential application of water splitting from solar energy to produce hydrogen fuel. The inert basal plane of GaSe and low absorption of the solar light due to the wide bandgap are the major challenges to use it as an efficient photocatalyst for water splitting reaction. For practical applications, it is necessary to narrow down the bandgap and enhance the basal plane reactivity of GaSe by controlling external parameters. Here, oxygen as a dopant atom ($\text{GaSe}_{1-x}\text{O}_x$; $x=6\%$, 11% , 17% , and 22%) and tensile strain applied along *a*- on *b*-direction ($T_s= 1, 2, 3,$ and 4%) was used to study the feasibility of enhancing GaSe water-splitting catalytic activity. A computational study using density functional theory (DFT) revealed that O atom and tensile strain created a local charge separation on surface GaSe that plays an essential role in increasing the surface-activity of the catalyst. The bandgap significantly reduced due to O-doping from 2.78 eV (GaSe) to 2.38 eV for $\text{GaSe}_{1-x}\text{O}_x$ ($x=6\%$) system. In general, combining tensile strain and O dopant further reduced the bandgap size of GaSe. The computational search over candidate $\text{GaSe}_{1-x}\text{O}_x$ ($x = 6\%, 11\%, 17\%,$ and 22%) suggests that 17% of O dopant concentration could lead to materials that exhibit enhanced HER activity. This result reveals that GaSe, with an optimized combination of doping and strain, exhibits hydrogen adsorption free energy closed to 0 eV, exceeding those of pristine GaSe (2.2 eV

(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Molecular Marker-based source apportionment of PM_{2.5} by Positive
Matrix Factorization at six sampling sites in Hong Kong**

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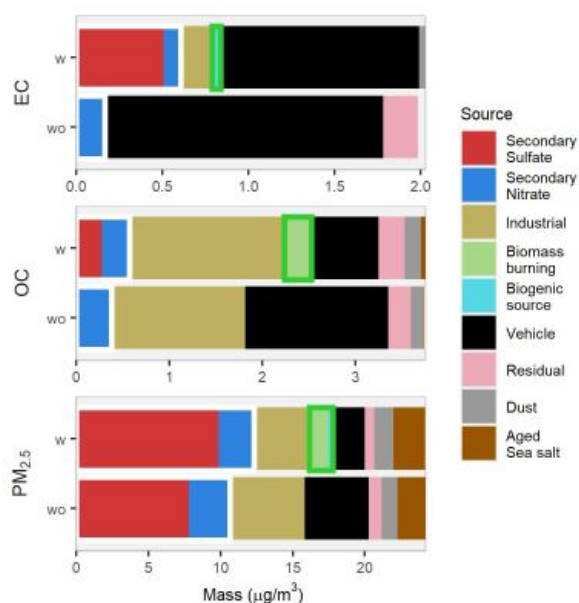
Abstract

Air pollution is a critical concern on environmental protection. In Hong Kong, the Hong Kong Environmental Protection Department (HKEPD) established several policies on vehicular, shipping, power plant emission control and reduction of PM_{2.5}, a particulate matter with aerodynamic diameter less than 2.5 μm, was successfully achieved¹. Understanding the emission properties in different environments could further aid on policies reviews and developments. In our study, we utilized a factorization method called positive matrix factorization² (PMF) for source identification of PM_{2.5} in six different sites located at roadside, suburban and urban areas coupled with air back trajectory analysis to trace the mass origin. Nine factors were resolved, including secondary sulfate, secondary nitrate, industrial emission, biomass burning, primary biogenic sources, vehicle emissions, residual oil combustion, dust and aged sea salt. Majority of PM_{2.5} was contributed by secondary inorganic aerosol which originated from northern continental area particularly in the wintertime. Industrial source, biomass burning and dust were also identified as regional source based on its higher-in-winter pattern and mass origin mainly from continental area. Local vehicular emissions were found higher at roadside station than that at the rest of stations by 16% of total PM_{2.5}. While the primary biogenic source was found more contributed in highly populated area like Mong Kok and Tsuen Wan, implying the significance of human activities effect on biogenic source.

Importance of organic tracers on PMF source apportionment was also examined. Overestimation on vehicular emission as well as absent of biomass burning were observed in the attempt of PMF without organic tracers. A newly applied tracer – unresolved complex mixture, a mixture of GCMS unidentified branched and cyclic hydrocarbons sourced from the combustion of fossil fuels^{3,4}, was well correlated with vehicular source-specific tracer hopanes

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and found also useful on resolving less biased vehicular source profile. Whilst traditional biomass burning tracer K^+ ions were better correlated with Zn/Pb than organic tracer levoglucosan, resulting in source mixing between biomass burning and industrial sources. These results emphasized the vital selection of tracers especially organic tracers as input species on achieving more reliable and comprehensive PMF results.



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(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Chemoproteomics and quantitative proteomics method development to facilitate
biological studies**

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Abstract

Recently, chemoproteomics and quantitative proteomics have emerged as important tools for the study of biological questions. Here, we present three of our current chemoproteomic and quantitative proteomic platforms. (1) Cysteine is the most intrinsically nucleophilic amino acid in proteins, where its reactivity is highly related to diverse biochemical functions. We have established a chemical proteomics approach to monitor 2810 reactive cysteine residues in a single experiment. By using 1.0 mg HeLa S3 cell lysate, not only the reactive cysteine-containing peptides, but also the exact modification sites can be detected and quantified by mass spectrometry. (2) To precisely quantify the dynamic phosphorylation levels at specific residues in a time-course experiment, a parallel reaction monitoring (PRM) method with high sensitivity has been established. The dynamic phosphorylation level changes highly agreed with structural biology characterization of the proteins, providing rich information to understand molecular events. (3) A multiplexing workflow with 10-plex tandem mass tags (TMT) was established to study phosphoproteome changes in myopia with great depth. In this study, 10856 phosphorylation sites from 7883 phosphorylated peptides have been quantified with a single MS injection.

This work was supported by the Hong Kong Research Grants Council (grant No. 25301518) and we acknowledge the State Key Laboratory of Chemical Biology and Drug Discovery and UCEA for the mass spectrometer platform.

Zoom to ask the author:

<https://zoom.us/j/7876396602?pwd=RU02dVgzam4zZE9waVNrN0V0MkpKUT09>

(Physical Chemistry & Analytical and Environmental Chemistry)
Oral Abstract

**Radical-Mediated Peptide Tyrosine Nitration: Structural, Energetic, Mechanistic,
and Spectroscopic Investigations**

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Protein tyrosine nitration (PTN), a hallmark of radical-mediated post-translational modification of proteins under nitrative stress *in vivo*, appears to occur regioselectively and site-specifically at diverse local sequences with no consensus modification *motif*.¹⁻² The mechanistic details governing site-specificity of ortho-tyrosine nitration are largely unknown. Fundamental factors governing the radical-mediated recombination ortho tyrosine nitration reactions were investigated using computationally tractable prototypical PTN sequences that mimic the local topological characteristics of actual peptides. We will present experimental and theoretical investigations into radical-mediated tyrosine nitration that integrate ion chemistry, ion–molecule reactions, isotopic-labelling, low-energy collision-induced dissociation experiments, infrared multiple photon dissociation action spectroscopy,⁴⁻⁵ in conjunction with density functional theory calculations to dissect the fundamental parameters that govern the radical-mediated PTN, which undergo various rearrangement processes, including hydrogen atom, proton, and electron transfer, in the absence of solvation. A hierarchical approach to PTN characterization has been employed, from the structures of the precursor and intermediates, to the locations of the charge and radical delocalized therein, to the energetics and kinetics along the reaction coordinates and their transition state(s) on the regioselectivity of 3-nitrotyrosine formation.³⁻⁵

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Oral Abstract

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Zoom to ask the author:

<https://hku.zoom.us/j/97557240099?pwd=K0VrZ25zam8vNkdSUE1ZMXZlYUZqZz09>

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(Physical Chemistry & Analytical and Environmental Chemistry)

Oral Abstract

Measuring Interactions between Particles and Polymer-grafted Surfaces with Total Internal Reflection Microscopy (TIRM)

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Abstract: Non-specific protein adsorption and deposition at medical device surfaces are problematic phenomenon. In order to prepare antifouling polymer-grafted surfaces for suppression of non-specific adsorption, it is vital to quantitatively investigate pollutant-polymer interaction and the response of grafted polymer to external environmental conditions. Herein, a self-built total internal reflection microscope (TIRM) with video microscopy (VM) was applied to directly measure $k_B T$ -scale interaction between probe particles and surfaces grafted with zwitterionic poly(carboxybetaine methacrylate) (PCBMA) or hydrophilic poly[oligo(ethylene glycol) methyl ether methacrylate] (POEGMA) at different ionic strength and pH values. The results demonstrate that long-range electrostatic interaction played a dominant role when either grafted PCBMA or POEGMA interacted with the probes. An additional attraction was also observed when the probes separated with the surface for less than 100 nm. In addition, by calculating the hindered diffusion coefficient in the direction perpendicular to the surface, the hydrodynamic thickness of grafted polymer layers was successfully measured with TIRM, implying the affinity of grafted polymer to surrounding solutions and the strength of intramolecular interaction under different conditions. To conclude, TIRM, as a characterization method with outstanding distance and force resolution, has shown not only its unique advantages in unmasking the antifouling mechanism of polymer-grafted surfaces but also its great potential in related research fields in the future.