Multifunctional solid@MOF nanohybrids toward surface-enhanced raman spectroscopy (SERS) and electrochemistry applications

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**MULTIFUNCTIONAL SOLID@MOF NANOHYBRIDS
TOWARD SURFACE-ENHANCED RAMAN
SPECTROSCOPY (SERS) AND ELECTROCHEMISTRY
APPLICATIONS**

HOWARD SIM YI FAN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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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

2021

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Chapter 2 is published as Howard Yi Fan Sim, Hiang Kwee Lee, Xuemei Han, Charlynn Sher Lin Koh, Gia Chuong Phan-Quang, Chee Leng Lay, Ya-Chuan Kao, In Yee Phang, Edwin Kok Lee Yeow, Xing Yi Ling. Concentrating immiscible molecules at solid@MOF interfacial nanocavities to drive an inert gas-liquid reaction at ambient conditions. *Angew. Chem. Int. Ed.* **57**, 17058 – 17062 (2018). DOI:10.1002/anie.201809813.

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 conducted the experiment and analyzed the results at the School of Physical and Mathematical Sciences.
- Dr Xuemei Han, Dr Charlynn Sher Lin Koh, Dr Gia Chuong Phan-Quang, Dr Chee Leng Lay, Ya-Chuan Kao, Dr In Yee Phang and A/Prof Edwin Kok Lee Yeow helped with the experimental setup and gave advice on the SERS analysis.
- All authors discussed the project.
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- All authors discussed the project.
- Dr Gia Chuong Phan-Quang wrote the manuscript draft and the draft was revised by Dr Lee Hiang Kwee, Dr Charlynn Sher Lin Koh, myself, and A/Prof Ling Xing Yi.

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- Jaslyn Ru Ting Chen and I conducted the experiment and analyzed the results at the School of Physical and Mathematical Sciences.

- Dr Srikanth Pedireddy and Dr Chee Leng Lay helped with the XPS data analysis.
- Dr Charlynn Sher Lin Koh and Dr Hiang Kwee Lee helped with the electrochemistry data interpretation.
- Dr Gia Chuong Phan-Quang, Jing Yi Pang, Dr In Yee Phang and A/Prof Edwin Kok Lee Yeow helped with the experimental setup and gave advice on the experiment.
- All authors discussed the project.
- I wrote the manuscript draft and the draft was revised by Dr Lee Hiang Kwee, Dr Charlynn Sher Lin Koh, and A/Prof Ling Xing Yi.

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Abstract

Solid-MOF nanohybrids are an emerging platform for applications in SERS detection, reaction monitoring and catalysis. However, current applications revolve either gas or liquid-based molecules, which deprive it for real-life multiphase applications. Notably, solid-MOFs have interfacial cavities where molecular interactions take place under the influence of both functional solid nanoparticles and MOFs. In this thesis, we address these challenges by designing multifunctional solid@MOF for SERS and electrochemical applications. In chapter 2, we showcase solid@MOF practicality in driving immiscible gas-liquid biphasic molecules with in-situ monitoring at ambient conditions. In chapter 3, we demonstrate real-time stand-off atmospheric monitoring where we integrate both remote detection and Raman spectroscopy to obtain the molecular fingerprints up to 10 m. In chapter 4 and 5, we exploit ZIF excellent gas sorbing ability and develop various metallic nanocatalyst@ZIF to drive ambient electrochemical nitrogen reduction. Finally, I end my thesis with a research summary and outlook for future work.

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Chapter 1: Introduction

Abstract. Solid-MOF is an emerging nanomaterial which fuses both solid functional nanoparticles and metal-organic framework (MOF). Owing to MOF's large surface area, tunability, and porous nature, functional solid-MOF has been employed across diverse potential applications ranging from molecular sensing and monitoring to catalysis. Consequently, various strategies have been developed in the fabrication of solid-MOF platforms. In this chapter, we first introduce solid-MOF and state its importance. We highlight the emerging strategies to design solid-MOF platforms which include solution-based and substrate-based solid@MOF core-shell fabrication. Subsequently, we give a review on the current applications involving solid@MOF platforms. Finally, we identify the key challenges associated in this field and describe the objectives of our thesis.

1.1 Solid@MOF core-shell nanohybrids

Metal-organic frameworks (MOFs) are an emerging type of porous with high crystallinity nanomaterial with tunable chemical properties.¹⁻¹¹ Notably, these nanomaterials are constructed through a network of metal ions or clusters and organic linkers coordination to result in a three-dimensional porous framework. These organic linkers are generally ditopic or polytopic nitrogen or oxygen-terminated donor ligands which coordinates to the metal ion or clusters to yield a robust crystalline framework with pore size up to 9.8 nm.¹² In comparison to other porous materials namely aluminosilicate zeolites and porous polymers, MOFs offer several advantages such as highly tunable pores sizes resulted from wide selection of organic linkers while preserving its framework topology, high surface specific area of $> 7000 \text{ m}^2 \text{ g}^{-1}$ and modifiable organic linkers.¹³⁻¹⁶ Hence, MOFs also function as a molecular sieve to enable molecular size selectivity effect and molecular storage in drug delivery.¹⁷⁻²¹ Interestingly, the modification of organic linkers incorporates a rich abundancy of chemical moieties into the framework which is extremely useful to create affinities to facilitate intrinsically weak adsorbing analytes for molecular adsorption. Furthermore, the presence of metal ions or clusters in framework can also exhibit as catalytic active site in the application of heterogenous catalysis.^{22, 23} By integrating MOF with functional solid surface to form solid@MOF, whereby MOF (shell) encapsulates the solid surface (core), such ensemble creates more opportunities and widens the application in the field of sensing, heterogenous catalysis and molecular storage (Figure 1.1).²⁴⁻²⁷ These functional solid surfaces encompass materials such as carbon nanostructures, graphene, metal oxides and other noble metal nanostructures.²⁸⁻³¹ Additionally, MOF coating on plasmonic surface strengthens plasmonic sensing for various environment detections by sorbing molecules close to plasmonic region. Moreover, MOF coating on these solid surfaces also serve as a protecting film which prevent

nanoparticles/nanostructures from aggregation and increases its chemical stability. In the next section, we introduce the various approaches to synthesize different types of solid-MOF platforms, followed by its potential applications.

Figure 1.1. Schematic of the fabrication of solid-MOF. Reproduced with permission from ref 43. Copyright 2014 American Chemical Society.

1.2 Emerging types of solid-MOF platforms

In general, there are four types of strategies to fabricate solid-MOF nanohybrids namely, 1) nanoparticles impregnation method, 2) nanoparticles deposited method, 3) solution-based fabrication of core-shell solid@MOF and 4) solid@MOF core-shell substrate-based method (Figure 1.2).³²

Figure 1.2. Overview scheme of the various types of solid-MOF platforms. Reproduced with permission from ref 32. Copyright 2021 American Chemical Society.

1.2.1 Nanoparticles impregnation method

One of the most straightforward ways to synthesize solid-MOF nanohybrid is via the impregnation method. This involves the diffusion of metal precursors into the MOF pores and reduction in the presence of reducing agent to result in the formation of nanoparticles encapsulated within MOFs (Figure 1.3A).³³⁻³⁶ This strategy involves first the formation of highly crystalline MOF nanoparticles via any conventional method, and then immersing the MOF into metal salt-growth solutions. Consequently, the MOF adsorbs the metal ions into its pores and cavity and the presence of reducing agents in situ reduces the ions into metallic nanoparticles within the MOF matrix. For instance, Au nanoparticle/MIL-101 nanocomposites are fabricated via the addition of sodium citrate as reducing agent into a series of different concentration of chloroauric acid solution with MIL-101.³⁶ This result in the formation of homogeneously dispersed Au nanoparticles within the octahedral MIL-

101 nanostructure (Figure 1.3B). Notably, the particle density of Au nanoparticles is tunable by varying the concentration of Au precursor solution, while altering sodium citrate concentrations results in differing Au nanoparticle sizes. Using similar methods, various Au-MOF nanocomposites including UiO-66, UiO-67 and MOF-199 can also be fabricated.³³⁻³⁶ Such impregnation method helps to retain the porosity and crystallinity of MOF and facilitate the prevention of nanoparticle aggregation during fabrication. However, there are a few drawbacks in such fabrication techniques. Firstly, the size of nanoparticle grown within MOF is restricted to the pore size of MOFs to host metal ions hence resulting in the formation of small nanoparticles size ranging in few nm to few ~10 nm.³³⁻³⁶ Despite its limitation to enable larger nanoparticle growth, such configuration is often being employed for catalysis owing to the small nanoparticle size and MOF synergistic effect to result in high performance catalysis.³⁷ Secondly, it is extremely challenging to achieve shape-controlled nanoparticles that is commonly employed due to its high catalytic activity and/or for plasmonic sensing-related application. Shape-controlled nanoparticles with steps and kinks can provide plasmonic hotspots and/or catalytic sites.^{38, 39} It is noteworthy that impregnating nanoparticles within the MOF pores can potentially decrease its adsorption surface area and also affecting the distribution of nanoparticles within the porous framework which is essential for significant plasmonic coupling in the application of plasmonic sensing.

Figure 1.3. Characterization of AuNPs/MIL-101 via nanoparticle impregnation method. (A) Scheme depicting AuNPs/MIL-101 platform for SERS detection and (B) TEM image. Reproduced with permission from ref 36. Copyright 2014 American Chemical Society.

1.2.2 Nanoparticles deposited method

A different kind of solid-MOF platform is the MOF@NP configuration where MOF surface is deposited with nanoparticles.^{40, 41} Similar to the impregnation strategy, MOF nanocrystals are first formed followed by the deposition of nanoparticles onto MOF surface while retaining MOF crystallinity. Typically, reducing agent is first selectively adsorbed onto the MOF surface followed by the addition of metal salts to synthesize metal nanoparticle-decorated MOF platform. The addition sequence of MOF precursors in this fabrication is crucial to avoid impregnation method which first involves the addition of metal salts. Hence to avoid impregnation method, it is important to ensure that the MOF surface possess available adsorption site for reducing agent to adsorb.⁴² For instance, AgNPs coated MIL-101(Fe) nanostructures can be fabricated by allowing tannic acid to functionalize MIL-101(Fe) surface via the complexation of its hydroxyl groups with the unsaturated Fe (III) ions at the MOF surface. Notably, tannic acid acts as a reducing agent which enables the immediate formation of AgNPs on MIL-101(Fe) surface upon addition of Ag⁺ ions (Figure 1.4).⁴⁰ The key advantage of such configuration involving AgNPs is the high-density packed nanoparticles which allows significant plasmonic coupling. However, it is extremely challenging to control the morphology and distribution of the decorated nanoparticles. Moreover, MOFs lose its molecular sieving functionality due to the presence of decorated NPs which may potentially block the MOF pores for the entry of molecules, hence narrowing its practicality for chemical kinetics studies. Nevertheless, the

employment of these various types of solid-MOF systems is dependent on the specific application of interest.

Figure 1.4. Schematic fabrication and SEM of AgNPs deposited on MIL-101. Reproduced with permission ref 40. Copyright 2015 American Chemical Society.

1.2.3 Solution-based solid@MOF core-shell fabrication

The formation of core-shell nanoparticle-encapsulated MOF (NP@MOF) in solution phase are commonly employed because such synthesis method provides good control of the composition and morphology of MOF and nanoparticles. In general, the nanoparticles are first synthesized before introducing MOF to nucleate and grow on its surface in the reaction media. Importantly, this strategy is versatile and can be established in substrate-based platforms such as close-packed assembled nanoparticle@MOF nanohybrids. In general, the dispersed nanoparticles exhibit as seeds to allow MOF precursor to adsorb on its surface. This adsorption then facilitates MOF growth which

eventually encapsulates the nanoparticles. The strategy to achieve complete MOF encapsulation of nanoparticles during MOF growth is to minimize the interfacial free energy between MOF and nanoparticles. To overcome its interfacial free energy, capping agents are coated onto nanoparticles surface to interact with MOF precursors through Van der Waals forces (hydrogen bonding, electrostatic or hydrophobic interactions). There are a few strategies to encapsulate nanoparticle surfaces; one of it is to employ charged capping agent on nanoparticle surface to facilitate adsorption of MOF precursors. For instance, mercaptoundecanoic acid (MUA)-capped AuNPs utilizes its COO^- to interact with copper nitrate (Cu^{2+}) in the presence of organic linker which eventually self-assembled to form $[\text{Cu}_3(\text{btc})_2]_n$ MOF onto the AuNPs via electrostatic interactions (Figure 1.5).^{25, 43, 44} However, this approach often encounters uncontrolled nanoparticles aggregation resulting from the interactions of MUA and metal ions, thus causing uneven distribution of nanoparticles in MOF nanocrystal. This raises the importance to tune the nanoparticles assembly and achieve highly reproducible and uniform platforms which is critical in the application of plasmonic and catalysis.

(A) Charged capping agents

Figure 1.5. (A) Schematic depicting the formation of MOF on mercaptoundecanoic acid (MUA)-AuNPs. Fabrication. (B) TEM characterization of MOF-encapsulated Au

nanoparticle. Reproduced with permission ref 43. Copyright 2011 American Chemical Society.

Another promising strategy to prevent nanoparticle aggregation while achieving controlled nanoparticle distribution during MOF encapsulation is to use polyvinylpyrrolidone (PVP) as a capping agent (Figure 1.6).^{24, 33, 45-47} For instance, the addition of PVP-capped nanoparticles during and after zeolitic imidazolate framework (ZIF) synthesis whereby ZIFs are a subclass of MOF which comprises of imidazolate linkers and metal ions. The difference in sequence can create a cluster of nanoparticles concentrated at the ZIF core and sparsely distributed nanoparticles within the ZIF core, respectively.²⁴ This is resulted from the interactions between PVP-capped nanoparticles and ZIF via its pyrrolidone using non-polar and polar interactions while adsorbing homogenously onto the growing ZIF hence preventing nanoparticles aggregation. Importantly, this encapsulation strategy is straightforward and versatile which can be extended to a library of nanoparticles of various morphologies and compositions.²⁴ Simultaneously, this approach also broadens the possibilities in designing new nanoparticle-MOF configurations. Thus far, most PVP-driven types of NP-MOFs formation are polycrystalline due to the randomly distributed PVP polymer chains on nanoparticle surface. Hence, it remains a challenge to control the initial ZIF formation/alignment at the nanoparticle-MOF interface. Single crystalline nanoparticle-MOF platforms are extremely useful in catalysis because it acquires highly oriented pore alignment which allow good control of guest molecules diffusing into the pores.

Polymeric capping agents

Figure 1.6. Schematic of various configuration of MOF-coated PVP-nanoparticles by changing the order of nanoparticle addition. Reproduced with permission ref 45. Copyright 2012 Springer Nature.

Besides MUA and PVP, hexadecyltrimethylammonium bromide (CTAB) is also employed owing to its ability to stabilize specific facets and promote nanoparticle-MOF interaction during synthesis to form highly aligned single crystalline NP-MOF nanohybrids.^{17, 48, 49} Notably, CTAB forms a layer of self-assembled monolayer (SAM) on nanoparticle surface which interacts with ZIF nuclei via hydrophobic interaction using its non-polar tail. For instance, {110} facets of ZIF nuclei prefers to grow on {100} of AuNP facet to result in a single crystalline Au nanocube-ZIF-8 core-shell nanoparticle (Figure 1.7).⁴⁸ In addition, this strategy can also be extended to Pd/Au nanooctahedral despite having eight {111} surfaces with few {100} surfaces. Notably, ZIF growth is kinetically controlled whereby ZIF nuclei need to first form followed by the addition of nanoparticles to result in nanoparticle-ZIF of single crystalline ZIF shell. Conversely, the concurrent addition of both nanoparticles and ZIF precursors will result in amorphous ZIF nuclei and hence polycrystalline shells. Nevertheless, the strategy of using CTAB to direct ZIF coating

is versatile and can be extended to a wide array of metallic nanoparticles of various morphologies and compositions.⁴⁹

Figure 1.7. (A) Schematic of quaternary ammonium surfactant directed nanoparticle@ZIF formation. (B) TEM image of single crystalline CTAB-Au nanooctahedron@ZIF-8. Reproduced with permission from ref 48. Copyright 2014 American Chemical Society.

Another method to encapsulate nanoparticles is via solution-based layer-by-layer (LBL) method. Typically, MOF precursor is adsorbed onto nanoparticle surface to form a thin MOF layer which eventually facilitates and controls the MOF growth.^{50, 51} The difference between previous surfactant-directed nanoparticle-MOF core-shell synthesis method and LBL method lies in the order of MOF precursor addition during MOF encapsulation of nanoparticles. Typically, nanoparticle-MOF core-shell synthesis involves the direct addition of nanoparticles into MOF precursors while LBL method achieves by dispersing the preformed NP-MOF nanohybrids sequentially into metal salt solution first and then later into organic linker solutions repeatedly. For instance, Au@Fe-MIL-100 with tunable MOF thickness of ~5 nm/cycle is achieved by mixing FeCl₃ salt and trimesic acid solutions with PVP-capped AuNPs into up to 7 cycles.⁵⁰ Although this synthesis approach enables highly controllable MOF thickness, polycrystalline MOF layer are usually formed.

In summary, the sequence of chemical/nanoparticle addition into the reaction mixture and the types of surfactants used are key parameters to determine the final configuration of the solution-based nanoparticle@MOF core-shell during synthesis. The core advantage of such configuration is the ability to retain its intrinsic nanopores without affecting the guest molecule diffusion within the pores. However, specific capping agents are required to promote heterogenous growth of MOF on nanoparticle surface. Moreover, some MOF synthesis which require high temperature and/or pressure may induce nanoparticle aggregation hence interfere MOF growth on solid surface. A solution to minimize nanoparticle aggregation is to assemble nanoparticles onto a solid support before MOF encapsulation.

1.2.4 Substrate-based solid@MOF core-shell fabrication

Core-shell solid@MOF substrate-based platforms can also be fabricated using similar strategies as solution-based synthesis. Instead of dispersing nanoparticles in the solution media, the nanoparticles are first assembled onto a flat solid surface and subsequently allow the heterogenous growth of MOF.⁵² Some key advantages of such platform involve the lack of nanoparticle aggregation that often occurs in solution-based fabrication and the ease to translate these platforms for practical applications because of the mechanical support. Furthermore, such configuration maximizes the interface between the nanoparticle surface and the MOF layer. In general, there are a few types of nanoparticle@MOF platforms. Surface-anchored metal-organic frameworks, SURMOFs, is a type of ultrathin MOF-encapsulated thin film substrate fabricated via a layer by layer method.⁵³⁻⁵⁵ SURMOF HKUST coated on Au nanodisk surface is fabricated via a repeated and alternated spraying of ethanolic copper acetate and 1,3,5 benzene tricarboxylic acid solutions through the interaction with hydroxyl-functionalized Au surface. Although the

MOF thickness is highly controllable with nm-precision, this process requires >10 cycles to ensure full encapsulation hence extremely time consuming. On the other hand, similar configuration can also be achieved by immersing the substrate directly into MOF precursors solution to form a polycrystalline MOF coating over nanoparticles (Figure 1.8A).⁵⁶⁻⁶⁰ This is demonstrated in the fabrication of Ag@ZIF platform whereby MOF thickness can be controlled up to 287 nm by tuning the MOF growth cycles (Figure 1.8B, C). Although such fabrication method seems easy for large scale synthesis, one of the major challenges revolves its ability to form an uniform ultrathin and continuous MOF layer which may be necessary to achieve faster molecular diffusion of guest molecules. Moreover, the surface chemistry of nanoparticles needs to be modified in order to promote MOF overgrowth. However, the presence of capping agents on nanoparticle surface may potentially hinder applications such as plasmonic-related sensing by preventing molecules from reaching the plasmonic region as well as deactivate potential active sites on nanocatalyst for catalysis.

Figure 1.8. Characterization of thin film Ag@ZIF core-shell platform. (A) Overall schematic Ag@MOF thin film core-shell platform as a plasmonic nose to sniff chemicals.

(B) SEM cross-section image of Ag@ZIF after 1 and 3 cycles. (C) Number of ZIF cycle coating to achieve n -thickness. Reproduced with permission ref 56. Copyright 2018 Royal Society of Chemistry.

1.3 Applications of solid-MOF platforms

Thus far, we have discussed various approaches to synthesize different types of solid-MOF platforms ranging from solution-based to substrate supported-based. In addition, we also elaborate on its advantages and disadvantages in affecting the guest-host chemistry within the platform. We also highlight the importance of capping agents in facilitating the MOF growth on nanoparticle surface to achieve either crystalline or polycrystalline structure. In this section, we will discuss some of the potential applications of these solid-MOF platform in Surface-enhanced Raman scattering (SERS) and electrocatalysis. Specifically for SERS, we will focus on how these nanohybrids impact conventional plasmonic applications such as real time reaction monitoring and chemical sensing. Additionally, we will also discuss on how the combination of both functional nanoparticles and MOF aids in enhancement of electrocatalysis.

1.3.1 Surface-enhanced Raman scattering (SERS)

Surface-enhanced Raman scattering (SERS) is a non-invasive and molecular specific spectroscopic technique which uses molecular vibrational fingerprints region ($400\text{--}1800\text{ cm}^{-1}$) to identify and quantify a library of chemical molecules (Figure 1.9).⁶¹⁻⁶⁴ However, Raman signals of molecules are weak due to their small Raman scattering cross-section and also the intrinsic weak Raman scattering whereby one in every 10^8 photons undergoes Raman scattering spontaneously.⁶⁵ Thus, to enhance Raman signals, SERS employs plasmonic nanoparticles (Ag, Au, Cu and Al) to boost signal up to 10^{10} -folds

Raman enhancement which enable the quantification of molecules down to ultratrace levels.⁶⁶ Specifically, SERS relies on the collective conduction bands of electrons which confines and oscillates at the plasmonic nanoparticle surface to result in an unique phenomenon known as localized surface plasmon resonance (LSPR).^{61, 67} Notably, coupling LSPR with incoming light generates a secondary electric field localized around the plasmonic surface, creating plasmonic hotspots which exhibits strong electromagnetic (EM) field near metal surface up to <10 nm. This strong EM field amplifies the scattered Raman signals of molecules up to 10^8 -fold. Both the LSPR resonance wavelength and strength of EM field are highly tunable. These factors depend on the dielectric functions, nanoparticle morphology and size, and plasmonic coupling among neighboring particles. Besides EM field, another important variable known as chemical enhancement accounts for up to 10^3 Raman signal amplification which results from the polarizability increment through the charge transfer among chemisorbed molecules and plasmonic metal surface.⁶⁸ However, the applications of chemical enhancement are limited to a short range of molecules which exhibit high affinity to metal surface such as thiolated molecules. Nevertheless, both mechanisms require molecules to be near to plasmonic metal surface and the synergy of both mechanisms is essential for SERS to achieve trace molecular detection with high sensitivity.

Figure 1.9. Schematic on the principle of SERS. (A) Normal Raman. (B) Localized surface plasmon resonance. (C) Electromagnetic enhancement mechanism in SERS. Reproduced with permission from ref 64. Copyright 2018 American Chemical Society.

1.3.1.1 Current developments in SERS platforms

The vast application of plasmonic nanoparticles across various fields have triggered tremendous efforts to design new configuration of plasmonic substrate so as to tailor the LSPRs.⁶⁹ This tailoring is crucial to achieve 1) increased EM field enhancements, 2) homogenous signal sensitivity and reproducibility and 3) match the LSPR with the irradiation wavelength for maximum resonance overlap and hence efficiency. Conventionally, 0D nanoantenna and nanoflowers which exhibits sharp tips and edges have been fabricated to achieve enhanced EM field confinement.^{70, 71} Their LSPR resonance wavelength can be tuned by modifying its morphology and size. In addition, plasmonic coupling between nanoparticles can also be achieved by assembling nanoparticles into 3D configurations and superlattices for enhance detection sensitivity.⁷²⁻⁷⁴ However, most plasmonic platforms suffer from extremely weak analyte detection of non-adsorbing

molecules. Typically, the surface of plasmonic nanoparticle is the region where its plasmonic effect is the strongest but decays rapidly as distance between molecules and plasmonic surface increases. Hence, these types of molecules are uncommonly employed in applications such as catalysis, photothermal, SERS reaction monitoring or detection related studies. Collectively, this leads in the limited development of platform design as non-adsorbing molecules are unable to reach plasmonic surface to experience any plasmonic effects. Currently, most applications involve non-adsorbing molecules, hence it is extremely important to tackle the bottleneck of weak analyte affinities to further broaden plasmonic-related applications. A solution to resolve this limitation is to integrate plasmonic platforms with MOFs to enable swift capturing and pre-concentration of molecules close to plasmonic region at the nanoparticle-MOF interface. In the following section, we discuss an emerging material known as plasmonic nanoparticle-metal-organic framework and its promising capability to boost SERS performance.

1.3.1.2 Chemical sensing

One of the key applications of SERS is chemical sensing whereby analytes are exposed to the plasmonic region with numerous hotspots which boost its molecular vibrational fingerprint spectra. Notably, chemical sensing is extremely important especially for environmental quality assurance, food safety and toxic volatile organic compounds (VOCs) leakage which affects the quality of our lives.^{17, 56, 75, 76} However, it is challenging to detect these analytes due to its poor surface affinity to plasmonic surface, small Raman cross section as well as low concentration level. Thus, the hybridization of plasmonic nanoparticle and MOF overcomes the limitations to enable the capturing of these analytes into the MOF and concentrating near the SERS-active surface (Figure 1.10A).⁵⁶ This is

demonstrated using Ag films-over-nanosphere (FON) coated with ZIF-8 (zeolitic imidazolate framework-8) to detect a series of volatile organic compound such as benzene, pyridine, nitrobenzene and 2,6-di-tert-butylpyridine down to ppm-levels.⁵⁷ To further enhance the SERS performance in plasmonic nanoparticle@MOF, it is necessary to optimize both the MOF coating thickness and the interparticle distance for plasmonic couplings. For instance, Ag nanocubes SERS signal enhances by 2.5-fold as ZIF coating thickness reaches 146 nm upon sorbing 4-methylbenzenethiol vapor compared to the absence of ZIF.⁵⁶ In addition, the systematic tune in the interfacial surface pressure during the assembly of Ag nanocubes from 4 to 16 mN m⁻¹ result in a ~5-fold linear enhancement in SERS sensitivity. (Figure 1.10B). Collectively, the enhancement in SERS sensitivity arises from the MOF preconcentrating effect which broadens SERS applications in the field of gas/vapor detection.

Figure 1.10. (A) Schematic depicting analyte concentrating effect in MOF. (B) Relationship of SERS intensity and analytical enhancement factor across various Ag@ZIF at different surface pressures. Reproduced with permission ref 56. Copyright 2018 Royal Society of Chemistry.

1.3.1.3 Interfacial sensing and reaction monitoring

Besides chemical sensing, SERS also enables the investigation of reaction occurring at the plasmonic surface which is necessary to understand the series of molecular events encompassing molecular adsorption, mechanism and heterogenous catalysis.⁷⁷⁻⁷⁹ However, it is extremely difficult to analyze the chemical reactions associating with poor adsorbing molecules by using bare plasmonic nanoparticle platforms. Thus, the incorporation of MOF into plasmonic nanoparticles can overcome these challenges. Typically, MOF sorbs the molecules near to the SERS-active site to allow SERS-active nanoparticles to monitor the molecular events. Owing to the strong plasmonic nanoparticles coupling, these hybrid SERS platforms enable kinetics investigations of molecular diffusion and adsorption into MOF. For example, real-time SERS monitoring of analyte diffusion (4-nitrobenzenethiol and 1-naphthalenethiol) into MOF can be achieved by using Au@Ag core-shell nanorods encapsulated with ZIF-8 (Figure 1.11).⁴⁹ Interestingly, large molecules up to 7.20 Å can diffuse into ZIF pore aperture of 3.4 Å. This phenomenon is also known as “gate-opening” effect attributed from ZIF’s highly flexible framework. Additionally, the adsorption kinetics investigation reveals the molecules follow a transient diffusion model with intracrystalline diffusion control which predicts a quasi-linear kinetic uptake curve. Hence, the hybridization of both materials serves an additional purpose to further reveal the molecular insights of MOF molecular sieving properties and the molecule diffusions within MOF pores. Collectively, these information are crucial to fundamentally understand the role of MOF and its working mechanism during catalysis, sensing and drug deliveries.

Figure 1.11. SERS performance of ZIF-encapsulated Au@Ag core-shell. (A) TEM characterization of Au@Ag@ZIF. (B) SERS detection of MBT, 1NAT and MGI in the presence (grey line) and absence (black line) of ZIF. (C) Adsorption kinetics of NBT entering ZIF. (D) Adsorption kinetics of 1NAT entering ZIF. Reproduced with permission ref 49. Copyright 2016 John Wiley and Sons.

Probing the behavior of gaseous molecules at the plasmonic nanoparticle-MOF interface using solid-MOF platform is also another important application. Notably, the formation of polycrystalline MOF on solid surface creates the presence of interfacial nanocavities. These interfacial nanocavities exhibit a pseudo high pressure microenvironment upon over accumulation of molecules during adsorption into MOF pores. This is observed through the prolong CO₂ exposure at Ag-ZIF-8 (zeolitic imidazolate framework; ZIF) interface which causes the transformation in CO₂ from linear-to-bent configuration using ZIF-8 encapsulated Ag nanocubes (Ag@ZIF-8) as a SERS platform at ambient conditions (Figure 1.12).⁸⁰ Time-dependent SERS analysis reveals the changes in

CO₂ free state SERS broad peak at $\sim 1365\text{ cm}^{-1}$ which narrows with peak appearance at 1289 cm^{-1} and 653 cm^{-1} . These new peaks are the bending and symmetric stretching of CO₂. Interestingly, this phenomenon can only occur at high pressure of $>60\text{ bar}$ and 313 K whereby CO₂ behaves as a quasi-condensed liquid state.⁸¹ Additionally, this concurrently highlight the presence of a pseudo high pressure environment at the nanoparticle-MOF interface. Notably, such transformation at ambient conditions can only be observed using SERS spectroscopy.

Figure 1.12. Real-time SERS monitoring between CO₂ and MBT-functionalized Ag surface at the Ag-ZIF interfacial cavities of Ag@ZIF-8. (i) under continuous CO₂ over 105

min and (ii) continuous N₂ purging for 35 min. Reproduced with permission from ref 80. Copyright 2017 American Chemical Society.

1.3.2 Electrocatalysis

Metallic nanoparticle-MOF can also be employed for electrocatalysis in the field of electrochemical nitrogen reduction reaction (NRR) for ammonia generation as a green fuel. NRR typically suffers from poor reaction selectivity and is hampered by the concurrent presence of hydrogen evolution reaction (HER) across catalysts. Moreover, ammonia (NH₃) generation via traditional Haber-Bosch process requires extreme conditions at 40 MPa and 400°C which is energy-consuming and unsustainable. A solution to overcome this is to use nanoparticle-MOF platforms whereby MOF can selectively capture and concentrate N₂ gas close to the electrocatalyst. Additionally, the presence of moisture entry into MOF can be suppressed by using a hydrophobic MOF. For instance, Ag-Au@ZIF-71 demonstrates extremely good NRR selectivity of ~90 % with an additional 10 % boost in Faradaic efficiency in dry tetrahydrofuran (THF) containing ethanol as proton source at ambient conditions.⁵⁹ In this application, Ag nanocubes exhibit both as a SERS platform and electrocatalyst with Au as a co-catalyst while the hydrophobic ZIF-71 aids to concentrate gaseous N₂ molecules close to electrocatalyst surface and repel water molecules to suppress HER. Notably, exposure to N₂ gives rise to a SERS peak at 2328 cm⁻¹ which is indexed to N-N stretching mode of N₂ hence indicating the successful capture of N₂ at the solid-ZIF interface.

By functionalizing the exterior and interior of ZIF with hydrophobic ligands, water molecules as a proton source, instead of an inhibitor, can be employed to promote NRR. This is demonstrated by designing a hydrophobic oleylamine-functionalized ZIF coating over Ag-Au@ZIF (M@ZIF-OAm) system to kinetically regulate water molecules entry into

and within ZIF (Figure 1.13).⁸² Notably, the platform achieves a faradaic efficiency (FE) of > 18% which is 4-fold higher than in the absence of water at ambient conditions. Moreover, functionalizing SERS-active Ag nanocubes with mercaptopyridine as a sensor for hydrogen bonding, it further reveals and verifies that the modified ZIF-71 is key to regulate water molecules to achieve better NRR performance. Hence, the corroboration of both SERS investigation and electrochemistry provides a powerful tool to elucidate the working mechanism behind water-assisted NRR. Concurrently, it also enables the identification of the major components within the platform to result in this phenomenon. It is noteworthy that such strategy which uses MOF encapsulation of electrocatalyst can be extended across various type of nanocatalysts to further improve NRR performance. Importantly, this work highlights the advantage of incorporating plasmonic nanoparticle into solid-MOF hybrid systems to enable the usage of SERS as an ultrasensitive surface characterization tool to monitor the diffusion of water molecules into MOF. This insight paves the way to integrate electrochemistry with SERS (EC-SERS) to potentially unravel real-time electrochemical nitrogen reduction reaction mechanism at the plasmonic nanoparticle-MOF interface which cannot be observed by other spectroscopic techniques such as nuclear magnetic resonance (NMR) spectroscopy. Furthermore, such configuration can easily investigate NRR chemical reaction kinetics as well as creating more opportunities for nanoparticle-MOF applications.

Figure 1.13. SERS monitoring of water molecule diffusion into ZIF layer by employing mercaptopyridine (MPy) as a sensor to detect water via hydrogen interaction. Reproduced with permission from ref 82. Copyright 2017 American Chemical Society.

Although current emerging NP-MOF electrocatalytic platforms demonstrate enhanced NRR performances and hold great promises for various electrocatalysis, it is important to identify and eliminate false positives in these reactions. In a recent work, three criteria are introduced to evaluate the reliability in a typical NRR experiment mainly, 1) NH_3 yield rate, 2) quantitative analysis of $^{15}\text{NH}_3$ production via $^{15}\text{N}_2$ reduction and 3) presence of oxidized forms of N_2 contaminant (NO_x).⁸³ To evaluate the practicality of the electrocatalyst based on NH_3 yield rate, it is necessary to achieve $\geq 10 \text{ nmol s}^{-1} \text{ cm}^{-2}$. Notably, NH_3 yield rate which falls below $0.1 \text{ nmol s}^{-1} \text{ cm}^{-2}$ is categorized as ambiguous and too low to be promising. In addition, it is imperative to include control experiment such as $^{15}\text{N}_2$ reduction and compare the generated $^{15}\text{NH}_3$ with $^{14}\text{N}_2$ experiments under identical conditions to affirm that the ammonia yield indeed arises from N_2 reduction and to evaluate the robustness of the electrocatalytical system.⁸⁴ Finally, it is also necessary to consider the effect contributed from the presence of atmospheric NO_x contaminants on exposed high

surface area material such as glasswares and working electrodes as well as electrolytes which may artificially boost the NRR performance.⁸⁵⁻⁸⁷ Furthermore, trace NO_x compound can also be identified in N₂ cylinders of highest purity level supplied by commercial suppliers. Hence, controls to take into account these factors are imperative and need to be implemented across future NRR work as more electrocatalytes for NRR are developed.

1.4 Motivations and Objectives

Nanoparticle-MOF nanohybrids are an emerging platform that has attracted paramount interest owing to its versatility to be applied across various fields in SERS and electrochemistry. By modifying functional nanoparticles with various morphologies of sharp tips and edges as building blocks and further assembling into 2D and 3D superlattices/supercrystals, such platforms offer multiple hotspots for SERS, catalytic active sites as well as adsorption sites. Importantly, the integration of MOF into these nanoparticles further strengthen its SERS and/or catalytic performance via capturing liquid and/or gas molecules of weak affinity into its MOF pores by bring it closer to nanoparticle surface. Collectively, such platform exhibits significant improvement in SERS detection and electrocatalysis which are important in the applications of environmental air quality analysis and green chemical generation, respectively.

Despite the rising development of solid-MOF nanohybrids, most of its applications revolve either gas or liquid-based molecules only which deprive solid-MOF practicality for real-life applications in chemical sensing and chemical generation that typically involve multiphase systems. Furthermore, there is a lack of molecular understanding at the solid-MOF interface which is a unique confinement where reactions and/or point of molecular interaction takes place under the influence of both solid nanoparticle and MOF materials. Likewise, various unprecedented observations arising from the synergistic effects of both materials are still left uninvestigated. On the other hand, SERS analysis are typically

conducted in an enclosed and close-up settings to eliminate light interferences thus limiting its practicality in long range outdoor chemical monitoring for applications in surveillance and toxic gas leakage detections. Their application for long range chemical monitoring is further impeded when involving gaseous analyte with poor affinities because of its intrinsic low concentration and dynamic nature. Although portable Raman spectroscopy can be deployed for on-site analysis, these instruments often suffer from poor spatial resolution hence not suitable for trace molecule detection and long-term exposure to toxic chemical can be detrimental to health. Therefore, given the advantages of MOF, it is most ideal to integrate with plasmonic platform to fabricate an ultrasensitive trace detection of gas and/or liquid analytes. By further coupling with SERS spectroscopy and other surface chemistry analytical tools, we can further investigate and elucidate the chemistry between molecules and solid-MOF materials at the solid-MOF interface. Moving forward, we foresee a significant increase in the design of solid-MOF interface which can propagate new scientific insights in this field.

The objective of my thesis is to utilize the unique properties of solid-MOF interface to overcome limitations in both chemical reactions and chemical sensing, and simultaneously showcase its potential practicality for real world applications. In chapter 2, we demonstrate a gas-liquid reaction involving two immiscible chemicals mainly CO₂ and aniline at ambient conditions. This is achieved by incorporating a molecular-sorbing ZIF layer over a closely packed assembled Ag nanocubes. ZIF serves as a sorbent to sorb these molecules into the interfacial cavities at the Ag-ZIF interface for close molecular interaction to result in an ambient reaction in the presence of pseudo high pressure environment near the plasmonic surface. In chapter 3, we further demonstrate Ag@ZIF capability to detect small volatile organic compounds (VOCs) at ppb-levels and gaseous CO₂ for real real-time atmospheric monitoring from a distance up to 10 m apart by incorporating long-range optics

Raman system and 3D Ag@ZIF assembly. The 3D assembly creates a large volume of hotspots for ultrasensitive detection while long-range optic system provides the in situ tracking of airborne molecules from afar. In chapter 4 and 5, we exploit the flexibility of integrating functional nanoparticle with ZIF to fabricate a catalytic solid@ZIF to drive ambient electrochemical nitrogen reduction reaction (EC-NRR) at the solid-MOF interface. In chapter 4, we employ ZIF to modify the d-band center of Pt nanocatalyst to favor Pt-N₂ interaction as well as ZIF's preconcentrating effect and hydrophobic pores to selectively sorb N₂ and repel moisture to favor and boost EC-NRR. In chapter 5, we further investigate the interaction between N₂ and the ZIF-modified Pt nanocatalyst at the Pt-ZIF interface and reveal its N₂ activation mechanism driven by the unique properties of Pt-ZIF interface. Lastly in chapter 6, I will end my thesis and provide a critical outlook of solid-MOF for future applications in chemical sensing and catalysis.

References

1. Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.
2. Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.
3. James, S. L. *Chem. Soc. Rev.* 2003, *32*, 276.
4. Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U. S. A.* 2006, *103*, 10186.
5. Cohen, S. M. *Chem. Sci.* 2010, *1*, 32.
6. Farha, O. K.; Hupp, J. T. *Acc. Chem. Res.* 2010, *43*, 1166.
7. Janiak, C.; Vieth, J. K. *New J. Chem.* 2010, *34*, 2366.
8. Stock, N.; Biswas, S. *Chem. Rev.* 2011, *112*, 933.
9. Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* 2012, *112*, 673.

10. Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. *Science* 2013, 341, 1230444.
11. Meek, S. T.; Greathouse, J. A.; Allendorf, M. D. *Adv. Mater.* 2011, 23, 249.
12. Deng, H.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gándara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; Kazumori, H.; O’Keeffe, M.; Terasaki, O.; Stoddart, J. F.; Yaghi, O. M. *Science* 2012, 336, 1018.
13. Senkovska, I.; Kaskel, S. *Chem. Commun.* **2014**, 50, 7089.
14. Shi, D.; Haw, K.-G.; Kouvatas, C.; Tang, L.; Zhang, Y.; Fang, Q.; Qiu, S.; Valtchev, V. *Angew. Chem. Int. Ed.* **2020**, 59, 19576.
15. Thomas, A. *Angew. Chem. Int. Ed.* **2010**, 49, 8328.
16. Slater, A. G.; Cooper, A. I. *Science*, **2015**, 348, aaa8075.
17. Qiao, X.; Su, B.; Liu, C.; Song, Q.; Luo, D.; Mo, G.; Wang, T. *Adv. Mater.* **2018**, 30, 1702275.
18. Della Rocca, J.; Liu, D.; Lin, W. *Acc. Chem. Res.* **2011**, 44, 957.
19. Zhuang, J.; Kuo, C. H.; Chou, L. Y.; Liu, D. Y.; Weerapana, E.; Tsung, C. K. *ACS Nano* **2014**, 8, 2812.
20. An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, 131, 8376.
21. Huxford, R. C.; Della Rocca, J.; Lin, W. *Curr. Opin. Chem. Biol.* **2010**, 14, 262.
22. Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, 110, 4606.
23. Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2011**, 112, 1196.
24. He, L.; Liu, Y.; Liu, J.; Xiong, Y.; Zheng, J.; Liu, Y.; Tang, Z. *Angew. Chem., Int. Ed.* **2013**, 52, 3741.
25. Sugikawa, K.; Nagata, S.; Furukawa, Y.; Kokado, K.; Sada, K. *Chem. Mater.* **2013**, 25, 2565.

26. Xiang, Z.; Hu, Z.; Cao, D.; Yang, W.; Lu, J.; Han, B.; Wang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 491.
27. Liu, J.; Strachan, D. M.; Thallapally, P. K. *Chem. Commun.* **2014**, *50*, 466.
28. Han, X.; Besteiro, L. V.; Koh, C. S. L.; Lee, H. K.; Phang, I. Y.; Phan-Quang, G. C.; Ng, J. Y.; Sim, H. Y. F.; Lay, C. L.; Govorov, A.; Ling, X. Y. *Adv. Funct. Mater.* **2021**, *31*, 2008904.
29. Choi, K. M.; Kim, D.; Rungtaweevoranit, B.; Trickett, C. A.; Barmanbek, J. T. D.; Alshammari, A. S.; Yang, P.; Yaghi, O. M. *J. Am. Chem. Soc.* **2017**, *139*, 356.
30. Wang, X.; Dong, A.; Hu, Y.; Qian, J.; Huang, S. *Chem. Commun.*, **2020**, *56*, 10809.
31. Liu, Y.; Tang, Z. *Adv. Mater.*, **2013**, *25*, 5819.
32. Koh, C. S. L.; Sim, H. Y. F.; Leong, S. X.; Boong, S. K.; Chong, C.; Ling, X. Y. *ACS Materials Lett.* **2021**, *3*, 557.
33. Chen, L.; Peng, Y.; Wang, H.; Gu, Z.; Duan, C. *Chem. Commun.* **2014**, *50*, 8651.
34. Cao, X.; Hong, S.; Jiang, Z.; She, Y.; Wang, S.; Zhang, C.; Li, H.; Jin, F.; Jin, M.; Wang, J. *Analyst* **2017**, *142*, 2640.
35. Zhang, B. B.; Shi, Y.; Chen, H.; Zhu, Q. X.; Lu, F.; Li, Y. W. *Anal. Chim. Acta* **2018**, *997*, 35.
36. Hu, Y.; Liao, J.; Wang, D.; Li, G. *Anal. Chem.* **2014**, *86*, 3955.
37. Xiang, W.; Zhang, Y.; Lin, H.; Liu, C-J. *Molecules* **2017**, *22*, 2103.
38. Leong, S. X.; Koh, C. S. L.; Sim, H. Y. F.; Lee, Y. H.; Han, X.; Phan-Quang, G. C.; Ling, X. Y. *ACS Nano* **2021**, *15*, *1*, 1817.
39. Naseem, F.; Lu, P.; Zeng, J.; Lu, Z.; Ng, Y. H.; Zhao, H.; Du, Y.; Yin, Z. *ACS Nano* **2020**, *14*, *7*, 7734
40. Jiang, Z.; Gao, P.; Yang, L.; Huang, C.; Li, Y. *Anal. Chem.* **2015**, *87*, 12177.

41. Li, D.; Cao, X.; Zhang, Q.; Ren, X.; Jiang, L.; Li, D.; Deng, W.; Liu, H. *J. Mater. Chem. A* **2019**, *7*, 14108.
42. Chen, J.; Zhang, B.; Qi, Long, Q.; Pei, Y.; Nie, R.; Heintz, P.; Luan, X.; Bao, Z.; Yang, Q.; Ren, Q.; Zhang, Z.; Huang, W. *ACS Appl. Mater. Interfaces* **2020**, *12*, 20, 23002.
43. Tsuruoka, T.; Kawasaki, H.; Nawafune, H.; Akamatsu, K. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3788.
44. Sugikawa, K.; Furukawa, Y.; Sada, K. *Chem. Mater.* **2011**, *23*, 3132.
45. Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C. J.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Huo, F. *Nat. Chem.* **2012**, *4*, 310.
46. Zhou, Z.; Li, M.; Zhao, J.; Di, Z.; Di, C.; Liu, B.; Zhang, C.; Yan, C.-H.; Li, L. *Chem. Commun.* **2018**, *54*, 8182.
47. Li, Q.; Gong, S.; Zhang, H.; Huang, F.; Zhang, L.; Li, S. *Chem. Eng. J.* **2019**, *371*, 26.
48. Hu, P.; Zhuang, J.; Chou, L.-Y.; Lee, H. K.; Ling, X. Y.; Chuang, Y.-C.; Tsung, C.-K. *J. Am. Chem. Soc.* **2014**, *136*, 10561.
49. Zheng, G.; de Marchi, S.; López-Puente, V.; Sentosun, K.; Polavarapu, L.; Pérez-Juste, I.; Hill, E. H.; Bals, S.; Liz-Marzán, L. M.; Pastoriza-Santos, I.; Pérez-Juste, J. *Small* **2016**, *12*, 3935.
50. Liao, J.; Wang, D.; Liu, A.; Hu, Y.; Li, G. *Analyst* **2015**, *140*, 8165.
51. Hinman, J. G.; Turner, J. G.; Hofmann, D. M.; Murphy, C. J. *Chem. Mater.* **2018**, *30*, 7255.
52. Gliemann, H.; Wöll, C. *Mater. Today* **2012**, *15*, 110.

53. Shekhah, O.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Wöll, C. *J. Am. Chem. Soc.* **2007**, *129*, 15118.
54. Gliemann, H.; Wöll, C.; Gulati, H.; Lindemann, P.; Heinke, L.; Liu, J.; Tsotsalas, M. *Tagungsband* **2015**, 234.
55. Munuera, C.; Shekhah, O.; Wang, H.; Woll, C.; Ocal, C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7257.
56. Koh, C. S. L.; Lee, H. K.; Han, X.; Sim, H. Y. F.; Ling, X. Y. *Chem. Commun.* **2018**, *54*, 2546.
57. Kreno, L. E.; Greeneltch, N. G.; Farha, O. K.; Hupp, J. T.; Van Duyne, R. P. *Analyst* **2014**, *139*, 4073.
58. Kreno, L. E.; Hupp, J. T.; Van Duyne, R. P. *Anal. Chem.* **2010**, *82*, 8042.
59. Lee, H. K.; Koh, C. S. L.; Lee, Y. H.; Liu, C.; Phang, I. Y.; Han, X.; Tsung, C. K.; Ling, X. Y. *Sci. Adv.* **2018**, *4*, eaar3208.
60. Hermes, S.; Schröder, F.; Chelmowski, R.; Wöll, C.; Fischer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13744.
61. Cardinal, M. F.; Vander Ende, E.; Hackler, R. A.; McAnally, M. O.; Stair, P. C.; Schatz, G. C.; Van Duyne, R. P. *Chem. Soc. Rev.* **2017**, *46*, 3886.
62. Ding, S.-Y.; You, E.-M.; Tian, Z.-Q.; Moskovits, M. *Chem. Soc. Rev.* **2017**, *46*, 4042.
63. Holler, S.; Mansley, E.; Mazzeo, C.; Donovan, M.J.; Sobrero, M.; Miles, B.A. *Biosensors* **2017**, *7*, 20.
64. Zong, C.; Xu, M.; Xu, L.-J.; Wei, T.; Ma, X.; Zheng, X. -S.; Hu, R.; Ren, B. *Chem. Rev.* **2018**, *118*, 10, 4946.
65. Jones, R.R.; Hooper, D.C.; Zhang, L.; Wolverson, D.; Valev, V. K. *Nanoscale Res. Lett.* **2019**, *14*, 231.

66. Moskovits, M. *Rev. Mod. Phys.* **1985**, *57*, 783.
67. Brus, L. *Acc. Chem. Res.* **2008**, *41*, 1742.
68. Otto, A. *J. Raman Spectrosc.* **2005**, *36*, 497.
69. Lee, H. K.; Lee, Y. H.; Koh, C. S. L.; Phan-Quang, G. C.; Han, X.; Lay, C. L.; Sim, H. Y. F.; Kao, Y.-C.; An, Q.; Ling, X. Y. *Chem. Soc. Rev.* **2019**, *48*, 731.
70. Jahn, M.; Patze, S.; Hidi, I. J.; Knipper, R.; Radu, A. I.; Mühlig, A.; Yüksel, S.; Peksa, V.; Weber, K.; Mayerhöfer, T.; Cialla-May, D.; Popp, J. *Analyst* **2016**, *141*, 756.
71. Chew, W. S.; Pedireddy, S.; Lee, Y. H.; Tjiu, W. W.; Liu, Y.; Yang, Z.; Ling, X. Y. *Chem. Mater.* **2015**, *27*, 7827.
72. Lee, Y. H.; Shi, W.; Lee, H. K.; Jiang, R.; Phang, I. Y.; Cui, Y.; Isa, L.; Yang, Y.; Wang, J.; Li, S.; Ling, X. Y. *Nat. Commun.* **2015**, *6*, 6990.
73. Kim, K.; Han, H. S.; Choi, I.; Lee, C.; Hong, S.; Suh, S.-H.; Lee, L. P.; Kang, T. *Nat. Commun.* **2013**, *4*, 2182.
74. Phan-Quang, G. C.; Han, X.; Koh, C. S. L.; Sim, H. Y. F.; Lay, C. L.; Leong, S. X.; Lee, Y. H.; Pazos-Perez, N.; Alvarez-Puebla, R. A.; Ling, X. Y. *Acc. Chem. Res.* **2019**, *52*, 1844.
75. Kim, R.; Jee, S.; Ryu, U.; Lee, H. S.; Kim, S. Y.; Choi, K. M. *Korean J. Chem. Eng.* **2019**, *36*, 975.
76. Hodnik, V.; Anderluh, G. *Sensors* **2009**, *9*, 1339.
77. Han, X.; Lee, H. K.; Lee, Y. H.; Hao, W.; Liu, Y.; Phang, I. Y.; Li, S.; Ling, X. Y. *J. Phys. Chem. Lett.* **2016**, *7*, 1501.
78. Phan-Quang, G. C.; Lee, H. K.; Ling, X. Y. *Angew. Chem., Int. Ed.* **2016**, *55*, 8304.
79. Yao, Y.; Zhu, S.; Wang, H.; Li, H.; Shao, M. *J. Am. Chem. Soc.* **2018**, *140*, 1496.

80. Lee, H. K.; Lee, Y. H.; Morabito, J. V.; Liu, Y.; Koh, C. S. L.; Phang, I. Y.; Pedireddy, S.; Han, X.; Chou, L.-Y.; Tsung, C.-K.; Ling, X. Y. *J. Am. Chem. Soc.* **2017**, *139*, 11513.
81. Besnard, M.; Cabaço, M. I.; Talaga, D.; Danten, Y. *J. Chem. Phys.* **2008**, *129*, 224511.
82. Koh, C. S. L.; Lee, H. K.; Sim, H. Y. F.; Han, X.; Phan-Quang, G. C.; Ling, X. Y. *Chem. Mater.* **2020**, *32*, 1674.
83. Choi, J.; Suryanto, B. H. R.; Wang, D.; Du, H. -L.; Hodgetts, R. Y.; Vallana, F. M. F.; MacFarlane, D. R.; Simonov, A. N. *Nat. Commun.* **2020**, *11*, 5546.
84. Kibsgaard, J.; Norskov, J. K.; Chorkendorff, I. *ACS Energy Lett.* **2019**, *4*, 12, 2986.
85. Andersen, S. Z.; Colic, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Norskov, J. K.; Chorkendorff, I. *Nature* **2019**, *570*, 504.
86. Ishibashi, T.; Himeno, M.; Imaizumi, N.; Maejima, K.; Nakano, S.; Uchida, K.; Yoshida, J.; Nishio, M. *Nitric Oxide*, **2000**, *4*, 516.
87. Li, L.; Tang, C.; Yao, D.; Zheng, Y.; Qiao, S. -Z. *ACS Energy Lett.* **2019**, *4*, 9, 2111.

Chapter 2: Concentrating Immiscible Molecules at Solid@MOF Interfacial Nanocavities to Drive an Inert Gas–Liquid Reaction at Ambient Conditions

Abstract. Gas–liquid reactions form the basis of our everyday lives, yet they still suffer poor reaction efficiency and are difficult to monitor in situ, especially at ambient conditions. Now, an inert gas–liquid reaction between aniline and CO₂ is driven at 1 atm and 298K by selectively concentrating these immiscible reactants at the interface between metal–organic framework and solid nanoparticles (solid@MOF). Real-time reaction SERS monitoring and simulations affirm the formation of phenylcarbamic acid, which was previously undetectable because they are unstable for post-reaction treatments. The solid@MOF ensemble gives rise to a more than 28-fold improvement to reaction efficiency as compared to ZIF-only and solid-only platforms, emphasizing that the interfacial nanocavities in solid@MOF are the key to enhance the gas–liquid reaction. Our strategy can be integrated with other functional materials, thus opening up new opportunities for ambient-operated gas–liquid applications.

2.1 Introduction

Gas–liquid reactions are crucial to sustain human civilization. They participate in various biological functions, such as photosynthesis¹ and gas exchange in the bloodstream,² and also industrial processes,³ including hydrogenation of unsaturated compounds and gas scrubbing.⁴ Notably, the key principle to drive high-performance gas–liquid reactions is to enforce efficient and frequent intermolecular collisions between these immiscible phases. However, such reactions still suffer poor efficiency, and tracking gas–liquid reaction in situ is challenging because of low gas concentration, especially at ambient/low pressure conditions. These performances are further aggravated by poor gas solubility and comparatively lower density of gas,⁵ whereby gas rapidly escapes a liquid medium and impedes efficient intermolecular interactions. To address these issues, conventional strategies involving flow chemistry,⁶ packed column and microbubbles have been developed to promote gas–liquid interactions by prolonging gas flow in liquid,⁷⁻⁸ or by increasing gas concentration/energy at >2 bar and >323 K.⁹ While these strategies have improved gas–liquid reactions, they are limited by the need of energy-intensive and/or long reaction procedures to drive the reaction, even at high temperature/pressure. Operating gas–liquid reaction at ambient conditions remains a formidable challenge.

Metal–organic frameworks (MOFs) are emerging porous materials that could address these limitations through their excellent sorptivity and selectivity toward small gas/liquid molecules.¹⁰⁻¹² When coated over a solid surface, the solid@MOF ensemble contains nanoscopic cavities at the solid–MOF interface.¹³⁻¹⁴ Gas sorption by solid@MOF platform continuously accumulates gas molecules in these confined cavities, eventually creating a pseudo high-pressure microenvironment even under ambient operations.¹³⁻¹⁴ We hypothesize that solid@MOF platform could also promote efficient gas–liquid reaction by concentrating biphasic molecules into close proximity to enhance their intermolecular

interactions. Besides enhancing a reaction, molecular enrichment in the interfacial cavities of a plasmonic solid@MOF platform will also enable ultrasensitive in situ reaction monitoring via surface-enhanced Raman scattering (SERS). This molecular-level information is essential to elucidate reaction dynamics and facilitate rationale design of gas–liquid reaction toward optimal performance and efficiency at ambient operations.

Herein, we drive an inert gas–liquid reaction at ambient conditions by integrating a gas-sorbing layer of zeolitic imidazolate framework-8 (ZIF) over an array of Ag nanocubes (Ag@ZIF). Our integrated platform involving ZIF (pore aperture 3.4 Å) selectively concentrates and forces the immiscible gaseous and liquid reactants together to promote molecular interactions at the solid-MOF interface (Figure 2.2A). Moreover, Ag also functions as a SERS platform to track gas–liquid reaction in situ at the molecular level. Our model gas–liquid reaction is the reaction between liquid aniline and gaseous CO₂ to form phenylcarbamic acid,¹⁰⁻¹² an industrially significant process that traditionally requires high operating pressure/temperature even in the presence of catalyst. We first investigate the selective enrichment of liquid aniline within the interfacial cavity of Ag@ZIF, which is vital for subsequent reaction with CO₂ gas. Corroborating experimental SERS and density functional theory (DFT) studies, we track the gas–liquid reaction in situ and demonstrate the unprecedented reaction of aniline and CO₂ at 1 atm and 298 K. Moreover, we reveal that the presence of interfacial cavities is the key to improve gas–liquid reaction efficiency by more than 28-fold, which cannot be achieved in standalone ZIF or Ag platforms. Our work offers valuable insights to realize ambient-operated gas–liquid reactions, which are highly sought after in diverse fields including air-to fuel conversion, chemistry, environmental remediation, and industrial chemical manufacturing.

2.2 Results and discussion

We begin by depositing an array of Ag nanocubes (edge length 126 ± 5 nm; Figure 2.1) on a Si substrate via the Langmuir–Blodgett technique. The Ag nanocube array is then surface-grafted with perfluorodecanethiol (PFDT) to provide a featureless SERS background in the region of 400 to 1800 cm^{-1} necessary for accurate reaction monitoring. PFDT-grafted Ag nanocube array is then coated with a ZIF layer by repeated immersions into methanolic zinc nitrate and 2-methylimidazole mixture. ZIF nucleates and eventually grows into a polycrystalline film that fully encapsulates the Ag nanocubes (Ag@ZIF; ZIF thickness 241 ± 45 nm; Figure 2.2B, 2.3). X-ray diffraction (XRD) analyses highlight the successful formation of Ag@ZIF platform (Figure 2.2C), where Ag@ZIF contains the unique XRD patterns of both ZIF and Ag nanocube. All Ag@ZIF platforms are activated using heat treatment prior to subsequent experiments (Figures 2.3, 2.4).

Figure 2.1. Characterization of PFDT-functionalized Ag nanocubes. (A) SEM image of PFDT-functionalized Ag nanocubes. (B) Extinction spectrum of PFDT-functionalized Ag

nanocubes. The peaks at 348, 412, 525 and 674 nm can be assigned to octupole (348 nm), quadrupole (412 nm and 525 nm), and dipole resonances (674 nm), respectively. (C) Size distribution of Ag nanocubes. (D) SERS spectra of PFDT-functionalized compared to PVP coated Ag nanocubes.

Figure 2.2. (A) Schematic depicting the importance of Ag@ZIF to capture and concentrate gas and liquid molecules in its interfacial cavities for enhanced gas-liquid reaction, using the reaction between CO_2 and aniline as a model. (B) Cross-sectional SEM image and (C) XRD pattern of Ag@ZIF. (D) Schemes and SERS spectra of (i) Ag@ZIF and (ii) Ag-only platforms when submerged in an aniline/decane mixture. (E) Time-dependent SERS intensity of aniline measured using Ag@ZIF or Ag-only platforms.

Figure 2.3. Characterization of Ag@ZIF before and after reaction. (A) As-synthesized Ag@ZIF, (B) Thermally activated Ag@ZIF and (C) Ag@ZIF after reaction. (i-ii) Cross-sectional SEM images in SEI and LBE modes respectively. (iii-iv) Top view SEM images in SEI and LBE modes respectively. (v) ZIF thickness distribution.

Figure 2.4. Substrate XRD diffraction pattern of as-synthesized Ag@ZIF, thermally activated Ag@ZIF and thermally activated Ag@ZIF after reaction (from bottom to top). XRD patterns at 7.5, 10.5, 12.8 and 18.0° coincide with ZIF's (011), (002), (112) and (222) facets,¹⁵ respectively. XRD peak at 44.4° can be indexed to the (100) facet of single crystalline Ag nanocube.¹⁶

There are two key criteria for solid@MOF to facilitate gas–liquid reaction: its abilities to 1) selectively sorb gas and liquid species from the reaction medium, and 2) subsequently enrich these reactants at the solid–MOF interface. To demonstrate its molecular selectivity and concentrating effects, we monitor the molecular components in solid@MOF interfacial cavity by immersing in 0.1M aniline/decane solution under N₂ environment using SERS. Only vibrational fingerprint of aniline is observed throughout the experiment, with SERS bands at 1274, 1387, 1594, and 1615 cm⁻¹ indexed to (ν_{CN}), (ρ_{NH2} +

ν_{CC}), ($\delta_{\text{NH}_2} + \nu_{\text{CC}}$) and ($\nu_{\text{CN}} + \delta_{\text{NH}_2} + \nu_{\text{CC}}$), (Figure 2.2D, 2.2E).¹⁷ The absence of other bands indicates that decane is not accessible to the SERS surface, and also eliminates the possibility of laser-induced processes on Ag@ZIF platform and/or aniline (Figure 2.5). The SERS intensity of aniline at 1387 cm^{-1} gradually increases from (31 ± 3) counts at 0 min to (463 ± 16) counts within the first 90 min, followed by a plateau at about 466 counts beyond 105 min. The initial rise and subsequent plateau of aniline's SERS intensity indicates the continuous accumulation and saturation of aniline near the SERS surfaces, respectively. Ag@ZIF exhibits a Lagergren pseudo first-order sorption kinetics model with a rate constant of 37.5 ms^{-1} , denoting the rapid sorption of aniline (Figure 2.5B). Conversely, no aniline SERS band is observed in control Ag platform without ZIF. Instead, we only observe three weak SERS bands at 1301, 1377, and 1448 cm^{-1} attributed to decane τ_{CH_2} , ω_{CH_2} and δ_{CH_2} ,¹⁸ respectively (Figure 2.2D, 2.2E, 2.6). These comparisons demonstrate the importance of creating a crack-free ZIF membrane to selectively capture and enrich target molecules over the encapsulated SERS active surfaces. The selective sorption of aniline over decane arises from the characteristic pore size (3.4 Å) and framework flexibility of ZIF to enable the diffusion of aniline (ca. 5.9 Å) into the SERS-active region,¹⁹⁻²² while blocking the access of larger solvent molecules such as decane (>7.2 Å). Furthermore, the rationale choice of solvent is another critical factor to ensure the selective capturing of reactant from liquid medium; the use of smaller solvent molecules (e.g. methanol) leads to competitive sorption with aniline by Ag@ZIF (Figure 2.7).

Figure 2.5. Time-dependent aniline concentrating effect in Ag@ZIF over 2 hrs. (A) SERS spectra under N₂ flushing. (B) SERS intensity measurement of aniline sorption comparing with (black) and without (green) ZIF film.

Figure 2.6. Control experiments using Ag platform for detection in aniline/decane mixture (i) with aniline and (ii) without aniline.

We highlight the importance of selecting an ideal solvent for our experimental setup by choosing small molecule solvent such as methanol which is undesirable as it will compete for sorption into interfacial cavities and post spectra interferences (Figure 2.7). Similarly, we immerse our Ag@ZIF substrate into 0.1 M aniline/methanol mixture and

monitor the capturing of methanol (3.6 Å) and aniline (~5.9 Å) via SERS detection.²³⁻²⁴ Our SERS spectra reveal the emergence of two additional peaks at 1032 and 1375 cm⁻¹ (Figure 2.7i), which can be indexed to (ν_{CO}) and (δ_{CH_2}) modes of methanol (Figure 2.7iii),²⁴ respectively. This indicates the diffusion of methanol into ZIF's pores hence causing spectra interference. Notably, we notice weak intensity SERS bands of aniline and methanol simultaneously in the absence of ZIF (Figure 2.7ii). Thus, this further emphasize on the importance of integrating ZIF onto Ag to concentrate and enrich liquid molecules near Ag surface for detection.

Figure 2.7. Molecule size selectivity in aniline/methanol mixture (i) with ZIF, (ii) without ZIF and (iii) SERS spectra of methanol.

We subsequently drive an inert gas–liquid reaction between CO₂ and aniline at ambient conditions and concurrently monitor the reaction in situ using our Ag@MOF platform. In a typical reaction set-up, we first immerse Ag@ZIF in aniline/decane mixture for 2 h to preconcentrate aniline in the interfacial cavities. Gas–liquid reaction is then initiated by bubbling CO₂ gas (5 sccm, 1 atm) into the reaction cell, and we track its progress

in real-time using SERS. At 0 min, the SERS spectrum shows only vibrational signatures of aniline at 1274 (ν_{CN}), 1387 ($\rho_{\text{NH}_2} + \nu_{\text{CC}}$), 1594 ($\delta_{\text{NH}_2} + \nu_{\text{CC}}$), and 1615 cm^{-1} ($\delta_{\text{NH}_2} + \nu_{\text{CN}} + \nu_{\text{CC}}$; Figure 2.8A). As CO_2 exposure increases, aniline SERS intensity decreases exponentially at 15 min and eventually diminishes by 45 min (Figure 2.8, 2.9). We also note the emergence of new SERS bands at 1335, 1427, 1556, and 1633 cm^{-1} at 30 min, whereby the intensities increase and ultimately dominate the SERS spectrum at 90 min. More importantly, subsequent purging with inert N_2 gas for 30 min does not revert these spectral evolutions. Our findings evidently demonstrate the spectral changes are due to irreversible chemical transformation of aniline. In contrast, control Ag platform in the absence of ZIF coating or Ag@ZIF under inert N_2 gas flow display no distinct spectrum changes (Figures 2.5B, 2.9B). Both control experiments highlight that ZIF is critical to enable gas–liquid reaction at ambient conditions and CO_2 functions as a gas reactant, respectively. The ZIF layer remains stable throughout the reaction with consistent thickness and XRD patterns before and after reaction (Figures 2.3, 2.4).

Figure 2.8. (A) SERS spectra and time-resolved contour plot recorded from Ag@ZIF (i) before reaction, (ii) after reaction and (iii) upon 30 min N_2 flush after reaction. (B) Temporal changes to SERS intensities of 1387 cm^{-1} and 1427 cm^{-1} bands when Ag@ZIF is submerged in 0.1 M aniline/decane mixture.

Figure 2.9. Time-dependent SERS spectra of reaction over 90 min (A) with ZIF and (B) without ZIF.

We use density functional theory (DFT) to identify the chemical species involved in the reaction and elucidate the molecular origins behind the observed spectral evolutions. We simulate the SERS spectra of various probable carboxylated products including phenylcarbamic acid, phenyl phenylcarbamate, 1,3-diphenylurea, and 2-aminobenzoic acid owing to the possibility of carbamates/urea formation as well as the presence of ortho-directing -NH_2 group (Figure 2.10A, 2.10B, 2.11). Experimental and DFT simulated SERS spectra of aniline (Figure 2.12; Table 2.1) are in close agreement,¹⁷ thus validating the accuracy of our DFT investigations. Most importantly, the experimental SERS spectrum at 90 min matches well to the simulated spectrum of phenylcarbamic acid. This is evident from the presence of unique amide and hydroxyl vibrational modes, whereby SERS features at 1427, 1335, and 1556 cm^{-1} are indexed to $(\nu_{\text{as,NC(OH)}} + \delta_{\text{COH}} + \nu_{\text{CO}})$, $(\nu_{\text{NCO}} + \nu_{\text{as,CCN}})$, and $(\nu_{\text{NCO}} + \nu_{\text{as,CNC}} + \delta_{\text{CNH}})$ (Figure 2.10B, Table 2.2), respectively. The formation of phenylcarbamic acid is also supported by similar work reporting the formation of carbamic acid using amine species and CO_2 .²⁵⁻²⁷ We exclude other carboxylated species as the product

owing to large spectral mismatch between our experimental and DFT simulated SERS spectra (Supporting Information, Figure 2.11).

Figure 2.10. (A) Molecular structures of aniline and phenylcarbamic acid near Ag surface. (B) Key spectral transformations involving amide and hydroxyl moieties. (i) Experimental SERS spectra at 0 and 90 min. (ii) Simulated SERS spectra of aniline and phenylcarbamic acid. (C) Depiction the gas-liquid reaction between aniline and CO₂ to form phenylcarbamic acid in the interfacial cavity.

Figure 2.11. Overview DFT-simulated Raman spectra of possible products with Ag₆ cluster. (A) Experimental product, (B) phenylcarbamic acid, (C) phenyl phenylcarbamate, (D) 1,3-diphenylurea and (E) 2-aminobenzoic acid.

Figure 2.12. Overview SERS spectra of aniline in comparison to DFT-simulation.

Table 2.1. SERS vibrational modes of aniline and their band assignments.

Experimental (cm^{-1})	Simulated Aniline (cm^{-1})	Assignment
1274	1265	$\nu(\text{C-N}) + \delta(\text{C-H})$
1387	1363	$\rho(\text{NH}_2) + \nu(\text{C-C}) + \delta(\text{C-H})$
1562	1540	$\nu(\text{C-N}) + \nu(\text{C-C}) + \delta(\text{C-H})$
1594	1654	$\delta(\text{NH}_2) + \nu(\text{C-C}) + \delta(\text{C-H})$
1615	1665	$\delta(\text{NH}_2) + \nu(\text{C-N}) + \nu(\text{C-C}) + \delta(\text{C-H})$

ν , stretching; δ , in-plane deformation; ρ , rocking

Table 2.2. DFT-Simulated SERS vibrational modes of phenylcarbamic acid and their band assignments.

Experimental (cm ⁻¹)	Simulated Phenylcarbamic acid (cm ⁻¹)	Assignment
1335	1351	$\nu_{as}(C=C-N) + \nu(N-C=O) + \text{aromatic ring stretch}$
1427	1458	$\nu_{as}(N-C-OH) + \delta(C-O-H) + \nu(C=O) + \text{aromatic ring stretch}$
1556	1547	$\nu_{as}(C-N-C) + \nu(N-C=O) + \delta(C-N-H) + \text{aromatic ring stretch}$
1633	1661	$\nu(C-N) + \text{aromatic ring stretch}$

ν , stretching; δ , in-plane deformation; ρ , rocking; as , asymmetric

Collectively, our experimental and DFT SERS studies clearly provide the first experimental verification to the formation of phenylcarbamic acid using liquid aniline and CO₂ gas (Figure 2.10C). In contrast, phenylcarbamic acid cannot be identified using conventional ex situ monitoring methods because it is unstable toward post-reaction treatments, such as molecular extraction. By enabling in situ gas–liquid reaction read-out at ambient conditions, our SERS-active Ag@ZIF platform addresses the limitations of modern characterization methods, which are typically non-molecular-specific and/or mandate pressurized system. Moreover, the realization of such gas–liquid reaction is unprecedented at ambient conditions; most carbamate-forming reactions are typically performed at high temperature and pressure. Our ability to drive inert gas–liquid reaction and perform real-time reaction monitoring are enabled by the abilities of Ag@ZIF to selectively concentrate target liquid and gas reactants within its interfacial cavities and near the plasmonic surfaces. This molecular concentrating process consequently forces biphasic reactants into proximity,

thereby enhancing their intermolecular interactions to drive chemical reactions in the absence of sophisticated set-up and/or elevated pressure/temperature.

Utilizing the critical reaction insights gained from our SERS and DFT investigations, we further apply Ag@ZIF platform at a larger reaction scale to demonstrate its versatility and scalability. Note that Ag@ZIF core-shell nanoparticles (2 mg; ZIF thickness, 47 ± 11 nm; Figure 2.13, 2.14) are used in this study, instead of Ag@ZIF substrate. This is to maximize their interactions with gas and liquid reactants throughout the reaction volume. We suspend Ag@ZIF particles in 0.1M aniline/decane mixture and initiate the reaction by bubbling CO₂ gas. The reaction is monitored over 5 h using UV/Vis absorption spectroscopy. We observe aniline's characteristic absorption peak at 234 nm (Figure 2.15A). With increasing CO₂ exposure from 0 min to 300 min, C/C₀ decreases linearly from 1 to 0.765 and corresponds to a reaction efficiency of 23.5% (Figure 2.15B). In contrast, control Ag-only platform and blank (neat aniline/decane mixture) exhibit apparent efficiencies of less than 6% (Figure 2.17), which are likely due to minor adsorption of aniline on reaction apparatus. The more than 4-fold improvement to reaction efficiency in Ag@ZIF eliminates the possibility of a catalytic effect arising from Ag or potential side reactions as the main contributor to its superior reaction performance. More importantly, Ag@ZIF exhibits a more than 2-fold superior reaction efficiency compared to pure ZIF-only crystallites (2 mg) with a reaction efficiency of 11.7% (Figure 2.15B; Supporting Information, Figures 2.16, 2.17). By further normalizing the aniline consumed with the mass of ZIF (Figure 2.15C; refer to Calculation 2.1), we ensure a fair comparison between Ag@ZIF and ZIF-only platforms to highlight the former's ability to facilitate gas-liquid reaction at the interfacial nanocavities. The Ag@ZIF exhibits an aniline consumption of about $9.6 \text{ mg}_{\text{aniline}}\text{mg}_{\text{ZIF}}^{-1}$ over 5 h, which is notably more than 28-fold higher than the consumption by ZIF of about $0.3 \text{ mg}_{\text{aniline}}\text{mg}_{\text{ZIF}}^{-1}$. The superior reaction performance of Ag@ZIF is also supported by its

2-fold higher apparent reaction rate constant (k) of 4.8mms^{-1} as compared to ZIF-only platform ($k=2.4\text{mms}^{-1}$; Figure 2.15B). These observations highlight the enhanced gas–liquid reaction in Ag@ZIF is primarily due to the presence of interfacial cavities rather than intrinsic ZIF pores.

Figure 2.13. SEM characterization in the optimization of ZIF coating onto Ag nanocubes for the formation of Ag@ZIF nanocubes (A) 0 min, (B) 20 min, (C) 40 min, (D) 1 hour, (E) 2 hour, (F) 3 hour, respectively.

Figure 2.14. Characterization of Ag@ZIF nanocubes. (A) As-synthesized Ag@ZIF nanocubes and (B) activated Ag@ZIF after reaction. (i) TEM image and (ii) ZIF thickness distribution.

Figure 2.15. (A) Aniline extinction spectra at predefined timings in presence of Ag@ZIF. Inset: a TEM image of our core-shell Ag@ZIF platform. (B) Changes to aniline C/C_0 under prolonged CO_2 exposure. Blank refers to absence of any nanoparticles. (C) Mass of aniline consumed per unit mass of ZIF in Ag@ZIF and ZIF-only platforms. (D) Mass of aniline consumed per unit mass of ZIF and interfacial area in Ag@ZIF and SiO_2 @ZIF systems.

Figure 2.16. Characterization of ZIF particles. (A) SEM image and (B) size distribution of ZIF particles.

Figure 2.17. Monitoring gas-liquid reaction using temporal UV-Vis absorption measurement. UV-Vis absorption spectra of respective reaction setups involving (A) Ag@ZIF, (B) ZIF only, (C) Ag only, (D) blank and (E) SiO₂@ZIF. (F) C/C₀ plot of reaction setups involving SiO₂@ZIF and SiO₂. All gas-liquid reactions are performed at a CO₂ flow rate of 5 sccm.

Calculation 2.1 - Calculation on the mass of aniline consume per mass of ZIF

For Ag@ZIF

We estimate the mass of ZIF in a Ag@ZIF nanoparticle by assuming that the ZIF layer conformally coats the entire Ag nanocube (AgNC). Hence, the volume of Ag@ZIF can be determined as followed:

$$\begin{aligned}\text{Volume}_{\text{Ag@ZIF}} &= (\text{Length}_{\text{Ag@ZIF}})^3 \\ &= (221.1 \text{ nm})^3 \\ &= 1.08 \times 10^7 \text{ nm}^3 \\ &= 1.08 \times 10^{-14} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Volume}_{\text{Ag}} &= (\text{Length}_{\text{Ag}})^3 \\ &= (126.7 \text{ nm})^3 \\ &= 2.03 \times 10^6 \text{ nm}^3 \\ &= 2.03 \times 10^{-15} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Volume}_{\text{ZIF}} &= \text{Volume}_{\text{Ag@ZIF}} - \text{Volume}_{\text{Ag}} \\ &= (1.08 \times 10^{-14} - 2.03 \times 10^{-15}) \text{ cm}^3 \\ &= 8.77 \times 10^{-15} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Mass}_{\text{ZIF}} &= \text{Density}_{\text{ZIF}} \times \text{Volume}_{\text{ZIF}} \\ &= 0.3 \text{ g cm}^{-3} \times 8.77 \times 10^{-15} \text{ cm}^3 \\ &= 2.63 \times 10^{-15} \text{ g}\end{aligned}$$

$$\begin{aligned}\text{Mass}_{\text{Ag}} &= \text{Density}_{\text{Ag}} \times \text{Volume}_{\text{Ag}} \\ &= 10.49 \text{ g cm}^{-3} \times 2.03 \times 10^{-15} \text{ cm}^3 \\ &= 2.13 \times 10^{-14} \text{ g}\end{aligned}$$

Given that the total mass of Ag@ZIF used = 2 mg

$$\text{Mass}_{\text{ZIF in Ag@ZIF}} = \frac{\text{Mass}_{\text{ZIF}}}{\text{Mass}_{\text{Ag}} + \text{Mass}_{\text{ZIF}}} \times 2 \text{ mg}$$

$$= \frac{2.63 \times 10^{-15}}{2.13 \times 10^{-14} + 2.63 \times 10^{-15}} \times 2 \text{ mg}$$

$$= 0.22 \text{ mg}$$

From the extinction spectra obtained, C/C_0 of aniline at $t = 300 \text{ min}$ is quantified to be 0.765 which denotes that 23.5 % of aniline has been consumed. By benchmarking against blank control experiment, the effective consumption of aniline in Ag@ZIF is calculated to be 17.4 %. Since the initial aniline concentration is 0.1 M, the mass of aniline consumed during the reaction duration of 300 min is estimated as followed:

$$\text{Mass}_{\text{aniline}} = \text{Volume}_{\text{aniline}} \times \text{Initial Concentration}_{\text{aniline}} \times \text{Molecular Weight}_{\text{aniline}}$$

$$\times \% \text{ effective aniline consumed}$$

$$= 1.3 \times 10^{-3} \text{ L} \times 0.1 \text{ M} \times 93.13 \text{ g mol}^{-1} \times 17.4 \% \times 1000$$

$$= 2.11 \text{ mg}$$

$$\text{Mass}_{\text{Aniline consumption normalized with Mass}_{\text{ZIF}}} = (2.11 \text{ mg}_{\text{aniline}} \div 0.22 \text{ mg}_{\text{ZIF}})$$

$$= 9.6 \text{ mg}_{\text{aniline}} \text{ mg}_{\text{ZIF}}^{-1}$$

For ZIF only

From the extinction spectra obtained, C/C_0 of aniline at $t = 300$ min is quantified to be 0.883 which denotes that 11.7 % of aniline has been consumed. By benchmarking against blank control experiment, the effective consumption of aniline in ZIF is calculated to be 5.7 %. Since the initial aniline concentration is 0.1 M, the mass of aniline consumed during the reaction duration of 300 min is estimated as followed:

$$\begin{aligned}\text{Mass}_{\text{aniline}} &= \text{Volume}_{\text{aniline}} \times \text{Initial Concentration}_{\text{aniline}} \times \text{Molecular Weight}_{\text{aniline}} \\ &\quad \times \% \text{ effective aniline consumed} \\ &= 1.3 \times 10^{-3} \text{ L} \times 0.1 \text{ M} \times 93.13 \text{ g mol}^{-1} \times 5.7 \% \times 1000 \\ &= 0.686 \text{ mg}\end{aligned}$$

$$\begin{aligned}\text{Mass}_{\text{Aniline consumption normalized with Mass}_{\text{ZIF}}} &= (0.686 \text{ mg}_{\text{aniline}} \div 2 \text{ mg}_{\text{ZIF}}) \\ &= 0.343 \text{ mg}_{\text{aniline}} \text{ mg}_{\text{ZIF}}^{-1}\end{aligned}$$

Our strategy building on the interfacial cavities of solid@MOF to promote gas–liquid reaction is also easily extended to other functional material. As a proof of concept, we synthesize SiO_2 @ZIF (ZIF thickness, 14 ± 4 nm; Figure 2.18) and subject them to identical reaction procedures. Using the absorption peak of aniline at 234 nm, SiO_2 @ZIF demonstrates a reaction efficiency of 20% (Figure 2.17E, 2.17F) at 300 min, which is also about 3-fold higher compared to control SiO_2 -only and blank systems (<7% efficiency). This again implies negligible contribution from the encapsulated solid to the decrease in aniline concentration. We further normalize the aniline consumption in both Ag@ZIF and SiO_2 @ZIF against interfacial area to exemplify that our strategy is independent on the nature of encapsulated solid. Both SiO_2 @ZIF and Ag@ZIF platforms exhibit similar aniline

consumption of about 90.9 and 99.7 $\text{mg}_{\text{aniline}}\text{mg}_{\text{ZIF}}^{-1} \mu\text{m}_{\text{interfacial area}}^{-2}$, respectively (Figure 2.15D; refer to Calculation 2.2). This is a direct evidence that the interfacial cavities between MOF and any solid materials is the key factor to achieve high performance gas–liquid reaction. Our solid@MOF strategy is versatile and can be potentially integrated with many functional materials, such as solid catalyst, to promote diverse fluid–fluid reactions.

Figure 2.18. Characterization of SiO₂ and SiO₂@ZIF nanoparticles. (A) As-synthesized SiO₂ nanoparticles. (i) SEM image and (ii) particle diameter distribution. (B) As-synthesized SiO₂@ZIF and (C) activated SiO₂@ZIF after reaction. (i) TEM image and (ii) ZIF thickness distribution.

Calculation 2.2 - Calculation on the mass of aniline consumed per mass of ZIF and per interfacial area

For Ag@ZIF

Based on the calculation achieved in Supporting Text 1 for Ag@ZIF, we further normalized it with the interfacial area by assuming that interfacial area is approximately the total surface area of cube surface.

$$\begin{aligned}\text{Interfacial Area}_{\text{Ag}} &= 6 \times (0.1267 \mu\text{m})^2 \\ &= 9.62 \times 10^{-2} \mu\text{m}^2\end{aligned}$$

Mass_{Aniline} consumption normalized with Mass_{ZIF} and Mass_{interfacial area}

$$\begin{aligned}&= 2.11 \text{ mg} \div [0.22 \text{ mg} \times 9.62 \times 10^{-2} \mu\text{m}^2] \\ &= 99.7 \text{ mg}_{\text{aniline}} \text{ mg}_{\text{ZIF}}^{-1} \mu\text{m}_{\text{interfacial area}}^{-2}\end{aligned}$$

For SiO₂@ZIF

We estimate the mass of ZIF in a SiO₂@ZIF nanoparticle by assuming that the ZIF layer conformally coats the entire SiO₂ nanosphere. Hence, the volume of SiO₂@ZIF can be determined as followed:

$$\begin{aligned}\text{Volume}_{\text{SiO}_2@\text{ZIF}} &= (4/3) \pi (\text{Radius}_{\text{SiO}_2@\text{ZIF}})^3 \\ &= (4/3) \pi (162 \text{ nm})^3 \\ &= 1.78 \times 10^7 \text{ nm}^3 \\ &= 1.78 \times 10^{-14} \text{ cm}^3\end{aligned}$$

$$\begin{aligned}\text{Volume}_{\text{SiO}_2} &= (4/3) \pi (\text{Radius}_{\text{SiO}_2})^3 \\ &= (4/3) \pi (148 \text{ nm})^3 \\ &= 1.36 \times 10^7 \text{ nm}^3 \\ &= 1.36 \times 10^{-14} \text{ cm}^3\end{aligned}$$

$$\text{Volume}_{\text{ZIF}} = \text{Volume}_{\text{SiO}_2@\text{ZIF}} - \text{Volume}_{\text{SiO}_2}$$

$$= (1.78 \times 10^{-14} - 1.36 \times 10^{-14}) \text{ cm}^3$$

$$= 4.25 \times 10^{-15} \text{ cm}^3$$

$$\text{Mass}_{\text{ZIF}} = \text{Density}_{\text{ZIF}} \times \text{Volume}_{\text{ZIF}}$$

$$= 0.3 \text{ g cm}^{-3} \times 4.25 \times 10^{-15} \text{ cm}^3$$

$$= 1.28 \times 10^{-15} \text{ g}$$

$$\text{Mass}_{\text{SiO}_2} = \text{Density}_{\text{SiO}_2} \times \text{Volume}_{\text{SiO}_2}$$

$$= 2.65 \text{ g cm}^{-3} \times 1.36 \times 10^{-14} \text{ cm}^3$$

$$= 3.59 \times 10^{-14} \text{ g}$$

Given that the total mass of $\text{SiO}_2@\text{ZIF}$ used = 2 mg

$$\begin{aligned} \text{Mass}_{\text{ZIF}} \text{ in } \text{SiO}_2@\text{ZIF} &= \frac{\text{Mass}_{\text{ZIF}}}{\text{Mass}_{\text{SiO}_2} + \text{Mass}_{\text{ZIF}}} \times 2 \text{ mg} \\ &= \frac{1.28 \times 10^{-15}}{3.59 \times 10^{-14} + 1.28 \times 10^{-15}} \times 2 \text{ mg} \\ &= 0.069 \text{ mg} \end{aligned}$$

From the extinction spectra obtained, C/C_0 of aniline at $t = 300$ min is quantified to be 0.8 which denotes that 20 % of aniline has been consumed. By benchmarking against blank control experiment, the effective consumption of aniline in $\text{SiO}_2@\text{ZIF}$ is calculated to be 14.2 %. Since the initial aniline concentration is 0.1 M, the mass of aniline consumed during the reaction duration of 300 min is estimated as followed:

$$\begin{aligned} \text{Mass}_{\text{aniline}} &= \text{Volume}_{\text{aniline}} \times \text{Initial Concentration}_{\text{aniline}} \times \text{Molecular Weight}_{\text{aniline}} \\ &\quad \times \% \text{ effective aniline consumed} \\ &= 1.3 \times 10^{-3} \text{ L} \times 0.1 \text{ M} \times 93.13 \text{ g mol}^{-1} \times 14.2 \% \times 1000 \\ &= 1.71 \text{ mg} \end{aligned}$$

We normalized the aniline consumption with the mass of ZIF and the interfacial area by assuming that interfacial area is approximately the total surface area of sphere surface.

$$\begin{aligned}\text{Interfacial Area}_{\text{SiO}_2} &= (4\pi) (\text{Radius}_{\text{SiO}_2})^2 \\ &= 4\pi \times (0.148 \text{ }\mu\text{m})^2 \\ &= 0.275 \text{ }\mu\text{m}^2\end{aligned}$$

$$\begin{aligned}\text{Mass}_{\text{Aniline}} \text{ consumption normalized with Mass}_{\text{ZIF}} \text{ and Mass}_{\text{interfacial area}} \\ &= 1.71 \text{ mg} \div [0.069 \text{ mg} \times 0.275 \text{ }\mu\text{m}^2] \\ &= 90.9 \text{ mg}_{\text{aniline}} \text{ mg}_{\text{ZIF}}^{-1} \text{ }\mu\text{m}_{\text{interfacial area}}^{-2}\end{aligned}$$

2.3 Conclusion

In conclusion, we drive an inert gas–liquid reaction between aniline and CO₂ at ambient conditions and realize its in situ reaction monitoring by selectively concentrating these biphasic molecules in the interfacial nanocavities of solid@MOF platform. Experimental and DFT SERS investigations jointly highlight the formation of phenylcarbamic acid in our model reaction. Notably, such molecular-level identification of phenylcarbamic acid is unprecedented because this chemical species is unstable to post-reaction treatment and can only be tracked in situ. Moreover, solid@MOF improves reaction efficiency by more than 28-fold as compared to solid-only or MOF-only platforms, highlighting that the interfacial cavities present in solid@MOF is the origin behind its superior reaction performance. Such solid@MOF system tackles the long-standing bottleneck in gas–liquid reaction monitoring by enriching immiscible reactants locally without requiring elevated temperature/pressure operations. Together with its high versatility to integrate with other functional materials, we envisage our solid@MOF strategy as a cornerstone to realize efficient and ambient-operated fluid–fluid

reactions/processes critical in diverse fields including chemistry, heterogeneous catalysis, greenhouse gases removal, and gas-to-fuel conversions.

2.4 Materials and methods

Chemicals. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55,000), decane ($\geq 98\%$), aniline (ACS reagent, $\geq 99.5\%$), zinc nitrate hexahydrate (reagent grade, 98%), 2-methylimidazole (99%), 1H,1H,2H,2H-perfluorodecanethiol (PFDT; 97%) and tetraethyl orthosilicate (99.999% trace metals basis) were purchased from Sigma Aldrich; copper (II) chloride ($\geq 98\%$) was from Alfa Aesar; methanol (ACS reagent, $\geq 99.8\%$) was from J.T.Baker®; ethanol (ACS, ISO, Reag. Ph Eur) and ammonia (ACS, Reag. Ph Eur) was from EMSURE®; dimethylformamide (HPLC grade) was obtained from Fisher Scientific; nitrogen (N_2 ; ALPHAGAZ 1; 99.999%) and carbon dioxide (CO_2 ; 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 were synthesized of high yield via polyol method described in literature.²⁸ 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 $190\text{ }^\circ\text{C}$ 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 then redispersed in ethanol (10 mg/mL) and stored in fridge.

Assembly of Ag nanocubes via Langmiur-Blodgett method. The preparation of Ag nanocubes assembled on Si substrates were prepared as described in literature.²⁹ Briefly, Si (100) substrates were cleaned prior to assembly of Ag naocubes using oxygen plasma (FEMTO SCIENCE, CUTE-MP/R, 100 W) for 5 min. The surface pressure was zeroed before addition of PVP-caped 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 Langmiur-blodgett trough (KSV NIMA, KN1002). The surface pressure can be tuned by moving the mechanical barrier of the machine. Surface pressure of 16 mN/m were employed, 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 Zeolitic Imidazolate Framework – 8 (ZIF) film on PFDT-capped Ag nanocubes array. ZIF film was grown on the nanocubes array using a procedure reported from literature.³⁰ 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 crystals. The procedure was repeated 2 more times using fresh $\text{Zn}(\text{NO}_3)_2$ and 2-methylimidazole solutions to obtain ZIF film 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 were used immediately after activation.

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.

Synthesis of silica beads. Silica beads were synthesized using a modified Stober process. 1500 μL of pure water and 1500 μL of ammonia were added dropwise into 760 μL of tetraethylorthosilicate ethanolic solution (0.35 M) respectively under vigorous stirring for 30 mins. The water-soluble silica beads were then washed with ethanol and water and subsequently redispersed in methanol.

Synthesis of SiO₂@ZIF core-shell. 250 μ L of Zn(NO₃)₂ (25 mM) was added to a vial of 1.3 mL methanol and stirred at 500 rpm for 5 minutes. 250 μ L of methanolic 2-methylimidazole (50 mM) was then added, followed by the immediate addition of 200 μ L SiO₂ nanospheres 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 evaluation. The thermal-activated platforms were placed inside a custom-made gas flow cell for SERS examination. The gas flow cell was first flushed with N₂ gas (5 sccm) for 30 min to displace air from our experimental set-up. Following which, CO₂ gas (5 sccm) was flown through the gas flow cell and SERS analysis was performed in-situ for a duration of 90 min. Subsequent purging of the experimental set-up with N₂ gas and simultaneous SERS analysis were conducted until characteristic SERS bands remain constant in the SERS spectra (30 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) and their SERS intensities (I) were based on the relative intensity on respective SERS bands.

Density functional theory (DFT) simulation. The calculation on the interaction of Ag surface with possible products were carried out using the unrestricted B3LYP exchange-correlation functional, as implemented in the Gaussian 09 computational chemistry package. The 6-31g (d p) basis set was used for all atoms except Ag, for which the LANL2DZ basis set was employed. The Ag surface was modelled using a reported triangle consisting of 6 Ag atoms.³¹ After geometry optimization of the triangular Ag cluster, possible product molecule was then placed near the Ag cluster ($< 2 \text{ \AA}$) and the entire system was re-optimized.

ZIF was excluded from the simulation owing to its nanoscopic separation from the SERS-active surface, as demonstrated experimentally via the lack of ZIF's vibrational features during SERS evaluations.

Ex-situ UV-Vis reaction monitoring. Solid@ZIF core-shell nanoparticles were dispersed in 1.3 mL aniline/decane mixture (0.1 M) solution. The gas flow cell was first flushed with N₂ gas (5 sccm) for 30 min to displace air from our experimental set-up. Following which, CO₂ gas (5 sccm) was introduced through the gas flow cell and UV-Vis analysis was performed at pre-defined timings of 0, 30, 60, 120, 150, 180, 240 and 360 min for UV-vis measurements to quantify the concentration of aniline. The apparent rate constant (k) can be determined based on the multiplication between the concentration of the reaction medium and the gradient of the C/C_0 plot exhibited by solid@ZIF and ZIF.

Characterization. Scanning electron microscope (SEM) imaging was performed using JEOL-JSM-7600F microscope. Transmission electron microscope (TEM) imaging was performed using JEOL-2100 at an accelerating voltage of 200 kV. 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 0.07 mW. A 50 $\times$ objective lens (N.A. = 0.55) with 5 s acquisition time was used for data collection. All SERS spectra were obtained by averaging the individual SERS spectra within the SERS image.

References

1. Xiong, J.; Bauer, C. E. *Annu. Rev. Plant Biol.* **2002**, *53*, 503.
2. Philippe, H. *J. Physiol.* **2014**, *592*, 453.
3. Franke, R.; Selent, D.; Börner, A. *Chem. Rev.* **2012**, *112*, 5675.
4. Prabhansu, M. K.; Karmakar, P.; Chandra, P. K.; Chatterjee, J. *Environ. Chem. Eng.* **2015**, *3*, 689.
5. Lei, Z.; Dai, C.; Chen, B.; *Chem. Rev.* **2014**, *114*, 1289.
6. Brzozowski, M.; O'Brien, M.; Ley, S. V.; Polyzos, A. *Acc. Chem. Res.* **2015**, *48*, 349.
7. Wang, M.; Joel, A. S.; Ramshaw, C.; Eimer, D.; Musa, N. M. *Appl. Energy* **2015**, *158*, 275.
8. Huang, J.; Cheng, F.; Binks, B. P.; Yang, H. *J. Am. Chem. Soc.* **2015**, *137*, 15015.
9. Peterson, S. L.; Stucka, S. M.; Dinsmore, C. *J. Org. Lett.* **2010**, *12*, 1340.
10. Wang, B.; Côté, A. P.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2008**, *453*, 207.
11. Xu, X.; Zhang, Z.; Wang, X. *Adv. Mater.* **2015**, *27*, 5365.
12. Zhuang, J.; Kuo, C.-H.; Chou, L.-Y.; Liu, D.-Y.; Weerapana, E.; Tsung, C.-K. *ACS Nano* **2014**, *8*, 2812.
13. Lee, H. K.; Lee, Y. H.; Morabito, J. V.; Liu, Y.; Koh, C. S. L.; Phang, I. Y.; Pedireddy, S.; Han, X.; Chou, L.-Y.; Tsung, C.-K.; Ling, X. Y. *J. Am. Chem. Soc.* **2017**, *139*, 11513.
14. Kobayashi, H.; Mitsuka, Y.; Kitagawa, H. *Inorg. Chem.* **2016**, *55*, 7301.
15. Zhang, W.; Lu, G.; Li, S.; Liu, Y.; Xu, H.; Cui, C.; Yan, W.; Yang, Y.; Huo, F. *Chem. Commun.* **2014**, *50*, 4296.

16. Zhou, X.; Huang, X.; Qi, X.; Wu, S.; Xue, C.; Boey, F. Y. C.; Yan, Q.; Chen, P.; Zhang, H. *J. Phys. Chem. C* **2009**, *113*, 10842.
17. Qi, Y.; Hu, Y.; Xie, M.; Xing, D.; Gu, H. *J. Raman Spectrosc.* **2011**, *42*, 1287.
18. Fawcett, V.; Long, D. A. *J. Raman Spectrosc.* **1975**, *3*, 263.
19. N. A. A. A, R. K. Kampara, P.K, R., B.G, *J. Appl. Surf. Sci.* **2018**, *449*, 244.
20. Fairen-Jimenez, D.; Moggach, S. A.; Wharmby, M. T.; Wright, P. A.; Parsons, S.; Düren, T. *J. Am. Chem. Soc.* **2011**, *133*, 8900.
21. Ryder, M. R.; Civalleri, B.; Bennett, T. D.; Henke, S.; Rudić, S.; Cinque, G.; Fernandez-Alonso, F.; Tan, J.-C. *Phys. Rev. Lett.* **2014**, *113*, 215502.
22. Kuo, C.-H.; Tang, Y.; Chou, L.-Y.; Sneed, B. T.; Brodsky, C. N.; Zhao, Z.; Tsung C.-K. *J. Am. Chem. Soc.* **2012**, *134*, 14345.
23. Borjigin, T.; Sun, F.; Zhang, J.; Cai, K.; Ren, H.; Zhu, G. *Chem. Commun.* **2012**, *48*, 7613.
24. Anasthasiya, A. N. A.; Kampara, R. K.; Rai, P. K.; Jeyaprakash, B. G. *Appl. Surf. Sci.* **2018**, *449*, 244.
25. Inagaki, F.; Matsumoto, C.; Iwata, T.; Mukai, C. *J. Am. Chem. Soc.* **2017**, *139*, 4639.
26. Flaig, R. W.; Osborn Popp, T. M.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **2017**, *139*, 12125.
27. Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365.
28. Lee, H. K.; Lee, Y. H.; Phang, I. Y.; Wei, J.; Miao, Y. E.; Liu, T.; Ling, X. Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5054.
29. Koh, C. S. L.; Lee, H. K.; Han, X.; Sim, H. Y. F.; Ling, X. Y. *Chem. Commun.* **2018**, *54*, 2546.

30. Lu, G.; Hupp, J. T. *J. Am. Chem. Soc.* **2010**, *132*, 7832.
31. You, T. T.; Yin, P. G.; Jiang, L.; Lang, X. F.; Guo, L.; Yang, S. H. *Phys. Chem. Chem. Phys.* **2012**, *14*, 6817.

Chapter 3: Tracking Airborne Molecules from Afar: Three-Dimensional Metal-Organic-Framework - Surface-Enhanced Raman Scattering (MOF-SERS) Platform for Stand-Off and Real-Time Atmospheric Monitoring

Abstract. Stand-off Raman spectroscopy combines the superior advantages of both Raman spectroscopy and remote detection to retrieve molecular vibrational fingerprints of chemicals at inaccessible sites. However, it is currently restricted to the detection of pure solids and liquids and not widely applicable for dispersed molecules in air. Herein, we realize real-time stand-off SERS spectroscopy for remote and multiplex detection of atmospheric airborne species by integrating a long-range optic system with a 3D molecular trapping metal-organic framework (MOF)-integrated SERS platform. Formed *via* the self-assembly of Ag@MOF core-shell nanoparticles, our 3D plasmonic architecture exhibits micrometer-sized thick hotspot to allow active sorption and rapid detection of aerosols, gas and volatile organic compounds down to parts-per-billion level, notably up to 10 meters. The platform is also highly sensitive to changes in atmospheric content as demonstrated in the temporal monitoring of gaseous CO₂ in several cycles. Importantly, we demonstrate the remote and multiplex quantification of polycyclic aromatic hydrocarbons (PAH) mixtures in real-time under outdoor daylight. By overcoming core challenges in current remote Raman spectroscopy, our strategy creates enormous opportunity in the long-distance and sensitive monitoring of air/gaseous environment at the molecular level, especially important in environmental conservation, disaster prevention and homeland defense.

3.1 Introduction

Stand-off Raman spectroscopy combines the advantages of both Raman spectroscopy and long-range detection to identify chemicals at distant and/or inaccessible sites,^{1, 2} providing an early indication of potential disasters and/or unhealthy air quality.^{3, 4} Typically performed at meter-range distances, stand-off Raman measurements give rise to molecular-specific vibrational fingerprints that can differentiate molecules of similar chemical structures and thus avert false signals.⁵ It also benefits from no interference from water in the common fingerprint region between 600 – 1700 cm^{-1} , thereby rendering it highly appealing for outdoor detection even in humid conditions.⁶ However, stand-off Raman suffers from intrinsically weak intensity (10^{-6} scattering probability) which further aggravates with increasing distance (intensity $\propto 1/d^2$).^{2, 7} As such, current stand-off Raman detection is restricted to the detection of pure solids/liquids and it is still not possible to detect diluted airborne species (such as gases and aerosols), even using high laser power (~ 400 mW) and long integration time (> 1 minute).^{2, 8} This weak sensitivity greatly hampers the use of stand-off Raman for remote threat/chemical detection and air quality monitoring because majority of explosives, volatile organic compounds and greenhouse gases exist in highly dispersed airborne conditions.⁹

Surface-enhanced Raman scattering (SERS) can potentially address the above problems by enhancing Raman signals of target airborne molecules by $>10^8$ -fold when they are in close proximity to the surface of plasmonic nanostructures.¹⁰⁻¹³ Using 2D plasmonic substrates of Ag and/or Au nanoparticles, ultrasensitive detections of small airborne molecules such as CO_2 and toxic aromatic compounds have been realized using significantly lower operating laser power of tens of mW.^{4, 14, 15} Hence, we hypothesize that the integration of plasmonic-active platform with stand-off Raman spectroscopy can achieve ultrasensitive stand-off SERS system to remotely detect airborne species. However,

the facile coupling of conventional 2D SERS platforms and stand-off Raman system remains a huge challenge owing to the following two main reasons. First, stand-off Raman system has large focal depth, typically in the range of mm to cm. When coupled with SERS, this large focal depth will be underutilized because most 2D SERS platforms have nanometer thick plasmonic hotspot along the z-direction, which are previously designed for microscopic Raman systems with sub-micrometer resolution.^{12, 16} Correspondingly, this inefficient utilization of stand-off laser excitation volume will lead to poor signal read-out due to the signal contribution from ambient interferences present in the laser volume. Second, current attempts in stand-off SERS rely on plasmonic particles that are unable to actively capture analytes from the air,¹³ making it unsuitable for the detection of randomly dispersed airborne molecules that have no affinity to metal, especially in an open ambient environment. Hence, resolving both hotspot focal depth and poor analyte affinity issues are crucial to achieve rapid and univocal stand-off SERS detection of highly-dynamic airborne species at the molecular level.

To accomplish this goal, we hereby develop a 3D multilayered Ag@MOF (MOF=metal-organic-framework) core-shell particle platforms that possesses micron-scale large hotspot depth and large analyte-sorbing ability. The MOF-SERS platform is then coupled with the stand-off Raman system for remote analyte detection to realize real-time stand-off SERS detection of multiplex airborne species, with sensitivity at parts-per-billion (ppb) level at 2 - 10 meters away (Figure 3.1). Our platform displays superior sensitivity and response time in the detection of airborne chemicals over other Ag-MOF configurations, as illustrated by the rapid recognition of aerosols and gases in 10 seconds. We also highlight the advantage of our platform in remote air monitoring applications as demonstrated by its ability to rapidly track chemical changes in atmospheric content when CO₂ and N₂ gases are exposed to the platform in repeated cycles. By corroborating with principal component

analysis (PCA), our robust stand-off SERS system achieves real-time and remote multiplex quantification of polycyclic aromatic hydrocarbons (PAH) mixtures even in strong outdoor daylight background and ambient air. These valuable insights to realize ultrasensitive stand-off SERS detection is critical to expedite future application of long-range molecular detection in various important sectors including atmospheric/environmental sciences, disaster prevention and homeland defense.

Figure 3.1. Overview schematic display of our stand-off MOF-SERS platform for real-time air monitoring.

3.2 Results and discussion

In the fabrication of the 3D MOF-SERS platform, we employ Ag nanocubes (edge length, 121 ± 5 nm; Figure 3.2) as the plasmonic nanoparticle building blocks due to its strong SERS enhancement arising from their sharp tips and edges.^{17, 18} The Ag nanocubes are first treated with an ethanolic solution of hydrochloric acid to remove polyvinylpyrrolidone surfactant on as-synthesized Ag particles. This is to provide a featureless SERS background in the region of 600 to 1700 cm^{-1} which is necessary for accurate analyte detection. The Ag nanocubes are then encapsulated with molecule-sorbing zeolitic imidazolate framework-8 (ZIF, Figure 3.3A(i), 3.4)¹⁹ due to the excellent ability of ZIF to concentrate a wide range of molecules (*e.g.* bicyclic compounds) on the plasmonic

surface for efficient SERS sensing.^{4, 19, 20} Using a ZIF overgrowth method, we synthesize polycrystalline Ag@MOF particles with a continuous ZIF coating at a thickness of 44 ± 5 nm (Figure 3.3A(i), 3.5, 3.6).

Figure 3.2. (A) SEM image of as-synthesized Ag nanocubes and (B) its size distribution (121 ± 5 nm). (C) Extinction spectrum of colloidal Ag nanocubes. The peaks at 348, 412, 525 and 674 nm can be assigned to octupole (348 nm), quadrupole (412 nm and 525 nm), and dipole resonances (674 nm), respectively.

Figure 3.3. 3D MOF-SERS platform. (A)(i) SEM image showing Ag@MOF particles, (ii) cross-sectional SEM image showing the side view of multilayered Ag@MOF platform and (iii) 3D x-y-z SERS image of a segment of the platform (performed with 20× confocal objective lens). (B)(i) Schemes and (ii) cross-sectional SEM images showing the structure and how airborne molecules are absorbed and detected in different platform configuration. Half of the images in (ii) are overlapped with x-z SERS hyperspectral images (with 100× objective lens) showing the penetration of gaseous 4-MBT into the platform (Ag in the platforms has no 4-MBT surface groups prior to exposure). (C)(left) SEM images overlapped with x-z SERS images (with 100× objective lens) of Ag@MOF platforms with increasing thickness and (right) schemes showing the hotspot and analyte density within the

fixed laser focal volume in when platforms of different thickness are used. (D) Effective SERS active depth and stand-off intensity (at 2 m) of 4-MBT's 1077 cm^{-1} obtained from platforms with thickness ranges from 0.2 – 9.2 μm (using Ag pre-functionalized with 4-MBT).

Figure 3.4. Multilayer substrate fabrication protocol.

Figure 3.5. XRD diffraction patterns of Ag particles, MOF, and as-synthesized Ag@MOF (with no surface groups or with 4-MBT on Ag surface), thermally activated Ag@MOF and thermally activated Ag@MOF after reaction (from bottom to top). XRD patterns at 10.5,

12.8 and 18.0° coincide with ZIF's (002), (112) and (222) facets, respectively. XRD peak at 44.4° can be indexed to the (100) facet of single crystalline Ag nanocube.¹⁹ The Ag@MOF platforms contains unique XRD patterns of both MOF and Ag nanocube, which indicates the successful formation and the high stability of Ag@MOF platform during thermal activation and reaction.

Figure 3.6. Transmission electron microscope (TEM) images of a single core-shell Ag@MOF particle, and clusters of multiple Ag particles within a collective MOF shell. This indicates that the Ag cubes can form close-packed structures that allows tip-to-tip and edge-to-edge plasmonic coupling, even with the MOF coating on each individual Ag@MOF particle.

Our 3D SERS platform is subsequently fabricated *via* the self-assembly of these Ag@MOF particles into a multilayered ensemble simply by drying a droplet containing 5 mg/mL Ag@MOF solution at ambient conditions.²¹ The resulting platform is a 1.3 ± 0.2 μm thick (10-15 layers) close-packed assembly of multiple Ag cores within a collective MOF shell structure (Figure 3.3A(ii), 3.6) with interparticle distance of < 10 nm. Such small interparticle distance is commonly observed in hard-core soft-shell structures,²² and is advantageous for our subsequent SERS application because it allows strong plasmonic

coupling among neighboring Ag cubes to form intense SERS hotspots for ultrasensitive sensing.¹¹ We then characterize our 3D Ag@MOF platform in terms of SERS hotspots using confocal Raman microscopy. We employ 4-methylbenzenethiol (4-MBT) as the probe molecule due to its strong and distinct vibrational fingerprints at 1077 cm^{-1} (ν_{CS} , β_{CCC} , Figure 3.7) for SERS characterization/imaging. Hyperspectral x-y-z SERS imaging reveals the 3D SERS active volume of our multilayered platform (Figure 3.3A(iii)), clearly indicating that plasmonic hotspots are intense and distributed homogeneously over all spatial directions. It is noteworthy that the relative standard deviation (%RSD) of SERS intensity using our 3D Ag@MOF platform is only < 9 % over a large x-y area of several mm^2 , and < 10 % along its x-z plane (Figure 3.8). To the best of our knowledge, our assembly methodology produces the largest and thickest homogeneous wafer-type 3D SERS platforms which offer large plasmonic hotspot volume to fully exploit the mm-scale excitation volume in stand-off Raman systems essential for sensitive molecular read-out.²¹

Figure 3.7. 4-MBT SERS spectra clearly displays signature vibrational fingerprints of 4-MBT at 1077 cm^{-1} (ν_{CS} , β_{CCC}) and 1595 cm^{-1} ($\nu_{\text{C}=\text{C}}$), among which we use the former as the main signal for analysis.

Figure 3.8. (A) Tilted 3D SEM image and (B) Top view SEM image showing a large area of multilayered Ag@MOF platform. (C) x-y and x-z hyperspectral SERS imaging of Ag@MOF platform over large area (with 4× and 20× objective lens respectively). (D) Intensity profile of 4-MBT signal across random areas in x-y and x-z images showing the homogeneity of the platform.

To illustrate the superior analyte-sorbing capability of our platform, we compare it with two other common 3D SERS platforms involving (1) pre-assembled Ag nanocubes top-coated with a MOF layer (~ 200 nm) (Figure 3.9A(ii)) and (2) pre-assembled Ag nanocubes without MOF (Figure 3.9A(iii)). Briefly, the SERS platforms are initially exposed to gaseous 4-MBT for 2 h and subsequently analyzed by tracking the signature 4-MBT signal along the z-direction to determine the penetration depth of analyte molecules into respective platforms upon saturation (Figure 3.3B, 3.9). Using 4-MBT's characteristic band at 1077 cm^{-1} , we observe that Ag@MOF platform allows the deepest analyte penetration with a depth of $1.3 \pm 0.1\text{ }\mu\text{m}$, as determined by the full-width half-maximum (FWHM) of the SERS intensity-distance profile scanned along the x-z plane. In contrast,

the two control platforms exhibit > 2-fold shorter penetration depths at $\sim 0.5 \pm 0.1 \mu\text{m}$ (Figure 3.9). These observations affirm that the multilayered Ag@MOF is able to absorb analyte molecule more efficiently, thereby giving the higher apparent penetration depth. We attribute the better performance of multilayered Ag@MOF platform to its porous and more homogeneous distribution of analyte-sorbing MOF moiety throughout the whole platform, which allows airborne molecules to populate the entire 3D hotspot volume. One additional factor contributing to the intensity is that the MOF coating in Ag@MOF enables a more spaced assembly, which allows better laser penetration than the highly close-packed assemblies in other platforms. On the other hand, Ag assembly top-coated with MOF does not possess MOF moiety throughout its z-direction and it can only sorb molecules at its top layer. Bare Ag assembly without MOF platform does not have any analyte capturing ability and only relies on chemisorption of 4-MBT on Ag surfaces. Such excellent analyte-sorbing ability of multilayered 3D Ag@MOF configuration is crucial to accumulate high density of analyte molecules within the large stand-off laser excitation volume for ultrasensitive SERS read-out.

Figure 3.9. x-z SERS map of absorbed 4-MBT on different platforms. (A) Scheme and x-y SERS images showing 4-MBT (tracked with 1077 cm^{-1} signal) penetration depth in the 3 platform types. (B) The full-width half-maximum (FWHM) of the obtained x-z intensity profiles.

Upon affirming the optimal MOF-SERS configuration for efficient analyte capture, we further tune the thickness of our multilayered 3D Ag@MOF platform to maximize analyte signals for ultrasensitive and reliable molecular detection. To evaluate the optimal

thickness of Ag@MOF particle ensemble, we pre-modified Ag surfaces with 4-MBT and perform x-z hyperspectral SERS imaging on various MOF-SERS platforms with thickness ranging from $\sim 0.2 \pm 0.1 \mu\text{m}$ (1-2 layers) to $9.2 \pm 0.8 \mu\text{m}$ (40-45 layers, Figure 3.3C, 3.10). We determine the effective SERS-active depth using the FWHM value of SERS intensity-distance profile obtained during x-z SERS imaging. Notably, the SERS-active depth, also average SERS intensity, increases from $0.5 \mu\text{m}$ to $1.2 \mu\text{m}$ as the physical platform's thickness increases from $0.2 \mu\text{m}$ (1-2 layers) to $1.3 \mu\text{m}$ (10-15 layers). The hotspot thickness and SERS intensity eventually plateaus at $\sim 1.2 \mu\text{m}$ (Figure 3.3D, 3.10) even when the platform's thickness increases beyond $1.3 \mu\text{m}$. The plateau in SERS-active depth and intensity is probably due to limited laser penetration depth through the close-packed assembly nanocubes, as commonly reported in multilayered platforms.^{23, 24} Nevertheless, our results evidently highlight the importance of thicker SERS platforms to larger SERS hotspot volume to better utilize the laser excitation volume as compared to thin platforms (Figure 3.3C). From here onwards, we use the best performing 3D multilayered Ag@MOF platform with optimal thickness of $1.3 \mu\text{m}$ (10-15 layers) for our subsequent stand-off detection demonstrations.

Figure 3.10. Efficient SERS-active thickness determined from x-z image using confocal lens. (A)(i) Cross-sectional SEM images, (ii) x-z SERS imaging of the multilayer Ag@MOF substrates of different thickness (Ag surface is modified with probe molecule 4-MBT), and (iii) their respective cross-sectional profile tracing 4-MBT 1077 cm⁻¹ signal from region (1) to (2). (B) The full-width half-maximum of the intensity profiles, showing the efficient SERS-active thickness and (C) SERS intensity of different multilayer platforms.

We realize stand-off SERS detection by integrating our 3D Ag@MOF platform with a stand-off Raman system with large collection volume of 1 mm × 1 mm × 3.9 mm for x, y, z, respectively (Figure 3.11A, 3.12). We begin by positioning our stand-off Raman system at a distance of 2 meters (which is also our standardized distance used for demonstrations, unless otherwise stated) and measure 4-MBT signals across all Ag@MOF platforms of various thicknesses. Notably, we observe a ~5-fold increase in intensity when the MOF-SERS platform thickness increases from 0.2 μm to 1.3 μm (237 ± 30 counts to 1041 ± 150

counts), which corresponds to an increment of stand-off SERS enhancement factor (EF) from 3.5×10^6 to 6.4×10^6 (Figure 3.11B; refer to Calculation 3.1). The stand-off SERS signal intensity and calculated EF plateaus at ~ 1000 counts and $\sim 6.2 \times 10^6$ as the platform thickness increases further from $1.3 \mu\text{m}$ to $4.1 \mu\text{m}$ and $9.2 \mu\text{m}$. This stand-off result is in agreement with the aforementioned trend in confocal SERS imaging, affirming that the optimal thickness for multilayered Ag@MOF platform is $1.3 \mu\text{m}$, equivalent to 10-15 layers of Ag@MOF nanoparticles. In overall, our finding indicates that thick Ag@MOF platforms with micron-size hotspot volume are essential to maximize the hotspot population within the laser collection volume and further boost the SERS intensity of target molecules.

Figure 3.11. Stand-off SERS with 3D MOF-SERS platform (A) Set-up of our stand-off SERS system. (B) Stand-off intensity (at 2 m) of 4-MBT's 1077 cm^{-1} obtained from platforms of thickness ranges from $0.2 - 9.2\text{ }\mu\text{m}$ (with Ag pre-functionalized with 4-MBT). (C) Scheme showing the stand-off SERS detection of aerosolized 4-MBT (500 ppm, Ag in the platforms has no 4-MBT surface groups). (D) Real-time 4-MBT intensity obtained in the stand-off SERS detection using different platforms. (E) 4-MBT intensity obtained at distances from 2 to 10 m using our A@MOF SERS platform and normal Raman detection. (F) Partial least square calibration graph of different 4-MBT airborne concentrations detected using our stand-off SERS system (at 2 m). (G) Consistent real-time stand-off

spectra of 4-MBT on Ag@MOF substrate for continuous 300 seconds after the substrate has reached saturation.

Figure 3.12. Schematic showing the optical set-up of the stand-off Raman system with excitation and collection beam aligned in the same path. We employ a portable stand-off Raman spectrophotometer that couples the excitation laser and collection light through the same path *via* a camera lens. This provides automated alignment and better flexibility for on-site measurements than other telescopic systems whereby laser is excited from a different angle and requires tedious re-alignment for every sample.

Calculation 3.1 – Calculation of enhancement factor (EF) for multilayered Ag@MOF platform with different hotspot thickness.

With reference to our reported EF calculation method,^{21, 23} we calculate the EF for multilayered Ag@MOF platform from their measured stand-off intensity of the probe molecule 4-MBT pre-functionalized on Ag surface. We assume the 4-MBT molecules assembled as a monolayer on the particle surface.

$$\text{SERS EF} = I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}}$$

Platform thickness (μm)	0.3	0.7	1.3	4.1	9.2
I_{SERS} (counts)	237	638	1041	991	1026
I_{solution} (counts)	62.8 (1884 seconds over 30 seconds, 1M 4-MBT solution)				

Laser beam: x- and y- spot diameter $r = \sim 1 \text{ mm}$ (10^{-3} m), y- focal depth $h = \sim 3.9 \text{ mm}$ ($3.9 \times 10^{-3} \text{ m}$)

$$\begin{aligned}
 N_{\text{solution}} &= \text{number of molecules in solution within the measured laser spot} \\
 &= V_{\text{solution}} \times \text{Concentration of molecules} \times \text{Avogadro number} \\
 &= \pi r^2 h \times 1\text{M} \times 6.022 \times 10^{23} \\
 &= 3.142 \times (1/2 \text{ mm})^2 \times 3.9 \text{ mm} \times 1000 \text{ mol/m}^3 \times 6.022 \times 10^{23} \\
 &= \mathbf{1.84 \times 10^{18}}
 \end{aligned}$$

N_{SERS} = number of 4-MBT molecules on surface of Ag cubes within the measured laser volume.

$$\text{Area of laser spot} = \pi r^2 = 7.855 \times 10^{-7} \text{ m}^2$$

Particle density estimated from counting the particle number: $\sim 38 \text{ particles}/\mu\text{m}^2$

$$\Rightarrow \text{Number of Ag within the laser spot: } 7.855 \times 10^{-7} \text{ m}^2 \times 38 \text{ particles}/\mu\text{m}^2 = 2.99 \times 10^7$$

Surface area of 1 side of Ag cube: $121 \text{ nm} \times 121 \text{ nm} = 14641 \text{ nm}^2$

Taking 4.5 molecules/nm² for a monolayer of 4-MBT on Ag,²⁵ number of 4-MBT molecules adsorbed on the particles surface within the laser volume for 0.2 μm substrate (the thinnest substrate with ~1 layer of Ag cube) is:

$$\begin{aligned} N_{\text{SERS}} &= 4.5/\text{nm}^2 \times 14641 \text{ nm}^2 \times 2.99 \times 10^7 \\ &= 1.97 \times 10^{12} \end{aligned}$$

Taken into account the determined laser penetration depth in Figure 3.10, we project the total number of 4-MBT molecules present in the laser excitation volume for substrates of different thicknesses as followed:

Platform thickness (μm)	0.2	0.7	1.3	4.1	9.2
Laser penetration depth (μm)	0.5	0.9	1.2	1.2	1.2
N_{SERS}	1.97E+12	3.55E+12	4.73E+12	4.73E+12	4.73E+12

$$\begin{aligned} \text{SERS EF (0.2 } \mu\text{m)} &= I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}} \\ &= 237/62.8 \times 1.84 \times 10^{18} / 1.97 \times 10^{12} \\ &= \mathbf{3.52 \times 10^6} \end{aligned}$$

$$\begin{aligned} \text{SERS EF (0.7 } \mu\text{m)} &= I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}} \\ &= 638/62.8 \times 1.84 \times 10^{18} / 3.55 \times 10^{12} \\ &= \mathbf{5.27 \times 10^6} \end{aligned}$$

$$\begin{aligned} \text{SERS EF (1.3 } \mu\text{m)} &= I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}} \\ &= 1041/62.8 \times 1.84 \times 10^{18} / 4.73 \times 10^{12} \\ &= \mathbf{6.45 \times 10^6} \end{aligned}$$

$$\begin{aligned} \text{SERS EF (4.1 } \mu\text{m)} &= I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}} \\ &= 991/62.8 \times 1.84 \times 10^{18} / 4.73 \times 10^{12} \\ &= \mathbf{6.14 \times 10^6} \end{aligned}$$

$$\begin{aligned} \text{SERS EF (9.2 } \mu\text{m)} &= I_{\text{SERS}}/I_{\text{solution}} \times N_{\text{solution}}/N_{\text{SERS}} \\ &= 1026/62.8 \times 1.84 \times 10^{18} / 4.73 \times 10^{12} \\ &= \mathbf{6.36 \times 10^6} \end{aligned}$$

Importantly, our 3D Ag@MOF platform is able to swiftly capture and identify airborne molecules at a stand-off distance, providing real-time monitoring of atmospheric changes to allow prompt remediation to be taken. We demonstrate the ability to detect airborne species of our platform by introducing aerosolized 4-MBT (500 ppm) near the SERS platform and concurrently measure the time-dependent and stand-off SERS responses from the analyte molecules. It is noteworthy that this experiment is performed using Ag nanocubes cleaned with HCl and not with Ag particles that are pre-modified with 4-MBT. This is to ensure a more accurate evaluation on the overall sorption kinetics of Ag@MOF ensemble (Figure 3.11C). Our multilayered Ag@MOF platform rapidly records 4-MBT SERS signature within 10s, which gradually reaches an intensity of >5000 counts within 30s (Figure 3.11D) of aerosol exposure. In contrast, control platforms comprising of pre-assembled Ag top-coated with MOF and pre-assembled Ag without MOF exhibit 6-fold poorer signals within similar time periods of 30s (Figure 3.11D). Using a Lagergren pseudo first-order adsorption kinetics,²⁶ we find that the multilayered Ag@MOF platform displays the highest sorption constant of $k = 55 \text{ ms}^{-1}$, which is 10-fold higher than the other control platforms (refer to Calculation 3.2). This observation again demonstrates the better analyte sorptivity and corresponding SERS sensitivity of multilayered Ag@MOF platform over other platform configurations towards the detection of airborne species in both aerosolized and gaseous forms (Figure 3.13). It is also noteworthy that no signal is detected in the absence of plasmonic particles, indicating that normal stand-off Raman detection is inapt for airborne analyte detection (Figure 3.11D). Collectively, both stand-off and confocal Raman microscopic experiments are in close agreement and jointly affirms that multilayered Ag@MOF with 1.3 μm thickness is the optimal 3D SERS platform essential for remote molecular sensing.

Calculation 3.2 – Calculation of sorption kinetics of different platforms

The intensity-time curves in Figure 3.11D can be fitted using a Lagergren pseudo first-order adsorption kinetics,²⁶ based on linear driving force model, which is inclined to physisorption of the analyte and follows the equation: $I = I_{\max}(1 - e^{-kt})$ where I is the time-dependent SERS intensity (in counts) at time t , $I_{\max}$ is the final equilibrium intensity and k (s^{-1}) gives the pseudo first-order adsorption rate constant.

Conversion of the above equation allows us to calculate k as:

$$k = -\ln \left(1 - \frac{I}{I_{\max}} \right) / t$$

As such we obtain the sorption kinetic constants as follow:

k (s^{-1})		
Ag@MOF	Ag coat MOF	Ag
0.05493	0.005204886	0.00656

This indicates that Ag@MOF platform displays up to 10 times faster sorption of airborne molecules across the entire platform hotspot volume ($k = 5.5 \times 10^{-2} s^{-1}$) than the other two platforms ($k = 5 \times 10^{-3} s^{-1}$ and $6 \times 10^{-3} s^{-1}$ for multilayer Ag coated with MOF and Ag without MOF respectively).

(This calculation is based on the measured stand-off intensity and may not accurately present the actual quantity of molecules sorbed within the platform, because the intensity is also governed by the total hotspot density within the laser collection volume. Nevertheless, it provides a good estimation on how efficiently the platforms absorb and provide stand-off SERS signals simultaneously.)

Figure 3.13. Absorption of gaseous 4-MBT sublimed from solid. Comparison of 4-MBT intensity obtained in real-time in the 4-MBT vapor detection between different substrates, and without substrate, with a scheme showing the detection of 4-MBT vapor molecules subliming from 4-MBT solid (estimated concentration of 4-MBT ~1000 ppm).

We also like to highlight that the detection can be performed at further stand-off distances, exemplifying the immense potential of our strategy in the real-life detection tasks at border, river or mountainous geographical areas. Our platform exhibits 4-MBT signals at extended stand-off distances from 2 meters up to 10 meters and outperforms the normal Raman detection at every distance (Figure 3.11E, 3.14). While the signal intensity decreases with distance (Raman intensity $\propto 1/d^2$), it is noteworthy that we are using 8-fold lower laser power (≤ 55 mW) than other common stand-off Raman techniques with ultrahigh laser power of > 400 mW.^{2, 7} This feature is a significant advancement in stand-off Raman spectroscopy, especially in enhancing safety for operator's eye and skin. Moreover, the platform can detect down to 50 ppb of aerosolized 4-MBT, at which we observe > 100 counts of distinct 4-MBT's vibrational signature at 1077 cm^{-1} (Figure 3.15). This detection limit corresponds to a high analytical enhancement factor (AEF) of 5×10^6 (Figure 3.16;

refer to Calculation 3.3). Importantly, the SERS spectra collected across different concentrations from 500 ppm to 50 ppb enables us to construct a standard calibration curve using partial least square (PLS) regression, which in turn allows subsequent quantification of analyte concentration (Figure 3.11F). The calibration curve exhibits an ideal 0.997 linear coefficient, highlighting our stand-off SERS design as a reliable platform to identify and quantify highly dispersed molecules in air. Furthermore, we observe stable and consistent signal intensity (relative standard deviation in intensity is $\leq 1.8\%$) for a continuous period of 300 seconds after the platform has been saturated with 4-MBT molecules (Figure 3.11G). This clearly indicates that both the Ag@MOF SERS platform and the stand-off instrument are highly robust and not affected by external disturbances, such as air perturbation, that could contribute to intensity fluctuation during prolonged measurements. By combining analyte-sorbing MOF scaffold and dense 3D plasmonic hotspot, our integrated approach resolves the bottleneck in stand-off Raman detection to enable the quantification of airborne molecules up to 10 meters away, even at low laser power of ≤ 55 mW,

Figure 3.14. (A) Scheme and (B) Stand-off SERS in comparison with (C) stand-off Raman spectra of the captured 4-MBT upon airborne detection on substrate with and without Ag@MOF, at different distances.

Figure 3.15. Quantitative detection of 4-MBT. SERS spectra of airborne 4-MBT detection from 50 ppb to 500 ppm.

Calculation 3.3 – Calculation of airborne concentration of 4-MBT, and analytical enhancement factor determination.

An aerosolized pulse of 4-MBT contains $\sim 50 \mu\text{L}$ of solution.

Therefore, a 10^{-6} M stock solution introduces $n = 10^{-6} \text{ M} \times 50 \mu\text{L} = 5 \times 10^{-11} \text{ mol}$ of 4-MBT, or $m = 5 \times 10^{-11} \text{ mol} \times 124 \text{ g/mol} = 6.2 \times 10^{-3} \mu\text{g}$ of 4-MBT into the chamber whose volume is $V = 5 \text{ cm} \times 5 \text{ cm} \times 5 \text{ cm} = 0.125 \text{ L}$.

Hence, the airborne concentration of a pulse of aerosolized 4-MBT is $c = 6.2 \times 10^{-3} \mu\text{g}/0.125 \text{ L} = 50 \text{ ppb}$.

To calculate the analytical enhancement factor (AEF) of our SERS sensor, we perform a normal Raman sensing of aerosolized 4-MBT produced from the stock solution of 1 M (50000 ppm), which yields the following Raman spectrum (upon 10 second of collection time).

Figure 3.16. Normal Raman of aerosolized 4-MBT.

With reference to the 1077 cm^{-1} SERS band, we calculate the analytical enhancement factor of 4-MBT detection as followed:

$$\begin{aligned}\text{Analytical EF} &= [(I_{\text{SERS}}) / (I_{\text{Raman}})] \times [(C_{\text{Raman}}) / (C_{\text{SERS}})] \\ &= [153 / (310 / 10)] \times (1 / 10^{-6}) \\ &= 5 \times 10^6\end{aligned}$$

where C_{SERS} and C_{Raman} are the corresponding concentrations of the stock solution to prepare aerosolized 4-MBT to be measured using our platform (10^{-6} M ; 50 ppb) and normal Raman of 4-MBT(1 M, 50000 ppm), respectively. I_{SERS} and I_{Raman} are the time-normalized intensities measured using SERS and normal Raman, respectively, at their corresponding concentration.

One potential application of our 3D Ag@MOF platform is its usage as a highly responsive remote air monitoring device to provide real-time readout of specific vibrational fingerprints of small gaseous molecules that do not have specific affinity with metal surface. Commercial air monitoring devices installed in households and buildings rely heavily on photoelectric method that does not provide molecular fingerprints, prone to false alarms, and usually requires > 15 minutes to recognize abnormal air composition.^{27, 28} As a proof-of-concept, we demonstrate the remote and real-time SERS sensing of gaseous carbon dioxide (CO₂) with high molecular specificity and showcase the potential of our platform as an ideal alternative to conventional detectors. Our 3D SERS platform is positioned within a gas flow cell that is connected to CO₂ source (50 sccm and 1 atm) and SERS signals are recorded in consecutive CO₂-vacuum cycles (Figure 3.17A). In this demonstration, Ag surface is pre-modified with 4-MBT as internal standard, whereby all spectra are standardized against 4-MBT's 1077 signals to eliminate signal fluctuations (Figure 3.17B). We choose 4-MBT as our internal standard because it can bond to Ag surface *via* strong Ag-S covalent bond, thus do not undergo detachment/reattachment during evacuation and provides consistent signal. As CO₂ exposure increases, we note the emergence of a broad SERS band centered at 1360 cm⁻¹ rapidly within ≤ 5 min (Figure 3.17B). Notably, this broad band diminishes as soon as the cell is evacuated under vacuum. Repetitive appearance and disappearance of the 1360 cm⁻¹ band is observed when Ag@MOF SERS platform is subjected to continuous cycling between CO₂ flow and vacuum evacuation, respectively. This observation clearly denotes the high reversibility of the sorption and desorption of CO₂ gas molecules in our 3D Ag@MOF platform, a feature critical for application in real-time and reusable stand-off SERS monitoring of airborne species. In contrast, control experiment involving nitrogen gas (N₂) does not exhibit any vibrational feature near the 1360 cm⁻¹ region (Figure 3.17C). Principle component analysis (PCA, an analysis to differentiate

spectra based on algorithms applied on their spectral features) further affirms that SERS signatures obtained when exposed to CO₂ or N₂ are statistically different. We therefore attribute the SERS band centered at 1360 cm⁻¹ to the symmetric stretching mode of CO₂ (ν_{CO2}) molecules accumulated at solid-MOF interface.¹⁴ Our approach thus offers a rapid and molecular-specific recognition of small gas molecules to prevent/minimize false positive, even for molecules that do not have specific affinity with metal surface using their specific vibrational fingerprints. Moreover, our stand-off SERS detection gives real-time results without tedious air sampling procedures, which is a significant advantage over conventional sensors which require pre-concentration of gas molecules using electrodeposition or¹⁰ ultralow temperature (-80°C).²⁹

Figure 3.17. Remote SERS-based gas detector. (A) Scheme showing remote tracking of CO₂ in real time for several cycles with multilayered Ag@MOF platform. (B) Time-resolved SERS intensity profile of 1360 cm⁻¹ band, showing the absorption and detection of CO₂ in several cycles. (C)(i) Spectroscopic observation of CO₂ vibrational modes (shown with respect to internal standard peak of 4-MBT embedded on the particle) in the detection of CO₂, which is not observed in the control experiments with N₂ flow and no gas (blank), (ii) Principle component analysis (PCA) score plot of stand-off spectra observed in the presence of CO₂ and N₂.

In addition, we would like to emphasize that the ability to absorb and desorb concentrated airborne molecules depends on the types of molecules and their affinity towards Ag surface. Small gaseous molecules with low affinity to Ag, such as CO₂, can be desorbed from the Ag@MOF system *via* vacuum and heat activation and the substrate can be reused for another detection. Bigger molecules like naphthalene and toluene can be trapped within the MOF network and harder to be completely removed. On the other hand, molecules with high affinity to Ag surface, such as 4-MBT that can form Ag-S covalent bond, remain on the Ag surface upon absorption. Hence, for the two latter cases, the substrates should be for one-time usage.

To simulate a real-life multiplex sensing scenario in air quality monitoring, we perform a series of outdoor detection of aerosolized mixture of (poly)cyclic aromatic hydrocarbons (PAH), naphthalene and toluene (Figure 3.18A,B), which are major pollutants commonly found in haze.³⁰ We first construct a signal-to-concentration calibration under controlled laboratory conditions for various compositions of a mixture of naphthalene (Nap) and toluene (Tol), ranging from Nap/Tol 15:85 (mol/mol, airborne concentration 850:3500 ppm, respectively) to Nap/Tol 1:99 (49:3500 ppm) (refer to

Calculation 3.4; Figure 3.19). By introducing the aerosol mixture in vicinity to the Ag@MOF platform, we are able to collect multiplex spectra exhibiting characteristic vibrational fingerprints of each analytes within 10 s. We observe the SERS bands of naphthalene at 763 cm^{-1} (δ_{CH}) and 1380 cm^{-1} ($\nu_{\text{C-C}}$) as well as toluene signatures at 786 cm^{-1} (δ_{CH}) and 1004 cm^{-1} (symmetric $\nu_{\text{C-C}}$ (ring)) in different intensity ratio according to the mixture composition (Figure 3.19A). For instance, the intensity ratio of Nap (763 cm^{-1}) / Tol (786 cm^{-1}) increases from (0.12 ± 0.05) to (0.86 ± 0.1) as we increase the Nap/Tol ratio from 1:99 to 15:85 (Figure 3.19), respectively. Such spectral features enable the accurate quantification of each component content within the multiplex detection, as shown in our predicted PLS model and PCA score plot (Figure 3.19C, 3.20). These results demonstrate that we are able to remotely measure the concentration of airborne molecules down to tens of ppm level, which is also the permitted threshold set by the Occupational Safety and Health Administration (OSHA).¹⁸

Figure 3.18. Outdoor remote sensing of airborne polycyclic aromatic hydrocarbon (PAH) mixture. (A)(i) Outdoor stand-off detection set-up. (B) Scheme showing the stand-off detection of aerosolized toluene and naphthalene. (C) Stand-off multiplex spectra obtained in outdoor condition with natural light, for Nap/Tol 5:95 and 15:85 mixture, with reference to individual naphthalene and toluene SERS spectra. (D) Spectral analysis of characteristic signals of the analytes within the dotted region in (C). (E) Comparison of Nap/Tol signal intensity ratio between calibration spectra and outdoor spectra, using 763 and 786 cm⁻¹ signals.

Calculation 3.4 – Calculation of airborne concentration of polycyclic aromatic hydrocarbons (PAH).

Aerosolized PAH are introduced into the chamber over a period of 5 second, equivalent to 250 μ L.

The solution used for spraying contains 3 mL (2.61 g) of toluene and several concentrations of naphthalene (0.632 g for Nap/Tol 15:85 sample, 0.384 g for Nap/Tol 10:90 sample, 0.19 g for Nap/Tol 5:95 sample, 0.0362 g for Nap/Tol 1:99 sample). With this the amount of each components in the stock solution and in 250 μ L of aerosol can be determined, which allows the calcution of airborne concentration in ppm (or ppb) by taking into account the volume of the chamber (0.125 L).

	Sample			
	Nap/Tol 15:85	Nap/Tol 10:90	Nap/Tol 5:95	Nap/Tol 1:99
Toluene (ppm)	3500	3500	3500	3500
Naphthalene (ppm)	850	515	255	49

Figure 3.19. Calibration of multiplex (poly)aromatic hydrocarbon detection (indoor)

(A) Stand-off multiplex SERS spectra obtained with just toluene (Tol), naphthalene (Nap) and Nap/Tol mixture at different composition for calibration (performed indoor, within 100 μ L of Tol aerosol, accounting for 7000 ppm Tol and 97-1700 ppm of Nap). (B) Spectrum deconvolution of the yellow-highlighted area in (A), showing the relative ratio between Nap 763 cm^{-1} and Tol 786 cm^{-1} signals at different composition. (C) Calibrated PLS prediction model constructed from the SERS spectra of various Nap/Tol composition from 0 to 100% (with a blue-highlighted magnification of Nap/Tol 85 to 99% region).

Figure 3.20. PCA score plot constructed from the SERS spectra obtained from the detection of Nap/Tol mixture of various composition from Nap/Tol 0/100 to 100/0. The spectra can clearly be differentiated due to the ratio between the vibrational fingerprints of each compound.

More importantly, we further exploit the multiplexing capability of our stand-off SERS system to remotely identify and quantify PAH composition in an outdoor setting, under strong daylight intensity during afternoon time. Real-time SERS spectra evidently display the signature vibrational signals of target molecules amidst the background interference (Figure 3.18C,D, 3.21). Upon background subtraction and baseline correction, the outdoor spectra of Nap/Tol 15:85 and 5:95 samples match well with the calibration spectra, whereby the relative intensity ratio of Nap/Tol SERS bands at $763\text{ cm}^{-1}/786\text{ cm}^{-1}$ or $1380\text{ cm}^{-1}/1004\text{ cm}^{-1}$ are tallied with the calibration graph (Figure 3.18E, 3.22). This result clearly showcases a high performance stand-off SERS sensor capable of remotely quantifying multiple airborne species in both lab-based and outdoor environments at high accuracy. Such rapid sorption and identification of foreign molecules in the atmosphere allows timely and adequate actions to be taken in the event of adverse weather, disaster and terrorism, while ensuring safety of operators when performed at remote distances.

Figure 3.21. Background correction and baseline subtraction for SERS spectra obtained in outdoor condition with strong background light interference.

Figure 3.22. Comparison of Nap/Tol signal intensity ratio between calibration spectra and outdoor spectra, using the alternative 1380 and 1004 cm^{-1} signals.

3.3 Conclusion

In conclusion, we have achieved real-time stand-off SERS detection of airborne molecules by integrating stand-off Raman with a 3D Ag@MOF platform with micron-scale hotspot volume and high molecule sorbing ability. By providing large hotspot population within the stand-off laser collection volume, our platform enables rapid quantitative detection of aerosolized chemicals with parts-per-billion (ppb) detection limit at 2 - 10 meters away. We are also able to achieve real-time stand-off monitoring of small gas molecules in multiple on-off cycles, exemplifying the potential application of our platform in prolonged atmospheric monitoring. Notably, our stand-off 3D platform can rapidly elucidate the fingerprints of multiple airborne polyaromatic hydrocarbons in an outdoor environment under strong daylight intensity, demonstrating its ability to afford target analyte signals in spite of background interference. These collective advantages of our platform tackle the current limitations in remote Raman spectroscopy and sets pathways in air monitoring at the molecular level, which also creates a paradigm in employing SERS as the next-generation sensing technology to address the pressing issues in the field of remote

monitoring for atmospheric/environmental sciences, disaster prevention and homeland defense.

3.4 Materials and methods

Materials. Silver nitrate ($\geq 99\%$), anhydrous 1,5-pentanediol (PD, $\geq 97\%$), poly(vinylpyrrolidone) (PVP, average MW = 55,000), decane ($\geq 98\%$), zinc nitrate hexahydrate (reagent grade, 98%), 2-methylimidazole (99%), 1H,1H,2H,2H-perfluorodecanethiol (PFDT; 97%), Methylbenzenethiol (4-MBT, 98%), naphthalene (99%), 1-propanol (anhydrous, 99.7%) were purchased from Sigma Aldrich; copper (II) chloride ($\geq 98\%$) was from Alfa Aesar; methanol (ACS reagent, $\geq 99.8\%$) was from J.T.Baker®; ethanol (ACS, ISO, Reag. Ph Eur) and ammonia (ACS, Reag. Ph Eur) was from EMSURE®; dimethylformamide (HPLC grade) was obtained from Fisher Scientific; 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.

Determining the laser focal depth of stand-off instruments. A substrate of 100 nm fluorescent microspheres is positioned at 2 meters from the stand-off instruments, the substrate is then moved along the z-axis forward and backward a few centimeters from the original position. The full-width half-maximum of the intensity profile is then obtained.

Synthesis and purification of silver nanocubes. The preparation of Ag nanocubes were synthesized of high yield *via* polyol method described in literature.¹⁸ 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 μ L 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 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 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 then redispersed in ethanol (~5 mg/mL) and stored in fridge.

4-Methylbenzenethiol (4-MBT) functionalization of Ag nanocubes. The removal of surfactant from Ag nanocubes surface was done by functionalizing the assembled Ag nanocubes with 4-MBT. The assembled Ag nanocube array was immersed in 5 mM of 4-MBT methanolic solution for at least 3 hours.

HCl treatment of Ag nanocubes. The removal of surfactant from Ag nanocubes surface was referred to method in literature.³¹ This is to provide a featureless SERS background in the region of 600 to 1700 cm^{-1} which is necessary for accurate analyte detection. 100 μ L of purified Ag nanocubes in ethanol suspension (10 mg/mL) was added to 5 mL hydrochloric acid (0.01 M) in water under stirring condition. After 3h, the Ag nanocubes colloidal

suspension was then washed with copious amount of pure water and ethanol to remove excess HCl. The HCl-treated Ag nanocubes were subsequently re-dispersed in ethanol for further use. *Either 4-MBT functionalization or HCl treatment can remove the surfactants. Nonetheless, 4-MBT functionalization will form a layer of 4-MBT probe on the surface. This is for characterization or detection experiment that needs 4-MBT signals as ‘internal’ standards to base on. HCl treatment will only remove the surfactant and leave a clean surface. This is for experiments where ‘internal’ 4-MBT signals is not required, such as the detection of 4-MBT, or toluene and naphthalene from the external environment.

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, Ag nanocubes can be functionalized with 4-MBT to have 4-MBT probe internal standard, or HCl-treated to remove surface groups). The mixture was stirred for another 90 minutes at 500 rpm. Excess reagents were removed by centrifugation and the core-shell nanocubes were then washed twice with methanol and then finally re-dispersed in methanol.

Assembly of Ag@MOF nanocubes into multilayered substrates (substrate 1 / Ag@MOF substrate). Briefly, 0.5 cm $\times$ 0.5 cm Si (100) substrates were cleaned prior to assembly of Ag@MOF using oxygen plasma (FEMTO SCIENCE, CUTE-MP/R, 100 W) for 5 minutes. 20 μL of the 1-propanol solution of Ag@MOF particles (with concentration of 0.5 – 20 mg/mL for different Ag@MOF thickness) was dispensed *via* pipette on the substrates and let dry. It is noteworthy to mention that the concentration of Ag@MOF particles required also varies when used on varying areas of Si substrates for the same

Ag@MOF thickness. For example, if a larger substrate is used, a higher concentration of Ag@MOF particles is required to obtain the same thickness.

Multilayered Ag nanocube substrate, and growth of Zeolitic Imidazolate Framework – 8 (ZIF) film on multilayered Ag nanocube substrate (substrate 3 and 2). Briefly, 0.5 cm × 0.5 cm Si (100) substrates were cleaned prior to assembly of Ag nanocubes using oxygen plasma (FEMTO SCIENCE, CUTE-MP/R, 100 W) for 5 min. 20 µL of the 1-propanol solution of Ag nanocubes (after filtration, with concentration of 0.5 – 20 mg/mL) was dispensed *via* pipette on the substrates and let dry. The coated substrate was submerged in hydrochloric acid (0.01 M) for 3 hours to remove PVP surface groups on Ag nanocubes. Multilayered Ag nanocube substrate (substrate 3) was obtained.

For substrate 2 preparation, ZIF coating was performed. 2 ml of methanolic Zn(NO₃)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 Ag nanocube substrate (9~10 layers, ~5 mg/mL Ag nanocube solution was used) 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 crystals. The procedure was repeated 2 more times using fresh Zn(NO₃)₂ and 2-methylimidazole solutions to obtain ZIF film of ~ 200 nm (standardized Ag/MOF ratio with Ag@MOF platform). The ZIF film on multilayered Ag nanocube substrate achieves a thickness of 1.3 µm with ~10 layers of Ag cube and 200 nm MOF, which is standardized with the Ag@MOF substrate of 1.3 µm with ~ 12 layers of Ag@MOF cube.

Activation of substrates. All MOF-modified 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 were used immediately after activation.

Preparation of 3D-printed chamber for airborne chemicals. 3D models were designed in AutoDesk 3Ds Max 2016, and exported to and printed with FormLabs 1+ 3D printer using clear resins FL02. The chamber was designed such that the airborne analyte can be sprayed into from top down. The chamber interior and the laser source (objective lens) is separated with a quartz slide to limit chemical dispersion in lab-based experiments. For outdoor experiments, the quartz slide is removed to minimize loss of laser power and signal intensity.

SERS detection of aerosolized chemicals. Solutions of analytes are loaded into commercially available ‘Nano Handy Mist Spray’ (SKG brand), and expelled out as aerosols. Typically, our measurement estimates that 1 second of spraying produces a total of 50 μ L of airborne aerosol. Aerosols were introduced into the chamber in which the SERS platforms are mounted at one side of the walls. Stand-off SERS measurement was performed *in situ* for the entire duration (before, during and after spraying of airborne analytes). SERS spectra are obtained with time-lapsed mode every 1 second with 1 second collection time – for characterization of 4-MBT pre-modified substrates, or every 10 seconds with 10 seconds collection time – for detection of airborne 4-MBT. About 5-10 SERS spectra were averaged and baselined for each analyte concentration. To measure the distance-dependent signal intensity at different distances, the measurement is performed as the substrate is positioned at 2 meters to 4, 6, 8 and 10 meters away from the lens (Figure S11). Spectra when the substrate is saturated (maximum intensity) are analyzed for intensity.

SERS detection of gaseous 4-MBT. Instead of aerosolized 4-MBT, 0.5 g solid 4-MBT was put in the chamber. Stand-off SERS measurement was performed *in situ* as the solid sublimed. SERS spectra are obtained with time-lapsed mode every 10 second with 10 second collection time. To determine the penetration depth of gaseous 4-MBT (Figure 1B), the substrates are collected after 2 hours and subjected to confocal x-z hyperspectral imaging.

SERS detection of CO₂ in Gas detector. The thermal-activated SERS platforms were placed inside a custom-made gas flow cell 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. Following which, CO₂ gas (50 sccm) was flown through the gas flow cell and stopped after 15 - 20 minutes. The cell was then vacuumed for 15- 20 minutes. CO₂ gas (50 sccm) was flown through again and the cycle was repeated. Stand-off SERS measurement was performed *in situ* for the entire duration (time-lapsed mode every 5 minutes with 30 seconds collection time). Subsequent purging of the experimental set-up with N₂ gas and simultaneous SERS analysis were conducted until characteristic SERS bands remain constant in the SERS spectra (30 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) and their SERS intensities (I) were based on the relative intensity of 4-MBT internal standard.

Stand-off outdoor experiment. The experiment was performed in daytime before 5 pm (Singapore time) at level 6 open area within the Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, NTU. The experimental

procedures for the detection of aerosolized analytes were performed accordingly to lab-based experiments.

Material characterization. Scanning electron microscope (SEM) imaging was performed using JEOL-JSM-7600F microscope. SEM images of Ag@MOF particles are overlapping images of two sets of images with the same magnification, taken with (1) secondary electron imaging (SEI) mode which reveals the MOF coating, and (2) low-angle backscattered electrons (LBE) mode which reveals the Ag core, to fully visualize the core-shell structure in 3D. Titled SEM image was performed at 10° tilt angle (Figure 1A(ii)). Transmission electron microscope (TEM) imaging was performed using JEOL-2100 at an accelerating voltage of 200 kV. 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. Stand-off SERS was performed on a portable stand-off Raman spectrophotometer with a mounted 200 mm Nikon lens, at ≤ 55 mW laser power, 532 nm wavelength, 1 mm $\times$ 1 mm $\times$ 3.9 mm laser volume (Technospex Pte. Ltd, Singapore). Hyperspectral SERS imaging were performed using x-y, x-z and x-y-z hyperspectral imaging mode of the Ramantouch microspectrometer (Nanophoton Inc., Osaka, Japan) with an excitation wavelength of 532 nm and laser power of 0.06 mW. A 100 $\times$ objective lens (N.A 0.90), 20 $\times$ objective lens (N.A 0.45) and a 4 $\times$ objective lens (N.A 0.13, for large scale imaging) with 1 s acquisition time was used for data collection. For x-y-z image (Figure 1A(iii)), original data was obtained over 400 horizontal pixels and cropped to ~ 150 horizontal pixels. All confocal and stand-off SERS spectra are subjected to background subtraction and baseline correction.

References

1. Fan, M.; Andrade, G. F. S.; Brolo, A. G., *Anal. Chim. Acta* 2011, 693, 7.
2. Hobro, A. J.; Lendl, B., *TrAC, Trends Anal. Chem.* 2009, 28, 1235.
3. Chou, A.; Jaatinen, E.; Buividas, R.; Seniutinas, G.; Juodkazis, S.; Izake, E. L.; Fredericks, P. M., *Nanoscale* 2012, 4, 7419.
4. Koh, C. S. L.; Lee, H. K.; Han, X.; Sim, H. Y. F.; Ling, X. Y., *Chem. Commun.* 2018, 54, 2546.
5. Phan-Quang, G. C.; Lee, H. K.; Ling, X. Y., *Angew. Chem. Int. Ed.* 2016, 55, 8304.
6. Carey, D. M.; Korenowski, G. M., *J. Chem. Phys.* 1998, 108, 2669.
7. Wallin, S.; Pettersson, A.; Östmark, H.; Hobro, A., *Anal. Bioanal. Chem.* 2009, 395, 259.
8. Moros, J.; Lorenzo, J. A.; Novotný, K.; Laserna, J. J., *J. Raman Spectrosc* 2013, 44, 121.
9. Gopalsami, N.; Raptis, A. C., *IEEE Trans. Microwave Theory Tech.* 2001, 49, 646.
10. Mosier-Boss, P. A., *Nanomaterials* 2017, 7, 142.
11. Lee, H. K.; Lee, Y. H.; Koh, C. S. L.; Phan-Quang, G. C.; Han, X.; Lay, C. L.; Sim, H. Y. F.; Kao, Y.-C.; An, Q.; Ling, X. Y., *Chem. Soc. Rev.* 2019, 48, 731.
12. Phan-Quang, G. C.; Lee, H. K.; Teng, H. W.; Koh, C. S. L.; Yim, B. Q.; Tan, E. K. M.; Tok, W. L.; Phang, I. Y.; Ling, X. Y., *Angew. Chem. Int. Ed.* 2018, 57, 5792.
13. Scaffidi, J. P.; Gregas, M. K.; Lauly, B.; Carter, J. C.; Angel, S. M.; Vo-Dinh, T., *Appl. Spectrosc.* 2010, 64, 485.

14. Lee, H. K.; Lee, Y. H.; Morabito, J. V.; Liu, Y.; Koh, C. S. L.; Phang, I. Y.; Pedireddy, S.; Han, X.; Chou, L.-Y.; Tsung, C.-K.; Ling, X. Y., *J. Am. Chem. Soc.* 2017, 139, 11513.
15. Lee, M. R.; Lee, H. K.; Yang, Y.; Koh, C. S. L.; Lay, C. L.; Lee, Y. H.; Phang, I. Y.; Ling, X. Y., *ACS Appl. Mater. Interfaces*. 2017, 9, 39584.
16. Sharma, S. K., *Spectrochim. Acta, Part A*. 2007, 68, 1008.
17. Phan-Quang, G. C.; Lee, H. K.; Phang, I. Y.; Ling, X. Y., *Angew. Chem. Int. Ed.* 2015, 54, 9691.
18. Lee, H. K.; Lee, Y. H.; Phang, I. Y.; Wei, J.; Miao, Y.-E.; Liu, T.; Ling, X. Y., *Angew. Chem. Int. Ed.* 2014, 53, 5054.
19. Sim, H. Y. F.; Lee, H. K.; Han, X.; Koh, C. S. L.; Phan-Quang, G. C.; Lay, C. L.; Kao, Y.-C.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y., *Angew. Chem. Int. Ed.* 2018, 57, 17058.
20. Yin, H.; Kim, H.; Choi, J.; Yip, A. C. K., *Chem. Eng. J.* 2015, 278, 293.
21. Lee, Y. H.; Lay, C. L.; Shi, W.; Lee, H. K.; Yang, Y.; Li, S.; Ling, X. Y., *Nat. Commun.* 2018, 9, 2769.
22. Rauh, A.; Rey, M.; Barbera, L.; Zanini, M.; Karg, M.; Isa, L., *Soft Matter* 2017, 13, 158.
23. Chen, M.; Phang, I. Y.; Lee, M. R.; Yang, J. K. W.; Ling, X. Y., *Langmuir* 2013, 29, 7061.
24. Li, X.; Lee, H. K.; Phang, I. Y.; Lee, C. K.; Ling, X. Y., *Anal. Chem.* 2014, 86, 10437.
25. Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M., *Chem. Rev.* 2005, 105, 1103.

26. Kodiyath, R.; Malak, S. T.; Combs, Z. A.; Koenig, T.; Mahmoud, M. A.; El-Sayed, M. A.; Tsukruk, V. V., *J. Mater. Chem. A* 2013, 1, 2777.
27. Qualey, J. R., *Fire Technol.* 2000, 36, 89.
28. Cleary, T., *Fire Technol.* 2014, 50, 775.
29. Oh, M.-K.; De, R.; Yim, S.-Y., *J. Raman Spectrosc.* 2018, 49, 800.
30. Cao, R.; Zhang, H.; Geng, N.; Fu, Q.; Teng, M.; Zou, L.; Gao, Y.; Chen, J., *Sci. Total Environ.* 2018, 625, 1486.
31. Zong, S.; Wang, Z.; Yang, J.; Cui, Y., *Anal. Chem.* 2011, 83, 4178.

Chapter 4: ZIF-Induced d-Band Modification in a Bimetallic Nanocatalyst: Achieving Over 44% Efficiency in the Ambient Nitrogen Reduction Reaction.

Abstract. The electrochemical nitrogen reduction reaction (NRR) offers a sustainable solution towards ammonia production but suffers poor reaction performance owing to preferential catalyst–H formation and the consequential hydrogen evolution reaction (HER). Now, the Pt/Au electrocatalyst d-band structure is electronically modified using zeolitic imidazole framework (ZIF) to achieve a Faradaic efficiency (FE) of >44% with high ammonia yield rate of $>161 \mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$ under ambient conditions. The strategy lowers electrocatalyst d-band position to weaken H adsorption and concurrently creates electron-deficient sites to kinetically drive NRR by promoting catalyst–N₂ interaction. The ZIF coating on the electrocatalyst doubles as a hydrophobic layer to suppress HER, further improving FE by >44-fold compared to without ZIF (ca. 1%). The Pt/Au–N_{ZIF} interaction is key to enable strong N₂ adsorption over H atom.

4.1 Introduction

The ambient electrochemical nitrogen reduction reaction (NRR) offers a promising and eco-friendly approach to produce ammonia as a green fuel directly from atmospheric abundant nitrogen (N_2) in contrast to the energy-consuming Haber–Bosch process (400 °C, 40 MPa).^{1, 2} However, the greatest limitations in NRR are its poor Faradic efficiency ($\text{FE} \approx 10\%$) and ammonia (NH_3) yield rate, which restrict its practical application, especially under ambient conditions.³⁻⁵ This performance bottleneck is mainly attributed to 1) poor selectivity and 2) poor activity of current NRR electrocatalytic designs. First, the poor NRR selectivity is due to competing hydrogen evolution reaction (HER) that dominates over NRR and affects virtually all traditional NRR metal electrocatalysts. The lower energy barrier of hydrogen (H) adsorption over N_2 causes preferential adsorption of H on catalyst which kinetically favors HER over NRR.^{6, 7} Second, the poor NRR catalytic activity arises from the weak affinity of N_2 to catalyst owing to the chemical inertness and the lack of electron deficient sites on catalyst to accept N_2 lone-pair electrons, impeding N_2 activation and corresponding NRR efficiencies.^{2, 8, 9} To overcome these limitations, it is necessary to overturn traditionally favored H adsorption and improve intrinsic catalytic activity towards NRR.

An emerging strategy to kinetically boost NRR performance is to improve catalyst affinity toward N_2 by creating electron-deficient catalytic sites via electronic structure modification. Co-doping carbon catalyst with electronegative heteroatoms (N and P) draws electron density away from carbon to facilitate N_2 adsorption for subsequent activation, but is limited by its energy-intensive process and difficulty in achieving high and uniform dopant concentrations.¹⁰ On the other hand, the NRR catalytic activity for metal catalysts largely depends on the intrinsic N_2 binding ability of metals.⁵ For instance, platinum (Pt) and iridium (Ir) can adsorb both N_2 and H, but favor H adsorption over N_2 owing to strong

metal–H formation because the metal d-band states are close to the Fermi level (E_f), hence leading to high HER and low NRR activities.^{11, 12} Therefore, it is imperative to strategically design an electronically modified electrocatalytic system which possesses 1) lower d-band position to weaken H adsorption and 2) abundant electron-deficient sites with strong N₂ affinity to kinetically drive NRR at ambient conditions.

Herein, we use zeolitic imidazole framework (ZIF) to modify the d-band electronic structure of bimetallic electrocatalyst to favor NRR and enhance its N₂ adsorption affinity to boost NRR performance, attaining a high FE of >44% and a NH₃ yield rate of >161 $\mu\text{mg}_{\text{cat}}^{-1} \text{h}^{-1}$ at ambient conditions. We achieve this by encapsulating our model Pt/Au electrocatalyst with a layer of ZIF to induce their direct chemical/ electronic interactions, which lowers the d-band to weaken H adsorption and concurrently creates electron-deficient catalytic sites with strong affinity toward N₂. Moreover, ZIF also serves two additional functions: i) concentrating N₂ molecules at the catalyst-ZIF interface to enhance catalyst–N₂ interactions and ii) serving as a hydrophobic barrier to suppress HER by restricting the access of trace water to electrocatalytic sites.¹³⁻¹⁶ X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) investigation reveal a negative shift of Pt/Au d-band center to weaken catalyst–H interaction and highlight the preferential N₂ adsorption over H atom at the electron deficient sites to kinetically boost NRR performance. Notably, our electrocatalytic design exhibits excellent NRR activity across a wide range of applied potentials (-2.1 V to -2.9 V), achieving FEs >44-fold better than bare Pt/Au catalyst (FE $\approx$ 1%). Our electrocatalytic design is straightforward and can be potentially extended to a library of metal electrocatalysts to improve NRR performance and/or other water-sensitive reactions for diverse applications, such as in air-to-fuel conversion and greenhouse gas remediation/valorization.

4.2 Results and discussion

Our electrocatalytic design comprises of a Pt nanosphere (PtNS)-deposited Au electrode that is coated with a layer of ZIF. The ZIF serves three functions, namely 1) modifying Pt/Au d-band structure to weaken H adsorption, 2) inducing electron deficient sites on Pt to enhance its affinity towards N_2 adsorption, and 3) concentrating N_2 to promote Pt/Au- N_2 interactions for NRR while repelling moisture to suppress competing HER (Figure 4.3A). We chose Pt as our primary metal catalyst owing to its excellent electrochemical stability and high intrinsic catalytic activities.¹⁷ Briefly, a series of PtNSs with different sizes (60 nm to 231 nm) are synthesized using a seed-mediated synthesis method and subsequently treated with HCl to remove surfactant prior to their depositions on Au electrode (co-catalyst) (Figures 4.1, 4.2). Our Pt/Au@ZIF electrode is then fabricated by encapsulating the Pt/Au ensemble with a polycrystalline ZIF layer (thickness, 433 ± 36 nm) via an overgrowth method (Figure 4.3B, 4.4). The successful formation of Pt/Au@ZIF platform is affirmed through the unique diffraction patterns of Au@ZIF and Pt obtained using X-ray diffraction (XRD) analysis (Figure 4.3C, 4.5).¹⁸ All of the Pt/Au@ZIF electrodes are thermally activated prior to subsequent experiments.

Figure 4.1. SEM images of Pt nanospheres with an average particle size of (i) 231 ± 17 nm, (ii) 140 ± 9 nm and (iii) 60 ± 7 nm. (iv) TEM image of Pt seeds with an average size of 29 ± 8 nm.

Figure 4.2. SEM characterization of Pt nanospheres coverage on Au electrode. (A) 60 nm, (B) 140 nm, (C) 231 nm and (D) Estimated particle density on Au electrode. (i) Representative SEM low magnification of PtNS coverage on Au electrode. (ii) Particle count distribution over three scanning areas.

(A) ZIF-induced electron deficient sites on Pt via Pt-ZIF interactions

(D) ZIF-induced Pt/Au d-band modification to weaken metal-H

Figure 4.3. The key concept of our strategy to modify the nanocatalyst surface electronic structure for enhanced electrochemical nitrogen reduction reaction at 1 atm and 298 K. A) The functions of ZIF: i) induce electron deficient sites on Pt via electron density migration from Pt to ZIF and ii) lower the d-band of Pt/Au to weaken metal–H interactions while facilitating metal–N₂ interaction. B) Cross-sectional SEM image of Pt/Au@ZIF. C) XRD patterns of Pt/Au@ZIF, Pt, and Au@ZIF, respectively. D) i) d-band center of 60 nm Pt/Au before and after ZIF encapsulation and ii) illustrating the shift of d-band away from the Fermi level to weaken the metal–H interaction. The black line represents the d-band center.

Figure 4.4. SEM characterization of Pt/Au@ZIF. (A) Cross sectional SEM of Pt/Au@ZIF. (B) ZIF thickness distribution.

Figure 4.5. XRD patterns of Pt/Au@ZIF, Pt, Au@ZIF, ZIF and Au, respectively. The successful formation of Pt/Au@ZIF platform is affirmed through the unique diffraction patterns of Pt, Au@ZIF, ZIF and Au obtained using X-ray diffraction (XRD) analysis.¹⁸

To improve NRR performances, it is important to 1) overturn traditionally favored H adsorption and 2) improve intrinsic catalytic activity towards NRR. These can be achieved by electronically modifying catalyst d-band center to reduce catalyst–H interactions and by creating electron deficient catalyst to improve N₂ adsorption and

activation, respectively. We first modify the electronic structure of Pt/Au to impede the formation of H-adatoms on Pt/Au catalyst, a key factor leading to HER side reaction. We hypothesize that such modification of the electrocatalyst valence band can be achieved through the synergistic effect arising from the electronic interaction between Pt/Au and ZIF. To probe the synergistic effects between Pt/Au and ZIF at the metal–ZIF interface, we examine the d-band center of Pt/Au upon ZIF encapsulation by performing valence band X-ray photoelectron spectroscopy (XPS) analysis in the range of 0–10 eV.¹⁷ The d-band model relates the adsorption strength between catalyst and adsorbate to the catalyst d-band position, which can predict reactivities and catalysis. The initial d-band center of all PtNSs (size: 60–231 nm) on Au at -4.88 eV experiences a negative shift upon ZIF encapsulation with a lowest d-band center of -5.56 eV (using 60 nm Pt/Au@ZIF) (Figure 4.3D, 4.6 refer to Calculation 4.1). We ascribe the lowering in d-band centers (from -4.88 to -5.56 eV) as PtNS size decreases to the increasing surface area/volume ratio of PtNS, whereby a smaller PtNS size allows more ZIF coverage and therefore increases the corresponding Pt-ZIF chemical interactions (Figure 4.7). Notably, the negative shift of Pt/Au d-band away from its Fermi level after ZIF encapsulation denotes that the Pt/Au–H interaction is weakened.¹⁹ This is a critical factor to suppress the formation of Pt/Au–H and associated HER (Figure 4.3D). Moreover, the Pt/Au–N₂ interactions and consequential NRR are further promoted by exploiting the high gas sorptivity of ZIF to concentrate N₂ molecules directly at the Pt/Au@ZIF interface (Figure 4.3A). We also eliminate the possibility that the change in d-band center is due to Pt–Au interaction because control XPS Au 4f analyses before and after PtNS deposition on Au electrode demonstrate negligible spectral change (Figure 4.8). Furthermore, we also calibrate our XPS observation to C 1s (Figure 4.9). Our observations thus highlight that ZIF is effective in lowering the electronic d-band center of Pt/Au to alleviate the strong competitive adsorption of H on Pt/Au for subsequent NRR analysis.

Calculation 4.1 – Determination of d-band center in valence band spectra

Center of d-band electronic structure is determined from valence band XPS spectra in the range from 0 to 10 eV. All spectra have been baseline-corrected by subtracting background using software CasaXPS. The d-band center position can be determined by first integrating the area of the valence band spectra in the range from 0 to -10.0 eV after background subtraction. The d-band center position is then determined to be at the value which cuts the integrated area exactly into half.

Figure 4.6. Analysis of d-band center. Comparison of valence band XPS spectra of various Pt/Au platforms (i) without and (ii) with ZIF encapsulation. Black lines indicate the positions of calculated d-band centers.

Figure 4.7. ECSA of Pt nanospheres. (A) Cyclic voltammograms of various Pt nanospheres in 0.1 M H_2SO_4 . (B) ECSA of various diameter of Pt nanospheres.

Figure 4.8. XPS Au 4f spectra investigation on various Pt/Au platforms upon fabrication.

(i)

60 nm Pt/Au, (ii) 140 nm Pt/Au, (iii) 231 nm Pt/Au and (iv) Au control platforms.

Figure 4.9. XPS C 1s characterization of 60 nm Pt/Au@ZIF.

Next, we investigate the generation of electron-deficient sites on Pt/Au catalyst upon ZIF encapsulation by analyzing the high-resolution XPS spectra of Pt 4f before and after ZIF coating. Using 60 nm Pt/Au as an example, we observe two broad peaks at about 75.5 eV and about 72 eV corresponding to Pt 4f_{5/2} and Pt 4f_{7/2} spin-orbit states, respectively (Figure 4.10A, 3.11A). The two broad XPS features can be further deconvoluted to three sets of peaks corresponding to the metallic state Pt⁰ (71.7 eV and 75.0 eV), Pt²⁺ oxide state (72.4 eV and 75.7 eV) and Au satellites (74.5 eV and 76.4 eV).²⁰ The presence of Pt oxidized state is commonly observed in small nanoparticles.²¹ Upon ZIF encapsulation, the XPS peaks of Pt⁰ and Pt²⁺ shifts positively by 0.2 eV and 0.3 eV, respectively. This indicates a reduction in Pt surface electron density, and is also a clear evidence that ZIF is in direct interaction with Pt surface. To further affirm the presence of interaction between Pt and ZIF, we also perform N 1s XPS analysis on ZIF with and without Pt/Au (Figure 4.10B; 4.11B). The broad N 1s peak of ZIF can be deconvoluted into three peaks which is attributed to ZIF imidazole linker -N= (399.7 eV), -NH- (400.5 eV) and quaternary N (401.3 eV). When ZIF encapsulates Pt/Au, the binding energy of -NH- and -N= peaks exhibit a negative shift of 0.4 eV and 0.3 eV, respectively, hence highlighting a direct chemical interaction between

ZIF and Pt/Au. More importantly, the direct chemical interaction results in the emergence of 398.7 eV, which is indexed to metal-N (Pt/Au-N) coordination bond upon ZIF encapsulation of metal.¹⁰⁻¹² Notably, this metal-N coordination bond serves as a bridge for the flow of electrons from Pt/Au to ZIF. This could be attributed to the electron migration from Pt to ZIF via metal-N (Pt/Au-N) coordination bond that is affirmed by the presence of its characteristic XPS feature at 398.7 eV.²¹⁻²³ Similar peak shifts/emergence are also observed when using PtNS of different sizes (Figure 4.12). From these observations, the positive shift of Pt 4f and the negative shift of N 1s spectra clearly highlight an electron density transfer from Pt to ZIF framework via Pt-N_{ZIF} interaction. Such Pt-to-ZIF electron migration in turn creates electron-deficient sites on Pt surface, which are necessary to promote the interactions between N₂ and catalyst for enhanced NRR.

Figure 4.10. XPS investigations on the 60 nm Pt/Au@ZIF platform. A) Changes in Pt 4f spectra of Pt/Au upon ZIF encapsulation. B) Changes in N 1s spectra of ZIF upon encapsulating Pt/Au. C) Electron density distributions: i) before and ii) after ZIF interaction, iii) corresponding changes in Mulliken charges on Pt₆, N1, and N2, respectively, after ZIF encapsulation. D) Gibbs free energy for i) free and ii) adsorbed states of N₂ and H onto Pt/Au@ZIF at the metal/ZIF interface. * denotes adsorbed states.

Figure 4.11. XPS investigation at the Pt/Au-ZIF interface in 60 nm Pt/Au@ZIF platform.

(A) Changes in Pt 4f spectra of Pt/Au upon ZIF encapsulation. (B) Changes in N 1s spectra of ZIF upon encapsulating Pt/Au.

Figure 4.12. XPS investigation at the Pt/Au-ZIF interface in 140 nm Pt/Au@ZIF platform.

(A) Changes in Pt 4f spectra of Pt/Au upon ZIF encapsulation. (B) Changes in N 1s spectra of ZIF upon encapsulating Pt/Au.

To elucidate the effect of Pt-to-ZIF electron migration, we further perform density functional theory (DFT) simulations between Pt catalyst and ZIF, and unravel the molecular origins behind the observed XPS spectral changes. We use 4,5-dichloroimidazole (dcim)–Zn and Pt₆ molecular clusters to represent ZIF and Pt surfaces, respectively, and to simulate the interfacial interaction between the two at the molecular level.²⁴ Upon ZIF encapsulation on Pt, the Mulliken charge distribution of Pt experiences a 0.131 positive increase, while the charges of N1 and N2 of ZIF become more negative by 0.054 and 0.122, respectively (Figure 4.10C-iii, 4.13). These changes in charge distribution on the atoms indicate the lost and gain in electron density on Pt and N, respectively, thereby validating our experimental XPS observations that electron density is transferred from Pt to ZIF framework via Pt–N linkage. Conversely, when anchoring Pt with a dcim organic layer (with no ZIF formation), the dcim–Pt system exhibits weaker electron withdrawing effect (Figures 4.14, 4.15). Hence, all results clearly signify the importance of ZIF in modifying the surface electron density of Pt. The coordination of Zn to dcim to form ZIF scaffold creates a greater electron withdrawing effect, hence drawing more electron density from Pt and resulting in a more electron deficient Pt.²⁵

Figure 4.13. Mulliken charge distribution (A) before and (B) after ZIF encapsulation on Pt surface. (i) schematic of the conformation and (ii) mulliken charge distribution table.

Figure 4.14. Mulliken charge distribution (A) before and (B) after dcim functionalization on Pt surface. (i) schematic of the conformation and (ii) mulliken charge distribution table. (C) Changes in mulliken charge distribution on Pt, N1 and N2, respectively, after dcim functionalization.

Figure 4.15. XPS Pt 4f investigation on Pt/Au before and after 4,5-dichloroimidazole functionalization.

To further highlight the importance of the aforementioned electronic modification in our design, we investigate the adsorption energy profile of both N₂ and H in their free and adsorbed states via DFT. Our simulations indicate that the change in Gibbs free energy (ΔG) are -1.45 eV (favorable adsorption) and 1 eV (unfavored adsorption) for N₂ and H adsorption on our electron-deficient Pt, respectively, as compared to its free-state (Figure 4.10D-ii; refer to Calculation 4.2, Table 4.1). The results affirm that the coating of ZIF lowers the energy barrier for N₂ adsorption relative to H which supports our hypothesis that N₂ adsorption is favored using our strategy.

Calculation 4.2 – Calculation of change in Gibbs free energy (ΔG)

The change in Gibbs free energy (ΔG) of adsorb *N₂ and *H were calculated using Eq. 1:

Equation (1)

$$\Delta G = G_{Pt-ZIF-X} - (G_{Pt-ZIF} + G_X)$$

where X is the adsorbed species, $Pt-ZIF-X$ is the adsorbed species on Pt@ZIF and $Pt-ZIF$ is the Pt@ZIF.

Table 4.1. Calculated Gibbs free energy of free and adsorbed species on electrocatalyst.

Reaction Progress	Δ Gibbs free energy (eV)
Adsorption of N ₂ on Pt@ZIF	$G_{Pt@ZIF (*N)} - G_{Pt@ZIF (free N)}$ = -1.45
Adsorption of H on Pt@ZIF	$G_{Pt@ZIF (*H)} - G_{Pt@ZIF (free H)}$ = 1.00

To assess the effect of the ZIF-induced Pt/Au surface modification on NRR performance, we perform cyclic voltammetry (CV) analysis using Pt/Au@ZIF electrode to elucidate the electrochemical processes occurring at the interfacial nanocavities. Briefly, our electrocatalysis setup comprises a three-electrode system (working electrode, 60 nm Pt/Au@ZIF; counter electrode, Pt wire; reference electrode, Ag/AgCl) immersed in dry tetrahydrofuran (THF) solution containing lithium trifluoromethanesulfonate as the electrolyte.¹⁴ Furthermore, 1% v/v ethanol is spiked in the electrolyte as a proton source for NRR. CV is performed under open ambient operations by first scanning towards the cathodic direction with a potential range from -0.5 V to -3.0 V under constant nitrogen (N₂) or argon (Ar) bubbling at 3 sccm (Figure 4.16A). Under N₂ bubbling, Pt/Au@ZIF exhibits a distinct reduction peak at about -2.6 V and subsequently demonstrates two electrochemical oxidation peaks at about -1.6 V and about -0.85 V. In contrast, control

experiment using the same Pt/Au@ZIF electrode but under Ar bubbling only exhibits the oxidation peaks at about -1.6 V and about -0.85 V. The distinct differences in electrochemical responses from both experiments (N₂ or Ar) affirm that the reduction peak at -2.6 V (onset at -2.1 V) arises from N₂-related reduction processes rather than potential interferences arising from ZIF, electrode and electrolyte. The two oxidation peaks during anodic scans in both gases are likely due to alcohol-related oxidation (Figure 4.17).¹⁴ In contrast, control Pt/Au electrodes without ZIF coating in the presence of N₂ or Ar bubbling exhibit distinct cathodic peak at -1.8 V that is attributed to HER and there is no N₂-related reduction peak at -2.6V (Figure 4.18). Collectively, these results ascertain that our Pt/Au@ZIF design is effective in driving NRR while suppressing competing HER owing to the presence of hydrophobic ZIF encapsulation (0.2 mmol g⁻¹ water uptake) to repel moisture (18 gm⁻³) as well as electronically tuned catalyst to promote N₂ adsorption.²⁶ More importantly, the high NRR selectivity in Pt/Au@ZIF electrocatalyst is unprecedented compared to other Pt-based catalysts because traditional Pt materials favor the formation of Pt-H and are commonly employed for HER.⁵

Figure 4.16. Evaluating the NRR performance across various Pt/Au@ZIF platforms. A) Representative cyclic voltammograms recorded from Pt/Au@ZIF working electrodes under N₂ or Ar gas bubbling at 3 sccm using a mass flow controller. B) UV/Vis spectra quantifying the ammonia produced by various platforms after 6 h. C) Effective Faradaic efficiency (FE) and rate of ammonia formation by various Pt/Au@ZIF platforms. D) Evaluating NRR performance using 60 nm Pt/Au@ZIF platform at various electrochemical potentials.

Figure 4.17. Cyclic voltammograms investigation of Pt/Au@ZIF working electrode in the presence and absence of ethanol under Ar bubbling at 3 sccm using a mass flow controller.

Figure 4.18. Cyclic voltammograms investigation of Pt/Au working electrode (in the absence of ZIF encapsulation) under N₂ or Ar gas bubbling at 3 sccm using a mass flow controller.

We evaluate the NRR performance of our Pt/Au@ZIF working electrode across various PtNS sizes to demonstrate the effect of our nanocatalyst d-band structure modification on NRR. NRR performance is evaluated based on two metrics, namely 1) effective Faradaic efficiency (FE) and 2) effective rate of ammonia formation, whereby the

effective values are obtained by comparing against control experiments performed under Ar bubbling. The subtraction of the ammonia formed under Ar conditions is necessary to determine the actual NH_3 that are formed by NRR using Pt/Au@ZIF, and eliminates potential contributions from any dissolved nitrogenous contaminants from the environment to prevent false positive results. In a typical reaction setup, the system is bubbled with N_2 gas for at least 15 min and ammonia is generated by applying a potential at -2.9 V, unless stated otherwise, for 6 h under a continuous supply of N_2 at 3 sccm in open ambient conditions. The electrosynthesized ammonia in the dry THF is determined via Berthelot's reaction to form indophenol blue, which has a characteristic absorption peak at about 647 nm that can be quantified via UV/Vis spectroscopy (Figure 4.16B, 4.19). NRR performance of Pt/Au@ZIF generally increases with lower d-band center as size of PtNS decreases. When PtNS size decreases from 231 nm to 60 nm, the FE increases significantly by >4-fold from $(9.6 \pm 1.1)\%$ to $(44.8 \pm 4.2)\%$. The NH_3 yield rate also achieves a notable >60-fold improvement from (2.5 ± 1.1) to $(161.9 \pm 16.7) \mu\text{g mg}_{\text{cat}}^{-1}\text{h}^{-1}$ (Figure 4.16C, 4.20), respectively. Among all Pt/Au@ZIF, 60 nm Pt/Au@ZIF is the best performing NRR electrocatalyst with the highest FE of $(44.8 \pm 4.2)\%$ and NH_3 yield rate of $(161.9 \pm 16.7) \mu\text{g mg}_{\text{cat}}^{-1}\text{h}^{-1}$ (Figure 4.16C; refer to Calculation 4.3, Table 4.2). This is because 60 nm Pt/Au@ZIF has the lowest d-band center of -5.56 eV, which greatly weakens the formation of metal-H while facilitating N_2 adsorption to promote NRR (Figure 4.3D, 4.6, 4.7). Notably, our high NRR performance is a direct correlation to the d-band observations.

Figure 4.19. UV-Vis and calibration curve of indophenol blue.

Figure 4.20. UV-Vis spectrum exhibited by various platforms after 6 h under 3 sccm of (i) N₂ and (ii) Ar gases.

Calculation 4.3 – Calculation of rate of ammonia formation and faradiac efficiency (FE)

The rate of ammonia formation and Faradaic efficiency were calculated using Eqs. 1 and 2, respectively:

Equation (1)

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

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

Equation (2)

$$\text{Faradaic efficiency (\%)} = \frac{3F \times r\text{NH}_3}{I}$$

where $r\text{NH}_3$ is the rate of ammonia formation, I is the current density at constant applied voltage, and F is the Faraday constant.

Table 4.2. Tabulating the current density of various Pt/Au@ZIF platforms determined using chronoamperometry under respectively N_2 or argon flow.

Electrode Platforms	Type of Gas	Current Density ($\mu\text{A}/\text{cm}^2$)
231 nm Pt/Au@ZIF	N_2	18.4 ± 1.9
	Ar	35.6 ± 3.6
140 nm Pt/Au@ZIF	N_2	7.2 ± 0.4
	Ar	25.4 ± 1.3
60 nm Pt/Au@ZIF	N_2	3.3 ± 2.1
	Ar	4.4 ± 2.8
Au@ZIF	N_2	8.1 ± 0.2
	Ar	9.2 ± 0.2
dcim-60 nm Pt/Au	N_2	4.3 ± 0.3
	Ar	7.6 ± 0.5
60 nm Pt/Au	N_2	5.2 ± 0.3
	Ar	9.3 ± 0.6

It is noteworthy that the high FE of >44% and ammonia yield rate of $>161 \mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$ achieved with 60 nm Pt/Au@ZIF is one of the highest reported thus far under ambient conditions.^{6, 27, 28} Importantly, our study provides the first direct evidence that ZIF is capable of modifying metal catalyst electronic structure to achieve high-performance NRR. We eliminate the contribution from Pt surface defects as defects are typically present in alloy

or core@shell nanomaterials.²⁹ These performances are possible through ZIF-induced d-band modification to weaken metal–H formation prior N₂ adsorption, with negligible contribution by the presence of nitrogenous impurities (ppb) in N₂ gas.³⁰ Furthermore, the Berthelot's reaction for NRR quantification is selective towards ammonia/ammonium and cannot be affected by other nitrogenous species because the latter forms a sterically-hindered intermediate that inhibits subsequent indophenol formation.³¹ By subtracting all FE and NH₃ yield rate against control Ar experiments, we also effectively eliminate background interferences arising from ZIF, electrolyte and gases. We further exclude the possibility of contaminants from N₂ gas source because the maximum possible ammonia from potential contaminants in N₂ gas was reported to be <2%.¹⁴ Hence, the ammonia quantified is definitively attributed to NRR and we employ 60 nm Pt/Au@ZIF for the remaining analysis due to its highest NRR performance. Moreover, we evaluate Pt/Au@ZIF NRR activity and isolate the preferential potential to boost NRR performance by examining across various applied potentials (-1.7 V to -3.3 V) (Figure 3.21). From -1.7 V to -2.1 V, FE increases significantly from (29.8 ± 4.7) % to (42.5 ± 4.6) % and plateau at -2.9 V (FE; 44.8 ± 4.2 %). Correspondingly, the NH₃ yield rate increases from (64.3 ± 15.6) µg mg_{cat}⁻¹ h⁻¹ to (161.9 ± 16.74) µg mg_{cat}⁻¹ h⁻¹ (Table 4.3). Subsequently the performance decreases slightly at -3.3 V with FE and NH₃ yield rate at (23.8 ± 4.2) % and (116.5 ± 18.7) µg mg_{cat}⁻¹ h⁻¹, respectively. The lower FE at -1.7 V might be because the reducing potential is before the onset potential of NRR (-2.1 V) while at -3.3 V, the FE decreases due to the influence from Li ion reduction.³² More importantly, the best NRR activity is identified to occur between -2.5 V to -2.9 V, which is consistent with our observed CV during N₂ bubbling, whereby a distinct broad N₂ reduction peak appears between -2.1 V to -2.9 V with an onset potential at -2.1 V (Figure 4.3A, 4.3D, Table 4.3, Figure 4.21). Notably, our ZIF coating remains intact even after NRR which demonstrates its durability (Figure 4.22).

Figure 4.21. Evaluating NRR performance using 60 nm Pt/Au@ZIF platform at various electrochemical potential.

Table 4.3. Tabulating the current density of 60 nm Pt/Au@ZIF platforms at various potential determined using chronoamperometry under respectively N₂ or Argon flow.

Potential (V vs Ag/AgCl)	Type of Gas	Current Density (μA/cm ²)
-3.3 V	N ₂	5.0 ± 0.3
	Ar	5.3 ± 0.3
-2.9 V	N ₂	3.3 ± 2.1
	Ar	4.4 ± 2.8
-2.5 V	N ₂	3.7 ± 0.3
	Ar	6.6 ± 0.4
-2.1 V	N ₂	3.2 ± 0.2
	Ar	7.7 ± 0.5
-1.7 V	N ₂	3.1 ± 0.2
	Ar	7.6 ± 0.5

Figure 4.22. SEM characterization of Pt/Au@ZIF. (A) Before reaction and (B) After reaction.

Our Pt/Au@ZIF is highly durable even after 6 h of reaction. This is demonstrated through the intact of ZIF coating on Pt/Au electrocatalyst.

In our Pt/Au@ZIF system, ZIF is postulated to exhibit multiple functionalities, and we classify them based on 1) the surface electronic modification of Pt for N_2 adsorption and 2) the physical concentration of N_2 and moisture-repelling effect. To ascertain the contribution of each effect, we fabricate and assess the NRR performances of three control electrocatalytic systems comprising 1) dichloroimidazole (dcim) monolayer-functionalized Pt/Au, 2) non-functionalized Pt/Au electrocatalysts, and 3) Au@ZIF (Figure 4.23A). Functionalizing Pt/Au with a monolayer of dcim (dcim-Pt/Au) modifies the electronic structure of Pt but does not highlights the effect of ZIF without d-band modification and Pt catalytic effect. The NH_3 yield rates are normalized against electrochemical active surface area (ECSA) for fair comparison.

Figure 4.23. Elucidating the importance of ZIF to enhance NRR performance. A) Comparing the effects present in various electrocatalytic systems: i) Pt/Au@ZIF, ii) dcim-Pt/Au, iii) Pt/Au, and iv) Au@ZIF. B) Evaluation of d-band position and C) corresponding effective Faradaic efficiency and rate of ammonia formation for each system, respectively. D) Proposed NRR mechanism at the Pt/Au@ZIF interfacial cavities. Imidazolate species coordinate to metal surface and distort surface electronic configuration to improve N₂ adsorption.

We first isolate the contribution of d-band modification by comparing NRR performance of dcim-Pt/Au with the nonfunctionalized Pt/Au system (Figure 4.23A(ii,iii)). Successful functionalization of dcim monolayer onto Pt/Au is affirmed via XPS where an additional peak corresponding to the characteristic imidazole at the N 1s spectrum (Figure

4.24). Dcim-functionalization of Pt/Au results in a distinct d-band center shifting from -4.88 eV to -5.32 eV, denoting strong metal–N imidazole interaction, while non-functionalized Pt/Au control indicates no d-band shift at -4.88 eV (Figure 4.23A(ii,iii), 4.23B(ii,iii)). The smaller extent of shift exhibited in dcim-Pt/Au (-0.44 eV) compared to Pt/Au@ZIF (-0.68 eV) could be due to the lack of coordination of Zn to dcim to create the ZIF network to significantly modify Pt/Au d-band (Figure 4.13-4.15). Hence, dcim-Pt/Au NRR achieves FE of 4.2%, which is >4-fold higher than non-functionalized Pt/Au (FE 0.9%). The NH₃ yield rate is also >1.7-fold higher for dcim-Pt/Au (0.731 mgm⁻²h⁻¹ and 0.414 mgm⁻²h⁻¹, respectively) (Figure 4.23A(ii,iii), 4.23C). Therefore, this comparison demonstrates the importance of d-band modified Pt/Au to improve NRR activity via the weakening of metal–H formation.

Figure 4.24. XPS N 1s characterization of dcim-Pt/Au (i) before dcim functionalization and (ii) after dcim functionalization.

Subsequently, we compare the NRR performance between Au@ZIF and Pt/Au@ZIF to determine the contribution of Pt and the effects of surface d-band modifications (Figure 4.23A(i,iv)). Our Pt/Au@ZIF system exhibits a d-band center -5.56

eV, indicating strong metal–N_{ZIF} interaction. In contrast, Au@ZIF with no surface electronic modification interaction demonstrates negligible d-band shifting (-5.29 eV) in comparison to Au film (-5.20 eV) (Figure 4.6). In terms of NRR performances, Pt/Au@ZIF achieves >4-fold higher FE as compared to our Au@ZIF system (44.8% compared to 9.6%), with NH₃ yield rate exhibiting >2-fold higher from 1.64 to 3.39 mgm⁻²h⁻¹ (Figure 4.23A(i,iv), 4.23C). This demonstrates that the presence of catalytic PtNS in our Pt/Au@ZIF system is necessary to enhance NRR performance. Although Pt is known for its high affinity for H atom to promote HER,^{11, 12} we successfully use the ZIF coating to weaken the Pt–H interaction and enhance the preferential adsorption of N₂ through the metal–N_{ZIF} interaction.

Finally, the Pt/Au@ZIF exhibits >10-fold and >4-fold higher FE and NH₃ yield rate as compared to dcim-Pt/Au system (Figure 4.23A(i,ii), C). This clearly demonstrates that the three-dimensional network structure of ZIF is more superior to a monolayer of dcim. In addition to the electronically modified Pt/Au surfaces, the Pt/Au@ZIF exhibits catalyst-ZIF interfacial cavities to concentrate N₂ gas directly on the catalyst surface to further promote their binding/interaction with N₂ molecules, which is unachievable using dcim-Pt/Au alone. Collectively, all three control experiments support our hypothesis that ZIF encapsulation is critical to boost NRR by >40 percentage points by modifying the metal catalyst electronic structure and by imparting N₂ concentrating and water repelling properties (Figure 4.23C). This valuable insight can help to boost the performance of traditional electrocatalysts and tune them toward high NRR activity.

Corroborating experimental results and calculations unravel the molecular event occurring at the catalyst-ZIF interfacial cavity during NRR and affirm that the Pt–N_{ZIF} interaction is crucial to kinetically promote NRR performance (Figure 4.23D). The Pt–N_{ZIF} interaction induces d-band modification of Pt/Au nanocatalyst, which weaken Pt–H

formation and simultaneously creates electron deficient affinity sites for favorable N₂ adsorption. Subsequently, N₂ gas and ethanol (proton source) are selectively infused into the ZIF scaffold and concentrated near the electrocatalyst surface for adsorption while the hydrophobic ZIF pores prevent trace water/moisture from reaching the electrocatalytic sites. The strong intermolecular interactions between N₂ and ethanol near Pt/Au surface in the presence of an external voltage thus activates the electrochemical reduction of N₂ to ammonia at ambient conditions.

4.3 Conclusion

Our work highlights the importance of ZIF electronic surface modification on the electrocatalyst to enhance NRR while suppressing HER by overturning the primarily favored H atom adsorption for N₂ and restricting access of trace water to the electrocatalyst surface. Importantly, our strategy successfully modifies the d-band structure of Pt/Au catalyst to kinetically boost the FE of NRR by >44-fold compared to the absence of ZIF (ca. 1%). We also showcase the superiority of our electrocatalyst by achieving a high FE of >40% and a high NH₃ yield rate of >130 $\mu\text{g mg}_{\text{cat}}^{-1}\text{h}^{-1}$ across wide reducing potentials. Experimental and DFT investigations jointly highlight the presence of N₂ adsorption sites through the creation of electron deficient regions on Pt catalyst in Pt/Au@ZIF via the Pt/Au-NZIF interactions. Importantly, our calculated adsorption energy profile rationalizes the origin of our improved NRR performances to the now favorable adsorption of N₂ over H atom. Our ZIF modified electrocatalytic design thus offers an attractive approach to effectively tackle the long-standing bottleneck in NRR: competing HER. Notably, our design is universal and can allow the facile integration with emerging active catalyst to further boost both NRR activity and selectivity. These valuable insights create enormous

opportunities to design an ideal electrocatalytic system for high-performance and sustainable NRR even when utilizing atmospheric air as N₂ and proton source.

4.4 Materials and methods

Materials. Chloroplatinic acid hexahydrate (ACS reagent), sodium citrate tribasic dihydrate ($\geq 99\%$, ACS reagent), citric acid, L-ascorbic acid (99%), zinc acetate dihydrate ($\geq 98\%$, ACS reagent), 4,5-dichloroimidazole ($\geq 98\%$), lithium trifluoromethanesulfonate (LiCF₃SO₃, 99.995%), sodium nitroprusside dihydrate ($\geq 99\%$, ACS reagent, Reag. Ph. Eur), sodium dichloroisocyanurate dihydrate ($\geq 98.0\%$) and phenol ($\geq 99\%$, purified by redistillation) were purchased from Sigma-Aldrich; sodium borohydride (97+%) from Alfa Aesar; methanol ($\geq 99.9\%$) and THF ($\geq 99.0\%$, ACS reagent) were from Fulltime; ethanol (ACS, ISO, Reag. Ph Eur) and sodium hydroxide (NaOH, $\geq 99.0\%$) were from EMSURE; *N,N'*-dimethylformamide (DMF, ACS reagent) was obtained from Tedia; sulfuric acid ($\geq 95\%$) and hydrochloric acid (37%) were from VWR Chemicals; and 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 an inert N₂ environment. All other chemicals were applied without further purification. Milli-Q water ($>18.0\text{ M}\Omega\text{ cm}$) was purified with a Sartorius Arium 611 UV ultrapure water system.

Synthesis of Platinum Nanoparticle Seeds. The preparation of platinum nanospheres was carried out following the method modified from literature.³³ Briefly, Pt nanoparticle seeds were synthesized by adding 3.6 mL of 0.2% chloroplatinic acid hexahydrate to 92.8 mL of boiling water. After 1 min, a 1.1 mL solution containing 1% sodium citrate and 0.05% citric

acid was injected into the mixture, followed by 0.55 mL of freshly prepared NaBH_4 (0.08%) solution containing 1% sodium citrate and 0.05% citric acid. The reaction mixture was heated for 10 mins at 100°C and then cooled to room temperature.

Synthesis of 29 nm Platinum Nanospheres. A seed-mediated synthetic approach was adopted to grow platinum nanospheres from 5 nm nanoparticle seeds to 29 nm nanospheres. 1 mL of as-synthesized Pt seed solution was added to 29 mL of ultrapure water, followed by the addition of 0.4 M chloroplatinic acid solution (0.045 mL) and 0.5 mL of a solution containing 1% sodium citrate and 1.25% L-ascorbic acid. The mixture was stirred and heated slowly to 100°C for 30 mins and then cooled to room temperature.

Synthesis of 60 nm, 140 nm and 231 nm Platinum Nanospheres. To synthesize 60 nm platinum nanospheres, 2 mL of 29 nm platinum nanospheres was added to 26 mL ultrapure water and 0.4 M chloroplatinic acid solution (0.045 mL) at room temperature, followed by 0.5 mL of a solution containing 1% sodium citrate and 1.25% L-ascorbic acid. The mixture was heated slowly to 100°C for 60 mins and then cooled to room temperature. The resultant solution was washed and redispersed in ultrapure water. To obtain 140 nm and 231 nm nanospheres, the synthesis was repeated by adding 1 mL and 0.25 mL of the 29 nm nanospheres to 26 mL of ultrapure water respectively. SEM imaging was carried out, and the diameter of 100 Pt nanoparticles were measured and analyzed using ImageJ software.

Preparation of Pt/Au Electrode. To prepare the Pt/Au electrode, 1.25 μL of Pt nanoparticle solution was drop-casted onto pre-polished Au electrodes (2 mm diameter). The working electrode was subjected to acid treatment and immersed in 0.1 M HCl solution (20% ethanol in water) for 3 h. The as-prepared Pt/Au electrode was then washed with a

copious amount of methanol and dried using a stream of nitrogen gas and stored under inert nitrogen conditions.

Encapsulation of the Pt/Au electrode with zeolitic imidazolate framework-71 (Pt/Au@ZIF electrode). A layer by layer overgrowth method of ZIF on the Pt/Au electrode was performed. Prior to ZIF synthesis, methanolic solutions of zinc acetate dihydrate (0.2 M) and 4,5-dichloroimidazole (0.4 M) were prepared separately. The as-prepared Pt/Au electrode was subsequently immersed in a reacting ZIF-71 solution containing 0.125 mL of DMF, 0.375 mL of MeOH and 0.25 mL of the respective methanolic solutions of zinc and imidazole precursors for 40 mins. The electrode was then washed with a copious amount of methanol and dried using a stream of nitrogen gas. ZIF formation reaction was repeated for a total of 6 cycles to achieve a complete encapsulation of ZIF over the Pt/Au surface. The electrode was stored under inert nitrogen conditions.

Thermal Activation of Various Platforms. Before their application in electrochemical nitrogen-to-ammonia conversion, all platforms were thermally activated under vacuum at 120 °C for 2 hours to remove residual methanol residing in the ZIF's intrinsic pores after its synthesis. This heat treatment does not affect the structural and chemical identity of our platforms, ensuring the integrity of its respective constituents for efficient and selective electrochemical reaction.

Electrochemical NRR. Electrolyte solutions were prepared using LiCF_3SO_3 (0.2 M) in a solvent mixture containing ~1% ethanol in “dry” THF. For each Pt/Au@ZIF electrode, the prepared electrolyte solutions were bubbled with respective N_2 gas or Ar gas for at least 15 min before electrochemical experiments. All gas flow rates were precisely controlled at ~3

sccm using mass flow controllers (model number MC-100SCCM-D) obtained from Alicat Scientific, Inc.

A three-electrode electrochemical setup was employed, where the counter electrode and the reference electrode comprised of a Pt wire and silver/silver chloride electrode (Ag/AgCl; 1M KCl solution), respectively. Working electrodes composed of thermal activated Pt/Au@ZIF electrodes. Cyclic voltammetry measurements were recorded at a scan rate of 50 mV/s between applied potential range from -3.0 V to -0.5 V (versus Ag/AgCl). The type of gas used was varied to identify the electrochemical peaks recorded from different working electrodes. Electrochemical conversion of nitrogen to ammonia for determination of the FE and rate of ammonia formation were then conducted using chronoamperometry at a constant applied potential of -2.9 V for 6 h using respective combinations of working electrode and types of gas. All electrochemical experiments were conducted under a constant gas flow and at open ambient conditions (1 bar, 298 K).

Preparation of Reagents for the Indophenol Blue Method. The preparation of indophenol blue method was followed according to previous studies.³⁴ Two precursor solutions were prepared for indophenol blue method, namely reagent A and B. Reagent A was prepared by dissolving phenol (0.1 M) and sodium nitroprusside dihydrate (0.2 mM) in ultrapure water. Reagent B was prepared by dissolving sodium dichloroisocyanurate dihydrate (2.8 mM) and sodium hydroxide (0.13 M) in ultrapure water. Both reagents were stored in a fridge before use.

Detection of Ammonia Using the Indophenol Blue Method. A calibration curve relating the extinction intensity with ammonia/ammonium concentration was first established for latter quantification of ammonia produced in the electrochemical reaction. Ammonium

sulfate (10 mM) was dissolved in an aqueous sulfuric acid solution (10^{-3} M). The ammonium sulfate was then serially diluted to various concentrations between 10^{-6} M and 10^{-4} M. This was followed by an addition of an equivalent amount of “dry” THF electrolyte (containing 1% ethanol) to all the ammonium sulfate standard solutions. Individual ammonium sulfate standard solutions (0.2 mL) were added to a glass vial containing 1 mL of reagent A. Reagent B (1 mL) was then added into the solution and allowed to react for 1 h 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). This solution (2 mL) was added to a glass vial containing 1 mL of reagent A. Reagent B (1 mL) was then added into the solution and allowed to react overnight while being stirred at 500 rpm. The 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 Electrochemical Surface Area. The electrochemical surface area (ECSA) of the Pt/Au electrodes was conducted according to previous studies.³⁵ Cyclic voltammetry measurements were recorded in 0.1 M H₂SO₄ and the ECSA was determined from the H⁺ absorption peak.

X-ray photoelectron spectroscopy (XPS) Characterization. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. The scanning range was from 0 – 10 eV. The C

1s binding energy peak at 284.5 eV was used for XPS calibration. ZIF-related samples are coated with 1 cycle of ZIF and thermally activated prior XPS analysis.

Density functional theory (DFT) simulation. The calculation on the interaction of Pt surface with ZIF cluster as well as the interaction of Pt-ZIF interface with *H and *N₂ molecules were conducted using unrestricted B3LYP exchange-correlation functional, as implemented in the Gaussian 09 computational chemistry package. The 6-31g (d p) basis set was used for all atoms except Pt, for which the LANL2DZ basis set was employed. The Pt surface was modelled using a reported triangle consisting of 6 Pt atoms. After geometry optimization of the Pt₆ cluster, the ZIF cluster was then placed near the Pt cluster and the entire system was re-optimized. *H and *N₂ molecules were subsequently placed near the Pt-ZIF system to study their interactions.

Characterization. Scanning electron microscope (SEM) imaging was carried out using JEOL-JSM-7600F microscope. UV-vis spectroscopic measurements were obtained using a Cary 60 UV-vis spectrometer. Substrate XRD patterns were recorded on a Bruker General Area Detector Diffraction System (GADDS) XRD diffractometer with Cu K α radiation. XPS spectra were measured using a Phoibos 100 spectrometer with a monochromatic Mg X-ray radiation source. All electrochemical experiments were performed using Metrohm Autolab potentiostat instrument.

References

1. Liu, C.; Sakimoto, K. K.; Colln, B. C.; Silver, P. A.; Nocera, D. G. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 6450.

2. Bao, D.; Zhang, Q.; Meng, F.-L.; Zhong, H.-X.; Shi, M.-M.; Zhang, Y.; Yan, J.-M.; Jiang, Q.; Zhang, X.-B. *Adv. Mater.* **2017**, *29*, 1604799.
3. Lv, C.; Qian, Y.; Yan, C.; Ding, Y.; Liu, Y.; Chen, G.; Yu, G. *Angew. Chem. Int. Ed.* **2018**, *57*, 10246.
4. Song, P.; Kang, L.; Wang, H.; Guo, R.; Wang, R. *ACS Appl. Mater. Interfaces* **2019**, *11*, 12408.
5. Wang, S.; Ichihara, F.; Pang, H.; Chen, H.; Ye, J. *Adv. Funct. Mater.* **2018**, *28*, 1803309.
6. Wang, M.; Liu, S.; Qian, T.; Liu, J.; Zhou, J.; Ji, H.; Xiong, J.; Zhong, J.; Yan, C. *Nat. Commun.* **2019**, *10*, 341.
7. A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff, J. K. Nørskov, *ACS Catal.* **2017**, *7*, 706.
8. Lv, C.; Yan, C.; Chen, G.; Ding, Y.; Sun, J.; Zhou, Y.; Yu, G. *Angew. Chem. Int. Ed.* **2018**, *57*, 6073.
9. Zhang, L.; Ji, X.; Ren, X.; Ma, Y.; Shi, X.; Tian, Z.; Asiri, A. M.; Chen, L.; Tang, B.; Sun, X. *Adv. Mater.* **2018**, *30*, 1800191.
10. Zhao, S.; Lu, X.; Wang, L.; Gale, J.; Amal, R. *Adv. Mater.* **2019**, *31*, 1805367.
11. Calle-Vallejo, F.; Koper, M. T. M.; Bandarenka, A. S. *Chem. Soc. Rev.* **2013**, *42*, 5210.
12. Li, F.; Han, G.-F.; Noh, H.-J.; Jeon, J.-P.; Ahmad, I.; Chen, S.; Yang, C.; Bu, Y.; Fu, Z.; Lu, Y.; Baek, J.-B. *Nat. Commun.* **2019**, *10*, 4060.
13. Koh, C. S. L.; Lee, H. K.; Sim, H. Y. F.; Han, X.; Phan-Quang, G. C.; Ling, X. Y. *Chem. Mater.* **2020**, *32*, 1674.
14. H. K. Lee, C. S. L. Koh, Y. H. Lee, C. Liu, I. Y. Phang, X. Han, C.-K. Tsung, X. Y. Ling, *Sci. Adv.* **2018**, *4*, eaar3208.

15. Sim, H. Y. F.; Lee, H. K.; Han, X.; Koh, C. S. L.; Phan-Quang, G. C.; Lay, C. L.; Kao, Y.-C.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y. *Angew. Chem. Int. Ed.* **2018**, *57*, 17058.
16. Koh, C. S. L.; Lee, H. K.; Han, X.; Sim, H. Y. F.; Ling, X. Y. *Chem. Commun.* **2018**, *54*, 2546.
17. Yang, Z.; Pedireddy, S.; Lee, H. K.; Liu, Y.; Tjiu, W. W.; Phang, I. Y.; Ling, X. Y. *Chem. Mater.* **2016**, *28*, 5080.
18. Dong, X.; Lin, Y. S. *Chem. Commun.* **2013**, *49*, 1196.
19. Pan, Y.; Sun, K.; Lin, Y.; Cao, X.; Cheng, Y.; Liu, S.; Zeng, L.; Cheong, W.-C.; Zhao, D.; Wu, K.; Liu, Z.; Liu, Y.; Wang, D.; Peng, Q.; Chen, C.; Li, Y. *Nano Energy* **2019**, *56*, 411.
20. Ma, J.; Habrioux, A.; Luo, Y.; Ramos-Sanchez, G.; Calvillo, L.; Granozzi, G.; Balbuena, P. B.; Alonso-Vante, N. *J. Mater. Chem. A* **2015**, *3*, 11891.
21. Melke, J.; Peter, B.; Haberer, A.; Ziegler, J.; Fasel, C.; Nefedov, A.; Sezen, H.; Wöll, C.; Ehrenberg, H.; Roth, C. *ACS Appl. Mater. Interfaces* **2016**, *8*, 82.
22. Jin, H.; Liu, X.; Chen, S.; Vasileff, A.; Li, L.; Jiao, Y.; Song, L.; Zheng, Y.; Qiao, S.-Z. *ACS Energy Lett.* **2019**, *4*, 805.
23. Wang, L.; Zhang, W.; Zheng, X.; Chen, Y.; Wu, W.; Qiu, J.; Zhao, X.; Zhao, X.; Dai, Y.; Zeng, J. *Nat. Energy* **2017**, *2*, 869.
24. Jennings, P. C.; Johnston, R. L. *Comput. Theor. Chem.* **2013**, *1021*, 91.
25. Zheng, B.; Zhu, Y.; Fu, F.; Wang, L. L. J. Wang, H. Du, *RSC Adv.* **2017**, *7*, 41499.
26. Zhang, K.; Lively, R. P.; Dose, M. E.; Brown, A. J.; Zhang, C.; Chung, J.; Nair, S.; Koros, W. J.; Chance, R. R. *Chem. Commun.* **2013**, *49*, 3245.
27. Yang, Y.; Wang, S.-Q.; Wen, H.; Ye, T.; Chen, J.; Li, C.-P.; Du, M. *Angew. Chem. Int. Ed.* **2019**, *58*, 15362.

28. Wang, H.; Chen, Y.; Fan, R.; Chen, J.; Wang, Z.; Mao, S.; Wang, Y. *Research* **2019**, *12*.
29. Dubau, L.; Nelayah, J.; Moldovan, S.; Ersen, O.; Bordet, P.; Drnec, J.; Asset, T.; Chattot, R.; Maillard, F. *ACS Catal.* **2016**, *6*, 4673.
30. Mitsui, Y.; Kambara, H.; Kojima, M.; Tomita, H.; Katoh, K.; Satoh, K. *Anal. Chem.* **1983**, *55*, 477.
31. Ngo, T. T.; Phan, A. P. H.; Yam, C. F.; Lenhoff, H. M. *Anal. Chem.* **1982**, *54*, 46.
32. Chen, W.; Hu, Y.; Lv, W.; Lei, T.; Wang, X.; Li, Z.; Zhang, M.; Huang, J.; Du, X.; Yan, Y.; He, W.; Liu, C.; Liao, M.; Zhang, W.; Xiong, J.; Yan, C. *Nat. Commun.* **2019**, *10*, 4973.
33. Bigall, N. C.; Hartling, T.; Klose, M.; Simon, P.; Eng, L. M.; Eychmuller, A. *Nano Lett.* **2008**, *8*, 4588.
34. Tsuneto, A.; Kudo, A.; Sakata, T. *J. Electroanal. Chem.* **1994**, *367*, 183.
35. Nash, J.; Yang, X.; Anibal, J.; Wang, J.; Yan, Y.; Xu, B. *J. Electroanal. Chem.* **2017**, *164*, F1712.

Chapter 5: Modifying Molecular Orbitals of Metals in Metal@ZIF to Boost N₂ Activation in Electrochemical N₂ Reduction at Ambient Conditions

Abstract. In this chapter, we perform a molecular level analysis to understand ZIF's ability to modify electrocatalyst's electronic structure for enhance NRR, In particular, we elucidate how ZIF promotes the NRR reaction by performing an in-depth investigation on the Pt-N₂ frontier molecular orbitals (MOs), and how these orbitals are involved during interactions. The fundamental understanding of these MOs is extremely crucial as it build a core foundation to design high performing electrochemical NRR systems. Using 140 nm Pt nanocatalyst as our model, we identify and highlight that ZIF elevates Pt's highest occupied molecular orbital (HOMO_{Pt}) closer to the lowest occupied molecular orbital of N₂ (LUMO_{N₂}) to facilitate stronger π -backbonding is key to N₂ activation. Importantly, we also showcase the platform versatility across other noble nanocatalyst of similar sizes. These valuable insights at the solid-ZIF interface creates tremendous opportunities for various applications in industrial fine chemistry production, greenhouse gas remediation and gas valorization.

5.1 Introduction

Electrochemical nitrogen reduction reaction (EC-NRR) is a promising approach to produce ammonia (NH_3) as a renewable energy source directly from atmospheric nitrogen (N_2) compared to the energy-consuming Haber-Bosch process ($400\text{ }^\circ\text{C}$, 40 MPa).^{1, 2} However, NRR suffers from poor reaction selectivity arising from the preferential adsorption of H over N_2 across catalyst surface, hence resulting in hydrogen evolution reaction (HER) and poor NRR performance.^{3, 4} Current existing strategies focus on heteroatom doping and creating defects on catalyst surface to improve the performance by creating electron-deficient catalytic sites to attract N_2 onto catalyst surface and also tuning the catalyst- N_2 adsorption strength by varying the d-band center of catalyst.^{5, 6} Typically, N_2 molecules will first adsorb onto electron-deficient catalytic surface via its lone pair electrons and subsequently break its $\text{N}\equiv\text{N}$ bond to accept a proton source in the presence of applied potential to form NH_3 . Although these strategies demonstrate better NRR performance, most exhibits only either high faradaic efficiency ($>\text{FE} \sim 40\%$) or NH_3 yield rate hence limits its practical application.⁷ By solely relying on both electron deficient sites and adsorption strength are insufficient and do not resolve the fundamental bottleneck of NRR – poor N_2 activation, which is the rate determining step. Thus, for easy N_2 activation, electron density has to flow from catalyst's highest occupied molecular orbital (HOMO) to N_2 's lowest occupied molecular orbital (LUMO) to weaken $\text{N}\equiv\text{N}$ bond. Notably, the challenge to activate N_2 comprises of two important factors mainly 1) high-lying N_2 LUMO (π^*) and 2) strong $\text{N}\equiv\text{N}$ bond (944 kJ mol^{-1}) which inhibits catalyst- N_2 interaction. To overcome these limitations, it is necessary to modify N_2 electronic properties for N_2 activation in order to improve its catalytic activity and reaction selectivity towards NRR.

An emerging strategy to activate N_2 is to modify its electronic structure by lowering its π^* orbital energy level via the withdrawal of electron density from N_2 . This modification

is demonstrated by binding molecules with Lewis acidic moieties to N₂ but is limited by the low N₂ gas density which makes intermolecular interaction extremely challenging.⁸ An alternative method is to tune and narrow the orbital energies between catalyst and diatomic gases by modifying catalyst's frontier orbitals. For instance, simulated nitrogen vacancies created in BN anchor single Au atom catalyst lowers the highest occupied molecular orbital (HOMO) closer to the lowest occupied molecular orbital (LUMO) of O₂ to allow easy electron transfer for activation in oxygen reduction reaction (ORR).⁹ This electron transfer is also known as π -backbonding which is fundamentally crucial for bond breaking. However, strategies which employ vacancies in catalyst often require harsh conditions (>500 °C) and also stabilizing atomically dispersed single metal atoms is extremely challenging because of the inherently high surface energy thus often suffer from low loading of SACs.^{10, 11} Therefore, it is imperative to integrate both experimental and simulation studies to strategically design a feasible electronically-modified electrocatalytic system which possesses 1) a narrow HOMO_{catalyst}-LUMO_{N₂} gap for easy N₂ activation and 2) electron-deficient catalytic site for strong N₂ affinity to kinetically drive NRR at ambient conditions.

Herein, we employ zeolitic imidazole framework (ZIF) to modify the HOMO energy level of Pt electrocatalyst for greater π -backbonding with N₂ and concurrently enhance catalyst's N₂ affinity to collectively activate N₂, achieving high FE of >35 % and high NH₃ yield rate of 4706.4 mg h⁻¹m⁻² at ambient condition. We achieve this by coating our model 140 nm Pt/Au electrocatalyst with a layer of ZIF to directly modify Pt HOMO (HOMO_{Pt}), increasing HOMO_{Pt} nearer to LUMO_{N₂} energy level by 0.7 eV and narrowing HOMO_{Pt}-LUMO_{N₂} gap for effective π -backbonding upon N₂ adsorption electron-deficient site. We choose nanocatalyst of ~140 nm due to its easy fabrication and fairer comparison to other noble nanocatalyst. In additional, ZIF serves two additional functions: i) a hydrophobic barrier to suppress HER and boost NRR selectivity by restricting entry of trace water to

electrocatalyst surface and ii) concentrate N_2 molecules at the metal-ZIF interface to facilitate N_2 adsorption and metal- N_2 interaction. Our density functional theory (DFT) investigation reveals the 0.7 eV positive shift in $HOMO_{Pt}$ in Pt/Au upon ZIF encapsulation to enhance metal-to- N_2 π -backbonding for better N_2 activation. We also showcase our platform design versatility across noble metals through the fabrication of Pd-, Ag- and Au/Au@ZIF. Furthermore, these electrocatalytic design is straightforward and can easily incorporated into emerging catalysts to improve NRR performance and expedite progress towards nitrogen-to-ammonia conversion from atmospheric air.

5.2 Results and discussion

Our strategic design comprises of metal nanocatalyst deposited Au electrode (metal/Au) that is encapsulated with a layer of ZIF. ZIF serves three crucial functions, mainly 1) modify the HOMO of metallic nanocatalyst surface ($HOMO_{catalyst}$) to strengthen π -backbonding with N_2 , 2) create electron deficient sites on nanocatalyst surface to enhance N_2 -affinity and 3) N_2 sorber to concentrate N_2 and promote metal/Au- N_2 cohesive interaction for NRR while repelling moisture to suppress competing HER (Figure 5.1). Briefly, Pt nanospheres (PtNS; ~ 140 nm) are synthesized via seed-mediated method and subsequently treated with HCl to remove surfactant prior deposition on Au (co-catalyst) electrode (Figure 5.2). Pt is chosen as our model catalyst owing to its high electrochemical stability and excellent intrinsic catalytic activities. Our Pt/Au@ZIF is fabricated by encapsulating Pt/Au with a polycrystalline ZIF layer (thickness, 333 ± 41 nm) via an overgrowth method to ensure complete encapsulation of ZIF over catalyst surface. X-ray photoelectron spectroscopy (XPS) analysis highlights the successful fabrication of Pt/Au@ZIF platform which comprises of Pt/Au at the range of 71 – 77 eV in Pt 4f XPS spectra and also ZIF in the range of 398 – 403 eV in N 1s XPS spectra (Figure 5.3). The N

1s broad peak can be further deconvoluted to three peaks which is attributed to ZIF imidazole linker -N= (399.7 eV), -NH- (400.5 eV) and quaternary (401.3 eV). Upon ZIF encapsulation of PtNS, the XPS peaks of -N= and -NH- shift negatively by 0.2 eV with an emergence peak at 398.7 eV which index to metal-N coordination bond (Figure 5.3). This indicates a gain in electron density of ZIF and a clear evidence that ZIF is interacting with Pt surface electronic structure which is similarly observed in previous study.⁶ Similar phenomenon using Pt 4f XPS spectra is also observed, whereby XPS peaks of Pt⁰ (71.7 eV and 75.0 eV) and Pt²⁺ (72.4 eV and 75.7 eV) shifts positively by 0.2 eV, respectively (Figure 5.3). Notably, the positive shift in Pt 4f spectra indicates a lost in electron density whereby the electron density migrates from Pt to ZIF via the metal-N (Pt/Au-N) coordination bond. Concurrently, this electron density migration from Pt to ZIF in turn creates electron deficient regions on Pt surface which is necessary to enhance N₂-affinity. Collectively, the positive and negative shifts in Pt 4f and N 1s XPS spectra highlights the importance of ZIF to modify the surface electronic configuration of Pt.

Figure 5.1. Key concept of our strategy to activate N_2 by tuning using ZIF to tune the surface electronic structure of metal catalyst and facilitate strong interactions between metal- N_2 upon N_2 adsorption in the presence of (i) ZIF and (ii) without ZIF.

Figure 5.2. SEM characterization of 140 nm Pt/Au@ZIF

Figure 5.3. XPS investigation at the Pt/Au-ZIF interface in 140 nm Pt/Au@ZIF platform.

(A) Changes in Pt 4f spectra of Pt/Au upon ZIF encapsulation. (B) Changes in N 1s spectra of ZIF upon encapsulating Pt/Au.

To investigate the molecular interactions between N_2 and the ZIF-induced electronic-modified Pt surface at the Pt-ZIF interface, we perform density functional theory (DFT) simulation to obtain molecular insights of its $HOMO_{Pt}$ - $LUMO_{N_2}$ frontier orbitals. We use Pt_3 and 4,5-dichloroimidazole (dcim)-Zn molecular clusters to represent Pt and ZIF surfaces, respectively, in the presence of N_2 to simulate N_2 -Pt interactions at the Pt-ZIF interface. $Cluster_3$ is employed as a basis in this study owing to its stabilized configuration.¹²⁻¹⁵ We notice that our simulated N_2 has a high LUMO energy level of -0.6 eV which is also observed in similar study, hence validating the accuracy of our simulation (Figure 5.4).⁸ Upon ZIF interaction with Pt during encapsulation, $HOMO_{Pt}$ experiences a 0.7 eV positive increase in energy level from -5.9 eV to -5.2 eV which narrows the $HOMO_{Pt}$ - $LUMO_{N_2}$ gap to 4.55 eV (Figure 5.4 A). Conversely, in the absence of ZIF, we notice poor interaction between Pt and N_2 resulting from the poor orbital overlapping between Pt and N_2 (Figure 5.4 (ii)). Notably, the narrowed $HOMO_{Pt}$ - $LUMO_{N_2}$ energy level resulting from the increment in $HOMO_{Pt}$ causes the intrinsic N_2 bond length to elongate from 1.105 Å to 1.119 Å (Figure 5.4B). This N_2 bond length elongation highlights the presence of π -backbonding between our Pt@ZIF catalyst and N_2 at the Pt-ZIF interface. Although our simulated $N\equiv N$ bond length slightly deviate from literature value of 1.0976 Å, the relative change in orbital energies between N_2 interaction with Pt in the presence and absence of ZIF eliminates all possible source of biasness during simulation and strongly highlight ZIF's unique property to enhance Pt- N_2 interaction.¹⁶

Figure 5.4. Density functional theory simulating interactions between Pt-ZIF and/or Pt with N_2 . (A) (i) Frontier molecular orbitals arising from orbital interactions between HOMO of Pt@ZIF and LUMO of N_2 and (ii) Poor interaction between Pt and N_2 . HOMO of Pt shifts to higher energy level in the presence of ZIF which narrows the $HOMO_{Pt}$ - $LUMO_{N_2}$ energy gap, thus allowing enhanced metal- N_2 interaction and stronger N_2 activation. (B) Schematic visualization in the N_2 bond length changes for N_2 activation.

To assess ZIF effectiveness on Pt to elongate N_2 bond length and its NRR performance, we perform cyclic voltammetry (CV) analysis using Pt/Au@ZIF electrode to elucidate the electrochemical process occurring at the solid-ZIF interface. Similar to our previous work, the reaction setup comprises of Pt/Au@ZIF working electrode with Au as co-catalyst, Ag/AgCl reference electrode and Pt wire counter electrode are immersed in dry tetrahydrofuran (THF) solution containing lithium trifluoromethanesulfonate as the

electrolyte (Figure 5.5A). Additionally, 1% v/v ethanol is spiked in THF as the proton source. CV is performed in open ambient conditions and scanned between -0.5 V to -3.0 V in the cathodic direction under consistent N₂ or Ar flow at 3 sccm (Figure 5.5B). During N₂ bubbling, Pt/Au@ZIF exhibits a reduction peak at -2.6 V and two oxidation peaks at -1.6 V and -0.85 V. Conversely, during Ar bubbling, only oxidation peaks at -1.6 V and -0.85 V are observed. Hence, the clear differences between the two electrochemical system highlights that the peak appearance at -2.6 V is related to N₂-related reduction processes. Meanwhile, the two oxidation peaks are likely due to alcohol-related oxidation. Control experiment involving Pt/Au without ZIF in the presence N₂ or Ar bubbling exhibits a cathodic peak at -1.8 V which is attributed to HER and no N₂-related reduction peak is observed at -2.5 V (Figure 5.5C). We then proceed to evaluate Pt/Au@ZIF NRR performance based on two major metrics, namely 1) effective Faradaic efficiency (FE) and effective rate of NH₃ formation whereby these values are obtained by comparing to control experiments (Ar bubbling). This comparison is important and necessary to determine the actual NH₃ production contributing from the electrocatalyst platform and eliminate any source of interference such as dissolved nitrogenous contaminant from the environment that may affect the actual ammonia yield. Typically, the immersed electrocatalyst is bubbled for at least 15 min with N₂ prior the start followed by reduction at -2.9 V for 6 h under continuous supply of 3 sccm of N₂. The electrosynthesized ammonia is then quantified using Berthelot's indophenol blue indicator which is further characterized by UV-Vis spectroscopy that exhibits an absorption peak at 647 nm (Figure 5.6). Pt/Au@ZIF NRR performance demonstrates an effective Faradaic efficiency of (35 ± 3.3) % with an ammonia yield rate of (4706.4 ± 622.9) mg h⁻¹m⁻². Notably, this is 35-fold and 10-fold improvement in FE and yield rate, respectively, in comparison to the absence of ZIF (FE 0.9 ± 1.0 %; NH₃ yield 414.3 ± 283.6 mg h⁻¹m⁻²) (Figure 5.5D, Table 5.1).

Figure 5.5. Evaluating the electrochemical process of 140 nm Pt/Au@ZIF at the Pt-ZIF interface and its NRR performance. (A) Schematic of the electrochemical setup. (B) Representative cyclic voltammograms recorded from Pt/Au@ZIF working electrodes under N₂ or Ar gas bubbling at 3 sccm using mass flow controller. (C) Representative cyclic voltammograms recorded from Pt/Au working electrodes under N₂ or Ar gas bubbling at 3 sccm using mass flow controller. (D) Evaluating NRR performance using 140 nm Pt/Au@ZIF at ambient conditions.

Figure 5.6. UV-Vis and calibration curve of indophenol blue. (A) UV-Vis spectrum of extinction (a.u.) against wavelength (nm) for known NH_4^+ concentrations. (B) Plot of extinction (a.u.) against NH_4^+ concentrations (M).

Table 5.1. Tabulated current density of various electrode platforms determined using chronoamperometry under respectively N_2 or argon flow at -2.9 V applied potential.

Electrode Platforms	Type of Gas	Current Density ($\mu\text{A}/\text{cm}^2$)
Au/Au@ZIF	N_2	$3.2 \pm 1.7 \times 10^{-2}$
	Ar	$5.7 \pm 2.6 \times 10^{-2}$
Ag/Au@ZIF	N_2	$0.2 \pm 1.1 \times 10^{-3}$
	Ar	17.5 ± 5.7
Pd/Au@ZIF	N_2	1.0 ± 0.1
	Ar	3.6 ± 0.4
Pt/Au@ZIF	N_2	7.2 ± 0.4
	Ar	25.4 ± 1.3

Next, we showcase our strategy versatility by extending to various metals such as Pd, Ag and Au which are commonly employed for catalysis owing to its electrochemical stability and good catalytic performance. These Pd, Ag and Au nanospheres (NS) are

synthesized via a modified seed-mediated method and kept its particle sizes in the range of 140 nm for fair comparison to PtNS (Figure 5.7). Similarly, we also perform its CV and evaluate its respective electrochemical processes by scanning between -0.5 V to -3.0 V towards the cathodic direction under consistent N₂ or Ar supply (Figure 5.8). In particular to Ag/Au@ZIF system, it exhibits a reduction peak at ~ -2.4 V which stretches between -2.1 V to -2.6 V with an oxidation peak at -1.7 V in the presence of N₂ while only an oxidation peak is observed at -1.5 V in Ar bubbling (Figure 5.8(i)). These oxidation and reduction peaks correspond to the alcohol-related oxidation and N₂-related reduction, respectively, which is also observed in similar studies.¹⁷ On the other hand, in the case of Au/Au@ZIF, an oxidation peak at -1.7 V is clearly observed in the presence of both N₂ and Ar which attributes to alcohol-related oxidation (Figure 5.8(ii)). Notably, only N₂-reduction onset potential is observed at ~-2.25 V with a weak N₂-related reduction peak. Additionally, this is also observed in the case of Pd/Au@ZIF, whereby only N₂-reduction onset potential is observed at ~-2.25 V with a weak N₂-related reduction peak while oxidation peaks are observed at -1.7 V and -0.9 V which are similar to the case of Pt/Au@ZIF (Figure 5.8(iii)). The slight differences in the N₂ reduction potential across metals indicate a possible presence of different reaction mechanism.¹⁸ We also evaluate its NRR performance through a similar reaction setup whereby the electrocatalyst working electrodes are subjected to 6 hours reduction at -2.9 V in both N₂ and Ar bubbling, followed by quantifying the electrosynthesized NH₃ with indophenol blue. The performance across Pd/Au@ZIF, Ag/Au@ZIF and Au/Au@ZIF exhibits a FE of (21.7 ± 3.8), (6.5 ± 1.7) and (11.5 ± 3) %, respectively, with an ammonia yield rate of (31.5 ± 9.8), (5.5 ± 1.4) and (23.6 ± 6.1) µg mg_{cat}⁻¹h⁻¹, respectively (Figure 5.9). Notably, Pt and PdNS as the primary catalyst exhibits greater NRR performance than Ag and Au. A possible reason can be due to Pt and Pd belongs to the same d-block column group 10 while Ag and Au belongs to group 11. Hence,

the difference in its electron configuration may affect the electron donating and electron withdrawing process between metal and N₂ which in turn affects the N₂ activation.¹⁵

Although our findings hold promises to perform N₂-related reduction, a series of in-depth analysis and controls are imperative to evaluate the working mechanism of our electrocatalyst and reaffirm that the electrocatalyst is indeed NRR-active. Therefore, as part of our future work, we will first employ DFT simulations to investigate the interactions between metals and N₂ at the metal-ZIF interface. We will adopt a larger metal cluster as a representative model to study the molecular interaction involving our metallic NPs. In addition, we will adopt Mulliken charge distribution analysis to quantify the electron flow between metals and N₂ in the presence of ZIF which is necessary for N₂ bond elongation. Next, we will analyze the changes in the HOMO_{metal}-LUMO_{N₂} energy level and the changes affecting on the N₂ bond length as these are fundamentally important to activate N₂. Additionally, we will perform XPS analysis to investigate the electronic configuration changes across these metals upon ZIF encapsulation as demonstrated that ZIF can induce surface electronic modification of metallic NS.

Besides surface characterization, we will perform in-depth CV analysis across metallic NS during N₂ and Ar bubbling and rationalize the changes. We will also identify the preferred NRR reducing potential across these metals and correlate to its activity. Notably, we will also assess the likelihood of possible effect arising from the rate of lithium plating on the production of NH₃ by varying the applied current density. Lithium plating occurs at -3.04 V vs Ag/AgCl, hence the presence of lithium metal can react with proton carrier to form hydrogen or with N₂ to result in lithium nitride which is protonated quickly to form NH₃.¹⁹ More importantly, to further evaluate the reliability of our reaction and eliminate false positive results, we will conduct similar control experiments as mentioned in recent NRR studies.²⁰⁻²³ Firstly, we will quantitatively analyze ¹⁵NH₃ formation from

$^{15}\text{N}_2$ reduction over several experimental durations and compare the performance to our $^{14}\text{N}_2$ experiments under identical conditions. These experiments will comprise of metal/Au, metal/Au@ZIF and ZIF-only. Using $^{15}\text{N}_2$ isotope ensures that the $^{15}\text{NH}_3$ produced is indeed from N_2 (or N_2 source) and not other external contaminants. Next, we will investigate the effects of trace NO_x contaminants present in our reaction. Notably, it is vital to confirm that the NH_3 detected is not originated from NO_x contaminants in gas supply and/or nitrate/nitrite in electrolyte. This can be done by using a NO_x sensor to quantify the concentration of NO_x and removing possible sources of NO_x contaminants. Finally, we will compare the NH_3 yield generated by our platforms to established standards whereby rate $\geq 10 \text{ nmol s}^{-1} \text{ cm}^{-2}$ is classified as practically promising and reliable.

Figure 5.7. SEM characterization of various noble metal nanospheres. (A) Pd, (B) Ag and (C) Au.

Figure 5.8. Representative cyclic voltammograms recorded by Ag/Au@ZIF, Au/Au@ZIF and Pd/Au@ZIF under constant 3 sccm N_2 or Ar gas bubbling

Figure 5.9. Effective Faradaic efficiency (FE) and rate of ammonia formation by various metal/Au@ZIF platforms.

5.3 Conclusion

Our preliminary work showcase the benefits of incorporating ZIF into metallic NS for potential NRR and reveals molecular insights at the solid-ZIF interface to potentially result in N₂ activation for enhance NRR performance. Our strategy involves the elevation of HOMO_{metal} energy level upon ZIF encapsulation to create greater metal-N₂ π -backbonding. We demonstrate such potential approach through DFT investigation which reveals the HOMO_{Pt} increment by 0.7 eV upon ZIF encapsulation and further brings the energy level closer to LUMO_{N₂} for greater interaction. Notably, this causes N₂ bond length to elongate from 1.10 Å to 1.119Å. Additionally, our Pt/Au@ZIF electrocatalyst is able to achieve a performance of FE (35 ± 3.3) % and NH₃ yield rate of (39.5 ± 4.3) $\mu\text{g mg}_{\text{cat}}^{-1}\text{h}^{-1}$. We also showcase our platform design versatility through the facile integration across different metallic NS. Although our DFT investigation supports our experimental studies in the case of Pt/Au@ZIF, more investigation is required to reaffirm the metal-N₂ interaction mechanism at the metal-ZIF interface. Furthermore, controls such as ¹⁵N₂ and NO_x contaminant will have to be included to assess the reliability of our electrocatalyst. Our findings can potentially boost the development of solid@MOF electrocatalyst with functional interfaces for enhance NRR performance especially when adopting atmospheric air as the main source of N₂ and proton.

5.4 Materials and methods

Materials. Hydrochloric acid (37%) and sulfuric acid ($\geq 95\%$) were from VWR Chemicals. Chloroplatinic acid hexahydrate (ACS reagent), citric acid, sodium citrate tribasic dihydrate ($\geq 99\%$, ACS reagent), L-ascorbic acid (99%), zinc acetate dihydrate ($\geq 98\%$, ACS reagent), silver nitrate ($\geq 99\%$), gold (III) chloride trihydrate ($\geq 99.9\%$), poly(vinylpyrrolidone) (average MW = 55,000), hexadecyltrimethylammonium bromide ($\geq 98\%$),

hexadecyltrimethylammonium chloride, (25 wt. % in H₂O), lithium trifluoromethanesulfonate (LiCF₃SO₃, 99.995%), sodium dichloroisocyanurate dihydrate ($\geq 98.0\%$), copper (II) chloride, potassium iodide ($\geq 99\%$), 4,5-dichloroimidazole ($\geq 98\%$), sodium nitroprusside dihydrate ($\geq 99\%$) and phenol ($\geq 99\%$) were from Sigma-Aldrich. Sodium borohydride ($>97\%$) was purchased from Alfa Aesar. Tetrahydrofuran ($\geq 99.0\%$, ACS reagent) and methanol ($\geq 99.9\%$) were from Fulltime. Sodium hydroxide ($>99\%$) and ethanol were from EMSURE. Argon (99.9995%) and nitrogen (99.999%) were obtained from Singapore Oxygen Air Liquide Pte Ltd. *N,N'*-dimethylformamide (ACS reagent) was purchased from Tedia. Only tetrahydrofuran undergoes further distillation in the presence of benzophenone, sodium and inert N₂. Ultrapure water from Sartorius Arium 611 UV ultrapure water system was used for all experiments.

Synthesis of Platinum Nanoparticle Seeds. Platinum nanospheres synthesis were conducted and modified based on a literature.²⁴ Briefly, Pt nanoparticle seeds were synthesized by adding 3.6 mL of 0.2% chloroplatinic acid hexahydrate to 92.8 mL of boiling water. After 1 min, a 1.1 mL solution containing 0.05% citric acid and 1% sodium citrate was injected into the mixture, followed by 0.55 mL of freshly prepared NaBH₄ (0.08%) solution with 0.05% citric acid and 1% sodium citrate. The reaction mixture was heated for 10 mins at 100°C and then cooled to room temperature.

Synthesis of 140 nm Platinum Nanospheres. 60 nm platinum nanosphere is needed to be synthesized as seed to synthesize 140 nm platinum nanospheres. Firstly, 2 mL of 29 nm platinum nanospheres was added to 26 mL ultrapure water and 0.4 M chloroplatinic acid solution (0.045 mL) at room temperature, followed by 0.5 mL of a solution containing 1.25% L-ascorbic acid and 1% sodium citrate. The mixture was heated slowly to 100 °C for 60

mins and then cooled to room temperature. The resultant solution was washed and redispersed in ultrapure water. To obtain 140 nm nanospheres, the synthesis was repeated by adding 1 mL of the 29 nm nanospheres to 26 mL of ultrapure water respectively.

Synthesis of Palladium Nanoparticle. 20 μL of Au cluster seeds were added into 10 mL of 1 mM H_2PdCl_4 , followed by the addition of 1.2 mL of 100 mM ascorbic acid. The resulting mixture was stirred for 3 mins at 500 rpm in room temperature. The synthesized mixture is centrifuge at 8000 rpm and redispersed in ultra purewater.

Synthesis of Silver Nanoparticle. The preparation of silver nanospheres was carried out following the method modified from previous study. Silver nanocubes were first formed using similar protocol.²⁵ 250 μL of the resulting mixture is redispersed in 2 mL of 3 M KI and stirred at 500 rpm for 2 h.

Synthesis of 140 nm Gold Nanoparticle Seed. The preparation of gold nanospheres was carried out following the method modified from literature.²⁶ Synthesis of 140 nm gold nanosphere comprises of repetitive growth steps. Firstly, CTAB-capped Au clusters were needed to be synthesized. This was prepared by adding 0.6 mL of 10mM NaBH_4 into 10 mL of 0.25 mM HAuCl_4 . The resultant solution was then stirred at 300 rpm for 2 min and left undisturbed for 3 h.

Au cluster seeds were then further grown into 80 nm Au nanoparticles as another set of seeds by mixing 2 mL of 100 mM CTAC, 130 μL of 10 mM ascorbic acid and 10 μL of seed cluster. The reaction was stirred at 300 rpm and 2 mL of 0.5 mM HAuCl_4 was added dropwise into the mixture. 140 nm Au nanoparticles were synthesize using similar approach

using 80 nm as the seed by adding 250 μ L of seeds into the reaction mixture while keeping the rest of the addition constant.

Preparation of metal/Au Electrode. 1.25 μ L of various Pt, Pd, Au or Ag nanoparticle solution was dispensed onto polished Au electrodes (metal/Au). Metal/Au electrode was subjected to acid treatment by submerging in HCl solution for 3 h containing 20% ethanol, 0.1M HCl and ultrapure water. The as-prepared metal/Au electrode was then washed with a MeOH and gently dry using nitrogen gas before storing under inert nitrogen conditions.

Fabrication of metal/Au@ZIF electrode. A layer by layer overgrowth method of ZIF on the metal/Au electrode was performed. The metal/Au working electrode was inserted into a ZIF-71 solution comprising of 0.375 mL of MeOH, 0.125 mL of DMF and 0.25 mL of 4,5-dichloroimidazole (0.4 M) and zinc acetate dihydrate (0.2 M), respectively, for 40 mins. All as-synthesized metal/Au@ZIF electrodes were washed with a MeOH and gently dry using nitrogen gas. ZIF formation reaction was repeated for a total of 6 cycles and the working electrode was stored under inert nitrogen conditions.

Thermal Activation of ZIF-encapsulated electrodes. ZIF-encapsulated working electrodes were activated under vacuum at 120 $^{\circ}$ C for 2 h to remove all chemicals trapped in the pores of ZIF after its synthesis.

Electrochemical NRR. Electrolyte solutions (LiCF₃SO₃, 0.2 M and 1% EtOH in dry THF) will undergo ~15 min of either N₂ or Ar gas bubbling at ~3 sccm prior any immersion of working electrode.

The electrochemical setup comprises of a Pt wire, Ag/AgCl reference electrode (1M KCl solution) and metal/Au or metal/Au@ZIF working electrode. Cyclic voltammetry measurements were recorded between -3.0 V and -0.5 V (versus Ag/AgCl) at 50 mV/s. Different working electrodes were employed to identify the electrochemical peaks changes in both N₂ and/or Ar gases. To determine the NRR performance (Faradiac efficiency (FE) and NH₃ yield rate), we employ chronoamperometry over a duration of 6 h at an applied potential of -2.9 V under 3 sccm gas flow in ambient conditions.

Preparation of Reagents for the Indophenol Blue Method. The preparation of indophenol blue method was followed according to previous studies.²⁷ In general, indophenol blue was prepared by mixing reagent A and B. Reagent A comprises of 0.1 M phenol and 0.2 mM sodium nitroprusside dihydrate in ultrapure water. Reagent B comprises of 2.8 mM sodium dichloroisocyanurate dihydrate and 0.13 M sodium hydroxide in ultrapure water.

Ammonia Detection via the Indophenol Blue Method. A concentration calibration curve was first established to quantify the amount of ammonia generated in the reaction. Briefly, 10 mM ammonium sulfate was dissolved in 1 mM sulfuric acid aqueous solution as stock solution, followed by the preparation of 10⁻⁶ M to 10⁻⁴ M standard solutions via serial dilution. A similar amount of dry THF electrolyte with 1% ethanol mixture was injected across all standard solutions. In a typical sample preparation, 0.2 mL of ammonium sulfate standard solution was mixed with 2 mL of 1:1 reagent A and B in a vial for 1 h at 500 rpm. The resultant indophenol blue solution was then analyzed with UV-Vis spectroscopy.

To determine amount of ammonia synthesized from a typical EC-NRR, 1 mL of reacted solution was added to 1 mL of aqueous 1 mM sulfuric acid solution. Following

which, 2 mL of 1:1 reagent A and B was injected into the mixture and left overnight at 500 rpm. The resulting indophenol blue solution was then analyzed with UV-Vis spectroscopy.

X-ray photoelectron spectroscopy (XPS) Characterization. Phoibos 100 spectrometer was employed for all analysis to retrieve XPS spectra and calibrated to C 1s binding energy peak at 284.5 eV. ZIF-related samples are coated with 1 cycle of ZIF and thermally activated prior XPS analysis.

Density functional theory (DFT) simulation. We employ Gaussian 09 computational tool to investigate the interactions between Pt surface with ZIF cluster and Pt-ZIF interface with *N₂ molecules using unrestricted B3LYP. We use 6-31g (d p) as the basis set while Pt uses LANL2DZ basis set. The Pt surface was constructed in a triangular fashion consisting of three Pt atoms (Pt₃ cluster). Upon geometric optimization of the ZIF and Pt clusters, both clusters are placed closely and re-optimization of the entire system. *N₂ molecules were subsequently placed near the Pt-ZIF system to study their interactions.

Characterization. JEOL-JSM-7600F scanning electron microscope (SEM) were operated to analyze the morphology and topography of the working electrode platforms. Cary 60 UV-Vis spectrometer was employed for UV-Vis measurements. Bruker General Area Detector Diffraction System (GADDS) X-ray diffractometer was operated to obtain all XRD spectra. Metrohm Autolab potentiostat was used to perform all electrochemical experiments.

References

1. Liu, C.; Sakimoto, K. K.; Colln, B. C.; Silver, P. A.; Nocera, D. G. *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 6450.
2. Bao, D.; Zhang, Q.; Meng, F.-L.; Zhong, H.-X.; Shi, M.-M.; Zhang, Y.; Yan, J.-M.; Jiang, Q.; Zhang, X.-B. *Adv. Mater.* **2017**, *29*, 1604799.
3. Wang, M.; Liu, S.; Qian, T.; Liu, J.; Zhou, J.; Ji, H.; Xiong, J.; Zhong, J.; Yan, C. *Nat. Commun.* **2019**, *10*, 341.
4. A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff, J. K. Nørskov, *ACS Catal.* **2017**, *7*, 706.
5. Zhao, S.; Lu, X.; Wang, L.; Gale, J.; Amal, R. *Adv. Mater.* **2019**, *31*, 1805367.
6. Sim, H. Y. F.; Chen, J. R. T.; Koh, C. S. L.; Lee, H. K.; Han, X.; Phan-Quang, G. C.; Pang, J. Y.; Lay, C. L.; Pedireddy, S.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y. *Angew. Chem. Int. Ed.* **2020**, *59*, 16997.
7. Shen, H.; Choi, C.; Masa, J.; Li, X.; Qiu, J.; Jung, Y.; Sun, Z. *Chem*, **2021**, *7*, 1.
8. Geri, J. B.; Shanahan, J. P.; Scymczak, N. K. *J. Am. Chem. Soc.* **2017**, *139*, 5952.
9. Li, Q.; Zhang, T.; Yu, X.; Wu, X.; Zhang, X.; Lu, Z.; Yang X.; Huang, Y.; Li, L. *Front. Chem.* **2019**, *7*, 674.
10. Liu, Y.; Deng, P.; Wu, R.; Zhang, Z.; Sun, C.; Li, H. *J. Mater. Chem. A*, 2021, **9**, 6694.
11. Cheng, N.; Zhang, L.; Doyle-Davis, K.; Sun, X. *Electrochem. Energ. Rev.* 2019, *2*, 539.
12. Jennings, P. C.; Johnston, R. L. *Comput. Theor. Chem.* **2013**, *1021*, 91.
13. Xing, X.; Hermann, A.; Kuang, X.; Ju, M.; Lu, C.; Jin, Y.; Xia, X.; Maroulis, G. *Sci. Rep.* **2016**, *6*, 19656.

14. Rincon, L.; Hasmy, A.; Marquez, M.; Gonzalez, C. *Chem. Phys. Lett.* **2011**, *503*, 171.
15. Liu, L.; Corma, A.; *Chem. Rev.* **2018**, *118*, 4981.
16. La Placa, S. J.; Hamilton, W.C. *Acta Cryst.* **1972**, *B28*, 984.
17. Lee, H. K.; Koh, C. S. L.; Lee, Y. H.; Liu, C.; Phang, I. Y.; Han, X.; Tsung, C. K.; Ling, X. Y. *Sci. Adv.* **2018**, *4*, eaar3208.
18. Guo, X.; Du, H.; Qu, F.; Li, J. *J. Mater. Chem. A*, **2019**, *7*, 3531.
19. Lazouski, N.; Schiffer, Z. J.; Williams, K.; Manthiram, K. *Joule*, **2019**, *3*, 1127.
20. Choi, J.; Suryanto, B. H. R.; Wang, D.; Du, H. -L.; Hodgetts, R. Y.; Vallana, F. M. F.; MacFarlane, D. R.; Simonov, A. N. *Nat. Commun.* **2020**, *11*, 5546.
21. Kibsgaard, J.; Nørskov, J. K.; Chorkendorff, I. *ACS Energy Lett.* **2019**, *4*, 12, 2986.
22. Andersen, S. Z.; Colic, V.; Yang, S.; Schwalbe, J. A.; Nielander, A. C.; McEnaney, J. M.; Enemark-Rasmussen, K.; Baker, J. G.; Singh, A. R.; Rohr, B. A.; Statt, M. J.; Blair, S. J.; Mezzavilla, S.; Kibsgaard, J.; Vesborg, P. C. K.; Cargnello, M.; Bent, S. F.; Jaramillo, T. F.; Stephens, I. E. L.; Nørskov, J. K.; Chorkendorff, I. *Nature* **2019**, *570*, 504.
23. Suryanto, B. H. R.; Du, H. -L.; Wang, D.; Chen, J.; Simonov, A. N.; MacFarlane, D. R. *Nat. Catal.* **2019**, *2*, 290.
24. Bigall, N. C.; Hartling, T.; Klose, M.; Simon, P.; Eng, L. M.; Eychmüller, A. *Nano Lett.* **2008**, *8*, 4588.
25. Sim, H. Y. F.; Lee, H. K.; Han, X.; Koh, C. S. L.; Phan-Quang, G. C.; Lay, C. L.; Kao, Y.-C.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y. *Angew. Chem. Int. Ed.* **2018**, *57*, 17058.
26. Zheng, Y., Zhong, X., Li, Z. and Xia, Y. *Part. Part. Syst. Charact.* **2014**, *31*, 266.
27. Tsuneto, A.; Kudo, A.; Sakata, T. *J. Electroanal. Chem.* **1994**, *367*, 183.

Chapter 6: Conclusion and Future Work

6.1 Conclusion

Solid-MOF nanohybrids are an emerging platform that has demonstrated great potential in applications such as SERS detection, reaction monitoring and catalysis. However, most of its application revolve either gas or liquid-based molecules which deprive its practicality for real-life applications such as a sensor and catalyst. Moreover, there is a lack of molecular understanding at the solid-MOF interface where interfacial cavities are present. Notably, these interfacial cavities are a unique confinement where reactions and/or point of molecular interaction take place under the influence of both solid and MOF materials. In this thesis, we showcase solid-MOF practicality for chemical synthesis involving gas-liquid biphasic molecules, the production of ammonia as green fuel as well as an ultrasensitive VOC and gas sensor. More importantly, we also reveal solid-MOF interfacial cavities molecular insights and breakthroughs which can potentially applied to existing applications toward new realms.

In chapter 2, we perform an inert ambient gas-liquid reaction. This is achieved by incorporating a molecular-sorbing ZIF layer over a single layer closely packed assembled Ag nanocubes. ZIF captures and concentrates both immiscible liquid and gas molecules into the Ag-ZIF interfacial cavities to promote high molecular interactions. The SERS-active Ag nanocubes enable the real-time molecular level monitoring of chemical reaction. We employ gaseous CO₂ and liquid aniline as the model reactants to form phenylcarbamic acid which typically requires high operating pressure/temperature, we demonstrate the capability of our Ag@ZIF to track and facilitate the reaction at 1 atm and 298 K. Importantly, the presence of interfacial cavities play a crucial role to enhance the efficiency of reaction by > 28-fold in comparison to ZIF and/or Ag control platforms. These findings offer beneficial

insights to achieve ambient gas-liquid reactions of great demand in the field of industrial chemical production and air-to-fuel conversion.

In chapter 3, we further extend the application of Ag@ZIF to real-time stand-off atmospheric monitoring where we combine the advantages of both remote monitoring and Raman spectroscopy to extract molecular vibrational fingerprints of chemicals at remote sites. This is accomplished by developing a 3-dimensional (3D) multi-layered Ag@ZIF core-shell particle platform that possesses micron-scale large hotspot depth and excellent analyte-sorbing ability. Notably, our system enables the real-time rapid SERS detection of airborne species, including polycyclic aromatic hydrocarbons mixtures, with a sensitivity down to ppb level at 2-10 m away in 10 s even in the presence of strong daylight background and ambient air. In addition, it is also able to perform remote air-monitoring via its ability to track chemical changes in the atmosphere content when expose to CO₂ gas. Our two-pronged approach thus offers a breakthrough solution to expedite future application of long-range molecular detection in various sectors including atmospheric sciences, disaster prevention and homeland defense.

In chapter 4 and 5, we further exploit ZIF excellent gas sorbing ability and develop various metallic nanosphere@ZIF to drive ambient electrochemical NRR at the nanosphere-ZIF interface. In chapter 4, we design an electronically modified Pt nanosphere electrocatalyst encapsulated by ZIF to achieve high FE of >44 % and an effective NH₃ generation rate of >161 $\mu\text{g mg}_{\text{cat}}^{-1} \text{h}^{-1}$. Our strategy uses ZIF to lower the d-band electronic structure of electrocatalyst to weaken H adsorption and simultaneously create electron-deficient catalytic regions with strong affinity toward N₂. Furthermore, ZIF also serves additional two functions which involves the concentrating of N₂ molecules to enhance catalys-N₂ interaction and as a hydrophobic barrier to restrict access of trace water to electrocatalytic sites. Our electrocatalytic design can be extended to a library of metals and

offers a new perspective from current electrochemical systems to produce ammonia as a source of green fuel from the atmosphere.

In chapter 5, we employ DFT simulations to design a nanocatalyst-ZIF interface for NRR by using ZIF to modify $\text{HOMO}_{\text{metal}}$ energy level closer to LUMO_{N_2} . In our model Pt nanocatalyst, we highlight that the small $\text{HOMO}_{\text{Pt}}\text{-LUMO}_{\text{N}_2}$ energy gap is key to activate N_2 triple bond. Our simulation also highlights that the elevation of HOMO_{Pt} enables π -backbonding between Pt- N_2 which leads to the elongation of N_2 bond length from 1.105 Å to 1.119 Å during the interaction at the Pt-ZIF interface. Collectively, this enables us to achieve a great performance of $\text{FE} > 35\%$ with an ammonia yield rate of $4706.4 \text{ mg h}^{-1}\text{m}^{-2}$ at ambient conditions. We also demonstrate the platform versatility by extending to other noble metallic catalyst. Moving forward, more in-depth simulation and experimental work will be conducted to further understand the changes in performances across these noble metals.

6.2 Future work

This thesis offered several insights of solid@MOF and its applicability in both SERS and electrocatalysis applications. Nonetheless, progressive research should be conducted to further explore and expand towards real-life applications. We identify a few areas of research interest involving solid-MOF and its future work.

Firstly, the ability to integrate MOFs onto nanoparticle surface remains a challenge. This is necessary to diversify the types of analytes used and applications. Currently, most MOF synthesis proceeds at harsh conditions hence makes MOF growth process on nanoparticle challenging because nanoparticles may experience aggregation or degradation. In this aspect, we notice the fabrication of AuNR@NU-901, which uses Zr-based MOFs at room temperature.¹ Notably, such Zr-based exhibits exceptionally good thermal and

chemical stability.^{2,3} Hence as part of our future work, we will employ Zr-based solid-MOF configurations and expands its application in the field of high temperature catalysis and toxic chemical sensing. We foresee an emerging development of various solid-MOF nanohybrids at ambient conditions. In addition, the competing growth rate between homogenous MOF nucleation and heterogenous overgrowth of MOF onto nanoparticle surface often leads to low solid-MOF yield. Although studies have demonstrated the incorporation of surfactants to guide the MOF growth, it can only be applied to a limited cluster of MOFs. In general, the MOF growth mechanism on nanoparticle surface is extremely complex. Moving forward, we will employ surface characterization techniques such as SERS and XPS to elucidate the MOF growth mechanism on plasmonic surface as a model and identify the determining factor to favor heterogenous growth of MOF on nanoparticle surface over homogenous of bulk MOF nanocrystals.

Second, in addition to our gas-liquid reaction involving Ag@ZIF. Current solid-MOF platform can be further employed for practical applications such as tandem multiphasic reactions and various toxic gas scrubbing. MOF comprise of three components mainly metal nodes, organic linkers and pores chambers.⁴ We propose that by post modifying the MOF, these metals nodes can exhibit unsaturated metal centers for catalysis or adsorption site while the organic linkers can create affinity to attract molecules towards these catalytic or adsorption sites.⁵ Collectively, its performance can be further enhanced with plasmonic and/or catalytic nanoparticles encapsulated within the MOF. Till date, various types of tandem catalyst are developed in gas-related reaction because of its ability to provide high turnover and product yield. However, limited studies are performed involving the use of plasmonic surface to track the molecular changes and derive the reaction pathway during the tandem reaction. Thus, as a continuation to our previous study

on gas-liquid reaction, we will strategically design a MOF-encapsulated nanoparticles for multiphasic reactions as well as gas scrubbing.

Another future direction in the application of plasmonic solid-MOF nanohybrids is the early detection of lung-related respiratory diseases via human breath samples. Human breath profile consists of a wide profile of volatile organic compounds which is also known as breath volatile organic compounds (BVOCs). Notably, BVOC profile changes during the pathological process of disease hence providing an indication of a person's health.⁶⁻⁸ More importantly, such analysis using breath sample is non-invasive, convenient, and non-intrusive by patients in comparison to serology test. Currently, BVOCs analysis are analyzed using mass spectrometry as part of the gold standard. However, such analysis is typically time consuming and unable to perform mass screening. SERS is an extremely powerful technique with high detection sensitivity.⁹ By incorporating chemometrics tools such as principal component analysis (PCA) and partial least squares discriminant analysis (PLA-DA), useful information can be extracted from the massive data to further analyze and classify test subject.¹⁰ The combination of both techniques will enable subject diagnosis. Hence, by employing plasmonic solid-MOF platform, it is possible to overcome these limitations whereby MOF will capture the BVOCs of weak affinity that can easily desorb from surfaces close to plasmonic region for detection.¹¹ Till date, current plasmonic solid-MOF platform for lung cancer diagnosis are only a proof of concept which is far from actual practical use.¹² Therefore, by integrating SERS with machine learning models, plasmonic solid-MOF platforms will be a promising platform for medical diagnosis and also as a medical kit. As part of our future work, we will employ solid-MOF to first detect smoker from non-smoker via breath analysis and finally correlate the presence of metabolites to the breath profile using chemometric analysis.^{10, 13} Such study is extremely important as it

builds the fundamental understandings towards medical diagnosis using both SERS and machine learning.

Lastly, another area of research is electrochemical nitrogen reduction. In our previous study, we reveal that ZIF can potentially modify the surface electronic configuration of nanocatalyst and simultaneously create binding sites to strengthen the adsorption of N_2 over H atom.¹⁴ When compared to conventional heteroatom dopings in catalyst, such strategy is preferred as it is less energy- and time- consuming. Besides the modification in the d-band of Pt nanocatalyst upon ZIF encapsulation, we also realize that the HOMO energy level of Pt nanocatalyst shifts closer to LUMO of N_2 . This narrows the $HOMO_{Pt}$ - $LUMO_{N_2}$ energy gap indicates a better π -backbonding between nanocatalyst and N_2 , thus leading to the elongation of N_2 bond length for better N_2 activation. This HOMO energy level increment could be underlying reason of our high NRR performance. However, current study only demonstrates on Pt nanocatalyst and will have to explore the possibility of employing other noble metallic catalysts. As a continuation to our current study, we have selected some commonly employed catalysts involving Pd, Ag and Au owing to its good electrochemical stability. We will first analyze its d-band and core-level XPS spectra to first identify the presence of electron-deficient sites for N_2 binding. Next, we will perform density functional theory simulation across these nanocatalyst of similar cluster size by observe the interaction between metal and ZIF via its frontier orbitals and movement in electron density via Mulliken charge distribution. Subsequently, we will also perform control electrochemical experiments to highlight the effect of ZIF on the NRR performance. More importantly, we will also conduct N_2^{15} isotope experiment to reaffirm the formation of our electrosynthesized ammonia.

References

1. Osterrieth, J. W. M.; Wright, D.; Noh, H.; Kung, C.; Vulpe, D.; Li, A.; Park, J. E.; Van Duyne, R. P.; Moghadam, P. Z.; Baumberg, J. J.; Farha, O. K.; Fairen-Jimenez, D. *J. Am. Chem. Soc.* **2019**, *141*, 3893.
2. Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850.
3. Choi, K.M.; Kim, D.; Rungtaweevoranit, B.; Trickett, C.A.; Barmanbek, J.T.; Alshammari, A.S.; Yang, P.; Yaghi, O.M. *J. Am. Chem. Soc.* **2017**, *139*, 356.
4. Qin, J. -S.; Yuan, S.; Lollar, C.; Oang, J.; Alsalme, A.; Zhou, H. -C. *Chem. Commun.* **2018**, *54*, 4231.
5. Thomas, R.; Bensalah, A.; Li, B.; Jeffery, B.*; **Tsung, C.-K.** *J. Am. Chem. Soc.* **2021**, *143*, 1630.
6. Peled, N.; Barash, O.; Tisch, U.; Ionescu, R.; Broza, Y. Y.; Ilouze, M.; Mattei, J.; Bunn, P. A.; Hirsch, F. R.; Haick, H. *Nanomedicine* **2013**, *9*, 758.
7. Phillips, M.; Altorki, N.; Austin, J. H. M.; Cameron, R. B.; Cataneo, R. N.; Kloss, R.; Maxfield, R. A.; Munawar, M. I.; Pass, H. I.; Rashid, A. *Clin. Chim. Acta* **2008**, *393*, 76.
8. Geng, S.; Tao, Q.; Hu, L.; Xu, G. B.; Pan, Y. Y.; Xiong, F. X.; Gu, K. S.; Sun, G. P.; Chen, Z. D. *Lung Cancer* **2009**, *67*, 227. Zhao, S.; Lu, X.; Wang, L.; Gale, J.; Amal, R. *Adv. Mater.* **2019**, *31*, 1805367.
9. Shikuan Yang, S.; Dai, X.; Stogin, B. B.; Wong, T. -S. *PNAS* **2016**, *113*, 268.
10. Worley, B.; Powers, R. *Curr. Metabolomics* **2013**, *1*, 92
11. Rascon, C.; Parry, A. O. *Nature* **2000**, *407*, 986.
12. Qiao, X.; Su, B.; Liu, C.; Song, Q.; Luo, D.; Mo, G.; Wang, T. *Adv. Mater.* **2018**, *30*, 1702275.

13. Capone, S.; Tufariello, M.; Forleo, A.; Longo, V.; Giampetruzzi, L.; Radogna, A. V.; Casino, F.; Siciliano, P. *Biomed. Chromatogr.* **2018**, *32*: e4132.
14. Sim, H. Y. F.; Chen, J. R. T.; Koh, C. S. L.; Lee, H. K.; Han, X.; Phan-Quang, G. C.; Pang, J. Y.; Lay, C. L.; Pedireddy, S.; Phang, I. Y.; Yeow, E. K. L.; Ling, X. Y. *Angew. Chem. Int. Ed.* **2020**, *59*, 16997.