Engineering of two-dimensional materials for energy storage and conversion

Koh, See Wee

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SINGAPORE

**ENGINEERING OF TWO-DIMENSIONAL MATERIALS FOR
ENERGY STORAGE AND CONVERSION**

KOH SEE WEE

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

2021

**ENGINEERING OF TWO-DIMENSIONAL MATERIALS FOR
ENERGY STORAGE AND CONVERSION**

KOH SEE WEE

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

A thesis submitted to the Nanyang Technological University

in partial fulfilment of the requirement for the degree of

Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Koh See Wee

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 2 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 3 is published as S. W. Koh, J. Hu, J. Hwang, P. Yu, Z. Sun, Q. Liu, W. Hong, J. Ge, J. Fei, B. Han, Z. Liu and H. Li, Two-dimensional palladium diselenide for the oxygen reduction reaction, *Materials Chemistry Frontiers*, 2021, **5**, 4970-4980. DOI: 10.1039/D0QM01113D

The contributions of the co-authors are as follows:

- Prof Li Hong and Dr Hu Jie provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts with Dr Hu Jie, Ms Hwang Jeemin and Dr Yu Peng.
- Dr Yu Peng provided the material for the study, and A/Prof Liu Zheng provided advice to the process.
- I co-designed the study with Dr Hu Jie and made modifications to the material, Dr Sun Zixu provided guidance to the modifications and interpretation of data.
- Dr Hu Jie performed the electrochemical measurement while I assisted the measurement.
- Dr Hong Wei and Mr Fei Jipeng assisted in the rebuttal process and additional electrochemical measurements.
- I conducted the X-ray characterization (XRD and XPS) in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr Liu Qiunan conducted the TEM characterization.
- Ms Ge Junyu assisted in the material characterization (SEM and TEM) during rebuttal process
- Ms Jeemin Hwang conducted the DFT measurements and Prof Han Byungchan advised the process
- Prof Li Hong, Prof Han Byungchan and Prof Liu Zheng provided guidance and support for the whole work

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Abstract

Negative impacts of reliance on fossil fuel on both environment and economy are becoming more apparent and urgent. This calls for a severe paradigm shift and serious actions toward sustainable energy supply chain. Developing clean and green energy especially from non-carbon generating sources is a crucial step in the direction. To this end, renewable energies such as solar and wind energy are perfect solutions. Energy conversion devices such as solar cell and wind turbine can convert these natural energy forms to electricity. Nevertheless, renewable energies are intermittent, which necessitates energy storage devices such as batteries that store the renewable electricity in terms of chemical energy. However, this chemical energy storage is not stable and self-discharge of batteries is inevitable. A more stable energy storage is to store renewable electricity in the form of chemical fuels. For instance, solar-to-hydrogen conversion effectively stores solar energy in stable hydrogen chemical bonds, which are stable for centuries.

A key component of these energy conversion and storage device is catalyst, particularly hydrogen and oxygen reaction catalysts. For instance, hydrogen and oxygen evolution catalysts play critical roles in water electrolysis for green hydrogen generation. Oxygen reduction reaction (ORR) catalyst is widely employed in metal-oxygen batteries, a high-capacity energy storage device. An ideal catalyst should have high activity and stability, low cost, and great abundance. The high activity is often achieved by high intrinsic activity of active sites, and high density of these active sites (per unit geometric area), which needs high surface area. High surface area also improves utilization rate of the catalyst materials, which is very crucial for reducing the cost of precious metal catalysts. The high activity also strongly depends on the electrical conductivity of the catalyst.

To this end, two-dimensional materials (2DMs) has gained traction for catalysing energy conversion and storage due to their high specific surface area, excellent mechanical properties, great electrical and thermal conductivity. The most alluring feature of 2DMs is their ability to be modified to exhibit different functions. In this thesis, 2DMs are modified to improve their applicability in energy applications, especially for oxygen reduction reaction and solar energy conversion/storage. I will present a showcase of how lithiation activation technique for PdSe_2 can balance the stability and performance of the material for ORR catalysis. Moreover, an unprecedented palladium phosphoronitride-based ORR catalyst is produced by a simple annealing of $\text{Pd}_3\text{P}_2\text{S}_8$. Lastly, I will present the functionalisation of MXene that can tune the work function in a wide range, which could find wide application in optoelectronic devices, e.g., solar cell. Additionally, the functionalisation of a new class of 2DM, MXene, had achieved highly efficient solar light to heat conversion for water desalination.

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Figure 19 Schematic nitrogen substitutional process. The grey, pink, yellow and blue balls represent Pd, P, S and N atoms. Dotted circles represent vacancy sites.

Figure 20 Total energy change with different lattice constants for (a) Pd₃P₂S₈ and (b,c) N doping on Pd₃P₂S₈. When nitrogen is doped in Pd₃P₂S₈, the equilibrium lattices get smaller.

Figure 21 (a,b) Model system of Pd₃P₂S₈ in (a) top view and in (b) side view with N doping sites of S(a) and S(s). (c) Thermodynamic energy convex hull of substitutional doping of N in Pd₃P₂S₈, where the doping sites are shown on the right, and N atoms are represented in blue. (d) Reaction energy diagram of different N doping pathways. Circled integers represent the considered routes. (e) Reaction pathways with respect to the N concentration and the corresponding changes in the energy of the system.

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Figure 23 (a) XRD indicates the (002) peak reduced after nitridation suggesting the process breaks the crystalline structure of the pristine Pd₃P₂S₈ and (b) Raman spectra of Pd₃P₂S₈ (upper), N-5h-Pd₃P₂S₈ (middle) and N-10h-Pd₃P₂S₈ (lower) shows Pd-S bond disappearing and Pd-N bond appearing indicating substitution of S (c) Deconvoluted Raman Spectrum for Pd₃P₂S₈.

Figure 24 (a) XPS spectrum of Pd₃P₂S₈, N-5h- Pd₃P₂S₈, N-10h- Pd₃P₂S₈ normalised to Pd peak shows S 2p diminishing after nitridation, the high level of carbon signal is due to the adhesive used for fixing powder sample. High resolution XPS spectra with deconvoluted peaks for elements (b) Pd 3d indicating the appearance of Pd-N bond and diminishing Pd-S bond, (c) S 2p shows the reduction of signals based on the signal to noise ratio indicating loss of S, (d) N 1s shows increase in adsorbed N-H indicating increasing difficulty for the N to replace S.

Figure 25 High resolution XPS spectra with deconvoluted peaks for elements (a) O 1s indicates higher adsorption of O which is beneficial for ORR, (b) P 2p shows multiple oxidation states of P in Pd₃P₂S₈ evolving to a strong peak at 133.8 eV assigned to P-N bond in N-10h-Pd₃P₂S₈ and 134.9 eV assigned to P-O bond, indicating significant change to the oxidation states of P. The P-S bond at around 132.2 eV in the pristine Pd₃P₂S₈ is observed to have diminished which could be due to the loss of sulfur and (c) C 1s used to shift the energy to the reference 284.8 eV (d) Crystal orbital Hamiltonian population (COHP) curves of Pd₃P₂S₈ and Pd₃P₂S₇(NH). The horizontal line at 0 eV represents the Fermi level (E_F).

Figure 26 Electrochemical ORR performances of Pd₃P₂S₈, N-5h-Pd₃P₂S₈, N-10h-Pd₃P₂S₈ and Pt/C. (a) ORR polarisation curves shows increase in current density after nitration, (b) Tafel plots for ORR shows a slight improvement (blue line, 83 mV dec⁻¹) compared to that of Pt/C (black line, 85 mV dec⁻¹) indicating faster kinetics, (c) ECSA of N-10h-Pd₃P₂S₈ is superior compared to that of Pt/C indicating increase in active sites, and (d) Chronoamperometric curves in O₂-saturated 0.1M KOH solution at 400 rpm under a potential of 0.6 V versus RHE. N-10h-Pd₃P₂S₈ (blue line) shows the lowest lost in current over time, indicating higher stability.

Figure 27 LSV curves of (a) Pd₃P₂S₈, (b) N-5h-Pd₃P₂S₈, (c) N-10h-Pd₃P₂S₈, and (d) Pt/C catalysts in O₂-saturated 0.1 M KOH solution at different rotation speeds with a sweep rate of 10 mV s⁻¹. Inset: Koutecky-Levich plots (i^{-1} vs. $\omega^{-1/2}$) relationship. Inset shows the transfer number which indicates the electron steps involved. n=4 indicates 4-electron pathway.

Figure 28 CV curves in the region of 1.06 - 1.17 V at scan rates from 40 to 100 mV s⁻¹ and corresponding linear fitting of capacitive current for (a,b) Pd₃P₂S₈, (c,d) N-5h- Pd₃P₂S₈, (e,f) N-10h- Pd₃P₂S₈, and (g,h) Pt/C. Cdl indicates electrochemical double-layer capacitance. The higher the Cdl the higher the ECSA which means presence of more active materials.

Figure 29 DFT calculation. (a) Oxygen reduction reaction free energy diagram of 4N, 6N and 7N doped Pd₃P₂N_x (4N, 6N and 7N represent x = 4, x = 6 and x = 7, respectively). (b) Correlation between the change in Pd charge state and OOH adsorption energy (ΔG^*_{OOH}), the horizontal dotted line represented the previously suggested optimal value of ΔG^*_{OOH} (3.9 eV). (c) Oxygen reduction reaction free energy diagram of referenced models (Pd₃P₂S₈ (pristine) and 8N). (d) Defect mechanism/ pathway for formation of Pd₃P₂S₆(NH). N doping induces stability to pristine material with S defect. (e) The illustration of pristine and N-doping paths.

Figure 30 (a) Adsorption configurations of intermediates for 4N model system. (b) 6N model system. (c) 7N model system (d) 8N model system. Circle indicates absorption configuration. Grey = Pd, Blue = N, Yellow = S, Pink = P, Red = O, White = H.

Figure 31 Optical photographs (a-c) and SEM images (d-i) of MXene before and after treatment. Colour difference after treatment, (a) as-etched MXene is slightly hued towards purple, (b) Ar-annealed MXene is much darker in hue tending towards black but shows slight blue hue under certain condition. (c) nitrogen-doped MXene has obvious changes towards reddish brown. SEM images of (b,g) as-etched, (e,h) Ar-annealed, (f,i) nitrogen-doped MXene.

Figure 32 Potential energy diagram for functionalised Ti₃C₂ with nitrogen coverages (ML) of (a) 0.25 (b) 0.5 (c) 0.75 (d) 1. Single-point calculations were performed to observe the effect of interlayer spacing on total energy of the slab. Interlayer distance, d, depends on surface concentration of nitrogen atoms on the slab and are listed in the Table S1 above. The y-axis

corresponds to the difference in total energy of a double and a single layered slab. Lowest point of the hill corresponds to the most stable configuration.

Figure 33 TEM images and corresponding HRTEM images of (a,d) as-etched, (b,e) Ar-annealed and (c,f) nitrogen-doped MXenes. Insets are corresponding Fourier transform patterns. Hexagonal spots represents clusters of TiO_2 particles.

Figure 34 (a) XRD indicates loss of 002 peak (centered at around 8.91° in as-etched) for both Ar-annealed and nitrogen-doped MXenes (b) Raman spectrum shows distinct peaks at 141, 217, 283, 378, 620, 692 cm^{-1} which is typical for as-etched MXene (c) XPS spectrum for As-etched MXene, Ar-annealed MXene and nitrogen-doped MXene shows that F signal at around 684 eV is diminished after the treatments.

Figure 35 High resolution XPS spectrum and deconvolution of as-etched MXene, Ar-annealed MXene and nitrogen-doped MXene of (a) Ti 2p signals indicates a new Ti-N peak and increase in Ti-O₂ peaks suggesting increase in terminations or oxidation, (b) N 1s signals indicates that N is bonded mainly to Ti and some indication of edge terminated with C, (c) C 1s signals shows peaks shows that annealing in high temperature had broken the C-Ti bond and forming more C-O and C-O-C bonds that are consistent with the expectation that surface carbon reacts with oxygen, (d) F 1s signal diminishes after annealing as shown by the lower signal to noise ratio indicating removal of F, and (e) O 1s signals show decrease in O-H bond which could indicate that O-H is removed together with F.

Figure 36 UPS measurement and corresponding extraction for (a,b) Work Function, and (c,d) Valence Band Maximum (VBM), insets are the extraction figure of single sample of each type. The onset of the respective energy measured (Kinetic energy for Work Function and Binding energy for VBM) gives the minimum energy for the removal of electron representing the . The yellow demarcation indicates the range of tunability of the work function based on polynomial fitting.

Figure 37 UPS spectrum of selected samples of each type. The presence of 2 onset values could be due to the presence of different phase of the material.

Figure 38 (a) Effect of terminations and thickness on work function (eV) of Ti_3C_2 . Blue and orange bars represent the PBE-D3 calculated work functions for a one- and a two-layered slab. These values were computed on a (2x2) unit cell. Work function depends on the surface terminations as clean slab has the lowest and N*-terminated slab has the highest value. These values are independent of the thickness of the slab as seen in the figure. (b) Scatter plot depicts the change in work function (eV) with respect to coverage of N* in $\text{Ti}_3\text{C}_2\text{-N}^*/\text{O}^*$ slab. As the coverage of O* decreases, there is a linear rise in the work function. As the thickness do not influence the work function, data points overlap for the same coverage of N*.

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Figure 40 (a) conductivity measurement based on van der Pauw's method, inset contains the samples for measurement (b) Structures of Ti_3C_2 , TiN (111) and TiN (100) (c) Density of states of F^* , O^* , N^* , TiN (100) and TiN (111) between -1 to 1 eV of Fermi level. The higher the density of states at Fermi level indicates higher conductivity.

Figure 41 Schematic illustration of overall solar steam generation setup based on CAM membrane absorber. Below the CAM membrane, water transport to the interface is facilitated by capillary force and swelling of the channels in the water pumper. The designed 2D pathway is part of the water pumper that enables sustainable water supply for steam generation, as well as for minimising heat spreading into the bulk water. Inside the porous polymeric network of CAM membrane (lower dotted box), the MXene flakes (atomic structure shown in upper dotted box) efficiently harvest solar energy and then generate heat for vaporising water molecules in the membrane to enhance water evaporation (see CAM membrane working mechanism in the middle). Coated with light blocking layer, PMMA plate with a circular opening is employed to precisely define the evaporation area, as well as to avoid direct sunshine on water bulk.

Figure 42 Characterizations of the as-prepared MXene materials and membrane. (a) UV-vis absorbance spectrum of different MXene powder, DI water as background solvent reference. Insets are SEM images of MXene flakes: Pristine MXene (left), Li-MXene (right); Scale bars are 1 μm . (b) HRTEM image of Li-MXene surface structure, where the dotted circle delineates the grains of defective region. Scale bar is 5 nm. Inset: the corresponding FFT pattern; (c) HRTEM image of pristine MXene surface structure showing the homogeneous surface structure. Scale bar is 5 nm. Inset: the corresponding FFT pattern. (d) XRD patterns of pristine and Li-MXene flakes showing the shifted (002) peak position which denotes larger layer gaps after intercalation of Li^+ specie.

Figure 43 (a) SEM images of CAM membrane surface to show the surface morphologies and distribution of MXene flakes, enlarged at right is the details of blank area (b) Cross-sectional SEM image of the CAM (sample 3) with micro- and nano-pores (sample 3); Scale bars are 20 μm , 50 μm and 1 μm from left to right image, respectively; (c) Cross-sectional optical microscopic images of sample 3 during (i) dry and (ii) wet state, which shows a stable porous structure.

Figure 44 (a) Contact angle test of the CAM surfaces: (i) sample 3; (ii) sample 5; (iii) sample 1. The contact angle of sample 3 and 5 are nearly the same, where sample 1 has much lower value.

All three samples possess hydrophilic surface. (b) Water content characterization of the CAM before and after drying (0.025 g) from saturated state (0.059 g). Annotation means the saturation water content of the tested sample. Sample is dried in air at 70 °C for 45min (c) UV-vis absorbance spectrum of pure CA and CAM membrane, insets are the optical images of corresponding membranes, scale bars are 2 cm; (d) Mechanical property tested under the same extension rate (e) Thickness measurement of the CAM and pure CA for comparison of mechanical property. (i) Thickness of the CAM sample is 330 μm ; (ii) Thickness of the pure CA membrane is 340 μm . (f) CAM structural recovery capability before and after drying. (i) Tested CAM sample in saturated state, showing a flat condition; (ii) Dried CAM sample after keeping at 70 °C for 45 min, showing a rolling state owing to water loss; (iii) Flat CAM sample after ultrasonication in water bath for 30 min, showing a recovery capability. (g) Evaporation performances of foldable membrane under condition of RH = 67%, T = 23 °C. Recovery means ultrasonic treatment to recover to the flat condition. Negligible variation is shown in sample 3 where a little decrease is shown in sample 5.

Figure 45 Working mechanism illustration and thermal performance evaluation. (a) Schematic of the designed solar steam generator, showing basic components and steam generating process; (b) Water pumper under the CAM which transport water from bulk to the interface and Top view heat distribution of the solar steam generator under exposure to 1 sun illumination continuously; (c) Temperature profile along the vertical direction, showing excellent heat localization performance (sample 3). Inset: the IR image from the side view [the “Center Point (+)” corresponds to the + marker in the IR image], recorded range is shown by the arrow; (d) Temperature change comparison of seawater, pure CA membrane, and the CAM membrane evaporator under continuous 1-h solar illumination.(e) IR images of samples with different MXene-to-CA ratios: (a) sample 4; (b) sample 2; (c) sample 1; (d) sample 3; (e) sample 5. Samples are illuminated continuously for 5 min.

Figure 46 Desalination performance of solar steam generator with the CAM membrane under 1 sun illumination, 57% relative humidity, and room temperature. (a) Mass change comparison for 1-h illumination of different setups with 3.5% seawater; (b) Mass change of samples with different MXene/ CA ratio under condition of RH = 67%, T = 23 °C. (c) Continuous evaporation rate and mass change test for 6 h showing the steam generating speed and stability (30 min per cycle); (d) Energy conversion efficiency evaluation during continuous 6-h illumination.

Figure 47 (a) Salt deposition effect on the evaporation performance under condition of RH = 67%, T = 23 °C, which shows a stable steam generation after seawater purification. (b) Evaporation performance of the CAM under harsh condition for 30 min. RH = 67%, T = 23 °C. (c) Salt rejection rate revealed by ion concentration comparison before and after desalination

showing the capability to produce drinkable water. (d) Benchmark comparison among related works with 2D interfacial membrane structure.

Figure 48 MXene EM absorber (a) schematic of MXene EM absorber (b) Experimental set up in reflection mode, S parameter measures the reflected EM, the energy not recorded is deemed to be absorbed, (c) Reflection parameter converted from S_{11} parameter read from network analyser (d) $|S_{11}|^2$ converted from S_{11} parameter indicating reflection and absorption power ratio for functionalised MXenes.

Figure 49 MXene Particle Alignment for Electromagnetic Absorption (a) Schema for particle alignment, (b) SEM images of (i) $Ti_3C_2T_x$ decorated with magnetic particles (ii) $Ti_3C_2T_x/Fe_3O_4$ -pva film on Cu foil (iii, iv) $Ti_3C_2T_x/Fe_3O_4$ -PVA film on Cu foil aligned under different orientation of rotating magnetic field, yellow line indicate general alignment direction (c) XRD comparison of Aligned and Not Aligned MXene on Cu foil (d) schema of EM wave within the Film.

Table Captions

Table 1 Engineering Precious-Metal Based electrocatalyst.

Table 2 Engineering Non-precious-metal based electrocatalyst.

Table 3 MXene based Electromagnetic Absorbers.

Table 4 Free energy change for each reaction steps of pristine and defective models with different active sites.

Table 5 Fitting of 002 peak on XRD spectrum.

Table 6 Atomic% of Pd and Se and Se:Pd Ratio in PdSe₂ and I-PdSe₂ calculated from XPS spectrum.

Table 7 Half-wave potentials, mass activities and electron transfer number of as prepared catalysts.

Table 8 Performance of I-PdSe₂ catalyst and several representative results about Pd compound from recent published works.

Table 9 ICOHP value of the bond between Se and Pd on the surface.

Table 10 Bond length between Se and adjacent Pd.

Table 11 Energy correction for the calculation of change in free energy taken from previous studies.⁶⁶

Table 12 Atomic Ratio from XPS.

Table 13 Half-wave potentials and specific and mass activities of Pd₃P₂S₈, N-5h-Pd₃P₂S₈, N-10h-Pd₃P₂S₈ and Pt/C catalysts.

Table 14 Performance of N-Pd₃P₂S₈ catalyst and several representative results about Pd compound from recent published works.

Table 15 Structural model of Ti₃C₂ functionalised with mixed terminations of N* and O* (0.25 ML and 0.5 ML coverage of N*). Top and perspective views of fcc adsorption sites of T_x are shown in the above figure. The interlayer distance is 6.7 Å in a two-layered slab converged

structure. The atomic elements Ti, O*, N* and C* are depicted in grey, red, turquoise, and brown respectively. Table shows Interlayer distance for a two-layered symmetric $\text{Ti}_3\text{C}_2\text{-Tx}$. The terminations are added on both sides of the slab and initial distance is maintained as 7 Å among the layers. This distance varies in the converged structure based on functional groups present on the surface of Ti_3C_2 .

Table 16 Atomic model of a bilayer of Ti_3C_2 MXene functionalised with N* on both ends. The interlayer distance is initially maintained as 7 Å, which decreases to 1.3 Å in the converged structure. The atomic elements Ti, N* and C* are depicted in grey, turquoise, and brown, respectively. Table shows a list of work function values predicted using PBE-D3 functional for a one and a two-layered $\text{Ti}_3\text{C}_2\text{-Tx}$. Surface terminations are added on both ends of the slab. The trend was predicted based on thickness of the MXene for full monolayer and mixed terminations. The interlayer distance for a two-layered MXene is maintained as 7 Å which decreases in the converged structure as listed in Table 15. These work function values are computed on a (2x2) unit cell.

Table 17 List of work function values predicted using PBE functional for a one-layered $\text{Ti}_3\text{C}_2\text{-Tx}$. These values are computed on a (2x2) unit cell with surface terminations on both ends of the slab.

Abbreviations

*	Terminations, functional groups, intermediates
#	Number of
2D	Two dimensional
2DM	Two Dimensional Materials
a	Constant
A	Surface Area
A	Ratio of absorbed power by material
at	Atomic
B	Reciprocal of slope of Koutecky-Levich (K-L) equation
b	Tafel slope
CA	Chronoamperometry
CA	Cellulose Acetate
CAM	Cellulose Acetate MXene
Cdl	Double layer capacitance
Cdl_{ref}	Reference double layer capacitance
C_o	O ₂ volume concentration
COHP	Crystal Orbital Hamilton Populations
CO₂RR	Carbon Dioxide Reduction Reaction
CV	Cyclic voltammetry
CVD	Chemical Vapour Deposition
CVT	Chemical Vapour Transport
D	Diameter
Δ	Change in
ΔE	Reaction energy
DFT	Density Function Theory
DI	Deionised
D_o	Diffusion coefficient
DOS	Density of States
E	Energy or applied potential
E_{ads}	Adsorption Energy
E_{surface+adsorbate}, E_{surface}, E_{adsorbate}	Ground state total energy of modelled slab
ECSA	Electrochemical Surface Area
E_D	Ground state energy of defected model
E_f	Defect formation energy
E_f	Energy at Fermi Level
η	Overpotential

η_{RHE}	Overpotential based on Reversible Hydrogen Electrode
E_{P}	Ground state energy of pristine model
EM	Electromagnetic
EMS	Electromagnetic shielding
ε	Emissivity
F	Faraday constant
FCC	Face Centered Cubic
FFT	Fast Fourier Transform
G	Gibbs free energy
GGA	Generalised Gradient Approximation
$G_{\text{H}_2\text{O}}$	Free energy of H ₂ O
G_{pH}	Energy correction of H ⁺ free energy
G_{U}	Energy correction based on electrode potential
G_{w}	Stabilization energy by water molecules
h	Planck's constant
HER	Hydrogen Evolution Reaction
h_{lv}	Latent heat of vaporisation
HOR	Hydrogen Oxidation Reaction
HRTEM	High Resolution Transmission Electron Microscopy
I	Input solar power
ICOHP	Integrated Crystal Orbital Hamilton Populations
i_{dl}	film diffusion-limiting current density
i_{k}	Kinetic limiting current density
IR	Infrared
j	Current density
j_{k}	Kinetic current density
K-L	Koutecky-Levich
Kα	X-ray energy
k_{B}	Boltzmann constant
λ	Wavelength
MILD	Mild Intensity Layer Delamination
μ_{Se}	chemical potential of Se
n	Number of electrons in oxygen reduction
NIR	Near Infrared Range
NMP	N-methyl-2-pyrrolidone
NRR	Nitrogen Reduction Reaction
N_{Se}	Number of defected Se atoms
v	Kinematic viscosity
v	frequency of the electromagnetic radiation
OER	Oxygen Evolution Reaction

ω	Angular velocity
ORR	Oxygen Reduction Reaction
P	Pressure
P₀	Atmospheric pressure
PAW	Projected Augmented Wave
PBE	Perdew-Burke-Ernzerhof
PEG	Poly(ethylene glycol)
pH	Power of Hydrogen
PMMA	Poly(methyl methacrylate)
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride
Q	Heat energy
Q	Swelling ratio
Q_{vapor}	Total utilised heat energy for evaporation
Q_{ref}	Reflected heat loss
Q_{cond}	Conduction heat loss
Q_{rad}	Radiation heat loss
R	Ideal gas constant
R	Ratio of power reflected by material
R	Net evaporation rate
RAM	Radar absorbance material
RFid	Radio frequency identification
RHE	Reversible Hydrogen Electrode
R_{sh}	Sheet Resistance
S	Entropy
SE	Shielding effectiveness
SEM	Scanning electron microscopy
σ	Conductivity
σ	Stefan-Boltzmann Constant
t	thickness
t	Time/ duration
T	Temperature
T_{amb}	Ambient Temperature
TBAOH	Tetrabutylammonium hydroxide
TEM	Transmission electron microscopy
TMD	Transition Metal Dichalcogenides
TMO	Transition Metal Oxides
T_{sur}	Surface Temperature
U	Potential energy
U⁰	Equilibrium potential

UPS	Ultraviolet Photoelectron Spectroscopy
UV	ultraviolet
VASP	Vienna Ab-initio Simulation Package
VBM	Valence Band Maximum
vdW	Van der Waals
W	Sample weight in saturated water absorption
W_d	Sample weight in dry state
WF	Work Function
WHO	World Health Organisation
wt	Weight
XRD	X-ray diffraction spectroscopy
XPS	X-ray Photoelectron spectroscopy
ZPE	Zero-point energy

Chapter 1: Introduction

The greatest concern facing the world today largely stems from the future of energy sustainability. Amid heavy dependency on fossil fuels, inevitable negative impacts on both environment and economy had surfaced and are getting more critical over time. Hence, this calls for a severe paradigm shift and serious actions toward sustainable energy supply chain. Although the impact of such shift could not be felt in the short term, the long-term benefit is definite. As part of the sustainable energy supply chain, developing and storing clean and green energy such as energy from sources like electrochemical, solar, thermal, hydro, wind, bio and many other renewable and non-carbon-generating sources is a crucial step in the direction.

One of the most popular sustainable energy supply chains focuses on tapping the most abundant renewable resource, which is the energy from the Sun. In terms of solar energy, the most untapped resource is the photo energy component.¹ This is due to the limited energy efficiency facing photoelectrical converters such as solar cells. There is a need to improve the technology and develop new technologies for more efficient and long-lasting solutions to tap into these resources.

1.1 Significance of electrochemical conversion to green energy

Among various clean and green energy solutions, electrochemical energy conversion and storage plays a significant role and the demand for such technology had seen tremendous increase over the years. Electrocatalytic conversion does not produce undesirable by-products and serves as a mean to store energy for later use. The fact that the source of electrical input can be of

renewable sources as aforementioned, provides greater incentive to develop the technology. In this aspect, the key electrochemical reactions such as hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) which are the fundamental reactions in electrolysis and fuel cells that had been commercialised; yet they still serve a great deal in research for better and more efficient electrochemical systems. Other forms of electrocatalytic conversion such as carbon dioxide reduction (CO_2RR), nitrogen reduction reaction (NRR) and many other forms of conversions that targets the valuable products such as formic acid^{2, 3} had also garnered interest. The main issue that limited the widespread application largely remains with the over-reliance on precious metals which are scarce and hence very expensive to implement in the large scale.

Recently, the shift towards wide adoption of electric vehicles has seen the demand to develop metal-air batteries such as Li-air and Zn-air batteries.⁴⁻⁶ Due to their higher theoretical energy density and much safer operation, metal-air batteries are potential alternatives to the current Li-ion batteries. This brings to consideration, the need for better ORR catalyst which is the limiting reaction; and the catalyst will have to traverse between the cathodic and anodic operation during the charge-discharge operation cycle.

1.2 Two-dimensional materials for energy conversion and storage

The rapid development in clean energy sees two-dimensional materials (2DMs) based catalysts gaining traction over the years ever since the discovery of graphene in 2004.^{7, 8} 2DMs generally refer to materials that are confined to single plane and are of one or few atomic layers thick.⁹ Their unique structure gives them alluring properties such as high specific surface area,

excellent mechanical properties, electrical and thermal conductivity.¹⁰ Applications for 2D materials are widespread, from energy storage/conversion applications such as supercapacitors,¹¹ batteries,¹² electrocatalysts,¹³ to electrical applications such as sensors,¹⁴ radio frequency identification (RFid),¹⁵ electromagnetic interference shields,¹⁶ to mechanical applications such as filters for seawater desalination, water purification,¹⁷⁻²¹ as well as thermal applications.²²

What fascinates most is their potential to be modified to fit into different functions. This ensures that the potential of their development will not stagnate but result in more interesting materials being developed year on year. Modifications on graphene is the classical example of functionalising on 2DMs which is made possible because of the unique structure and affinity of the 2D network, such as through sp hybridisation.²³ These opened the doors to opportunities as they can act as a substrate that welcomes functional ligands or replace their empirical build to effect different properties. For example, nitrogen doped graphene,^{24, 25} continues to expand the applications in electrochemical energy conversion.

In the 2D materials class, transition metal dichalcogenides (TMDs) such as molybdenum disulfide (MoS₂) and tungsten disulfide (WS₂) are the go-to material for electrical applications due to their versatile properties as semiconductors and their ease of handling and there are still endless applications for these 2 materials where they continue to garner interests. In fact, MoS₂ and WS₂ had been widely researched for their use as electrocatalyst as well because of the ability to tune sulfur vacancies through defects engineering.^{26, 27} Precious metal TMDs such as that based on platinum (Pt) and palladium (Pd) are well known for their electrical properties and electrochemical capability,²⁸ yet, there is a need to activate the material to increase the mass activity and to boost the efficiency.

The most recent discovery sees the development of a new class of 2DM coined “MXene” by its founder due to its structure resembling that of graphene.⁷ It is a family of hexagonal layered ternary transition metal carbides, carbonitrides and nitrides where the M stands for an early transition metal (such as Ti, V, Cr, Nb, *etc.*), the A stands for a group A element (such as: Al, Si, Sn, In, *etc.*), and X stands for carbon and/or nitrogen.⁷ Due to its layered structure and unique build, to date, this class of 2D material had seen potential applications across multiple fields including energy storage,^{29, 30} energy conversion,³¹⁻³³ supercapacitors,³⁴ sensors,³⁵ construction,³⁶ among others. The material alone could achieve outstanding performance, yet the most alluring property is that by modifying the termination, different functions can be achieved.

Termination groups on MXenes are crucial to their electronic properties, both electrical and electrochemical properties. Various literatures³⁷⁻⁴⁰ had displayed that by modifying the termination groups, electrical conductivity can be tuned, and different functions can be attained. Meanwhile, because of the unique structure of MXenes, additives can be easily incorporated into the structure in the form of intercalant to alter the electrical properties and state of the material. Many researchers had started investigating the functionalisation of MXene for use with energy application such as catalysts,^{31, 32} batteries,^{11, 29} microwave absorption and electromagnetic shielding,⁴¹⁻⁴⁴ and their potential as a component for solar cell.⁴⁵⁻⁴⁷

1.3 Motivation for the Thesis

To this end, 2D materials continue to intrigue due to that they can be tuned to suit different functionality. The research into 2D materials engineering is imperative for innovative and practical-focused development of energy conversion and storage. Improving 2DMs for their

applications seeks to close the gap between laboratory studies and the industrial needs. With their unlimited potential, 2D materials will open doors to many other opportunities.

1.4 Organisation of Thesis

. In this Thesis, 2DMs are modified to improve their applicability in energy conversion applications. Starting with a literature review, in Chapter 2, the basis and outlook of engineering 2DMs for different energy applications will be highlighted.

Subsequently, in Chapter 3 and Chapter 4, precious metal based 2DMs (in particular Pd based 2DMs) are investigated and engineered to improve their utility. In Chapter 3, a showcase of lithiation activation technique for PdSe₂ that balanced the stability and performance of the material for Oxygen Reduction Reaction (ORR). In Chapter 4, an unprecedented palladium nitride based (Pd₃P₂N_x) ORR catalyst is produced through simple annealing of Pd₃P₂S₈ guided by rational design.

To shift away from the reliance on precious metal, alternative non precious 2DMs are investigated. In this case, MXene, for their rich surface chemistry, can be engineered to fit different function. Hence, in Chapter 5, the functionalisation of MXene to tune the physical properties such as work function and conductivity is showcased. Such tunability can find useful applications in, take for example, solar cell. Subsequently, Chapter 6 demonstrates one of such application of functionalisation where highly efficient photothermal conversion to tackle water desalination problem is achieved by functionalisation of MXene. Finally, the thesis will end off with a conclusion and future work on the 2DM modification for energy applications.

Chapter 2: Literature Review

2.1 Engineering 2D materials for hydrogen and oxygen electrocatalysis

2DMs comprises of multiple families of materials such as graphene and their derivatives, transition metal oxides (TMOs) and dichalcogenides (TMDs) including precious metal based TMDs such as PtSe₂, PtTe₂, PdTe₂,^{48, 49} and multiple other ultrathin materials.⁵⁰ As 2DMs have the versatility to be modified and the resultant modifications shows great performance towards electrocatalysis. In this Chapter, the modification techniques for 2D materials electrocatalysts and the benchmarks for the modified catalysts will be reviewed. Firstly, the commercial relevance of electrocatalysis will be briefly discussed. Followed by the introduction on precious-metal based catalysis modification, and a discussion on the trend towards non-precious-metal based two-dimensional 2D catalysts will be presented. The last part will introduce and discuss MXene, techniques for functionalisation, and their relevance in energy applications.

Figure 1 Overview of 2D materials for energy conversion/storage, and their engineering methods.

Since, electrocatalysis is a superficial reaction, which means that the reaction takes place on the surface, hence, the larger the area on the catalysts is exposed to the reactant, the more favourable the reaction. Furthermore, the charge transfer to the interface and their affinity towards the reactants will affect the kinetics of process drastically. Strategies to improve the activity of electrocatalysts can be broadly classified into three classes, defect engineering, interface engineering and strain engineering (**Figure 1**). Defects such as edges, vacancies, grain boundaries are known to be active to increase carrier density and facilitate carrier transfer. Hence, by

increasing the number of defects, the catalysts can be tuned for the electrocatalysis.⁵¹ The interface between different solid-state material contains rich chemistry and the synergistic effect between the heteroatoms is beneficial for catalysis. The different components may induce electron transfer between each other, and the electron redistribution will modulate the electronic or band structures of the components, which improves the catalytic activities. Hence, by tackling the interfaces, it is possible to increase number of active sites, improve selectivity and mass transport.⁵² Straining a 2DM is to provide distortion or stretching in the lattice of the material to effect a change in the electronic structure and band structure which in turn improves the affinity and selectivity of the catalyst, effecting greater chemical activity.⁵³

The strategies usually take on multi-prong approach and can be a mix of the three classes. Essentially, almost all techniques can be classified within the broad headings. These modification techniques seek to meet a set of objectives, *i.e.*, 1) to improve the amount of defect and active sites on the material, 2) to increase the activities at the active sites through tailoring the electronic structures, 3) to improve the conductivity of the electrocatalysts, 4) to improve the selectivity and affinity of the reactants. Recent advances in the electrocatalytic energy research makes use of the inherent properties of 2DMs and by modifying them to further activate their potential for high performance and stable electrocatalysts.

Energy conversion and storage are key factors towards the sustainable energy chain. One of the promising solutions for energy conversion is through catalytic electrochemical reactions due their relatively low impact to environment and high throughput. Electrochemical energy conversion comprises of various reactions such as HER, HOR, ORR, OER, CO₂RR, NRR and many other forms of conversions that targets organic products such as formic acid, acetic acid,^{2, 3,}

⁵⁴ and hydrogen peroxides.⁵⁵ In these processes, the by-products (or products) are generally useful and safe, such as water, hydrogen and oxygen. The products can also be stored for on demand application, such as that of fuel cells or metal air battery, where energy is stored in the form of hydrogen or as ions in electrolyte until operation needs. Furthermore, the energy that are used to perform the conversions can be from renewable sources,⁵⁶ which adds to the advantage of these solutions.

Commercial processes should be the aim of electrocatalysis for where the demand and the utilization can be justified. Processes such as water splitting is important for the hydrogen fuel economy⁵⁷ because of the abundance of water, while as part of the hydrogen energy chain, the downstream application for it will be fuel cells. HER and OER are the cathodic and anodic processes for water splitting/electrolysis, and their reverse process HOR and ORR are the anodic and cathodic counterpart in a fuel cell. As fuel cells are becoming increasingly prominent with the increase in demand for hydrogen (fuel cell) vehicles.⁵⁸ Moreover, whilst the discovery of metal-air batteries brings forth a new rise in demand for electric vehicles and various high-power applications,⁴ ORR playing an indispensable role for both systems becomes a crucial limiting factor.

2.1.1 Mechanisms of HER, HOR, OER, ORR

HER and HOR follows the well-known Volmer–Heyrovský mechanism and Tafel mechanism.^{59, 60} Starting from HER, the overall half equation of $2H^+ + 2e^- \rightarrow H_2$ in acidic condition and $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ in alkaline condition, the reverse of the equation will be that for HOR. These reactions have the simplest mechanism out of all the electrolytic

reactions,⁵⁹ yet, to achieve by 2DMs catalysts remains a challenge due to the lack or excess of affinity to adsorb and release hydrogen.^{61, 62}

OER at the other end of water electrolysis follows a much more complicated process. The overall half equation is $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ in acidic condition while $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ in alkaline and neutral condition, conversely, ORR is the reverse process. Although the actual mechanism is still up for debate, most researchers agree with the traditional adsorbate approach proposed by Man *et al*⁶³ and the lattice approach.⁶⁴ These processes consist of multiple steps and multiple electron transfer which plagued the processes with slow kinetics and high energy barriers. The design of OER and ORR catalysts is thus aimed at improving these aspects to effect a better conductivity for electron transport and to overcome the high energy requirement for transfer of electrons.⁶⁵

Precious metals such as Pt are considered the benchmark electrocatalyst for HER and ORR, whereas RuO₂ and IrO₂ are considered the most active electrocatalysts for OER.^{51, 66} This means that practical implications of electrocatalysis are still fixated with the approach to improve the utilization of precious metals in the electrocatalysis, despite a call for precious-metal free electrocatalyst.⁶⁷ Such practical implications possess multitude of issues, ranging from cost to efficiency, especially that the biggest challenge facing the large-scale application could be the scarcity and cost. On this aspect, various efforts are made to improve the utilization of the precious metal and to improve the longevity of the precious metal electrocatalysts.

On the other hand, the demand for sustainable energy through electrocatalytic conversion still drives the development for cheap and highly efficient electrocatalysts. On this aspect, 2DMs

has great potential to achieve high performance for commercial implementations. To date, they have shown to play important roles to the success of batteries and electrocatalysis.¹⁰

2DMs are usually one or several atoms thick with strong covalent bonds extending through the atoms within the plane, like graphene. They can be exfoliated from their layered bulk structure, *i.e.*, graphite, which is held on by weak Van der Waals interactions.⁶⁸ Graphene can be made thin, light and extremely small. Furthermore, due to their anisotropic nature, they possess many advantages over their bulk structure that complements the state-of-the-art technology. First, 2DMs has large surface area that can be full of exposed active sites. Second, 2DMs serves as a good support for catalysts due to the synergy and compatibility between the surface electronic structure and the catalysts' electronic structure Third, 2DMs have rich surface chemistry that can be modified for multifunctionalities, enhancements, amongst many more.

2.1.2 Engineering precious metal-based catalysts

Currently, precious metals (Pt, Pd, Ir, Ru, etc) are known to produce the benchmark catalysts. They are highly regarded for their high activity especially to hydrogen and oxygen. Coupled with the dissociative adsorption, the reactants H and O could easily react and release on the metal surface, achieving balance between adsorption and desorption of the reactant and products. Precious metals hence show high performance as electrocatalysts. Furthermore, they are practically robust under acidic and alkaline conditions, so they do not dissolve in either of them,⁶⁹ which makes them ideal for many electrocatalysis reactions. However, there are still limited adoption in the industry despite the advantages. The main problem echoed by the research community on using precious metal is the cost and scarcity of such materials.

In retrospect, the problem could possibly lie in the effectiveness of the process instead. Take for example, the current cost for hydrogen production via alkaline water electrolysis is around 5.5 USD/kgH₂ (using China as a benchmark), where the cost of electricity overwhelms the capital cost.⁵⁷ Whilst comparing to other forms of hydrogen production, it is much cheaper and effective. Nevertheless, the fact of the matter is that precious metal are scarce and hence shifting from the reliance on precious metal should still be prioritised but tackling the effectiveness of the process can encourage more widespread application as the operation becomes more economically sound.

In the effort to reduce the cost, finding alternatives within the precious metal class for a more abundant precious metal (such as Pd to replace Pt) is widely researched.⁷⁰ To tackle the issues on effectiveness, various techniques aimed at improving the utilization of precious metals. For instance, stabilising the precious metals within supports, forming alloys or compounds, and doping compounds with electron rich atoms, amongst others. These techniques try to make use of the synergy between the precious metal and the partner component to achieve greater kinetics and effective electron transfers between the reactants for the electrocatalytic processes; and most importantly, to reduce the overall use of precious metals.

2.1.2.1 Stabilising precious-metals in supports

The basic approach is to mix precious metals with supports such as carbon black,⁷¹ however, the effectiveness depends greatly on the dispersion and structure of the support as explored by Park *et al.*⁷² The performance of the cell is highly dependent on the accessible electrocatalytic area. Any agglomeration of the particles results in a drastic reduction of performance. Furthermore, the dissociation of the dispersed particles poses a challenge to have a long-term stability of the catalyst, such as the common problem of Pt dissociating from its carbon black support.⁷³

Looking at the recent years, the advancement in the stabilisation of precious-metal catalyst takes into consideration of 2DMs. The main aim is to improve the material utilization by exploiting high specific area 2DMs to load the precious metal, and then to essentially increase the mass activity of precious metal whence enhances the efficiency. The general trend for precious metal-based catalyst is to find an optimal dispersion of nanoparticles to the point of isolating single atom on a supporting 2D matrix that is both active and conductive such as graphene or nitrogen doped graphene.

The advantage of using 2DMs in this case is to make use of the surface chemistry to provide an anchor for the nanoparticles to prevent agglomeration and provide stabilisation.⁷⁴ In this aspect, nitrogen doped graphene is a good candidate to provide such anchor due to the compatibility of electron interaction between N-dopant and Pt.⁷⁵ Cheng *et al*⁷⁶ established a 37-fold increase in catalytic activity for HER with around 10% of performance drop after 1000 cycles, by controlling the atomic layer deposition of Pt onto nitrogen-doped graphene nanosheet which kept the agglomeration problem at bay. Mahmood *et al*⁷⁷ dispersed Ru in a nitrogenated holey 2D C₂N structure for HER for the first time and made use of the affinity between Ru and C₂N to effect fast H₂O reduction and product desorption and hence achieving superior HER performance (small overpotentials 13.5 mV in acidic and 17.0 mV in alkaline condition) compared to regular Pt or Pd.

In another experiment Begum and Kim⁷⁸ tried to tackle the dispersion issue using graphene as the substrate and exploited the inherent activity of graphene due to its sp² hybridisation, and its ability to anchor the platinised carbon. Essentially using the optimised graphene and Pt/C composite (onset potential shifted positively from 0.95 to 1.01 V vs RHE) electrode to improve the mass activity (252 mA mg⁻¹_{Pt}) and kinetics of ORR in fuel cells while maintaining the stability.

Zuo *et al*⁷⁹ investigated the effect of Pd grown on MoS₂, the dispersion of Pd particles can be controlled by controlling the concentration of NaH₂PO₂. The higher the concentration, the smaller the particles of Pd formed. The resulting dispersion achieved a half wave potential (~0.75 V vs RHE) and a higher mass activity 0.533 mA mg⁻¹_{Pd}.

2.1.2.2 Forming alloys or compounds

Forming alloys or compounds via the introduction of a secondary transition metal had been shown to improve the adsorption of reactant species through alteration of electronic structure and improving the charge transfer. Despite a good performance, the alloy usually suffers from low stability as bimetal is prone to the leaching of the secondary metal, however in a short-term usage, the reverse might happen, *i.e.*, an increase in activity due to dealloying. Gunji *et al*⁸⁰ showed that combining the effect of transition metal such as Fe, Co, and Ni into Pd changes the electronic structure of the material and leads to an improved ORR activity. The best result comes from the combination of Pd and Ni, the process achieved high half wave potential (~0.88 V) and high mass activity of around 0.151 mA μg⁻¹_{Pd}. In this case, for the observed range, the material exhibited increasing activity which was postulated to be due to the increasing exposure of interlayer Pd which participated in the activity increment after the dealloying of the secondary metal.

Bimetal can be made very thin which allows great degree of exposure of active precious metal atom. Take, for example, Saleem *et al*⁸¹ made ultrathin bimetallic 2D nanosheet from Pt and Cu that can be made into a special cone shape with improved surface area. The nanoalloy outperformed Pt in direct ethanol fuel cell for ethanol oxidation. Jiang *et al*⁸² combined Ni and Pd to form core-shell structure which exhibited good electrocatalysis performance, comparable to that of the benchmark catalyst Pt/C. Depending on the synthesis route, Ni or Pd can both form the core

with the other forming the shell. The best performance is observed to from the structure made of Pd shell, which can be attributed to the exposure of Pd. In this case, the ligand effect of Ni which serves as the substrate for the dispersion of Pd coupled with the strain in Pd favours the oxygen adsorption and desorption. The high half wave potential of the optimised Ni@Pd₃ core shell structure (~0.87 V (vs RHE) in acidic condition, ~0.86 V (vs RHE) in alkaline condition) is comparable to that of Pt/C and well exceeds that of Pd/C. Unfortunately, the problem of leaching secondary metal hinders the stability, the compound had exhibited an 8 mV drop in half wave potential after 3000 cycles of CV with substantial loss of Ni. Concomitantly, the stability is compromised further when there is higher percentage of Ni in the starting material.

Figure 2. PdMo Bimetallene extracted from Luo et al.⁴⁰ (a) SEM image (b) TEM image (c) AFM Image (d) Thickness analysis from AFM image (e) EDS imaging of PdMo Bimetallene (f) LSV curve at scan rate of 20 mV s^{-1} in 0.1 M KOH (g) Mass activity and specific activity (h) ECSA (i) LSV of PdMo bimetallene/C before and after 15000 and 30000 CV cycles (j) Normalised Mass activity for commercial Pd/C, Pt/C, Pd metallene/C and PdMo bimetallene/C. Credit: all figures extracted from Luo et al.⁸³

Luo et al.⁸³ showed that by alloying Pd with Mo, PdMo bimetallene can be made and serve as a superior ORR catalyst, with a half wave potential of 0.95V (vs RHE) which is far superior to most precious-metal based catalyst (**Figure 2**). It is found that the super thin 2D structure gives it fast kinetics and favourable electron transfer, furthermore, the electronic interaction between the bimetal makes the dissociation of oxygen atoms much easier. In this case, the bimetallene has the benefit of alloying, strains, and quantum size effects, with alloying effect contributing the most to the performance improvement. The bimetallene exhibits high stability during ORR with only a small loss in ECSA ($\sim 8\%$) after 30000 cycles. Such stability could be due to the large lateral size

of its 2D nanostructure which contains multiple anchoring points to the carbon support, with a small proportion of defected surface atoms at the edges, and less oxophilic surface Pd atoms due to the electronic interaction with molybdenum.

In other experiments, Yao *et al*⁸⁴ prepared Ru and Cu bimetallic 2D nanosheet that made use of the band structure difference between the bimetal to offer good HER and OER performance. The Cu 3d band energy is lower than the 4d band of Ru which allows electron to be transferred to Ru more easily and hence allows faster reaction for the OER and HER to take place. The optimised RuCu nanosheet exhibits robust stability in both alkaline and acid condition, achieved low overpotential for OER (~240 mV in both alkaline and acidic condition), and HER (~30 mV in both alkaline and acidic conditions). Similarly, Chen *et al*⁸⁵ established a bimetal between Pd and Cu which exhibited half wave potential of around 0.81 V and a comparable overpotential.

Precious metal can also be the secondary metal, in fact, it could be a potential direction to alleviate the impact on Pt. Other precious metals, especially Pd are highly sought after as the secondary metal. Xiong *et al*⁷⁰ epitaxially grown two atoms thick Pt onto Pd in a core-shell like structure which improved the stability and ORR performance compared to pure Pt catalyst, and uses less of Pt. The synergistic effect between the Pd and Pt propelled the ORR performance from ~0.85 V half-wave potential to more than 0.92 V half wave potential (vs. RHE). The performance is found to be highly dependent on the shape of the core as it acts as a dispersion for the surface Pt and provides the strain in the Pt lattice. Interestingly, the stability for this combination is remarkable at mere ~0.1V reduction in half-wave potential after 30000 cycles, however, the mass activity shows a loss of 23.6% indicating that there is a significant degradation. Although

combining two sets of precious metals shows promising performance elevation, it fundamentally does not diverge from the reliance on precious metal.

2.1.2.3 Doping with electron-rich donors

The process of the alloying could achieve good performance, yet the bane on the method is the leaching of component metal in highly acidic and alkaline solution, potentially poisoning the electrolyte solution or proton exchange membrane.⁸⁶ Alternative route to improving the performance and maintaining stability of electrocatalyst while avoiding aggregation and migration is to introduce electron rich anion such as P which forms crystal structure with precious metal which provides stabilisation to the structure.⁸⁷ Furthermore, introducing P changes the electronic structure of the precious metal that improves the affinity with the reactant of the electrolysis process⁸⁸⁻⁹⁰ or to stabilise the amorphized phase which is crucial for the activity of the catalyst.^{91,}

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Figure 3 PtP₂@PNC (a) synthesis pathway (b) SEM of PtP₂ dispersed on PNC (c) HRTEM image of PtP₂@PNC, PNC are indicated by the white arrows (e) Mass activity for ORR in 0.1 M KOH (f) Current versus time (i-t) chronoamperometric curves of the PtP₂@PNC and Pt/C at the rotation speed of 1,600 rpm and the constant potential of -0.3 V. Credit: all figures extracted from Pu *et al.*⁸⁸

Pu *et al.*⁸⁸ investigated PtP₂ dispersed on P and N co-doped Carbon (PtP₂@PNC) for HER and ORR reaction. The inculcation of P into Pt effected a lower binding energy between Pt and H atoms which improved the desorption of H₂ in HER, similarly the trend was observed for Pt and O atoms which encourages the reduction of O₂ during ORR operation. Due to the low loading of Pt, the mass activity of PtP₂ (150 mA mg⁻¹ Pt) is more than twice as high as that of a commercial Pt/C (~75 mA mg⁻¹ Pt). The catalyst is observed to be better performing in alkaline solution than

acidic solution which could be attributed to the reactants involved. However, based on comparison by mass activity and electron transfer number, the material still exhibited higher mass activity and near ideal electron transfer suggesting overall good performance. The interaction between the Pt-P and PNC stabilised the material which increases its stability which compared to Pt/C, the PtP₂@PNC exhibited only 8% decrease after 24 hours of CV while Pt/C suffered a 14% decrease within the first 3 hours. The reduction is determined to be from the detachment of PtP₂ during the vigorous activity (**Figure 3**).

Similarly, Luo *et al*⁹³ investigated the effect of PdP₂ for HER and OER and found that the Pd-P bonding weakened the binding energy between Pd and H atoms. Furthermore, inculcating of more P induces more active sites which is beneficial for the reactions. The HER and OER performance are outstanding as compared to commercial Pt/C and IrO₂ (for HER: overpotential of 27.5 mV in acidic media, 35.4 mV in alkaline media, for OER: overpotential of 270 mV in alkaline, 277 mV in neutral). The stability of the PdP₂ was also enhanced due to the negative Pd-P bonding which prevents poisoning by intermediate species.

It is worth noting that earlier experiments by Kucernak *et al*⁹² investigated the effect of increasing P content in Pd and P compounds, namely Pd₅P₂ and PdP₂ for HER, HOR, ORR and formic acid oxidation. The stabilising effect of P is prominent in all the reactions, but the performance on HER and ORR is slightly poorer compared to commercial Pt/C for HER and ORR. However, since the method that the group used to create PdP₂ is different (more facile method compared to the chemical method used by the former), the synthesis conditions could be responsible for the discrepancy. Accordingly, the facile method could have introduced a larger amount of oxide which impedes the performance.

2.1.2.4 Benchmarking precious metal-based electrocatalysis

Overall, the improvements made to precious-metal catalysts are successful on reducing the amount of precious-metal without compromising their activity. In **Table 1**, a list of precious-metal catalysts is compiled for an overview of the advances of precious metal-based catalysts.

Table 1 Engineering Precious-Metal Based electrocatalyst.

Type	Compound	Modification Technique	Activity/ Condition	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave (v) or overpotential (V) or current density j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA μ g ⁻¹ s)	Ref
Pt	Pt/C	-	ORR / Alkaline	(0.88)	14% loss (3 hours)		0.148 (Pt)	88
	Pt/C	-	ORR / Acidic	(0.85)	Undetermined		0.482 (Pt)	88
	Pt/C ₈ :G ₂	Stabilising on Graphene	ORR / Alkaline	0.22	25% decrease after 30000s	4.02	0.252 (Pt)	78
	PtP ₂ @PNC	P-doping and Stabilising on P and N doped carbon	HER / Acidic	0.012	$\Delta\eta$ +0.003 V (2000)	-	loading = 0.01785 mg cm ⁻²	88
	PtP ₂ @PNC	P-doping and Stabilising on P and N doped carbon	ORR / Alkaline	(0.82)	8% activity loss (24 hours)	3.96	0.1486(Pt)	88
	PtP ₂ @PNC	P-doping and Stabilising on P and N doped carbon	ORR / Acidic	(0.74)	Undetermined	~4	0.0176 (Pt)	88
	ALD Pt NGN	Stabilising on N doped Carbon	HER / Acidic	~0.04	10% loss in activity (1000)	-	2120 (Pt)	76
	Ni@Pd ₃	Coreshell	ORR / Acidic	(0.87)	E _{1/2} -0.008 V (3000)	3.93	0.105 (Pt)	82
	Ni@Pd ₃	Coreshell	ORR / Alkaline	(0.86)	E _{1/2} -0 V (3000)	3.99	0.095 (Pt)	82
	Pt-Fe/Fe ₂ O ₃	Heterointerface, Alloying	ORR / Alkaline	(1.05)	<4.2% loss after 180h	3.96	14.9 (Pt)	94
Pd	Pd/C	-	ORR / Alkaline	(0.76)	undetermined	~4	0.098 (Pd)	95

Type	Compound	Modification Technique	Activity/Condition	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave (v) or overpotential (V) or current density j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA μ g ⁻¹ s)	Ref
	Pd/C	-	ORR / Alkaline	(0.84)	50% loss in ECSA (30000)	-	0.006 (Pd)	83
	PdP ₂ /C	P-doping	OER / Alkaline	0.27	$\Delta\eta$ +0.008 V (5000)	-	loading = 0.285 mg cm ⁻²	93
	PdP ₂ /C	P-doping	OER / Neutral	0.277	$\Delta\eta$ +~0.007 V (5000), reduced ECSA by ~0.4 mF cm ⁻²	-	loading = 0.285 mg cm ⁻²	93
	PdP ₂ /C	P-doping	HER / Alkaline	0.0354	$\Delta\eta$ +0.01 V (5000)	-	loading = 0.285 mg cm ⁻²	93
	PdP ₂ /C	P-doping	HER / Acidic	0.0275	$\Delta\eta$ +0 V (5000) but reduced ECSA by ~1.3 mF cm ⁻²	-	loading = 0.285 mg cm ⁻²	93
	PdP ₂ /C	P-doping	HER / Neutral	0.0846	$\Delta\eta$ +0.007 (5000)	-	loading = 0.285 mg cm ⁻²	93
	PdMo	Alloying, Bimetallene	ORR / Alkaline	(0.95)	$\Delta\eta$ +0 V (30000), ~8% loss in ECSA	3.95	16.37 (Pd)	83
	Pd@Pt	Coreshell	ORR / Acidic	(0.92)	E _{1/2} -0.1 V (30000)	-	3.48 (Pt)	70
	Pd-B/C	B-doping	ORR / Alkaline	(0.883)	Undetermined	~4	0.145 (Pd)	95
	Pt-Pd/RGO	Alloying and stabilising	ORR / Alkaline	(0.84)	46% activity loss (500)	4.05	0.211 (Pd)	96
	Pd ₃ Fe NPs/CB	Alloying and stabilising in carbon black	ORR / Alkaline	0.870 (0.79)	E _{1/2} +0.1 V (1500)	3.78	0.125 (Pd)	80
	Pd ₃ Ni NPs/CB	Alloying and stabilising in carbon black	ORR / Alkaline	0.901 (0.88)	E _{1/2} +0.1 V (1500)	3.21	0.151 (Pd)	80
	MoS ₂ /Pd	Stabilising in MoS ₂	ORR / Alkaline	(0.75)	-0.2 V (4000)		0.533 (Pd)	79

Type	Compound	Modification Technique	Activity/ Condition	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave (v) or overpotential (V) or current density j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA μ g ⁻¹ s)	Ref
	Ni@Pd ₃	Coreshell	ORR / Alkaline	(0.86)	+0.1 V (3000)	3.99	0.098 (Pd)	82
	Pd/FePt	Alloying and coreshell	ORR / Alkaline	(0.7)	+1.0 V (10000)		0.067 (Pd)	97
	PdNiSn/NG	Alloying and stabilising on N doped graphene	ORR / Alkaline	(0.75)	0 V (5000)		0.164 (Pd)	98
	Pd-g- C ₃ N ₄	Stabilise on graphitic N doped Carbon	ORR / Alkaline	(0.7)	8% activity loss after 40000s		0.072 (Pd)	99
	Pd-Pt /C	Alloying and stabilising in carbon	ORR / Alkaline	(0.75)	+0.2 V (10000)		0.224 (Pd)	100
	Pd-Fe	Alloying	ORR / Alkaline	(0.77)	Undetermined		0.085 (Pd)	101
	Pd-Co/C	Alloying and stabilisation in carbon	ORR / Alkaline	(0.75)	Undetermined		0.063 (Pd)	102
	Pd ₂ -Co alloy	Alloying	ORR / Alkaline	(0.71)	Undetermined		0.041 (Pd)	103
	Cu-Pd multipod	Alloying	ORR / Acidic	(0.81)	+0.006 V (1000)		0.0423 (Pd)	85
	PdP ₂	P-doping	ORR / Acidic	(0.77)	Undetermined		Loading = 20 μ gPdcm ⁻²	92
	Pd/Ni	Alloying	ORR / Alkaline	(0.65)	60% loss in ECSA (400)		0.141 (Pd)	104
	Ag _{0.1} Pd _{0.9}	Alloying	ORR / Alkaline	0.977	40% loss in activity after 2h	3.98	0.011 (Pd)	105
Ru	Ru/C ₂ N	Stabilising in C ₂ N	HER / Alkaline	0.170	$\Delta\eta$ +~0.02 V (10000)	-	Loading = 0.285 mg cm ⁻²	77

Type	Compound	Modification Technique	Activity/ Condition	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave (v) or overpotential (V) or current density j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA μ g ⁻¹ s)	Ref
	Ru/C ₂ N	Stabilising in C ₂ N	HER / Acidic	0.135	$\Delta\eta$ -0.010 V (10000)	-	Loading = 0.285 mg cm ⁻²	77
	RuCu Nanosheet	Alloying	HER / Alkaline	0.020	Maintain nearly 45h	-	Undetermined	84
	RuCu Nanosheet	Alloying	HER / Acidic	0.019	Maintain nearly 20.5h	-	Undetermined	84
	RuCu Nanosheet	Alloying	OER / Alkaline	0.234	Small increase after 21.5h	n > 4	Undetermined	84
	RuCu Nanosheet	Alloying	OER / Acidic	0.236	Small increase after 13.5h	n > 4	Undetermined	84

2.1.3 Engineering the shift towards nonprecious metal-based electrocatalysts

The advancement on precious metal-based electrocatalysts is still making good headway, but the issue of overreliance on them is not sustainable. Hence, shifting towards nonprecious metal-based electrocatalyst remains an imperative to reduce the pressure towards precious metal. However, adopting nonprecious metal-based electrocatalysts is not without its limitations. The commercial implementation of nonprecious metal-based electrocatalysts still has a long way to go. This is because of their inherently low efficiency and low stability compared to those of precious metals. Take for example, graphene, being the predecessor for the booming list of 2DMs, which possesses every aspect of a good electrocatalyst (high specific surface area, excellent mechanical properties, high thermal and electrical conductivity) is surprisingly inert electrochemically. However, with a few modifications, including doping with nitrogen and increasing the number of active sites, graphene had become one of the promising 2D electrocatalysts for ORR.¹⁰⁶

Similarly, TMDs such as MoS₂ and WS₂ are considerably inert when they are perfect crystals. However, through various defect creation and engineering, and band structure modifications, TMDs performed well for HER and ORR.^{107, 108} Recently, the rise of 2D MXenes brought new hope towards electrocatalysts with its rich surface chemistry.¹⁰⁹ The rich terminations groups and excellent conductivity have shown to be crucial to their electrochemical activity.¹¹⁰ Yet, their performance had been mediocre with low stability and will require further enhancements to improve their performances.

Improving the effectiveness of 2DMs is necessary to facilitate the shift towards the nonprecious metal-based catalysts. A great advantage over precious metal-based system could be

easily reducing the capital and maintenance cost, which will encourage more adoption. In this aspect, to improve 2DMs for electrocatalysis, the techniques revolve around 1) creating defects such as edges and vacancies, 2) heteroatom doping and functionalisation, and 3) heterostructure and interface engineering.

2.1.3.1 Edges and vacancies

The simple act of creating an edge in graphene switched the material from an inert electrocatalyst to an active one.^{106, 111, 112} The main argument is that the edge consists of higher electronic density of states, or rather strong localised charge density distribution in graphene, although the increase in charge density favours only the zigzag site (*i.e.*, the site that exposes a single C atom from the hexagon network). Deng *et al*¹⁰⁶ tested the idea by ball-milling graphene into different size for ORR followed by DFT calculations. The ORR activity is observed to increase with increasing hours of ball-milling up from (halfwave potential vs RHE) ~0.28V pristine to ~0.14 V after 20 hours. The complementary DFT suggests that only the zigzag sites are suitable for ORR because -OH species are able to be desorbed much more easily at zigzag sites as opposed to the armchair sites (*i.e.*, edge site where two consecutive C atoms are exposed) and the generally inactive planar base. Similarly, the edge effect is apparent in the TMDs. TMDs such as MoS₂ and WS₂ have electrocatalytic activity on the basal plane, but the edge S site shows better affinity towards hydrogen making them good HER catalysts¹¹³ while the edge Mo site shows better affinity to oxygen making them good for ORR.¹⁰⁸ Hence tuning the quantity of such edges and defects can tailor the material for the intended applications.

Defects and active sites are usually formed from destructive processes, such as plasma bombardment, dealloying, chemical etching, and heteroatom doping. Other processes such as

solvothermal and template synthesis are also used to design various active sites. Vacancies can be considered edges, which possesses similar dangling bonds or accumulation of charges that are responsible for regulating the electronic configurations and physiochemical properties. To date, O vacancies are known to creates an electron rich environment that acts as a donor to the surrounding atoms.^{114, 115} Depending on the nature of the vacancies and the environment the vacancies are in, the resultant change in electron density can be modulated.

Figure 4 Singular Vacancy MoS₂ (a) Schematic for synthesis of singular vacancy MoS₂ (b,c) STEM image together with the line profiles extracted from the areas marked with purple rectangles of a CVD grown monolayer MoS₂ flake film after etching. The yellow dotted circles represent the S-vacancies. (d) (e,f) SEM image of pristine MoS₂ and MoS₂ after etching in H₂O₂ for 60s (g) TEM image of pristine and etched MoS₂ (h) LSV curve at a scan rate of 2 mV s⁻¹. (i) Tafel Plot (g) Linear fits of half capacitive currents versus scan rates for the extraction of Cdl (h) LSV curves of MoS₂-60 s before and after 1000 cyclic potential scans at a scan rate of 50 mV s⁻¹ in the potential range of 0 to (-0.35) V vs (RHE) in 0.5M H₂SO₄. Inset: chronoamperometric test of MoS₂-60 s at the current density of 10 mA cm⁻². Credit: all figures extracted from Wang et al.¹¹⁶

By engineering more vacancies and different types of vacancies, the performance and selectivity can henceforth be controlled. Usually, the defects formed are practically random and uncontrollable, but this does not pose a huge problem because overall active sites can be increased. Until a new paradigm on controlling the vacancies that can selectively create useful vacancies could generate less waste while improving the performance. Interestingly, Wang *et al*¹¹⁶ introduced a targeted approach to selectively remove S atoms from MoS₂ crystal plane that creates singular vacancies. The resultant material has well defined structure with singular S vacancies well dispersed on the plane. The team adopted a facile and mild etching of MoS₂ using H₂O₂ and controlled the number of vacancies by systematically adjusting the duration, temperature, and etching solution concentration. They found that there is an optimal loading of vacancies of around 12.5% which will balance the distribution of the vacancies and prevent agglomeration of the vacancies, furthermore the electrical conductivity will also be enhanced. The effect of controlled vacancies is tested on HER with an overpotential decrease from 220 mV in the pristine MoS₂ to 131 mV in the optimal etching time of 60s. The stability was further enhanced and there is only a minimal overpotential increase of around 20 mV after a continuous hydrogen generation process at current density of 10 mA cm⁻² for 12 h (**Figure 4**). The reason was due to the robustness of the structure, and well distributed singular vacancies which suppressed the agglomeration of the vacancies unlike vacancies created from other methods.

2.1.3.2 Heteroatom doping and functionalisation

To improve the electrocatalytic activity, a series of transition metal atoms (e.g., Ni, Co, Fe, Zn) and/or nonmetal atoms (e.g., C, N, O, P, Se) have been doped into the 2DMs to activate or strain the inert basal plane and minimising the band gap, thus boosting their catalytic performance.

Generally, the introduction of secondary atom is to improve the adsorption of reactant species or intermediates to encourage direct electron transfer. Take for example, N doping in graphene is widely accepted to induce charge delocalization or alter spin distribution of the sp^2 carbon plane, which facilitates the adsorption of O_2 and the O–O bond cleaving.^{117, 118} In this case, the N doping altered the electrical properties and create active sites for ORR.

In the effort to investigate the doping efficacy, Wang *et al*¹¹⁹ introduced a new process, deemed LI-PLI (low intensity pulsed-laser irradiation), which involves using laser to induce defects on graphene which will be more susceptible to nitrogen doping. They have found preferential doping of pyridinic N which is favourable for adsorption of O and intermediates for ORR and OER. The nitrogen doping on the laser-treated graphene can be tuned and the resultant materials were tested for their ORR activity. The optimised nitrogen-doped laser treated (NL) graphene shows a moderate ORR performance (halfwave potential ~ 0.80 V vs RHE) although much better than non-laser-treated nitrogen-doped graphene (halfwave potential ~ 0.68 V vs RHE). Using the NL graphene as a substrate, the group grew NiCo nanoparticles via hydrothermal method with $NiCo_2O_4$ precursor to obtain a synergistic effect between the pyridinic N-C bond and Co atom. The group confirmed that the dominant contribution towards the absorption of oxygen was from the Co-pyridinic N-C bond in the hybrid material. Hence, improving the ORR (halfwave potential ~ 0.83 V) and OER (~ 0.4 mV negative shift in overpotential) performance. Due to the synergistic effect between the substrate and the nanoparticle, the overall stability of the hybrid exceeds that of the commercial Pt/C reference (9% compared to 23% current density loss after 10-h stability test).

Following the work of Wang, Qin *et al*¹²⁰ dispersed MoS_2 into nitrogen doped mesoporous carbon via hydrothermal method to investigate the bonding preference on the edge and its effect

on HER. They found that out of the three types of N bonds (pyridinic, pyrrolic and graphitic N), pyridinic N, is more likely to bond with edge-Mo to form Mo–pyridinic-N coordination. Furthermore, with the help from laser, the graphene substrate could be made more mesoporous and promotes doping of pyridinic N onto the edge-Mo site. Such modification can be tuned to optimise hydrogen absorption free energy and to promote water dissociation on the edge-Mo of 2H-MoS₂ by tuning the charge density of edge-Mo. The overpotential is hence reduced from 313 mV in acid, 488 mV in alkaline in pristine MoS₂ to 110 mV in acid, 145 mV in alkaline in the laser induced sample (MoS₂/NLG-3). The catalyst is stable for over 150 hours.

Huang *et al*¹²¹ doped P into MoS₂ which caused the surface to be more nucleophilic for O₂ to be reduced to water. By introducing P into the Mo-S matrix, the more electronegative P is polarised by the S to become more positively charged. This favours the attraction of dissolved O₂. Furthermore, this process shifted the frontier/ surface orbital energy towards more positive side which encourages the surface electron transfer towards the reactant and improves the reduction of O₂ into water, endowing the doped material high selectivity and good performance (overpotential ~270 mV, half wave potential ~0.8V vs RHE). Unfortunately, although the P-MoS₂ has good performance, the facile synthesis could not keep up in stability, it had fell below commercial Pt/C in stability after a mere 7400s.

Bolar *et al*²⁷ investigated the doping strategy of MoS₂ using V and N as the cationic and anionic dopant to improve HER. The doping caused strain and vacancies in the MoS₂ crystal lattice and facilitated the alteration of electronic structure and reduction in the bandgap. The group compared pristine MoS₂ with N-doped (NMS), V-doped (VMS) and both V and N doped (VNMS) made using hydrothermal method. They observed a reduction in bandgap MoS₂ > NMS > VMS >

VNMS calculated from the tangents of the Tauc plot which promotes charge transfer, resulting in a decreasing trend of overpotential, MoS₂ (133 mV in acidic, 194 mV in alkaline) > NMS (114 mV in acidic, 175 mV in alkaline) > VMS (103 mV in acidic, 150 mV in alkaline) > VNMS (51 mV in acidic, 122 mV in alkaline). Due to the change in charge transfer, the kinetics improved as well, the Tafel slopes are observed to follow a downward trend. Understandably, the increase in overpotential and more sluggish kinetics in alkaline as compared to the acidic medium is due to the higher binding energy of hydrogen caused by the higher entropic barrier for the formation of dipoles and strong water association. Despite the doping effect of V and N, the VNMS material shows a mere moderate stability within 10 hours of test with a drop of around 40% after 4 hours, albeit the current density stabilises afterwards. It also exhibited an increase in overpotential after 10000 cycles of CV.

2.1.3.3. Heterostructure and interface engineering

Another strategy to improve the catalytic activity on 2DMs is to create a synergistic effect between two or more foreign elements or materials at their interface. The advantage of using this technique is mostly due to the facile nature for synthesis. Recently, Garino *et al*¹¹⁷ investigated Cu functionalised N-doped reduced graphene oxide (rGO) via a simple microwave synthesis method. Combining the effect of N doping in graphene with the introduced Cu⁺ ion on the surface, the new states are introduced near the Fermi level in the density of states (DOS). The more electron rich surface Cu-N-rGO improved the adsorption of O₂ to encourage direct four electron transfer process of ORR. The onset potential for Cu-N-rGO increased from 0.8 V (vs RHE) in N-rGO to 0.91 V (vs RHE) which gives it an overpotential of 0.32 V which is slightly higher than that of Pt/C (0.29 V) but a comparably better halfwave potential of 0.78 V (vs RHE). Unfortunately, due to the facile

synthesis method and lack of chemical bond between Cu and C, the Cu^+ is not secured onto the substrate, the performance is expected to be not robust due to possible leaching and dissociation. Nevertheless, it exhibited higher stability compared to Pt/C within 10000s of operation (with a reduction of 8% in current density).

Figure 5 Fe-N-C/MXene Superlattice (a) schematic of synthesis based on polarity (b) SEM image of Fe-N-C/MXene (c) EDS mapping (d) Surface area from Methylene blue adsorption measurements of Fe-N-C/MXenes in comparison to Fe nanoparticles (NPs) and Fe-N-C (e) Zeta potential in relation to the feeding ratios (w/w) of its precursors (Fe and C_3N_4); inset shows the charge donation from Fe to N sites of carbon nitride. (f) LSV plots at the scan rate of 5 $mV s^{-1}$ in O₂-saturated 0.1 M KOH electrolyte. (g) Histogram of half-wave potentials (h) LSVs at different rotate speeds. (i) K-L plots at different applied potentials (j) Electron transfer numbers at different applied potentials. (k) Chronoamperometric response at 0.7 V (vs RHE) for 20 h. Credit: all figures extracted from Jiang *et al.*¹²²

In this aspect, researchers are moving towards considering the newcomer in 2DM, MXene. The rich surface chemistry of MXene can form synergistic effect with foreign atoms. Jiang *et al.*¹²² showed that Fe doped C_3N_4 can be combined with $Ti_3C_2T_x$ MXene to form a synergistic interface for ORR. The heterostructure was made by assembling the two materials using electrostatic force between the two materials. Due to the difference in zeta potential of the Fe-N-C and MXene, a superlattice was formed. The halfwave potential of the Fe-N-C/MXene is a high 0.84 V vs RHE

(in alkaline condition) with comparable limit current density to that of Pt/C. The electron transfer was around 3.96 at low potential, suggesting a good efficient electron transfer for ORR. Furthermore, due to the strong polarity between the two materials, the moiety is considerably stable. This translates to a super stable electrocatalyst with almost no reduction in activity after 20 hours (**Figure 5**).

Yu *et al*¹²³ exploited the rich surface termination of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene and hydrophilicity of the material to capture oxygen for the reaction. The group combined g- C_3N_4 with the MXene via vigorous mixing to attain a heterostructure configuration. The combination makes use of the inherent difference in polarity (also known as zeta potential) to successfully bind together the two nanosheets. The heterostructure exhibited good ORR performance (halfwave potential ~ 0.79 V vs RHE) and a strong stability and methanol tolerance even after 40000s.

2.1.3.4 Benchmarking nonprecious material-based electrocatalysis

Modifications on 2D nonprecious metal-based catalysts had been successful at tackling the performance issues, with many being comparable to commercial Pt/C and IrO_2 . Unfortunately, the best activity achievable by nonprecious metal-based catalysts is still inferior to moderately improved precious metal-based catalyst. Economically speaking, the most suitable nonprecious metal-based catalysts should have superior stability with comparable performance instead of superior performance at the expense of stability. In **Table 2**, a list of nonprecious metal catalysts is compiled for an overview of the development of nonprecious metal-based catalyst.

Table 2 Engineering Non-precious-metal based electrocatalyst.

Type	Compound	Modification Technique	Condition/ Activity	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave, j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA mg ⁻¹ x)	Ref
Mo	P-MoS ₂	P-doping	ORR / Alkaline	(0.80)	Stable before 7400s -18.8% after 10000s	3.6	Loading = 0.283 mg cm ⁻²	121
	Singular Vacancy MoS ₂	Selective etching with H ₂ O ₂ for vacancy control	HER / Acidic	0.131	$\Delta\eta$ +<0.010 V (1000)	-	5.43	116
	CoMoS _x	Alloying	HER / Alkaline	0.158	$\Delta\eta$ +~0.03 V (500)	-	Loading = 0.05 mg cm ⁻²	124
	Ni ₃ S ₂ /MoS ₂	Heterointerface tuning	ORR / Alkaline	(0.885)	12% loss in activity after 200000s	~4.0		125
	MoS ₂	Creating edges	ORR / Alkaline	(0.72)	~30% loss in activity after 20000s	3.6	Loading = 0.2 mg cm ⁻²	108
	MoS ₂ /NLG	Creating vacancies, doping, heterointerface	HER / Alkaline	0.145	10% loss after 150h	-	Loading = 0.293 mg cm ⁻²	120
	VN-MoS ₂	V and N doping	HER / Alkaline	0.122	40% loss after 4 hours	-	Loading = 0.5 mg cm ⁻²	27
C	Graphene	Creating edges	ORR / Alkaline	(0.86)	Undetermined	Undetermined	-	106
	NiCo/NLG	Creating vacancies, doping and heterointerface	ORR / Alkaline	(~0.825)	9% loss in activity after 10h	3.96	Loading = 0.4 mgcm-2	119
	P-g-C ₃ N ₄	P-doping of N doped graphene	ORR / Alkaline	(0.67)	2.2% loss in activity after 30h	3.92	Loading = 0.2 mg cm ⁻²	126

Type	Compound	Modification Technique	Condition/ Activity	Overpotential or (Half-wave potential) (V vs RHE)	Stability Δ half-wave, j (mA cm ⁻²) (after x cycles)	Electron Transfer Number n	Mass Activity (mA mg ⁻¹ x)	Ref
	Cu-N-rGO	Cu functionalised N-doped graphene	ORR / Alkaline	(0.78)	8% loss in activity after 10000s	~4	Undetermined	117
	Fe-N-C/MXene	Fe doped C ₃ N ₄ heterostructure with MXene	ORR / Alkaline	(0.84)	<5% loss in activity after 20h	3.96	Loading = 0.1 mg cm ⁻²	122
	Co ₂ C-rGO	Heteroatom doping	ORR / Alkaline	(0.99)	0.05% loss in activity after 5000s	3.9	Loading = 0.1 mg	127
Other Transition Metals	Exfoliated WS ₂	Creating edges and vacancies	HER / Acidic	0.08	<20% loss in activity after 120h	-	Loading = 0.28 mg cm ⁻²	128
	Mg-N-C	Heterointerface tuning	ORR / Alkaline	(0.91)	0.2% loss in activity after 25000s	~4	Loading = 0.4 mg cm ⁻²	129
	CoOOH-N-C	Heterointerface tuning	ORR / Alkaline	(0.76)	E _{1/2} -0.019 V (5000)	3.9	Loading = 0.28 mg cm ⁻²	130

2.1.4 Outlook for 2DM electrocatalysis

Electrocatalytic conversion consists of a broad spectrum of reactions, and it is a promising lead towards sustainable energy. The strategies discussed in this section of the literature review pertain to general strategies that can be used for water splitting, fuel cells and metal-air batteries which are the important commercial applications for the near future; notwithstanding the fact that it can be applied to other (electro)catalysis applications. Looking at the overall trend of research and improvement towards electrocatalysts, the techniques and strategies are mostly converging, *i.e.*, the strategies comprise of similar techniques and revolve around solving the performance issue.

On the hindsight, the main obstacle to adopting electrocatalysis could be the impracticality due to the low stability of the catalysts. The low stability of the catalysts, conversely the durability of the system, results in unsustainable maintenance and replacement cost. This applies to both precious metal and nonprecious metal-based electrocatalysts as they possess this same Achilles' heel. Considering this aspect, more effort can be put into tackling the stability and durability rather than focusing on the performance. Although, to be fair, researchers do pick up the important trend of tackling stability, such that current drive of precious metal electrocatalyst research seeks to make use of 2DMs to provide supplement to the aspects that it lacks, especially on the aspect of stability where 2DMs are very suitable to become an anchor and substrate for dispersion. Meanwhile, the trend for research on nonprecious metal electrocatalyst seeks to move towards improving the stability of 2DMs for long term usage. However, there remains a huge gap to mass adoption of electrocatalytic conversion.

2.2 Engineering MXene for energy application

This section covers the rising trend of 2DM research where MXene is involved. Due to the extensive types of MXenes and applications, engineering of representative Ti based MXene will be emphasised. MXene is a novel 2DM that was discovered in 2011 by Gogotsi *et al.*⁷ Its graphene-like structure gives it its name, and the strong physical and chemical properties, referencing the most commonly researched MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) - high mechanical stiffness ($\approx 0.33 \text{ TPa}$),¹³¹ high electrical conductivity ($\approx 1.4 \times 10^5 \text{ S m}^{-1}$)¹³² and rich surface terminations - which brought it into the limelight of the new era research for functional materials for electrocatalysis,^{133, 134} supercapacitors,³⁴ batteries,¹³⁵ photoluminescence,¹³⁶ photothermal conversion¹³⁷ and many more. To date interest in energy conversion and storage remains keen

MXene is a class of 2D carbonitrides derived from the parent MAX phase. The MAX phases which are hexagonal layered transition metal carbides and nitrides of space group $\text{P6}_3/\text{mmc}$ ⁷ and have the general formula of $\text{M}_{n+1}\text{AX}_n$. The variable n can take up $n=1, 2$ or 3 depending on the number of layers of M , resulting in three types of structures of MAX phase namely, 211, 312 and 413.^{11, 138} Generally, the M multilayers are made up of closely packed M atoms with the X layers occupying the octahedral sites between the M atomic layers in the fashion of $M-X-M$. The A layers interleave the $M-X-M$ periodic units as the A atoms take up the centers of trigonal prisms.¹¹

Figure 6 MXenes reported so far. NA = not available. Credit: figure extracted from Anasori *et al.*²⁹

Different combination of M and X had been predicted and synthesised (**Figure 6**). The more well-known MAX phases are the carbides of Ti, V^{139, 140} and Nb^{141, 142} that see potential applications in energy storage and conversion. MAX phases also exist in the form of solid solution or an ordered phase of multiple different metallic elements, M'MAX.¹⁴³ An example of ordered phase is the combination of Ti and Mo that forms Mo₂Ti₂AlC₃. MXene produced from such MAX phases have different electrical properties. After various prediction from DFT calculations, Anasori *et al.*¹⁴⁴ demonstrated the replacement of outer layer of Ti in Ti₃C₂ and Ti₄C₃ MXenes with Mo layers to produce Mo₂TiC₂T_x and Mo₂Ti₂C₃T_x. The research team further investigated the electronic properties of the synthesised material. They showed that the inclusion of Mo changed the properties of the basal plane of MXene from metallic into a semiconductor with a narrow band

gap of around 0.05 eV, furthermore, using magnetoresistance measurement the team concluded that the electrical transport mechanism in the material is not the same as that of pristine Ti_3C_2 .

2.2.1 MXene synthesis

Processing MAX phase is straightforward where the synthesis routes mainly aim to remove the interleaved A atom. Anasori *et al*²⁹ pointed out that, due to the metallic M-A bonds, it is not possible to isolate the M-X-M unit via mechanical shearing. Fortunately, such structure of M-X-M-A contains both strong covalent M-X bonds and relatively weak ionic M-A bonds¹³⁸ which means that the M-A bonds are chemically more active than the M-X bonds. This enables selective etching of A layer chemically.²⁹

Predominant choice of synthesis of MXene remains to be etching their precursor MAX phases with aqueous HF or the in-situ formation of HF using fluorine salt such as LiF, KF and NH_4HF_2 .²⁹ However, it is noted that due to the difference in the bonding, MXenes such as Ti_2N ¹⁴⁵ and Ti_4N_3 ¹⁴⁶ which required elevated temperature and molten salt, are not able to be synthesised this way.

Although processing with HF directly is well known to be a quick and simple process,^{7, 147} it is nevertheless a hazardous one. Hence, various groups attempted to produce MXenes without HF, but the processes are plagued with limitations that deterred widespread adoption. Li *et al*¹⁴⁸ used molten salt of ZnCl_2 to remove the interleaved Al however the experiment was plagued with low repeatability. Yang *et al*¹⁴⁹ performed etching using a binary aqueous solution containing Cl^- instead of F^- but found that the etching was limited to the surface and was ineffective for large scale adoption. Li *et al*¹⁵⁰ produced $\text{Ti}_3\text{C}_2\text{T}_x$ with 92% purity through hydrothermal reaction with

NaOH, however the yield for the process was limited by the capacity and hazard of the hydrothermal process. Furthermore, notably Xu *et al*¹⁵¹ devised a bottom-up strategy to synthesise MXene using the CVD technique, unfortunately as much as it was successful in creating low defect MXene without termination groups, it was unable to be scaled to useful quantity. These means that HF remains as the most successful route of synthesis.

Alhabeab *et al*¹⁵² established the guidelines for synthesis and processing of the titanium carbide MXene which collated the typical synthesis and are regarded as standard protocols for preparing the material. It is noted from the guidelines that different synthesis route will have different effect on the properties of the MXene, hence, to achieve the desired outcome for one's application, one must employ the appropriate synthesis routes. It is imperative to note that precursor MAX phase's synthesis method will influence the quality of the MXene as well.

2.2.2 Characteristic of $Ti_3C_2T_x$ MXene

Figure 7 SEM images of Ti_3AlC_2 MAX phase powder at different magnification showing compact layered structure at (a, b) lower and higher magnification (c, d) extracted from ¹¹⁴ and XRD (e) spectrum for MAX phase, Ti_3AlC_2 (black line), HF etched Ti_3C_2 MXene (purple), delaminated Ti_3C_2 (pink), simulated $Ti_3C_2F_2$ (gold) and simulated $Ti_3C_2(OH)_2$ (red). Credit: all figures extracted from Naguib et al.⁷

Figure 8 Sem images of Ti_3C_2 MXene synthesised under different conditions (a) Ti_3AlC_2 MAX powder, (b-d) Multi-layered $Ti_3C_2T_x$ powder synthesised with 30 wt%, 10 wt% and 5 wt% respectively, (e) Multi-layered $Ti_3C_2T_x$ synthesised with ammonium hydrogen fluoride, (e) multi-layered $Ti_3C_2T_x$ etched with 10M LiF in 9M HCl. Credit: all figures extracted from Alhabeab et al.¹⁵²

Although each synthesis route results in different physical and chemical properties^{11, 152} the characteristic opening of the lamellas makes for a quick identification of the material. **Figure 7** shows a typical SEM image of Ti_3AlC_2 MAX phase which exhibits prominent layered structure. Etching in various conditions (**Figure 8**) shows obvious lamella opening in the material. It is noted that only with higher concentration ($>30 \text{ wt\%}$) of HF will the accordion shape be prominent, otherwise, with milder concentration ($<10 \text{ wt\%}$) of HF, the material will exhibit more compact structure and small lamella opening.¹⁵² Usually, this result is not adequate to determine the successful exfoliation.

Another way to determine the successful formation of MXene is the characteristic shift towards a lower angle and the weakening of the (0001) peak in the XRD spectrum due to the larger c lattice parameter and the lower intensity of the peak indicates a better exfoliation of the A element.¹⁵³ **Figure 7e** shows both the simulated and experimental XRD results from Naguib *et al.*⁷ The purple line spectrum is associated with the HF-etched MAX phase and the slight shifts in the (002) plane and (004) plane indicate an increase in c lattice parameter, meanwhile, the absence of the large peak at around 39° indicates that the phase of Ti_3AlC_2 is entirely converted. The experimental HF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ exhibits characteristic peaks from the simulated $\text{Ti}_3\text{C}_2(\text{OH})_2$ and $\text{Ti}_3\text{C}_2\text{F}_2$, red and gold line respectively, which suggests that there is a mixture of -F and -OH termination group on the basal plane.⁷ The presence of termination groups works to improve the characteristic of the material and will be discussed in the later section.

2.2.3 MXene functionalisation

The most alluring properties of MXenes where surface chemistry can be modified to affect the electronic properties of the material inspired this work. MXenes are usually terminated with surface functional groups such as -OH, -O and -F or -Cl depending on the synthesis methods. The latest tally by Pang *et al*¹¹ puts another 256 more members to the MXene family that can be attained by modifying the surface chemistry, *i.e.*, the -O, -F, -OH groups. It remains that the basal plane or monolayer MXenes are metallic, however with the influence of the surface functional groups, usually fluorine or hydroxyl groups, the material exhibits semiconductor properties.^{7, 29, 37, 38, 138}

Surface terminations plays an important role to the electrical properties and contributes to the high capacitance and the catalytic activities on the surface of the material. Fluorine termination is known to improve the proton adsorption kinetics for hydrogen evolution reaction (HER).¹⁵⁴ Oxygen termination is known to play a significant role at improving the lithiation capacity of MXene,¹⁵⁵ to help to improve HER by reducing the overpotential,¹⁵⁶ and to increase the capacitance of the material,¹⁵⁷ Nitrogen termination was known to improve the conductivity and the capacitance of the material,³⁴ very useful for supercapacitors.^{158, 159} The possibility to inculcate other terminations such as aryl diazonium termination¹⁶⁰ inspires innovative methods and novel terminations for use for other functions.

Over the years, the study of surface termination modification and effect of intercalation on the material had gained traction. By extending the functional groups on the surface of the material, the material has the potential to alter its electronic properties and volumetric capacitance; and by introducing intercalation molecules, the extension of the interlayer spacing improves the energy

storage capacity. Hart *et al*³⁹ established the relationship between the surface termination and intercalation through the use of in-situ annealing in TEM. The research group found that the surface termination can be tuned by gradually increase the temperature of the material in vacuum. The termination groups will be removed in the order of adsorbed atmospheric O₂ and H₂O, followed by the functional groups -OH and -F, and then -O as the temperature increases up to 800 °C, which will result in the improvement in electrical conductivity. This is consistent with the finding from DFT calculations that the basal plane is indeed more conductive. They also found that intercalant plays a significant role at reducing the conductivity of the sample, but deintercalation can happen at higher temperature which will reverse the trend. Generally, there are 3 main parameters that need to be balanced to tune the electrical properties of the material, namely, the basal plane defects, surface functional groups and the type of intercalant.

Oxygen termination is known to be a more stable form of termination because of the strong affinity between Ti and O. By annealing Ti₃C₂T_x under inert environment or vacuum, the yield will be highly likely oxygen terminated Ti₃C₂O_x due to the adsorbed -OH group and adsorbed O₂. Lai *et al*¹⁶¹ annealed as-etched Ti₂C MXene under Ar/H₂ atmosphere at 1100°C to obtain oxygen terminated Ti₂CO_x and found that the material has a band gap of 80 meV and a sheet resistance of 250 Ω sq⁻¹ contrary to that of as-etched Ti₃C₂T_x with band gap of 10 meV and sheet resistance of 280 Ω sq⁻¹. Zhang *et al*,¹⁵⁷ on the other hand, used a two-step reaction to produce oxygen termination. By first treating the Ti₃C₂T_x MXene in KOH, the research group tried to replace as much relatively stable -F terminations with the less stable -OH terminations, followed by annealing under argon at 400°C.

Nitrogen termination can be obtained by annealing under ammonia flow similar to that of Wen *et al.*,³⁴ or N atom can be introduced during synthesis using NH_4F and HCl followed by annealing at the temperature required.¹⁵⁹ Basically, the adsorbed NH_3 undergoes a different degree of oxidation converting itself from adsorbed γNH_3 to oxidised NO_2 group (in the form of Ti-O-N) and to the final Ti-N bond as the replacement goes into completion at elevated temperature. The downside of adopting annealing under elevated temperature is the formation of rutile TiO_2 that would have adverse effect on the electrical conductivity, however in the application of EM shielding, rutile TiO_2 is preferred for its ability to absorb EMI,^{41, 162} which will be detailed later.

Chlorine termination can be obtained by annealing excess ZnCl_2 with Ti_3AlC_2 MAX phase.^{148, 163} The reaction follows a mechanism similar to Lewis acid as proposed by Li *et al.*,¹⁴⁸ from which the Zn^+ and Cl^- dissociate to react with the weakly bonded Al^{3+} forming a Ti_3ZnC_2 MAX phase. The Zn-MAX phase is then broken down due to its instability at high temperature and engaging in a redox reaction with the excess ZnCl_2 to form chlorine terminated MXenes, $\text{Ti}_3\text{C}_2\text{Cl}_2$ and Ti_2CCl_2 . Due to the high temperature synthesis process, the resultant material has a more orderly structure and practically clean surface with only Cl as termination as compared to that from solution-based synthesis which is expected to introduce more species in ambient environment. The bonding between Ti and Cl is found to be stronger than that of F and N which suggests that it is much more difficult to remove. The electronic structures (DOS and band structures) of $\text{Ti}_3\text{C}_2\text{Cl}_2$ and Ti_2CCl_2 show a Ti d orbital dominated Fermi level which means that they are metallic. However, due to the lesser amount of Ti and C bands in Ti_2CCl_2 , it displays a bandgap of around 0.9 eV in contrast with $\text{Ti}_3\text{C}_2\text{Cl}_2$ which exhibits no bandgap.¹⁶³

2.2.4 Engineering MXene for energy applications

Figure 9 MXene development over the years, year when the application using MXene was reported. Credit: figure extracted from Gogotsi and Anasori.¹⁶⁴

MXenes are the rising star when it comes to energy application, **Figure 9** shows the timeline of development for MXene in multiple applications for when the first papers for each application was published and the large proportion of MXene research revolves around energy application.¹⁶⁴ Most of which belongs to $\text{Ti}_3\text{C}_2\text{T}_x$ MXene due to its versatility and ease of obtaining. The material is known to have rich surface chemistry that consists of various density of states which contributes to the high activity and electrical and photo responses. MXene has been

favoured as conductive substrates for adhering electrochemically active nanoparticles due to their active surface chemistry. In the field of batteries, they are favoured as layered ion storage and capacitors due to their electrical conductivity and malleable layer.

Recent advancements of MXenes are in the electromagnetic energy conversion, which includes electromagnetic absorption and solar energy conversion. MXene had been favoured for their ability to provide shielding against microwave in the K-band (18 GHz- 27GHz),¹⁶⁵ and recently, MXene had been found to convert light into heat energy (photothermal conversion).³³ Furthermore, MXene had been deemed as a suitable hole transport material for perovskite solar cells.^{45, 46}

2.2.4.1 Electromagnetic (EM) absorber

MXene, unlike most of its predecessors 2DMs, is considered more metallic due to the band structure and is comparable to that of graphene, giving it the advantage of both metal and 2DM for EM shielding.¹⁶⁶ The added advantage of using MXene is that the material's rich surface chemistry and terminations can be easily modified and tuned to the specific function, as discussed previously. Furthermore, MXene layered structure is favourable for EM waves to undergo multiple internal reflection which is understood to be the main mechanism of EM attenuation.^{167, 168} During which, the energy from the EM is dissipated as heat.

EM shielding and absorption is generally measured by two quantification techniques, *i.e.*, total shielding effectiveness (SET) and reflection Loss (RL) which tells similar story but has explicit difference in the two measurements and their results are not directly comparable, however, the trend they follow will be consistent within the methods. Essentially, RL measurements relies upon

impedance to explain the interaction between the EM wave and the surface of the material and to understand how the EM wave is encouraged to propagate into the material to be attenuated. Whereas the shielding effectiveness (SE) takes direct measurement of the total energy change of the supplied EM wave followed by a conversion to logarithmic term to exemplify the order of attenuation. Hence, the comparison of SEA must be coupled with the basis SET to derive the absolute absorption. Take for example, graphene has high SE of 45 dB, blocking 99.9968% of incoming energy, which is much higher than the benchmark of 20 dB (equivalent to blocking 99.0% of energy), with the corresponding absorption efficiency (SEA) of 33 dB (equivalent to absolute absorption of merely 6.3%).¹⁶⁹ However, the material does fare well in absorption only measurement at a mere 8.9 dB based on RL measurement but translating to 87% of absorption, but yet it is not up to the standard of lower than the 10 dB (90% absorption) benchmark. This exhibits the stark difference in the measurements and the standards used to determine the capability of absorption. To be fair, the different methods can be applicable for different applications, hence it remains debatable for which the developed material can be used for actual application.

Nevertheless, researchers around the world, had been engaging in the modification of this material to achieve unprecedented high EM shielding and absorption using the same benchmark. In this aspect, Han *et al*¹⁶² had achieved the few highest recorded EM absorption using the most common MXene, $\text{Ti}_3\text{C}_2\text{T}_x$, in pure form, reaching a 76.1 dB (SE) with 67.3 dB (SEA), at 1 μm thickness. In the same report, a similar sample using the RL measurement method yielded 30 dB (RL) which can be translated to 99.9% of absorption. The results are remarkable for they have yet to be replicated by others on the same material. In objectiveness, the benchmark should be taken to be the average value from most experiments,^{44, 132, 162, 165, 170, 171} at around 30.2 dB (SET) with

22.06 dB (SEA) using pure $\text{Ti}_3\text{C}_2\text{T}_x$ MXene without any modifications (calculated spanning multiple thicknesses between 100 μm to 1mm).

MXenes' unique metallic surface coupled with surface terminations that can alter the dielectric properties of the surface combines both reflection and absorption to provide effective shielding of EMI.¹⁷² Furthermore, their layered structure gives them a unique edge when it comes to attenuating EMI via multiple reflections unlike conventional shielding materials.¹⁶⁵ Since Shazad *et al*¹⁶⁵ reported the highest attained shielding effect of MXene, the material had become a popular one studied for EMI shielding. More intriguingly, majority of MXenes' EMS capability is contributed by absorption, Qing *et al*⁴² investigated the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene at the Ku band (12.4 to 18 GHz) and found that at the 14.6 GHz, a 1.4mm thick MXene can absorb about 98% of the incoming power. Whilst Liu *et al*¹⁷³ investigated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene from 2.0 GHz to 18 GHz and showed that a 2mm thick sample at 18 GHz has absorption contributing to 75% of the total shielding effect. This means that there is a huge possibility for the material to be adopted into more intricate circuitries, or other applications that requires the absorption capability, such as for energy conversion or radio masking.

Due to the layered structure, fillers can be introduced into the MXene layers to improve its EM absorption capability. The improvement in absorption comes from the improved impedance matching resulted from the changes in permittivity and permeability.¹⁷⁴ Liu *et al*⁴¹ incorporated Fe_3O_4 particles into the MXene matrix via hydrothermal to produce a hierarchical composite. The 1.9mm thick Fe_3O_4 decorated MXene sample has maximum absorption of -57.3 dB at 10.1 GHz and absorption range from 9.1-11.1 GHz. Feng *et al*¹⁷⁵ incorporated Ni^+ ions onto the MXene surface through the same process and showed that the composite has a broad absorption range of

6.9-18 GHz at 3 mm thickness, and 9-18 GHz at 2 mm thickness where the absorption is more than 90% and a peak corresponding to 99.5% absorption within the range. Alternatively, inculcating intrinsic conductive polymer could be incorporated into the material to improve the conductivity and surface activity on the material. Wei *et al*¹⁷⁶ incorporated polyaniline (PANI) in order to improve the electrical conductivity, they postulated that the difference in the electrical conductivity of the material could induce a capacitance effect to further attenuate the incoming EM wave. They found that by incorporating PANI, they could attain more than 90% of absorption with their best result at 99.8% absorbed at 13.8Hz at 1.8 mm thick.

Apart from fillers, surface modifications had been attempted on MXene to tune the dielectric properties and then to tune the absorption characteristic. Han *et al*¹⁶² converted the surface termination of as-etched $\text{Ti}_3\text{C}_2\text{T}_x$ to primarily oxygen termination via annealing, although they observed that the absorption of EMI did not improve in the X band, they showed that this is a viable way to tune the absorption characteristic. Recently, Wang *et al*¹⁷⁷ managed to achieve a slightly higher absorption effect based on the same annealing technique but the results were comparable with that of Han *et al*. A reference table of previous works on MXene is tabulated in

Table 3

Table 3 MXene based Electromagnetic Absorbers.

MXene composition	MXene synthesis method	Sample Type	Frequency Range	Thickness (mm)	Surface Modification	Filler	Conductivity (S/m)	Peak frequency (GHz)	Shielding effectiveness (dB)	Absorption Value/ Percentage (dB)/(%)	Calculation Method (RL, SE _A , ϵ)	Ref
Ti₃C₂T_x	9M HCl + 1g LiF	Aerogel	X band (8-12.4 GHz)	NA	-	-	220	12.2	75	98.67	SE _T	172
Ti₃C₂T_x	6M HCl + 1g LiF	Film	X band (8-12.4 GHz)	0.006	-	-	46651	8.2	59	59.32	SE _T	165
100 wt% Ti₂CT_x/Paraffin	12M HCl + 1g LiF	Pressed Film	X band (8-12 GHz)	0.8	-	-	30	NA	61.1 or 76.375 dB/mm	84.75	SE _T	44
90 wt% Ti₃C₂T_x/Paraffin	40% HF	Pressed film	X band (8-12.4 GHz)	1	-	-	10	NA	76.1	88.44	SE _T	162
90% Ti₃C₂T_x/Paraffin	40% HF	Pressed film	X band (8-12.4 GHz)	1	Ar annealed 800°C 2h	-	10	NA	32	75.00	SE _T	162
60 wt% Ti₃CT_x/Paraffin	40% HF	Pressed Film	C to Ku Band (2 to 18 GHz)	2	-	-	NA	NA	39.1	74.94	SE _T	173
60 wt% Ti₃C₂T_x/SA	6M HCl + 1g LiF	Film	X band (8-12.4 GHz)	0.008	-	-	NA	8.2	40	60	SE _T	165
55wt% Ti₃C₂T_x/Paraffin	9M HCl + 1.32g LiF	Block	C to Ku Band (2 to 18 GHz)	4	-	-	NA	17.1	-27.5	99.82	RL	178
50 wt% Ti₃CT_x/Paraffin	49% HF	Donut/Toroid	C band (4-8 GHz) X band (8-12 GHz) Ku band (12-18 GHz)	2	-	-	NA	7.8	-40	99.94	RL	179

MXene composition	MXene synthesis method	Sample Type	Frequency Range	Thickness (mm)	Surface Modification	Filler	Conductivity (S/m)	Peak frequency (GHz)	Shielding effectiveness (dB)	Absorption Value/ Percentage (dB)/(%)	Calculation Method (RL, SE _A , ϵ)	Ref
50% Ti₃C₂T_x/ Epoxy	50% HF	Block	Ku band (12-18 GHz)	1.4	-	-	NA	14.6	-11	92	RL	42
15 wt% Ti₃C₂T_x/ Epoxy	9M HCl + 2g LiF	Block	X band (8-12 GHz)	2	5% H ₂ / Ar annealed 200°C 2h	-	105	NA	41	80.48	SE _T	177
Ti₃C₂T_x/ MWCNT/ PVA:PSS	9M HCl + 4.8g LiF	Flake	X band (8.2-12.4 GHz)	0.000170	-	-	13000	NA	2.81	NA	SE _T	180
70% TiO₂/ Ti₃C₂T_x/ Fe₃O₄/ Paraffin	50% HF	Donut/ Toroid	C to Ku Band (2 to 18 GHz)	1.9	Hydrothermal ^a facile synthesis 150°C 5h	20 wt% Fe ₃ O ₄	NA	10.1	-57.3	99.9998	RL	181
Ti₃C₂T_x/ Co₃O₄/ Paraffin	40% HF	Donut/ Toroid	C to Ku Band (2 to 18 GHz)	5.5	Hydrothermal ^a facile synthesis 120°C 24h	1:9 Co ₃ O ₄	NA	5.47	-55.4	99.9997	RL	182
50% Ti₃C₂T_x/ TiO₂/ NiO/ C/ Paraffin	49% HF	Donut/ Toroid	C to Ku Band (2 to 18 GHz)	2	Hydrothermal ^a facile synthesis 180°C 12h	1:1 NiO	NA	15.2	-25	99.5	RL	175
50% Ti₃C₂T_x/ Ni²⁺/ Paraffin	49% HF	Donut/ Toroid	C to Ku Band (2 to 18 GHz)	2	KOH	1M Ni ²⁺	NA	11.2	-22	99.36	RL	174
50% Ti₃C₂T_x/ Ni	9M HCl + 2g LiF	Donut/ Toroid	C to Ku Band (2 to 18 GHz)	2.8	-	50 wt% Ni Chains	NA	NA	57.4	87.11	SE _T	183

2.2.4.2 Photothermal conversion

Energy from the sun is the most abundant energy yet it is also considerably the most untapped resource due to limitations in the method to tap solar energy. In this aspect, MXene possesses almost 100% efficiency in light-to-heat conversion based on Li *et al*³³ laser experiment. MXenes' ability to effectively absorb the sunlight could have been due to their outstanding electromagnetic wave absorption ability since the photothermal behaviour stems from absorption of EM waves albeit at different frequency. This inspired further investigation into applications to exploit MXenes' ability to convert light to heat.

It is postulated that the main mechanism of light to heat conversion in MXene is the localised surface plasmon resonance (LSPR) effect similar to that of metallic nanoparticles.¹⁸⁴ MXenes' high electron density of state near the Fermi level endowed it with highly conductive nature which is favourable for collective oscillations of free electrons driven by the incident EM waves it absorbs at visible and infrared range.¹⁸⁵ In fact, Ti₃C₂ nanosheets show a strong absorption in NIR region of 750–850 nm similar to that of Au and Ag nanoparticles.¹⁸⁶

Figure 10 Solar steam generation with MXene/MF/PVA composite (a) Schematic illustration of the fabrication of the 3D MXene architecture (3DMA), which is achieved by assembling Ti3C2 MXene nanosheets onto the melamine foam (MF) skeleton through a simple two-step dip coating process. (b) Schematic illustration of steam generation with the 3DMA floating at the air–water interface. (c) The light absorption spectra of the pristine MF and 3DMA-5 in the dry and wet states. (d) The temperature increasing process of the pristine MF and 3DMA-5 under solar illumination of 1 sun in air. (e) Temperatures of bulk water and 3DMA-5 surfaces under solar illumination of 1 sun as a function of irradiation time tested using an IR camera. Inset in (e) is the typical IR image at 10 min (f) Mass change of water with 3DMA-5 under solar illumination of different intensities. Inset in (f) is the real photograph showing 3DMA-5 floating at the air–water interface and steam generation under 5 sun illumination (g) Water evaporation rates (left-hand side axis) and the corresponding solar steam efficiencies (right-hand side axis) of the 3DMA-5 system under solar illumination of different intensities. (h) Cycling performance of 3DMA-5 under solar illumination of 1 sun. Credit: all figures extracted from Zhao et al.¹⁸⁷

To utilise the strong light to heat conversion property of MXenes, Zhao *et al*¹⁸⁷ impregnated a novel floating melamine foam-polyvinyl alcohol (MF/PVA) based structure with MXene to effect water surface directed heating (**Figure 10**). The MXene-Melamine 3D macroporous architecture (3DMA) encourages water to be transported up via mechanism like transpiration pull. The MXenes in the structure enhances the flow of water to the surface due to its hydrophilicity endowed by its surface terminations. The thermal conductivity of the channels is slightly higher than that of water when wet ($0.674 \text{ W m}^{-1} \text{ K}^{-1}$) encouraging heat transport to the water in the structure. The 3D structure encourages internal reflection and scattering of the light within the structure which improves the efficiency of the conversion. The temperature of the structure in water increased from room temperature (24°C) to 39°C in a short time of 10min, whilst the temperature could reach a staggering 80°C in air, the difference in temperature is due to the heat loss to the bulk of water. With the help from the structure, the evaporation rate of water was improved by 3.07 times from $0.426 \text{ kg m}^{-2} \text{ h}^{-1}$, under solar illumination of 1 sun, to $1.309 \text{ kg m}^{-2} \text{ h}^{-1}$.

Similarly, Mo *et al*¹⁸⁸ developed a composite between $\text{Ti}_3\text{C}_2\text{T}_x$ and PVA to encapsulate polyethylene glycol (PEG) for phase change material based thermal energy storage. MXene in the structure effectively restricted the leakage of molten PEG due to the strong hydrogen bond interactions between the hydroxyl groups of PEG and the surface terminations of MXene. The MXene/PVA structure also has improved thermal conductivity (from $0.101 \text{ W m}^{-1} \text{ K}^{-1}$ to $0.428 \text{ W m}^{-1} \text{ K}^{-1}$), for high power delivery. The group found that the increase in temperature is proportional to the amount of MXene in the structure. Whence, in the optimal condition, the temperature of the structure increased by 36.3°C under 1 sun illumination (100 mW cm^{-2}) with a photothermal

conversion efficiency of 96.5%. However, it is noted that the total energy that can be stored is relatively compromised.

To further improve the effect of LSPR, Fan *et al*¹³⁷ introduced Ag nanoparticles to the $\text{Ti}_3\text{C}_2\text{T}_x$ surface through facile synthesis. By combining the LSPR effect on Ag and LSPR effect on the MXene, the system could effectively convert light to heat. As the Ag@MXene is well dispersed in a polyurethane (PU) matrix, the heat energy can be well dissipated. In the report, the group made use of the heat generation to induce self-healing property to the PU polymer matrix. The minimum required loading to reach the temperature above PU's melting point of 95°C within 3 minutes of exposure under illumination of 6 sun is around 0.8 wt% loading of the Ag@MXene hybrid particles. The healing efficiency is calculated by the ratio of tensile strength of healed material and tensile strength of the original material, and the healing can reach up to 98% for a 0.16 wt% loading (97% for 0.8 wt% loading) after 5 min of illumination. The material had almost fully recovered after merely 5 min of photothermal healing.

2.2.5 Outlook for MXenes in energy applications

Considering the multitude of applications and myriad of variation of MXenes. There is no doubt that the exploration of MXene is still at its nascent stage. It is a novel material with unlimited potential especially in energy conversion and storage. Over the years, MXene had undergone different modifications using strategies such as intercalation and surface modification to activate the potential of MXene. In this literature review, the showcase of applications of MXene is limited to electromagnetic absorber and photothermal conversion because they are most relevant to the research in this thesis. The material shows promising application in other energy applications as

well, especially in batteries. Notwithstanding the fact that the material is a 2DM which exhibits anisotropic properties, suggesting that it has potential to be exploited by tapping into the anisotropy, yet there are few papers studying this aspect of the material.

Chapter 3: Intercalating PdSe₂ for ORR Catalysis

As introduced in Chapter 2, ORR has wide application ranging from metal-air batteries to fuel cells. Typically, precious metals platinum (Pt)-based materials are used as the electrocatalysts, however, the high cost and scarcity of these precious metals are hindering their widespread implementation. Methods to reduce the usage of precious metals without compromising the catalytic activity are highly desirable.¹⁸⁹ A facile and effective way is to mix precious metals with nonprecious elements, *e.g.*, Pt mixed with carbon black.⁷¹ Another effective way is to forming precious metal alloy or compound, *e.g.*, Pt₃M alloys (M = Ni, Co, Fe, V, Ti, Sc, Y) show high ORR activity with significantly lowered Pt loading.¹⁹⁰⁻¹⁹⁵ Newly developed strategy is to introduce phosphorus (P) into the precious metal to reduce the precious metal loading such as RuP₂,⁹⁰ IrP₂,⁸⁹ and the most recent PtP₂.⁸⁸ By introducing P, the mass activity of PtP₂ had seen significant improvement for ORR in alkaline medium. Alternative to Pt, another superior ORR catalyst, palladium (Pd) has also been extensively studied.¹⁹⁶⁻¹⁹⁸ Being more abundant than Pt, Pd could serve as a perfect alternative to Pt. Phosphor (P)-doped Pd exhibits very high catalytic activity owing to its amorphous structure.^{91, 92} Electrodeposited palladium–gold (PdAu) alloys also show excellent performances in both acidic and basic medias.¹⁹⁹⁻²⁰¹

2DMs have atomic-thick layer as their basic unit cell, which could maximise the exposure of atoms to its surroundings, and thus maximise the catalyst surface with the same amount of material used. Moreover, 2D materials have much better stabilities than other nanomaterials of similar sizes as their surfaces are free of dangling bonds.²⁰²⁻²⁰⁶ Palladium diselenide (PdSe₂) is a Pd-based 2D TMD that is potentially a promising electrocatalyst due to its excellent electrical conductivity and containing Pd.^{207, 208} Moreover, the mass of Pd in PdSe₂ is 60% lower than that of pure Pd metal,

implying lower Pd loading for electrocatalysis. Monolayer PdSe₂ has recently been exfoliated from its bulk crystals and shows excellent electrical conductivity and stability in air.^{208, 209} 2D PdSe₂ has been employed to catalyse water-splitting,²¹⁰ and the PdSe₂ crystal prepared at high-temperature shows excellent electrical properties but limited catalytic activity, due to its perfect crystallinity (*i.e.*, free of defects) and inaccessible interlayer space. Generally, strategies to activate 2D catalysts include: (1) creating vacancies/defects,²¹¹⁻²¹³ (2) applying elastic strain,²¹⁴ and (3) doping or alloying.^{211, 215-218} One of the unique properties of 2D layered materials is that their layered geometry allows guest species, *e.g.*, lithium (Li), sodium, magnesium, copper, *etc.*,²¹⁹⁻²²² to be inserted between the layers via intercalation to alter the physical and chemical properties of the pristine materials.

Figure 11 Schematic of electrochemical intercalation process of PdSe₂.

In this chapter, we employed electrochemical intercalation process to activate PdSe₂ for ORR catalysis. Li ions are controllably inserted and extracted from the PdSe₂ crystal *in situ* without modifying the electrode morphology or the phase of the material. The schematic PdSe₂ before (pristine) and after the electrochemical activation process (I-PdSe₂) is illustrated in **Figure 11**. The activated PdSe₂ shows greatly improved electrocatalytic activity including more than 100%

increase in current density, 250 mV positive shift of potential, and 5 times decrease in Tafel slope. Though typically there is a trade-off between activity and stability of catalyst because high activity indicate stronger chemical interaction between reaction intermediates and catalyst surface, it is noted that the stability is also greatly enhanced, attributed to the sustained *2L* phase,²⁰⁸ which is different from other TMD electrocatalysts that experience a *2H*-to-*1T* phase change during intercalation.²²³⁻²²⁵ With the complementary theoretical modelling, the electrochemical activation of PdSe₂ ORR catalyst is attributed to two factors: (1) the electric potential-forced Li insertion/extraction creates defects that facilitate the adsorption of oxygen molecules, and (2) the intercalation process increases the interlayer distance and makes much more surface accessible for oxygen species.

3.1 Experimental section

3.1.1 Synthesis of intercalated PdSe₂ (I-PdSe₂)

Bulk PdSe₂ single crystals were grown by a self-flux method through melting stoichiometric amounts of Pd powder and Se powder.²⁰⁸ I-PdSe₂ was obtained by activating PdSe₂ via electrochemical intercalation with lithium hexafluorophosphate, as schematically illustrated in **Figure 11**. A certain amount PdSe₂ and polyvinylidene fluoride (PVDF) were dispersed in 10 ml N-methyl-2-pyrrolidone (NMP) and ultrasonicated for 24 h (the ratio of PdSe₂: PVDF was 9:1), and then coated on copper foil to about 3 cm by 4 cm. The sample was then attached to a Land Battery tester in argon atmosphere to perform the intercalation. After which, the sample was removed from the copper foil through a few rounds of ultrasonication and centrifugation. The sample preparation method was repeated with intercalation current (current density) of 25 μ A (2.08

$\mu\text{A cm}^{-2}$), 50 μA (4.17 $\mu\text{A cm}^{-2}$) and 100 μA (8.33 $\mu\text{A cm}^{-2}$), where the samples were denoted as I-PdSe₂-25, I-PdSe₂ and I-PdSe₂-100, respectively.

3.1.2 Physical characterizations

The crystal phase and structure were examined by X-ray diffraction (XRD, Panalytical Xpert Pro) with Cu K α ($\lambda = 0.15406$ nm) radiation in the range of 10–90°. Raman spectra were obtained using a WITec CRM200 confocal Raman microscopy system with the excitation line of 488 nm. The morphology of the samples was examined by transmission electron microscopy (TEM, JEOL-2010) at an acceleration voltage of 200 KV. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Kratos AXIS Supra with an Al Ka source ($h\nu = 1486.6$ eV).

3.1.3 Electrochemical measurements

Electrochemical measurements were carried out with a conventional three-electrode system on an electrochemical workstation (Gamry Potentiostat Reference 600) at room temperature. Platinum wire and Ag/AgCl (Saturated KCl) electrode were used as the auxiliary and reference electrodes, respectively. All potentials in this study were given versus reversible hydrogen electrode (RHE) according to the following equation

$$E(RHE) = E(Ag/AgCl) + 0.059 \times pH + 0.198$$

The working electrode was prepared as follows: 4 mg of material (the ratio of the as-prepared catalyst: acetylene black was 1:1) and 12 μL of Nafion solution (5 wt%) were dispersed in 2 mL isopropanol solution by sonication for 30 min. Then, 25 μL of the catalyst ink was dropped on the

glassy carbon electrode surface ($D = 5$ mm). For comparison, the commercial Pt/C (20 wt% Pt, Alpha Aesar) catalyst ink was prepared by following the same procedure.

A rotating disk electrode (RDE) measurement was performed in O₂-saturated 0.1 M KOH solution at different rotation rates (400-1600 rpm) with a scan rate of 5 mV s⁻¹ from -1 V to 0.2 V (vs. Ag/AgCl).

The number of transferred electrons (n) calculated from RDE test was based on the Koutecky-Levich (K-L) equation:

$$I_d^{-1} = i_{dl}^{-1} + i_k^{-1} = \left(B \omega^{\frac{1}{2}} \right)^{-1} + i_k^{-1}$$

$$B = 0.62nFCo(D_o)^{\frac{2}{3}}\nu^{-\frac{1}{6}}$$

where i_d is the measured current density, i_k and i_{dl} are the kinetic and film diffusion-limiting current densities, and B is the reciprocal of the slope, ω is the angular velocity of the disk ($\omega = 2\pi N$, where N is the linear rotation speed), n is the number of electrons in oxygen reduction, F is the Faraday constant (96500 C · mol⁻¹), Co is O₂ volume concentration in 0.1 M KOH (1.14×10^{-6} mol · cm⁻³), ν is the kinematic viscosity of the electrolyte (0.01 cm² · s⁻¹), and Do is the diffusion coefficient of O₂ in 0.1 M KOH (1.73×10^{-5} cm² · s⁻¹).

Tafel slope was calculated according to Tafel equation:

$$E = a + b \log(j_k)$$

where E is the applied potential in the LSV test, a is a constant, b is the Tafel slope and j_k is the kinetic current density.

The electrochemically active surface areas (ECSA) were estimated from the electrochemical double-layer capacitance (Cdl) by collecting cyclic voltammograms (CV) in a non-Faradaic region of 1.06 – 1.16 V vs RHE following the equation

$$ECSA = \frac{Cdl}{Cdl_{ref}}$$

where Cdl is the double layer capacitance measured by CV scan in non-Faradaic potential window. The reference Cdl_{ref} is typically around 20 to 80 $\mu\text{F}\cdot\text{cm}^{-2}$,^{226, 227} and thus we adopted the Cdl_{ref} around the middle value of 60 $\mu\text{F}\cdot\text{cm}^{-2}$ which is consistent with those of reported precious metals including Pd.²²⁸⁻²³⁰

The CV tests were recorded over an applied potential range of 1.06 to 1.17 V vs RHE. The potential range is constant for all catalysts and the same scan rates of 40, 60, 80, and 100 mV s^{-1} were selected.

3.1.4 Computational details

The density function theory (DFT) calculations were performed by Vienna Ab-initio Simulation Package (VASP).²³¹ The exchange-correlation energy functional was described within the generalised gradient approximation (GGA)²³² in the Perdew-Burke-Ernzerhof (PBE) functional.²³³ The projector augmented wave (PAW)²³⁴ potentials were used with a 520 eV cut-off energy and the Brillouin zone integration was sampled by a $3\times 3\times 1$ k-grid mesh for a unit cell.

The van der Waals interactions were described by DFT-D2 approach of Grimme,²³⁵ and spin polarisation effect was considered. The convergence criteria for the energy and force were set to 1×10^{-5} eV and 0.02 eV/Å, respectively.

The defect formation energy (E_f) of Se was calculated using following equation:

$$E_f = E_D - E_P + N_{Se}\mu_{Se}$$

where E_D and E_P are the calculated ground state energy of defected and pristine model, respectively; N_{Se} corresponds to the number of defected Se atoms; and μ_{Se} represents the chemical potential of Se which was obtained from bulk octaselenium ring structure.

The overall reaction of O₂ reduction to OH⁻ in alkaline media is as follows:

To examine ORR performance, following associative mechanism with the four-electron reaction pathway is considered in the calculations:

The sign * refers to an active site on the catalyst models. The Gibbs free energy of adsorption is calculated by following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_w$$

where ΔE is the adsorption energy which can be directly obtained from the calculations; ΔZPE is the zero point energy corrections and ΔS is the vibrational entropy contribution at room temperature ($T = 298.15$ K).²⁸ $\Delta G_U = -eU$, where U is the electrode potential; ΔG_{pH} is the correction of the H⁺ free energy where $\Delta G_{pH} = -k_B T \ln(10) \times pH$ (k_B is Boltzmann's constant and $pH = 13$); ΔG_w is the stabilization energy by water molecules calculated by implicit solvation model.²³⁶ The free energy of O₂ was derived from $G_{O_2} = 2G_{H_2O(l)} - 2G_{H_2} + 4.92$ eV. The free energy of H₂O_(g) and H₂ was calculated in the gas phase at room temperature. The free energy of H₂O_(l) was calculated by $G_{H_2O(l)} = G_{H_2O(g)} + RT * \ln(\frac{p}{p_0})$, where R is the ideal gas constant, $T = 298.15$ K, $p = 0.035$ bar, and $p_0 = 1$ bar.

The overpotential was calculated by $\eta_{RHE} = 1.23 - \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]$. Free energy changes of each reaction step are shown in **Table 4**.

Table 4 Free energy change for each reaction steps of pristine and defective models with different active sites.

	ΔG_1	ΔG_2	ΔG_3	ΔG_4
PdSe₂	0.353 eV	-2.582 eV	-0.718 eV	-1.973 eV
I-PdSe₂	0.482 eV	-2.697 eV	-0.007 eV	-2.698 eV
I-PdSe₂ (L1)	-1.075 eV	-2.892 eV	-0.246 eV	-0.707 eV
I-PdSe₂ (L2)	0.419 eV	-2.629 eV	-0.008 eV	-2.702 eV
I-PdSe₂ (2L)	0.318 eV	-2.524 eV	-0.347 eV	-2.366 eV
I-PdSe₂ (L1_2L)	0.300 eV	-2.536 eV	-0.103 eV	-2.581 eV
I-PdSe₂ (L2_2L)	-1.249 eV	-2.717 eV	-0.090 eV	-0.865 eV

3.2 Results and discussion

Figure 12 (a) XRD pattern shows that the (002) peak of PdSe₂ at 23.1° remains almost unchanged suggesting that interlayer spacing increment is small after delithiation which is crucial for electrode stability (b) Raman spectra shows the main peaks of PdSe₂ occurs around ~143.65,

206.62, 222.27 and 257.32 cm^{-1} while that of I-PdSe₂ occurs at ~142.86, 205.06, 220.70 and 256.54 cm^{-1} , indicating a redshift which suggests the bond length increasing (c,d) TEM images (e,f) HRTEM images of PdSe₂ and I- PdSe₂ show high degree of crystallinity with no obvious defects, arising from the high-temperature growth process. Insets of (c) and (d): the corresponding Fourier transform pattern indicating high degree of crystallinity.

When the as-prepared PdSe₂ is subjected to the Li intercalation forced by an electric potential, the interlayer distance increases due to the relatively larger diameter of Li ion compared to the van der Waal gap. This expands the volume of the crystal, and thus allows the diffusion of the ions between layers and encourages oxygen diffusion into the interlayer space.²³⁷ Subsequently, the chemically active parts of the crystal, *e.g.*, the edge, grain boundaries, are activated by the reactive and energetic Li ions, and structure defects such as Se vacancies are created.

X-ray diffraction (XRD) and Raman spectroscopy were performed to establish the crystal structure, as shown in **Figure 12a** and **Figure 12b**, respectively. Despite the lithiation process, the XRD shows that the major PdSe₂ peaks have been retained after intercalation, suggesting similar crystallinity. It is noted that there is no obvious shift of the (002) peaks at 23.1° but an overall change of 0.1° (**Table 5**), suggesting that the interlayer spacing increment is small after delithiation, which is crucial to maintaining the electrode integrity after activation process. However, the presence of newly formed bump on the left the (002) peak evidently suggests strain broadening of the lattice which can be attributed to the intercalated foreign species that could have been lodged in between the plane.²³⁸ The lodged molecules in this case could have contributed to exposing the interplanar layers to increase activity through improved oxygen diffusion²³⁹ as evident from the improvement of electrochemical surface area (ECSA), which will be discussed later.

Table 5 Fitting of 002 peak on XRD spectrum.

	I-PdSe₂	PdSe₂
FWHM	0.1686	0.1385
Peak Position	23.22	23.09449
Area	150.06131	16399.5184
Interlayer distance	0.38275 nm	0.3848 nm
Est. # layers	2.19344	2.655

The Raman spectrum in **Figure 12b** shows negligible change of peak position or width, suggesting no dramatic chemical composition/structure change has occurred. The main peaks of PdSe₂ occurs around ~143.65, 206.62, 222.27 and 257.32 cm⁻¹ while that of I-PdSe₂ occurs at ~142.86, 205.06, 220.70 and 256.54 cm⁻¹, indicating a redshift which suggests the bond length increasing. This could be attributed to the effect of introducing lithium into the structure that induced strain on the layer²⁴⁰ and loosening the chemical bond of the structure which is consistent with the XRD characterisation. Transmission electron microscopy (TEM) images in **Figure 12c** and **Figure 12d** further confirm that there is no obvious difference in morphology between flakes of PdSe₂ and I-PdSe₂, suggesting the maintaining of structural integrity after activation process.

The high-resolution TEM (HRTEM) image of pristine PdSe₂ (**Figure 12e**) and the corresponding Fourier transform pattern (Inset of **Figure 12e**) show high degree of crystallinity with no obvious defects, arising from the high-temperature growth process, which ensures the superior electrical properties. The interlayer spacing is 0.29 nm, corresponding to the (002) face of PdSe₂. The HRTEM image of I-PdSe₂ in **Figure 12f** confirms the structural integrity and good crystallinity of PdSe₂ after the activation process. Moreover, the corresponding Fourier transform pattern (inset of **Figure 12f**) supports the slight variation of crystallinity after the activation.

Figure 13 XPS spectra of PdSe₂ and I-PdSe₂ (a) shows no notable difference before and after activation, the presence of F 1s and change in C 1s signals is due to the intercalation agent (PVDF) in the sample. The high-resolution XPS curves of (b) Pd 3d spectrum shows a minor downshift which could be caused by decrease of Pd oxidation state due to the new Se vacancies, (c) Se 3d spectrum peaks tend to merge due to weakening of Se peak intensity, and (d) O 1s spectrum corresponding to the lattice oxygen species, hydroxide species and the surface adsorbed oxygen. The increase in adsorbed oxygen suggests the structure defects created during intercalation enhances the affinity to oxygen intermediates that promotes ORR.

The detailed chemical composition was further examined by X-ray photoelectron spectroscopy (XPS). No notable difference can be seen in the XPS spectrum before and after activation (**Figure 13a**), indicating that all the elements and chemical bonds have been preserved in I-PdSe₂ during activation. The emerging F 1s peak after intercalation at the high energy region

could come from the residual of intercalation agent (*i.e.*, PDVF) in the sample, which agrees with the new carbon peaks in C 1s spectrum.

The Pd 3d XPS spectrum of PdSe₂ crystal (**Figure 13b**), exhibits doublet peaks at around 335.5 eV and 340.8 eV, corresponding to the 3d_{5/2} and 3d_{3/2} components of PdSe₂, respectively. The minor downshift of Pd peaks in I-PdSe₂ could be caused by the decrease of Pd oxidation state arising from Se vacancies created in the activation process. As suggested in previous report,²⁰⁸ the Li⁺ species could have formed bonds with Se during the lithiation process hence allows the easy dissociation of Se during de-lithiation.

The Se 3d spectrum (**Figure 13c**) consists of two peaks corresponding to Se 3d_{5/2} and 3d_{3/2}, respectively, and they tend to merge due to weakening of Se peak intensity, which can be ascribed to Se vacancies formed during intercalation. Fitting of XPS spectra indicates decreasing of Se:Pd ratio from 1.6947 to 1.5867 due to intercalation (**Table 6**), suggesting the loss of Se. Introducing Se vacancies allows ORR intermediates to contact the interlayer Pd more easily. As a precious metal, Pd's high selectivity and affinity to oxygen^{69, 241, 242} plays a huge part at capturing O₂ for further reduction process as O₂ binds and dissociates readily on Pd.²⁴¹ This means that the O-O bonds in the ORR intermediates could actively interact with the newly exposed interlayer Pd.

Table 6 Atomic% of Pd and Se and Se:Pd Ratio in PdSe₂ and I-PdSe₂ calculated from XPS spectrum.

	<i>Element</i>	<i>At%</i>	<i>Se:Pd Ratio</i>
PdSe₂	Pd	37.74	1.6497
	Se	62.26	
I-PdSe₂	Pd	38.66	1.5867
	Se	61.34	

The O1s spectrum (**Figure 13d**) was deconvoluted into three peaks located at 530.4, 531.9 and 533.4 eV, corresponding to the lattice oxygen species, hydroxide species and the surface adsorbed oxygen, respectively.²⁴³ The increase in lattice oxygen in I-PdSe₂ sample, further supports that activation process generated surface vacancies that are prone to be oxidised. At the same time, the intercalation increased the amount of adsorbed oxygen, suggesting the structure defects created during intercalation have good affinity to oxygen species. And the enhanced affinity to oxygen intermediates can promote catalytic oxygen reduction reaction.

Figure 14 Electrochemical performances of PdSe₂, I-PdSe₂-25, I-PdSe₂-50, I-PdSe₂-100, and Pt/C. (a) ORR polarisation curves shows that the highest increase in half-wave potential is around 250 mV in I-PdSe₂-50 (green line) compared to that of pristine PdSe₂ (black line) and (b) corresponding Tafel plots of I-PdSe₂-50 shows a smaller Tafel slope of 64 mV dec⁻¹ (green line) compared to Pt/C 74 mV dec⁻¹ (blue line) indicates better kinetics (c) ECSA of I-PdSe₂ is around 8 times more than that of PdSe₂ indicating more active sites are created, and (d) chronoamperometric curves in O₂-saturated 0.1 M KOH solution at 400 rpm under a potential of 0.55 V versus RHE indicates that I-PdSe₂-50 is very stable (green line, <1% drop after initial drop)

compared to that of Pt/C (blue line, more than 35% continuous drop) (e) LSV after 28800s Chronoamperometric test for I-PdSe₂

Figure 14a shows the LSV curves of PdSe₂, I-PdSe₂-25, I-PdSe₂-50, I-PdSe₂-100 and commercial 20 wt% Pt/C, where the number at the back signifies the intercalation current applied (in μA), and a summary of the performances is presented in **Table 7**. Apparently, I-PdSe₂-50 exhibits more positive potentials (both onset and half-wave potentials) and larger diffusion-limited current density than PdSe₂, I-PdSe₂-25 and I-PdSe₂-100, indicating I-PdSe₂-50 has an optimised ORR activity.

Table 7 Half-wave potentials, mass activities and electron transfer number of as prepared catalysts.

Catalyst	Half-wave Potentials (V)	Mass activities ($\text{mA } \mu\text{g}^{-1}_{\text{Pd}}$)	Electron Transfer Number (n)
PdSe ₂	0.58	0.030	2.58
I- PdSe ₂ -25	0.74	0.042	2.69
I- PdSe ₂ -50	0.76	0.054	3.67
I- PdSe ₂ -100	0.71	0.040	2.89
Pt/C	0.79	0.063	3.97

Figure 15 LSV curves of (a) PdSe₂, (b) I-PdSe₂ -25, (c) I-PdSe₂ -50, (d) I-PdSe₂ -100 and (e) Pt/C catalysts in O₂-saturated 0.1 M KOH solution at different rotation speeds with a sweep rate of 10 mV s⁻¹. Inset: Koutecky-Levich plots (j^{-1} Vs $\omega^{-1/2}$) relationship. Inset shows the transfer number which indicates the electron steps involved. $n=4$ indicates 4-electron pathway.

To further unravel the reaction kinetics for ORR, the LSV measurements at 400-1600 rpm were performed, and the kinetic parameters were calculated by Koutecky-Levich (K-L) equation, as shown in **Figure 15**. The diffusion-limited current densities of different samples show an increasing trend due to the higher rate of diffusion. The fitting K-L plots show linear relationships between j^{-1} and $\omega^{-1/2}$ under each potential. The number of transferred electrons n for I-PdSe₂-50 was calculated to be 3.67 at different potentials from 0.2 V to 0.6 V (inset of **Figure 15**), indicating a four-electron dominated transfer pathway for ORR. The higher electron transfer number of I-PdSe₂-50, than those of I-PdSe₂-25 and I-PdSe₂-100, indicates a better suppression of formation of HO₂⁻ during the conversion of O₂ into OH⁻, in turn translating to the better performance of ORR conversion since the desired four-electron pathway is dominant.²⁴⁴

Figure 16 CV curves in the region of 1.06-1.17 V at scan rates from 40 to 100 mV s⁻¹ and corresponding linear fitting of capacitive current: (a) and (b) for PdSe₂, (c) and (d) for I-PdSe₂; (e) and (f) for Pt/C. Cdl indicates electrochemical double-layer capacitance. The higher the Cdl the higher the ECSA which means presence of more active materials.

Optimization at intercalation current density of $4.17 \mu\text{A cm}^{-2}$, *i.e.*, current of $50 \mu\text{A}$, could be a result of balanced rate of intercalation. A high intercalation current density of $8.33 \mu\text{A cm}^{-2}$ (current of $100 \mu\text{A}$) decreases the effectiveness of intercalation where the intercalation could be incomplete due to drastic interlayer ion drifting and hence insufficient to expose all interlayer active sites.²⁴⁵ On the other hand, a low current density of $2.08 \mu\text{A cm}^{-2}$ (current of $25 \mu\text{A}$) enables a milder intercalation and might have been insufficient to create abundant active sites. Moreover, a slow rate of intercalation could allow the build-up of solid electrolyte interface from the breakdown of electrolyte on the surface of the PdSe₂,^{246, 247} which creates a protective layer that shields the material from defects formation or blocks the active sites.²⁴⁸

The corresponding Tafel slope (**Figure 14b**) of I-PdSe₂-50 was calculated to be 64 mV dec^{-1} , smaller than that of Pt/C (74 mV dec^{-1}), suggesting the faster kinetics process than Pt/C. The electrochemical double-layer capacitance (*C_{dl}*) was measured to obtain ECSA. Cyclic voltammetry (CV) was performed to evaluate *C_{dl}* and then to calculate the ECSA of various catalysts. The CV curves recorded at different scan rates for all catalysts, and the linear fitting of current density versus scan rate are displayed in **Figure 16**. The summary of ECSA values is shown in **Figure 14c**, and I-PdSe₂ has a much greater ECSA than pristine PdSe₂, confirming that the ORR active sites density has been dramatically increased by intercalation.

Next, the stability of the catalysts was examined. As shown in **Figure 14d**, I-PdSe₂ exhibits 14.5% decrease after 28800-s continuous operation, showing a much better durability and stability than Pt/C which displays a faster current loss about 35% under the same conditions. The change in half-wave potential and loss of diffusion-limited current density are almost negligible, as shown in **Figure 14e**, further supporting the stability of I-PdSe₂-50. The lack of durability of the Pt/C

relative to I-PdSe₂-50 can be attributed to the loose carbon black constituent in the commercial Pt/C catalyst that leads to easily dissolved Pt particles and aggregation under working conditions.⁷³ The excellent stability of I-PdSe₂-50 is attributed to the retained thermodynamically stable *2L* phase after intercalation, which is different from *2H*-to-*1T* phase transition caused by Li interaction in other TMD electrocatalysts including molybdenum sulfide, tungsten sulfide etc.^{223-225, 237} To benchmark the optimised catalyst I-PdSe₂, the catalytic performance of some other Pd-based ORR electrocatalysts are compared in **Table 8**, which shows that I-PdSe₂-50 is among the best in terms of balanced performance and stability despite the ease of activation process. It is worth noting that, despite the robustness and durability of the material, it is still based on precious metal catalysts, thus it is unable to resist the methanol crossover during ORR process.²⁴⁹⁻²⁵¹

Table 8 Performance of I-PdSe₂ catalyst and several representative results about Pd compound from recent published works.

Catalyst	Half-wave	Mass	Stability		Ref
	Potentials (V)	activities (mA mg ⁻¹ _{Pd})	Δhalf-wave,j (mA cm ⁻²) (after x cycles)	ΔE (mV) (after x cycles)	
I- PdSe ₂	0.76	0.112	+0.2	-20	This work
Pd ₃ Fe NPs/CB	0.79	0.298	+0.1 (1500)	+40 (1500)	80
MoS ₂ /Pd	0.75	0.553	-0.2 (4000)	0 (4000)	79
Ni@Pd ₃	0.75	0.098	+0.1 (3000)	-1 (3000)	82
Pd/FePt	0.7	0.067	+1.0 (10000)	0 (10000)	97
PdNiSn/NG	0.75	0.164	0 (5000)	+0.1 (5000)	98
Pd-g- C ₃ N ₄	0.7	0.072	8% activity loss (40000s)	-	99
Pd-Pt /C	0.75	0.224	+0.2 (10000)	-20 (10000)	100
Pd-Fe	0.77	0.085	undetermined	undetermined	101
Pd-Co/C	0.75	0.063	undetermined	undetermined	102
Pd ₂ -Co alloy	0.71	0.041	undetermined	undetermined	103
Cu-Pd	0.81	0.0423	+0 (1000)	-6 (1000)	85
Pd/Ni	0.65	0.141	60% loss in ECSA (400)	-	104

Figure 17 (a) Model systems of PdSe₂ and I-PdSe₂. (Pd: blue, Se: yellow). The top view of the first (L1) and second (L2) layer and the lateral views of PdSe₂, I-PdSe₂. (b) Defect formation energy for each defective models. Insets: The corresponding schematic models of 5 different defect types. (c) Gibbs free energy of the oxygen reduction reaction (ORR) at equilibrium potential (U₀) for pristine and defective models with various active sites.

Density functional theory (DFT) calculations were further calculated to evaluate the stability and ORR activity for PdSe₂ and I-PdSe₂. In our calculations, bulk PdSe₂ structure has lattice parameters of $a = 5.82 \text{ \AA}$, $b = 5.91 \text{ \AA}$ and $c = 7.40 \text{ \AA}$, consistent with experimental values.²⁵² For I-PdSe₂ model, the interplanar distance was doubled as depicted in **Figure 17a** to observe the ORR activity between layers. The (001) facets of 2×2 supercell for both PdSe₂ and I-PdSe₂ were modelled with periodically repeating 4-layer slab with a vacuum of about $15 \text{ \AA}$ along the direction

normal to the sheet plane to avoid interaction between the periodic images, as shown in **Figure 17a**. The bottom two layers were fixed in their bulk positions.

Figure 18 (a) COHP of the bond between Se and Pd on the surface for PdSe₂ (black) and I-PdSe₂ (blue). The Fermi energy is set to 0 eV (b) Top view of the second layer (2L) for pristine and defective I-PdSe₂ with adsorbed intermediates (i) O, (ii) OH and (iii) OOH.

To evaluate the stability, the defect formation energy for PdSe₂ and I-PdSe₂ with various defect formation pathways were calculated, as presented in **Figure 17b**. Since it is well known that defect formation of a Se is more favourable than that of Pd, the models with Se defects were constructed. There are 5 types of defective models as shown in the inset of **Figure 17b**. Two of them are the models with one Se defect on the first (L1) and the second layer (L2) each. Since there is a high chance that the first Se defect is already formed during de-lithiation, the formation energy of the second Se defect was also analysed to evaluate the stability during ORR process. Therefore, rest of the models have two Se defects, *i.e.*, two defects on the first layer (L1L1), one defect on each layer (L1L2), and two defects on the second layer (L2L2). I-PdSe₂ shows greater

defect formation energy than PdSe₂, suggesting higher stability against defect formation. To obtain more insights into the Se defect formation energy and the nature of chemical bond between Pd and Se, the defect formation on the surface was examined by Crystal Orbital Hamilton Populations (COHP) analysis, which separates the band structure energy into bonding (negative value), nonbonding, and antibonding (positive value) contributions.²⁵³ As shown in **Figure 18a**, COHP plot of PdSe₂ (black) is positioned at lower energy than that of I-PdSe₂ (blue) indicating more electrons are involved in Pd-Se bonding because of the covalent-like quasi-bond between layers.²⁵⁴ As the anti-bonding orbitals are crossing the Fermi energy, more electrons are occupying anti-bonding orbital for PdSe₂ than I-PdSe₂ leading to weaker bond strength. The integrated COHP (ICOHP) in **Table 9**, which summarises the electrons filled in states up to the Fermi energy in COHP, also indicates Pd-Se bonding in I-PdSe₂ is more stable than that in PdSe₂. Additionally, bond length between Se and two adjacent Pd are compared in **Table 10**, where I-PdSe₂ has slightly smaller Pd-Se bond length than PdSe₂, implying stronger bond strength between Pd and Se.

Table 9 ICOHP value of the bond between Se and Pd on the surface.

<i>ICOHP</i>	<i>PdSe₂</i>	<i>I-PdSe₂</i>
Se-Pd1	-1.027	-1.048

Table 10 Bond length between Se and adjacent Pd.

Bond length	PdSe₂	I-PdSe₂
Se-Pd1	2.46 Å	2.45 Å
Se-Pd2	2.48 Å	2.47 Å

For PdSe₂, a Se defect formation on the first layer (L1, 1.71 eV) is more difficult than that on the second layer (L2, 1.68 eV). After the formation of the Se defect on the first layer (L1), subsequent Se defect can be formed on both layers with less energy, *i.e.*, the first layer next to the already formed one (L1L1, 1.57 eV) or the second layer (L1L2, 1.58 eV). For the case when a defect is formed on the second layer (L2), it is easier for the second Se defect to be formed on the same layer (L2L2, 1.14 eV) than on the first layer (L2L1, 1.71 eV). The defect formation energy on I-PdSe₂ for L1 (2.21 eV), L1L2 (2.25 eV), L2 (2.24 eV) and L2L1 (2.22 eV) are similar as the interlayer interaction is weaker than that of PdSe₂ due to the larger interlayer distance. The second Se defect forms relatively easier on the layer with existing first defect (L1L1, 2.03 eV; L2L2, 2.05 eV); however, these defect formations are still endothermic which requires high energy to overcome. In other words, even a Se defect is formed during de-lithiation process, the subsequent Se defect formation is still unfavourable which leads to the high stability of I-PdSe₂.

Next, the influence of the defect and increased interlayer distance on ORR activity for I-PdSe₂²⁵⁵ was examined. **Figure 17c** shows the Gibbs free energy diagrams on the associative 4e⁻ reaction pathways in alkaline medium (pH = 13) calculated using previously developed method⁶⁶ for pristine PdSe₂, pristine I-PdSe₂, I-PdSe₂ (L1) and I-PdSe₂ (L2) models. Due to the larger interlayer distance of I-PdSe₂ than that of PdSe₂, we assumed that O₂ can access interlayer space and the catalytic reaction can occur on the second layer (2L), as shown in **Figure 18b**. Therefore, ORR not only on the first layer (solid line) but also on the second layer (2L, dotted line) of I-PdSe₂ were also presented. The Gibbs free energy diagram exhibits the lowest overall reaction energy change at equilibrium potential (U^0), suggesting their theoretical ORR performance. For pristine PdSe₂ (black) and I-PdSe₂ (blue), the rate-determining step is evaluated as the first electron transfer step to form chemisorbed OOH* from H₂O (ΔG_1) for both models. The first electron transfer step

is the adsorption of OOH which is an endothermic reaction with overpotential of (η_{RHE}) of 1.58 V for PdSe₂ and 1.71 V for I-PdSe₂. The rate-determining steps are determined as the first electron transfer step for all but two models. The two exceptions are the I-PdSe₂ with a defect on the first layer (I-PdSe₂ (L1)) and I-PdSe₂ with a defect on the second layer whose active site is also on the second layer (I-PdSe₂ (L2_2L)). I-PdSe₂ (L1) and I-PdSe₂ (L2_2L) show high ORR performance with different rate-determining step, the third electron transfer step (ΔG_3) where overpotential is 0.98 eV and 1.14 eV, respectively. These two models are the ones that intermediates adsorbed on the defect site. The defect increases the adsorption energy of OOH which changes the rate-determining step and decreases the overpotential of ORR. The ORR overpotentials on the I-PdSe₂ are similar or smaller to those of the PdSe₂ indicating the surface area with similar or better activity compared to PdSe₂ have increased for I-PdSe₂. Therefore, one can conclude that the conversion from PdSe₂ to I-PdSe₂ activates the ORR by enriched and diversified active sites. Also, defects on I-PdSe₂ improve the ORR activity by tuning electronic structure.²⁵⁶

The strategy employed in this work shows that 2D crystals with robust phase can be achieved with the development of more controllable in situ intercalation method, e.g., mild intercalation process that allows one to fine tune the activity and stability of 2D catalyst, without damaged or drastic phase/structural changes during intercalation which is highly desirable. Therefore, exploring of in situ characterization tools to monitor the evolution of activity and stability during intercalation is crucial for reaching optimal balance between activity and stability.

3.3 Summary

2D PdSe₂ has been activated for ORR catalysis using lithium intercalation. The good crystallinity and 2*L* phase of pristine PdSe₂ are well retained, offering the greatly enhanced activity as well as superior stability. The de-lithiation process forces weak Pd-Se bonding to dissociate to create active sites by exposing more Pd element. Furthermore, the lithiation process introduces intercalation that improves the oxygen diffusion. Our complementary DFT calculation indicates Li-intercalation induces active sites that enhance ORR activity. Furthermore, the high bond energy between Pd and Se beneath the surface layers ensures that further defect formation is unfavourable, making it more stable. These complementary experimental and theoretical studies indicate that lithiation/de-lithiation cycle can activate PdSe₂ for ORR without significantly degrading the original good crystallinity of PdSe₂ synthesised at high temperature, in obvious contrast to the lithium intercalation of other TMD electrocatalysts where stable 2*H* phase is usually converted to metastable 1*T* phase accompany with structural defects. The immediate benefit of the retained crystallinity and stable phase is the greatly enhanced activity without significantly compromising stability, which could effectively address the activity-stability dilemma in electrocatalysts.

Chapter 4: Ternary Palladium Phosphoronitride for Oxygen Reduction

Ternary palladium thiophosphate ($\text{Pd}_3\text{P}_2\text{S}_8$) is a layered compound with an interlocked layered structure that is notorious for its electrochemical inactivity since the first reported synthesis in 1971.^{257, 258} The lack of activity indicates that $\text{Pd}_3\text{P}_2\text{S}_8$ is practically not useful for catalytic applications. Though several theoretical studies have suggested the potential activation of $\text{Pd}_3\text{P}_2\text{S}_8$ by strain engineering or atomic doping,^{257, 259, 260} it had only been demonstrated recently by Zhang *et al.*² who activated the material for hydrogen evolution reaction (HER) using a self-developed lithiation method to form amorphous nanodots with rich sulfur (S) and phosphorous (P) vacancies. 2D ternary palladium phosphoronitride could also have catalysis applications, but its synthesis has not yet been reported.

As discussed in Chapter 3, the best-known ORR catalysts are based on precious metal platinum (Pt) and its compounds.^{70, 71, 261} Yet, the high cost and scarcity of precious Pt hinder the widespread implementation of these catalysts. To this end, palladium (Pd) has been a promising alternative to Pt due to its relatively higher abundance. Various methods have been developed to reduce the usage of precious metals without compromising the catalytic activity, such as 1) mixing of precious metals with nonprecious elements, e.g., Pt mixed with carbon black,⁷¹ 2) forming alloys^{262, 263} or compounds, e.g., electrodeposited palladium–gold (PdAu) alloys¹⁹⁹⁻²⁰¹ which showed excellent performances in both acidic and alkaline medias, 3) introducing electron donor groups such as P to improve the electrocatalytic activity by modifying the electronic structure of the catalyst⁸⁸⁻⁹⁰ or to stabilise the amorphized phase which is crucial for the activity of the

catalyst,^{91, 92} and 4) employing lithiation and de-lithiation process to improve the exposure of Pd in palladium diselenide while maintaining its stability.²⁶⁴ Despite these advances on engineering of palladium-based materials,¹⁹⁶⁻¹⁹⁸ there is still a lack of method to improve the utilization of the materials. The emerging atomically thin 2D catalysts^{68, 265-267} show extraordinary efficiency in terms of mass loading because of their high surface area and effective electron transfer.^{268, 269} The 2D geometry enables almost all of the atoms to be exposed to electrolytes and thus offers abundant active sites; holding great promise to increase material utilization.

Figure 19 Schematic nitrogen substitutional process. The grey, pink, yellow and blue balls represent Pd, P, S and N atoms. Dotted circles represent vacancy sites.

In this chapter, we introduce a new 2D ORR catalyst based on ternary palladium phosphoronitride $\text{Pd}_3\text{P}_2\text{N}_x$. As $\text{Pd}_3\text{P}_2\text{N}_x$ is challenging to be synthesised via chemical vapor deposition/transport (CVD/CVT) methods, we adopt a post-synthesis substitutional doping of nitrogen to replace sulfur in CVT $\text{Pd}_3\text{P}_2\text{S}_8$. **Figure 19** shows the schematic of the substitutional doping process exemplifying the structural modification to enhance the activity of the material. In the very reductive ambient of ammonia (NH_3) gas, sulfur atoms can be effectively reduced, and

then progressively substituted by nitrogen atoms, which have strong bonding with Pd atoms. The sulfur vacancies created during this process is also favourable for increased ORR activity, as will be discussed later.

First-principles density functional theory (DFT) calculations are employed to guide the substitutional doping process, followed by experimental synthesis of $\text{Pd}_3\text{P}_2\text{N}_x$. The mass activity of as-synthesised $\text{Pd}_3\text{P}_2\text{N}_x$ of $0.151 \text{ mA } \mu\text{g}^{-1}_{\text{Pd}}$ shows fivefold improvement from that of $\text{Pd}_3\text{P}_2\text{S}_8$. The ORR diffusion-limited current density of $\text{Pd}_3\text{P}_2\text{N}_x$ reaches 6.2 mA cm^{-2} , outperforming commercial Pt/C ($\sim 5 \text{ mA cm}^{-2}$) with fast kinetics and excellent stability. DFT results suggest that the doped nitrogen has altered the charge states of Pd atoms that regulate the binding energies of the ORR intermediate, and relieve the sulfur vacancy formation energy which were identified as the detrimental factors for catalytic stability.

4.1 Experimental section

4.1.1 Synthesis of the $\text{Pd}_3\text{P}_2\text{S}_8$

Single crystals of $\text{Pd}_3\text{P}_2\text{S}_8$ were grown by chemical vapour transport method (CVT) with I as the transporting agent. The amounts of Pd (powder, 99.9%, Sigma-Aldrich) : P (powder, 99.9%, Sigma-Aldrich) : S (powder, 99.99%, Sigma-Aldrich) = 1 : 1.5 : 3 with a total weight of 450 mg plus extra 55 mg I as the transport gas were sealed in an evacuated 20 cm-long quartz tube under vacuum at 10^{-6} Torr, which was placed in a three-zone furnace. The reactants were kept at 850°C for 30 h to allow pre-reaction while preheating the growth zone to 900°C to prevent the transportation of the gas. Then, the temperature was raised to 1030°C while maintaining the growth zone at the lower temperature 900°C to provide the temperature gradient necessary for the

transportation of the gas and growth of the single crystals. The furnace was then let to naturally cool down to room temperature after 5 days. Red transparent single crystals of $\text{Pd}_3\text{P}_2\text{S}_8$ were obtained in the growth zone, which had been confirmed by the powder XRD.²

4.1.2 Synthesis of the N- $\text{Pd}_3\text{P}_2\text{S}_8$

The N- $\text{Pd}_3\text{P}_2\text{S}_8$ was synthesised via one-step ammonization and the process schematically illustrated in **Figure 19**. The temperature of tube furnace was elevated to 600°C at a heating rate of 10°C·min⁻¹ and the samples were kept at that temperature for 5 h or 10 h denoted as N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$ and N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$, respectively.

4.1.3 Physical characterization

Transmission electron microscopy (TEM) was done on a JEOL-2010 TEM at an acceleration voltage of 200 KV. X-ray diffraction (XRD) was done on a Panalytical Xpert Pro with Cu K α ($\lambda = 0.15406$ nm) radiation in the range of 10–90°. Raman spectroscopy was performed using a WITec CRM200 confocal Raman microscopy system with the excitation line of 488 nm. X-ray photoelectron spectroscopic (XPS) were performed on a Kratos AXIS Supra with Al K α source ($h\nu = 1486.6\text{eV}$).

4.1.4 Electrochemical measurements

The measurements were done in a conventional three-electrode system at room temperature, using Platinum wire and Ag/AgCl (Saturated KCl) electrode as the auxiliary and reference electrodes, respectively. Gamry Potentiostat Reference 600 workstation was used to carry out

electrochemical measurements. All potentials in this study are referenced to reversible hydrogen electrode (RHE) according to the following equation:

$$E(RHE) = E(Ag/AgCl) + 0.059 \times pH + 0.198$$

The working electrodes and the comparison catalyst [Commercial Pt/C (20 wt% Pt, Alpha Aesar)] were prepared using 4 mg of material (the ratio of the as-prepared catalyst: acetylene black was 1:1) with 12 μ L of Nafion solution (5 wt%) dispersed by ultrasonication for 30 mins in 2 mL isopropanol solution. 25 μ L of the catalyst ink was dropped on the glassy carbon electrode surface ($D = 5$ mm).

Rotating disk electrode (RDE) measurements were performed under O_2 -saturated 0.1M KOH solution at different rotation rates (400-1600 rpm) at scan rate of 5 mV s⁻¹ from -1 V to 0.2 V (vs. Ag/AgCl).

The number of transferred electrons (n) was calculated based on the Koutecky-Levich (K-L) equation based on the results from the RDE tests:

$$I_d^{-1} = i_{dl}^{-1} + i_k^{-1} = \left(B \omega^{\frac{1}{2}} \right)^{-1} + i_k^{-1}$$

$$B = 0.62nFCo(D\omega)^{\frac{2}{3}}\nu^{-\frac{1}{6}}$$

where i_d is the measured current density, i_k and i_{dl} are the kinetic and film diffusion-limiting current densities, and B is the reciprocal of the slope, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the linear rotation speed), n is the number of electrons in the oxygen reduction, F is the Faraday constant (96500 C · mol⁻¹), Co is O_2 volume concentration in 0.1 M KOH (1.14×10^{-6} mol · cm⁻³),

ν is the kinematic viscosity of the electrolyte ($0.01 \text{ cm}^2\cdot\text{s}^{-1}$), and Do is the diffusion coefficient of O_2 in 0.1 M KOH ($1.73 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$).

The Tafel slope was calculated with the Tafel equation:

$$E = a + b \log(j_k)$$

Where E is the applied potential in the LSV test, a is a constant, b is the Tafel slop and j_k is the kinetic current density.

The electrochemically active surface areas (ECSA) were estimated from the electrochemical double-layer capacitance (Cdl) by collating the cyclic voltammograms (CV) in the non-Faradaic region of 1.06 – 1.16 V vs RHE following the equation

$$ECSA = \frac{Cdl}{Cdl_{ref}}$$

where Cdl is the double layer capacitance measured from the CV scans in non-Faradaic potential window. As the reference Cdl_{ref} is typically around 20 to 80 $\mu\text{F}\cdot\text{cm}^{-2}$,^{226, 227} thus the Cdl_{ref} used in the calculation of ECSA takes on the value around the middle value (60 $\mu\text{F}\cdot\text{cm}^{-2}$) which is consistent with that of other reported precious metals including Pd.²²⁸⁻²³⁰

4.1.5 Computational details

All calculations were performed via spin-polarised density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP).²³¹ The projector-augmented-wave (PAW)²³⁴ basis set and cut-off energy of 520 eV were set to describe core-electron interaction. The generalised

gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional²³³ was used to treat the exchange-correlation interaction. The total energy and force were converged within 10^{-4} eV and 0.02 eV/Å, respectively, for all calculations. Γ -centered $5 \times 5 \times 1$ k-point scheme was used to integrate the first Brillouin zone for slab models and Γ -point was used for the molecules.

Figure 20 Total energy change with different lattice constants for (a) $\text{Pd}_3\text{P}_2\text{S}_8$ and (b,c) N doping on $\text{Pd}_3\text{P}_2\text{S}_8$. When nitrogen is doped in $\text{Pd}_3\text{P}_2\text{S}_8$, the equilibrium lattices get smaller.

A pristine $\text{Pd}_3\text{P}_2\text{S}_8$ slab model was constructed from the fully relaxed bulk lattice parameters of $\text{Pd}_3\text{P}_2\text{S}_8$ with the unit cell size of $6.794 \text{ \AA} \times 6.794 \text{ \AA} \times 22.03 \text{ \AA}$. N- $\text{Pd}_3\text{P}_2\text{S}_8$ slab was modelled by computing the equilibrium a and b lattice parameters as shown in **Figure 20**. Nitrogen doping at side site induced the lattice contraction, while that in apical site exhibited marginal difference in equilibrium lattice compared to $\text{Pd}_3\text{P}_2\text{S}_8$. All slab models ensure the vacuum space

of 15 Å to exclude the interaction of periodic images. The adsorption energy (E_{ads}) of the adsorbed was calculated as

$$E_{ads} = E_{surface+adsorbate} - E_{surface} - E_{adsorbate}$$

where, $E_{surface+adsorbate}$, $E_{surface}$, and $E_{adsorbate}$ are the DFT ground state total energy of the modelled slab with adsorbate in the active site, the modelled slab, and the adsorbate in the vacuum. The crystal orbital Hamilton population (COHP) analysis was conducted using lobster4.0.0.^{253, 270, 271}

To evaluate free energy diagram of the oxygen reduction reaction, we used the methods by Nørskov *et al.*⁶⁶ The change in free energy of each elementary step was defined as follows,

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S - neU + \Delta G_{pH}$$

where ΔE is the reaction energy from DFT calculations, ΔZPE and ΔS is the change in zero-point energy and vibrational entropy. Some gaseous molecules' entropies were obtained from the NIST-JANAF thermochemical Table.²⁷² Energy correction was summarised in **Table 11**. U is the electrode potential referenced to the standard hydrogen electrode and n is the number of electrons participate in the reaction. ΔG_{pH} is $k_B T \ln 10 \times pH$ where k_B is the Boltzmann constant. Yet, the overpotential is invariant to the pH value, the free energy diagram was plotted with $pH=0$. We also neglected the effect of electrochemical double layer in this study.

ORR free energy diagram was obtained via DFT calculations considering the four-electron associative ORR pathways (equation 1-4) as the basis mechanism of ORR.

The free energy of O_2 was calculated from the experimental value of reaction $O_2 + 2H_2 \rightarrow 2H_2O$, -4.92 eV at 298.15 K and 0.035 bar.⁶⁶ Also, the difference in Gibbs free energy of OH^- , e^- and other gaseous intermediates (*i.e.*, O, OH and OOH) were calculated from H_2 and H_2O .

Table 11 Energy correction for the calculation of change in free energy taken from previous studies.⁶⁶

	$\Delta ZPE-TAS$	ΔG_{solv}
*OH	0.05	0.05
*O	0.35	0.30
*OOH	0.40	0.30

4.2 Results and discussion

Figure 21 (a,b) Model system of Pd₃P₂S₈ in (a) top view and in (b) side view with N doping sites of S(a) and S(s). (c) Thermodynamic energy convex hull of substitutional doping of N in Pd₃P₂S₈, where the doping sites are shown on the right, and N atoms are represented in blue. (d) Reaction energy diagram of different N doping pathways. Circled integers represent the considered routes. (e) Reaction pathways with respect to the N concentration and the corresponding changes in the energy of the system.

To guide the N doping process, we conducted first-principles DFT calculations as detailed in section 3.1.5. In pristine $\text{Pd}_3\text{P}_2\text{S}_8$ depicted in **Figure 21a** and **Figure 21b**, the substitutional doping sites for N can be S(a) and S(s). To evaluate the thermodynamic stability of N doping into $\text{Pd}_3\text{P}_2\text{S}_8$, energy convex hull was calculated for 256 different 2D structures (**Figure 21c**). DFT calculations indicated that N substitution for S is thermodynamically feasible until its concentration reaches 50 atomic percent (*at%*), *i.e.*, $\text{Pd}_3\text{P}_2\text{S}_4\text{N}_4$. At such dilute concentration, N was more likely located at S(s) site, resulting in the lattice contraction due to its smaller size than S (**Figure 20**). This transformation process can be plausible through the NH or N pathways, as depicted in the computation routes. Seven routes for the process as a function of N concentration were identified and represented by the energy change in each path (see details in **Figure 21d** and **Figure 21e**).

The most thermodynamically favourable route for the substitution is the **Route 1** due to its lowest energy cost. Nevertheless, the transformation mechanism would be greatly affected by the energy input. In this case, by increasing thermal energy, it is seemingly sufficient to increase the level of doping, which implies that the **Route 2** and **Route 3** can be also possible. We hypothesise that NH is involved in the initial doping process to replace the S sites, and the level of doping is not limited to that of **Route 1** as observed from the synthesis results (will be detailed later), which are more consistent with that of **Route 3** (highlighted in **Figure 21d**). In general, our DFT calculations indicate that the transformation process *via* the NH doping is thermodynamically more feasible than the direct N doping. Thus, it is difficult to achieve the direct N doping, instead NH doping is thermodynamically more feasible. Hence, using NH_3 would make the synthesis much more attainable than nitrogen.

Figure 22 HRTEM, TEM and corresponding Fourier transform patterns of (a,b) $\text{Pd}_3\text{P}_2\text{S}_8$, (c,d) $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$, and (e,f) $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$. Two crystal domains are labelled using dashed circles in (e).

As suggested by these DFT calculations, we employed NH_3 as the N source for substitutional doping of $\text{Pd}_3\text{P}_2\text{S}_8$ via nitridation in thermal furnace (see Section 3.1 for details). The CVT-grown $\text{Pd}_3\text{P}_2\text{S}_8$ crystal was well-defined in its plate-like shape, as seen in the high-resolution transmission electron microscopy (HRTEM) image in **Figure 22a** and **Figure 22b**, which signifies high degree of crystallinity with no obvious defects [see FFT (fast Fourier transform) pattern in the inset of **Figure 22a**]. The lattice spacing of 0.619 nm corresponds to the (100) facet of $\text{Pd}_3\text{P}_2\text{S}_8$ (**Figure 22a**), consistent with previous report.²⁵⁸ After nitridation process for 5 hours, the plate-like feature of N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$ was preserved (**Figure 22c** and **Figure 22d**) but showed obvious defects and much lower crystallinity (**Figure 22c**), suggesting that the structure of $\text{Pd}_3\text{P}_2\text{S}_8$ became distorted due to the nitridation process. Further evidence of the structural distortion from the nitridation can be seen from the TEM image of N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$ that has prolonged exposure to NH_3 and heat for 10 h (**Figure 22e** and **Figure 22f**). Notably, the material remained layered and became nearly amorphous, as seen from the FFT pattern (inset of **Figure 22e**).

Figure 23 (a) XRD indicates the (002) peak reduced after nitridation suggesting the process breaks the crystalline structure of the pristine $\text{Pd}_3\text{P}_2\text{S}_8$ and (b) Raman spectra of $\text{Pd}_3\text{P}_2\text{S}_8$ (upper), $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$ (middle) and $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$ (lower) shows Pd-S bond disappearing and Pd-N bond appearing indicating substitution of S (c) Deconvoluted Raman Spectrum for $\text{Pd}_3\text{P}_2\text{S}_8$.

X-ray diffraction (XRD) spectrum of $\text{Pd}_3\text{P}_2\text{S}_8$ in **Figure 23a** is consistent with the simulated XRD from Zhang *et al.*²⁵⁸ The XRD spectrum of $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$ corroborates the TEM images since (001) and (002) peak retains, suggesting the integrity of the 2D morphology albeit the crystallinity had been degraded. This degradation could have positive effect towards activation of the material for ORR as it breaks the crystalline structure to expose the interlocked Pd. Furthermore, the XRD spectrum of $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$ shows that both peaks disappeared, suggesting the material has been significantly amorphized with nanodomains of crystal (see dotted circles in **Figure 22e**). It is worth

noting that the 2D morphology of the material remains, as corroborated by the TEM images (**Figure 22b,d and f**), which indicates that most of the atoms are still exposed to the ambient.

It is also evident from the Raman spectrum (**Figure 23b**) that the transformation of the material becomes much more complete as the nitridation duration increases. The pristine material consists of peaks (see deconvoluted Raman peaks in **Figure 23c**) centered between 90 and 400 cm^{-1} which suggest the predominant Pd-S bonding.²⁷³ With different doping levels, the disappearance of Pd-S bond is accompanied by the appearance of peaks at around 472 to 476 cm^{-1} corresponding to pyrite-Pd-N bond due to nitrogen.²⁷⁴ As shown by Åberg *et al*,²⁷⁴ the calculated T_g^3 , E_g , and T_g^2 peak frequencies at low pressure (<3 GPa) range from 300 to 460 cm^{-1} . Moreover, the bending mode of Pd-N in palladium complex was calculated to be 245 cm^{-1} .²⁷⁵ In our experiment the peaks positions of N-10h-Pd₃P₂S₈ are 177.82 and 472.32 cm^{-1} , which reasonably fall in this range considering the difference in phases. Thus, the Raman peaks at 177.82 and 472.32 cm^{-1} are ascribed to the Pd-N bond vibrations.

Figure 24 (a) XPS spectrum of $\text{Pd}_3\text{P}_2\text{S}_8$, N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$, N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$ normalised to Pd peak shows S 2p diminishing after nitridation, the high level of carbon signal is due to the adhesive used for fixing powder sample. High resolution XPS spectra with deconvoluted peaks for elements (b) Pd 3d indicating the appearance of Pd-N bond and diminishing Pd-S bond, (c) S 2p shows the reduction of signals based on the signal to noise ratio indicating loss of S, (d) N 1s shows increase in adsorbed N-H indicating increasing difficulty for the N to replace S.

X-ray photoelectron spectroscopy (XPS) characterizations offer quantitative doping level, as shown in **Figure 24a**. Apart from the signals of Pd, P, and S, additional N 1s peak appears in N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$. This becomes more apparent when the nitridation duration increases to 10 h, suggesting the increase in N doping level. The intensity of S 2p peak in N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$ becomes much weaker in contrast to that in $\text{Pd}_3\text{P}_2\text{S}_8$, eventually the peaks of S become negligible in N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$,

suggesting that S atoms have been mostly removed. Quantitative analysis in **Table 12** shows that around 97% sulfur atoms had been removed with trace amount remained, which is ascribed to the residual S atoms and those S binding to N via S-N bond.

Table 12 Atomic Ratio from XPS.

SAMPLE\AT%	PD	P	S	N
10h-N-Pd₃P₂S₈	19.34	46.04	3.43	31.19
5h-N-Pd₃P₂S₈	17.02	34.77	19.73	28.47
Pd₃P₂S₈	21.96	30.59	47.45	0

Drastic changes are evident on the high-resolution Pd 3d and S 2p spectra (**Figure 24b** and **Figure 24c**). The Pd 3d XPS spectrum of the pristine Pd₃P₂S₈ crystal consist of a doublet corresponding to the Pd²⁺ 3d_{5/2} and Pd²⁺ 3d_{3/2} components and can be deconvoluted into 4 peaks around 336.6, 337.6, 342.8 and 342.9 eV that can be assigned to Pd-O, Pd-S and Pd-Pd bonds. The evolution of Pd peaks suggests the significant alteration of the charge state of Pd. It is noted that there are shifts in the binding energy of Pd-O and Pd-N which could have been caused by the destruction of the crystallinity, which have led to the change in surface electronic structure. It is postulated that as the nitridation happens, the electron transfer between the Pd and the dopant N as well as the absorbed O could have altered the chemical coupling and hence the shift in binding energy.^{276, 277} In this case, the contribution from O could have caused a shift of the Pd spectrum towards a lower binding energy, whereas contribution from N could have caused a shift otherwise.

On the S 2p spectrum of Pd₃P₂S₈ (**Figure 24c**), the S-P peaks at 161.9 eV and 162.8 eV seemingly combined into a single peak and the S-Pd peak at 163.9 eV which weakens as a new S-N peak emerges after nitridation. A closer look reveals that the signal-to-noise^{278, 279} ratio of S 2p

peak decreased to ~ 8.7 after 10-h nitridation, where the intensity is reaching detection limit of XPS, suggesting the replacement of S is almost complete. The almost complete loss of S atoms is attributed to the reductive ambient of NH_3 at elevated temperature. Such reduction reactions remove S, resulting in abundant S-vacancy defects as well as drastic structural change, which are consistent with the XRD and TEM characterizations.

The high-resolution N 1s spectrum (**Figure 24d**) of N-5h- $\text{Pd}_3\text{P}_2\text{S}_8$ can be deconvoluted into four peaks, centered at 397.8, 399.3, 400.1 and 402.4 eV, corresponding to N-Pd, N-P, N-O and N-H, respectively.²⁸⁰ As nitridation is prolonged, the doping process shows saturation as evident by the increase in area of the peak around 402 eV from the adsorbed NH_2 , which suggests that it has become more difficult for the N to replace S. The presence of N-O bond which can be attributed to the resultant increase of lattice oxygen species.

Figure 25 High resolution XPS spectra with deconvoluted peaks for elements (a) O 1s indicates higher adsorption of O which is beneficial for ORR, (b) P 2p shows multiple oxidation states of P in $\text{Pd}_3\text{P}_2\text{S}_8$ evolving to a strong peak at 133.8 eV assigned to P-N bond in N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$ and 134.9 eV assigned to P-O bond, indicating significant change to the oxidation states of P. The P-S bond at around 132.2 eV in the pristine $\text{Pd}_3\text{P}_2\text{S}_8$ is observed to have diminished which could be due to the loss of sulfur and (c) C 1s used to shift the energy to the reference 284.8 eV (d) Crystal orbital Hamiltonian population (COHP) curves of $\text{Pd}_3\text{P}_2\text{S}_8$ and $\text{Pd}_3\text{P}_2\text{S}_7(\text{NH})$. The horizontal line at 0 eV represents the Fermi level (E_F).

The most interesting feature is the strong O_2 adsorption capability of the material as seen in the high-resolution O 1s spectrum (**Figure 25a**). The effective peaks in the pristine material centers at the 532.1, 533.7 and 535.3 eV, corresponding to the lattice oxygen species, hydroxide species and adsorbed oxygen respectively.²⁴³ With nitridation, there is evident increase in the amount of

lattice oxygen. As pure NH_3 balanced in argon was employed during the nitridation, it is not possible to introduce oxygen during nitridation. Thus, the increased oxygen content is most likely ascribed to the conversion of the adsorbed oxygen species, consistent with the deconvoluted XPS peaks. The high temperature annealing broke the crystallinity of the pristine material and would have invited active sites to accept the oxygen that was physiochemically absorbed in $\text{Pd}_3\text{P}_2\text{S}_8$, giving rise to the lattice oxygen species. It is worth noting that the oxygen adsorption capability remains that can be seen from the adsorbed oxygen ($\text{O}=\text{O}$) peaks at around 534.4 eV. Since the adsorbed oxygen is the active oxygen species in ORR, the strong capability of O_2 species absorption is very beneficial for high ORR activity that will be detailed later.

There are obvious changes in the oxidation states of P atoms too, as suggested by the high-resolution P 2p spectrum depicted in **Figure 25b**. The multiple oxidation states of P in $\text{Pd}_3\text{P}_2\text{S}_8$ evolves to a strong peak at 133.8 eV assigned to P-N bond in N-10h- $\text{Pd}_3\text{P}_2\text{S}_8$ and 134.9 eV assigned to P-O bond, indicating significant change to the oxidation states of P. The P-S bond at around 132.2 eV in the pristine $\text{Pd}_3\text{P}_2\text{S}_8$ is observed to have diminished which could be due to the loss of sulfur. The variety of oxidation state of P in $\text{Pd}_3\text{P}_2\text{S}_8$ contributes to producing S vacancies and then to promoting the transformation to nitride. To gain more theoretical insight on S vacancy formation, the integrated COHP (ICOHP) values of P-S bonding were calculated by the summation of the filled electrons up to the Fermi energy in COHP. The more negative ICOHP indicates the weaker bonding between P-S in $\text{Pd}_3\text{P}_2\text{S}_7\text{NH}$, suggesting that creation of S vacancies becomes easier as the nitridation progresses. The ICOHP for the pristine $\text{Pd}_3\text{P}_2\text{S}_8$ was -4.39 eV while -4.55 eV for the $\text{Pd}_3\text{P}_2\text{S}_7\text{NH}$. The result was further confirmed by the COHP curves that the P-S bonding energy peak of $\text{Pd}_3\text{P}_2\text{S}_7(\text{NH})$ is smaller than that of $\text{Pd}_3\text{P}_2\text{S}_8$ (**Figure 25d**) It is noted that there are

relatively weak signals at the lower binding energy of the P 2p spectrum of the nitrated samples which can be attributed to the trace amount of remaining sulfur.

These detailed XPS measurements suggest the formation of ternary palladium phosphoronitride ($\text{Pd}_3\text{P}_2\text{N}_x$) becomes more favourable as nitridation progresses albeit with defects. The conversion is consistent with a temperature-dependent process as laid out in the theoretical postulation.

Figure 26 Electrochemical ORR performances of $\text{Pd}_3\text{P}_2\text{S}_8$, $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$, $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$ and Pt/C . (a) ORR polarisation curves shows increase in current density after nitration, (b) Tafel plots for ORR shows a slight improvement (blue line, 83 mV dec^{-1}) compared to that of Pt/C (black line,

85 mV dec⁻¹) indicating faster kinetics, (c) ECSA of N-10h-Pd₃P₂S₈ is superior compared to that of Pt/C indicating increase in active sites, and (d) Chronoamperometric curves in O₂-saturated 0.1M KOH solution at 400 rpm under a potential of 0.6 V versus RHE. N-10h-Pd₃P₂S₈ (blue line) shows the lowest lost in current over time, indicating higher stability.

Motivated by the observed significant oxygen absorption, the ORR activities of the synthesised samples were measured. **Figure 26a** shows the linear sweep voltammetry (LSV) curves of Pd₃P₂S₈, N-5h-Pd₃P₂S₈, N-10h-Pd₃P₂S₈ and commercial 20 wt% Pt/C as the reference. N-10h-Pd₃P₂S₈ exhibits relatively positive onset potential, half-wave potential, and larger diffusion-limited current density, which are much better than the pristine Pd₃P₂S₈ and N-5h-Pd₃P₂S₈. Notably, both N-5h-Pd₃P₂S₈ and N-10h-Pd₃P₂S₈ exhibit higher diffusion-limited current density than that of commercial Pt/C. Although it is noted that the performance of the Pt/C in the experiment is low, it is consistent with other reported results.²⁸¹ The mass activity of N-10h-Pd₃P₂S₈ shows a 5 (2.4) fold improvement from Pd₃P₂S₈ (20 wt% Pt/C), as summarised in **Table 13**. To benchmark the ORR activity of N-10h-Pd₃P₂S₈, ORR catalyst based on some other Pd-based compounds are compared in **Table 14**, which shows that the N-10h-Pd₃P₂S₈ is comparable or superior to others in alkaline medium. The outstanding ORR activity of N-10h-Pd₃P₂S₈ is attributed to its high affinity towards oxygen species,^{69, 241, 242} as suggested by the O 1s XPS peak.

Table 13 Half-wave potentials and specific and mass activities of Pd₃P₂S₈, N-5h-Pd₃P₂S₈, N-10h-Pd₃P₂S₈ and Pt/C catalysts.

Catalyst	Half-wave Potentials (V)	Specific activities (mA cm ⁻²)	Mass activities (mA μg ⁻¹ Pd)
Pd ₃ P ₂ S ₈	0.65	0.76	0.030
N-5h-Pd ₃ P ₂ S ₈	0.73	0.44	0.142
N-10h-Pd ₃ P ₂ S ₈	0.76	0.45	0.151
Pt/C	0.79	0.43	0.063

Table 14 Performance of N-Pd₃P₂S₈ catalyst and several representative results about Pd compound from recent published works.

Catalyst	Half-wave Potentials (V)	Mass activities (mA $\mu\text{g}^{-1}_{\text{Pd}}$)	Reference
N-10h-Pd ₃ P ₂ S ₈	0.76	0.151	This work
Pd-B/C	0.78	0.145	95
Pd/C	0.76	0.098	95
Pd-g-C ₃ N ₄	0.70	0.072	99
Pt-Pd/RGO	0.84	0.211	96
Pd-Pt /C	0.75	0.224	100
Pd-Fe	0.77	0.085	101
Pd-Co/C	0.75	0.063	102
Pd ₂ -Co alloy	0.71	0.041	103
Cu-Pd	0.81	0.042	85
Pd/Ni	0.65	0.141	104

Figure 27 LSV curves of (a) $\text{Pd}_3\text{P}_2\text{S}_8$, (b) $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$, (c) $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$, and (d) Pt/C catalysts in O_2 -saturated 0.1 M KOH solution at different rotation speeds with a sweep rate of 10 mV s^{-1} . Inset: Koutecky-Levich plots (j^{-1} vs. $\omega^{-1/2}$) relationship. Inset shows the transfer number which indicates the electron steps involved. $n=4$ indicates 4-electron pathway.

To unravel the ORR reaction kinetics, LSV measurements at 400-1600 rpm were performed and the kinetic parameters were calculated by Koutecky-Levich (K-L) equation, as shown in **Figure 27**. The diffusion-limited current densities of all samples exhibit an increasing trend due to the faster diffusion. The fitted K-L plots show linear relationships between j^{-1} and $\omega^{-1/2}$ under each potential. The number of transferred electrons n for $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$ is estimated to be ~ 4 at different potentials from 0.2 V to 0.6 V , which approached the theoretical value of 4 of Pt/C

measured under the same condition, indicating a dominant four-electron transfer pathway for ORR. This means that there is practically negligible intermediate forming during the process, and the ORR is efficient with almost a 100% efficiency. Furthermore, the corresponding Tafel slope (**Figure 26b**) of N-10h-Pd₃P₂S₈ is calculated to be 83 mV dec⁻¹, which is smaller than those of Pd₃P₂S₈ (125 mV dec⁻¹), N-5h-Pd₃P₂S₈ (91 mV dec⁻¹) and Pt/C (85 mV dec⁻¹), indicating the fastest ORR kinetics among all.

Figure 28 CV curves in the region of 1.06 - 1.17 V at scan rates from 40 to 100 mV s^{-1} and corresponding linear fitting of capacitive current for (a,b) $\text{Pd}_3\text{P}_2\text{S}_8$, (c,d) $\text{N-5h-Pd}_3\text{P}_2\text{S}_8$, (e,f) $\text{N-10h-Pd}_3\text{P}_2\text{S}_8$, and (g,h) Pt/C .

10h- Pd₃P₂S₈, and (g,h) Pt/C. Cdl indicates electrochemical double-layer capacitance. The higher the Cdl the higher the ECSA which means presence of more active materials.

Electrochemical active surface area (ECSA) effects the total ORR activity, and thus the electrochemical double-layer capacitance (Cdl) was tested to estimate ECSA. Cyclic voltammetry (CV) was performed over an applied potential range of 1.06 to 1.17 V vs reversible hydrogen electrode (RHE), where negligible Faradic current appears, to evaluate the Cdl. The potential ranges were kept constant for all catalysts and the same scan rates of 40, 60, 80, and 100 mV s⁻¹ were selected. The CV curves recorded at different scan rates for all samples, and the corresponding linear fitting curves of current density versus scan rate are displayed in **Figure 28**. The ECSA values are summarised in **Figure 26c**, and N-10h-Pd₃P₂S₈ shows the highest value, exemplifying the abundant active sites caused by substitutional doping.

Durability of the catalyst is another key parameter for practical application. As shown in **Figure 26d**, N-10h-Pd₃P₂S₈ exhibits 12.8% degradation after 28800-s continuous operation. This decrease could be due to the material detaching from the electrode after prolonged operation. In contrast, Pt/C displays a 35% degradation under the same conditions, indicating the worse stability than N-10h-Pd₃P₂S₈. The poorer durability of Pt/C is ascribed to the poor stability of the carbon black constituent in commercial Pt/C catalyst, leading to easy detachment of Pt particles and their aggregation under working conditions.⁷³ In contrast, the stability of the N-5h-Pd₃P₂S₈ and N-10h-Pd₃P₂S₈ could be attributed to the presence of N which forms better affinity with carbon atoms in carbon black.²⁸² Thus, the N doping process inherently improved the catalytic stability of the catalyst.

Figure 29 DFT calculation. (a) Oxygen reduction reaction free energy diagram of 4N, 6N and 7N doped Pd₃P₂N_x (4N, 6N and 7N represent $x = 4$, $x = 6$ and $x = 7$, respectively). (b) Correlation between the change in Pd charge state and OOH adsorption energy (ΔG_{*OOH}), the horizontal dotted line represented the previously suggested optimal value of ΔG_{*OOH} (3.9 eV). (c) Oxygen reduction reaction free energy diagram of referenced models (Pd₃P₂S₈ (pristine) and 8N). (d) Defect mechanism/ pathway for formation of Pd₃P₂S₆(NH). N doping induces stability to pristine material with S defect. (e) The illustration of pristine and N-doping paths.

DFT calculations were employed to shed light into the mechanism of high ORR activity of N-10h-Pd₃P₂S₈. Three different models were considered of N-Pd₃P₂S₈ with increasing nitrogen doping level, *i.e.*, 4N, 6N, and 7N, respectively, as shown in **Figure 29a**. The onset potential (U_{ORR}) increases as the nitrogen doping concentration increases (4N: 0.62 V, 6N: 0.67 V, and 7N: 0.70 V), consistent with the experimental observations. For these ORR free energy diagrams, only the N doped model was considered because during the process of ORR, hydrogen can be easily desorbed in the alkaline media with abundant OH⁻, otherwise the incoming oxygen can easily attract pre-adsorbed hydrogen from Pd₃P₂NH_x.

Figure 30 (a) Adsorption configurations of intermediates for 4N model system. (b) 6N model system. (c) 7N model system (d) 8N model system. Circle indicates absorption configuration. Grey = Pd, Blue = N, Yellow = S, Pink = P, Red = O, White = H.

The active site of ORR was nitrogen in hollow site (*i.e.*, side site), and the rate determining step for all models was OH adsorption. As the experimental observation had shown that sulfur hardly remained in N-10h-Pd₃P₂S₈, it is reasonable to compare the effect of sulfur defect on onset potential to determine if the number of vacancy sites plays a significant role. Since defect site strongly binds oxygen, the free energy diagram of sulfur defect in Pd₃P₂N₇ with oxygen passivated into sulfur defect site was calculated. Notably, the onset potential did change about 0.03 V, suggesting that the sulfur defect indeed plays a role in ORR process. Due to the difference in valence electrons of nitrogen and sulfur, it is natural to expect that the charge state of Pd will be affected by the doping concentration. Recently, it was reported²⁸³ that the atomic level modification of the charge state of cobalt (Co) in Co-N₄/graphene regulated the H₂O₂ production reaction, which is a slightly different reaction from ORR. Thus, the charge state of Pd was calculated using Bader charge analysis²⁸⁴ as nitrogen doping level increases (1N ~ 8N), as shown in **Figure 29b**. The more the nitrogen is doped, the more Pd depletes the electron, and this directly affects the Gibbs free energy of OOH adsorption ($\Delta G^{*}_{\text{OOH}}$). It was shown that as the N doping concentration increases, $\Delta G^{*}_{\text{OOH}}$ decreases from 5.21 eV to 3.99 eV, the stronger adsorption strength, due to larger number of charge transfer from Pd to the ligand (S or N). Both 7N and 8N exhibit $\Delta G^{*}_{\text{OOH}}$ (4.03 eV and 3.99 eV, respectively) close to the optimum (3.9 eV)²⁸³, yet 8N showed over-binding of O led to low onset potential (-0.586 eV) as shown in **Figure 29c** and **Figure 30**. Accordingly, there is an optimal nitrogen doping occurs around 0.875 per formula unit, *i.e.*, seven N atoms substitute the original eight S atoms to achieve a balance between nitrogen doping and sulfur vacancies, *i.e.*, Pd₃P₂N₇.

To further understand the role of nitrogen in durability enhancement, the reaction diagrams of nitrogen doping and sulfur defect formation were calculated, as shown in **Figure 29d** and **Figure**

29e. Sulfur defect formation is thermodynamically feasible, indicating the low stability of $\text{Pd}_3\text{P}_2\text{S}_8$, which facilitates the N substitutional doping. This result has also been reported in molybdenum disulfide (MoS_2), where H_2S formation from lattice sulfur to create sulfur vacancies.²⁸⁵

4.3 Summary

In summary, a new 2D material of ternary palladium phosphoronitride have been synthesised, which shows outstanding mass activity, kinetics, and stability for ORR catalysis. As it is challenging to directly synthesise $\text{Pd}_3\text{P}_2\text{N}_x$, a post-synthesis substitutional doping in CVT-grown 2D $\text{Pd}_3\text{P}_2\text{S}_8$ was performed, as guided by a DFT-based rational design. Owing to the thermodynamically unstable sulfur in $\text{Pd}_3\text{P}_2\text{S}_8$, around 97% sulfur has been replaced by N and vacancies. The mass activity of pristine $\text{Pd}_3\text{P}_2\text{S}_8$ has been improved from 0.03 to 0.151 $\text{mA } \mu\text{g}^{-1}_{\text{Pd}}$ in $\text{Pd}_3\text{P}_2\text{N}_x$. The ORR diffusion-limited current density (6.2 mA cm^{-2}) has exceeded that of commercial Pt/C ($\sim 5 \text{ mA cm}^{-2}$). The superior ORR activity is attributed to the strong oxygen affinity of $\text{Pd}_3\text{P}_2\text{N}_x$, as indicated by XPS characterization. The detailed ORR mechanism of $\text{Pd}_3\text{P}_2\text{N}_x$ is revealed by complementary DFT study, which suggests the dominant ORR active site is N in hollow sites, complemented by sulfur vacancies. DFT calculations also shed light on the stability improved by N doping, suggesting the ideal N doping to be $\text{Pd}_3\text{P}_2\text{N}_7$.

Chapter 5: Tuning Work Function of MXenes via Functionalisation

In the previous chapters, inert precious metal compounds were activated via defects engineering to become effective electrocatalysts. In the following chapters, the focus will be on engineering nonprecious 2DM MXenes for potential solar energy conversion applications.

As a new member of the family of 2D material, MXenes are interesting material, known to be versatile, multifunctional, strong, robust, and has many advantages over its counterparts in terms of applicability. Despite being discovered since 2011, MXenes can still be considered novel for the exploration into the material's application in electromagnetic shielding, electrical and electronic devices, and energy conversion. To date, this class of 2D material had seen potential applications across multiple fields including energy storage,^{29, 30} sensors,³⁵ construction,³⁶ energy conversion,^{31-33, 286} supercapacitors,³⁴ among others.

Their characteristic layered structure, metallic behaviour, and interesting surface chemistry made them one of the most prominent novel materials in the recent years. Given their unique structure, additives can also be easily incorporated into them in the form of intercalant to alter the electrical properties of the material.³⁹ Yet, the most alluring property is in its surface terminations, also known as functional groups. In a typical synthesis, there are usually a combination of termination groups denoted T_x for simplicity in $M_{n+1}X_nT_x$, where T can be $-OH$, $-F$, or $-O$.^{8, 34, 152, 161} It had been well known that by modifying the functional

groups^{34, 39, 161, 287} on the material, it is possible to attain different functional properties, making it one of the most versatile materials.

Termination groups on MXenes are crucial to their electronic and electrical properties, where various literatures³⁷⁻⁴⁰ had demonstrated that by modifying the termination groups, electrical conductivity can be tuned to fit different functions. Many researchers had picked up on the investigation of functionalising MXenes for use with energy applications such as catalysis^{31, 32}, batteries^{11, 29, 163} and the effect on microwave absorption and electromagnetic shielding⁴¹⁻⁴⁴. Hart *et al*³⁹ observed the changes of electrical conductivity as a result of thermal annealing using In-situ TEM technique and found that the resistance decreases after the termination groups had been removed via thermal reduction in vacuum. Meanwhile, Schultz *et al*²⁸⁸ investigated the work function (WF) changes in the process with respect to temperature. These findings demonstrated consensus that stripping the termination will improve the electrical properties.

In retrospect, there are indeed other reported successful functionalization of MXenes gearing towards adding or modifying the existing functional group, using techniques such as 1) nitrogen doping by solvothermal¹⁵⁸ or annealing it under ammonia environment³⁴ to inculcate nitrogen, 2) annealing the MAX phase with ZnCl to effect Cl termination,¹⁶³ 3) annealing in inert mixture gas to control oxidation,¹⁶¹ and 4) annealing under CO₂ to effect decomposition of the pristine structure.²⁸⁹ Yet, the degree to the change in WF is underexplored.

In this work, through simple gaseous annealing techniques, we show that it is possible to treat MXenes in the bulk with consistent modification to the surface morphology that induced changes in the WF and electrical properties. Ti_3C_2 MXenes with different terminations on the surface were computationally explored to understand how their chemistry influences the WF values. The trends obtained via experiment were further confirmed using Density Functional Theory (DFT) calculations. These modifications enable and inspire further investigations into widespread usage for this material in applications such as perovskite solar cells, electromagnetic absorber, electromagnetic shield coating and other devices.

5.1 Experimental section

5.1.1 Synthesis of MXene

Ti_3AlC_2 MAX phase was purchased from Y-Carbon Ukraine and etched in 48 wt% Hydrofluoric Acid (Sigma Aldrich/695068) for around 5 days to achieve MXene. This is to ensure the material is etched fully with high saturation of fluorine on the surface. The resultant MXene was retrieved via multiple centrifuge (6000 rpm for 20mins) and dilution cycle to which the pH was around 5 to 6, keeping the residue. It was then dried in vacuum oven at 60°C for a day.

5.1.2 Annealing and doping of MXene

300 mg of the dried MXene powder was sonicated in methanol for around 60mins to achieve delamination. The solution was centrifuged at 3500 rpm for 10 mins to separate the

MXene from the methanol, and the residue was dried to retrieve the MXene. The dried sonicated MXene (hereafter referred to as “as-etched MXene”) was then separated into different alumina crucibles to be treated in a tube furnace. Nitrogen-doped MXene was obtained by annealing around 100 mg of as-etched MXene under constant flow (10 sccm) of 10% Ammonia in Argon (10% NH_3 : 90%Ar, Air Products) for 7 hours. While Ar-annealed MXene was obtained by annealing the same amount of as-etched MXene under same conditions except that the gas used was 99.9999% Argon (Leeden National Oxygen Ltd).

5.1.3 Material characterisation

The samples were characterised with SEM (FESEM JEOL JSM-7600F), TEM (TEM JEOL 2100F), XRD (Panalytical Xpert Pro), XPS and UPS (Kratos AXIS Supra).

5.1.4 WF and VBM measurement

Powder samples of the treated MXenes were dispersed in methanol and drop casted onto eletro-deposited gold (<100 μm) on Si wafer to achieve a thin layer covering the entirety of the surface. The samples were measured via UPS (Kratos Axis Supra) using He I_α ($h\nu = 21.22 \text{ eV}$) as radiation source at the range of -5 to 10 eV Kinetic Energy and Binding Energy.

5.1.5 Conductivity measurement

Samples were sprayed onto approximately 5 cm by 2 cm by 0.05 cm Alumina plate in the pattern of 0.5 cm by 0.5 cm squares. Silver paste was applied to the corners of the squares

to create a Van Der Pauw measurement set up. The sheet resistance was then measured using a 4-probe measurement set up, the conductivity (σ) was then converted from the sheet resistance using the formula $\sigma = \frac{1}{R_{sh}t}$, where R_{sh} is the sheet resistance measured, and t is the nominal thickness of the layer of MXene. The nominal thickness was measured using the laser profiling mode on the surface profiler (Taylor Hobson Talyscan 150). The thickness was estimated from the profile obtained.

5.1.6 Computational details

First-principle DFT calculations are performed using Quantum ESPRESSO package²⁹⁰ within the Atomic Simulation Environment (ASE)²⁹¹ to confirm the trend. The experimental doped structure was modelled by putting the terminations on surface of Ti_3C_2 and investigated its electronic properties. The plane-wave basis sets have kinetic and density cut-offs of 500 eV and 5000 eV, respectively. Electronic interactions are described using projector augmented wave (PAW) method. The self-consistent total energies are obtained using Perdew-Burke-Ernzerhof (PBE) and PBE-D3 exchange-correlation functional,^{233, 292} the latter of which accounts for dispersion interactions. Vanderbilt ultra-soft pseudopotentials²⁹³ was used to represent core states. As functionalised $Ti_3C_2T_x$ MXene and TiN are non-magnetic, spin paired calculations were performed.²⁹⁴ Spin-polarised calculations with the PBE+U functional was employed for anatase and rutile TiO_2 using a U value of 3.0 eV. K -points. For surface calculations, a dipole correction was included to mitigate spurious interactions between periodic images separated by vacuum. VESTA²⁹⁵ was used to create graphics of the structures.

Bare Ti_3C_2 MXenes and MXenes terminated by F^* , O^* , N^* , and mixed O^*/N^* terminations were considered, hereafter the materials will be referred to as $\text{Ti}_3\text{C}_2\text{-F}^*$, $\text{Ti}_3\text{C}_2\text{-O}^*$, $\text{Ti}_3\text{C}_2\text{-N}^*$ or $\text{Ti}_3\text{C}_2\text{-O}^*/\text{N}^*$ for the various terminations. The terminations were placed at the fcc hollow site, which is the most stable adsorption site, as shown in **Table 15**. The interlayer distance depends on the surface terminations, as observed via experiment. For Ti_3C_2 MXenes, the interlayer spacing corresponding to the most stable bi-layered structures was determined by computing the potential energy as a function of the bilayer distance.

To compute the work function, the charge density file was first generated using a symmetric slab. Then, the surface averaged local potential was determined from the charge density. The work function is given by the energy difference between upper vacuum and the fermi level. Since all MXene, TiN , and TiO_2 structures are symmetric, either vacuum level can be used to compute the work function. For computing the total density of states, we performed non-self-consistent calculations using a denser Monkhorst Pack²⁹⁶ k-point grid with the tetrahedron method. The k-point grids for these density of states calculations was individually converged for the $\text{Ti}_3\text{C}_2\text{-T}_x$, TiN , and TiO_2 structures.

5.1.7 Bulk calculations

The initial structure of Ti_3C_2 is obtained from the Materials Project. The (001) surface of Ti_3C_2 represents a bulk structure with 20 Å of vacuum in the z-direction to avoid interactions between the periodic images. Lattice parameter of the MXenes is optimised using $14 \times 14 \times 1$ k-points in reciprocal space generated with the Monkhorst-Pack method.²⁹⁶ The optimised lattice

constant of Ti_3C_2 is 3.07 Å. Functionalised structures were constructed by creating an epitaxial film of terminations ($\text{F}^*/\text{N}^*/\text{O}^*$) on the bare Ti_3C_2 . Dipole correction along the z-direction to alleviate spurious electrostatic interactions. The total energy and force convergence threshold are 10^{-6} eV and 0.05 eV/Å respectively. These electronic structure calculations are converged using a Fermi-Dirac smearing of 0.1 eV for all structures. Structural relaxations were performed using the Perdew-Burke-Ernzerhof exchange-correlation functional with and without inclusion of vdW interactions, PBE-D3 and PBE, respectively.

5.1.8 Geometric optimisation

For each $\text{Ti}_3\text{C}_2\text{-T}_x$ system, we observe the fcc hollow site of the slab to be the most thermodynamically stable site. The effect of thickness on the work function using one and two-layered MXene with functional groups present both sides of the surfaces. The interlayer distance is initially maintained as 7 Å in a two-layered slab which changes based on surface terminations, as listed in **Table 15**. **Table 15** Structural model of Ti_3C_2 functionalised with mixed terminations of N^* and O^* (0.25 ML and 0.5 ML coverage of N^*). Top and perspective views of fcc adsorption sites of T_x are shown in the above figure. The interlayer distance is 6.7 Å in a two-layered slab converged structure. The atomic elements Ti, O^* , N^* and C^* are depicted in grey, red, turquoise, and brown respectively. Table shows Interlayer distance for a two-layered symmetric $\text{Ti}_3\text{C}_2\text{-T}_x$. The terminations are added on both sides of the slab and initial distance is maintained as 7 Å among the layers. This distance varies in the converged structure based on functional groups present on the surface of Ti_3C_2 .

Termination (T_x)	Coverage (ML)	Interlayer distance (Å)
Bare	1	7.22
O*	1	2.98
N*/O*	0.25	6.73
N*/O*	0.5	6.7
N*/O*	0.75	N*-N*=1.31, O*-O*=2.16
N*	1	1.3
F*	1	5.46

5.2 Results and discussion

Figure 31 Optical photographs (a-c) and SEM images (d-i) of MXene before and after treatment. Colour difference after treatment, (a) as-etched MXene is slightly hued towards purple, (b) Ar-annealed MXene is much darker in hue tending towards black but shows slight blue hue under certain condition. (c) nitrogen-doped MXene has obvious changes towards reddish brown. SEM images of (b,g) as-etched, (e,h) Ar-annealed, (f,i) nitrogen-doped MXene.

MXene, $\text{Ti}_3\text{C}_2\text{T}_x$ (as-etched MXene) was made by etching its precursor MAX, Ti_3AlC_2 , in 48 wt% Hydrofluoric acid (HF). The product was cleaned via centrifuge and dilution in a typical synthesis, dried and placed into alumina crucible to be annealed in gaseous environment, in argon (Ar-annealed), or ammonia (nitrogen-doped). Physical change can be observed after

annealing and can be used to indicate if the doping is successful. As-etched MXene expresses a tint of purple (**Figure 31a**). After annealing in argon, it turned bluish black (not apparent in photo, **Figure 31b**). Whilst, on the other hand, annealing in ammonia changed the colour towards reddish brown (**Figure 31c**). It is well noted that right after the doping process, the tint can be obvious, and are in different range of the visible region and it is consistent throughout multiple sources of MAX phase. This indicates the high repeatability of the doping and there is a relationship between the change in dopant on the properties of the material.

On closer inspection, the SEM images (**Figure 31d** to **Figure 31di**) indicate changes to the layer distance between the 3 types of MXene. This is consistent with the XRD results which will be discussed later. The starting material, as-etched MXene (**Figure 31d** and **Figure 31g**), well known for its accordion-like structure, has collapsed under the high temperature annealing. The resultant materials, Ar-annealed MXene (**Figure 31e** and **Figure 31h**) and nitrogen-doped MXene (**Figure 31f** and **Figure 31i**), have lower interplanar distance apparent from the close-up images. At this point, it can be observed that the planar structures are still preserved. The change is mainly attributed to the loss of interlayer water molecules; however, the degree of change is proposed to be due to the interactions between the surface termination including intermolecular van der Waals forces and electrostatic forces or the lack thereof and warrants a further investigation.

Figure 32 Potential energy diagram for functionalised Ti₃C₂ with nitrogen coverages (ML) of (a) 0.25 (b) 0.5 (c) 0.75 (d) 1. Single-point calculations were performed to observe the effect of interlayer spacing on total energy of the slab. Interlayer distance, d , depends on surface concentration of nitrogen atoms on the slab and are listed in the Table S1 above. The y-axis corresponds to the difference in total energy of a double and a single layered slab. Lowest point of the hill corresponds to the most stable configuration.

There are various changes to the topology of the material which is consistent with process that is disruptive in nature. Such disruptive process effected changes to the structure of the material. The obvious bumps on the surface of the Ar-annealed MXene (**Figure 31h**) are much more prominent as compared to that of the as-etched MXene (**Figure 31g**) which are due to the further formation of TiO₂ nanoparticles. This is in consistent with computationally derived calculations where we observe the interlayer distance in the converged structures to be as low as 2.98 Å and 1.3 Å for Ti₃C₂-O* (O-terminated MXene, i.e., Ar-annealed MXene) and Ti₃C₂-N* (N-terminated MXene, nitrogen-doped MXene), respectively. This interlayer

spacing for $\text{Ti}_3\text{C}_2\text{-O}^*$ is similar to the gap between bilayers of 2D metal oxides like MoO_3 .²⁹⁷ This distance is dependent on the surface terminations. As we increase the concentration of surface nitrogen atoms, the interlayer spacing decreases for the slab. We further confirmed this trend by building a potential energy diagram for different coverages of N^* and O^* . Single-point calculations were performed to obtain the effect of interlayer spacing on total energy of the slab (**Figure 32**).

Figure 33 TEM images and corresponding HRTEM images of (a,d) as-etched, (b,e) Ar-annealed and (c,f) nitrogen-doped MXenes. Insets are corresponding Fourier transform patterns. Hexagonal spots represents clusters of TiO_2 particles.

These TiO_2 nanoparticles formation can be seen clearly from TEM analysis in **Figure 33a** and **Figure 33b** as hexagonal spots²⁹⁸ consistent with the understanding of the oxidation of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene.²⁸⁹ The degree of oxidation is limited to the amount of adsorbed oxygen on

the as-etched MXene since there is no other oxygen source introduced during the process. This is further exemplified as the oxidation observed on the nitrogen-doped MXene (**Figure 33c**) is much less prominent, which is expected due to the reductive environment. However, the remnants of the TiO_2 phase formed during the etching process prior might still be seen, which will appear as dark spots in the TEM albeit much lesser. There is in stark contrast between reported annealing results^{39, 288, 299} with the results from this experiment which could be due to fact that such bulk treatment provides enough oxygen source to form the TiO_2 nanoparticles unlike monolayer or few layers treated under high vacuum. Just as Naguib *et al*²⁸⁹ pointed out that there were observed clustering of Ti atoms during annealing, this effect could have been further exacerbated by sufficient O sources forming TiO_2 clusters.

After the annealing process, **Figure 33d** to **Figure 33f**, shows that there are obvious changes in the crystallinity of the MXene under different doping. The as-etched MXene (**Figure 33d**) shows that the material does start with mostly crystalline structure, with various terminations randomly lined on the basal plane consistent with the understanding of the structure of MXene.²⁹ Through annealing in Ar atmosphere (**Figure 33e**) the crystallinity seemed to be reduced. This is consistent with high temperature treatment of $\text{Ti}_3\text{C}_2\text{T}_x$ that causes the migration of Ti atoms towards the surface as carbon breaks down into amorphous carbon.²⁸⁹ On the other hand, annealing in ammonia environment maintains the crystallinity better as seen from **Figure 33f**. It does suggest that nitrogen doping could have stabilised the material or altered the structure of the material.

Figure 34 (a) XRD indicates loss of 002 peak (centered at around 8.91° in as-etched) for both Ar-annealed and nitrogen-doped MXenes (b) Raman spectrum shows distinct peaks at 141, 217, 283, 378, 620, 692 cm^{-1} which is typical for as-etched MXene (c) XPS spectrum for As-etched MXene, Ar-annealed MXene and nitrogen-doped MXene shows that F signal at around 684 eV is diminished after the treatments.

XRD (**Figure 34a**) characterisation indicates loss of 002 peak (centered at around 8.91° in as-etched) for both Ar-annealed and nitrogen-doped MXenes, with the latter having the most drastic reduction. It is noted that there are some extents of 002 peak present (centered at around 9.05°) but it is very near the noise level of the data. The shift of the XRD towards a higher 2θ value indicates a reduction in interlayer spacing which is consistent with the SEM mentioned

earlier. This could mean that the newly formed nitrogen-doped MXene is less planar than expected. Furthermore, due to the high temperature for nitridation, it is reasonable based on the XRD comparison^{300, 301} to believe that TiN was formed. Overall, the peaks are consistent with that of mixture between TiN, Ti₃C₂ MXene and TiO₂. The upshift is more apparent in the Ar-annealed MXene, centered at around 9.11°, suggesting the interlayer distance is much reduced. This indicates that although the crystallinity is less obvious in the Ar-annealed MXene, the planar structure is still preserved. This could be due to the obscured view in the TEM due to the large quantity of TiO₂ lining the surface.

Raman spectroscopy (**Figure 34b**) characterization of as-etched MXene indicates distinct peaks at 141, 217, 283, 378, 620, 692 cm⁻¹, which is consistent with previous report.¹⁷⁵ The peaks are consistent with the presence of TiO₂ both rutile and anatase.³⁰² The results from the Raman are overwhelmed by the Ti-O signal, suggesting significant amount of O on the surface Ti. The increase in amorphous carbon can be observed with the prominent increase in the D and G peak¹⁶¹ which is consistent with breaking down of C from the inner surface effecting the Ti migration as shown by Naguib *et al.*²⁸⁹ With nitridation of MXenes, the prominent changes of the pristine peaks into that of TiN³⁰³ further supports the formation of TiN.

XPS was used to investigate the surface termination of MXenes. Since the surface-sensitive technique is widely accepted with its 12-nm penetration depth, it can identify the chemical states of multiple layers of functionalised MXenes. This versatile approach gives an

indication of the chemical bonding on the targeted MXenes surfaces. However, it must be noted that the randomness of the surface doping will affect the XPS results, although the trend will be consistent since the annealing of MXenes happens from every direction. From the wide spectrum (**Figure 34c**), it can be observed that F is practically substituted in both treatments by O and/or N. In the Ar-annealed sample, there is an overall increase in O signal, which suggests that O termination is significant on the surface. This expectation is consistent with Ar treatment on MXenes.¹⁶² On the other hand, the nitrogen-doped sample is dominated by N termination as expected from NH_3 treatment.³⁴ It is noted that there is considerably small quantity of F which could be the remnant from the by product, AlF_3 ,³⁰⁴ or the partial removal of the -F terminations.³⁹

Figure 35 High resolution XPS spectrum and deconvolution of as-etched MXene, Ar-annealed MXene and nitrogen-doped MXene of (a) Ti 2p signals indicates a new Ti-N peak and increase in Ti-O₂ peaks suggesting increase in terminations or oxidation, (b) N 1s signals indicates that N is bonded mainly to Ti and some indication of edge terminated with C, (c) C 1s signals shows peaks shows that annealing in high temperature had broken the C-Ti bond and forming more C-O and C-O-C bonds that are consistent with the expectation that surface carbon reacts with oxygen, (d) F 1s signal diminishes after annealing as shown by the lower signal to noise ratio

indicating removal of F, and (e) O 1s signals show decrease in O-H bond which could indicate that O-H is removed together with F.

Deconvolution of high-resolution Ti 2p_{3/2} signal (**Figure 35a**) shows that as-etched MXene consist of mainly of peaks centered at 455.0, 455.6, 456.4, 457.3, 460.0 eV which can be assigned to Ti-C, Ti-F, Ti (II)-O, Ti (III)-O, and Ti-O₂. This is consistent with the structural model where Ti-C acts as the skeletal structure with surface termination as ligand of -F, -O and -OH. When the as-etched MXene was treated at high temperature, the oxidation states of Ti shifted towards higher oxidation number with the most drastic change forming TiO₂. The formation of the TiO₂ phase is less obvious in the nitrogen-doped sample compared to Ar-annealed sample because of the reductive environment that is suppressing the formation of oxide, nevertheless, due to the former being a mixture environment, the formation is inevitable. The disappearance of Ti-C and Ti-F bond and appearance of the Ti-N bond in the nitrogen-doped sample suggest that Ti-N has dominated the surface in place of Ti-C and Ti-F. Such change is similar to the findings from Wen *et al.*³⁴ Hence, it is reasonable to assume that the effect of annealing in ammonia had successfully doped nitrogen into the surface. The deconvolution of N 1s signal (**Figure 35b**) concurs with the results showing that the primary peak can be observed to at 396.8 eV corresponding to N-Ti. While minor peaks corresponding to N-O and N-C appeared at 399.0 and 401.4 eV which could be due to the intermediate or doping at the edges, the large amount of N-Ti indicates that the functionalization happened right at the surface.

Furthermore, **Figure 35c** shows the deconvolution of high-resolution C 1s signal. On the as-etched, the peaks are centered at 282.4, 282.6, 284.8, 285.7 with a minute peak at 289.4 eV which correspond to C-Ti, C-O-C, C-C, C-O and C=O. Annealing in high temperature had broken the C-Ti bond and forming more C-O and C-O-C bonds that are consistent with the expectation that surface carbon reacts with oxygen. Notably, the C-Ti peak disappeared in the nitrogen-doped sample which shows that the previous assumption where Ti-N was dominating is valid. Nevertheless, it is hard to tell the atomic percentage of Ti-N and N-MXene on the surface.

The deconvolution of the high-resolution F 1s signal (**Figure 35d**) shows peaks centered at 685.3 and 687.0 eV corresponding to F-Ti and F-C respectively. After annealing, drastic reduction in the intensity of F signal can be observed (not shown in figure). There is a slight shift of the F signal in the nitrogen-doped sample and could probably be attributed to the effect from the incoming nitrogen.

The breaking of the weak Ti-F bond was crucial to the substitution mechanism. It is known that the first modification of the surface termination group happens at the Ti-F bond.³⁹ It is also known that the synthesis condition will determine the concentration of Ti-F³⁰⁵ and hence affecting the degree of substitution. To increase the substitution by maximising the quantity of Ti-F population, the MAX was submerged in etchant for a week. This means that the quantity of Ti-F would have been saturated with the etching coming to completion in the

excess of HF. Although there were concerns over the oxidation of the material during the long period of etching, it is considerably minute as seen from the material characterizations.

The deconvolution of O 1s signal (**Figure 35e**) shows peaks centered at 530.0, 530.7, 531.3, 532.1, 533.1, 534.2 eV corresponding to O-Ti, TiO₂, O-H, O-C, O-O and O=C. After annealing at high temperature, the termination -OH was removed together with the -F group as expected from high temperature annealing, forming TiO₂. It is also apparent that the quantity of O-C bonding had been reduced. This reduction could be attributed to the breaking down of carbon which could have been lost during the high temperature annealing.

Figure 36 UPS measurement and corresponding extraction for (a,b) Work Function, and (c,d) Valence Band Maximum (VBM), insets are the extraction figure of single sample of each type. The onset of the respective energy measured (Kinetic energy for Work Function and Binding energy for VBM) gives the minimum energy for the removal of electron representing the . The yellow demarcation indicates the range of tunability of the work function based on polynomial fitting.

These transformation results in interesting modification to the electrical structure of the material. WF represents the energy barrier to free space (or vacuum level) that prevents an electron at Fermi level from escaping the solid³⁰⁶ and is extracted from the onset of the UPS spectrum^{307, 308} (**Figure 36a**). These values obtained were summarised in **Figure 36b**. As WF

is highly surface sensitive, the slight difference in surface morphology affects the reading widely, hence it is reasonable for the spread of readings. Based on the results, the WF increases from minimum 4.0 eV in as-etched MXene to maximum 4.75 eV in nitrogen-doped MXene. The reference gold WF is ~ 4.7 eV which is consistent with previous report for polycrystalline film gold.³⁰⁶

On average, after the annealing in Ar, the WF of MXene is shifted upwards by about 0.37 eV to 4.5 eV, whilst after annealing in NH_3 the shift is more apparent to 4.7 eV. This trend of the shift in WF, is consistent with the trend exhibited from the calculation. The increase in WF could be attributed to the introduction of more electronegative species as termination. The partial electron transfer increases surface dipole and raises the vacuum level energy.³⁰⁶ The wide range of shift is visualised with the light demarcation where it is possible to tune the WF within the range as seen experimentally. The largest change of 0.75 eV had been obtained by doping the as-etched MXene with nitrogen.

Figure 37 UPS spectrum of selected samples of each type. The presence of 2 onset values could be due to the presence of different phase of the material.

To understand the band structure, VBM was measured (**Figure 36c**) and summarised in **Figure 36d**. The intersection point of tangents from the leading edge of the valence band onset and the zero line is taken as the valence band onset point. The difference between the Fermi level ($BE=0$) and the intersection point gives position of VBM with respect to the Fermi level ($E - E_f$).³⁰⁹ On average, the VBM of the as-etched MXene is 3.77 eV, but, after annealing in Ar, the VBM shifted downwards to 3.66 eV. The VBM is reduced further after annealing in NH_3 to 3.43 eV. The drop in VBM indicates a smaller energy difference between the valence

band and the Fermi level, indicating a reduction in the potential barrier for flow of holes and increased contribution of hole conduction. It is noted that there are double onsets on certain samples of the different type of treatment (**Figure 37**) indicates the presence of multiple phases.³¹⁰ Especially on nitrogen-doped samples, the presence of multiple phases supports the observation that a mixture of TiN and $\text{Ti}_3\text{C}_2\text{-N}$ is present. The presence of multiple phases on the as-etched could be due to the presence of various functional groups in the pristine MXene. On the Ar-annealed sample on the other hand, there is no sign of double onset suggesting that the sampled locations are mostly made up single termination.

Figure 38 (a) Effect of terminations and thickness on work function (eV) of Ti_3C_2 . Blue and orange bars represent the PBE-D3 calculated work functions for a one- and a two-layered slab. These values were computed on a (2x2) unit cell. Work function depends on the surface terminations as clean slab has the lowest and N*-terminated slab has the highest value. These values are independent of the thickness of the slab as seen in the figure. (b) Scatter plot depicts the change in work function (eV) with respect to coverage of N* in Ti_3C_2 -N*/O* slab. As the coverage of O* decreases, there is a linear rise in the work function. As the thickness do not influence the work function, data points overlap for the same coverage of N*.

Experimental results had shown how the WF of Ti_3C_2 can be modulated by functionalizing the MXene. The evolution of WF values and trends of Ti_3C_2 functionalised with different terminations such as F*/O*/N* are investigated using DFT. WF (Φ) is calculated as the energy difference between the potential of the slab in the vacuum region and the Fermi level.^{47, 306} Using the self-consistency calculations, the charge density file is generated, which is further used to get work function using post-processing scripts provided in Quantum ESPRESSO. The work function of a one-layered and a two-layered slab using PBE and PBE-D3 functionals was predicted. Symmetric slabs were used with terminations on both sides of

the slab. A fundamental understanding of the work function trends was obtained by relating them to the conductivity.

From the calculation, WF is dramatically high with a value of 7.37 eV in case of N-terminated ($\text{Ti}_3\text{C}_2\text{-N}^*$) and lowest in the case of bare slab with a value of 4.46 eV, for a one-layered symmetric slab determined using PBE-D3 functional. F-terminated ($\text{Ti}_3\text{C}_2\text{-F}^*$) and O-terminated ($\text{Ti}_3\text{C}_2\text{-O}^*$) slabs have intermediate values of 4.78 eV and 5.85 eV, respectively. A similar trend with respect to terminations is observed for thicker slabs. The WF value, 7.42 eV, is the highest in a two-layered $\text{Ti}_3\text{C}_2\text{-N}^*$ slab, calculated using PBE-D3 functional as shown in **Figure 38b**. In all these cases, terminations are homogeneously distributed on surface of the slab. In addition to this, the trend for mixed terminations of O^* and N^* on the surface was investigated. The WF values for these structures are intermediate between $\text{Ti}_3\text{C}_2\text{-N}^*$ and $\text{Ti}_3\text{C}_2\text{-O}^*$ are significantly higher than the bare slab. As the surface nitrogen atoms increases, the WF increases. Hence in **Figure 38c**, an increasing trend is obtained between WF and coverage of N^* . The data is included in **Table 16**.

Table 16 Atomic model of a bilayer of Ti_3C_2 MXene functionalised with N^* on both ends. The interlayer distance is initially maintained as 7 Å, which decreases to 1.3 Å in the converged structure. The atomic elements Ti, N^* and C^* are depicted in grey, turquoise, and brown, respectively. Table shows a list of work function values predicted using PBE-D3 functional for a one and a two-layered $Ti_3C_2-T_x$. Surface terminations are added on both ends of the slab. The trend was predicted based on thickness of the MXene for full monolayer and mixed terminations. The interlayer distance for a two-layered MXene is maintained as 7 Å which decreases in the converged structure as listed in Table 15. These work function values are computed on a (2x2) unit cell.

Termination (T_x)	Coverage (ML)	One-layered slab	Two-layered slab
Bare	1	4.46	4.45
O^*	1	5.85	5.84
N^*/O^*	0.25	6.29	6.29
N^*/O^*	0.5	6.81	6.8
N^*/O^*	0.75	7.15	7.17
N^*	1	7.37	7.42
F^*	1	4.78	4.77

Figure 39 The trend in the work function for a one layered thick slab based on surface terminations. The substrate is covered with a full monolayer of functional groups. Work function is the highest in N-terminated and lowest in clean slab. This trend is independent of the functional used.

The trends in WF obtained via theoretical calculations agree qualitatively with experimental observations. Using a second DFT functional, PBE, for different terminations, the WF is computationally predicted to see the influence of the functional chosen in the model. The data is presented in **Table 17** and the trend with respect to surface terminations can be observed in **Figure 39**. The most striking feature is that the functionals and thickness of the slab do not affect the work function. Instead, it can be modulated by just tuning the terminations present on the surface.

Table 17 List of work function values predicted using PBE functional for a one-layered $Ti_3C_2-T_x$. These values are computed on a (2x2) unit cell with surface terminations on both ends of the slab.

Termination (T_x)	Coverage (ML)	One-layered slab
Bare	1	4.45
O*	1	5.99
N*/O*	0.25 (N*)	6.04
N*/O*	0.5 (N*)	6.1
N*/O*	0.75 (N*)	6.15
N*	1	6.31
F*	1	4.67

Figure 40 (a) conductivity measurement based on van der Pauw's method, inset contains the samples for measurement (b) Structures of Ti_3C_2 , TiN (111) and TiN (100) (c) Density of states of F^* , O^* , N^* , TiN (100) and TiN (111) between -1 to 1 eV of Fermi level. The higher the density of states at Fermi level indicates higher conductivity.

To further understand the effect of functionalisation on the electrical conductivity. The electrical conductivity was measured via a van der Pauw set up (results are summarised in **Figure 36e**), Annealing in Ar reduced the electrical conductivity by almost 6 fold, from 72.9 Sm^{-1} in the as-etched to 11.5 Sm^{-1} . This could be due to the TiO_2 formed within the Ar-annealed that impedes the electrical conductivity. Furthermore, the electron withdrawing effect of O could be another reason for the reduction in charge carrier density. On the other hand, electrical

conductivity after annealing in NH_3 was increased by ~ 170 fold to 12432.44 Sm^{-1} . The increase in conductivity of nitrogen-doped sample can be attributed to two factors 1) the reduction of the layer distance during the formation could have led to more conductive pathway, and 2) the electron donating effect of N could have resulted in the increase in carrier density.

To gain more insight into the electronic structure change, density of states (DOS) was calculated using DFT. Density of states are normalised by the volume of the metal atoms, calculated as the cross-sectional area times the slab thickness. As the conductivity is proportional to the number of states available at the Fermi level ($E - E_f = 0$). The density of states of O^* , N^* , and F^* terminated Ti_3C_2 MXene near the Fermi level are similar indicating that changing the termination alone is unlikely to drastically alter the electrical conductivity.

As corroborated by the DOS of TiN, especially TiN (100) (**Figure 40b** and **Figure 40c**), significantly higher DOS near the Fermi level indicates a higher conductivity than $\text{N}^*/\text{O}^*/\text{F}^*$ terminated Ti_3C_2 . The experimentally observed high conductivity of Ti_3C_2 annealed in NH_3 maybe partially contributed by the formation of TiN on the surface. Even with the presence of TiN, the improvement of the conductivity limits in the range capped at $1\text{E}4 \text{ Sm}^{-1}$ compared to the expectations of $1\text{E}6 \text{ Sm}^{-1}$,³¹¹ suggesting the polycrystalline nature of the crystal.

5.3 Summary

Termination on MXene is one of the most intriguing and important properties for the material. The surface termination of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ can be changed to tune its work

function and electrical properties by simple annealing in oxidative or reductive environment. Although the largest shift in work function obtained was ~ 760 meV by doping nitrogen into the pristine $\text{Ti}_3\text{C}_2\text{T}_x$. DFT calculations suggested that a complete replacement of termination into N^* can achieve a WF of more than 7 eV, showing the great potential of MXene as high-WF metal, alternative to platinum.

Though the termination on MXene has minor effect on the DOS, hence should not have effect on the electrical conductivity of the material, the experimentally observed electrical conductivity varies by orders of magnitude. This discrepancy suggests that formation of TiN may play a nonnegligible role in the increase in conductivity, while the presence and influence of TiO_2 plays a countering role.

This wide range of tuning is beneficial to engineering its application in energy conversion such as perovskite solar cells, where MXene can act as both the electron transfer layer and or the hole transport material in the same cell which reduce the complexity of fabrication.

Chapter 6: MXenes Modification for Light-to-Heat Conversion

Modification of MXene also affects its photothermal conversion properties as shown in this chapter. More than one billion people lack access to clean freshwater, and freshwater scarcity is a critical challenge worldwide. Extensive research efforts have been devoted to technologies for freshwater generation.³¹²⁻³¹⁸ Technologies like reverse osmosis by micro-filter membrane and thermal distillation (*e.g.*, in power plant) are developed for mass production of freshwater in centralized systems with energy-intensive processes.^{319, 320} However, most of the areas lacking fresh water are in developing countries and have very limited access to intensive energy that powers centralised systems. Thus, decentralised systems that are energy saving and easy to operate are highly desirable for freshwater generation in the developing and/or remote areas. Seawater desalination exhibits great feasibility due to the seemingly infinite availability of seawater. Meanwhile, solar energy is widely utilised in renewable technologies including solar cell and photocatalysis.³²¹ Combining a traditional distillation system with an energy-saving process such as solar steam generation is promising owing to its excellent scalability, high efficiency, and environmental friendliness.³²²⁻³²⁶ Therefore, the development of an efficient solar steam generator has gained ever-increasing attention.

Both volumetric and interfacial solar steam structures have been deployed to achieve high energy conversion efficiency. Despite the simple process of volumetric structure, where photothermal absorbers are dispersed in the bulk of water to be heated up, it faces challenges

such as substantial energy wastage and inefficient photothermal material recycling. Compared to volumetric structure, interfacial structure confines heat near the distillation interface, leading to much higher energy efficiency.^{327, 328} Moreover, photothermal materials are embedded in a membrane absorber, facilitating photothermal material recycling. Membrane designation serves as efficient a way to eliminate factors inhibiting the evaporations. An ideal solar steam generator can be obtained through: (1) optimising photothermal efficiency of the absorber; (2) localising heat within the absorber; and (3) minimising heat lost into the bulk water or surrounding.^{325, 327, 329, 330} Researchers also employ integrated Janus structure for isolating functional parts in membrane, which significantly enhances steam efficiency.³²⁶

Various photothermal materials with wide adsorption band and low dimensional structures (for high surface-to-volume ratio) including carbon nanotube, two-dimensional (2D) semimetal graphene or bulk Graphite, graphene-like molybdenum disulfide, organic membrane and plasmonic metal nanoparticle have been studied in solar steam generator for high light absorption capability.^{187, 331-342} Besides, organic hydrogel is also an novel system which can effectively tuning the water state to lower the latent heat for ultrahigh evaporation.^{343, 344} MXene, an emerging graphene-like material has been theoretically predicted to be a superior photothermal material with nearly 100% photo-to-thermal conversion efficiency.³³ As discussed in Chapter 5, MXene has wide applications in catalysis, photocatalysis, photothermal conversion, and electromagnetic shielding.^{7, 11, 33, 345, 346} Owing to its unique layered structure and metal-atom-terminated surface, its rich surface chemistry and can be easily functionalised

by surface modification. Various functionalisation can significantly tailor its physical properties including photothermal properties. Despite these advantages of MXene for photothermal conversion, its application in solar steam generation is yet to be demonstrated.

Apart from improving the high photothermal efficiency, minimising heat dissipation is also crucial. By optimising absorber's inner structure, one can effectively prevent heat from spreading in polymers and composite membranes.^{347, 348} Furthermore, insulated structure made of materials with low thermal conductivity such as plastics and foams were employed to confine the generated heat (from solar energy) locally at the distillation interface. Water desalination without excess energy input can be realised through such solar steam generation. Although high solar steam efficiency under concentrated solar irradiance has been achieved through optimising the materials and device configuration, that under natural solar irradiance (around 1 sun) still has room for significant improvement.^{328, 349} Several key challenges hamper the practical applications of interfacial solar steam generation. These are (a) high solar steam efficiency with scalable fabrication process is required, (b) sustaining adequate and continuous water evaporation at the interface is challenging, (c) long lifespan, cost-effective photothermal absorber materials with robust mechanical property are needed, and (d) low water content within the absorber (inner water transport channels) is desirable.

In this chapter, we introduce an insulated interfacial solar steam generator with high solar steam conversion efficiency made from cellulose acetate-MXene (CAM) membrane. The CAM membrane is facilely fabricated by dispersing functionalised MXene flakes in the

polymeric network of cellulose acetate. Within the 3D cross-linked polymeric networks, these homogeneously dispersed MXene flakes are integrated into the structure to improve the mechanical strength; this enables efficient light-to-heat conversion. As such, a high net evaporation rate of $1.47 \text{ kg m}^{-2} \text{ h}^{-1}$ under 1 sun illumination with 92% solar steam conversion efficiency was achieved with a robust thin photothermal membrane. Moreover, the CAM membrane exhibited a high desalination rate up to 97.5%. The increased light absorbance by functionalised MXene efficiently improves the heat generation and activation, which offers a cost-effective photothermal material. Besides, the integrated structure and polymeric wrapping structure extends the lifespan of MXene flakes, leading to a stable and durable membrane system.

6.1 Experimental section

Figure 41 Schematic illustration of overall solar steam generation setup based on CAM membrane absorber. Below the CAM membrane, water transport to the interface is facilitated by capillary force and swelling of the channels in the water pumper. The designed 2D pathway is part of the water pumper that enables sustainable water supply for steam generation, as well as for minimising heat spreading into the bulk water. Inside the porous polymeric network of CAM membrane (lower dotted box), the MXene flakes (atomic structure shown in upper dotted box) efficiently harvest solar energy and then generate heat for vaporising water molecules in the membrane to enhance water evaporation (see CAM membrane working mechanism in the middle). Coated with light blocking layer, PMMA plate with a circular opening is employed to precisely define the evaporation area, as well as to avoid direct sunshine on water bulk.

The experimental setup and main components are illustrated in **Figure 41**. Water evaporation is accelerated at the CAM membrane surface due to the rapid conversion of solar energy to heat. The porous polymeric heat insulator keeps the heat localised and support capillary water transport, which sustains the water supply to the surface. A water pumping pathway is formed in the bulk water for efficient water supply enabled by capillary pressure in

the pores. The cross-linked molecule meshes of CAM membrane and the poly(methyl methacrylate) (PMMA) insulator form pathways that encourage dynamic ion diffusion, endowing the generator stable evaporation performance for long-time usage.³⁴⁷ The evaporation area is defined by a PMMA plate with a circular opening in the center. This is surrounded by a light blocking layer to prevent light shining onto the bulk water that may increase its temperature.

6.1.1 Materials

Cellulose acetate ($M_n \sim 30000$) and polyethylene glycol (PEG, $M_w \sim 1500$) were purchased from Sigma-Aldrich. Solvents including acetone and N-methyl-pyrrolidone (NMP) were purchased from VWR Chemicals. MAX phase Ti_3AlC_2 was purchased from Y-Carbon Ukraine.

6.1.2 Fabrication of pristine MXene

MAX phase Ti_3AlC_2 was exfoliated via etching under 48 *wt%* HF for 1 week under constant stirring. MXene were retrieved after sequential process of washing with DI water, centrifuging at 3500 rpm, and then drying under vacuum at 60°C.

6.1.3 Fabrication of Li-MXene

MAX phase Ti_3AlC_2 was exfoliated using the MILD method with the etchant consisted of 100 ml of 6 M HCl with 3.96 g LiF. The material was etched for 1 week under constant stirring. MXene was retrieved in the same way as that of pristine MXene.

6.1.4 Fabrication of CAM membrane

Proper amount of Cellulose acetate and PEG were dried under 50 °C for 30 min to remove the absorbed water. Then, all the dried powder was dissolved in acetone and NMP in a sealed beaker under 55 °C with stirring for 1 h. The as-prepared Li-MXene powder was grinded for several times followed by dispersion in 2.5 mL acetone in ultrasonication. Then, the dispersed Li-MXene was added into the organic gel at 45 °C with stirring. Afterward, homogeneous mixture was poured into the glass mould ($D = 5.0$ cm) and then placed on a balance. When the weight reached a stable state, the mould was immersed into cold water immediately for phase changing around 1 h to obtain the CAM membrane. Water bath treatment (50 °C) was applied to the CAM membrane after the phase change to remove the unstable chemicals inside. Here, the template method was employed for better evaluation of Li-MXene loading. Spray coating method is also applicable in the fabrication of CAM membrane. Details of sample fabrication are as follows: sample 1: 1.2 g cellulose acetate and 0.3 g PEG with 50 mg Li-MXene; sample 2: 0.8 g cellulose acetate and 0.2 g PEG with 50 mg Li-MXene; sample 3: 0.4 g cellulose acetate and 0.13 g PEG with 50mg Li-MXene; sample 4: 0.4 g cellulose acetate and 0.13 g PEG with 30 mg Li-MXene; sample 5: 0.4 g cellulose acetate and 0.13 g PEG with 80 mg Li-MXene.

6.1.5 Physical characterizations

The absorption spectra of MXene powder and membranes were characterised by a UV-vis spectrometer coupled with an integrating sphere (Shimadzu, UV-1800). The powder

measurements were corrected by baseline correction with only solvent. Microstructures of MXene and membrane were taken by a field-emission SEM (JEOL 7600F). Heat distribution map was obtained through an IR camera (NEC F30W) with black background (emissivity = 1.0). X-ray diffraction characterization was carried out using Bruker D8 Advance ($\text{Cu K}\alpha = 0.154\text{nm}$). Mechanical robustness was tested by a tensile machine (Instron-5569). Microscopic images are taken by OLYMPUS BX53M series. Contact angle is measured by LMS Scientific Solution Sdn Bhd OCA 200.

For desalination property characterization, a balance (OHAUS- Pioneer Series) was used for the tracing of weight change. Natural light was simulated by a solar simulator from ORIEL (LCS-100). The actual solar intensity was calibrated by a photometer from Silicon Lab. Ion concentrations were precisely evaluated by ion concentration meters for Na^+ and Cl^- (Hang Zhou, Qiwei Equipment-DWS 51).

6.1.6 Desalination performance measurement

The steam generation experiments were conducted in our lab with average temperature of 27°C and relative humidity of 57%. Solar steam generator was placed on balance (with 0.01 g resolution) under continuous solar illumination generated from solar simulator. Precise solar flux intensity was characterised by a photometer to keep the absorber under 1.0 kWm^{-2} solar irradiation. To avoid light nonuniformity, we utilise the center of the illuminated area ($5 * 5\text{ cm}^2$) by confining the evaporation area into 12 cm^2 by PMMA shadow mask. A glass chamber was used to collect the purified water for salt concentration test. Before the solar irradiation,

the setup was kept in the dark condition to take the weight change as the reference. All the evaporation rate stated above is net evaporation rate, which excluded that in the dark condition as the background.

Foldable test is conduct as follows: desalination is test after the sample is fully swollen in seawater. Then swollen sample is dried under 60 °C to make it folded. After that, dried sample is ultrasonicated in seawater for recovery.

Harsh condition test: (1) samples are boiled (100 °C) for 1 h before evaporation test is conducted; (2) samples are immersed in acidic solution (H_3PO_4 , pH = 3) for 1 h before evaporation test is tested; (3) samples are immersed in alkaline solution (KOH, pH = 13) before evaporation test is conducted.

6.1.7 Solar steam efficiency calculation

Solar steam energy conversion efficiency is calculated by considering the h_{lv} as the latent heat of the liquid-vapor phase change (2256 Jg^{-1}) instead of combination with water sensible heat (315 Jg^{-1} derived from 25 °C to 100 °C). The reason is that latent heat of vaporization is the total heat requirement during a constant temperature process, which corresponds to the working principle of the solar steam generator. Besides, the water sensible heat is precisely evaluated in the following energy transformation analysis.

6.1.8 Steam generator energy consumption evaluation

To better evaluate the energy output of solar steam generator, the detailed energy pathways were calculated from the data recorded within 1h. The total solar energy input with 1.0 kWm^{-2} for 1h is $3.6 \times 10^5 \text{ J}$. Several types of conversions are included in this thermal-dynamic system.²⁸

1. Heat for evaporation: Q_{vapor}
2. Reflected heat loss: Q_{ref}
3. Conduction heat loss: Q_{cond}
4. Radiation heat loss: Q_{rad}

Q_{vapor} represents the total utilised heat energy converted from solar input. In other words, it's the heat that is consumed by the liquid-vapor phase changing process. Thus, the Q_{vapor} equals $2256 \text{ Jg}^{-1} * 1.47 \text{ kg m}^{-2} \text{ h}^{-1}$, which is 92.1% of input solar energy.

Q_{ref} is the total energy loss caused from reflection at the CAM surface. The average reflection rate measured in 400 nm - 1100 nm is around 5%.

Q_{cond} denotes the energy loss during conduction process especially to the water heat capacity, which can be defined as $Q_{\text{cond}} = Cm\Delta T$, where C is the specific heat capacity, m is the weight of bulk water (~55 g), ΔT (0.3 °C) is the temperature change before and after illumination. The overall conduction heat loss can be calculated as $4.2 \text{ Jg}^{-1}\text{K}^{-1} * 45 \text{ g} * 0.3 \text{ °C}$, which represents 1.9% of input solar energy.

Q_{rad} represents the heat loss during the irradiation to ambient atmosphere, which can be calculated as $Q_{rad} = \varepsilon A \sigma (T_{sur}^4 - T_{amb}^4) * t$, where ε is the estimated emissivity (0.92) of the CAM, A (12 cm^2) is the illuminated surface area, σ is the Stefan-Boltzmann constant ($5.67 * 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$), T_{sur} ($48 \text{ }^\circ\text{C}$) is the surface temperature, T_{amb} ($27 \text{ }^\circ\text{C}$) is the ambient temperature, t (1 h) is the illumination time. Thus, Q_{rad} is calculated to be 1.07 J, corresponding to 0.03% of the total input solar irradiation.

The overall calculated energy consumption above is around 99.03% of the total input solar energy (excluding measurement and calculation errors), other pathways of heat loss may also exist during the thermal-dynamic process.

6.2 Results and discussion

Figure 42 Characterizations of the as-prepared MXene materials and membrane. (a) UV-vis absorbance spectrum of different MXene powder, DI water as background solvent reference. Insets are SEM images of MXene flakes: Pristine MXene (left), Li-MXene (right); Scale bars are 1 μm. (b) HRTEM image of Li-MXene surface structure, where the dotted circle delineates the grains of defective region. Scale bar is 5 nm. Inset: the corresponding FFT pattern; (c) HRTEM image of pristine MXene surface structure showing the homogeneous surface structure. Scale bar is 5 nm. Inset: the corresponding FFT pattern. (d) XRD patterns of pristine and Li-MXene flakes showing the shifted (002) peak position which denotes larger layer gaps after intercalation of Li^+ specie.

MAX phase of titanium carbide with $n=2$, i.e., Ti_3C_2 , was selected in this investigation for its well-studied properties, wide availability, high reproducibility, and ease of production. To search for the MXene with high photothermal efficiency, we have employed various methods

to prepare and functionalise MXenes. For instance, hydrogen fluoride was used to etch MAX powder to obtain MXenes (denoted as pristine MXene). Lithium fluoride (LiF) was also employed to etch MAX materials as well as intercalation of Li into MXene (named as Li-MXene). Nitrogen (denoted as N-MXene) and O (named as O-MXene) surface functionalization were performed on the pristine MXene. **Figure 42a** shows the UV-vis spectrum of various MXenes that were homogeneously dispersed in aqueous solution. It is noted that Li-MXene and N-MXene possessed high absorption rate; and Li-MXene has relatively higher absorption within the visible range. Since most of the sun light is in the range of 400 - 1000 nm, Li-MXene is expected to act as a better absorber for solar steam generation.

Pristine and Li-MXene have very similar morphology under scanning electron microscopy (SEM), as shown in the inset of **Figure 42a**. The intercalated Li⁺ species cannot be detected by Energy Disperse Spectroscopy (EDS) due to the lack of K α , but similar material was proved to contain Li in previous work.^{152, 350} High-resolution transmission electron microscopy (HRTEM) images (**Figure 42b** and **Figure 42c**) confirm the similar morphology. However, Li-MXene has more defects (see dotted circles in **Figure 42b**) with poorer crystallinity, as seen from the Fast Fourier Transform (FFT) patterns (insets of **Figure 42b** and **Figure 42c**). The DFT calculations of Bai *et al*³⁵¹ predicted that the presence of defects improves the in-plane adsorption of visible light. X-ray diffraction (XRD) characterization (**Figure 42d**) reveals that the (002) peak of Li-MXene is much stronger and appears at a smaller angle than that of pristine MXene, suggesting that the interlayer distance of Li-MXene is larger

than that of pristine MXene. This is attributed to the intercalation of Li species into the interlayer space in Li-MXene, consistent with previous report.¹⁵² It is worth noting that this larger interlayer distance can be very beneficial for light penetration, and more adsorption in the membrane.

Figure 43 (a) SEM images of CAM membrane surface to show the surface morphologies and distribution of MXene flakes, enlarged at right is the details of blank area (b) Cross-sectional SEM image of the CAM (sample 3) with micro- and nano-pores (sample 3); Scale bars are 20 μm, 50 μm and 1 μm from left to right image, respectively; (c) Cross-sectional optical

microscopic images of sample 3 during (i) dry and (ii) wet state, which shows a stable porous structure.

To systematically investigate factors affecting the CAM performance, 5 samples with different MXene-to-CA ratios (sample 1-5) were prepared. The CAM structure fabricated using a mould with diameter of 4 cm. Lower MXene-to-CA ratio means high crosslink density (compared among samples #1-#3) and higher MXene-to-CA ratio represents higher MXene concentration (compared among samples #3-#5). The SEM image of CAM membrane surface (**Figure 43a**) implies that Li-MXene flakes (dotted circle) are homogeneously dispersed on the surface, leaving blank area (see inset for enlarged view) with interconnect pores for water transport. The cross-sectional SEM image of CAM membrane (**Figure 43b**) reveals an integrated nano/ micro pore structure is exhibited inside the polymeric networks. Furthermore, this porous structure is stable during transition from dry to wet state, as shown in the optical microscopic images (**Figure 43c**). As one can see, the swollen membrane exhibits the same structure as that in dry state. Both micropores and nanopores play important roles owing to the capillary forces.³⁵² Such a porous structure can effectively generate weak water bonds with polymeric chains, which facilitates the steam generation.^{353, 354} Interpenetrated Li-MXene flakes are fully wrapped and completely blended inside the polymeric network, as depicted in the SEM image (**Figure 43a** and **Figure 43c**), where no obvious naked flakes can be identified. Such a complete wrapping significantly reduced exposure of MXene flakes to water and oxygen molecules, which effectively prevents MXene degradation, and thus increased its stability to more than 6 months.

Figure 44 (a) Contact angle test of the CAM surfaces: (i) sample 3; (ii) sample 5; (iii) sample 1. The contact angle of sample 3 and 5 are nearly the same, where sample 1 has much lower value. All three samples possess hydrophilic surface. (b) Water content characterization of the CAM before and after drying (0.025 g) from saturated state (0.059 g). Annotation means the saturation water content of the tested sample. Sample is dried in air at 70 °C for 45min (c) UV-vis absorbance spectrum of pure CA and CAM membrane, insets are the optical images of corresponding membranes, scale bars are 2 cm; (d) Mechanical property tested under the same

extension rate (e) Thickness measurement of the CAM and pure CA for comparison of mechanical property. (i) Thickness of the CAM sample is 330 μm ; (ii) Thickness of the pure CA membrane is 340 μm . (f) CAM structural recovery capability before and after drying. (i) Tested CAM sample in saturated state, showing a flat condition; (ii) Dried CAM sample after keeping at 70 $^{\circ}\text{C}$ for 45 min, showing a rolling state owing to water loss; (iii) Flat CAM sample after ultrasonication in water bath for 30 min, showing a recovery capability. (g) Evaporation performances of foldable membrane under condition of $\text{RH} = 67\%$, $T = 23^{\circ}\text{C}$. Recovery means ultrasonic treatment to recover to the flat condition. Negligible variation is shown in sample 3 where a little decrease is shown in sample 5.

Contact angle test shows that samples #1, #3, and #5 are all hydrophilic, and higher MXene-to-CA ratio results in more hydrophilicity (**Figure 44a**). The integrated pore structure also promotes water extraction, as well as salt exchange owing to the capillary effect throughout the polymeric network.³⁴⁷ The swelling ratio Q is obtained from water content measurement by equation:

$$Q = \frac{W}{W_d} \quad (1)$$

where W and W_d represent sample weights in saturated water absorption and dry state, respectively. The swelling experiment (**Figure 44b**) shows that CAM membrane possesses much lower swelling ratio ($\sim 2.3 \text{ gg}^{-1}$) compared to that of 3D gel-based absorber ($3\sim 8 \text{ gg}^{-1}$).^{347,}

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Next, the photothermal performance of CAM membrane was investigated. The pure CA membrane is white in colour while the CAM membrane appears completely black owing to the addition of black Li-MXene flake (insets of **Figure 44c**). The ultraviolet-visible (UV-vis) absorbance spectrum presented in **Figure 44c** shows that, compared to pure CA membrane,

the CAM membrane exhibits nearly 100% increase in absorbance. The absorbance of both spectra shows obvious increase of about 25% from 400 to 1100 nm, indicating an enhanced absorption in the visible region. This phenomenon may be ascribed to the increase by cellulose acetate networks.³⁵⁵ Two other factors also account for the excellent light absorption: (1) the change in overall colour from white to black due to homogeneous dispersion of Li-MXene that reduces the light reflection; and (2) the interpenetrated Li-MXene flakes efficiently absorb photons in its layered structure.³³ The mechanical robustness (crucial for practical application) of the CAM membrane was evaluated through mechanical testing (**Figure 44d**). Lateral forces were applied on two membranes with the same size and thickness $\sim 340\ \mu\text{m}$ (**Figure 44e**), with a piece of commercial A4 paper ($80\ \text{gm}^{-2}$) of the same dimensions as the reference. Under consistent extension rate, the CAM membrane shows promising mechanical strength with the maximum loading of around 12 N. Excellent extension reveals higher tolerance to strains and lower risk of potential mechanical damage. This improvement in ductility can be attributed to the cross-linked polymeric network in CAM membrane. It's worth noting that CAM membrane is naturally flat and can be folded even under saturated swelling condition. Moreover, the folded dry CAM membrane can recover to its original flat condition upon complete wetting in water with slightly decrease in evaporation performance (**Figure 44f** and **Figure 44g**). Sample #5 showed more degradation during the folding test, which is attributed to the too high MXene-to-CA ratio leading to a poor mechanical stability.

Figure 45 Working mechanism illustration and thermal performance evaluation. (a) Schematic of the designed solar steam generator, showing basic components and steam generating process; (b) Water pumper under the CAM which transport water from bulk to the interface and Top view heat distribution of the solar steam generator under exposure to 1 sun illumination continuously; (c) Temperature profile along the vertical direction, showing excellent heat localization performance (sample 3). Inset: the IR image from the side view [the “Center Point (+)” corresponds to the + marker in the IR image], recorded range is shown by the arrow; (d) Temperature change comparison of seawater, pure CA membrane, and the CAM membrane evaporator under continuous 1-h solar illumination. (e) IR images of samples with different MXene-to-CA ratios: (a) sample 4; (b) sample 2; (c) sample 1; (d) sample 3; (e) sample 5. Samples are illuminated continuously for 5 min.

Lastly, the CAM membrane in a solar steam generator prototype was examined. As illustrated in the schematic of our solar steam generator (**Figure 45a**), capillary pressure extracted water through the T-shaped water pathway (the water pumper) working as the sustainable water supplier to CAM membrane/ pumper interface (see **Figure 45b** for optical image). Meanwhile heat was localised within the thick PMMA spacer acting as the heat insulator. Light-to-heat conversion within the CAM membrane accelerated steam generation in the channels. It encourages transpiration pull as shown by the steam flow, and hence the replacement of water in the channel. IR heat maps under 1 sun illumination are shown in **Figure 45b** and inset of **Figure 45c** from different perspective views. Top view temperature difference within the generator is depicted in Figure 3b, where the CAM membrane reached 50 °C in 1 h within the evaporation area defined by the PMMA opening. From the side view (inset of **Figure 45c**), one can observe an abrupt temperature drop of more than 20 °C between the surface and the bulk water; this verified that heat was efficiently localised within the surface of the evaporating area. The overall thickness of the CAM membrane and foam pumper was around 1 mm. The homogeneous colour contour below the spacer further revealed the negligible heat loss into the bulk water. Plots in Figure 3c quantitatively presents the temperature change along the vertical direction from the top of the CAM membrane to the bottom of the beaker (as labelled by the dotted line in the side view IR image). The photothermal performance of CAM membrane was further analysed with the activation time trace, as depicted in **Figure 45d**. Under continuous 1-sun illumination, bulk water was slightly warmed while the pure CA gradually rose to 38 °C after 12 min. In contrast, the CAM membrane reached 43 °C within 5

min owing to its superior light-to-heat energy conversion capability, indicating a fast activation performance. Moreover, the temperature of CAM membrane kept increasing in the first hour and peaked at 50 °C. The similar temperatures of samples #1 to #3 (CA amount decreases with constant MXene amount) suggest that (1) the samples temperature depends on the MXene loading, and (2) the CA amount used is sufficient to effectively isolate heat from dissipating to bulk water in the optimised condition (sample #3), as shown in **Figure 45e**. Whereas the low temperature of sample #4 than that of sample #3, which have the same CA amount, indicates insufficient heat generation in sample #4 due to the less MXene used.

Figure 46 Desalination performance of solar steam generator with the CAM membrane under 1 sun illumination, 57% relative humidity, and room temperature. (a) Mass change comparison for 1-h illumination of different setups with 3.5% seawater; (b) Mass change of samples with different MXene/CA ratio under condition of RH = 67%, T = 23 °C. (c) Continuous evaporation rate and mass change test for 6 h showing the steam generating speed and stability (30 min per cycle); (d) Energy conversion efficiency evaluation during continuous 6-h illumination.

To systematically evaluate the potential of CAM membrane for water desalination, series of experiments were conducted to record mass change, evaporation rate, efficiency, stability, and salt rejection rate. The mass change was measured under continuous solar illumination.

Figure 46a displays the real-time mass loss curves of different conditions. Mass losses of 0.72 g and 0.44 g were recorded for water with and without CA membrane, respectively, under

continuous 1-sun illumination. This result suggests that the insulation structure significantly enhanced steam generation by localising heat at the surface. In obvious contrast, the setup with the CAM membrane exhibited mass loss of 1.5 g, which is 108% (240%) more than that with pure CA (without membrane). This superior performance is attributed to the excellent photothermal property of the interpenetrated Li-MXene. The abruptly increased mass change within the first 300 s corresponds to the fast activation performance, as shown in Figure 3d. As shown in **Figure 46b**, the inferior evaporation performances of control samples (#1, #2, #4, #5) than the optimised sample (#3) is ascribed to the following factors. Firstly, higher CA amount results in thicker membrane structure, leading to longer water transport path and more water exchange, thus low evaporation rate (*e.g.*, sample #1). Secondly, lower MXene amount (*e.g.*, sample #4) generates less heat (Fig. S10), resulting in insufficient energy for steam generation. Thirdly, too high MXene loading (sample #5) can generate more heat, but shorter water path due to smaller CA ratio. Therefore, one should balance the MXene loading (then cost) and the MXene-to-CA ratio.

Stability test was conducted under continuous illumination for 6 h and recorded every 30 min. As shown in **Figure 46c**, more than 10 g weight loss was accumulated in a linear trend, showing an outstanding stability in long-term steam generation. In the first 30-min cycle, the total recorded weight loss was only 0.75 g with an evaporation rate of $1.25 \text{ kg m}^{-2} \text{ h}^{-1}$, corresponding to the result in **Figure 46a**. This can be ascribed to the activation process when the membrane-vapor interface temperature rose from room temperature. The following cycles

show that the evaporation rate levels off with negligible variance revealing great stability for long-time steam generation for seawater. To further evaluate the performance of the steam generator quantitatively, energy conversion efficiency was calculated. Since solar irradiance provides the energy during water vaporization, the solar-to-steam energy utilization efficiency can be evaluated as.³⁵⁶

$$\eta = \frac{R \times h_{lv}}{I \times t} \quad (2)$$

where R is the net evaporation rate; h_{lv} represents the latent heat of liquid-vapor phase change of water (2256 Jg^{-1}); I denotes the total input solar power that is calculated by multiplying the optical concentration with nominal solar power density of 1.0 kWm^{-2} , and the evaporation duration t is fixed at 1 h. **Figure 46d** visually compares the efficiencies for the 12 cycles together with evaporation variance. Within the first activation cycle, the total efficiency is calculated to be 78.3%. Afterward, the generator shows great stability and efficiency (up to 92.1%) during the following 11 cycles recorded with negligible variation.

Figure 47 (a) Salt deposition effect on the evaporation performance under condition of $RH = 67\%$, $T = 23\text{ }^{\circ}\text{C}$, which shows a stable steam generation after seawater purification. (b) Evaporation performance of the CAM under harsh condition for 30 min. $RH = 67\%$, $T = 23\text{ }^{\circ}\text{C}$. (c) Salt rejection rate revealed by ion concentration comparison before and after desalination showing the capability to produce drinkable water. (d) Benchmark comparison among related works with 2D interfacial membrane structure.

As salt deposition is always a concern for porous structure, we evaluated the recycling feasibility by washing the CAM in freshwater after solar steam generation testing, and it showed a stable evaporation performance after washing (**Figure 47a**). Harsh condition stability of the CAM was also investigated including high temperature boiling ($100\text{ }^{\circ}\text{C}$), acidic ($\text{pH} = 3$) and alkaline ($\text{pH} = 13$) conditions, which revealed a stable performance of steam generation under harsh conditions (**Figure 47b**). To better evaluate efficiency systematically, forms of

heat loss are estimated with respect to the recorded parameter during continuous steam generation. The overall estimation of heat flows depicts clear view of heat utilization which provides possible directions for efficiency optimization. Furthermore, we have precisely evaluated the ion concentrations from a simulated sea water and compared the results with the standard specified by WHO, as displayed in **Figure 47c**. A salinity of 3.5% seawater (corresponding concentrations of Na^+ and Cl^- are both around 18000 mg L^{-1}) was prepared for the evaluation of salt rejection efficiency. After 6-h continuous steam generation, purified water was collected by clean chamber for ion concentration test. The ion concentrations in evaporated water decreased to 400 mg L^{-1} , as depicted in **Figure 47c**. This result indicates that up to 97.7% ions (Na^+ , Cl^-) were rejected by the polymeric networks. As a result, the ion concentration was significantly lower than the WHO drinkable water standard (800 mg L^{-1}).³³¹

To benchmark our device performance, evaporation rates of similar reported devices (*i.e.*, 2D interfacial structure) are compared in **Figure 47d**. Various photothermal materials including carbon nanotube,³³²⁻³³⁴ two-dimensional (2D) semimetal graphene or bulk Graphite,^{335, 336} graphene-like molybdenum disulfide,³⁴² organic membrane,³³⁷ plasmonic metal nanoparticle^{331, 338, 340, 341} as well as MXene¹⁸⁷ are presented, which shows evaporation rate ranging from 1.0 to $1.35 \text{ kg m}^{-2} \text{ h}^{-1}$. Our solar steam generator shows unprecedented $1.47 \text{ kg m}^{-2} \text{ h}^{-1}$ during continuous 1-sun illumination. The functionalised MXene lowers the loading of photothermal materials in CAM without compromising its performances, holding great

promise for solar steam generation in rural areas that lack of fresh water. The excellent durability and stability in harsh conditions also enhance the potential of functionalised MXene.

6.3 Summary

Efficient steam generation under 1-sun illumination was achieved in our steam generator with the MXene containing CAM membrane. It promoted water transport through embedded channels and exhibited superior mechanical robustness. The engineered Li-MXene possessed a suitable absorption window within the visible-NIR range as an excellent photothermal material. The steam generator confined heat around its desalination surface, and thus avoided heat loss effectively. In addition, the integrated porous structure of CAM membrane offered proper water content balancing between transport and evaporation. This designed setup enabled an unprecedented steam generation rate of $1.47 \text{ kg m}^{-2} \text{ h}^{-1}$ with very high efficiency of 92.1% under continuously 1-sun illumination, thus it is suitable for operation under natural sunlight. Furthermore, cost-effectiveness, scalability, and great robustness suggest the great promise for practical application. Due to practically no additional input energy is required as compared to commercial reverse osmosis process, the CAM serves as potential complement to the energy intensive water purification system. These features, coupled with high salt rejection rate, endow the CAM membrane a promising candidate for seawater desalination. It is worth noting that the new photothermal absorber of MXene has applications beyond solar steam generation such as solar disinfection and photothermal reactions.

Chapter 7: Conclusion and Future Work

7.1 Conclusion

There are countless ways to engineer 2D materials, and while various techniques to modify 2DMs for energy conversion had been showcased in this Thesis, they are just the tip of the iceberg. The methods introduced in the chapters are facile techniques which caused huge improvements to the functionality, rendering remarkable performance to their respective applications. In a nutshell, the Thesis contributes to the understanding of 2DM engineering towards energy application, essentially, closing gaps in the usability of precious metal 2DMs, and functionalisation leveraging rich surface chemistry of 2DMs.

The first showcase was a lithiation activated PdSe_2 that achieved a balance between performance and stability for ORR catalysis. Following that, by annealing $\text{Pd}_3\text{P}_2\text{S}_8$ in NH_3 , an unprecedented ternary palladium phosphoronitride ($\text{Pd}_3\text{P}_2\text{N}_x$) was produced and showed outstanding ORR activity. Subsequently, the work function of $\text{Ti}_3\text{C}_2\text{T}_x$ was tuned in a wide range through functionalisation with O and N which could potentially be used on perovskite solar cell as its electron or hole selection/transport material. Finally, MXene $\text{Ti}_3\text{C}_2\text{T}_x$, was investigated for its photothermal conversion and was demonstrated for its application in a highly efficient photothermal water desalination set up.

The biggest hindrance to the practical adoption of electrochemical catalysts is the durability. Subsequently, the lack of performance limits the use case. To put in perspective, it will be ideal to have a long lasting yet high power producing energy convertor. Hence, the first two showcases

addressed the electrochemically inert 2D precious metal-based materials through various activation techniques. The focus is to assess their applicability in the ORR catalysis in metal-air batteries, and to improve the utility of the scarce precious metals based catalysts.

In Chapter 3, to improve the performance yet maintain durability, *in-situ* lithiation-and-delithiation cycle was used to activate an originally electrochemically inert PdSe₂ by inducing Se vacancies in its chemically inert atomic structure that encourages adsorption of oxygen. Moreover, the accessibility of interlayer space was increased during the process to allow electrolyte to reach the interlayer Pd for catalysing ORR. The lithiation can be controlled to optimise the defect formation without damaging the structural stability of the PdSe₂; such that mild intercalation will not cause any improvement, yet over intercalation will destroy the crystal and compromise the stability. The electrochemically activated PdSe₂ exhibits greatly enhanced electrocatalytic activities as the current density doubled with a 250 mV positive shift of potential. The kinetics of the ORR process was also determined to be much faster (5 times smaller Tafel slope compared to pristine structure), while the stability was greatly improved. DFT calculations complement the experimental studies revealed the mechanisms of electrochemical activation and concurred that the increase in activities would have been derived from the activated surface and easy access of interlayer space for reaction intermediates. Furthermore, the calculations support that the robustness of the PdSe₂ stemmed from the Pd-Se bonding endowing it excellent resistance to degradation.

Subsequently, after understanding how to improve the utility of Pd based 2D catalyst, in Chapter 4, the intrinsic properties of 2D Pd based material was investigated. 2D ternary palladium phosphoronitride (Pd₃P₂N_x) was synthesised, for the first time, via a post synthesis substitutional

doping of ternary palladium thiophosphate ($\text{Pd}_3\text{P}_2\text{S}_8$) as guided by rational design using first-principles DFT calculations. The process almost completely replaced the sulfur atoms with nitrogen atoms, yet the 2D morphology was not destroyed. As pristine $\text{Pd}_3\text{P}_2\text{S}_8$ is inert, the doping greatly improved the usability of the material by improving the ORR activity of the material. The annealing in NH_3 ambient exposed the interlocked Pd atoms of $\text{Pd}_3\text{P}_2\text{S}_8$ and introduced ligands that improved the affinity of oxygen intermediates. As a result, the ORR kinetics was improved, and the activation energy was reduced. The mass activity of the pristine $\text{Pd}_3\text{P}_2\text{S}_8$ was dramatically increased as much as fivefold (from 0.03 to 0.151 $\text{mA } \mu\text{g}^{-1} \text{Pd}$ in $\text{Pd}_3\text{P}_2\text{N}_x$). The ORR diffusion-limited current density of $\text{Pd}_3\text{P}_2\text{N}_x$ (6.2 mA cm^{-2}) exceeded that of commercial Pt/C (5 mA cm^{-2}) with fast kinetics and robust long-term stability. The DFT calculation in the study guided the synthesis and unravelled the mechanism behind the doping that enhanced ORR activity.

To shift away from the reliance of precious metal, the latter two showcases addressed the functionalisation of MXene for which the rich surface chemistry of the material, owing to the metal Ti surface termination, allows for tunability of physical properties. In Chapter 5, MXene $\text{Ti}_3\text{C}_2\text{T}_x$ was modified to change the work function and electrical conductivity. The termination makes it a versatile material and can be modified to tune its physical properties, endowing the ability to fine tune its interaction with electromagnetic waves. Coupled with the unique layered properties, MXene opened up many opportunities in the field of electrical and electromagnetic shielding. By simple modification technique, the surface termination of the pristine $\text{Ti}_3\text{C}_2\text{T}_x$ can be changed to tune its work function and electrical properties. Effectively, by simple annealing technique, as-etched $\text{Ti}_3\text{C}_2\text{T}_x$ can be modified to carry O and N terminations which results in a shift of work functions from average of 4.20 eV (as-etched) to 4.52 eV (O terminated) and 4.69 eV (N

terminated). The largest shift in work function obtained was ~ 0.75 V by doping nitrogen into the pristine $\text{Ti}_3\text{C}_2\text{T}_x$. DFT calculations were performed to further understand the influence of the different terminations on the surface on the work function values. This wide range of tuning coupled with the good conductivity, can allow it to act as both the electron transfer layer and or the hole transport material in the same cell which improves the utility of the material.

Unfortunately, due to its rich chemistry, it is overly active and unstable for electrochemical application and found unsuitable for prolonged electrochemical applications. Hence, in Chapter 6, the functionalised MXenes-were demonstrated for their application in heat to light conversion. The functionalised MXenes were homogeneously dispersed and encapsulated in polymeric networks of cellulose acetate which were crosslinked to make a polymeric membrane based solar steam generator. As compared to commercial reverse osmosis process, the designed CAM structure exploited the dispersed MXenes' light absorption for effective heat localisation for efficient water harvesting and desalination system. Water was automatically pumped through the absorber, which contained the embedded nano/micro channels, via capillary action and heated up. As such, the fabricated solar steam generator shows a net evaporation rate (with respect to that in dark condition) of $1.47 \text{ kg m}^{-2} \text{ h}^{-1}$ with 92.1% efficiency under 1 sun illumination. Furthermore, as a viable water desalination membrane, the salt rejection rate for high salinity seawater (original Na^+ concentration is 18000 mg L^{-1}) reached up to 97.5%, generating drinkable water that meets the WHO standard. Such new photothermal membrane absorber is cost-effective, scalable, washable, and stable under harsh conditions, holding great promise for practical solar desalination applications.

7.2 Future Work

Despite the successful modification of 2DMs including PdSe₂, Pd₃P₂S₈, and MXene Ti₃C₂T_x, the investigation on 2DM is practically limitless. In line with the theme on energy conversion, further exploration on MXenes absorption of electromagnetic (EM) waves can be promising due to their rich surface chemistry. Hence, the future work is targeted at the effect of functionalisation of MXenes for EM absorption.

7.2.1 Functionalising MXene for EM absorption

Figure 48 MXene EM absorber (a) schematic of MXene EM absorber (b) Experimental set up in reflection mode, S parameter measures the reflected EM, the energy not recorded is deemed to be absorbed, (c) Reflection parameter converted from S_{11} parameter read from network analyser (d) $|S_{11}|^2$ converted from S_{11} parameter indicating reflection and absorption power ratio for functionalised MXenes.

MXenes are known to be good EM shield material with the highest recorded of 92 dB (Shielding Effectiveness, SE) at thickness of $45\mu\text{m}$.¹⁶⁵ Furthermore, multiple literatures^{44, 132, 162, 165, 170, 171} had established that MXenes are promising EM absorbers, notably that from Han *et al.*¹⁶² Generally, the incident EM wave will attenuate in the material as it is converted into heat energy due to the strong EM interaction in the material,^{357, 358} such conversion is the basis of a radar absorbance material (RAM). The added benefit from using MXene is that the layered structure encourages further internal reflection which promotes further absorption in the material. **Figure 48a** shows the schematic of MXenes in response to incoming EM wave.

Although it is well known that MXene is a good absorber, using MXene in a RAM has not been investigated so far. Preliminary experiments had established key parameters for the designing of MXene based absorber layer by tuneable material properties. As a start, functionalisation plays a huge part in tuning the surface electrical responses as established in Chapter 6. This warrants further investigation into the EM properties of functionalised MXenes. Furthermore, the composition of MXenes is crucial to the surface impedance matching which determines the extent of attenuation of EM waves.³⁵⁹ Essentially, designing MXene-based absorber using the effect of functionalisation to enable a matching of input impedance for effective transverse of EM waves and its attenuation, is essential to high EM absorber.

In this case, typical samples were prepared by spraying functionalised MXenes onto alumina plate. These prepared chips were measured using a waveguide connected to a network analyser to measure the S-parameters. Minimum of 2 samples per treatment was made to establish the trends. The S-parameters were measured in the reflection mode where the incoming EM wave was confined within the material by the aluminium backing (**Figure 48b**). The results were extracted between 18 to 26 GHz (K band).

S parameters measured from the network analyser were converted into $|S|^2$ based on the formula [equation (1) – (3)], where S_{11} is the raw data, and R is the ratio of power reflected by the material and A is the ratio of power absorbed by the material.

$$|S_{11}| = 10^{\frac{S_{11}}{20}} \quad - (1)$$

$$R = |S_{11}|^2 \quad - (2)$$

$$A = 1 - R \quad - (3)$$

The results are summarised in **Figure 48c** and **Figure 48d** which shows that there is an increasing trend in the absorption due to the change in surface impedance matching. Generally, nitrogen doped sample exhibits high reflection in the K band whereas Ar-annealed sample exhibits high absorption within the band. Hence, by tuning the function on the MXene, it is possible to design effective broadband absorber based on the material with different functionalization.

7.2.2 Exploiting the anisotropy of MXenes for EM shielding and absorption

Aligning MXenes in specific direction is hypothesised to be able to allow tuning of the electromagnetic shielding (EMS) capability by affecting the impedance matching and through the change in incident angle of the EM wave to effect polarisation or change in the degree of penetration. This idea is to leverage on the anisotropy of the material however this aspect of the material has not been investigated so far.

One of the strategies is to introduce magnetic particles for alignment. Fe_3O_4 magnetic particles had been known to be used as fillers for EMS application due to their ultrasmall size resulting in effective interfacial polarisation and significant scattering and reflection of EM waves.¹⁸¹ Liu *et al* in separate articles^{41, 181} showed that by optimising the composition of Fe_3O_4 magnetic particles in MXenes, the interaction between the former and the latter can both improve the dielectric loss which contributes to the high EM absorption of the material. However, aligning MXenes with magnetic particles and the effect of alignment on EMS were not investigated.

Hence, the investigation serves to close the gap on the anisotropy and interfacial effect on EMS using MXenes. The approach will consider the size of the Fe_3O_4 magnetic particles to be inculcated into the MXene matrix, the composite matrix with the aligned MXene flakes, and the variable incident angle of the EM wave.

Figure 49 MXene Particle Alignment for Electromagnetic Absorption (a) Schema for particle alignment, (b) SEM images of (i) $\text{Ti}_3\text{C}_2\text{T}_x$ decorated with magnetic particles (ii) $\text{Ti}_3\text{C}_2\text{T}_x/\text{Fe}_3\text{O}_4$ -pva film on Cu foil (iii, iv) $\text{Ti}_3\text{C}_2\text{T}_x/\text{Fe}_3\text{O}_4$ -PVA film on Cu foil aligned under different orientation of rotating magnetic field, yellow line indicate general alignment direction (c) XRD comparison of Aligned and Not Aligned MXene on Cu foil (d) schema of EM wave within the Film.

Preliminary investigation showed that MXene inculcated with Fe_3O_4 is responsive under influence of rotating magnetic field, and the result is promising to achieve high EM absorption.

Figure 49a shows the schematic of the alignment process. Magnetic-MXene (m-MXene), was

prepared by exfoliating $\text{Ti}_3\text{C}_2\text{T}_x$ MXene in Tetrabutylammonium hydroxide (TBAOH) and dried in vacuum oven, followed by dispersing it in an aqueous solution with Fe_3O_4 particles. The resultant m-MXene was filtered using vacuum filtration and dried in vacuum oven. m-MXene was then dispersed via vigorous shaking and stirring in water containing 20 mg ml^{-1} of poly(vinyl alcohol) PVA at a ratio of 1:49 PVA:MXene by weight. The resultant composite was spread on a thin Cu foil for manipulation and dried for characterisation and testing.

SEM was taken to see the profile of the alignment. It is clear that the flake alignment of the magnetised MXene [**Figure 49b(i)**] have been changed drastically under the effect of rotating magnetic field. In the absence of magnetic field, Ti_3C_2 flakes exhibit random packing arrangement [**Figure 49b(ii)**] while with the presence of magnetic field, particles align themselves in an orderly manner [**Figure 49b(iii)**]. By changing the orientation of the magnet, another set of well aligned MXene was obtained [**Figure 49b(iv)**]. This indicates that the alignment direction of MXene flakes could be controlled by adjusting the direction of magnetic field. To further understand the alignment, XRD was performed on the aligned and not aligned MXene samples (**Figure 49c**). The disappearance of the (001) peak at around 7° in the aligned MXene is due to a significant change in orientation of Ti_3C_2 particles.

Figure 49d shows the hypothesised EM interaction with different MXene that is 1) fully aligned 2) partially aligned, and 3) not aligned at all. As such, the incident EM wave can be directed according to the orientation of the MXene particles. With a full alignment, it is expected that there will be perfect reflection due to the lack of interactions with the MXene particles. In the case of partial alignment, it is expected that there are some energies passing through the material which will attenuate via multiple internal reflection and redirection of reflection. Whereas a non-aligned

sample will not have the advantage of directed reflection and will have to rely mostly on the interactions with the magnetic particles. The ability to control orientation patterning of MXene under dynamic magnetic field would open new explorations of tuneable EM shielding or absorber.

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