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**HYBRID NANOPARTICLE PLATFORMS TOWARD
MULTIFUNCTIONAL SURFACE-ENHANCED RAMAN
SCATTERING (SERS) SPECTROSCOPY APPLICATIONS**

KOH SHER LIN CHARLYNN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

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MULTIFUNCTIONAL SURFACE-ENHANCED RAMAN
SCATTERING (SERS) SPECTROSCOPY APPLICATIONS**

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SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Doctor of Philosophy

2020

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Chapter 2 is published as Charlynn Sher Lin Koh, Hiang Kwee Lee, Gia Chuong Phan-Quang, Xuemei Han, Mian Rong Lee, Zhe Yang, Xing Yi Ling. SERS- and Electrochemically-Active 3D Plasmonic Liquid Marble for Molecular-Level Spectroelectrochemical Investigation of Microliter Reaction. *Angew. Chem. Int. Ed.* **56**, 8813 – 8817 (2017) DOI: 10.1002/anie.201704433

The contributions of the co-authors are as follows:

- A/Prof Ling Xing Yi came up with the research direction, supervised the research direction and revised the manuscripts.
- A/Prof Ling Xing Yi, Dr Lee Hiang Kwee, and I designed the research. I performed the laboratory work at the School of Physical and Mathematical Sciences and analyzed the results.
- Dr Yang Zhe and Dr Lee Mian Rong helped with the experimental setup and gave advice on the interpretation of the electrochemical data.
- All authors discussed the project.
- I wrote the manuscript drafts and the draft was revised by Dr Lee Hiang Kwee, Dr Gia Chuong Phan-Quang and Dr Han Xuemei.

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- Dr Lee Hiang Kwee and Howard Yi Fan Sim helped with experimental design and gave suggestions in the analysis of data.
- All authors discussed the project.
- I wrote the manuscript and the draft was revised by Dr Lee Hiang Kwee and Dr Han Xuemei.

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- All authors discussed the project.
- I wrote the manuscript and it was revised by Dr Lee Hiang Kwee, Dr Han Xuemei and Dr Gia Chuong Phan-Quang.

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- Dr Lee Hiang Kwee and I did the research work at the School of Physical and Mathematical Sciences and analyzed the data.
- Dr Yejing Liu and I performed X-ray photoelectron spectroscopy (XPS).
- All authors discussed the project.
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Koh Sher Lin Charlynn

Abstract

Surface-enhanced Raman scattering (SERS) spectroscopy is a highly sensitive spectroscopy technique that can boost the Raman fingerprint signals of molecules. However current SERS applications are limited to dye/thiolated molecules sensing or monitoring spontaneous reactions, mainly due to poor analyte-plasmonic surface affinities. In this thesis, we address these challenges by designing hybrid plasmonic platforms for multifunctional SERS applications. In chapter 2, we demonstrate the fabrication of hybrid SERS- and electrochemically-active three-dimensional plasmonic liquid marble for in-situ monitoring of an electrochemical redox reaction. In chapter 3, we incorporate metal-organic frameworks (MOFs) with Ag nanocubes superlattice array to preconcentrate non-adsorbing vapor molecules for SERS detection. For chapter 4 and 5, we exploit plasmonic nanoparticles-MOF hybrids for gas-based applications, realizing catalysis and SERS investigation of interfacial processes for ambient electrochemical nitrogen reduction and CO₂ carboxylation reaction, respectively. Lastly, I conclude my thesis with a summary of my research works and identify potential future work.

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List of Abbreviations

2D	Two-dimensional
3D	Three-dimensional
AEF	Analytical enhancement factor
Ag	Silver
Ar	Argon
ATR	Attenuated total reflectance
Au	Gold
CE	Counter electrode
CHEM	Chemical (enhancement)
CO₂	Carbon dioxide
CV	Cycle voltammogram
DFT	Density functional theory
DMF	Dimethylformamide
DNA	Deoxyribonucleic acid
EC	Electrochemical
EDS	Energy-dispersive X-ray spectroscopy
EF	Enhancement factor
EG	Ethylene glycol
EM	Electromagnetic
FE	Faradaic efficiency
FTIR	Fourier-transform infrared
HCl	Hydrochloric acid
HER	Hydrogen evolution reaction
HKUST	Hong Kong University of Science and Technology

HOMO	Highest Occupied Molecular Orbital
KCl	Potassium chloride
LMB	Leucomethylene blue
LOD	Limit of detection
LSPR	Localized surface plasmon resonance
MB	methylene blue
MBT	methylbenzenethiol
MIL-100	Material from Institut Lavoisier-100
mIM	2-methylimidazole
MOF	Metal-organic framework
MP	Mercaptophenol
MPy	4-mercaptopyridine
MUA	Mercaptoundecanoic acid
MW	Molecular weight
N₂	Nitrogen
NaOH	Sodium hydroxide
NH₃	Ammonia
NP	Nanoparticle
NRR	Nitrogen reduction reaction
NSEGSO	Non-selectively Au deposited-Ag octahedra
NT	Naphthalenethiol
OAm	Oleylamine
OSHA	Occupational Safety and Health Administration
PAH	Poly(cyclic) aromatic hydrocarbons
PD	Pentanediol

PFDT	1H,1H,2H,2H-perfluorodecanethiol
PLM	Plasmonic liquid marble
PLS	Partial least square
ppm	Parts per million
PVP	Polyvinylpyrrolidone
RE	Reference electrode
RH	Relative humidity
RSD	Relative standard deviation
sccm	Standard cubic centimeters per minute
SEGSO	Selective edge Au-deposited Ag octahedra
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman Scattering
SFG	sum-frequency generation
SLM	Silica liquid marble
SOMO	Singly Occupied Molecular Orbital
SVR	Support vector regression
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
UV	Ultraviolet
VOC	Volatile organic compound
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction
ZIF	Zeolitic imidazolate framework

Chapter 1: Introduction

Abstract. Surface-enhanced Raman scattering (SERS) spectroscopy is a surface-sensitive spectroscopic technique whereby the molecular vibrational fingerprint of analyte close to plasmonic nanoparticles are significantly enhanced. The high sensitivity, non-invasive nature and low water interference of SERS has resulted in diverse potential applications ranging from molecular sensing to reaction monitoring. Consequently, increased focus has been placed on manipulating and designing plasmonic nanoparticles and platforms to expedite the development of SERS for diverse applications. In this chapter, we introduce the principles of SERS, discussing the factors that affect SERS enhancements. We highlight the emerging strategies to design plasmonic platforms, including nanoparticle assembly and hybridization, and subsequently give a review on current SERS applications. Lastly, we identify the key challenges associated in this field and describe the objectives of our thesis.

1.1 Introduction to surface-enhanced Raman scattering (SERS)

1.1.1 Principles of SERS

The advent of SERS significantly enhances the inherently weak Raman signals of molecules close to plasmonic nanostructures, leading to an increase research interest to Raman spectroscopy as a viable and effective analytical tool.¹⁻³ This surface-sensitive phenomenon is widely proposed to arise from two mechanisms: 1) electromagnetic (EM) and 2) chemical enhancements (CHEM) where EM enhancement is postulated to contribute to majority of the enhancement (up to 10^8) as compared to the latter (10^3).⁴⁻⁶ Extensive EM enhancement is achieved by the utilization of plasmonic noble metal nanoparticles, whereby light is amplified due to the excitation of localized surface plasmon resonances (LSPRs), which is the collective oscillation of the electrons confined at the particle surface (Figure 1.1).^{7, 8} The incoming light couples with the LSPR to generate a secondary electric field, resulting in localized regions of intense electromagnetic (EM) field, also known as plasmonic hotspots, at/near the metal surface (<10 nm). As both the incident and scattered radiations are significantly magnified, the resultant SERS enhancement is scaled to the fourth power of field enhancement (E^4), leading to a $10^3 - 10^8$ -fold SERS signal enhancement. Conventionally, silver (Ag), gold (Au) and copper (Cu) and more recently aluminum (Al) are the most commonly utilized plasmonic material because they can support surface plasmons in the visible light to near-infrared wavelength range, where most Raman measurements occur.^{7, 9} Of these materials, Ag is established to possess the highest plasmon efficiency and hence greatest SERS activity.¹⁰

On the other hand, CHEM is based on a charge-transfer mechanism and arises from the enhanced polarizability between the analyte molecules and the metallic surfaces.^{5, 11} Consequently, CHEM largely depends on the chemical nature of the analytes, and their interaction with the plasmonic surface. This means that SERS enhancements via CHEM is

applicable only to narrow class of analytes such as thiols. Nonetheless, both mechanisms can give rise to significant enhancements only if the analyte is close to the plasmonic nanoparticles.

Figure 1.1. Schematic of the localized surface plasmon resonance (LSPR). Reproduced with permission from ref 8. Copyright 2014 Elsevier.

1.1.2 Factors affecting LSPR

The LSPRs of metallic nanoparticles can be modified based on the nanoparticle morphologies, compositions, dielectric functions, and interparticle plasmonic couplings. This highly tunable property is particularly favorable because the EM enhancement is maximized when the LSPR peak is in resonance with the irradiation wavelength. Amongst these factors, one of the most direct way to alter the LSPR is to change the morphology or shape of the nanoparticles. For example, due to its anisotropic shape, plasmonic nanorods possess multiple plasmon bands, namely the longitudinal and transverse plasmon bands that correspond to light absorption and scattering along the nanorod's long and short axes, respectively. Notably, the energy of the nanorod's longitudinal plasmon can be tuned from visible (~ 600 nm) to infrared (~ 1500 nm) region by altering the nanorod aspect ratio. The LSPR λ_{max} generally increases linearly with an increase in Au nanorod aspect ratio from 2 to 5.^{12, 13} Aside from manipulating single nanoparticles, individual nanoparticles can also

be arranged in close proximity so that their plasmons can interact to give rise to huge local EM enhancements at the interparticle gaps. Typically, these hotspots result in SERS enhancements of 5 – 6 orders of magnitude higher than single nanoparticle systems. In subsequent sections, we will discuss in depth current strategies to manipulate LSPRs and hotspots to achieve plasmonic platforms with strong SERS capabilities.

1.2 Strategies for designing SERS platforms

Owing to the large enhancements offered by EM mechanism, most strategies are focused on manipulating plasmonic nanoparticles to modulate the LSPRs and create plasmonic hotspots.¹⁴ For zero- and one-dimensional (0D/1D) nanostructures, researchers strategically design nanoparticles that possess sharp tips and edges, such as nanostars and nanoprisms, because these features can localize the LSPRs and create EM hotspots via the ‘lightning-rod’ effect.¹⁵ In addition, bottom-up self-assembly approaches to organize plasmonic nanoparticles into ordered 2/3-dimensional (2/3D) metacrystals are also increasingly employed so that the plasmonic hotspots can be scaled up from the nanometer scale to the macroscale. Nanoparticle self-assembly induces plasmonic coupling between neighboring nanoparticles, which in turn generates intense and homogenous EM field enhancements across centimeter-scale areas. However, the field enhancements engendered by these hotspot engineering strategies are only effective if the target analyte can access these hotspots because of the surface-sensitive nature of the enhancement mechanisms. To overcome this challenge, hybrid nanoparticle platforms are emerging solutions to enhance SERS signals and/or manipulate analyte close to the plasmonic surface. In this section, we discuss the contemporary strategies used to increase SERS performance.

1.2.1 Designer nanoparticles

Over the past several decades, advances in nanoparticle synthesis has resulted in various morphologies which can achieve intense light confinement on nanoparticle surfaces. Various shape-controlled metallic nanoparticles with regions of large curvatures can now be prepared through wet-chemical synthesis in high yields and excellent monodispersity (Figure 1.2A). Typically, molecular capping agents such as poly(vinylpyrrolidone) (PVP) are employed to selectively passivate specific crystal planes against further growth through molecular interactions to enable seed particles to grow into anisotropic, shape-controlled nanoparticles. Some examples of anisotropic nanoparticles include nanocubes and octahedra,¹⁶⁻¹⁸ nanorods,¹⁹ wires,²⁰ prisms,²¹ and bipyramids.²² These nanoparticles all possess sharp vertices which result in a ‘lightning-rod effect’ that confine the strong electromagnetic field enhancements. By tuning synthesis conditions, increasingly complex particle shapes can also be achieved, including bowls,²³ various star-like and flower-like structures,²⁴⁻²⁶ porous structures,^{27, 28} as well as high-index faceted tetrahedral nanorods,²⁹ rhombic dodecahedra³⁰ and concave cubes.³¹

In addition, various nanoparticles with unique structural features has been achieved by modifying as-synthesized shape-controlled nanoparticles, further enabling dynamic modulation of LSPR. There are two types of modifications: 1) additive and 2) subtractive methods. The additive method increases EM hotspot density through selective deposition of additional plasmonic nanoparticles on specific regions or facets of as-synthesized nanoparticle templates.³² For instance, Au nanoparticles are deposited on the sharp edges and vertices of Ag octahedra, creating selective edge Au-deposited Ag octahedra (SEGSO) (Figure 1.2B).³² Due to intra-particle plasmonic coupling between the Ag and Au surface plasmons, SEGSO demonstrates 15-fold stronger local EM field and 10-fold higher SERS enhancement factor (EF) along its Au-deposited edges and vertices than pure Ag octahedra.

Such precise decoration of original hotspot areas with additional hotspots, referred to as the ‘hotspot-over-hotspot’ approach, further enables a 3-fold increase in single-particle SERS EF over non-selectively Au deposited-Ag octahedra (NSEGSO).

The subtractive method heightens SERS enhancement through the controlled etching the nanoparticle surface to increase surface roughness and promote efficient plasmonic coupling.^{33, 34} For instance, smooth Ag nanowires are etched using a hydrogen peroxide/ammonia mixture to produce nanowires with rough surfaces resembling ‘beads-on-a-string’ (Figure 1.2C).³³ The etched nanowires generates intra-particle nanogaps for more efficient EM field localization at these engineered hotspots, enabling SERS activity to be observed along the entire etched nanowire length. This is in contrast to the original smooth Ag nanowires that only possess SERS activity at the tips, hence increasing single-particle SERS EF (6.4×10^4) by ~2-fold. Importantly, these post-synthetic morphological modifications do not affect the intrinsic crystallinity of the nanoparticles, ensuring a high quality (Q)-factor of the plasmon resonances.³⁵

Besides traditional Ag, Au and Cu, Al nanoparticles are emerging as promising plasmonic-active materials because of its low cost and ability to support LSPRs from the deep-UV to the visible region.³⁶⁻³⁹ However, the plasmonic-active areas on individual particles are limited to the nanometer length scale, thus presenting significant challenges in directly using these nanoparticles to address macroscopic applications such as in sensing or in catalysis. Hence, plasmonic nanoparticles are generally used as the basic building blocks to fabricate plasmonic metacrystals via assembly, which is akin to atomic analogues in the creation of bigger ‘molecules’.⁴⁰⁻⁴²

Figure 1.2. (A) Overview of the various strategies to achieve designer plasmonic nanoparticles. (B) SEM images of Ag octahedral (i) before and (ii) after selective Au-deposition, respectively. (C) SEM images of Ag nanowires (i) before and (ii) after etching, respectively. Reproduced with permission from (A) ref 14, (B) ref 32 and (C) ref 33. Copyright 2019 The Royal Society of Chemistry. Copyright 2014 John Wiley & Sons, Ltd. Copyright 2012 American Chemical Society.

1.2.2 Two-dimensional (2D) assembly of nanoparticles

Organizing nanoparticles into 2D assemblies introduces plasmonic coupling across the x-y plane to yield stronger and more consistent electromagnetic field enhancements, generating scalable SERS-active areas of up to centimeter-scale.⁴³ These 2D metacrystals can be transferred onto supporting substrates, or directly in interfacial SERS. In this section, we will discuss commonly used bottom-up interfacial nanoparticle self-assembly processes,

which are governed by various inter-nanoparticle interactions including van der Waals interactions, hydrogen bonding and electrostatic interactions.

Interfacial self-assembly is the go-to bottom-up technique to construct scalable 2D plasmonic metacrystals. This technique makes use of the interface between two immiscible fluid phases to control nanoparticle self-assembly. Common examples are fluid-fluid interfaces such as the liquid-air and liquid-liquid interfaces.⁴⁴ Nanoparticles spontaneously adsorb to these interfaces to minimize interfacial free energy, forming nanoparticle morphology-dependent close-packed metacrystals.⁴⁵⁻⁴⁷ The associated adsorption energy is usually few orders of magnitude larger than thermal energy. Such stable adsorption at the interfaces provide a versatile channel to tailor nanoparticle organization and by extension, the strength of electromagnetic field enhancements in the resulting metacrystal.

To form 2D array substrates at the liquid-air interface, Langmuir-Blodgett or Langmuir-Schaefer methods are generally used, whereby a non-polar nanoparticle solution is spread over the aqueous layer, and the compactness is modulated by systematically altering the surface pressure.⁴⁸ For example, when using Ag nanocrystals, as surface pressure becomes higher, the particle density of the Langmuir monolayer increases and the film color transits from yellowish to metallic silver, indicating the change in plasmon coupling between the particles.^{49, 50} While these techniques allow precise control of the packing densities of the 2D assembly, they can only provide limited modulation of metacrystal structure, despite the fact that shape-controlled nanoparticles with well-defined facets can pack in different ways to achieve maximum space filling.

In this aspect, assembly at the interface between two immiscible solvents presents a more versatile avenue to tune metacrystal structure. Such liquid-liquid interface is typically formed between water and a low polarity organic solvent such as liquid alkanes and chloroform. Unlike the air/liquid interface, the presence of two liquid phases introduces

additional hydrophobic and hydrophilic interactions between the nanoparticles and the respective liquid phases.^{44, 51} Such interactions can be used to control the interfacial behaviors of the nanoparticles, including nanoparticle interfacial position and orientation, in turn creating more flexibility in tuning metacrystal formation. A notable example utilizing the liquid/liquid interface to modulate metacrystal superlattice is via the ‘one nanoparticle morphology, multiple superlattices’ approach, achieved by employing shape-controlled Ag/Au nanoparticles (Figure 1.3, 1.4).⁵² Nanoparticle surfaces can be functionalized with a series of thiol-terminated molecules possessing varying hydrophobicity through ligand exchange reactions; increasing chain lengths of the alkylthiols increases the surface hydrophobicity. The respective nanoparticles are then dispersed and assembled at the oil/water interface via a gel-trapping technique (Figure 1.3). Hydrophilic Ag octahedra functionalized with PVP form a hexagonal close-packed superlattice (packing efficiency of 89 %) while functionalizing the Ag octahedra with a relatively hydrophobic 1-propanethiol results in an open hexagonal metacrystal (packing efficiency of 67 %) (Figure 1.4). Ag octahedra in both hexagonal metacrystals adopt a planar configuration at the interface. Further increasing the surface hydrophobicity of the Ag octahedra using 1-hexadecanethiol results in the formation of a square metacrystal (packing efficiency of 33 %), and the Ag octahedra adopt a standing configuration in this metacrystal. Thus, these 2D assembly methods hence enable the formation of large-scale nanoparticle superlattices with tunable interparticle distance and packing, which in turn allow controllable plasmonic couplings, and versatile application for practical devices.

Figure 1.3. Schematic of liquid-liquid interfacial assembly of nanoparticles via gel-trapping technique. Reproduced with permission ref 52. Copyright 2015 Springer Nature.

Figure 1.4. (A) Change in water contact angles of thiol functionalized Ag films. (B) Ag octahedra with increasingly hydrophobic surface results in the packing patterns to transit from hexagonal close-packed superlattice to the open hexagonal metacrystal and into the square packing. All scale bars, 200nm. (C) Schematic highlighting the transition process between the three superlattices. Reproduced with permission ref 52. Copyright 2015 Springer Nature.

1.2.3 Three-dimensional (3D) assembly of nanoparticles

Extending the self-assembly of nanoparticles along the z-axis results in the formation of 3D plasmonic platforms. 3D SERS platforms triumphs over 2D plasmonic platforms because it enables efficient utilization of the 3D excitation volume of the laser.⁵³ Furthermore, 3D platforms possess enhanced SERS performance due to an increase in effective spatial hotspot density (or SERS-active volume in other words) within the laser

excitation volume.⁵⁴ They also demonstrate improved detection sensitivities due to an increase in effective SERS-active surface area, which boost interactions between the plasmonic nanoparticles and target analyte. Moreover, 3D platforms also possess higher laser misfocus tolerance along the z-axis. This enables faster and more feasible on-site measurements, omitting the laborious laser alignment prior to SERS detection for practical application.

Typically, these 3D plasmonic metacrystals can be formed via layer-by-layer stacking of the as-synthesize 2D superlattice,^{55, 56} evaporation-induced assembly,⁵⁷⁻⁵⁹ Deoxyribonucleic acid (DNA)-programmable assembly,⁶⁰⁻⁶³ and droplet/emulsion interfacial assembly.⁶⁴⁻⁶⁹ In this section, we highlight the progress of droplet interfacial assembly of plasmonic nanoparticles into 3D plasmonic liquid marbles/colloidosomes. As with its 2D counterparts, the assembly of these 3D metacrystals are driven by the minimization of thermodynamic free energy. In turn, the self-assembly is governed by a combination of interactions including van der Waals' attractive forces, steric repulsion and capillary forces.⁷⁰

In general, plasmonic liquid marbles (PLMs) and colloidosomes are spherical millimeter-/micrometer-sized SERS platforms that are formed from the spontaneous assembly of nanoparticles at the immiscible liquid-liquid interface (Figure 1.5). For example, adding an aqueous droplet into a Ag nanocubes suspension in decane results in the spontaneous assembly of the Ag nanocubes onto the aqueous droplet to form a liquid marble.⁶⁴ The resultant PLM demonstrates excellent mechanical stability and robustness. Notably, the thickness of the nanoparticle shell in these milli-/micro-droplets can be readily modulated by tuning the nanoparticle concentrations during PLM/ colloidosome formation. Both platforms possess multiple layers of closely packed metallic nanoparticles to give rise to uniform and intense EM field across the entire 3D shell, due to extensive plasmonic coupling in all three Cartesian planes.

Coupled with greater access to analyte and laser penetration from all spatial directions, this enables better utilization of the 3D hotspot density to achieve high analytical enhancement factors (AEF) of $10^6 - 10^9$, which can be applied for ultra-trace SERS detection.⁷¹⁻⁷³

Figure 1.5. (A) SEM image of Ag nanocubes. (B, C) Schematic of the formation of a plasmonic liquid marble. (D) Digital image and (E) Contact angle of the PLM. (F) PLM submerged in hexane while floating on water (yellow). Reproduced with permission ref 64. Copyright 2014 WILEY-VCH Verlag GmbH & Co.

Evidently, the manipulation of plasmonic nanoparticles to engineer and design intense hotspots has evolved significantly since the advent of SERS. We have highlighted some of the recent nanoparticle platform strategies, including the synthesis of designer nanoparticles and techniques to fabricate 2D/3D metacrystals for efficient light confinement. Nevertheless, a major challenge still persists in SERS platforms – most analytes have poor or no affinities to the plasmonic nanoparticles and are not close enough to experience meaningful enhancements. As a result, weak/negligible SERS readout is expected even when using plasmonic platforms with intense SERS capabilities due to the distance-dependent exponential decay of the EM field. To overcome such limitation and to expedite the translation of SERS to real world applications, SERS research has also branched out to

introduce secondary functional nanomaterials to plasmonic systems so that the analyte can be manipulated close to the plasmonic surface.

1.2.4 Incorporation of MOFs to form hybrid materials

One up-and-coming class of material that can be incorporated with plasmonic nanoparticles is metal-organic frameworks (MOFs), which are porous crystalline structures made up of inorganic metal ions or clusters coordinated to organic linkers.⁷⁴ They possess extremely large internal surface areas and have unparalleled degree of tunability, enabling various functionalities to be conferred onto these frameworks. Notably, when integrated with plasmonic nanoparticles, their porous nature and their high surface areas enable MOFs to preconcentrate and confine small molecules right at the nanoparticle surface within the EM field enhancement.^{75, 76} Depending on the size of the pores, MOFs can also function as molecular sieves to confer specificity to the SERS substrate.

Generally, there are two approaches to fabricate plasmonic nanoparticles (NP)-MOF platforms. One straightforward method is the impregnation method whereby the MOF is synthesized first and then immersed in metallic salt solution. Addition of reducing agents reduces the metallic salts into small nanoparticles within the MOF framework.⁷⁷ For example, Au NP/MIL-101 nanocomposites are fabricated by suspending MIL-101 in chloroauric acid solution of varying concentrations followed by the addition of reducing agent, sodium citrate.⁷⁸ The resultant composite comprises of Au nanoparticles homogeneously distributed within the octahedral MIL-101 crystalline structures (Figure 1.6). However, it is challenging to control the nanoparticle morphology and distribution, which could potentially lead to low and inhomogeneous SERS hotspot distribution.

Figure 1.6. Schematic of plasmonic nanoparticle-MOF nanohybrid Au NP/MIL-101 formed by impregnation of Au precursors into MIL-101. Reproduced with permission ref 78. Copyright 2014 American Chemical Society.

Another approach involves first the formation of shape-controlled plasmonic nanoparticles, followed by the overgrowth of MOF layer.^{75, 79, 80} Due to the advantage of controlling the plasmonic properties, the second approach is often more favored. To promote the overgrowth of MOF over the nanoparticles, capping agents are employed to drive heterogenous nucleation. For example, the addition of mercaptoundecanoic acid (MUA)-capped Au nanorods to MOF-5 precursors enables the interactions of the Zn^{2+} ions with COO^- of MUA which promotes the self-assembly of MOF-5 onto Au nanorods (NR) clusters (Figure 1.7).⁸⁰ The resultant Au@MOF-5 nanohybrid exhibits size selective adsorption, where pyridine can diffuse through the MOF to access the plasmonic core (pore size $\sim 8 \text{ \AA}$) while poly(vinyl 4-pyridine) cannot. Notably, due to the ability to alter the types of plasmonic nanoparticle, the metal cluster and organic linker of MOF used, there is immense flexibility in novel structure design and ability to customize the MOF for specific analyte capture.

Figure 1.7. Schematic and TEM image of Au NR@MOF-5 formed by the overgrowth of MOF-5 around preformed Au NRs. Reproduced with permission ref 80. Copyright 2013 American Chemical Society.

1.3 Applications of SERS

Thus far, we have discussed various approaches to create numerous plasmonic platforms including 2D/3D assembled superlattices and hybrid NP-MOF nanoparticles, and how these different designs enable the modulation of hotspots and manipulation of analyte respectively. In this section, we discuss the applications of these assembled and hybrid platforms to SERS, focusing on how these designs directly impact the ability to achieve strong electromagnetic field confinements and superior SERS performance. Currently, there are two major applications of SERS; analyte sensing and reaction monitoring.

1.3.1 Analyte sensing

One of the main applications of SERS is analyte sensing or detection, where the analyte solution is exposed to the plasmonic platforms with strong hotspots to enhance its vibrational fingerprints. Besides single analyte sensing, SERS platforms have diverse applications in chemical sensing, including multiplex and online microfluidic sensing. These analytes also serve as model probe to assess the enhancement factors and performance of the plasmonic platforms.

For example, assembling nanoparticles of the same morphology but with different hydrophobicity at the liquid-liquid interface generates diverse metacrystals such as close-

packed and progressively open structures. Notably, despite having the lowest packing density of 33 %, the open square metacrystal assembled using Ag octahedra generates a SERS enhancement factor of 9.9×10^4 using 4-methylbenzenthionol as the probe. This enhancement factor is nearly 8-fold higher than the hexagonal arrays which have packing densities of 67 % and 89 %. Similarly, the open hexagonal metacrystal formed using Ag nanocubes (packing density 24 %) achieves a SERS enhancement factor of 1.5×10^6 , nearly 350-fold higher compared to the close-packed square metacrystal (packing density 100 %). This study evidently demonstrates that “more is not always better”, thus challenging the convention idea where highly compact nanoparticles are required to achieve higher SERS performance.

Another SERS application of 2D/3D assembled superlattice is interfacial multiplex sensing. The plasmonic nanoparticles array at the liquid-liquid interface enables the simultaneous detection of analytes in both of the immiscible phases, eliminating the need for phase separation procedures required in conventional high-performance liquid or gas chromatography analysis. For example, a “dual-phase tri-analyte” detection platform is first realized using plasmonic colloidosomes whereby three analytes dissolved in the aqueous and oil phase are simultaneously detected (Figure 1.8).⁷¹ Consequently, several industrial toxins including malachite green, rhodamine 6G, and dimethyl yellow can be detected down to the sub-femtomolar levels. Furthermore, the plasmonic colloidosomes can also be incorporated into a microfluidic channel for on-line and rapid high through-put multiplex detection.⁸¹ The dye analyte are isolated inside individual colloidosomes, averting contamination of the flow channel and analyte cross-talk for sequential detection. Notably, quantification of samples in concentrations ranging from 10^{-7} to 10^{-2} M can also be achieved. Therefore, SERS sensing using 2D/3D assembled platforms has diverse applications in clinical diagnosis, environmental monitoring, and toxin detections. However, in general,

despite advances in hotspot engineering, many studies are limited to Raman probes that have large Raman cross-sections and/or can adsorb easily onto the plasmonic surface because of the surface-sensitive nature of SERS.

Figure 1.8. (A) SERS quantification of toxic dyes. (B) Schematic illustrating the “dual-phase tri-analyte” detection. (C, D) SERS spectra and hyperspectral image of multiplex detection (black) and detections of rhodamine 6G (red), malachite green (green), and dimethyl yellow (yellow). Reproduced with permission ref 71. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

To achieve SERS sensing of low affinity analyte, MOFs can be incorporated with SERS platforms to capture analyte and further increase detection sensitivity, enabling ultratrace detection in liquid/aqueous media. This is attributed to the high sorption capabilities and porous matrices of MOFs, which efficiently confines and accumulates analytes near the plasmonic surface. For instance, MOF-5-coated Au (Au-MOF-5) gratings are employed to detect organophosphorus pesticides with a limit of detection of 10^{-12} M (2.8×10^{-7} mg L⁻¹), which is 4 orders of magnitudes lower than that of Au-COOH gratings

without MOF (10^{-8} M) (Figure 1.9).⁸² In another example, MOF-shell-isolated Au nanoparticles (Au@MIL-100) can quantitatively detect toxic malachite green in aquaculture water with a 10^{-9} M limit of detection (LOD) and realize *in situ* measurement of trace malachite green (5×10^{-8} M - 10^{-6} M) on fish bodies. Another important attribute of MOFs is its ability to preconcentrate target analyte onto plasmonic surfaces to enable specific detection even in the presence of interfering compounds. This is exemplified by the highly sensitive detection of polluting *p*-phenylenediamine at 1.3 ng mL^{-1} using AuNPs/MIL-101 nanocomposites, even in sewage and river water which contain numerous interfering contaminants. Hence, the design of various plasmonic platforms ranging from 2D superlattices to 3D plasmonic liquid marbles, and the incorporation of secondary functional material such as MOFs have brought about novel SERS applications in sensing.

Figure 1.9. (A, B) SERS detection of Paraoxon in different concentrations on Au@MOF-5 films. (C) Quantification of Paraoxon by plotting SERS peak intensity against analyte concentration. Reproduced with permission ref 82. Copyright 2019 Elsevier.

1.3.2 Reaction monitoring

Aside from chemical sensing, the non-invasive nature of SERS also permits in-situ investigation of reaction progress. In contrast with *ex situ* techniques, SERS enables real time investigation of molecular events during reaction without disrupting the reaction setup. The unique analyte vibrational fingerprints reflect the chemical events that are occurring within the solution, enabling the elucidation of reaction mechanisms. For example, the use of plasmonic liquid marbles as a microlab permits the real time investigation of the reaction kinetics of a multistep azo-dye formation (Figure 1.10).⁶⁷ Nitroaniline is first converted into diazonium nitrobenzene upon mixing two plasmonic liquid marbles containing the precursors, followed by reaction with arenes to form azo-dye. The plasmonic microreactor enables on-demand reaction-and-detection procedures where the molecular reactions are initiated and then tracked in situ in a non-disruptive manner. Furthermore, the plasmonic shell protects volatile or light-sensitive reactants from light degradation and improves reaction rates via hydrodynamic flow when merging the PLMs.

Figure 1.10. Schematic illustrating PLM as a microchemical reactor for on-demand reaction and SERS detection of a multistep reaction. Reproduced with permission ref 67. Copyright 2017 American Chemical Society.

In addition, the permeable 3D shells of plasmonic colloidosomes also enable the in situ SERS observation of interfacial protonation reaction of dimethyl yellow that is otherwise challenging to monitor when using other analytical techniques.⁸³ Moreover, the reaction rate constant can be derived through SERS spectral evolution. Notably, SERS

vibrational fingerprint permits the differentiation of isomers, which is not possible via high-performance liquid chromatography. Due to the highly catalytic nature of the plasmonic nanoparticles, they can also serve as a bifunctional platform where SERS spectroscopy can be employed to in-situ monitor plasmon-catalyzed reactions.⁸⁴⁻⁸⁶ For example, plasmon-driven catalytic reactions of 4,4'-dinitroazobenzene, 4,4'-diaminoazobenzene and 4-nitro-4'-aminoazobenzene can be investigated using electrochemical SERS spectroscopy. The study revealed that plasmon-driven reduction of the NO₂ groups to NH₂ occurs more readily compared to plasmon-driven oxidation of NH₂. Furthermore, the concomitant time-dependent SERS spectral changes can also reveal addition kinetics insights. Hence, in addition to simple SERS sensing of analyte, the strategic design of plasmonic platforms can enable novel SERS applications in reaction monitoring.

1.4 Motivations and Objectives

Therefore, the manipulation of plasmonic nanoparticles via assembly and hybridization has permitted significant improvement in SERS performance which has potential applications in diverse fields ranging from biomedical diagnosis to environmental detections. Using plasmonic nanoparticles as building blocks to form centimeter scale 2D and 3D metacrystals generates plasmonic platforms with strong hotspots and affords unique interfacial applications. Addition of MOFs to the plasmonic platforms also potentially overcomes the current bottleneck of poor analyte affinity. Collectively, these platforms allow SERS to be employed for multiplex sensing, microfluidic sensing and reaction monitoring.

Despite the improvements in SERS performance, there are still few challenges and research gaps that need to be addressed to translate SERS toward practical applications for chemical sensing, reaction monitoring and catalysis. Firstly, current SERS reaction

monitoring are still restricted to spontaneous reactions that are activated by the mixing of precursors. An important field that cannot be neglected is electrochemical reactions, which has crucial relevance in diverse applications, such as electrochemical energy generation/storage,⁸⁷ and biochemical charge transfer processes.⁸⁸ Current setups using roughened electrodes typically require the laser to penetrate through the bulk solution to reach the electrochemical-active surface, causing poor signal readout due to scattering and possible interferences. In this aspect, PLM is an ideal platform for microscale spectroelectrochemical analysis where the 3D Ag shell can serve as a hybrid platform for as a working electrode and plasmonic-active surface. Secondly, despite the integration of MOFs to plasmonic platforms, sensing of analyte with poor affinities remain a challenge. This problem is especially notable for vapor/gases because of their intrinsic low concentrations and dynamic nature, and this is reflected by the limited SERS reports on vapor detections. The detection of chemical species in vapor form have a myriad of important applications including environmental monitoring of volatile organic compounds and detection of disease biomarkers as breathalyzers. Given the advantage of nanoparticle assembly and incorporation of MOFs, it is thus ideal to combine both strategies to achieve an ultrasensitive plasmonic platform capable of capturing and detecting gaseous/vapor species. Moving beyond chemical sensing, we also anticipate the development of the plasmonic NP-MOF platforms to drive and monitor gas-based reactions and catalysis via SERS, creating a new niche area for practical and multifunctional SERS applications.

The objective of my thesis is therefore to overcome the aforementioned limitations and translate SERS to real world applications by hybridizing functional materials and assembling plasmonic nanoparticles to effect strong plasmonic coupling. In chapter 2, we demonstrate the fabrication of smallest hybrid SERS- and electrochemically active 3D PLM for the in-situ molecular level monitoring of an electrochemical redox reaction. The Ag

nanocubes shell serves as both the working electrode and highly sensitive SERS-active platform, enabling spectroelectrochemical analysis. We further highlight the importance of nanoparticle assembly in chapter 3, where we incorporate metal-organic frameworks (MOFs) with Ag nanocubes superlattice array to preconcentrate non-adsorbing vapor molecules for SERS detection at the ppm levels. In chapter 4 and 5, we exploit MOF for gas/vapor-based applications and develop plasmonic nanoparticles (NP)/MOF hybrids to drive catalysis and in situ investigate the interfacial processes via SERS. In chapter 4, we utilize the preconcentration effect and hydrophobicity of selected MOF for efficient electrochemical nitrogen reduction reaction (NRR) where hydrophobically modified MOF concentrates nitrogen to the Ag electrocatalyst while retarding water entry. In chapter 5, we further exploit the NP-MOF interface to drive the inert CO₂ carboxylation of arene moiety and in situ investigate its unconventional regioselectivity via SERS. Lastly, I conclude my thesis with a summary of my research works and provide a critical outlook for the future progress of SERS and plasmonic field.

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Chapter 2: SERS- and Electrochemically-Active 3D Plasmonic Liquid Marble for Spectroelectrochemical Investigations

Abstract. Liquid marbles are emergent microreactors owing to their isolated environment and the flexibility of materials used. Plasmonic liquid marbles (PLMs) are demonstrated as the smallest spectroelectrochemical microliter-scale reactor for concurrent spectro- and electrochemical analyses. The three-dimensional Ag shell of PLMs are exploited as a bifunctional surface-enhanced Raman scattering (SERS) platform and working electrode for redox process modulation. The combination of SERS and electrochemistry (EC) capabilities enables in situ molecular read-out of transient electrochemical species, and elucidate the potential-dependent and multi-step reaction dynamics. The 3D configuration of our PLM-based EC-SERS system exhibits 2-fold and 10-fold superior electrochemical and SERS performance than conventional 2D platforms. The rich molecular-level electrochemical insights and excellent EC-SERS capabilities offered by our 3D spectroelectrochemical system are pertinent in charge transfer processes.

2.1 Introduction

Liquid marbles are emerging lab-on-a-droplet platforms which efficiently isolate liquid reaction medium within a three-dimensional (3D) particle shell to impart robustness and overcome rapid evaporation typical in small-volume processes.¹⁻⁵ Attributing to these unique properties, liquid marbles are employed in vast applications as isolated micro-reactors,⁶ micro pumps⁷ and in sensing.⁸ These versatile microreactors can be further imbued with function-specific attributes, such as photothermal and catalytic properties,^{9, 10} via the selection of active encapsulating solids, and have diverse (bio)chemical applications.^{8, 11, 12} For instance, the plasmonic liquid marble (PLM) constructed using metallic nanoparticles has enabled the elucidation of critical reaction mechanism and dynamics using surface-enhanced Raman scattering (SERS) spectroscopy.¹²

Despite the vast potentials offered by liquid marbles, these reactors are limited to spontaneous chemical reactions driven intrinsically by the presence of multiple reactive reagents. Electrochemical (EC) reactions form the basis of important energy- and environmental-related applications, such as energy storage mechanisms in chemical batteries,¹³ and charge transfers in biochemical processes.¹⁴ The fusion of liquid marble with electrochemistry is hence tantalizing to expand its application for electrochemical activation of small-volume inert reactions. The spherical shell of the liquid marble also provides a unique geometry as a working electrode. However, it remains challenging to perform EC in liquid marbles due to the dearth of in-depth understanding of charge transfer properties across liquid marbles and the technical difficulties in incorporating commercial three-electrode system in a microliter droplet.

Due to its inability in giving structural and adsorption data, EC are often coupled with molecular-specific spectroscopy to provide unequivocal identification of species for comprehensive understanding of complicated redox systems.^{15, 16} Typically, vibrational

spectroscopic methods such as infrared (IR),^{17, 18} Raman,^{19, 20} and sum-frequency generation (SFG) spectroscopies are used together with EC to identify interfacial molecules and to study the nature of chemisorption bond.^{21, 22} Notably, SERS prevails other methods due to its ultrasensitive detection capability^{23, 24} while averting interfering signals from water, which is a common electrolyte in EC processes. A typical method to fabricate SERS-active electrodes is via metal oxidation-reduction cycle,^{25, 26} which often leads to inconsistent surface roughness and suffers from reproducibility issues. While methods are developed to prepare electrodes with tunable metallic nanostructured surfaces, e.g. metal film over nanosphere^{27, 28} and sphere segment void nanostructured films,²⁹⁻³¹ these designs often require multiple-step protocols and is difficult for the electrodes to be miniaturized down to microliter scale.

Herein, we demonstrate the PLM as an ideal micro test-bed for spectroelectrochemical analysis capable of circumventing the aforementioned limitations, leveraging on the plasmonic and electrically conductive metallic shell as a bifunctional SERS- and EC-active platform. Exploiting the Ag shell as the first miniaturized 3D spherical working electrode, we first highlight the ability of the PLM soft metallic shell to perform EC reactions at precise voltages, and demonstrate the excellent reproducibility of our improvised three-electrode microsystem over extended analysis period. PLM is then showcased as the smallest spectroelectrochemical cell capable of offering potential-dependent read-out of molecular vibrational fingerprints and electro-thermodynamics simultaneously, using the colorless hexaammineruthenium (III) chloride ($\text{Ru}(\text{NH}_3)_6\text{Cl}_3$) and environmental toxin methylene blue (MB^+) as model compounds. Remarkably, the synergistic electrochemical and SERS capability of the PLM enables the elucidation of critical insights on EC reaction mechanism, molecular structural changes, and quantitative temporal concentration for kinetic dynamics that cannot be accomplished with EC or SERS

alone. Finally, we exemplify the importance of our unique 3D electrode by comparing the superior EC and SERS performance of PLM over conventional 2D micro-platforms.

2.2 Results and discussion

HCl-treated Ag nanocubes (edge length of 133 ± 9 nm; Figure 2.1) are used as the metallic building blocks of the PLM due to the superior SERS enhancement arising from the intense localized electromagnetic fields at the sharp edges.³² Upon the addition of a 40 μ L aqueous droplet, the Ag nanocubes suspended in decane spontaneously assemble on the microdroplet surface to form a 3D encapsulating shell (Figure 2.2A) driven by the large interfacial energy between the aqueous and organic decane phases.³³ The Ag nanocube shell exhibits the appearance of bulk silver arising from the uniform and compact array at optimized Ag-to-water ratio of 7.5 μ g/ μ L (shell thickness $\sim$ 500 nm; Figure 2.3). X-y hyperspectral SERS evaluation of PLM demonstrate its intense SERS activity with an analytical enhancement factor (AEF) of 2.6×10^8 , and excellent homogeneity (< 10 % relative standard deviation (%RSD)) across a large evaluation area (Figure 2.4). The intense and homogeneous SERS responses directly affirm the compactness of the plasmonic shell, where plasmonic coupling of adjacent Ag nanoparticles in x-, y- and z- spatial direction create dense and strong electromagnetic hot-spots evenly distributed around PLM. Hereon,

all experiments are conducted in a 40 μL droplet using the optimal Ag-to-water ratio of 7.5 $\mu\text{g}/\mu\text{L}$ to ensure electrical continuity and high SERS readout.

Figure 2.1. Characterization of HCl-treated Ag nanocubes. (A) SEM image of HCl-treated Ag nanocubes. (B) Size distribution of Ag nanocube edge length. The average edge length is measured at (133 ± 9) nm. The decrease in edge length arises from the rounding of the edge and vertices by acid etching. The SERS enhancement capability of the Ag nanocubes is not affected by HCl treatment.¹² (C) UV-vis extinction spectra of the Ag nanocubes colloidal solution in ethanol. The peaks at 353, 400, 505 and 724 nm that can be assigned to octupole (353 nm), quadrupole (400 nm and 505 nm), and dipole resonances (724 nm).

Figure 2.2. (A) Fabrication of PLM. Inset shows digital image of PLM. (B) Schematic on the use of Ag shell as 3D working electrode (WE). (C) Digital image of the EC-SERS set up.

Figure 2.3. Optimization of Ag-to-water ratio. Microscopic images of the surface of plasmonic liquid marble prepared using an Ag-to-water ratio of (A) 5 μg/μL, (B) 7.5 μg/μL, (C) 10 μg/μL and (D) 12.5 μg/μL.

Figure 2.4. Evaluation on the SERS homogeneity over the Ag nanocubes shell. A) X-y hyperspectral SERS image of PLM across a wide evaluation area of $165\ \mu\text{m} \times 65\ \mu\text{m}$. (B) Comparison on the homogeneity of SERS intensity at 20 different random spots using the $1639\ \text{cm}^{-1}$ SERS band of methylene blue.

We then evaluate the PLM as a conductive 3D working electrode (WE) by performing CV using electroactive $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ as our model probe dissolved in the enclosed aqueous microdroplet. A three-electrode system is improvised to allow precise regulation of applied voltage. Pt electrode and Ag/AgCl wire serve as a counter and quasi-reference electrode, respectively (Figure 2.2B, C). In a forward scan, we observe the emergence of a cathodic peak at $-0.28\ \text{V}$ as the applied potential is regulated systematically from -0.05 to $-0.5\ \text{V}$ (Figure 2.5B). An anodic peak subsequently evolved at $-0.19\ \text{V}$ as the applied potential is reversed from $-0.5\ \text{V}$ back to the initial $-0.05\ \text{V}$. The peak separation is determined at $0.09\ \text{V}$, which is comparable with literature using similar droplet cell setup.^{34, 35} These finding clearly reflects a one-electron redox process involving the

electroreduction of Ru^{3+} to Ru^{2+} . Furthermore, we note the similar peak currents of cathodic and anodic electrochemical responses quantified at 27 and 30 μA , respectively, which can be attributed to the excellent reversibility of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ electroreduction. Such stable and well-defined redox peaks of our redox probe when using PLM as electro-active microreactor indicates the efficient electron transfer between the electrode and electroactive species. PLM as a working electrode is again affirmed on comparison with a control insulating silica liquid marble, which reveals featureless and negligible EC responses, signifying no redox reaction under identical CV conditions. The 3D metallic shell also demonstrates ~ 2 -fold higher peak current ($\sim 27 \mu\text{A}$) relative to the planar WE ($\sim 18 \mu\text{A}$) formed by dropcasting Ag nanocubes onto copper tape, which directly denotes the superior electrochemical performance of 3D PLM electrodes over conventional planar counterpart. This is due to the efficient utilization of electrode materials with higher specific electrode surface area in a 3D configuration. The similar symmetric shape of the CV compared to bulk EC also indicates minimal distortions arising from the high current density of the small CE. Our results therefore collectively emphasize the immense potential of PLM as a robust and efficient microsystem for practical EC applications.

PLM as a microliter-scale spectroelectrochemical cell is further demonstrated by in situ reaction monitoring using SERS which further provides both molecular-level identification and quantification of the entire electron-transfer processes occurring at the electrode surface. At the initial potential of -0.05 V , we observe one SERS band centred at 495 cm^{-1} (Figure 2.5C, D). The SERS intensity of the 495 cm^{-1} band remains relatively constant even as potential decreases to -0.15 V . As the potential reaches -0.25 V , the SERS intensity of 495 cm^{-1} band begins to decrease with the concomitant emergence of a new vibrational feature at a more red-shifted region of 455 cm^{-1} .^{26, 27} Further regulation of applied potential to -0.5 V leads to a 4-fold decrease of 495 cm^{-1} SERS intensity, whereas

the band at 455 cm^{-1} increase by 3-folds. The SERS spectral changes are indicative of a single-step reaction occurring at the electrode surface. The band at 495 cm^{-1} can be assigned to the Ru^{3+} -N stretching while the 455 cm^{-1} band arises due to the Ru^{2+} -N stretching.^{26, 27} This agrees with the fact that as the charge on Ru decreases, the polar interaction between amine ligand and Ru^{2+} metal center is reduced. Consequently, Ru-N bond strength decreases (lower vibrational force constant) and causes the bond to vibrate at lower frequency compared to Ru^{3+} . The lower intensity of Ru^{2+} -N stretching could be due to the decrease in polarizability of the bond arising from the reduction of Ru^{3+} to Ru^{2+} . Our SERS observations therefore clearly correlate to the CV cathodic peak at -0.28 V where Ru^{3+} is reduced to Ru^{2+} . This is further supported by the appearance of a broad NH_3 rocking mode (585 cm^{-1}) at -0.25 V ,³⁶ which gradually experiences an increase in its intensity at more negative potential. Such phenomenon could be due to electric field-induced adsorption reorientations of the complex, whereby the closer proximity of ammine ligands to the Ag surface enhances its SERS responses.^{37, 38} It is also noteworthy that changes in these spectral features are reverted as the applied potential is tuned from -0.5 to the initial -0.05 V , a clear indication on the reversibility of the redox reaction. SERS intensity of Ru^{3+} -N mode at 495 cm^{-1} increases back to its maximal intensity while the Ru^{2+} -N vibrational mode diminishes to negligible intensity (<3 counts). Collectively, SERS- and electrochemically-active PLM is important to track both molecular and concentration changes during EC reaction at the electrode surface, notably using just $40\text{ }\mu\text{L}$ of the reaction solution.

Figure 2.5. (A) Scheme depicting EC-SERS investigation using PLM, (B) CV of 3D PLM shell (red) and 2D Ag nanocube-based WE (black), and silica liquid marble (SLM; blue). (C) SERS spectra changes when applied potential is scanned from -0.05 to -0.5 V and back. (D) Plot of SERS intensity as a function of potential at the 495 cm^{-1} band (blue) and 455 cm^{-1} band (orange). The bands are assigned to the $\text{Ru}^{3+}\text{-N}$ and $\text{Ru}^{2+}\text{-N}$ stretchings, respectively.

Heterogeneous electroreduction of methylene blue (MB^+) toxin is also performed as a second electrochemical model to demonstrate the versatility of our system in analysing multi-electron redox systems (Figure 2.6). As the potential is cycled between -0.1 and -1 V, MB^+ exhibits two cathodic peaks at -0.42 and -0.56 V (peak 1 and 2) and two anodic peaks at -0.47 and -0.31 V (peak 3 and 4) during the forward (-0.1 to -1 V) and reverse scans, respectively. Peaks 1 – 4 possess complementary peak currents of 8.7, 14.0, 6.5, and 13.0 μA , respectively. These peaks and their matching currents jointly reflect the two one-electron transfers from the applied current to MB^+ , resulting in the final reduced product,

leucomethylene blue (LMB). MB^+ first receives an electron to form radical $\text{MB}^\bullet$ (peak 1; $\text{MB}^+ \rightarrow \text{MB}^\bullet$). This is followed by protonation of $\text{MB}^\bullet$ to yield radical cation ($\text{HMB}^{\bullet+}$), which is then reduced by receiving another electron to produce LMB (peak 2; $\text{HMB}^{\bullet+} \rightarrow \text{LMB}$). Correspondingly, the reversed reactions of LMB oxidation to $\text{HMB}^{\bullet+}$, and to the initial MB^+ are assigned to peak 3 ($\text{LMB} \rightarrow \text{HMB}^{\bullet+}$) and peak 4 ($\text{MB}^\bullet \rightarrow \text{MB}^+$), respectively.³⁹ We highlight the importance of PLM's Ag shell as an active electron relay center to resolve multi-step electron transfers by comparing the electrochemical responses with control experiment involving naked reaction microdroplet placed on top of the Cu tape (Figure 2.6B). The control CV reveals only one anodic peak and overall sluggish electron transfer, reflecting an irreversible process during the oxidation of LMB back to MB in the absence of Ag shell. This evidently emphasizes the importance of Ag nanocube shell as an efficient electron transfer modulator between the externally-applied current to electro-active species which enables a more efficient reduction and its subsequent reversible oxidation process, resulting in enhanced degradation and representative EC investigations.⁴⁰

Next, we quantitatively track the structural changes of MB^+ at the Ag nanocube shell using in situ SERS, and relate the molecular-level information with the EC insights from the CV (Figure 2.6C, 2.7). In the reduction pathway, the nitrogen atom (yellow) of $\text{MB}^\bullet$ gains a proton (H^+) and results in a structural change of the molecule where the $\text{C}=\text{N}$ bond is reduced to $\text{C}-\text{N}-\text{H}$ in LMB. Hence, the sharp and intense $\text{C}=\text{N}$ stretching mode at 1639 cm^{-1} is selected to represent the presence of MB^+ (and also $\text{MB}^\bullet$) during the potential-dependent SERS investigation.⁴¹ In the forward scan from -0.1 to -0.5 V , the SERS intensities remain constant (~ 347 counts, $< 3\%$ change) because $\text{C}=\text{N}$ bond remains present even as MB^+ is reduced to $\text{MB}^\bullet$ at -0.42 V . This is followed by the onset reduction of SERS intensity to a minimum of 213 counts at -0.8 V after applied potential is reversed at -0.9 V . On the reversal of the applied potential, the SERS intensity increases and eventually

reaching a plateau of ~ 393 counts after -0.3 V, corresponding to the reduction peak of MB[•] to MB⁺ in the CV. Such observations can be explained using the Nernst equation, where the ratio reactant:product is dependent on the applied potential:

$$E - E' = -\frac{RT}{nF} \ln \left(\frac{[LMB]}{[MB]} \right)$$

Where E is the applied potential, E' is the half cell reduction potential, R is the universal gas constant, T is temperature in kelvins, n is number of electrons, F is the faraday constant, [Red] is the concentration of molecules in the reduced form, and [Ox] is the concentration of molecules in the oxidised form (MB).

Hence, upon reversal of potential to less negative potentials, the reduction of MB to LMB still occurs but the ratio of [LMB]/[MB] decreases. This is also in close agreement with previous spectroelectrochemical investigations.^{31, 42} Owing to the surface-sensitive nature of SERS, these intensities are directly proportional to MB⁺ concentration at the Ag shell,⁴³ and the spectral changes reflect the potential-dependent molecular changes during the MB⁺ redox, congruent to the EC insights derived from CV. Quantitative examination using SERS thus holds an advantage over UV-vis absorption spectroscopy, where the latter usually reveals bulk concentration changes that are not representative of the actual concentration profile at the electrode interface, especially for diffusion-limited analysis.⁴⁴ More importantly, structural changes, which cannot be obtained from UV-vis spectroscopy, can be identified from the molecular fingerprints changes during the electroreduction of MB⁺ to LMB. For example, the C=N-C ring stretching (1410 cm⁻¹) that is only present in MB⁺ attenuates by 3-folds while the weak C-N-C stretching mode (1524 cm⁻¹) belonging to LMB red-shift by 6 cm⁻¹ and increases 2-folds due to the formation of LMB (Figure 2.8).

Figure 2.6. (A) Heterogeneous reduction mechanism of MB. Colored regions highlight the chemical moiety that undergo molecular changes during the redox reaction. (B) CV of aqueous MB when isolated within PLM (pink), and without PLM (black). (C) Correlation of the electrochemical responses from CV (top) with SERS intensity (bottom) of 1639 cm⁻¹ band.

Figure 2.7. (A) Typical SERS spectrum of methylene blue. (B) Raman shift assignment of the characteristic vibration modes of MB.³¹

Figure 2.8. (A) Change in band intensities when MB+ reduces to LMB. De-convolution of spectral feature at ca. 1405 cm^{-1} into 2 SERS bands centered at 1400 cm^{-1} and 1410 cm^{-1} , which corresponds to C=C ring stretching and C=N-C stretching respectively. (B) De-convolution of spectral features between $1420\text{ cm}^{-1} - 1560\text{ cm}^{-1}$ gives 3 SERS bands centered at 1450 cm^{-1} , 1490 cm^{-1} , and 1524 cm^{-1} which can be assigned to C-N asymmetric, C=C and C-N-C stretching respectively. The reduction of MB+ to LMB causes the intensities for all bands to decrease, except for the C-N-C stretching band, which down shifts by 6 cm^{-1} and increases in intensity.

We exclude any potential EC and SERS interference from the Ag shell, electrolyte or systematic signal fluctuations from the consistent and featureless spectra in the control, in the absence of MB+ (Figure 2.9). Possibilities of systematic signal fluctuations in Ag shell is also eliminated owing to the constant SERS intensity (%RSD = 4%) of identical control PLM in absence of potential. Thus, these controls assert the SERS intensity changes are instigated by applied potential. In addition, PLM also offers ultrasensitive SERS activities for the determination of potential-dependent reaction kinetics (Figure 2.10). At -0.3 V , the temporal SERS intensity of the 1639 cm^{-1} band remains constant, and when the potential is at -0.5 V , we note the exponential decrease of SERS intensity, reaching an

eventual plateau at 310 counts after 9 min. Such exponential relationship can be modelled using a pseudo-first order kinetics equation of $I = 307 + 38.6e^{-0.240t}$, where I is the intensity in counts and t is the time in minutes. The close fit of the experimental data to the kinetics model affirm the first-order behavior of the electroreduction of MB^+ followed by protonation, where the rate constant is determined at 0.240 min^{-1} . Therefore, the onsite read-out of potential-induced molecular transformation clearly demonstrates the immense advantages of PLM to definitively identify EC species in its native reaction environment.

Figure 2.9. (A) SERS spectra of PLM encapsulating microdroplets of aqueous MB solution in 0.1 M KCl (blue), aqueous 0.1 M KCl solution in the absence of MB (red), and also pure water (black). (B) SERS spectra recorded from control PLM, prepared using aqueous 0.1 M KCl solution, at different applied voltages. (C) Scheme depicting the control EC-SERS set-up without applying voltage. (D) Temporal evaluation of SERS intensity of aqueous MB solution encapsulated in PLM when no potential is applied.

Figure 2.10. Temporal SERS intensities of aqueous MB in PLM at applied potential of -0.3 (red) and -0.5 V (blue).

Lastly, we demonstrate superior SERS and EC capability of the PLM over controls involving conventional 2D micro-platform and non-plasmonic active silica liquid marble (SLM; Figure 2.11A - D). Notably, the SERS intensity using PLM is >10 -fold higher than its 2D counterpart, prepared by the pre-deposition of Ag nanocubes onto the copper tape, while SLM exhibits negligible SERS response. These two control micro-platforms therefore emphasize the importance of 3D Ag nanocube shell in PLM for SERS enhancements. The better SERS performance in PLM over other systems stems from the direct sensing of the analyte at the top of PLM's Ag nanocube shell, which enables a more accessible pathway for the excitation laser to reach the SERS platform and effective collection of Raman scattered lights back to the detector. In the contrary, the laser and Raman scattered light are required to travel through the aqueous solution to reach the control 2D SERS platform at the bottom and detector, respectively, which could be both attenuated by the light-absorbing dye solution and impede the successful recording of vital molecular signatures. The remarkable SERS capability of PLM is again highlighted via its ~ 5 -fold higher sensitivity (115 counts/ 0.1 V) compared to the conventional 2D control (24 counts/ 0.1 V) (Figure 2.11F), allowing the accurate distinction of minute concentration changes. This is especially

critical in temporal SERS measurements, where any low intensity and its associated high error (average %RSD = 63 %) of the SERS measurements could severely hinder the representative elucidation of temporal information and reaction kinetics (Figure 2.11G). Collectively, these comparisons therefore clearly reflect the ultrasensitivity of the PLM-based spectroelectrochemical micro-reactor necessary for efficient EC-SERS characterization, especially for EC processes with low species concentrations and/or weak Raman scattering.

Figure 2.11. Scheme of different WE using (A) PLM, (B) 2D layer Ag nanocubes deposited on Cu tape, and (C) SLM. (D) SERS intensity of MB using (A-C). (E-G) Comparing the performance of PLM (pink) and 2D Ag nanocube layer (blue) as a spectroelectrochemical platform; (E) SERS spectra of MB. (F) Plot of SERS intensity changes with voltage. (G) Temporal SERS intensities of aqueous MB solution at -0.5 V. All intensities are obtained based on MB's 1639 cm^{-1} C=N mode.

2.3 Conclusion

In conclusion, we utilize the highly versatile PLM as an isolated and smallest 3D miniature reactor for simultaneous molecular-level analysis of EC processes. Together with its dual functionalities as SERS-active platform and working electrode, PLM's Ag shell also facilitates electron relay and demonstrates immense potential for real-time molecular-level identification of transient species, using the electrodegradation of a toxin as a model. These insights are crucial for elucidation of tandem EC reactions dynamics, which is not possible via standalone EC methods. More importantly, our novel 3D electrode exhibits 2-fold and 10-fold better electrochemical- and SERS-activities than their conventional 2D counterparts. Despite the potential window limit of Ag, the rich information and excellent performance offered by PLM still serves as an important proof of concept, which can be easily extended to vast nanomaterials of various materials or shape to better cater for specific experiment conditions. This finding is valuable to impact future design of 3D electrode system for enhanced electrochemical performance relevant in the broad applications in environmental conservation, energy harvesting, and biochemical charge transfer.

2.4 Materials and methods

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1, 5-pentanediol ($\geq 97\%$), poly (vinylpyrrolidone) (PVP; average MW = 55000), hydrochloric acid (HCl; 37%), methylene blue ($\geq 82\%$), decane (anhydrous, $\geq 99\%$), potassium ferricyanide (99%), hexaammineruthenium (III) chloride (98%) were purchased from Sigma Aldrich; copper (II) chloride ($\geq 98\%$) was from Alfa Assar; ethanol (ACS, ISO, Reag. Ph. Eur) was from EMSURE®; Potassium chloride (AR) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals were used without further purification.

Milli-Q water ($> 18.0 \text{ M}\Omega \cdot \text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis and purification of Ag nanocubes. Ag nanocubes were synthesized in high yield via the polyol method according to literature.⁴⁵ Copper (II) chloride (8 mg/mL), poly (vinylpyrrolidone) (20 mg/mL) and silver nitrate (20 mg/mL) were separately dissolved in 10 mL 1, 5-pentanediol after repeated sonication and vortex mixing. 35 μL copper (II) chloride solution was subsequently added to the silver nitrate solution. 20 mL of 1,5-pentanediol was added into a 100-mL round bottomed flask and heated to 190°C for 10 min. 250 μL poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s while 500 μL silver nitrate precursor was injected every minute using a quick addition. The addition process continued until the greenish coloration of the mixture faded off.

HCl treatment of Ag nanocubes. The removal of surfactant from Ag nanocubes surface was referred to method in literature.⁴⁶ 100 μL of purified Ag nanocubes in ethanol suspension (10 mg/mL) was added to 5 mL hydrochloric acid (0.1 M) in water under stirring condition. After 3 h, the Ag nanocubes colloidal suspension was then washed with pure water and ethanol multiple times to remove excess HCl. The HCl-treated Ag nanocubes were subsequently re-dispersed in ethanol (10 mg/mL) for further use.

Preparation of plasmonic liquid marble (PLM). 30 μL ethanolic solution of HCl-treated Ag nanocubes (10 mg/mL) was added into a 2 mL centrifuge tube and dried with nitrogen gas. 300 μL decane was then added to the centrifuge tube and sonicated to uniformly disperse the Ag nanocubes in decane. A 40 μL water droplet containing nitrogen-purged hexaamineruthenium (III) chloride (5 mM) or methylene blue ($10^{-4} - 10^{-3} \text{ M}$) in KCl (0.1M), was dispensed into Ag nanocube-containing decane suspension and rolled to form plasmonic liquid marble.

Electrochemical studies. Three-electrode system was used. The working electrode (WE) used was Ag nanocubes shell of the liquid marble, the counter electrode (CE) was a Pt Wire, and silver/silver chloride (Ag/AgCl) wire was used as quasi-reference electrode (RE). The Ag/AgCl wire was removed from the glass frit in order to reduce its size so that it can be inserted into the small liquid marble. CE and RE were fitted with inert pipette tips, revealing only the ends of the electrode. Hexaamineruthenium (III) chloride (5 mM) or methylene blue (1 mM) was prepared and KCl (0.1M) was used as electrolyte (pH 6.3). Copper tape was used to draw electric charge to the PLM. Cyclic voltammetry measurements were taken at a scan rate of 50 mV/s from at different potential ranges.

In situ Electrochemical SERS. The schematic setup and actual setup were as shown in Figure 2 and 3. Copper tape (15-cm) was attached to the mid-point of a petri dish to facilitate electrical flow to the liquid marble. Copper tape (4x 1.5-cm) was also used to create a platform to stabilize the position of the plasmonic liquid marble. 30 mL decane was added, and the PLM (containing 10^{-4} M MB with 0.1 M KCl) was transferred into the petri dish. The petri dish was placed on the Raman sample stage and positioned such that the laser spot is in the middle of the marble. The CE and RE were fitted with inert pipette tip at the ends to prevent electrical contact with the Ag shell. The electrodes were tilted to an approximate angle of 30° respective to the stage and brought close to the plasmonic liquid marble. The Raman stage was then adjusted to focus the laser. Finally, the electrodes were carefully inserted into the plasmonic liquid marble. The potential was stepped from -0.1 V to -0.9 V and back to -0.1 V at 0.1 V intervals. At each interval, the potential was held constant for 10 minutes and Raman measurements were acquired at every 1-minute interval simultaneously.

SERS measurement on plasmonic liquid marble. The as-prepared plasmonic liquid marbles (40 μ L) encapsulating methylene blue were transferred onto the Raman

sample stage for SERS evaluations. The SERS characterization for plasmonic liquid marble encapsulating KCl (0.1M) and aqueous methylene blue solution were performed at room temperature ($\sim 22^{\circ}\text{C}$). SERS measurement is performed using a hyperspectral x-y imaging mode with an acquisition time of 1 s/line and a laser power of 0.065 mW.

Characterization. SEM imaging was performed using JEOL-JSM-7600F microscope. UV-vis spectra was measured with Cary 60 UV-vis spectrometer. SERS measurements were performed using x-y imaging mode of the Raman touch microspectrometer (Nanophoton Inc., Osaka, Japan) with an excitation wavelength of 532 nm and laser power of 65 μW . A 50 $\times$ objective lens (N.A. = 0.55) with 1 s acquisition time was used for data collection. All SERS spectra were obtained by averaging the individual SERS spectra within the SERS image. Microscopic images were taken with Olympus BX51 microscope under 10 $\times$ (0.30 BD) objective lens. Cyclic voltammetry, chronoamperometry and linear sweep voltammetry was performed using Metrohm Auto lab potentiostat instrument.

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Chapter 3: Plasmonic Nose: Integrating MOF-enabled Molecular Preconcentration with Plasmonic Array for Molecular-level Volatile Organic Compounds Recognition

Abstract. Timely detection of toxic vapor is vital in safeguarding people's lives. Herein, we design a plasmonic nose based on zeolitic imidazolate framework (ZIF)-encapsulated Ag nanocubes array for ultratrace recognition of VOCs vapor. The plasmonic nose enables in-situ adsorption kinetics and recognition of various VOCs at ppm levels, eliminating false-positives. Our approach provides a paradigm shift as next-generation, effective and specific gas sensor.

3.1 Introduction

Toxins are most potent in the vapor form as they can readily access our respiratory system to cause instantaneous harm even at the parts per million (ppm) level.¹ However, human olfactory systems are often inept at discerning these lurking dangers owing to limited sensitivity. To maintain environmental and industrial safety, surface-enhanced Raman scattering (SERS) spectroscopy-based sensor emerges as a powerful gas detection technique by offering molecular-specific information even at trace concentration.² Notably, these SERS-based sensors also address the limitations of commercial gas sensing devices³ such as high quantification limit, long response time and/or susceptibility to false positive response due to the lack of molecular specificity/recognition. Furthermore, SERS also surpasses other analytical methods such as surface plasmon resonance or refractive index which mostly depend on indirect physical changes and cannot provide molecular structure information.⁴ These multitude of benefits potentially allows SERS-based platforms to function as a ‘plasmonic nose’, capable of “sniffing” out gas components at the molecular-level with sensitivity far surpassing that of human’s nose. Despite the immense potential, current SERS-based gas detection must be coupled with additional pre-treatment system such as thermoelectric cooler to condense gas onto the analytical platform. Direct gas detection remains a challenge due to their low concentrations and poor affinity to the plasmonic-active surface.

The integration of metal-organic frameworks (MOFs) with SERS overcomes these limitations because MOFs can confine gas molecules directly at the SERS-active surfaces, even in the absence of gas condenser or specific gas-surface affinity. This imparts molecular preconcentration effect that greatly enhance SERS performance, allowing the detection of molecules down to femtomolar level.⁵⁻⁷ Thus far, most MOF-based SERS systems are utilized for aqueous/liquid sensing applications, while gas detection is still non-trivial due

to poor plasmonic enhancements and background interference problems. Such limitations arise from the typical use of impregnation-based particle synthesis, which is difficult to control particle size, shape and density for optimal SERS activities. More importantly, a critical drawback from all current methods is that they only focus on gas adsorption using MOFs, which alone do not fully utilize the three-dimensional (3D) spatial field enhancements and is insufficient to tackle the pressing sensitivity issue. A multifaceted approach to overcome MOF-SERS performance bottleneck is therefore required for sensitive and rapid molecular-level readout in practical vapor detections, and in kinetic studies involving gas molecules.

Herein, we design a plasmonic nose based on a zeolitic imidazolate framework (ZIF)-encapsulated Ag nanocube platform (Ag@ZIF) to concentrate both gas molecules and electromagnetic (EM) field at the nanometer-scale in three-dimensional (3D) space, achieving ultratrace SERS detection of non-adsorbing volatile organic compounds (VOCs) down to ppm level. Our plasmonic nose consists of multifaceted strategies to achieve low gas detection limit – (1) optimizing the effective preconcentration of gas, and (2) intensifying EM hotspots by manipulating plasmonic coupling between adjacent Ag nanocubes. We first maximize the SERS performance by modulating both the ZIF thickness and interparticle spacing, and further highlight the importance of intense EM field to better utilize the sorbed molecules in 3D space for SERS detection. Subsequently, we demonstrate MOF layer is critical for in situ kinetics investigations due to their excellent sensitivity and responsiveness towards gas detection compared to their absence. Exploiting the molecular vibrational fingerprint, our plasmonic nose is also able to “sniff out” and quantify several toxic VOCs and poly(cyclic) aromatic hydrocarbons (PAHs) vapors (such as toluene, 4-methylbenzenethiol (4MBT), 2-naphthalenethiol (2NT) and chloroform) below regulatory limits, surpassing the human nose. Together with its excellent recyclability, these valuable

insights are important to push for even better regulatory standards to enforce safety and conserve life.

3.2 Results and discussion

We design ultrasensitive Ag@ZIF-based plasmonic nose (Figure 3.1A) by leveraging on both ZIF's preconcentration effect for gas accumulation and concentrating plasmon-induced EM fields via organization of Ag nanocubes (Figure 3.2). Using a repeated growth method, we encapsulate the assembled Ag nanocubes array on Si substrate with ZIF film via immersion into a solution containing zinc nitrate and 2-methylimidazole.⁴ ZIF first nucleates onto the Ag nanocubes and silicon surface, and then thickens into a polycrystalline thin film over the array. By increasing growth cycles (from 1 to 5), the thickness of the pristine ZIF film above the nanocubes can be systematically controlled from 8 to 287 nm (Figure 3.1B, 3.1C). The ZIF film also becomes more continuous and homogenous as its coverage on the Ag nanocubes array increases from an initial 64% to an eventual 100% as the number of coating cycles increase (Figure 3.3). Henceforth, various Ag@ZIF platforms are described as 'Ag@ZIF-(X)', where X denotes the ZIF growth cycles to form respective Ag@ZIF.

Figure 3.1. (A) Scheme of “plasmonic nose” concept based on a two-pronged approach in tuning plasmonic hotspots and MOF thickness. (B) Cross-sectional SEM images of the ZIF film thickness after one (top) and three (bottom) ZIF growth cycles. Scalebar, 100 nm. (C) Thickness of ZIF film above the nanocubes as a function of growth cycles. (D) XRD characterization of Ag@ZIF before (blue) and after activation at 120 °C for 2 hours under vacuum (green), and also neat ZIF film (pink). (E) SERS spectrum of 4-methylbenzenethiol (4MBT) recorded from Ag@ZIF-(3). (F) Schemes depicting the SERS experimental set-up (left) and increased accumulation of gas with increasing thickness of ZIF film (right). (G)

SERS intensity of 4MBT vapor as a function of ZIF growth cycles. The SERS intensities are based on 4MBT's characteristic vibrational mode at 1079 cm^{-1} . Eye-guided dotted line represents the trend.

Figure 3.2. Characterization of as-synthesized PVP-coated Ag nanocubes. (A) SEM image of Ag nanocubes. (B) Size distribution of Ag nanocube edge length. The average edge length is measured at $(138 \pm 7)\text{ nm}$. (C) UV-vis extinction spectra of the PVP-coated Ag nanocubes colloidal solution in ethanol. The peaks at 353, 400, 505 and 724 nm that can be assigned to octupole (353 nm), quadrupole (400 nm and 505 nm), and dipole resonances (724 nm).⁸

Figure 3.3. (A-C) SEM images of ZIF-8 film growth after 1 - 3 cycles. Dotted lines show the ZIF-8 film growth over the nanocubes. The first cycle result in minimal film growth and individual ZIF-8 crystals are observed. Upon additional growth cycle, the film thickens and becomes more continuous but is insufficient to completely encapsulate the Ag nanocubes array. A minimum of 3 cycles is needed to allow complete and homogenous encapsulation of the nanocubes. Yellow lines outline the ZIF-8 film overgrowth on the Ag array.

The thickness and coverage of ZIF film over Ag nanocube array directly impact the volume of gas that can be preconcentrated near the plasmonic nanoparticles surface for enhanced SERS detection. We investigate this by assessing the SERS responses of gas

molecules recorded from Ag@ZIF platforms constructed from different ZIF growth cycles. We choose 4MBT as our probe because their distinct and consistent vibrational fingerprints allow representative comparison across various Ag@ZIF platforms. Prior to SERS measurement, Ag@ZIF platforms are thermally-activated and this treatment process does not affect Ag@ZIF's structural integrity (Figure 3.1D, 3.4). 4MBT solid is then incubated in an enclosed Raman cell with various platforms to allow vaporization of 4MBT into an equilibrium state in the closed system (Figure 3.1F). All Ag@ZIF platforms exhibit the characteristic peaks of 4MBT at 1079 cm^{-1} (ν_{CS} , β_{CCC}), 1181 cm^{-1} ($\nu_{\text{C=C}}$) and 1595 cm^{-1} ($\nu_{\text{C=C}}$) (Figure 3.1E).⁹ Using the most intense band at 1079 cm^{-1} , we observe a general increase in SERS intensity with thicker ZIF film. This is followed by the plateau of SERS intensity at (620 ± 84) counts beyond the third cycle ($d = 146\text{ nm}$) (Figure 3.1G). Consequently, the optimal ZIF thickness is determined at 146 nm , which demonstrates a notable ~ 2.5 -fold higher SERS activity compared to control Ag nanocube array without ZIF. This corresponds to an analytical enhancement factor (AEF) of 7.6×10^6 and 3×10^6 for Ag@ZIF-(3) and control platform, respectively (refer to Calculation 3.1).

Calculation 3.1: Calculation of Analytical Enhancement Factor (AEF)

Calculation of AEF using saturated methylbenzenethiol gas is as follows:

$$\text{Analytical EF} = [I_{\text{SERS}} / I_{\text{Raman}}] \times [C_{\text{Raman}} / C_{\text{SERS}}]$$

where C_{SERS} and C_{Raman} are the corresponding concentration measured using Ag@ZIF substrate and normal Raman respectively. I_{SERS} and I_{Raman} are the signals recorded using SERS and normal Raman at their respective concentration per unit time.

C_{SERS} is calculated by manipulating the terms in the ideal gas law:

$$C_{\text{SERS}} = \frac{n}{V} = \frac{p}{RT} = \frac{108}{8.31 \times 298} = 0.0434\text{ mol/m}^3$$

Where p is the partial pressure ($= 108\text{ Pa}$) at ambient temperature ($T = 298\text{ K}$), and R is the universal gas constant, 8.31 J/Kmol .

C_{Raman} is calculated by dividing the density of 4MBT by its molecular weight:

$$C_{\text{Raman}} = \frac{\rho}{\text{MW}} = \frac{1.022 \text{ g/mL}}{124 \text{ g/mol}} = 0.008228 \text{ mol/mL}$$

Hence, using Ag@ZIF substrate formed using surface pressure of 16 mN/ m as an example,

$$\begin{aligned} \text{AEF} &= [I_{\text{SERS}} / I_{\text{Raman}}] \times [C_{\text{Raman}} / C_{\text{SERS}}] = (660/ 18) \times (8228/ 0.0434) \\ &= 7.10 \times 10^6 \end{aligned}$$

The effect of ZIF growth cycles on Ag nanocubes highlights two contributing factors affecting SERS response – (1) an increase in film coverage and (2) in film thickness. While the increment in film coverage does increase the averaged SERS intensity, we note the sudden surge in SERS activity enabled by thicker ZIF film in Ag@ZIF-(3). This is due to the increased accumulation of gas along the z-depth (Figure 3.1F, 3.3) which maximizes the amount of analyte molecules within the intense and z-extended EM hot spots imparted by Ag nanocubes. Beyond the optimal thickness (3rd cycle), the SERS intensity remains constant because any further accumulation of 4MBT along the z-direction is too far to experience the enhanced EM field and therefore, contributes negligibly to the overall SERS responses. Our Ag@ZIF ensemble is a clear progress from previous MOF-SERS works involving core-shell Ag@ZIF, where the latter demonstrates an optimal shell thickness of only 3.2 nm using small (~ 54 nm) and pseudo-spherical nanoparticles.¹⁰ The better utilization of the sorbed gas molecules could potentially arise from the more intense EM field enhancements. This is achieved using larger and shape-controlled Ag nanocubes and the extensive plasmonic coupling among adjacent particles. Notably, these observations are also aligned with previous theoretical studies reporting that smaller nanoparticles are inherently weaker scatterer and experience faster electric field decay¹¹ because of surface plasmon damping via non-radiative processes.^{12, 13} Hereon, we use Ag@ZIF-(3) for optimization of SERS performance.

Figure 3.4. SEM images of Ag nanocubes assembled using surface pressure of 16 mN/ m after (A) functionalization with PFDT, followed by (B) (i) 3 cycles of ZIF-8 and then (C) (i) thermally activated under vacuum at 120°C for 2 hours. Scale bar, 200 nm. (ii) Thickness distribution of the ZIF film. Thermal stability of ZIF-8 film over Ag nanocubes is reflected by the minimal changes even after activation. (D) XRD spectra before and after activation shows minimal difference.

Plasmonic coupling modulation between Ag nanocubes is also key to effect intense EM field enhancements in 3D space and can be achieved by controlling the interparticle spacing (Figure 3.5A).¹⁴ Briefly, we use Langmuir-Blodgett as a liquid-air interfacial assembly technique to systematically vary the Ag nanocube packing density.^{15, 16} Our platform does not involve polymeric template, therefore eliminating potential background signal interferences.¹⁷ Uniform and large-scale array comprising of a monolayer of Ag nanocubes with precisely tunable compactness is realized via the isothermal compression by a mechanical barrier to alter interfacial surface pressure (Π). As Π is varied from 4 to 18 mN/m, the interfacial film evolves from light brown to metallic silver due to enhanced plasmonic coupling as its compactness increases from a particle density of 9 to 51

particles/ μm^2 , respectively (Figure 3.5B, C, 3.6).¹⁸ Using Ag@ZIF-(3) platform and 4MBT as gaseous probe, we observe an obvious ~5-fold linear enhancement to SERS sensitivity as Π increases from 4 to 16 mN/m owing to enhanced plasmonic coupling between adjacent particles (Figure 3.5D). Constant SERS intensity at 617 counts with negligible improvements are obtained for $\Pi = 18$ mN/m. This is possibly due to the balance between stronger plasmonic coupling with opposing effect arising from reduced molecular accessibility to the plasmonic surfaces at high particle compactness.¹⁹ It is also noteworthy that Ag@ZIF-(3) fabricated at a more compact $\Pi = 16$ mN/m enables a homogenous distribution of SERS activities across the entire platform while control substrate formed at $\Pi = 4$ mN/m are sporadically located. Collectively, our findings clearly demonstrate that both the MOF thickness and the intense EM field rendered by extensive plasmonic coupling within a compact Ag nanocube array are the keys to maximize SERS sensitivity crucial for ultrasensitive gas phase detection.

We further demonstrate the concept of the plasmonic nose to capture and direct gaseous analytes towards the ZIF-encapsulated plasmonic surface for rapid molecular detection. Time-dependent SERS monitoring on the sorption of vapor 4MBT is employed to reveal the sorption kinetics of gas to Ag surface in both Ag@ZIF-(3) and control Ag nanocube without ZIF coating (Figure 3.5E). For Ag@ZIF-(3) platforms, 4MBT's SERS intensity increases exponentially from (40 ± 10) to (432 ± 5) counts within 80 seconds and subsequently plateaus after equilibrium is reached (Figure 3.5F, G). More importantly, the additional ZIF film over the Ag nanocubes improves SERS performance by > 3-fold over the control, where the latter acquires a lower intensity of (136 ± 3) counts only after 120 s. Using a Lagergren pseudo first order sorption kinetics, we further determine that the sorption rate constant of Ag@ZIF-(3) is 66 ms^{-1} and notably ≥ 2 -fold higher than the control. This evidently underlines that Ag@ZIF platform is critical to impart intense and rapid SERS

response whereby ZIF swiftly captures and concentrates analytes to the plasmonic surface while the intense EM hot spots conferred by Ag nanocube array permits sensitive monitoring of temporal sorption events.

Figure 3.5. (A) Scheme shows reducing the interparticle spacing enhances the plasmonic coupling and the resultant EM field surrounding the Ag nanocubes. (B, C) (i) SEM images and (ii) SERS image of Ag nanocube array prepared at surface pressures of 4 and 16 mN/m. Scalebar of SEM, 200 nm. Scale bar of SERS image, 1 μm . (D) Comparison of SERS intensity and respective AEF using Ag@ZIF-(3) arrays prepared at various surface pressures. (E) Scheme depicting temporal gas sorption. (F) Time-dependent SERS

comparing platforms with (red) and without (black) ZIF film upon incubation of 4MBT vapor. (G) Graph depicting the rate constants of respective platforms. Intensities are based on 4MBT characteristic SERS band at 1079 cm^{-1} .

Figure 3.6. (A) (i-iii) Digital images of the visual changes observed as the compactness of the Ag nanocube array increases from 4, 10, 16 mN/m. (B) (i-vi) SEM images of assembled Ag nanocube array when surface pressure is 4, 10, 12, 14, 16, 18 mN/m respectively.

Using our optimized Ag@ZIF-(3) ensemble fabricated at $\Pi = 16\text{ mN/m}$ (hereon termed as Ag@ZIF plasmonic nose), we demonstrate the quantitative and molecular-level identification of VOCs, which are toxic yet prevalent in air due to their wide industrial usage (Figure 3.7A). We first use commonly-used toluene as our model VOC because it has no chemical affinity to Ag. This enables us to examine our platform as a universal gas sensor

for a wide range of toxic VOC and poly(cyclic) aromatic hydrocarbon (PAHs). SERS responses recorded from our Ag@ZIF plasmonic nose clearly exhibit vibrational features unique to toluene even at a remarkable detection limit down to 200 ppm ($AEF > 2 \times 10^5$), with distinctive peaks at 1002 cm^{-1} , 1030 cm^{-1} , and 1210 cm^{-1} indexed to $\nu_{C=C}$.²⁰ Ag@ZIF also permits the linear quantification of toluene vapor over three orders of magnitude (200 to 20000 ppm) (Figure 3.7B). Quantifying toluene concentration in this range is crucial as the hazardous vapor could lead to acute symptoms ranging from throat/eye irritation to even death. The detection limit is also well within the Occupational Safety and Health Administration (OSHA) exposure limit which is vital to drive continual revision of toxic gas threshold to ensure better industrial safety. Our plasmonic nose is also easily recycled owing to their reversible host-guest interactions upon subjecting to vacuum, as demonstrated from the reproducible SERS readout ($< 1\%$ standard deviation) and similar structural integrity after 4 cycles of detections (Figure 3.7C, 3.8).

Our Ag@ZIF plasmonic nose is also versatile and can discern a series of PAH and VOC including chloroform and 2NT, which are frequently emitted by the industry/laboratories and require constant monitoring. Both analytes exhibit their unique SERS vibrational features even at respective detection limits. For chloroform, the peaks at 363 cm^{-1} and 665 cm^{-1} correspond to the δ_{CCl} and ν_{CCl} respectively, while 2NT is identified by the peaks at 780 cm^{-1} ($\delta_{C=C}$), 1065 cm^{-1} (δ_{CH}) and 1375 cm^{-1} ($\nu_{C=C}$) (Figure 3.7D, 3.9).²¹,²² Notably, the limit of detection (LOD) of 2NT is down to the 50 ppb, 15-fold lower than the exposure limits of 5 mg/m^3 (0.7 ppm). The ability to distinguish different gas molecules via their vibrational signatures is vital to accurately attribute the gas and eliminate false positives – a function lacking in most commercial detectors. Importantly, our platform directly measures gas species from air which surpasses previous SERS-based gas detectors that typically requires post-treatment of gas.²³ We also note the consistent ~2-fold

enhancement to SERS intensity across all vapor analytes when compared to control platform without ZIF, further affirming the preconcentration effect imparted intrinsically by the ZIF film (Figure 3.7E).

Figure 3.7. (A) SERS spectrum of toluene vapor recorded using Ag@ZIF (B) Linear correlation of SERS intensities with toluene concentration. Dotted line represents the linear regression line. The potential acute health hazards are included. (C) Normalized SERS intensities measured from a single Ag@ZIF platform after exposure to toluene and vacuum repeatedly. The recyclability is reflected by the absence of toluene spectra after vacuum and consistent signals upon toluene incubation. The intensities are based on the band at 1002 cm^{-1} . (D) SERS spectra for 2NT (top) and chloroform (bottom) vapor. (E) Enhanced detection of toluene, 2NT, and chloroform of Ag@ZIF platforms when compared to control Ag nanocube array in the absence of ZIF.

Figure 3.8. SEM images of Ag@ZIF substrate (A) before and (B) after exposure to toluene for four cycles. ZIF film remains intact even after subjecting the substrate to toluene vapor and vacuum repeatedly. (C) Cross-sectional SEM image (top) and corresponding ZIF-8 film thickness distribution of (B) (bottom). Dotted line denotes the ZIF film layer.

Figure 3.9. (A – C) SERS spectrum comparing detection of 2-naphthalenethiol, chloroform and toluene in gaseous phase using Ag@ZIF substrate (red) and Ag only (black). Raman spectra (pink) of the liquid solvent is added for reference. Inset shows the molecular structure of each VOC. Carbon, Hydrogen, Sulphur and Chlorine atoms are represented by grey, beige, yellow and magenta spheres respectively.

We further compare the SERS performance of our Ag@ZIF plasmonic nose across other control platforms to highlight the importance of each individual components in our combinative approach. These control platforms include bare Ag nanocubes (absence of ZIF), core-shell Ag@ZIF dispersed onto a Si substrate (absence of intense plasmonic coupling), Ag film@ZIF and ZIF only platforms (Figure 3.10, 3.11). Generally, Ag@ZIF ensemble clearly outperforms all other platforms, achieving > 2-fold and 6-fold higher SERS sensitivity than Ag nanocubes only and Ag@ZIF core shell, respectively. The superior performance of our Ag@ZIF platform stems from its ability to concentrate both molecules and EM field cumulatively for better SERS enhancement compared to controls without ZIF or assembled arrays. We also note that control Ag film@ZIF and ZIF only platforms exhibit featureless spectra, again accentuating the need for high quality plasmonic crystal for sensitive SERS read-out. Our findings collectively highlight that MOF-enabled molecular preconcentration and intense EM field generated by extensive plasmonic coupling between Ag nanocubes are the key to ultrasensitive and swift vapor/gas detection. These benefits are highly sought after to ensure timely response necessary to protect the safety of the public in event of potential toxic gas leakage and/or air pollution from anthropogenic or natural sources.

Figure 3.10. Demonstration on the superior SERS performance of Ag@ZIF. (A) Scheme of the Ag@ZIF platform with other control platforms such as (B) Ag nanocubes only, (C) Ag@ZIF core-shell particles, (D) Ag film@ZIF and (E) neat ZIF platform, and (F) comparison of their SERS activity.

Figure 3.11. SEM images of the control platforms; (A) Ag@ZIF core-shell, (B) Ag film@ZIF and (C) ZIF film (cross-sectional view) only. Scale bar, 200 nm. Comparison of the SERS performance of different platforms. The SERS intensities are obtained from the 1002 cm^{-1} band of toluene.

3.3 Conclusion

In conclusion, we have designed a MOF-encapsulated Ag nanocubes-based plasmonic nose capable of ultrasensitive SERS recognition of multiple gaseous VOCs down to ppm levels. Two key factors are essential towards the realization of efficient plasmonic nose: (1) the thickness of the pristine ZIF film which directly influences the preconcentration of molecules in the z-depth, and (2) extensive plasmonic coupling arising from compact Ag nanocube array that allows 5-fold amplification in SERS signal. Notably, our plasmonic nose enables both in situ gas sorption kinetics analysis, and quantitative detection of non-adsorbing toluene vapor. Our plasmonic nose is also versatile and can discern a series of toxic VOCs at the molecular-level. These valuable insights could potentially provide a paradigm shift in the future design of MOF-SERS sensors, empowering ultrasensitive detection capability beyond boundaries which is critical in the shaping of better toxic gas regulation for industrial safety.

3.4 Materials and methods

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1, 5-pentanediol ($\geq 97\%$), poly (vinylpyrrolidone) (PVP; average MW = 55000), 1H,1H,2H,2H-perfluorodecanethiol (PFDT, $\geq 97\%$), zinc nitrate hexahydrate (98%), 2-methylimidazole (99%), 4-methylbenzenethiol (4MBT, $\geq 98\%$), 2-naphthalenethiol (99%), chloroform, toluene, decane (anhydrous, $\geq 99\%$), were purchased from Sigma Aldrich; copper (II) chloride ($\geq 98\%$) was from Alfa Assar; ethanol (ACS, ISO, Reag. Ph. Eur) was from EMSURE®. All chemicals were used without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis and purification of Ag nanocubes. Ag nanocubes were synthesized in high yield via the polyol method according to literature.²⁴ Copper (II) chloride (8 mg/mL),

poly (vinylpyrrolidone) (20 mg/mL) and silver nitrate (20 mg/mL) were separately dissolved in 10 mL 1, 5-pentanediol after repeated sonication and vortex mixing. 35 μ L copper (II) chloride solution was subsequently added to the silver nitrate solution. 20 mL of 1,5-pentanediol was added into a 100-mL round bottomed flask and heated to 190 °C for 10 min. 250 μ L poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s while 500 μ L silver nitrate precursor was injected every minute using a quick addition. The addition process continued until the greenish coloration of the mixture faded off.

For the purification of Ag nanocubes, 1, 5-pentanediol was first removed from the mixture through centrifugation and then washed with ethanol. The Ag nanocubes were then dispersed in 10 mL ethanol and 100 mL aqueous poly (vinylpyrrolidone) solution (0.2 g/L). The resulting solution was vacuum filtered using Durapore® polyvinylidene fluoride filter membranes (Millipore) with pore sizes ranging from 5000, 650, 450, and 220 nm, repeated several times for each pore size. The Ag nanocubes were then re-dispersed in ethanol (10 mg/mL) and stored in fridge for further use.

Assembly of Ag nanocubes via Langmuir-Blodgett method. Si (100) substrates were cleaned prior to assembly of Ag nanocubes using oxygen plasma (FEMTO SCIENCE, CUTE-MP/R, 100 W) for 5 min. The surface pressure was zeroed before addition of PVP-capped Ag nanocubes. 700 μ L of the ethanolic purified Ag nanocubes was dispersed in 1050 μ L of chloroform and then added carefully to the surface of the water in the Langmuir-Blodgett trough (KSV NIMA, KN1002). The surface pressure can be tuned by moving the mechanical barrier of the machine. Surface pressure of 4, 8, 10, 12, 14, 16, 18 mN/ m were performed, and the pull rates and compression rate were fixed at 2 mm/ s.

1H,1H,2H,2H-perfluorodecanethiol (PFDT) functionalization of Ag nanocubes. The removal of surfactant from Ag nanocubes surface was done by

functionalizing the assembled Ag nanocubes with PFDT. The assembled Ag nanocube array was immersed in 5 mM of PFDT methanolic solution for at least 15 hours.

Growth of ZIF-8 film on PFDT-capped Ag nanocubes array. ZIF-8 film was grown on the nanocubes array using a procedure reported from literature.⁴ 2 mL of methanolic $\text{Zn}(\text{NO}_3)_2$ (25 mM) was added to 2 mL of methanolic 2-methylimidazole (mIM; 50 mM) and mixed quickly for 5 s. For one growth cycle, the PFDT-capped Ag nanocubes substrate was immersed in the solution for 40 minutes, and then washed with copious amount of methanol and dried with nitrogen gas several times to remove excess ZIF-8 crystals. The procedure was repeated (1 – 5 times) using fresh $\text{Zn}(\text{NO}_3)_2$ and 2-methylimidazole solutions to obtain ZIF-8 films of increasing thickness.

Activation of Ag@ZIF substrate. The Ag@ZIF substrates were thermally activated to remove any solvent molecules within its pores by heating the substrate under vacuum at 120°C for 2 hours. The substrates are used immediately after activation.

Fabrication of Ag film@ZIF. 25-nm Ag film was deposited onto the O_2 plasma-treated Si wafer using a thermal evaporator deposition system from Syskey Technology Corporation (Taiwan) system. The deposition rate was 0.5 Å/s which was monitored using a quartz crystal microbalance. Ag target with 99.99% purity was purchased from Zhongnuo Advanced Material (Beijing) Technology co., Ltd. The Ag film was then functionalized with PFDT and then with 3 layers of ZIF-8 using the same procedures as above.

Fabrication of ZIF only. Silicon substrate was directly immersed in a fresh mixture containing 2 mL of methanolic $\text{Zn}(\text{NO}_3)_2$ (25 mM) and 2 mL of methanolic 2-methylimidazole (mIM; 50 mM) for 40 minutes, and then washed and dried under nitrogen flow. Additional 2 growth cycles were carried out to achieve ZIF film of similar thickness to Ag@ZIF platform.

Synthesis of Ag@ZIF core-shell. 250 μL of $\text{Zn}(\text{NO}_3)_2$ (25 mM) was added to a vial of 1.3 mL methanol and stirred at 500 rpm for 5 minutes. 250 μL of methanolic 2-methylimidazole (50 mM) was then added, followed by the immediate addition of 200 μL Ag nanocubes solution (4.7 mg/mL). The mixture was stirred for another 90 minutes at 500 rpm. Excess reagents were removed by centrifugation and the core-shell nanoparticles were then washed twice with methanol and then finally re-dispersed in methanol.

SERS measurement of VOCs and PAH vapors. The activated Ag@ZIF substrate or Ag nanocubes only substrate is incubated together with 200 μL or 0.05 g of solvent/solid at ambient conditions in an enclosed Raman cell printed using Form 1+ stereolithography 3D printer. The SERS detection was performed 10 or 30 mins after incubation of vapor at room temperature ($\sim 20^\circ\text{C}$). Time-dependent investigations were performed using Ag@ZIF-(3) fabricated at $\Pi = 12 \text{ mN/m}$. For VOCs detection, optimized Ag@ZIF-(3) fabricated at $\Pi = 16 \text{ mN/m}$ is employed. SERS measurement is performed using a hyperspectral x-y imaging mode with an acquisition time of 1 s/line or 15 s/line (for toluene and chloroform) and a laser power of 0.5 mW or 0.38 mW respectively, unless otherwise stated.

Characterization. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) imaging was performed using JEOL-JSM-7600F microscope. UV-vis spectra were measured with Cary 60 UV-vis spectrometer. Substrate X-ray diffraction patterns were recorded on a Bruker GADDS XRD diffractometer with Cu K α radiation. SERS measurements were performed using x-y hyperspectral imaging mode of the Ramantouch microspectrometer (Nanophoton Inc., Osaka, Japan) with an excitation wavelength of 532 nm and laser power of 0.5 mW or 0.38 mW. A 50 $\times$ objective lens (N.A. = 0.55) with 1 s or 15 s acquisition time was used for data collection. All SERS spectra were obtained by averaging the individual SERS spectra within the SERS image.

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Chapter 4: Turning Water from a Hindrance to the Promotor of Preferential Electrochemical Nitrogen Reduction

Abstract. Electrochemical nitrogen reduction reaction (NRR) offers a sustainable ammonia production but suffers from poor performance owing to favorable water electrolysis. Recent designs achieve better efficiency by eradicating water, but do not leverage on water as a readily-available NRR proton source. Herein, we design a hydrophobic oleylamine-functionalized zeolitic-imidazolate framework coated over electrocatalyst to achieve >18% NRR efficiency in the presence of water, a ~4-fold boost compared to without water. Our strategy kinetically regulates water availability at the electrocatalyst surface, suppresses direct water adsorption/electrolysis, and promotes preferential nitrogen adsorption to achieve water-assisted NRR. Conversely, control systems without hydrophobic modification experience drastic decrease in efficiencies (<3%) upon water addition. In-situ SERS investigation reveals that our hydrophobic system's ability in suppressing water accessibility to the electrocatalyst is the key to transform water from a hindrance to an NRR promotor. Our universal design is a paradigm shift from current approaches to achieve sustainable air-to-ammonia electrosynthesis.

4.1 Introduction

Electrochemical nitrogen reduction reaction (NRR) offers an attractive renewable approach to produce ammonia as green fuel and nitrogenous chemical precursors directly from abundant nitrogen.¹⁻⁴ Notably, a library of protic solvents can be used as the proton source to produce ammonia, as compared to H₂ obtained from energy-intensive steam reforming in Haber-Bosch process.^{1, 5-10} Among all protic solvents, water is the most ideal proton source because it is renewable and omnipresent in the form of atmospheric water vapor. While the use of water mimics the natural ammonia synthesis using nitrogenase, the efficient use of water in NRR is severely daunted by the interference from the two-electron hydrogen evolution reaction (HER), which is kinetically more favorable compared to a six-electron NRR.¹¹⁻¹³ This issue is further exacerbated by the preferential proton (water) adsorption on effectively all traditional metal NRR catalysts, making H₂ evolution the dominant reduction reaction as long as protons are readily available near the electrocatalyst surface.^{12, 14}

Theoretically, it has been proposed that regulating protons availability at the electrode can effectively deter direct proton adsorption and thus prohibits competing HER.^{13, 15, 16} This is because the rate-determining step of HER is first-order with respect to proton concentration while that of NRR has a zeroth-order relationship.¹¹ To efficiently suppress HER and enhance NRR, we hypothesize that it is critical to control and minimize direct proton adsorption at the electrocatalyst surface. As such, N₂ molecules can be first adsorbed onto electrocatalytic surfaces and subsequently be protonated by the incoming protons for preferential NRR. Current NRR strategies typically use non-aqueous electrolyte and completely exclude water from the reaction system.^{6,7,15-17} However, it is impractical in real applications to exclude trace water because water is omnipresent even in atmospheric air and its potential use as an NRR proton source directly from atmospheric vapor. For

instance, it has been shown that using hydrophobic fluorinated ionic liquid as electrolyte can achieve NRR efficiencies of 32%. However, the presence of trace moisture (>180 ppm) drastically reduces efficiencies to <10%.¹⁷ It is therefore crucial to design new NRR strategy that efficiently utilizes water as a proton source, rather than eradicating water, for the promotion of preferential NRR processes.

Herein, we kinetically regulate water availability at the conventionally water-intolerant NRR electrocatalyst surface to transform water into an efficient proton source, notably achieving enhanced efficiencies of >18% at ambient conditions that is 4-fold higher than in the absence of water. Our design involves the coating of a zeolitic-imidazolate framework-71 (ZIF) layer on NRR electrocatalysts to concentrate reactants and we further modify ZIF to impart water-regulating abilities via two ways: (1) surface modification with hydrophobic oleylamine to ensure both its exterior surfaces and interior pores are water repelling (Figure 1a (i)), and (2) inclusion of butanol that is preferentially absorbed in ZIF compared to water to further impede water transportation within the ZIF pores (Figure 1a (ii))¹⁸⁻²⁰. We hypothesize that by exploiting the hydrophobic ensemble to retard water (proton source) access, we allow first the preferential nitrogen adsorption and saturation on the electrocatalyst surface. The surface nitrogen can then react with the incoming water to realize a kinetically controlled water-assisted NRR. Our strategy uniquely controls water access directly at the point-of-use (at electrode surface) and differs from traditional approach that modifies the entire bulk electrolyte. When our electrolyte is spiked with water to mimic the trace water content in ambient air, our electrocatalyst platform improves efficiencies by ~4-fold compared to the absence of water, attaining a maximum faradaic efficiency (FE) of > 18% at 0.1% v/v. In contrast, control electrocatalyst without hydrophobic modification experiences drastic decrease of NRR FE to < 3% when spiked with similar water content. These findings clearly verify our hypothesis that the effective

regulation of water accessibility can transform it from a hindrance to an effective proton source for NRR. Corroborating extensive cyclic voltammetry and molecular-level surface-enhanced Raman scattering (SERS) investigations, we further elucidate the kinetics of water accessibility to the electrocatalyst surface and highlight the integral role of both oleylamine and butanol to promote water-assisted NRR while suppressing HER. Our electrocatalyst platform design is a universal and modular system, which can be easily integrated with various emerging NRR catalysts to expedite progress toward high catalytic performance and direct atmospheric nitrogen reduction.

4.2 Results and discussion

Our electrocatalyst design comprises two parts, using hydrophobic oleylamine (OAm)-functionalized ZIF to encapsulate the metallic electrocatalyst (M@ZIF-OAm) and enriching ZIF with butanol as a molecular filler to collectively impede water. We first fabricate the M@ZIF platform by using HCl-treated Ag nanocubes (119 ± 4 nm) on Au electrode as a bimetallic electrocatalyst and encapsulating it with ZIF coating. The ZIF coating serves two purposes; (1) ZIF can concentrate N_2 molecules and reactants close to the electrode surface for efficient reaction; (2) the intrinsic hydrophobic pores of ZIF can repel trace water to favor the NRR process.²⁰⁻²² Furthermore, the hydrophobic nature of ZIF-71 renders the material to be thermally and kinetically stable even in the long term.²³ The addition of Ag nanocubes acts as the electrocatalyst which is previously demonstrated to boost NRR.⁶ The nanocubes also function as a SERS platform to subsequently track the access of water to the electrocatalyst surfaces in real time. This bimetallic design is employed because of the synergistic effect between the Ag and Au that achieves higher catalytic performance.⁶ Briefly, the Ag nanocubes are dropcasted onto Au electrode and subsequently encapsulated with a ZIF layer via an overgrowth method to form M@ZIF

electrode (Figure 4.1a). The ZIF nucleates onto the Ag nanocubes and Au surface to form a polycrystalline thin film of thickness ca. (342 ± 31) nm. X-ray diffraction (XRD) analysis indicates the successful formation of M@ZIF (Figure 4.2, 4.3).

a Transforming water from hindrance to proton source

Figure 4.1. Characterization of oleylamine-functionalized zeolitic imidazole framework-71 encapsulating Ag nanocube array platform (M@ZIF-OAm). (a) Scheme depicting the strategy to transform water into efficient NRR proton source by regulating access of water to electrocatalytic surface. This is achieved by two integral strategies; (i) surface modification with oleylamine to restrict access of water molecules into the ZIF pores and (ii) addition of butanol as a molecular filler within the pores to further retard water molecules to enhance NRR instead of undergoing competing HER. (b) Cross-sectional

scanning electron microscope (SEM) image of oleylamine-functionalized M@ZIF substrate (M@ZIF-OAm). (c) ATR-FTIR spectra of the respective ZIF platforms. (d) Schematic of ZIF without and with surface modification by oleylamine functionalization, and its respective contact angle measurements.

Figure 4.2. Characterization of M@ZIF before and after oleylamine functionalization. (a) Before functionalization and (b) after functionalization with oleylamine. (i) Top view SEM image of ZIF. (ii) Cross-sectional SEM images of the M@ZIF platforms. (iii) ZIF thickness distribution.

Figure 4.3. Substrate XRD diffraction pattern of as-synthesized ZIF, M@ZIF, M@ZIF-OAm, thermal-activated M@ZIF-OAm and M@ZIF-OAm immersed in the THF-based electrolyte for approximately 6 h (from bottom to top).

We subsequently functionalize the M@ZIF electrode with a monolayer of hydrophobic oleylamine molecules on ZIF surface. Briefly, the M@ZIF platform is immersed into oleylamine solutions for an optimized duration of 40 min.^{24, 25} Cross-sectional SEM image depicts that the electrocatalyst remains fully encapsulated by the ZIF film after functionalization (Figure 4.1b, 4.2b). The presence of oleylamine on ZIF surface is affirmed by the emergence of characteristic oleylamine stretching peaks at 1643, 2853, and 2927 cm^{-1} characterized using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), and also the presence of $-\text{NH}_2$ species peak in surface-sensitive XPS measurements (Figure 4.1c, 4.4).²⁶⁻²⁹ Importantly, the increase in contact angle from 90° to 120° after immersion denotes the successful functionalization of oleylamine onto the ZIF film to render additional hydrophobic property to its surface (Figure 4.1d). We also note that these oleylamine molecules are only attached to the exterior ZIF surface but not within the interior ZIF pores. This is demonstrated via SERS characterization which indicates the absence of oleylamine vibrational signature at/near the Ag surface after the functionalization step (Figure 4.5). Both the surface functionalization and subsequent thermal activations do not change the ZIF intrinsic crystal structure as evident from the similar XRD patterns (Figure 4.3).

Figure 4.4. High resolution XPS scans of N 1s region of ZIF without (top) and with (bottom) oleylamine functionalization.

Figure 4.5. SERS spectra of M@ZIF before and after oleylamine functionalization. (a) Scheme (i) and SERS spectra (ii) when Ag@ZIF is functionalized with ZIF and (b) Ag-only platform functionalized with OAm. No oleylamine vibrational peaks are observed when Ag is encapsulated by ZIF. This is in contrast with the oleylamine peaks present after bare HCl-treated Ag is immersed under the same functionalization conditions.

To modulate water accessibility for suppression of HER, our strategy involves two integral parts; (1) using oleylamine as a molecular barrier (Figure 4.1a(i)) and (2) butanol as molecular filler within the ZIF network (Figure 4.1a(ii)). We affirm the importance of these two components by performing electrochemical investigations on three electrocatalytic systems in the presence of water, namely (1) oleylamine-functionalized M@ZIF (M@ZIF-OAm), (2) M@ZIF, as well as (3) M@ZIF-OAm in electrolyte without butanol (Figure 4.6). Our electrocatalysis setup comprises a three-electrode system (counter electrode, Pt wire; reference electrode, Ag/AgCl) immersed in dry tetrahydrofuran (THF) as the solvent and lithium trifluoromethanesulfonate as the conducting electrolyte. In addition, 1% v/v butanol is added into the electrolyte as a molecular filler within the ZIF pores to further impede water entry, unless otherwise stated. ZIF is known to possess selective adsorption of butanol over water deters water molecules from passing through easily.^{16,17} Butanol may also serve as a proton source for NRR when water is initially absent at the electrocatalytic surfaces. The electrolyte is subsequently spiked with 0.25% v/v water to simulate the total amount of moisture that may enter the electrolyte from the atmosphere (refer to Calculation 4.1). Cyclic voltammetry (CV) is subsequently performed under ambient open conditions by scanning toward the cathodic direction with a potential range from -0.5 V to -3.0 V under constant nitrogen (N₂) or argon (Ar) bubbling.

Firstly, when using M@ZIF-OAm working electrode with butanol under N₂ bubbling, the cathodic scan depicts a distinct reduction peak at -2.5 V. Subsequent reverse scan from -3 V to -0.5 V shows the presence of an oxidation peak at -1.8 V (Figure 4.6a). This is in contrast with control experiment performed under Ar bubbling, which exhibits only the oxidation peak at -1.8 V. We therefore attribute the reduction peak at -2.5 V (with onset potential at -2.0 V) as a nitrogen-related reduction process and eliminate the possibilities of the peak arising due to the ZIF-OAm or any electroactive species present in

the electrode/electrolyte system. The oxidation peak that is observed in both N₂ and Ar conditions is likely due to alcohol (butanol)-related oxidation, which is consistent with literature work.⁶

In contrast, control experiments involving M@ZIF in the presence of butanol and M@ZIF-OAm without butanol demonstrate different CV responses (Figure 4.6b, c). In both electrocatalytic systems, cathodic scans in the presence of N₂ result in a steep increase in current beyond onset potential at around -1.3 V. When the electrolyte is bubbled with Ar, the CV cathodic features of both electrocatalytic systems are similar with an almost identical onset potential. Together with the absence of NRR's characteristic cathodic peak at -2.5 V, our results in Figure 2b and c highlight that the cathodic responses starting at -1.3 V are due to a faradaic process that is not N₂-related and is possibly attributed to HER, as supported by previous literature.⁶ The slightly higher current observed in Ar conditions compared to in N₂ could indicate an increase in HER. This phenomenon is likely due to the absence of N₂ adsorption on the catalyst surface, which in turn allows water molecules to approach the catalyst surface more easily.³⁰ We note that using M@ZIF working electrode (Figure 4.6b) results in slightly higher current between -1.3 to -3.0 V compared to the use of M@ZIF-OAm without butanol (Figure 4.6c). This underlines the importance of hydrophobic oleylamine as surface barrier to reduce water accessibility to the system which in turn reduces the HER rate. Likewise, the replacement of butanol with ethanol also results in HER evolutions (Figure 4.7). This is because ZIF has a lower selectivity toward ethanol adsorption, the use of ethanol as the molecular filler is inept in modulating water entry. This further emphasizes the role of butanol as a molecular filler because it is preferably absorbed by ZIF to effectively block water accessibility to the electrocatalyst surface and suppress HER.^{16,17,31} Collectively, these observations highlight that the synergy between oleylamine

surface functionalization and butanol is essential to achieve efficient control of water accessibility to enhance NRR while suppressing HER.

Figure 4.6. Elucidation of the role of various components in water transport regulation across ZIF layer to electrode surface. (a – c) Schematic illustrations (left) and respective CV responses (right) of various electrochemical setup when employing M@ZIF-OAm electrode, and controls using M@ZIF only electrode, and M@ZIF-OAm electrode in the absence of butanol as a molecular filler. The electrochemical investigation is performed in a three-electrode electrochemical setup. Pt wire and Ag/AgCl (1 M KCl) are used as counter (CE) and reference electrodes (RE), respectively. All platforms are preactivated at 120 °C under vacuum for 2 h.

Figure 4.7. CV response of M@ZIF-OAm electrode in electrolyte containing ethanol instead of butanol as molecular filler. The same molecular size of ethanol makes it to be a less efficient molecular filler compared to butanol which results in HER evolution. The electrochemical investigation is performed in a three-electrode electrochemical setup. Pt wire and Ag/AgCl (1 M KCl) are used as counter (CE) and reference electrodes (RE), respectively.

Calculation 4.1 – Estimation of moisture content in air

The calculation of the moisture content in air is calculated below:

According to Guide to Meteorological Instruments and Methods of Observation, World Meteorological Organization, 2008, the saturation vapor pressure (e_w) at 298 K, 1 atm is 31.75 hPa. Given that the average relative humidity (RH) in Singapore is 80%, the actual vapor pressure (e) is given by:

$$e = e_w \frac{RH}{100} = 31.75 \times 0.80 = 25.4 \text{ hPa}$$

Using the ideal gas law,

$$pV = nRT$$

$$eV = \frac{m}{M}RT$$

Where p is the partial pressure ($= e$) at ambient temperature ($T = 298\text{ K}$), m is the mass of water, M is its molecular weight and R is the universal gas constant, 8.31 J/K.mol .

The mass of water vapor per unit volume of air can thus be obtained by rearranging the equation:

$$\frac{m}{V} = \frac{eM}{RT} = \frac{2450 \times 18.0152}{8.31 \times 298} = 18\text{ g/m}^3$$

Given that the nitrogen gas flow is 3 sccm for a total of 360 min, the total volume of gas is 1080 cm^3 . By determining the overall volume of gas used, this translates to the total mass of water accumulated if ambient air is used:

$$\text{Mass} = \frac{3 \times 360}{10^6} \times 18 = 0.0194\text{ g}$$

$$\%v/v = \frac{0.0194}{9} \times 100 = 0.216\%$$

Hence, when using ambient air as the N_2 source, the amount of water accumulating in the electrolyte reaches 0.216%. This estimated water content is crucial as a reference that should be taken in consideration when designing NRR systems that are geared toward realizing ambient air-to-ammonia conversion.

We then evaluate the NRR performance of our M@ZIF-OAm working electrode against M@ZIF without oleylamine functionalization to highlight the performance of our hydrophobic design in utilizing water for selective NRR. The NRR performance of each electrocatalyst system is assessed using two metrics, namely the effective rate of ammonia formation and faradaic efficiency (FE) (methods). In particular, high FE translates to efficient utilization of the total electrons supplied to form ammonia. To assess the effect of water content on the overall NRR efficiency, we systematically spike the electrolyte with 0 – 0.25% v/v water. Typically, the system is flushed with N_2 for at least 15 min and ammonia is electro-synthesized by applying a potential of -2.9 V for 6 hours under continuous N_2

bubbling (3 sccm at 298 K and 1 bar). The ammonia generated in the THF solvent is harvested via Berthelot's reaction to produce blue-colored indophenol blue, which can be quantified using UV-visible spectroscopy because of its strong absorbance at 638 nm (Figure 4.8a, 4.9). Notably, the indophenol blue method is a standard protocol to quantify ammonia with high reproducibility and remains widely used to assess NRR performance of electrocatalysts.³²⁻³⁵ In addition, Berthelot's reaction using hypochlorite/phenol to form indophenol blue dye is only selective to ammonium. Presence of other nitrogenous interferences including amine undergoes nucleophilic addition to form an intermediate that is sterically hindered and inhibits the formation of indophenol. Thus it is not affected by the presence of other nitrogenous interferences.³⁶ Nonetheless, to eliminate potential background interference that may arise from other nitrogenous sources possibly from the ZIF, electrolyte and gases, we subtract all rates of ammonia production and FEs achieved when bubbling N₂ with that of blank experiments performed under Ar.³⁷ Herein, the effective rate of production and FE which represents the ammonia originating from electrochemical nitrogen-to-ammonia conversion are discussed.

The FE of M@ZIF-OAm working electrode increases significantly from (5 ± 1)% to (18 ± 1)% from 0 – 0.1% v/v water (Figure 4.8b), and then decreases slightly to ~10 % beyond 0.1% v/v water. Similarly, the effective rate of ammonia increases from (8.4 ± 1.2) μg_{NH3} h⁻¹ mg_{cat.}⁻¹ to (45.3 ± 2.9) μg_{NH3} h⁻¹ mg_{cat.}⁻¹ as water content increases to 0.1% v/v before slightly decreasing to (18.6 ± 0.6) μg_{NH3} h⁻¹ mg_{cat.}⁻¹. The performance across all conditions spiked with water results in higher FE than in the absence of water. Notably, the peak FE of 18% in the presence of 0.1 % v/v trace water is ~4 -fold higher than the 5% FE obtained in the absence of water. The water content-dependency of the ammonia production rates and FE validates that varying the water amount within the electrode interface alters the kinetics between H- and N-adsorption. The slight decrease in FE upon the addition of

water beyond 0.1% v/v is likely because additional water encourages faster diffusion of water from the bulk electrolyte to the electrode surface, thereby promoting H⁺-adsorption for HER. Thus, this is a direct evidence that we kinetically control water accessibility and successfully allow preferential nitrogen adsorption followed by reaction with the incoming water for enhanced water-assisted NRR while deterring water adsorption that leads to HER.

Conversely, in the absence of hydrophobic surface modification, control M@ZIF working electrode achieves the highest performance in the absence of water, with the FE and ammonia production rate at $(5 \pm 0.2)\%$ and $(21 \pm 7.2) \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{mg}_{\text{cat.}}^{-1}$, respectively. A slight addition of water to the electrolyte from 0.05% v/v to 0.25% v/v results in a drastic decrease in both FE and ammonia production rate to almost 0% and $0 \mu\text{g}_{\text{NH}_3} \text{h}^{-1} \text{mg}_{\text{cat.}}^{-1}$ respectively. Such significant decrease in FE in the presence of water for M@ZIF system highlights the detrimental effects of water in conventional electrocatalyst system, where water is a persistent interference to NRR because competing water electrolysis is more favored over NRR. Our results show that while the ZIF interior is hydrophobic, it is insufficient to kinetically control water accessibility when higher concentrations of water are present. Correspondingly, M@ZIF-OAm working electrode achieves > 16-fold higher FE and > 75-fold increase in rate of ammonia production at 0.25% v/v water. In addition, we subject the electrode to continuous cyclic voltammetry over 80 cycles and achieve relatively consistent current density compared to initial at -2.9 V, demonstrating the stability of our M@ZIF-OAm design to sustain the catalysis over multiple cycles (Figure 4.10). Thus, given the strong propensity for water to undergo HER as highlighted in the control experiments and in other works^{7, 13, 14, 17} the ability of our design to boost the FE even in the presence of water is a paradigm shift from conventional knowledge.

Notably, we affirm that the ammonia produced is contributed by the electroreduction of N_2 gas because the values are obtained after being subtracted from control experiments using Ar gas under the same conditions. This thus eliminates any ammonia that could be form from N-containing materials/contaminants present. We further exclude the possibility of contaminants from N_2 gas source because the maximum possible ammonia from potential contaminants in N_2 gas was previously calculated to be $< 2\%$.⁶ In addition, our rate of ammonia generation is comparable to many reports.^{6, 30, 38-41} While there are indeed works that achieve higher ammonia yields, our main objective is to demonstrate a strategy to turn water into a promoter. This could potentially be incorporated with other engineered catalyst to give multiplicative improvement to NRR performance. Thus, our approach overcomes the longstanding bottleneck of NRR where the omnipresent trace water is no more a persistent interference. This improvement thus allows for more versatile designs and eventually paves the way for ambient air as a direct source for N_2 and proton.

Figure 4.8. Affirming the water-assisted NRR phenomenon by assessing the rate of ammonia production and faradaic efficiency. (a) Schematic depicting the three-electrode

electrochemical setup of electrochemical nitrogen reduction reaction in the presence of 0 – 0.25% v/v water. The potential was applied at – 2.9 V for 6 hours under nitrogen or argon bubbling. The indophenol reaction is used for ammonia quantification and the UV-vis calibration curve is formed using standard ammonium solutions. (b) Effective rate of ammonia production and effective faradaic efficiency when using M@ZIF-OAm working electrode as the amount of water in the electrolyte is regulated. Both rate of ammonia production and faradic efficiency increases as the spiked water content is systematically increased. (c) Control experiment using M@ZIF electrode, where HER is predominant instead of NRR.

Figure 4.9. Absorption spectra of indophenol blue at various concentration and the linear co-relation of the absorbance intensity to the effective concentration of ammonium ions present to enable indophenol blue formation.

Figure 4.10. (a)(i-iii) Continuous cyclic voltammograms depicting electrochemical responses under N_2 using M@ZIF-OAm electrode for 80 cycles. (b) Percentage of current density relative to initial current at -2.9 V as the M@ZIF-OAm is subjected to continuous cyclic voltammetry for 80 cycles. The consistent and sustained current density across the number of cycles demonstrate the high stability of our catalytic system.

To verify our hypothesis and understand the origin of the water-assisted NRR from our electrocatalytic design, we perform *in-situ* SERS spectroscopy to systematically monitor the water diffusion into the electrode interface (Figure 4.11a). In the *in-situ* SERS experiments, we specifically graft our electrocatalyst (Ag nanocubes) surfaces with 4-mercaptopyridine (MPy) as the probe. MPy is a known molecular probe for hydrogen bonding, where its ring breathing mode ($1000 - 1030\text{ cm}^{-1}$ region) blue shifts when interacting with water/protons.^{42, 43} By monitoring the SERS spectra shift of MPy as it interacts with water (Figure 4.11), we can therefore *in-situ* track water molecules as they

diffuse into the ZIF-OAm scaffold to reach the underlying electrocatalytic surfaces. Prior to spiking with water, the immersion of MPy-capped Ag nanocubes in “dry” electrolyte reveals a SERS peak at 1017 cm^{-1} that is attributed to the Li^+ -bonded ring breathing mode of MPy (Li^+ is from the electrolyte). As M@ZIF-OAm is immersed in the electrolyte, the initial presence of the hydrogen-bonded peak at 1006 cm^{-1} could be due to the concentration of butanol at the catalyst-ZIF interface while the sharp peak at 1028 cm^{-1} is ascribed to the breathing mode when MPy interacts with the ZIF network (Figure 4.11b, Figure 4.12). Upon the diffusion of water to the electrocatalyst surface, one can expect the increase of the ring breathing peak at 1006 cm^{-1} . Here, we use the relative peak intensities of the hydrogen-bonded mode (I_{H}) and Li^+ -bonded mode (I_{Li}) ($I_{\text{H}}/(I_{\text{H}}+I_{\text{Li}})$) to monitor the water diffusion as the initial interactions of MPy with Li^+ is replaced with water.

To obtain the kinetics of water regulation, we acquire and compare the temporal SERS changes in MPy’s ring breathing mode regions recorded from (1) MPy-capped M@ZIF-OAm, (2) M@ZIF-OAm without butanol and (3) M@ZIF-only experiments as water is added to the “dry” THF electrolyte (Figure 4.11b). We track the real-time SERS responses and investigate the kinetics of water transportation into the ZIF and ZIF-OAm film (Figure 4c). Note that lower SERS intensity ratio ($I_{\text{H}}/(I_{\text{H}}+I_{\text{Li}})$) indicates less water within the ZIF interface, and vice-versa. All three systems generally exhibit a “S” shaped adsorption curve due to the initial deterrence of the water entry into the hydrophobic ZIF pores which in turn causes a lagged increase in peak ratio. For our MPy-capped M@ZIF-OAm electrode, the time-resolved intensity ratio of hydrogen-bonded to Li^+ -bonded peaks exhibits small increase from 0.47 to 0.53 within the 2 hours (Figure 4.11c, Figure 4.13a). This indicates that less water enters the electrode surface when using our M@ZIF-OAm platform as compared to platforms in the absence of OAm or butanol due to the deterrence of water from both components. In contrast, the SERS intensity ratios of the MPy-capped ZIF-OAm

without butanol and the MPy-capped M@ZIF-only electrodes increase to 0.70 and 1.0, respectively (Figure 4.13b, c). Especially for MPy-capped M@ZIF-only electrode, the Li+-bonded peak at 1017 cm⁻¹ is eventually replaced entirely by the hydrogen-bonded peak at 1006 cm⁻¹. This observation verifies the diffusion of water molecules into the scaffold and saturates the surface of MPy, akin to the scenario using M@ZIF-only electrode during NRR where excessive water enters the ZIF pores and results in HER. We also highlight that the temporal SERS evaluation remains unchanged throughout the 2 hours in the absence of spiked water (Figure 4.14). Hence, the spectral changes observed are indeed due to varying water content at the surface rather than the changes in butanol concentration. Collectively, the water sorption kinetics using SERS highlights that our hydrophobic design achieves a 9-fold higher water suppression. This verifies our hypothesis that the synergistic effect of both oleylamine and butanol is essential for efficient water control into the electrode interface. Such water control is thus the key to prevent water adsorption on the electrocatalysts surface and enable preferential nitrogen adsorption to realize water-assisted enhanced NRR efficiencies.

Figure 4.11. Time-resolved SERS measurement of water diffusion through the ZIF interior cavities using mercaptopyridine (MPy) as a hydrogen bond probe. (a) Schematic depicting the diffusion of water into MPy-capped M@ZIF and M@ZIF-OAm platforms. (b) Deconvoluted Raman bands of the breathing mode of MPy-capped M@ZIF and M@ZIF-OAm platforms in electrolyte before and after addition of water. (c) The ratio of the peaks at 1006 and 1017 cm^{-1} which is ascribed to the water (I_H) and electrolyte peaks (I_{Li}), respectively, is plotted against time. The trend line is fitted using the Yoon-Nelson adsorption model.

Figure 4.12. Experimental and simulated SERS spectra of mercaptopyridine when immersed in THF electrolyte containing Li salt and in water, respectively.

Figure 4.13. (a – c) Time-resolved SERS spectra of Ag-MPy-Au@ZIF, MPy@ZIF-OAm and MPy@ZIF-OAm (without BuOH) samples immersed in THF electrolyte after the addition of water. Shaded regions depict the deconvoluted peaks at the breathing mode of the MPy probe. The peak at 1006 cm^{-1} is indexed to the hydrogen-bonded MPy breathing mode (red) that arises due to the diffusion of water molecules to the Ag surface. The peak

at 1017 cm^{-1} (blue) is ascribed to the MPy breathing mode when Li^+ ions from the electrolyte interacts with N-atom of MPy.

Figure 4.14. Control experiment involving the time-dependent SERS spectra of Ag-MPy-Au@ZIF substrate immersed in THF electrolyte without addition of water. Shaded regions depict the deconvoluted peaks at the breathing mode of the MPy probe. The peak at 1006 cm^{-1} is indexed to the hydrogen-bonded MPy breathing mode (red) that arises due to the diffusion of water molecules to the Ag surface. The peak at 1017 cm^{-1} (blue) is ascribed to the MPy breathing mode when Li^+ ions from the electrolyte interacts with N-atom of MPy.

Finally, the universal nature of our design is exemplified by showcasing improved NRR performance using various common electrocatalysts, including platinum and ruthenium (Figure 4.15). We replace Ag electrocatalyst with Pt and Ru nanoparticles of similar sizes ($110 \pm 12\text{ nm}$, $178 \pm 17\text{ nm}$, respectively, Figure 4.16) and functionalize the electrode with ZIF-OAm coating.^{44, 45} Similar to previous experiments, the electrode is subjected to 6 hours reduction at -2.9 V , with and without water. In the presence of 0.1%

v/v water, the water-assisted enhanced NRR performance is observed regardless of the electrocatalyst used whereby the FE achieved for Pt and Ru reaches $(19 \pm 5)\%$ and $(15 \pm 2)\%$, respectively. Notably, when compared to the same system in the absence of water (Pt: $(6 \pm 1)\%$; Ru: $(5 \pm 2)\%$), additional FE enhancements due to water is $\sim 3 - 4$ -fold across all three electrocatalysts. This is especially notable because platinum is typically the traditional go-to catalyst that is highly active for HER, and its ability to sustain such high FE, even in the presence of water, exemplifies the successful transformation of water from a hindrance to a promotor. Importantly, this similar boost in FE achieved using our strategy further justify that the effective kinetic control of water accessibility is the key to the observed enhancement, and also highlights that our two-pronged modular electrocatalytic design is universal regardless of the electrocatalyst used. Consequently, our strategy to transform water from a longstanding interference into a readily available proton source opens the doors to explore various types of electrocatalysts regardless of their activity for HER.

Figure 4.15. Comparison of NRR performance across various metallic catalysts. (a) Scheme depicting the versatility of our modular strategy; the electrocatalysts used can be interchangeable and all exhibit water-assisted NRR. (b) Comparison of effective faradaic efficiency across all metals with (yellow) and without adding water as an enhancer (cyan). (c) Effect of water-induced NRR faradaic efficiency boost across all catalysts.

Figure 4.16. Characterization of metallic electrocatalysts. Characterization of a Platinum nanoparticles and b Ruthenium nanoparticles. (i) SEM images and (ii) Size distribution of respective nanoparticles.

4.3 Conclusion

In conclusion, our work highlights the importance of controlling water accessibility at the electrocatalytic surfaces to realize enhanced NRR while suppressing HER by designing a synergistic two-pronged approach using oleylamine as a surface barrier and butanol as a molecular filler. Importantly, our strategy successfully exploits water as an efficient proton source for NRR to boost the faradaic efficiency by ~4-fold in the presence of water as compared to in dry conditions. In contrast, control experiments without hydrophobic surface modification falter in the presence of water addition whereby HER prevails over NRR. Correspondingly, our hydrophobic M@ZIF-OAm electrocatalyst design achieves > 16-fold higher efficiency and > 75-fold increase in rate of ammonia production compared to systems without hydrophobic modification. Hence, we achieve the unprecedented transformation of water as a persistent hindrance to an efficient NRR proton source under ambient conditions. Electrochemical and SERS investigations reveal the integral role of both oleylamine and butanol in kinetically controlling water into the ZIF

scaffold, which is essential in averting water adsorption while promoting water-assisted NRR when the subsequent incoming water molecules protonates the selectively adsorbed nitrogen. Notably, our design is highly universal and employs a modular approach that can integrate seamlessly with emerging catalyst design to further boost their efficiency, even in the presence of water. We expect that the parallel development of both electrocatalyst properties and electrode/electrochemical system design will be key to achieve selective NRR under ambient conditions. These valuable insights therefore create the potential to design an ideal electrocatalytic system for high-performance and sustainable NRR with the grander prospect of using atmospheric air as both the N₂ and proton source directly.

4.4 Materials and methods

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55,000), zinc acetate dihydrate ($\geq 98\%$, ACS reagent), ethylene glycol (EG), L-ascorbic acid (99%), sodium citrate tribasic dihydrate ($\geq 99\%$, ACS reagent), citric acid, chloroplatinic acid hexahydrate (ACS reagent), ruthenium (III) chloride hydrate (99.98% metal), 4,5-dichloroimidazole ($\geq 98\%$), lithium trifluoromethanesulfonate (LiCF₃SO₃, 99.995%), sodium nitroprusside dihydrate ($\geq 99\%$, ACS reagent, Reag. Ph. Eur), ammonium sulfate ($\geq 99.0\%$), sodium dichloroisocyanurate dihydrate ($\geq 98.0\%$), 4-mercaptopyridine (95%), phenol ($\geq 99\%$, purified by redistillation) were purchased from Sigma Aldrich; oleylamine (80 – 90%) was from Acros Organics; sodium borohydride (97+%), copper (II) chloride ($\geq 98\%$) was from Alfa Aesar; methanol ($\geq 99.9\%$) and tetrahydrofuran (THF, $\geq 99.0\%$, ACS) were from Fulltime®; ethanol (ACS, ISO, Reag. Ph Eur) and sodium hydroxide (NaOH, $\geq 99.0\%$) were from EMSURE®; N,N-dimethylformamide (DMF, ACS) was obtained from Tedia®; sulphuric acid ($\geq 95\%$) and hydrochloric acid (37%) were from VWR Chemicals; nitrogen (N₂, 99.999%,

ALPHAGAZ 1) and argon (Ar, 99.9995 %) were purchased from Singapore Oxygen Air Liquide Pte Ltd. THF was further dried by distilling commercial THF with sodium and benzophenone under inert N₂ environment. All other chemicals were applied without further purification. Milli-Q water (> 18.0 MΩ. cm) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis and purification of silver nanocubes. The preparation of Ag nanocubes was carried out following the method described in literature.⁴⁶ Briefly, 10 mL of copper (II) chloride (8 mg/mL), poly(vinylpyrrolidone) (20 mg/mL) and silver nitrate (20 mg/mL) were separately dissolved in 1,5-pentanediol. The chemicals were sonicated and vortexed repeatedly to dissolve them. 35 µL copper (II) chloride solution was then added to the silver nitrate solution. Then, 20 mL 1,5-pentanediol in a 100 mL round bottomed flask was heated to 190 °C for 10 min. 250 µL poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s while 500 µL silver nitrate precursor was injected every min using a quick addition. The addition process continued until the greenish coloration of the reaction mixture faded off.

For the purification of Ag nanocubes, 1,5-pentanediol was first removed from the mixture through centrifugation. The Ag nanocubes solution was then dispersed in 10 mL ethanol and 100 mL aqueous poly(vinylpyrrolidone) solution (0.2 g/L). The resulting solution was vacuum filtered using Durapore® polyvinylidene fluoride filter membranes (Millipore) with pore sizes ranging from 5000 nm, 650 nm, 450 nm and 220 nm, repeated several times for each pore size. The Ag nanocubes were later re-dispersed in ethanol. SEM imaging was performed and the edge lengths of 100 Ag nanocubes were measured and analyzed using ImageJ software.

Synthesis of Platinum nanoparticles. Platinum nanoparticles were synthesized following the method described in literature.³⁰ Briefly, Pt nanoparticle seed were prepared

by adding 3.6 mL of a 0.2% solution of chloroplatinic acid hexahydrate to 46.4 mL of boiling water. After 1 min, 1.1 mL of a solution containing 1% sodium citrate and 0.05% citric acid was added, followed half a minute later by a quick injection of 0.55 mL of a freshly prepared sodium borohydride (0.08%) solution containing 1% sodium citrate and 0.05% citric acid. After 10 min, the product was cooled down to room temperature. To form 29 nm seeds, to 1 mL of the platinum seed solution was added at room temperature to 29 mL of deionized water. 0.045 mL of a 0.4 M chloroplatinic acid solution was added, followed by 0.5 mL of a solution containing 1% sodium citrate and 1.25% L-ascorbic acid. Under stirring, the temperature was slowly heated to boiling. To obtain 100 nm nanoparticles, the synthesis was repeated by adding 0.25 mL of the 29 nm seeds to 29 mL water.

Synthesis of Ruthenium nanoparticles. Ruthenium nanoparticles were synthesized following the method described in literature.²⁹ Ruthenium chloride (3.48 mg) and PVP (18.6 mg) were added to 15 mL ethylene glycol. The solution was first heated to 160°C for 1.5 hours to form pale yellow seeds, and then heated at 180°C for 3 hours to form the larger nanoparticles.

Preparation of Ag-Au electrode. To prepare the Ag-Au electrode, 0.132 μ L of ethanolic PVP-capped Ag nanocube solution (3.5 mg/ml) was drop-casted onto a pre-polished Au electrode (2 mm diameter). The electrode was then immersed in 0.1 M HCl solution (20 % ethanol in water) for three hours and washed with copious amount of methanol. The as-prepared Ag-Au electrode was dried using a stream of nitrogen gas and stored under inert nitrogen condition.

Encapsulation of Ag-Au electrode with zeolitic imidazolate framework-71 (M@ZIF). Prior to ZIF synthesis, methanolic solutions of zinc acetate dihydrate (0.2 M) and 4,5-dichloroimidazole (0.4 M) were prepared separately. As-prepared Ag-Au electrode

was subsequently immersed into a 2 mL centrifuge tube containing 0.125 mL DMF, 0.375 mL MeOH and 0.25 mL of respective methanolic solutions of zinc and imidazole precursors. The reaction was allowed for 40 min and later washed with copious amount of methanol. ZIF formation reaction was repeated four more times to achieve a complete encapsulation over the Ag-Au surface. The electrode was dried using a stream of nitrogen gas and stored under inert nitrogen condition.

Functionalization of M@ZIF electrode. The M@ZIF electrode is further functionalized with oleylamine (OAm) by immersing the electrode into 1 ml oleylamine solution (0.1 M) for an optimized time of 40 min. The electrode was then washed with copious amount of methanol and dried using a stream of nitrogen gas.

Encapsulating Ag nanocube-dropcasted Au substrate with ZIF (M@ZIF substrate). Au films were first prepared using a thermal evaporator deposition system from Syskey Technology Corporation (Taiwan). A thickness of 18 nm Au film was deposited on an O₂ plasma-treated Si wafer (0.6 cm × 0.6 cm) at a deposition rate of 0.8 Å/s. The deposited rate was monitored in situ by a quartz crystal microbalance. Au source with 99.99% purity was purchased from Zhongnuo Advanced Material (Beijing) Technology co., Ltd.

Ethanol solution of Ag nanocubes was drop-casted onto the Au substrate (Ag-Au substrate) at a volume-to-area ratio of $\sim (4 \times 10^{-2}) \mu\text{L}/\text{mm}^2$, which is also similar to that used for M@ZIF-OAm electrodes. Upon drying, Ag-Au substrate was subsequently immersed into a 2 mL centrifuge tube containing 0.125 mL DMF, 0.375 mL MeOH and 0.25 mL of respective methanolic solutions of zinc (0.2 M) and imidazole (0.4 M) precursors. The reaction was allowed for 40 min and later washed with copious amount of methanol. ZIF formation reaction was repeated four more times to achieve a complete encapsulation over the Ag-Au surface. The substrate is then immersed in oleylamine

solution to functionalize the surface with oleylamine. M@ZIF-OAm substrate was dried using a stream of nitrogen gas and stored under inert nitrogen condition prior to subsequent cross-sectional SEM imaging and XRD characterizations.

For MPy-capped M@ZIF platforms, the Ag-Au substrates were first immersed in 5 mM mercaptopyridine solution for 15 min and then washed with copious methanol. After drying with N₂, the MPy-capped Ag-Au substrate is then immersed into the 2 mL centrifuge tube containing ZIF precursors to form encapsulate the substrate with ZIF as described earlier.

Thermal activation of various platforms. Prior to latter application in electrochemical nitrogen-to-ammonia conversion, all platforms were thermally activated at 120 °C under vacuum for two hours to evacuate residual methanol residing in ZIF's intrinsic pores after its synthesis. Such heat treatment does not alter the structural and chemical identity of our platform, ensuring the integrity of its respective constituents for efficient and selective electrochemical reaction.

Electrochemical nitrogen reduction reaction. Electrolyte solutions were prepared by adding LiCF₃SO₃ (0.2 M) in a solvent mixture containing ~ 1 % butanol in “dry” THF. The THF-based electrolyte solutions were bubbled with respective N₂ or Ar gas for at least 15 min prior to electrochemical experiments. These gas flows were also maintained during the electrochemical measurements. All gases flowrates were controlled at ~ 3 sccm using mass flow controllers (model number MC-100SCCM-D) obtained from Alicat Scientific, Inc. Water (0 – 0.25 v/v%) was also spiked into the electrolyte to access the effect of water on NRR.

A three-electrode electrochemical set-up was employed where the counter electrode and reference electrode comprised of a Pt wire and silver/silver chloride electrode (Ag/AgCl; 1 M KCl solution), respectively. Working electrodes were composed of thermal-

activated M@ZIF-OAm electrode as well as control platform M@ZIF electrodes. Cyclic voltammetry measurements were recorded at a scan rate of 50 mV/s between applied potential of -3 V and -0.5 V (versus Ag/AgCl). Electrolyte solutions and type of gas used were also varied to identify the electrochemical peaks recorded from different working electrodes. Electrochemical conversions of nitrogen to ammonia for evaluation of Faradaic efficiency and ammonia formation rate were subsequently conducted using chronoamperometry at a constant applied potential of -2.9 V for 6 hours using respective combinations of working electrode and gas types. Ammonia generated were quantified using the indophenol blue method (stated in the following sections). All electrochemical experiments were performed under constant gas flow and at ambient conditions of 1 bar and 298 K.

Preparation of reagents for indophenol blue method. Two precursor solutions were required in the indophenol blue method and were named as Reagent A and Reagent B, respectively¹. Reagent A was prepared by dissolving phenol (0.1 M) and sodium nitroprusside dihydrate (0.2 mM) in water. Reagent B was prepared by dissolving sodium dichloroisocyanurate dihydrate (2.8 mM) and NaOH (0.13 M) in water. Both reagents were stored in fridge prior to their use.

Detection of ammonia using indophenol blue method. A calibration curve relating extinction intensity with ammonia/ammonium concentration was first established for subsequent quantification of ammonia produced in the electrochemical reaction. 10 mM ammonium sulfate were dissolved in aqueous sulfuric acid solution (10^{-3} M). The ammonium sulfate was then serially diluted to various concentrations between 10^{-6} M to 10^{-4} M. After which, an equivalent amount of “dry” THF electrolyte (containing 1 % butanol) was added to all the ammonium sulfate standard solutions. 0.2 mL of individual ammonium sulfate standard solutions was added to a glass vial containing 1 mL of reagent A. 1 mL of

reagent B was then added into the solution and allowed to react for 1 hour while being stirred at 500 rpm. Indophenol blue generated was identified and quantified using UV-vis spectroscopy.

To determine the ammonia generated during the electrochemical nitrogen-to-ammonia conversion, the THF-based electrolyte solution was added to an equivalent amount of aqueous sulfuric acid solution (10^{-3} M). 2 mL of this solution was added to a glass vial containing 1 mL of reagent A. 1 mL of reagent B was then added into the solution and allowed to react for 1 hour while being stirred at 500 rpm. Indophenol blue generated was identified and quantified using UV-vis spectroscopy. THF electrolyte solutions were primarily examined for ammonia because THF readily dissolves ammonia up to a high concentration of 0.4 M.

Determination of rate of ammonia formation and Faradaic efficiency. The ammonia formation rate and Faradaic efficiency were calculated using equation S1 and equation S2, respectively.⁴⁷

$$r_{NH_3} = \frac{[NH_4^+] \times V}{t \times A} \quad (S1)$$

where r_{NH_3} is the rate of ammonia formation ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$), $[NH_4^+]$ is the concentration of produced ammonium ion (equivalent to ammonia concentration), V is the volume of THF-based electrolyte solution, t is time of collection, and A is the overall electrocatalyst's area.

$$\text{Faradic efficiency (\%)} = \frac{3F \times r_{NH_3}}{I} \quad (S2)$$

where r_{NH_3} is the rate of ammonia formation, I is current density at constant applied voltage and F is the Faraday constant.

SERS evaluations. The thermal-activated MPy-capped M@ZIF-OAm platform and the electrolyte solution were placed inside a petri dish for SERS examination. Temporal

SERS measurements were performed before (time = 0 min) and after water is added into the “dry” electrolyte.

Material characterization. Scanning electron microscopy (SEM) were performed with JEOL-JSM-7600F microscope. Contact angles were measured on a Theta Lite tensiometer equipped with a Firewire digital camera. Static contact angles were measured with a 3 μ L ultrapure water droplet. UV-vis spectroscopic measurements were conducted with a Cary 60 UV-Vis spectrometer. SERS measurements were performed using x-y hyperspectral imaging mode of the Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan) with an excitation wavelength of 532 nm. Using a 50 $\times$ (N.A. 0.55) objective lens, the laser power was pre-set at 0.3 mW with 5 s accumulation time for data collection between 200 cm^{-1} to 2600 cm^{-1} . All SERS spectra were the average of at least 20 individual spectra. XPS spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. Substrate ATR-FTIR spectra were measured using a Perkinelmer SpectrumTM 100 FT-IR spectrometer. XRD patterns were recorded on a Bruker GADDS XRD diffractometer with Cu Ka radiation. All electrochemical experiments were performed using Metrohm Auto lab potentiostat instrument.

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Chapter 5: Applying Nanoparticle@MOF Interface to Activate an Unconventional Regioselectivity of an Inert Reaction at Ambient Conditions

Abstract. Here, we design an interface between a metal nanoparticle (NP) and a metal-organic framework (MOF) to activate an inert CO₂ carboxylation reaction and in situ monitor its unconventional regioselectivity at the molecular level. Using a Kolbe-Schmitt reaction as model, our strategy exploits NP@MOF interface to create a pseudo high-pressure CO₂ microenvironment over the phenolic substrate to drive its direct C-H carboxylation at ambient conditions. Conversely, Kolbe-Schmitt reactions usually demand high reaction temperature (>125 °C) and pressure (>80 atm). Notably, we observe an unprecedented CO₂ meta-carboxylation of an arene that is previously deemed impossible in traditional Kolbe-Schmitt reactions. While the phenolic substrate in this study is fixed at NP@MOF interface to facilitate spectroscopic investigations, free reactants could be activated the same way by the local pressurized CO₂ microenvironment. These valuable insights create enormous opportunities in diverse applications including synthetic chemistry, gas valorization and greenhouse gas remediation.

5.1 Introduction

Applying metal-organic framework (MOF) on nanoparticle surfaces (NP@MOF) boosts the catalytic/reaction performances of the embedded material.¹⁻⁵ Notably, the nanoscopic NP@MOF interface has recently been demonstrated to be highly efficient gas concentrator.⁶⁻⁸ At this NP@MOF interface, gas molecules are selectively captured and accumulated into a quasi-condensed phase over the functional particle surfaces, even at ambient operating conditions. This unique phenomenon increases the gas concentration and molecular energy directly at the point-of-use,⁶ thereby enhancing gas-gas and solid-gas interactions which are the fundamental basis in all gas-based processes. By potentially mitigating the need of elevated operating pressure/temperature in traditional gas-based processes, NP@MOF interface offers an attractive approach to realize efficient gas-based applications at safer and greener ambient conditions.

Notably, the transformations of CO₂ into commodity chemicals are important gas-based reactions to address increasing global CO₂ emission and its detrimental effects as a major greenhouse gas.⁹⁻¹² However, CO₂ is thermodynamically stable with a high oxidation state which consequently mandates the use of energy-demanding reaction conditions involving high temperature/pressure, or the use of reactive substrates such as organolithium or Grignard reagent.⁹ Overcoming these limitations using NP@MOF systems is therefore a promising strategy to achieve high-performance and selective CO₂ valorization without needing elevated temperature/pressure. Meanwhile, the high local concentration of CO₂ at designed plasmonic NP@MOF interface could potentially improve the detection sensitivity of surface-enhanced Raman scattering (SERS) spectroscopy, making the in situ characterization of gas-based processes straightforward without requiring specialized equipment/apparatus.^{13, 14}

Herein, we drive an inert CO₂ carboxylation reaction at ambient conditions and in situ monitor the reaction using SERS at the nanoscopic interface formed between a plasmonic-active Ag nanoparticle and a zeolitic imidazolate framework-8 (ZIF) layer. We choose a Kolbe-Schmitt reaction as our model because it is an important process to synthesize benzoic acid moiety,¹² the structural backbone of many biologically-active molecules. In our strategy, ZIF functions as a CO₂ concentrator while Ag nanoparticle serves as a binding site for chemical substrates and a SERS platform to read-out the reaction in real time. To facilitate SERS investigations, we fix mercaptophenol (MP) substrates at the NP@MOF interface via their spontaneous self-assembly onto the Ag surfaces and subsequently coating the Ag-MP array with a layer of ZIF. Free reactants could be activated the same way at the functional NP@MOF interface. Corroborating experimental investigations and density functional theory (DFT) simulations, we observe the direct C-H carboxylation of arene at NP@MOF interface using CO₂ gas at 1 atm and 25 °C. In contrast, Kolbe-Schmitt reactions over conventional catalysts typically require elevated temperature (130-280 °C) and pressure (20-100 atm).⁹ More importantly, our ability to in situ monitor gas-based reaction allows us to observe an unprecedented meta-carboxylation of arene by CO₂ gas (Figure 1a). Such unconventional regioselectivity was never observed under traditional reaction conditions due to the dominant ortho-selectivity, which in turn arises from the formation of a stable six-membered ring intermediate with CO₂ at the ortho-position and the presence of ortho-/para-directors. Our findings offer valuable insights of reaction selectivity at a NP@MOF interface, as well as to realize ambient-operated gas-based processes/monitoring crucial for diverse applications including (bio)chemical synthesis, gas-to-fuel conversion and greenhouse gas removal.

5.2 Results and discussion

The interface between a SERS-active Ag nanocube and a CO₂-absorbing ZIF layer plays a central role to concurrently drive and monitor an inert Kolbe-Schmitt reaction at ambient conditions (Figure 5.1a).^{6, 9} Our design comprises an array of Ag nanocubes (edge length, 121±5 nm; Figure 5.1a-c, 5.2) and a monolayer of MP reaction substrates is grafted onto NP surfaces (Ag-MP) via Ag-S bond formation. The Ag-MP is then treated with aqueous NaOH solution to generate sodium phenoxide moiety while maintaining Ag nanocubes' structural integrity (Figure 5.3). Elemental X-ray photoelectron spectroscopy (XPS) analysis supports the deprotonation of MP's hydroxyl groups through the emergence of Na 1s XPS peak at 1068.1 eV (Figure 5.4). We also note that MP remains attached to Ag surfaces via Ag-S bond (162.7 eV and 164.0 eV), even after NaOH treatment. The NaOH-treated Ag-MP array is subsequently coated with a polycrystalline ZIF layer (Ag-MP@ZIF; thickness, 243±16 nm; Figure 5.1c) using a wet chemical deposition. Successful coating of ZIF layer over Ag-MP is affirmed by the presence of characteristic ZIF's XPS features (N 1s and C 1s) and XRD patterns (Figure 5.5, 5.6) in Ag-MP@ZIF.⁶

Having established the successful grafting of MP on Ag surfaces, we further investigate the chemical interactions between MP and ZIF using XPS characterization. We observe two distinct sets of Zn 2p XPS signatures in Ag-MP@ZIF, clearly highlighting the presence of two types of Zn constituents (Figure 5.1d, e). The first set of Zn XPS peaks at 1022.8 and 1046.0 eV corresponds to the Zn-N bonds in ZIF, while the other set positioned at 1021.0 and 1044.0 eV is indexed to Zn-O interactions between phenoxide and ZIF.^{6, 15} The formation of Zn-O bond is further supported by the disappearance of Na 1s XPS feature and corresponding shifts in binding energies of Ag, S and O elements (Figure 5.6, 5.7). In contrast, control methylbenzenethiol (MBT)-functionalized Ag nanocubes without chemical interaction with the ZIF layer only exhibit Zn-N XPS features (Figure 5.1e) and no change to the binding energies of other elements upon ZIF formation (Figure 5.8).

Moreover, Zn-O bond formation in Ag-MP@ZIF is also demonstrated by the appearance of an originally-weak MP's in-plane CH bending (β_{CH}) mode at 1170 cm^{-1} (Figure 5.9),¹⁶ possibly due to enhanced polarizability when phenoxide is connected to bulky transition metal.¹⁷ The sandwiched MP structure is expected to create molecular-scale cavities at the Ag@ZIF interface, which are in turn essential to generate a pseudo high-pressure microenvironment for the activation of gas-based reaction at ambient conditions.⁶

Figure 5.1. Key concepts and characterizations of our NP@MOF platform. (a) Schematic depicting the importance of a NP@MOF interface to activate an inert Kolbe-Schmitt (KS) reaction and in situ monitor its unconventional regioselectivity, notably at an ambient operation of 1 atm and 25 °C. (b) Overview on the fabrication of Ag-MP@ZIF platform. 2-mIM denotes 2-methylimidazole. (c) Cross-sectional SEM image of Ag-MP@ZIF. (d) Proposed molecular configuration at Ag-MP@ZIF interface. (e) Zn 2p XPS spectra of Ag-MP@ZIF and Ag-MBT@ZIF.

Figure 5.2. Characterization of Ag nanocubes. (a) SEM image of as-synthesized Ag nanocubes. (b) Size distributions of Ag nanocubes. (c) Extinction spectrum of an ethanolic solution of Ag nanocubes.

Figure 5.3. Characterization of NaOH-treated Ag-MP array. (a) SEM image of mercaptophenol (MP)-functionalized Ag nanocubes after NaOH treatment. (b) Comparison of Ag nanocube edge length before and after NaOH treatment.

Figure 5.4. High-resolution XPS spectra of NaOH-treated Ag-MP. (a) Na 1s XPS spectrum. (b) S 2p XPS spectrum.

Figure 5.5. Characterizations of Ag-MP@ZIF platform. (a) Distribution of ZIF's thickness in the Ag-MP@ZIF platform. (b) XRD spectra of various platforms.

Figure 5.6. XPS characterizations of NaOH-treated Ag-MP before and after ZIF formation. (a – e) High-resolution XPS spectra (S 2p, N 1s, C 1s, Ag 3d and O 1s) of NaOH-treated Ag-MP before and after ZIF formation. Shifts in binding energies of Ag, S and O elements are ascribed to the delocalization of electron density from O-Zn moiety to the entire Ag-MP@ZIF.

Figure 5.7. XPS characterizations of NaOH-treated Ag-MP after exposure to zinc precursor solution. Comparison of high-resolution Na 1s XPS spectra of NaOH-treated Ag-MP before and after exposure to zinc precursor solution.

Figure 5.8. High-resolution XPS characterizations of Ag-MBT before and after ZIF formation. (a) S 2p spectrum. (b) Ag 3d spectrum. MBT denotes methylbenzenethiol.

Figure 5.9. SERS evaluations on NaOH-treated Ag-MP before and after ZIF formation. (a) SERS spectra of NaOH-treated Ag-MP before and after ZIF formation. (b) DFT-simulated SERS spectra of Ag-MP(ONa) and Ag-MP@ZIF.

We subsequently apply the Ag-MP@ZIF ensemble to drive an inert Kolbe-Schmitt reaction involving CO_2 gas as the chemical precursor. Typically, the reaction platform is

placed in a sealed gas flow cell and the SERS responses are recorded in situ during CO₂ flow (Figure 5.10a). All SERS spectra are collected from the same spatial spot to accurately identify potential reactions between Ag-MP and CO₂. Note that the laser used for SERS experiment does not induce molecular changes to Ag-MP@ZIF, as evident from the consistent SERS features measured under N₂ gas flow (Figure 5.11). Initially at $t \leq 1$ min, only MP vibrational modes at 1079 and 1170 cm⁻¹ are observed (Figure 5.10b-i). The former is attributed to a combination of benzene ring breathing mode and C-S stretching ($\beta_{\text{CCC}} + \nu_{\text{CS}}$) while the latter corresponds to MP's β_{CH} mode.¹⁶ Temporal SERS investigation unveils continuous evolution of SERS spectra throughout the CO₂ sorption process. We identify three major time-dependent changes to the SERS spectra in three Raman shift regions; (a) 1050–1110 cm⁻¹, (b) 1150–1190 cm⁻¹, and (c) 1300–1400 cm⁻¹. First, as CO₂ exposure increases to 45 min, the SERS intensity of MP's ($\beta_{\text{CCC}} + \nu_{\text{CS}}$) mode at 1079 cm⁻¹ (region a) decreases and eventually diminishes while MP's β_{CH} mode (region b) red-shifts from 1170 to 1158 cm⁻¹. Second, further exposure to CO₂ for >45 min yields new SERS features in Raman shifts region (b) and (c). Using the SERS spectrum at $t = 60$ min as an example, we note the presence of a SERS feature at 1178 cm⁻¹ (region b) in addition to the original MP's β_{CH} mode at 1158 cm⁻¹. Notably, two SERS bands also emerge at 1335 and 1343 cm⁻¹ in region (c) where carboxylate's vibrational modes (ν_{COO^-}) are commonly reported.^{18, 19} Finally, prolonged CO₂ sorption for 105 min leads to four distinct vibrational modes within region (c) at 1317, 1337, 1373 and 1391 cm⁻¹. A broad SERS band also appears at 1172 cm⁻¹ (region b) which can be further deconvoluted into three constituting SERS features.

More importantly, these spectral features are largely retained (albeit slight red-shifted) even after subsequent purging of Ag-MP@ZIF with N₂ gas for 35 min (Figure 5.10b-ii). The observed red-shifting is likely due to the release of the pseudo high-pressure microenvironment at NP@MOF interface (to be discussed later) after N₂ flush, thereby

allowing surface-grafted MP to vibrate more easily which correspondingly lowers its vibrational energy.^{6, 20} Nevertheless, the permanent SERS signatures in the stipulated ν_{COO^-} region clearly attribute these spectral evolutions to irreversible chemical transformations involving CO_2 rather than weak physical interactions that are otherwise easily reverted.⁶ Conversely, control experiment in the absence of ZIF encapsulation does not demonstrate any spectral changes when exposed to CO_2 flow (Figure 5.12, 5.13), indicating ZIF is important to promote the interactions/reactions between Ag-MP and CO_2 gas. Together with the irreversibility of the spectral changes, the appearance of two sets of ν_{COO^-} vibrational signatures evidently indicates two sequential chemical transformations to the MP substrate at notable ambient operating conditions.

Figure 5.10. Time-dependent SERS spectra recorded from Ag-MP@ZIF during CO₂ infusion at 1 atm and 25 °C. (a) Experimental set-up for in situ SERS monitoring of potential MP carboxylation when exposing Ag-MP@ZIF to CO₂ gas flow. (b) Time-resolved SERS spectra recorded from Ag-MP@ZIF (i) under continuous CO₂ flow for 105 min. Representative SERS spectra at 1 min, 60 min and 105 min are included for comparison. (ii) Subsequent purging using N₂ gas for 35 min. All platforms are thermally activated under vacuum before experiment. Gas flows are controlled at 50 sccm. Red, yellow and green arrows denote redshift, emergence and disappearance of SERS bands, respectively.

Figure 5.11. Time-resolved SERS spectra recorded from Ag-MP@ZIF under continuous N₂ flow for 105 min.

Figure 5.12. Time-resolved SERS spectra recorded from NaOH-treated Ag-MP in the absence of ZIF under continuous CO₂ flow for 105 min.

Figure 5.13. Comparison of SERS spectra changes across different experimental conditions. Ag-MP@ZIF under CO₂ flow (black), Ag-MP@ZIF under N₂ flow (red) and NaOH-treated Ag-MP under CO₂ flow. All platforms are preactivated at 120 °C under

vacuum for 2 h. All SERS spectra are recorded after respective gas flow for 105 min. Gas flow rate, 50 sccm.

Next, we employ density functional theory (DFT) to identify probable intermediate and product species involved in the CO₂-based carboxylation reactions. A series of reaction intermediates/product species comprising carboxylate/carboxylic acid functional group(s) at the ortho and/or meta positions is proposed (Figure 5.14, 5.15). To facilitate comparison with traditional Kolbe-Schmitt reaction, we label phenoxide's carbon as C1, the next carbon atom as C2 (or ortho-position), and the following carbon as C3 (or meta-position) for all proposed species. Using representative vibrational signatures recorded at 1, 60 and 105 min, we corroborate our SERS investigations with simulation studies to decipher the chemical species present during different reaction stages (Figure 5.14 – 5.16). At $t = 1$ min, the experimental SERS spectrum matches the simulated spectrum of ZIF-encapsulated Ag-MP (Ag-MP@ZIF), whereby both SERS spectra are featureless between 1300 and 1400 cm⁻¹. At $t = 60$ min, the two SERS bands at 1335 and 1343 cm⁻¹ agree well with the simulated vibrational fingerprint of a meta-carboxylated Ag-MP derivative (denoted as Ag-MP@ZIF(1×C3OO⁻)). The experimental SERS band at 1335 cm⁻¹ is assigned to a combination of C-O stretching (ν_{C-O}) and phenyl ring vibration of Ag-MP@ZIF(1×C3OO⁻), whereas the 1343 cm⁻¹ band is indexed to the symmetric stretching of carboxylate group (ν_{COO^-}). The formation of Ag-MP@ZIF(1×C3OO⁻) intermediate is further supported experimentally by the appearance of its unique β_{CH} mode at 1178 cm⁻¹, and the disappearance of its ($\beta_{CCC} + \nu_{CS}$) mode at 1079 cm⁻¹ (Figure 5.16) owing to its reduced polarizability when bulky carboxylate group is present near the C-S bond.

Importantly, the chemical species present at $t = 105$ min is indexed to a Ag-MP moiety containing two carboxylate groups at each of its meta-carbons (denoted as Ag-MP@ZIF($2\times\text{C3OO}^-$)) because the experimental and simulated SERS spectra closely tally. Four experimental SERS signatures at 1317, 1337, 1373 and 1391 cm^{-1} are identified and indexed to (1) the combination of C-O stretching ($\nu_{\text{C-O}}$) and phenyl ring vibration of Ag-MP@ZIF($2\times\text{C3OO}^-$), (2) symmetric COO^- stretching alternating between two carboxylate groups ($\nu_{2\text{COO}^-,\text{alternating}}$), (3) synchronous symmetric COO^- stretching of two carboxylate groups ($\nu_{2\text{COO}^-,\text{synchronous}}$) and (4) phenyl vibration, respectively. The new δ_{CH} mode at 1172 cm^{-1} is unique to Ag-MP@ZIF($2\times\text{C3OO}^-$) (Figure 5.16). We note moderate deviations of the experimental SERS intensity/position from the DFT-simulated results which are likely due to differences in actual MP structure/orientation when compared to the simulated molecular configurations.²¹ Nevertheless, both the experimental and simulated SERS results collectively highlight the successive formation of Ag-MP@ZIF($1\times\text{C3OO}^-$) and Ag-MP@ZIF($2\times\text{C3OO}^-$). We exclude chemical species involving ortho-carboxylation and/or carboxylic acid formation as potential reaction intermediate/product because of large spectral mismatches (Figure 5.15). Our assumption that Ag-MP is stably locked to the ZIF layer is also validated because Zn-O interactions between Ag-MP and ZIF remain intact after the carboxylation reactions (Figure 5.17).

Figure 5.14. Unravelling reaction events at the Ag-MP@ZIF interface during CO₂ infusion.

(a) Experimental SERS spectra at 1, 60 and 105 min. (b) DFT-simulated SERS spectra (left) and associated molecular configurations (right) of Ag-MP@ZIF, Ag-MP@ZIF(1×C3OO⁻) and Ag-MP@ZIF(2×C3OO⁻).

Figure 5.15. Comparing experimental SERS spectra with DFT-simulated SERS spectra of various postulated chemical species. (a) Experimental SERS spectra at 60 and 105 min. (b – f) DFT-simulated SERS spectra of various postulated chemical species. For (b – f), each proposed chemical species and their respective DFT-simulated molecular configurations are illustrated at the top. The corresponding SERS spectra are depicted at the bottom.

Figure 5.16. Assigning experimental SERS features recorded from Ag-MP@ZIF under CO₂ exposure. (a, b) Vibrational mode assignment and characteristic SERS evolution of $(\beta_{\text{CCC}} + \nu_{\text{CS}})$ and β_{CH} , respectively. (Left) Magnified experimental SERS spectra of corresponding Raman shift regions at 15, 60 and 105 min. These SERS spectra are recorded from Ag-MP@ZIF under CO₂ flow. (Right) Magnified simulated SERS spectra of $(\beta_{\text{CCC}} + \nu_{\text{CS}})$ and β_{CH} at corresponding Raman shift regions. DFT-simulated molecular configurations of respective carboxylated arenes are also included.

Figure 5.17. XPS characterizations of Ag-MP@ZIF after CO₂ flow. High-resolution Zn 2p XPS spectra of Ag-MP@ZIF before and after CO₂ flow for 105 min.

Both experimental and simulation investigations clearly unveil a sequential, double meta-carboxylations of MP substrate by CO₂ gas. To further verify this proposed reaction pathway, we use XPS to characterize Ag-MP@ZIF before and after CO₂ infusion to ascertain two critical aspects of the reactions, namely (1) the presence of carboxylate groups and (2) their formation at MP meta-positions (Figure 5.18a). First, the presence of carboxylate group is evident through the emergence of its characteristic C 1s and O 1s XPS peaks at 289.7 and 531.9 cm⁻¹ (Figure 5.18b, c), respectively, after CO₂ infusion.²² Second, the formation of carboxylate groups is indeed at MP's meta positions due to a red-shift in Ag XPS peaks by 0.2 eV after exposing Ag-MP@ZIF to CO₂ flow (Figure 5.18d-i). This observation highlights that the Ag surfaces possess a higher electron density after CO₂ infusion, thereby indicating the presence of electron-donating carboxylate groups near the Ag surfaces.²³ DFT investigations on the ortho- and meta-carboxylated products reveal that only Ag-MP@ZIF(2×C3OO⁻) possesses a frontier orbital that is contributed from both the carboxylate groups and Ag surfaces (Figure 5.18d-ii; Figure 5.19). Such orbital interactions allow excess electrons from the negatively-charged carboxylates to easily delocalize to the Ag surface and reduces its binding energy. Control platforms without ZIF coating do not show any XPS changes even after prolonged CO₂ exposure (Figure 5.20–5.22), thus highlighting that ZIF encapsulation is necessary to drive CO₂-based meta-carboxylations. We eliminate the possibility that the unconventional meta-regioselectivity is caused by an increase in electron density at C3 atom of Ag-MP@ZIF. This is because C2 atom still possesses >3-fold negative Mulliken charge which should favor ortho-carboxylations instead of our observed meta-carboxylations (Figure 5.23).^{9, 24} Our Ag-MP@ZIF design thus achieves the first CO₂ meta-carboxylation of arene that is traditionally impossible in a Kolbe-Schmitt reaction; only the formations of ortho-/para-carboxylated products have been previously reported.^{9, 24-26}

Figure 5.18. Affirming the molecular transformations using X-ray photoelectron spectroscopy. (a) Mechanism depicting the two sequential carboxylations of MP in Ag-MP@ZIF under constant CO₂ flow at 1 atm and 25 °C. (b, c) C 1s and O 1s XPS peaks recorded from Ag-MP@ZIF before and after CO₂ infusion, respectively. Magnified C1s XPS spectra near 290 eV demonstrates the presence of COO⁻ moiety after CO₂ infusion. (d) Meta-carboxylation of MP moiety in Ag-MP@ZIF. (i) Ag 3d XPS spectra recorded from Ag-MP@ZIF before and after CO₂ flow. (ii) HOMO of Ag-MP@ZIF(2×C₃OO⁻) indicates that electrons from the carboxylate groups are able to delocalize to the underlying Ag layer.

Figure 5.19. Frontier orbitals of postulated products based on the dual carboxylation of MP moiety at C3 (top) and C2 (bottom) positions. HOMO denotes the highest molecular orbitals occupied by 2 electrons while SOMO refers to the molecular orbital filled by an unpaired electron.

Figure 5.20. XPS characterizations of Ag-MP@ZIF and NaOH-treated Ag-MP after CO₂ flow. (a, b) High-resolution Ag 3d XPS spectra of Ag-MP@ZIF and NaOH-treated Ag-MP before and after CO₂ flow for 105 min, respectively.

Figure 5.21. XPS characterizations of NaOH-treated Ag-MP after CO₂ flow. (a, b) High-resolution C 1s and O 1s XPS spectra of NaOH-treated Ag-MP before and after CO₂ flow for 105 min, respectively.

Figure 5.22. XPS characterizations of NaOH-treated Ag-MP that is further treated with a methanolic solution of zinc precursor [Ag-MP(OZn)]. (a, b) C 1s and O 1s XPS spectra before and after CO₂ flow for 105 min, respectively.

Figure 5.23. Mulliken charges on the C2 and C3 atoms of Ag-MP@ZIF.

To rationalize how the functional interface activates Kolbe-Schmitt reaction at ambient operations, we employ DFT to examine Ag-MP and CO₂ interactions prior to the first chemical transformation. From the experimental SERS signatures for $t < 45$ min, we infer that CO₂ molecule progressively approaches the Ag-MP surfaces whereby their intermolecular separation decreases from 3.9 to 1.7 Å (Figure 5.24a, 5.25). Meanwhile, the initially linear CO₂ molecule adopts a bent geometry to minimize steric repulsion with the Ag-MP surface.^{27, 28} Such linear-to-bent transformation of CO₂ geometry is also accompanied by a surge in molecular energy by ~230 KJ/mol (Figure 5.25). We attribute these phenomena to the continuous accumulation of CO₂ molecules at NP@MOF interface to create a pseudo high-pressure microenvironment directly over the Ag-MP substrate (Figure 5.24a), in accordance to our previous findings on NP@MOF systems.^{6, 7, 29} Enhancing both molecular energy and concentration directly at the point-of-use is the fundamental basis to activate and drive a reaction along its reaction coordinates.³⁰⁻³² We exclude the chemical interactions of MP with Ag and ZIF layers as the main driving force behind the carboxylation reaction because it is thermodynamically more-favorable for free mercaptophenoxide to undergo CO₂ carboxylation (Figure 5.26).

We further investigate the energy profiles of both ortho- and meta-carboxylations in Ag-MP@ZIF to potentially explain the unconventional meta-carboxylations in our Kolbe-Schmitt reaction. We postulate the formation of meta-carboxylated products to two possible reasons. First, the locking of Ag-MP's alkoxy group to ZIF via Zn-O bond could possibly inhibit the generation of a stabilized six-membered ring with CO₂ at the ortho-position, an important intermediate behind the dominating ortho-selectivity in conventional Kolbe-Schmitt reaction (Figure 5.24b, 5.27).^{9, 33} In contrast, surface-grafted MP in the absence of ZIF encapsulation (Ag-MP(OZn); Figure 5.28) is expected to favor traditional ortho-carboxylation because the Zn-O bond is free to form the aforementioned stable six-

membered ring intermediate. Second, the meta-carboxylation may be facilitated when excess electron densities of negatively-charged carboxylates are stabilized by delocalizing to nearby electron-accepting Ag surfaces. This is affirmed by the 48 and 109 KJ/mol lower Gibbs free energy of the first and second meta-carboxylation products than their ortho-carboxylation counterparts (Figure 5.24b; Figure 5.27, 5.28) respectively.

Figure 5.24. Rationalizing the reaction activation and unconventional regioselectivity using our NP@MOF material approach. (a) Proposed mechanism on how NP@MOF activates a chemical reaction that is otherwise inert at ambient operating conditions. This is achieved by creating a pseudo high-pressure gas microenvironment over the reactant at the point-of-use. (b) Molecular structure-energy correlations at various reaction stages in respective Ag-MP@ZIF and Ag-MP(OZn) platforms.

Figure 5.25. Demonstrating the pseudo high-pressure microenvironment at the Ag-MP@ZIF interface. (a) Experimental spectral evolution of (i) ($\beta_{\text{CCC}} + \nu_{\text{CS}}$) and (ii) β_{CH} recorded from Ag-MP@ZIF between 1 min and 30 min. (b) Simulated SERS spectra of corresponding Raman shift regions at intermolecular separations of 3.9 and 1.7 Å. (c) Variation of molecular system energy with the intermolecular separation between Ag-MP and CO₂. All energies are benchmarked against the optimized state (lowest molecular energy) at 3.9 Å.

Figure 5.26. Gibbs free energy of carboxylation reactions in respective platforms. Comparison of the simulated Gibbs free energy of reaction (ΔG) associated with the first lower-energy carboxylation using Ag-MP@ZIF and MP(ONa).

Figure 5.27. Gibbs free energy of different carboxylation products in Ag-MP@ZIF. Comparison of Gibbs free energy of meta- and ortho-carboxylated products formed at different reaction stages in Ag-MP@ZIF.

Figure 5.28. Gibbs free energy of different carboxylation products in Ag-MP(OZn). Comparison of Gibbs free energy of meta- and ortho-carboxylated products formed at different reaction stages in Ag-MP(OZn).

5.3 Conclusion

In this work, we realize the direct C-H carboxylation of arene using CO₂ gas at ambient conditions and in situ monitor its reaction events by exploiting the nanoscopic interface formed between a SERS-active Ag nanoparticle and a ZIF layer. By creating a pseudo high-pressure microenvironment of CO₂ over the phenolic substrate, our designed interface effectively circumvents the need of high temperature (130-280 °C) and pressure (20-100 atm) in conventional Kolbe-Schmitt reaction. Notably, we also observe an unprecedented CO₂ meta-carboxylation of a phenolic substrate that is previously deemed impossible using traditional chemical approaches. A comprehensive mechanistic study is currently in progress to rationalize the unconventional reaction regioselectivity observed at the NP@MOF interface.

Our work could potentially bring numerous benefits to the relevant fields. For instance, our NP@MOF design offers valuable insights to promote gas-based reactions without needing elevated temperature/pressure, which will in turn expedite our progress towards safer and more energy-efficient gas-based processes. Moreover, NP@MOF design could also provide a plausible material approach to identify and realize atypical reaction pathway that is previously inaccessible using conventional wet chemistry methods. Our strategy is generic and can be possibly extended to other gas/liquid-based processes by coating a layer of secondary functional/catalytic materials on SERS-active Ag surfaces, or simply by using these materials as the core particle. While our current study utilizes phenolic substrate fixed

at NP@MOF interface to facilitate spectroscopic investigations, free reactants could be activated the same way by the local pressurized CO₂ microenvironment. On a broader prospective, these insights are valuable to achieve the ultimate goal of realizing efficient, ambient-operated gas-based reaction/monitoring that can be extended to a wide range of important processes, such as industrial chemical manufacturing, functional surface engineering, gas-to-fuel conversion, as well as CO₂ removal and valorization.

5.4 Materials and methods

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55,000), 4-methylbenzenethiol (MBT, $\geq 98\%$), 4-mercaptophenol (MP; 97%), zinc nitrate hexahydrate (reagent grade, 98%) and 2-methylimidazole (99%) were purchased from Sigma Aldrich; copper (II) chloride ($\geq 98\%$) and sodium hydroxide (98%) were from Alfa Aesar; methanol (ACS reagent, $\geq 99.8\%$) was from J.T.Baker®; ethanol (ACS, ISO, Reag. Ph Eur) was from EMSURE®; nitrogen (N₂; ALPHAGAZ 1; 99.999%) and carbon dioxide (CO₂; ALPHAGAZ 1; 99.99%) were purchased from Singapore Oxygen Air Liquide Pte Ltd. All chemicals were applied without further purification. Milli-Q water ($> 18.0\text{ M}\Omega\cdot\text{cm}$) was purified with a Sartorius Arium® 611 UV ultrapure water system.

Synthesis and purification of silver nanocubes. The preparation of Ag nanocubes was carried out following the method described in literature.⁶ Briefly, 10 mL of copper (II) chloride (8 mg/mL), poly(vinylpyrrolidone) (20 mg/mL) and silver nitrate (20 mg/mL) were separately dissolved in 1,5-pentanediol. The chemicals were sonicated and vortexed repeatedly to dissolve them. 35 μL copper (II) chloride solution was then added to the silver nitrate solution. Then, 20 mL 1,5-pentanediol in a 100 mL round bottomed flask was heated to 190 °C for 10 min. 250 μL poly(vinylpyrrolidone) precursor was added to flask dropwise every 30 s while 500 μL silver nitrate precursor was injected every minute using a quick

addition. The addition process continued until the greenish coloration of the reaction mixture faded off.

For the purification of Ag nanocubes, 1,5-pentanediol was first removed from the mixture through centrifugation. The Ag nanocubes solution was then dispersed in 10 mL ethanol and 100 mL aqueous poly(vinylpyrrolidone) solution (0.2 g/L). The resulting solution was vacuum filtered through Durapore® polyvinylidene fluoride filter membranes (Millipore) with pore sizes of 5000 nm, 650 nm, 450 nm and 220 nm, repeated several times for each pore size. The Ag nanocubes were later redispersed in ethanol with a concentration of ~ 7 mg/mL. SEM imaging was performed and the edge lengths of 200 Ag nanocubes were measured and analyzed using ImageJ software.

Preparation of MP-grafted Ag nanocube array (Ag-MP). 1 cm × 0.8 cm Si (100) substrates were cleaned using oxygen plasma for 5 min prior to the assembly of Ag nanocubes. 1.6 μL ethanolic solution of Ag nanocube (7 mg/mL) was then drop-casted onto the O₂ plasma-treated Si wafer and dried under ambient conditions. The Ag nanocube array was further dried using a stream of nitrogen gas and subsequently functionalized via immersion in methanolic MP solution (4 mL, 5 mM) for at least 15 hours. MP-grafted Ag nanocube array was then washed with copious amount of methanol and dried using N₂ gas stream.

Fabrication of ZIF-encapsulated Ag-MP array (Ag-MP@ZIF). The MP-grafted Ag nanocube array was first treated with aqueous NaOH solution (0.1 M) for at least 30 min to generate the sodium phenoxide moiety. NaOH-treated Ag-MP array was washed with methanol and dried using nitrogen gas stream. The as-treated substrate was then immersed into a 20 mL glass vial. 2 mL methanolic solutions of Zn(NO₃)₂ (25 mM) and 2-methylimidazole (50 mM) were prepared separately and added into the glass vial sequentially. The solution was allowed to react for 40 min at room temperature. The

resulting Ag-MP@ZIF was washed with ample amount of methanol and subsequently dried under nitrogen flow. The protocol was repeated until the stipulated ZIF thickness was achieved. Prior to SERS investigations, the platform was thermally activated at 120 °C under vacuum for two hours to evacuate residual methanol residing in ZIF-8's intrinsic pores.

Preparation of ZIF-encapsulated Ag-MP film for XPS characterization. Ag films were deposited using a thermal evaporator deposition system from Syskey Technology Corporation (Taiwan). A 25 nm Ag was deposited on an O₂ plasma-treated Si wafer (1.5 cm × 1.5 cm) at a deposition rate of 0.8 Å/s. The deposited rate was monitored in situ by a quartz crystal microbalance. Ag source with 99.99% purity was purchased from Zhongnuo Advanced Material (Beijing) Technology co., Ltd. The Ag films were subsequently functionalized via immersion in methanolic MP solution (4 mL, 5 mM) for at least 15 hours. MP-grafted Ag films were then washed with copious amount of methanol and dried using N₂ gas stream. Similarly, the MP-grafted Ag film was treated with aqueous NaOH solution (0.1 M) for at least 30 min to generate the sodium phenoxide moiety. NaOH-treated Ag-MP film was washed with methanol and dried using nitrogen gas stream. The as-treated substrate was then immersed into a 20 mL glass vial. 2 mL methanolic solutions of Zn(NO₃)₂ (25 mM) and 2-methylimidazole (50 mM) were prepared separately and added into the glass vial sequentially. The solution was allowed to react for 40 min at room temperature. The resulting platform was washed with ample amount of methanol and subsequently dried under nitrogen flow.

We use MP-grafted Ag film to mimic the Ag-MP@ZIF platform owing to the larger Ag surface area necessary for XPS characterization. More importantly, such Ag film has underwent only one cycle of ZIF synthesis to yield a thin encapsulating layer which was

determined to be ≤ 10 nm in our previous study.⁶ This design is important to ensure efficient XPS characterizations of various platforms.

In situ SERS measurement. Various thermally-activated platforms were placed inside a custom-made gas flow cell with a quartz window suitable for SERS examination. The gas flow cell was first flushed with N₂ gas (50 sccm) for 30 min to displace air from our experimental set-up. For in situ SERS measurement, CO₂ gas (50 sccm) was first flown through the gas flow cell for 105 min and subsequently purged with N₂ gas (50 sccm) for 35 min. All gas flows were precisely controlled using precision gas mass flow controllers (model number MC-100SCCM-D) obtained from Alicat Scientific, Inc. All SERS spectra were normalized between 0 (min) and 1 (max).

Density functional theory (DFT) simulation. We employed DFT simulations to (1) elucidate the effect of increasing CO₂ concentration at the Ag-MP surface arising from the molecular concentrating effect of ZIF, and also (2) to identify probable carboxylated MP species. These calculations were carried out using the unrestricted B3LYP exchange-correlation functional, as implemented in the Gaussian 09 computational chemistry package. The 6-311g (d p) basis set was used for all atoms except Ag, for which the LANL2DZ basis set was employed.

The Ag-MP surface was modeled using a reported method,³⁴ whereby a MP molecule was attached onto a silver cluster consisting of five Ag atoms. After geometry optimization of the Ag-MP system, the Ag atoms were fixed. The hydrogen atom of the phenoxide moiety was replaced by a Zn atom and was subsequently relaxed. After which, the dihedral angle between the aromatic ring and the Zn-O bond was fixed to mimic the “locking” of the phenoxide moiety to the ZIF layer when the Zn²⁺ and imidazole precursors eventually assembled into a crystalline scaffold. The locking of the phenoxide moiety to ZIF was justified by XPS characterization (Figure 1e), whereby the presence of strong Zn-

O bonding to a rigid ZIF scaffold is expected to restrict the free rotation of the bond. Carboxyl functional groups were subsequently added to the MP's aromatic ring to simulate the SERS spectra of various probable carboxylated species.

To identify the molecular concentration effect of ZIF, we utilized a similar approach reported in literature.⁶ A CO₂ molecule was placed near the Ag-MP cluster ($< 2 \text{ \AA}$) and the whole system was relaxed with Ag atoms fixed. Using the relaxed Ag-MP/CO₂ system, the CO₂ molecule was brought nearer to the MBT molecule and the entire system was re-optimized while fixing the Ag-MP and CO₂ intermolecular separation systematically down to $\sim 1.7 \text{ \AA}$.

Material characterization. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) characterizations were performed with JEOL-JSM-7600F microscope. UV-vis spectroscopic measurement was conducted with a Cary 60 UV-Vis spectrometer. SERS measurements were performed using x-y hyperspectral imaging mode of the Ramantouch microspectrometer (Nanophoton Inc, Osaka, Japan) with an excitation wavelength of 532 nm. Using a 50 $\times$ (N.A. 0.55) objective lens, the effective laser power after the quartz glass was set at 80 μW with 5 s accumulation time. All SERS spectra were obtained via real-time tracking of SERS-active region for 105 min and were the average of at least 3 individual spectra. XPS spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. Substrate XRD patterns were recorded on a Bruker GADDS XRD diffractometer with Cu K α radiation.

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Chapter 6: Conclusion and Future Work

6.1 Summary

The continuous development and improvement of plasmonic platforms via nanoparticle assembly has significantly boosted the signal enhancements of SERS and extended its applicability in diverse fields including chemical sensing, reaction monitoring and catalysis. However, we identified two challenges and research gaps that are impeding the progress of SERS toward practical applications. Firstly, in terms of reaction monitoring, current applications are limited to spontaneous reactions while dynamic reactions such as electrochemical reactions are hardly investigated. Secondly, due to the poor surface affinity of most gases/vapor, SERS applications are largely limited to detections in aqueous/solution phase with dye molecules and/or molecules with strong affinities as target analyte. In this thesis, we overcome these challenges by improving both the intrinsic SERS capabilities of plasmonic platforms and the surface affinity of these platforms with the target analyte. By hybridizing functional MOFs and assembling plasmonic nanoparticles, we showcase the ability to push SERS applications toward new realms and achieve breakthrough in sensing, reaction monitoring and catalysis.

In chapter 2, we fabricate the smallest hybrid SERS- and electrochemically active 3D PLM for the real-time molecular level investigation of an electrochemical redox reaction. The Ag nanocubes shell functions as both the SERS-active platform and 3D working electrode, enabling highly sensitive spectroelectrochemical analysis. Using hexaammineruthenium (III) chloride and methylene blue as the model analyte, we demonstrate the capability of our PLM to perform in situ EC-SERS to track molecular changes and identify transient species during these reactions. Notably, our 3D electrode performs 2-fold higher electrochemical-activities and 10-fold strong SERS readout when compared to conventional 2D counterparts. Our findings are thus valuable to develop future

designs of 3D electrode system that are of relevance in the broad fields including energy storage, environmental conversions, and biochemical applications.

We further highlight the importance of nanoparticle assembly in chapter 3, where we incorporate MOFs with Ag nanocubes superlattice array to preconcentrate non-adsorbing vapor molecules for SERS detection. We established that two key factors are key to achieving high sensitivity. Firstly, the ZIF layer thickness is crucial because it directly affects the analyte preconcentrated in the z-layer. Secondly, the strong plasmonic coupling due to the assembled Ag nanocube superlattice is also necessary to boost SERS signal by 5-folds. Notably, our plasmonic nose design can recognize multiple VOCs, including toluene, chloroform, and naphthalenethiol down to ppm levels. Our two-pronged approach thus offers a breakthrough solution to expand detections toward analyte in gas/vapor phase.

In chapter 4 and 5, we exploit MOF for gas/vapor-based applications and develop plasmonic nanoparticles (NP)/MOF hybrids to drive catalysis and in situ investigate the interfacial processes via SERS. In chapter 4, we design a hydrophobically-modified ZIF encapsulating an electrocatalyst, achieving >18% NRR efficiency with addition of water, a ~4-fold improvement compared to dry conditions. Our strategy achieves such water-assisted NRR by kinetically regulating the availability of water to the electrocatalyst, thereby suppressing direct water adsorption and hence electrolysis while promoting nitrogen adsorption. Using in situ SERS investigations, we affirm that the key to transform water to boost NRR is the regulation of water entry to the electrode surface. Our plasmonic NP-MOF design thus offers a new perspective from current electrochemical systems to approach sustainable ammonia electrosynthesis directly from air.

Lastly, in chapter 5, we further exploit the interface between a metal nanoparticle (NP) and MOF to drive and in situ observe the unusual meta-carboxylation of CO₂ under

ambient conditions. Using a Kolbe-Schmitt reaction as model, we highlight that the pseudo high-pressure at the NP@MOF interface drive CO₂ close to the phenolic precursor for direct carboxylation. In comparison, typical reactions necessitate high pressure (>80 atm) and temperature (>125 °C). Importantly, using SERS spectroscopic investigations, we in situ observe meta-carboxylation of the aromatic ring for the first time, a phenomenon that is thermodynamically unfavored in traditional Kolbe-Schmitt reactions.

6.2 Future work

In this thesis, we have offered several novel insights to significantly boost the SERS performance and applicability of plasmonic platforms in diverse fields. Nevertheless, continuous research efforts should be maintained to further explore and drive the development of plasmonic SERS platforms toward real life sensing applications, as well as practical relevant applications including reaction investigations and mechanistic studies. We identify a few branches of SERS research that shows promising potential and discuss possible future works.

Firstly, a burgeoning area of research in SERS is gas/vapor analyte detection. With serious implications ranging from environmental issues due to VOCs in the air and potential defense applications to prevent chemical warfare, to breath analysis for early disease detection, there is a growing demand to develop SERS platforms as a viable and robust gas-based sensor. While several plasmonic platforms have utilized MOFs and other porous materials to capture gas analyte for ultratrace detection, many of these sensors are in their infancy stage and are still performed under controlled laboratory conditions.^{1, 2}

In this aspect, due to the versatility of MOFs as an absorbent layer, we anticipate the increase research on integrating MOFs into plasmonic platforms. One of the key challenges in these hybrid platforms is that current plasmonic-MOF ensembles for SERS are limited to a few types of MOFs (ZIFs, HKUSTs etc.).¹⁻⁴ While these MOFs are advantageous

because of their ease of fabrication and thermal/chemical stability, they also limit the range of properties. For example, ZIFs have nanoscale pore sizes that narrows the size of compatible guest molecules and are less stable in acidic conditions which may impede their applicability. To expand the class of analyte that can be detected, we will explore the facile development of MOFs with tailorable pores and have high stabilities. In addition, we will also consider the optical properties of the whole NP-MOF system, and investigate the effect of varying reflective index, irradiation wavelength and nanoparticle lattice structure on the effective Raman enhancement. Such systematic studies are crucial to improve the understanding of our plasmonic sensor so that the SERS capability can be further enhanced.

In addition, post synthetic modifications of the plasmonic-MOF structures are also emerging strategies that opens up a whole new avenue to generate new properties from current plasmonic-MOF platforms.⁵ We propose that the current plasmonic nose and Ag@ZIF platforms can be further functionalized with different chemical groups to render hydrophobicity/hydrophilicity or to increase affinity with analyte. Importantly, metal centers/organic linkers can be functionalized or exchanged after synthesis to tune pore sizes and alter chemical interactions between the analyte and the MOFs. Consequently, this will promote the design of plasmonic platforms with size and chemical selectivity toward target analyte, paving the way for real life vapor detection even in complex matrix/interferences. Upon the development of these gas/vapor-based SERS sensors, we will then be able to create new niche areas for SERS applications, including point-of-care disease breathalyzers, on site environmental monitoring and stand-off surveillance for defense.

Another future direction in the SERS field is electrochemical-SERS applications (EC-SERS), especially for gas-related reactions. Electrochemical reactions is of importance to a myriad of energy- and environmental-based applications, including energy storage,⁶ and biochemical charge transfer processes.⁷ In addition, there is a rise in using

electrochemical methods to drive the conversion gaseous species such as N_2 , CO_2 , H_2 , O_2 into useful chemicals at ambient conditions.^{8, 9} However, there is still a severe lack in understanding of the electrochemical processes and the underlying mechanisms at the electrode surface. Since plasmonic nanoparticles are both SERS-active and electrically conductive, SERS prevails other analytical methods because the redox reaction can be probed right at the electrode/plasmonic surface. Furthermore, SERS is highly ideal because it averts interfering signals from water, which is a common electrolyte in EC processes. Therefore, as an extension of our NRR work, we propose the combination of plasmonic nanoparticle superlattice with MOFs/adsorbent layers to achieve gas-based redox monitoring. Through the monitoring of the spectral changes upon applied potentials, we will be able to elucidate the adsorption states, intermediates and hence mechanistic pathways of NRR in our system. This will enable us to propose possible mechanisms for the dissociation of nitrogen and hydrogen at the active sites, and establish any changes in the kinetic rate of reactions. We will also investigate the effect of reaction conditions on reaction rates, by changing the temperature, pH and partial pressure of the gaseous reactants. The effect of the nanoparticle material and any facet-dependent enhanced activity can also be studied. As an extension, we can also study the mechanisms of important redox reactions including hydrogen evolution reaction, carbon dioxide fixation and oxygen reduction reaction. These insights are crucial to bridge the information gap between mechanistic process and results, and expedite the progress of these reactions toward industrialization. Additionally, with judicious design such as inclusion of selective MOF layers and/or catalytic metals, the plasmonic platform can also function beyond a monitoring platform to realize catalytic and selective reaction pathways.

Lastly, aside from platform design to expand SERS applications, another area of research that is gaining traction is the use of chemometric tools for analysis.^{10, 11} One of the

biggest bottlenecks that is preventing even the best plasmonic platform from transcending to real world applications is the need to manually acquire, preprocess and then analyze the data. While at the small scale, these procedures are feasible, such tedious protocols are not practical for high throughput analysis of samples. Furthermore, a single Raman fingerprint offers > 1000 wavenumbers and this vast information cannot be simply scrutinized using the human eye, resulting in small but important peak changes/shifts to be often overlooked. Using chemometric techniques such as exploratory principal component analysis (PCA), partial least squares (PLS), and machine-learning models such as support vector regression (SVR), useful information can be quickly extracted from the massive multivariate data obtained.¹⁰ Consequently, robust prediction models can be developed to expedite the automation of SERS analysis. However, despite being developed since the 1970s, chemometrics and statistical tools in SERS analysis is not employed until recently.¹² Hence, there is still much room for development in terms of preprocessing techniques and procedures, and the types of models to apply. It is thus crucial to establish a standard model and protocol to expedite the integration of chemometrics with SERS. Therefore, by combining high quality SERS data from plasmonic platforms with strong SERS readout together with a robust chemometric model, we anticipate the development of a commercial SERS sensor capable of high throughput and ultrasensitive identification and quantification of target analyte.

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