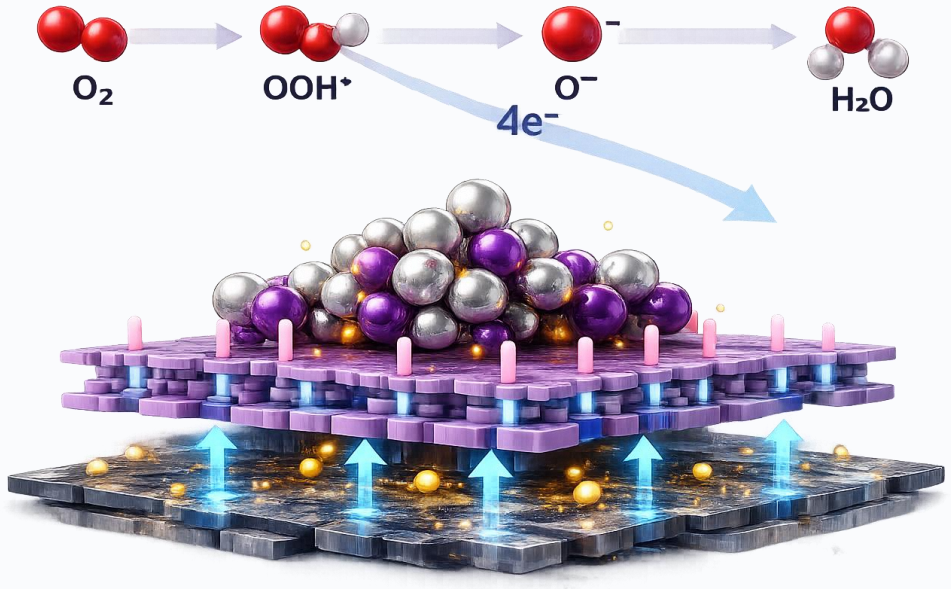
# Mechanochemical Synergy of a MOF–MXene–Hybrid Halide Composite Electrocatalyst for Oxygen Reduction

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University of Chemistry and Technology Prague, Czech Republic

**Advanced Nanomaterials 2026**

23.07.2026

# Designing Advanced Electrocatalysts for the Oxygen Reduction Reaction

*Balancing the trade–offs: conductivity, active sites and stability*

## PRESENTATION ROADMAP

1. **Motivation**
   Why ORR?
   The energy & environment challenge
2. **State of the Art**
   Challenges in catalyst design
3. **Our Strategy**
   Tribochemical transfer of hybrid halide on S-doped MXene
4. **Results**
   Structure, properties and electrocatalysis
5. **Conclusions**
   Key findings and perspectives
6. **Acknowledgements**

## THE "ROCK – PAPER – SCISSORS" GAME OF CATALYST DESIGN

**ROCK**
**High Conductivity**

Excellent electron transport



But usually few active sites

**PAPER**
**High Density of Active Sites**

Many sites for $O_2$ adsorption and reaction



But poor conductivity

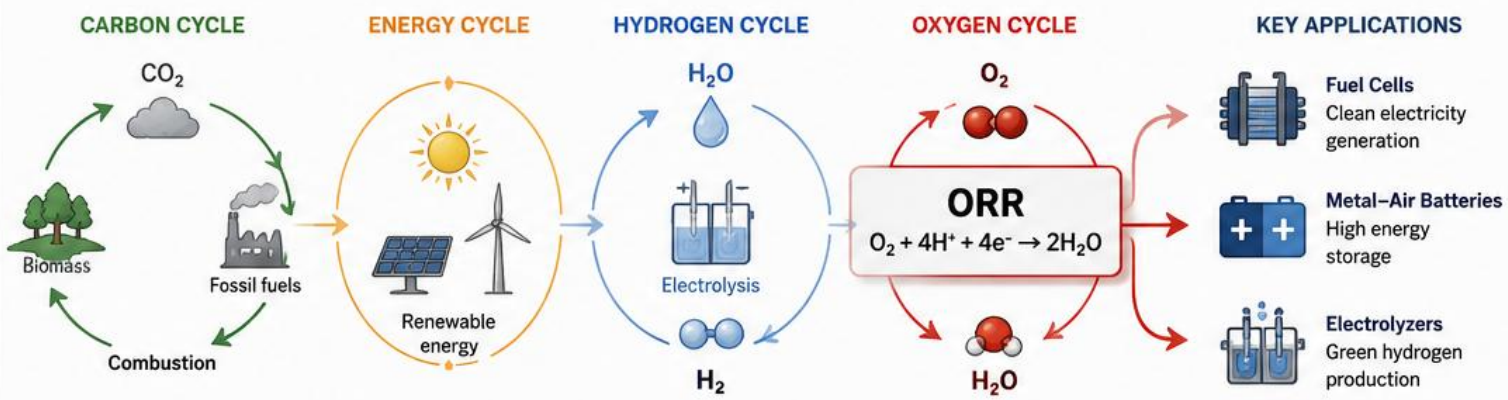
**SCISSORS**
**High Stability**



Resistant to corrosion and degradation

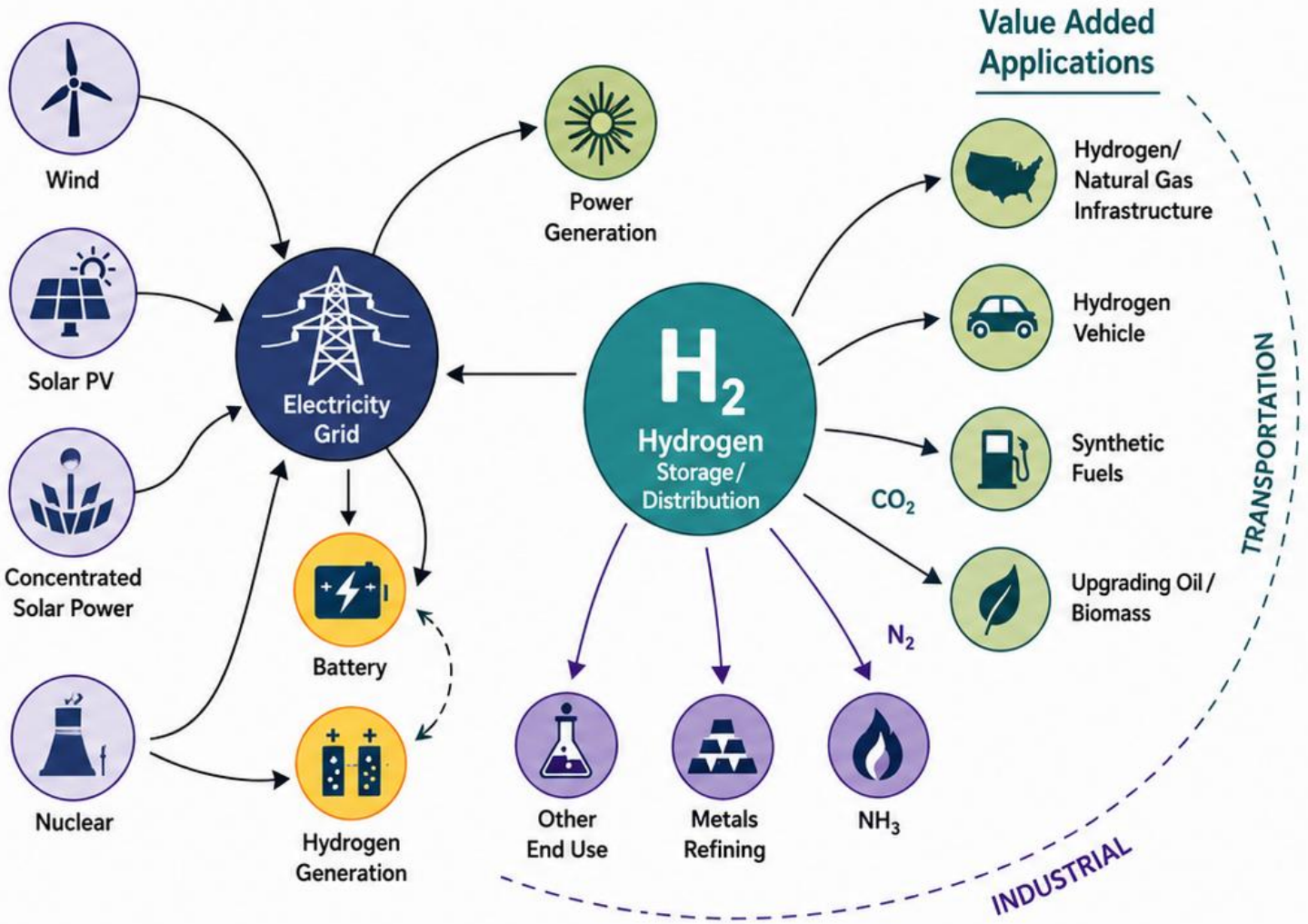
But often limited active sites and conductivity

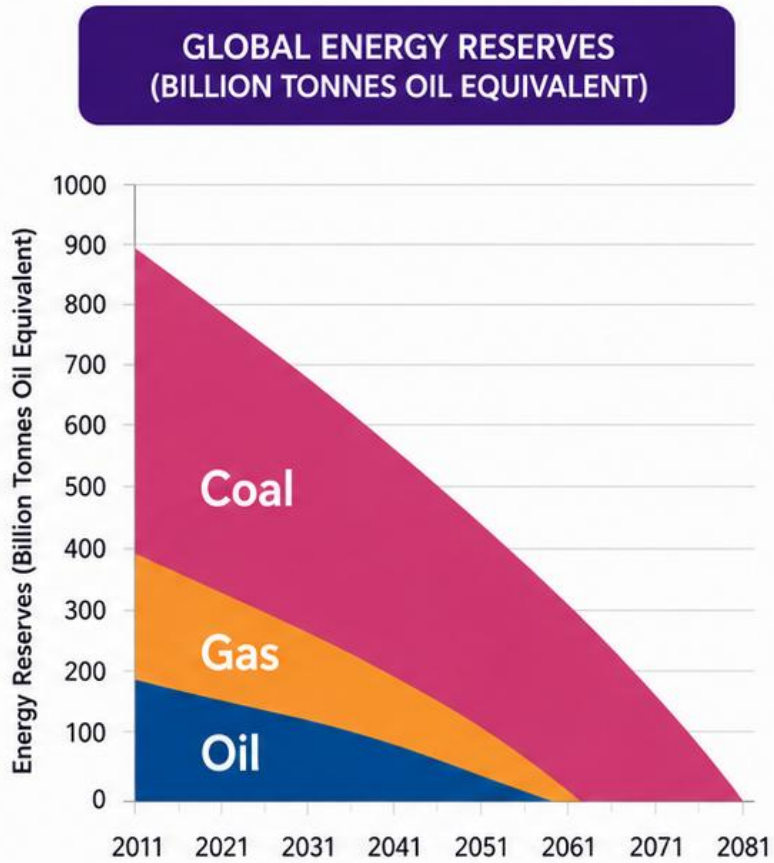
**Improving one property often worsens another.**
**The challenge: achieve the right balance!**




**Our goal: engineer hybrid interfaces that deliver conductivity, abundant active sites and long-term stability.**
**One catalyst. Balanced properties. Maximum performance.**

# The Concept of Hydrogen Economy



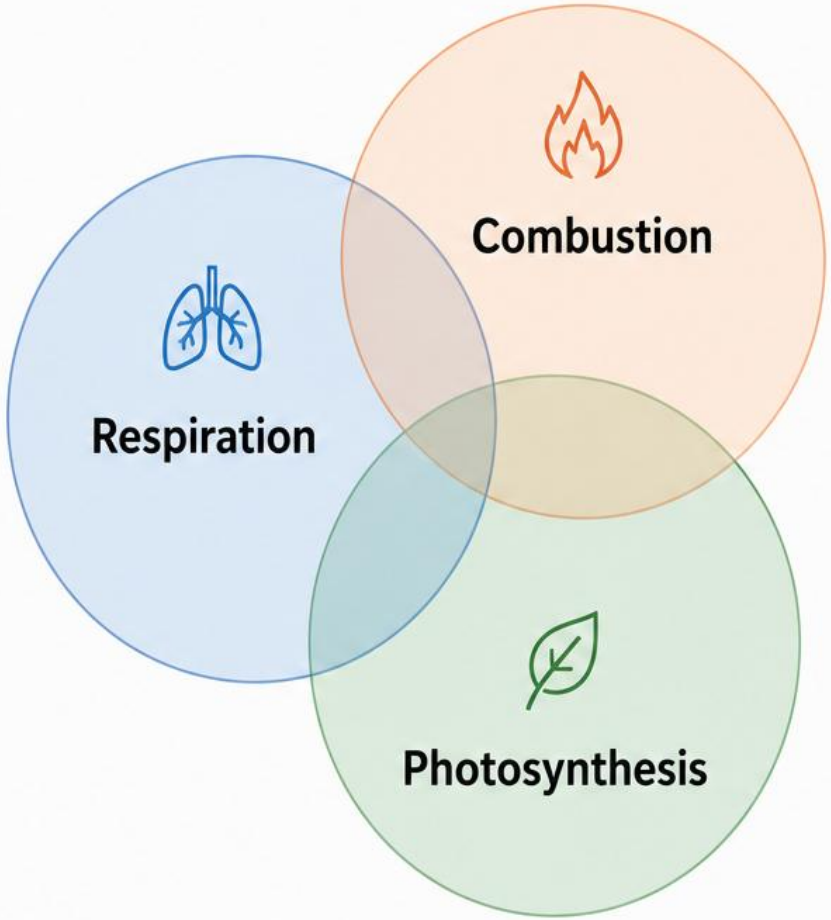




**Source:** World Energy 2017-2050: Annual Report

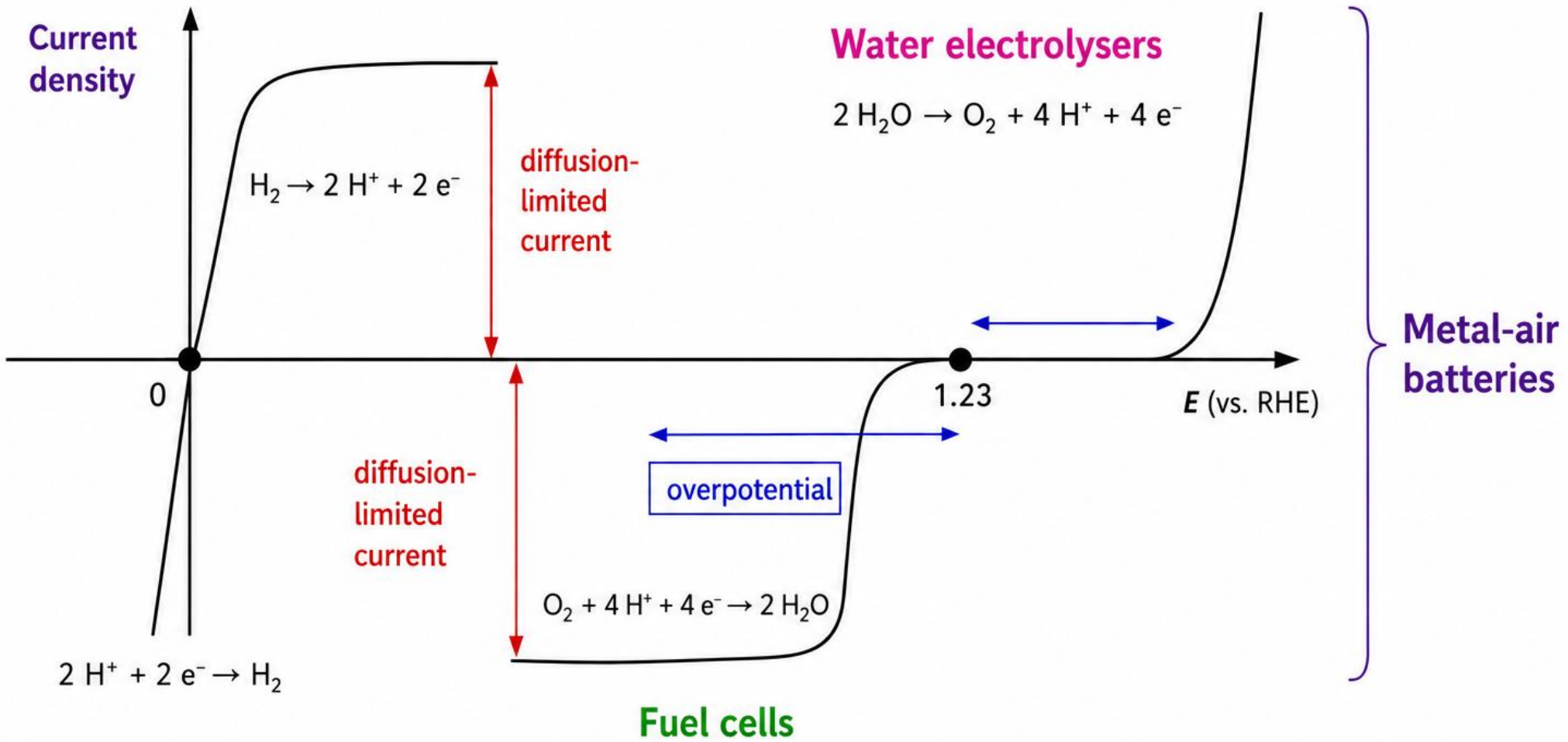
**Source:** Heinz J. Sturm in "Hydrogen Economy for Arab Countries: Perspectives"

# OXYGEN: A FEW INTRIGUING FACTS

- **3rd** most abundant element in the universe.
- Vigorously reactive in its nascent form and highly reactive in its molecular form.
- Always exist as a diatomic molecule **($O_2$)** in atmosphere.
- Earth's atmosphere has **20.95%** of **$O_2$**.
- Almost all elements exist as **oxides**.
- Half of the earth crust is made of **O**.
- Proteins, Carbs, Nucleic acids contain **O** in major proportion.
- Hard shells, bones and teeth of every living organism contain **O**.



# KINETICS OF $4e^-$ OXYGEN ELECTROCHEMISTRY




M.T.M. Koper, H.A. Heering, in "Fuel Cell Science", Eds. A. Wieckowski, J. K. Nørskov, Wiley (2010), P. 71–110.

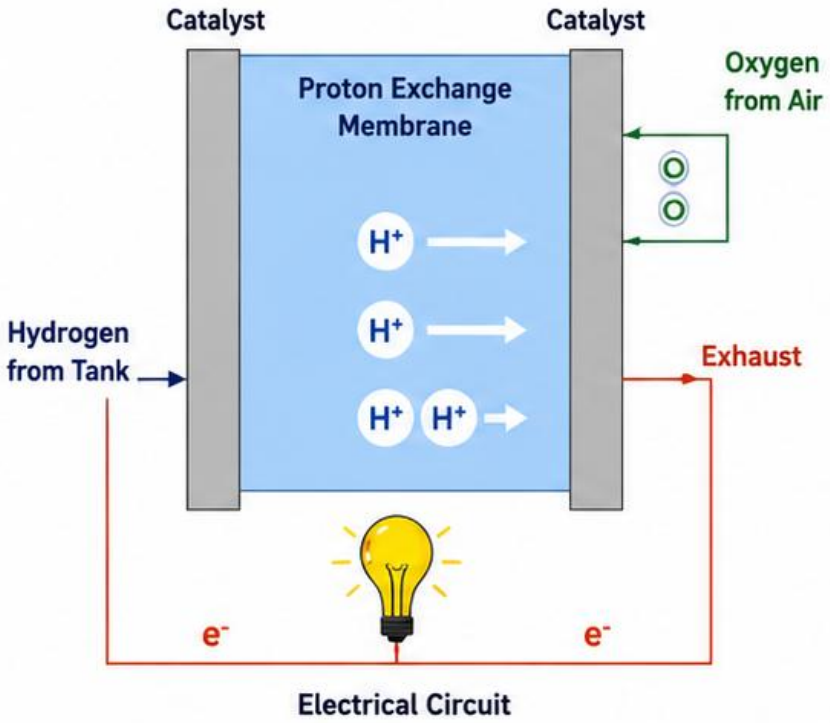
# OXYGEN ELECTROCHEMISTRY

| INVOLVING MOLECULAR $O_2$ | | | INVOLVING WATER | | |
|---|---|---|---|---|---|
| $4e^-$ path | $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | $E = 1.229$ V vs. RHE | $4e^-$ path | $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ | $E = 1.229$ V vs. RHE |
| $3e^-$ path | $O_2 + 3H^+ + 3e^- \rightarrow HO^{\cdot}$ | $E = 0.803$ V vs. RHE | $3e^-$ path | $2H_2O \rightarrow HO_2^{\cdot} + 3H^+ + 3e^-$ | $E = 1.655$ V vs. RHE |
| $2e^-$ path | $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ | $E = 0.700$ V vs. RHE | $2e^-$ path | $2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ | $E = 1.760$ V vs. RHE |
| $1e^-$ path | $O_2 + H^+ + e^- \rightarrow HO_2^{\cdot}$ | $E = 0.330$ V vs. RHE | $1e^-$ path | $H_2O \rightarrow HO^{\cdot} + H^+ + e^-$ | $E = 2.730$ V vs. RHE |

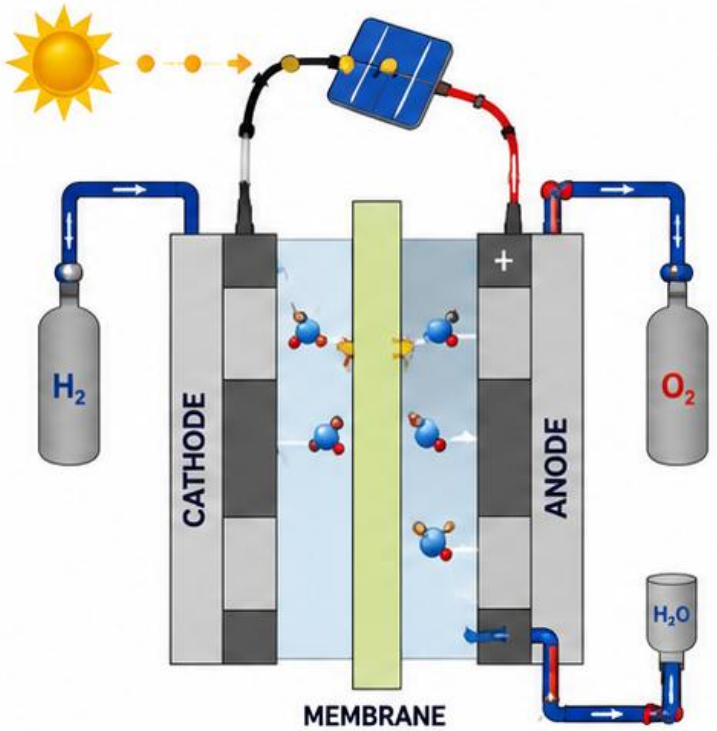
**PROS:** Partially reduced oxygen species / Potentially reactive oxygen species

# PROCESSES THAT DEPEND ON OXYGEN ELECTROCHEMISTRY

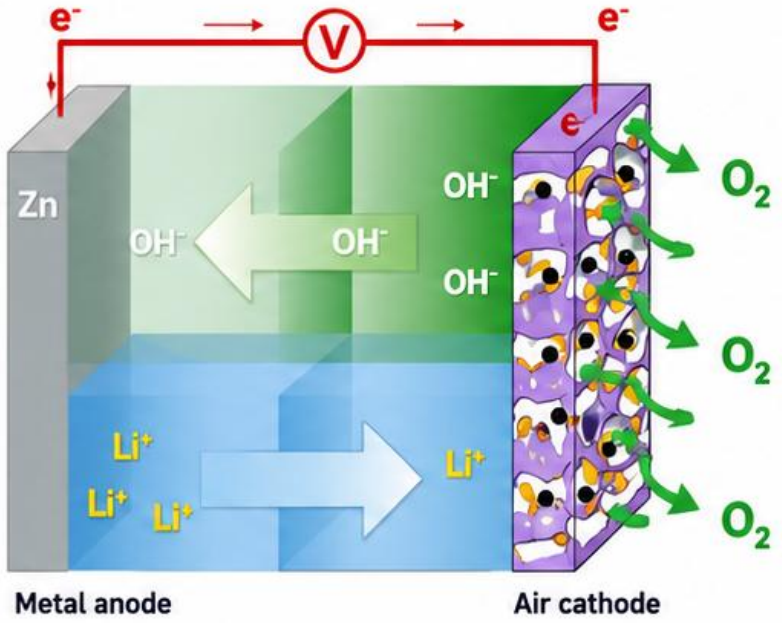
## FUEL CELLS




## WATER ELECTROLYSIS




## METAL-AIR BATTERIES




$OH^-$ : in aqueous Zn-air battery

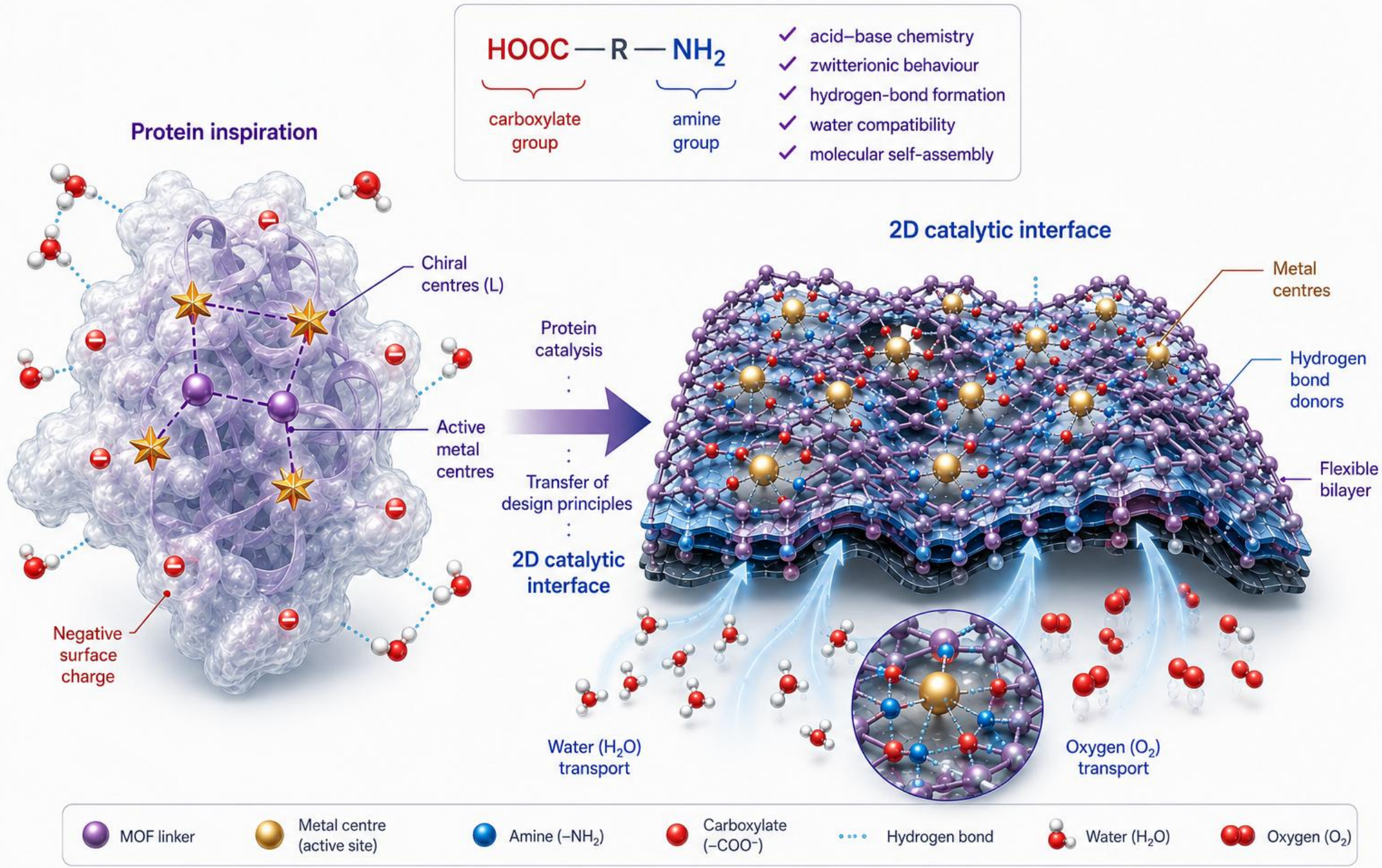
$Li^+$ : in non-aqueous Li-air battery

● : Oxygen catalysts

**Source:** https://en.wikipedia.org/

Wang et al. ***Chem. Soc. Rev.***, 2014, 43, 7975–7986.

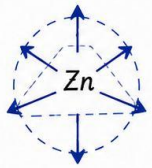
# DESIGN OF THE COMPONENTS OF THE HYBRID ELECTROCATALYST


HOOC — R — NH2
carboxylate group
amine group
acid–base chemistry
zwitterionic behaviour
hydrogen-bond formation
water compatibility
molecular self-assembly
Protein inspiration
Chiral centres (L)
Active metal centres
Negative surface charge
Protein catalysis
Transfer of design principles
2D catalytic interface
2D catalytic interface
Metal centres
Hydrogen bond donors
Flexible bilayer
Water (H2O) transport
Oxygen (O2) transport
MOF linker
Metal centre (active site)
Amine (–NH2)
Carboxylate (–COO⁻)
Hydrogen bond
Water (H2O)
Oxygen (O2)

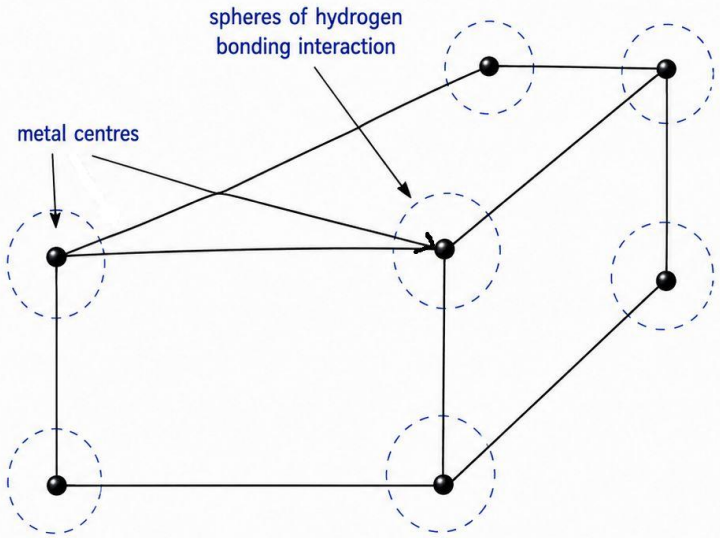
# DESIGN OF THE NEW CATIONIC BILAYER MOF

$HOOC-R-COOH$
*aliphatic diacid*

$NH_2NH(O)C-R-C(O)NHNH_2$
*aromatic dihydrazide*




*octahedral metal nodes*

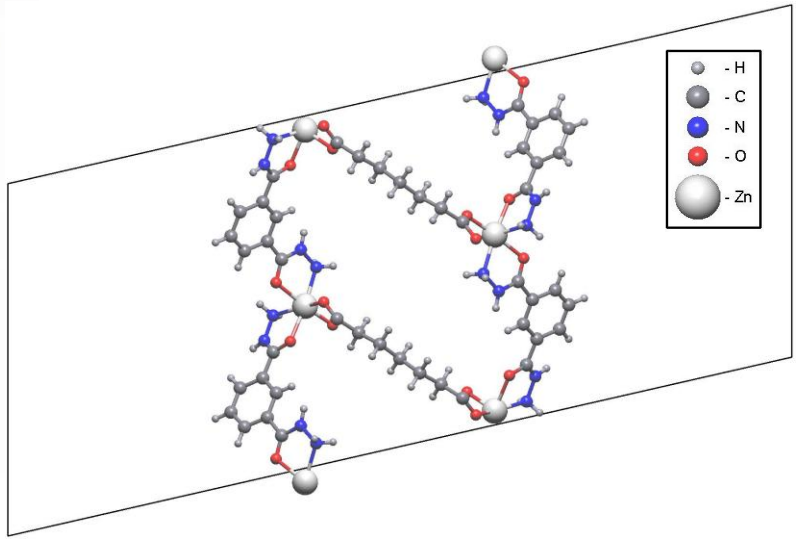



**Key concept:** Octahedral metal nodes (e.g., $Zn^{2+}$) are connected by aliphatic diacid and aromatic dihydrazide linkers, forming a cationic bilayer framework.

## UCT-1 CRYSTAL DATA

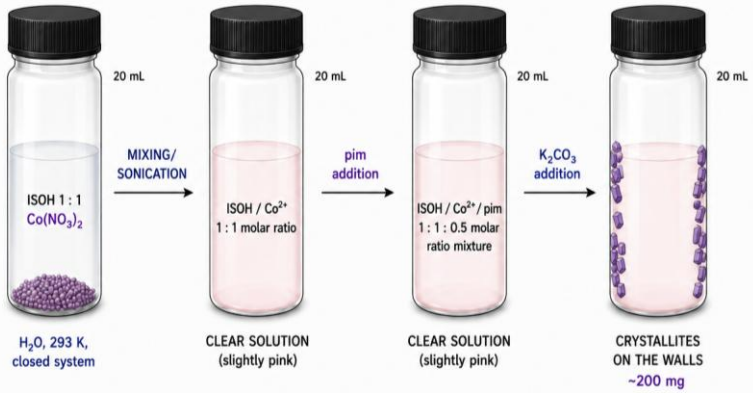
Space group: *C2/c*

$a$ = 41.753 Å
$b$ = 4.747 Å
$c$ = 18.201 Å
$\alpha$ = 90.0°
$\beta$ = 103.23°
$\gamma$ = 90.0°
$Z$ = 8
$R$ = 3.89 %

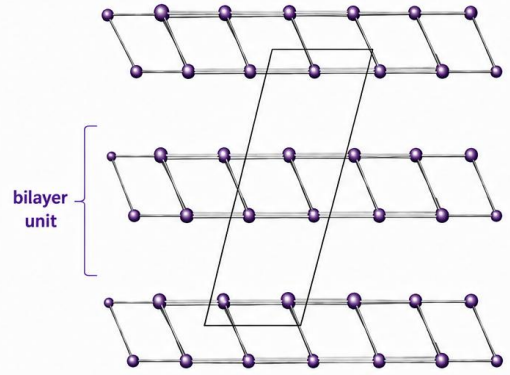



## PREPARATION OF UCT-1 MOF



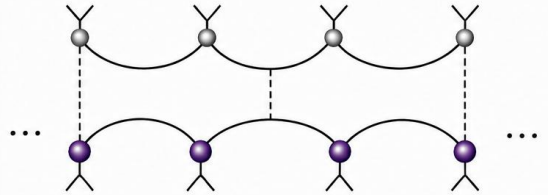




## BILAYER STRUCTURE




= metal centre ($Zn^{2+}$)

## 1D CHAIN STRUCTURE



= metal centre ($Zn^{2+}$)

**373 K, $H_2O$, 1 h**

$P2_1/n$ space group

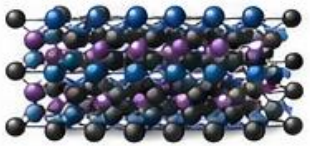
$a$: 11.620 Å  $b$: 7.665 Å  $c$: 18.590 Å
$\alpha$: 90.0°  $\beta$: 95.42°  $\gamma$: 90.0°
Z: 4  R: 2.88%

**Zhang, J., Liu, Y. and Wang, J., 2018.** Synthesis, structures, and properties of Co (II) and Zn (II) coordination polymers based on 1, 3-dicarbo-hydrazine benzene. *Journal of the Chinese Chemical Society*, 65(12), pp.1491-1494.

# Preparation of MXenes from MAX Phases

## 1 MAX phase

Layered ternary carbide/nitride ($M_{n+1}AX_n$)

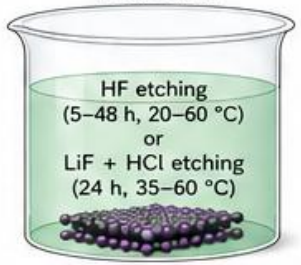


Example: $Ti_3AlC_2$

- M early transition metal
- A group 13–16 element
- X C and/or N

## 2 Etching (A removal)

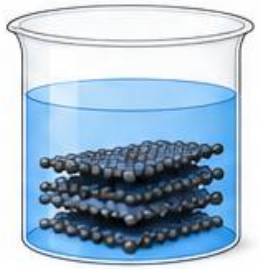
Selective etching of A layer (Al)




- Al (to be removed)
- $F^-$ / $Cl^-$

## 3 Washing

Removal of etchant and by-products



Washing with DI water until pH ~ 6

## 4 Multilayer MXene

Accordion-like multilayer MXene ($M_{n+1}X_nT_x$)



$T_x$ = –OH, –O, –F (surface terminations)

## 5 Intercalation (optional)

Intercalation of molecules/ions to expand interlayer spacing



e.g., TBAOH, DMSO, $Li^+$, $Na^+$, $K^+$, urea, etc.

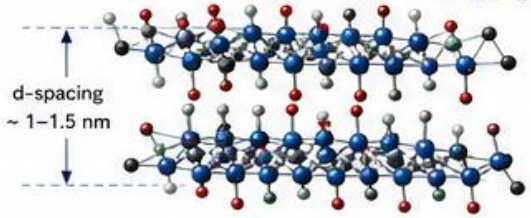
## 6 Delamination

Delamination to obtain few-layer or single-layer MXene



Sonication and/or stirring in water or suitable solvent

## Structure of MXene ($M_{n+1}X_xT_x$)




- M (Ti, V, Nb, Mo, etc.)
- X (C and/or N)
- –O
- –OH
- –F

$T_x$ = surface terminations

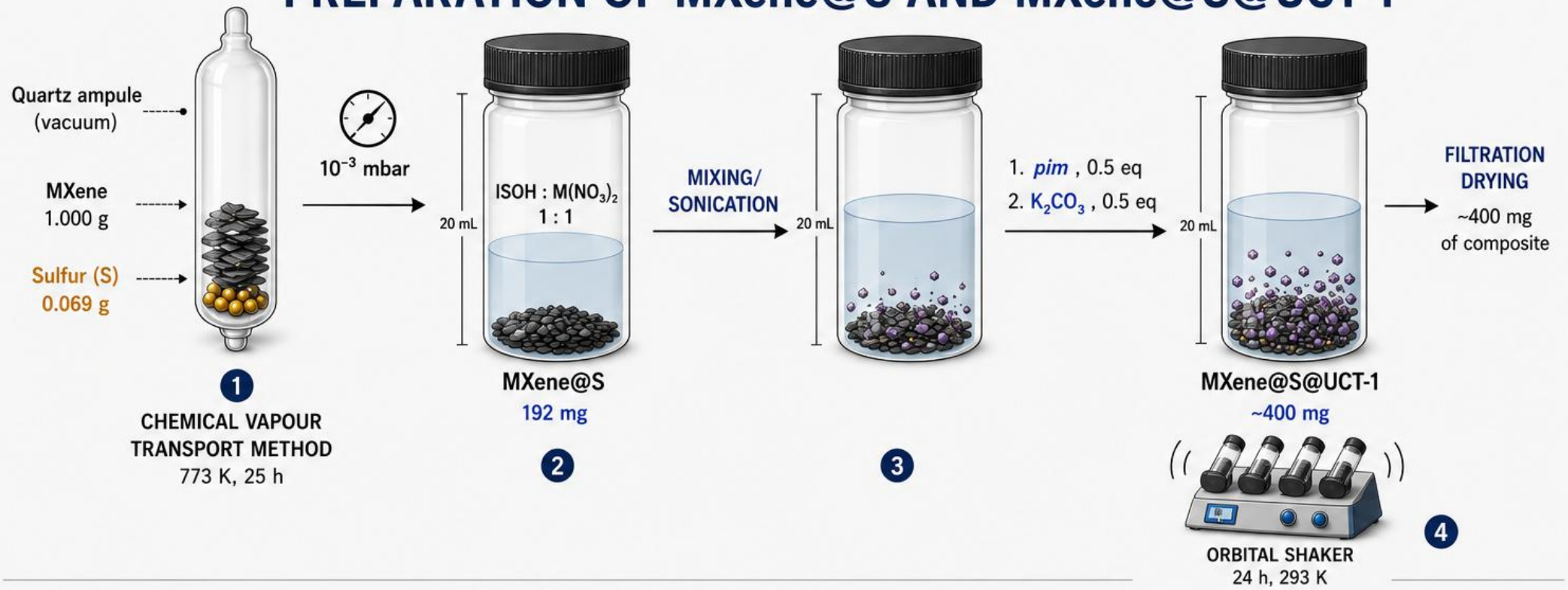
## Examples of MXenes from MAX phases

| MAX phase | Etchant | MXene product |
|---|---|---|
| $Ti_3AlC_2$ | HF | $Ti_3C_2T_x$ |
| $Ti_2AlC$ | HF | $Ti_2CT_x$ |
| $V_2AlC$ | HF | $V_2CT_x$ |
| $Nb_2AlC$ | HF | $Nb_2CT_x$ |
| $Mo_2TiAlC_2$ | HF | $Mo_2TiC_2T_x$ |
| ... | ... | ... |

## Key features of MXenes

- ✓ 2D transition metal carbides/nitrides
- ✓ Hydrophilic surface terminations (–O, –OH, –F)
- ✓ High electrical conductivity
- ✓ Large surface area and rich surface chemistry
- ✓ Excellent mechanical and chemical stability

# PREPARATION OF MXene@S AND MXene@S@UCT-1



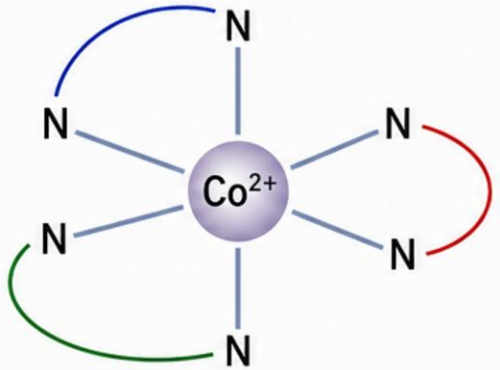

## CAN INSULATORS BE GOOD ELECTROCATALYSTS?




- Ultrathin MOF → shorter electron tunnelling distance
- Defects / grain boundaries → more conductive paths
- Strong interfacial contact → efficient charge transfer
- Is electron tunnelling through MOF possible?

**Hypothesis:**
Ultrathin MOF on S-doped MXene may allow **electron tunnelling**, enabling insulating MOFs to act as **active and selective electrocatalysts.**

# WHAT IS SPECIAL ABOUT NON-PEROVSKITE HYBRID HALIDES?

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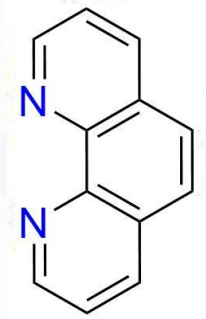
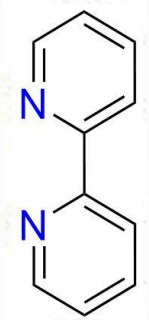



**phen**
1,10-phenanthroline




**bpy**
2,2'-bipyridine

$$AgX\ ,\ [Ag_nX_m]^{\{x-\}}$$

the clusters are only present in solid state

> "The critical coagulation concentration of $Ni^{2+}$ for a negatively charged silver bromide hydrosol is decreased by ca. **1000 times** when very small amounts of **2,2'-dipyridyl** are added to the sol"

> "(...) The results show that these ions $[ML_3]^{n+}$ are very efficient coagulation and reversal of charge agents!"

*Journal of Colloid and Interface Science, Vol.55, No.2, 1976*



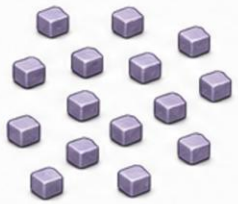
BULK SINGLE CRYSTAL

MECHANICAL FORCE →



FRAGMENTATION

MECHANICAL FORCE →



FURTHER SIZE REDUCTION

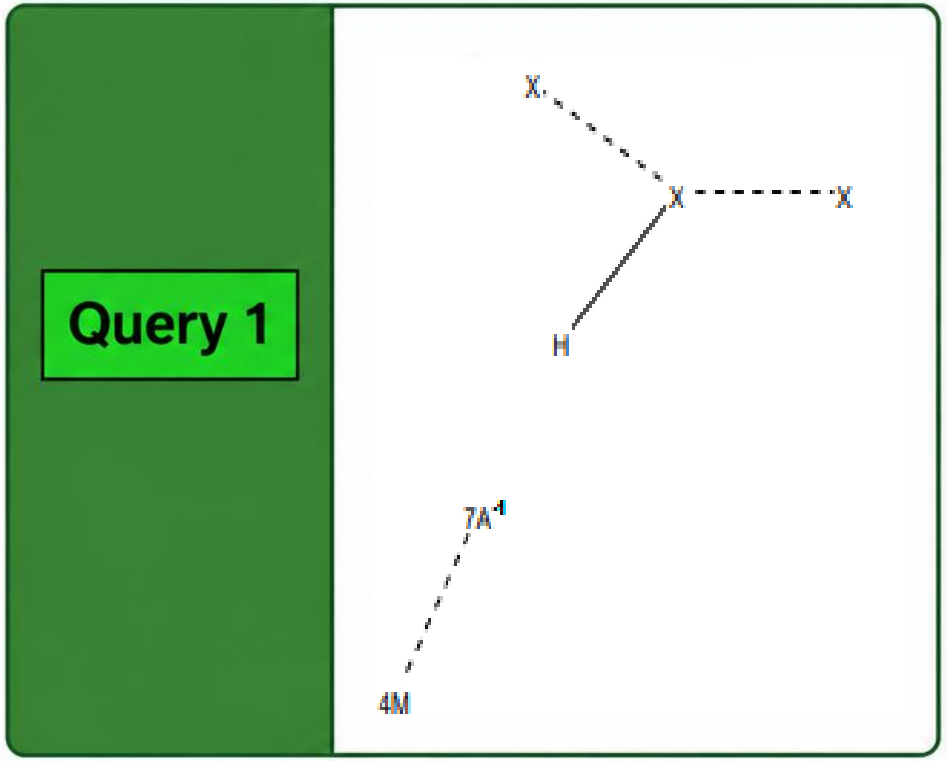
**SMALLER AND SMALLER CRYSTALLITES**

→ Mechanochemical grinding produces smaller crystallites, increasing surface area and facilitating interface formation.

Leads to enhanced ion exchange, charge reversal and improved interfacial interactions.

# CSD (Cambridge Structural Database) survey

- Hybrid halides templated with metal organic cations (27 514 structures) → 3567 structures (hybrid halides templated with metal-organic cations) → $[M_xL_y]_n[M_wX_z]_m$ non-perovskite hybrid halides (325 compounds) (**nuclearity 2 and higher**)

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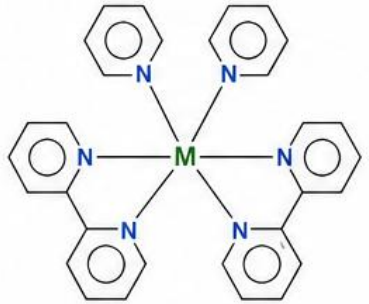
ACACUF

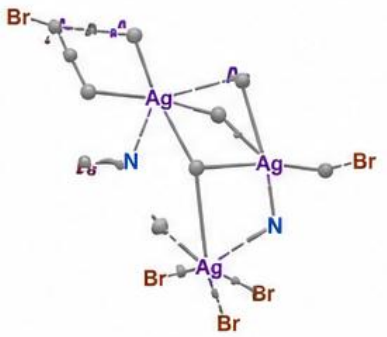
***Reference:*** Kang, Wei et al., CrystEngComm, 14, 2012, 7696
Ruiz-Garcia, Luis et al., Polyhedron, 67 (2014) 46, 133069

***Formula:*** $[C_6H_5Ag_6I_6\ N_{34}]\cdot 3C_6H_{10}\cdot Br_3\cdot(C_6H_{10})_2$

**Compound Name:** catena-poly[[2,2,2-tris(pyridin-2-ylmethyl)propane-1,3-diamminesilver(I)]

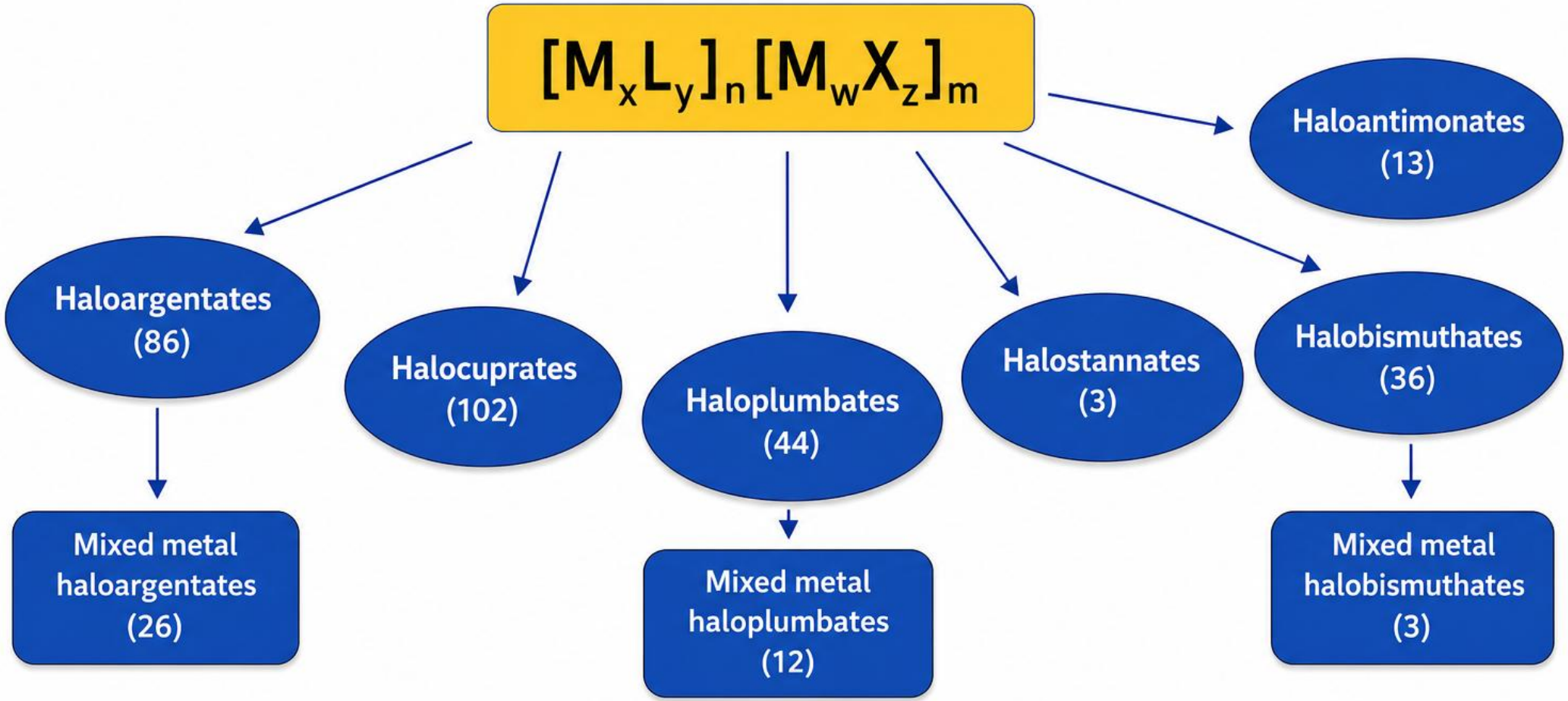
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Space Group:** | $P2_1/c$ | **Cell:** | **a** | 9.277(6) | **b** | 36.347(7) | **c** 16.637(3) |
| **Space Group No.:** | 14 | | α | 90 | β | 115.713(5) | γ 90 |
| ***R*-Factor (%):** | 6.64 | **Temperature(K):** | | 296 | **Density (g/cm³):** | | 2.350 |




At over 1.25 million curated entries, the Cambridge Structural Database (CSD) is a **vital resource** for scientific research around the world.

# $[M_xL_y]_n[M_wX_z]_m$ non-perovskite hybrid halides (325 compounds)

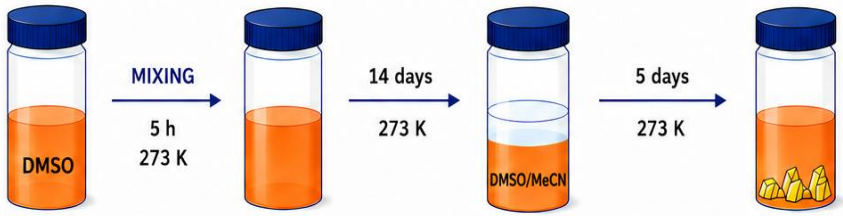



At over 1.25 million curated entries, the Cambridge Structural Database (CSD) is a **vital resource** for scientific research around the world.

# PREPARATION OF HH-1

**A**

| REAGENT | MOL. EQ. |
|---|---|
| phen | 1.5 |
| $Co(NO_3)_2$ | 0.5 |
| AgBr | 1.5 |
| KBr | 3.0 |



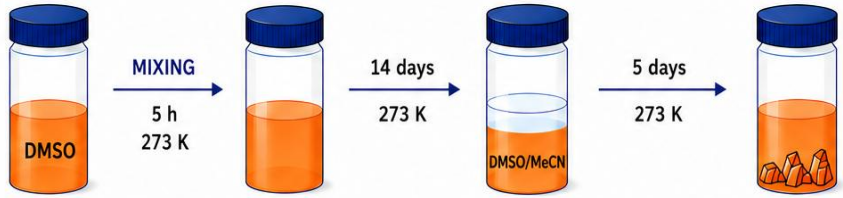

Crystals of
$[Co(phen)_3]_2[Ag_{13}Br_{17}]\cdot 2DMSO\cdot 3H_2O$

Shen, Y. et al.
*Eur. J. Inorg. Chem.*
**2018**, 6, 826–834.

$[Co(phen)_3]_2[Ag_{13}Br_{17}]\cdot 2DMSO\cdot 3H_2O$
$I2_13$ space group; $a$ = 22.13 Å; α = 90°
$Z$ = 4, $R_1$ = 4.79%

**B**

| REAGENT | MOL. EQ. |
|---|---|
| phen | 1.5 |
| $Co(NO_3)_2$ | 0.5 |
| $Ag(NO_3)_2$ | 1.5 |
| KBr | 4.5 |

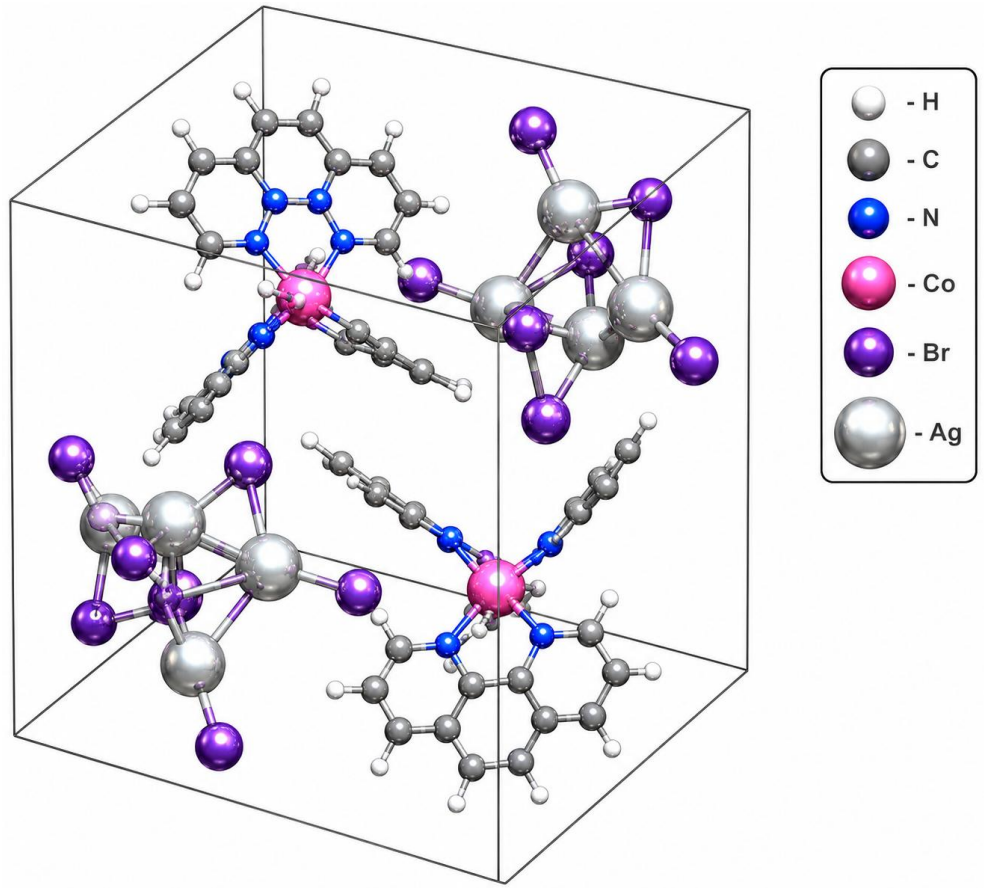



Crystals of (B)
$[Co(phen)_3]_2[Ag_4Br_8]\cdot 2DMSO\cdot 2H_2O$

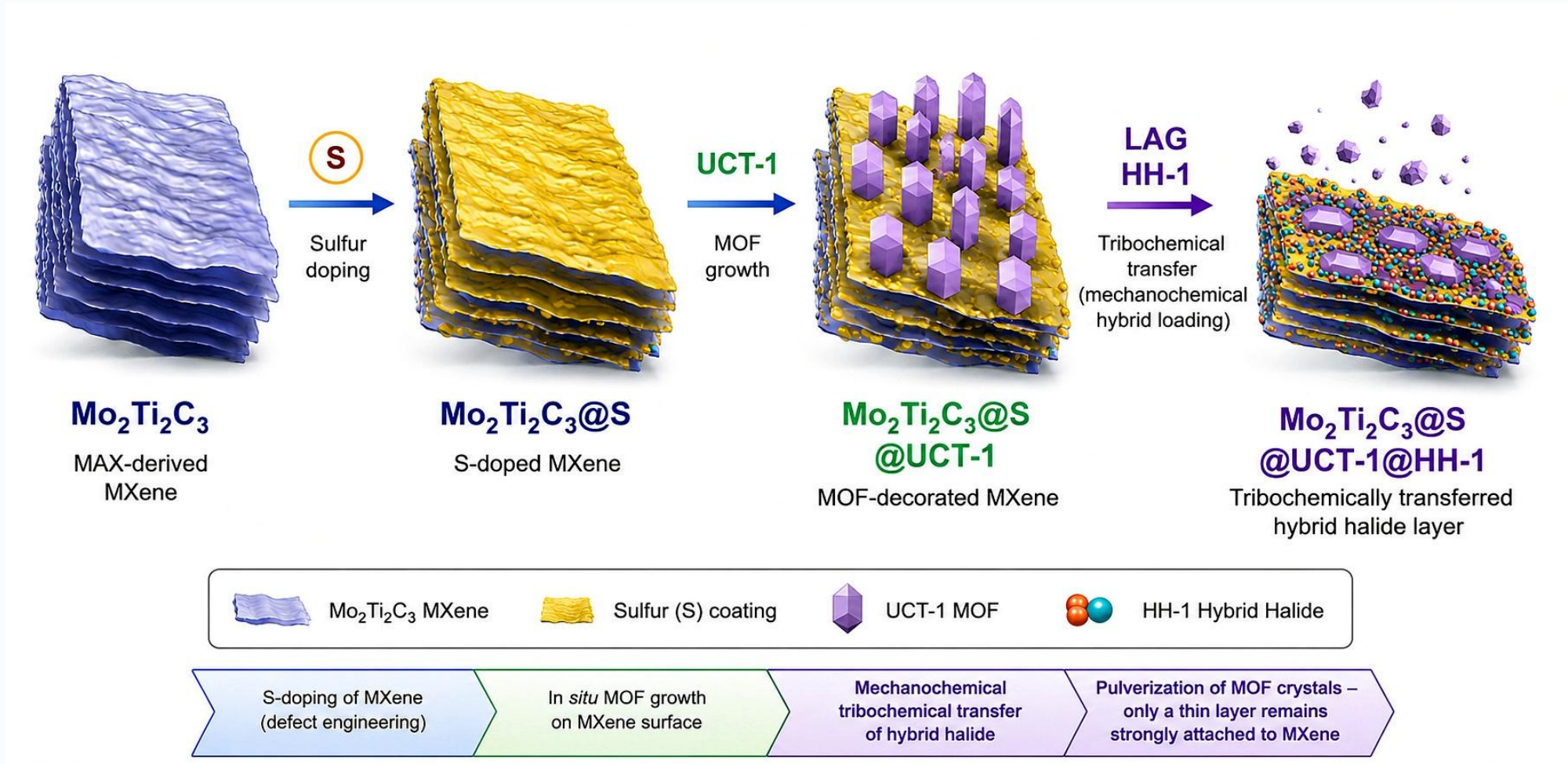
*This work*

$[Co(phen)_3]_2[Ag_4Br_8]\cdot 2DMSO\cdot 2H_2O$
$P1$ space group; $a$ = 14.41 Å, $b$ = 14.88 Å,
$c$ = 21.76 Å; α = 81.05°, β = 81.17°, γ = 75.65°
$Z$ = 8, $R_1$ = 9.4%

Importance of **silver source**, and **conditions of storage**.

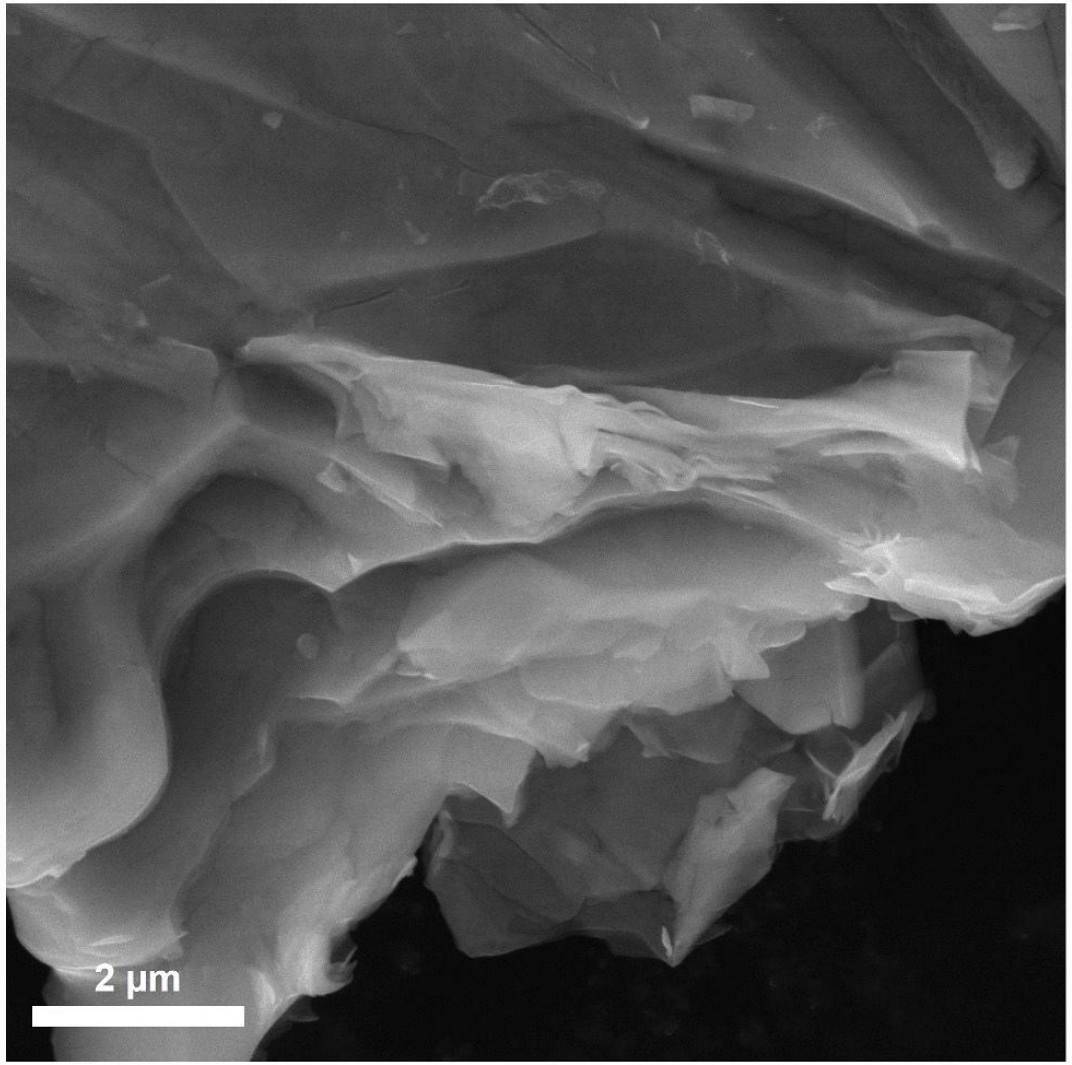


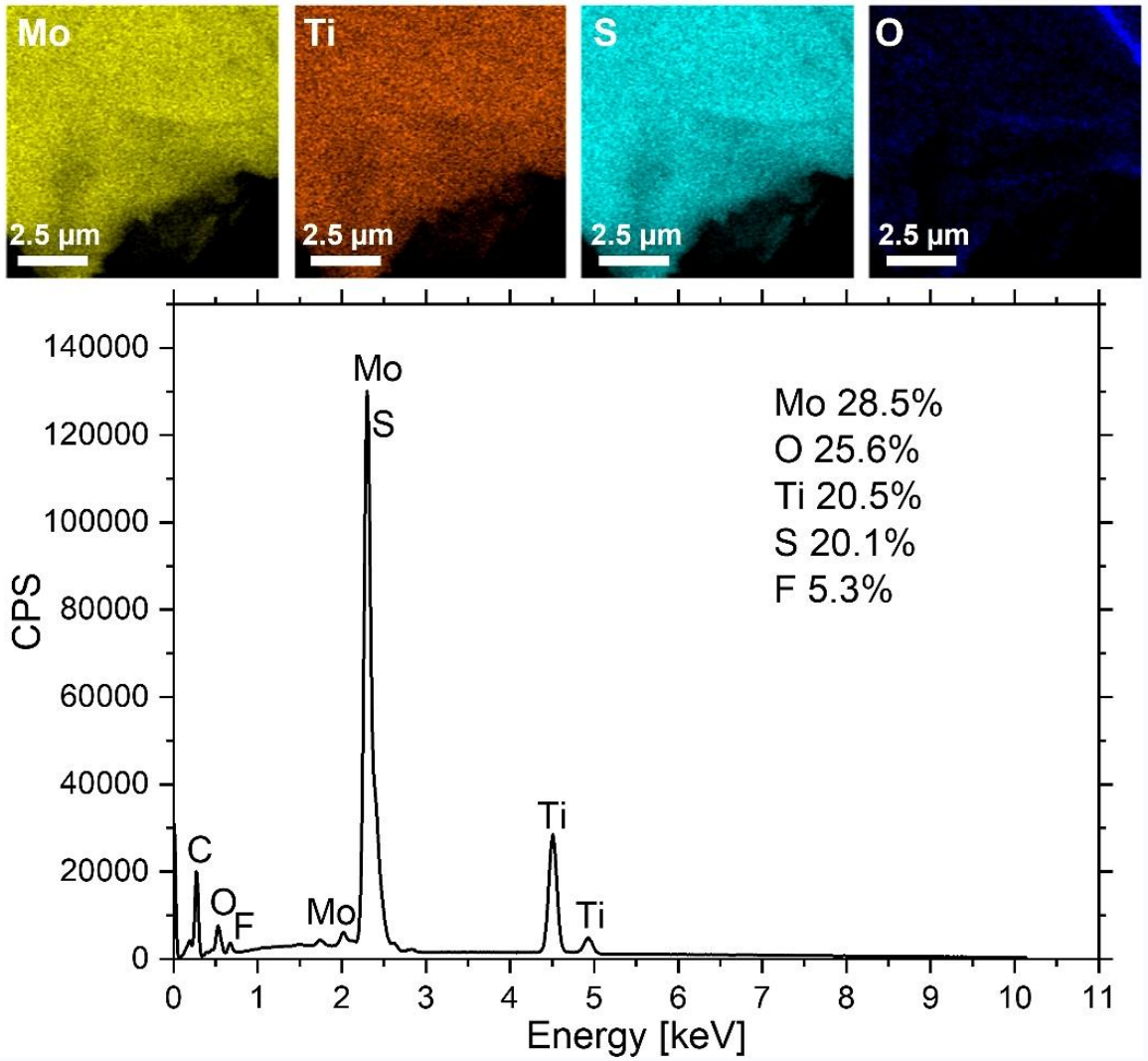
# Synthesis strategy: tribochemical assembly of the catalytic interface



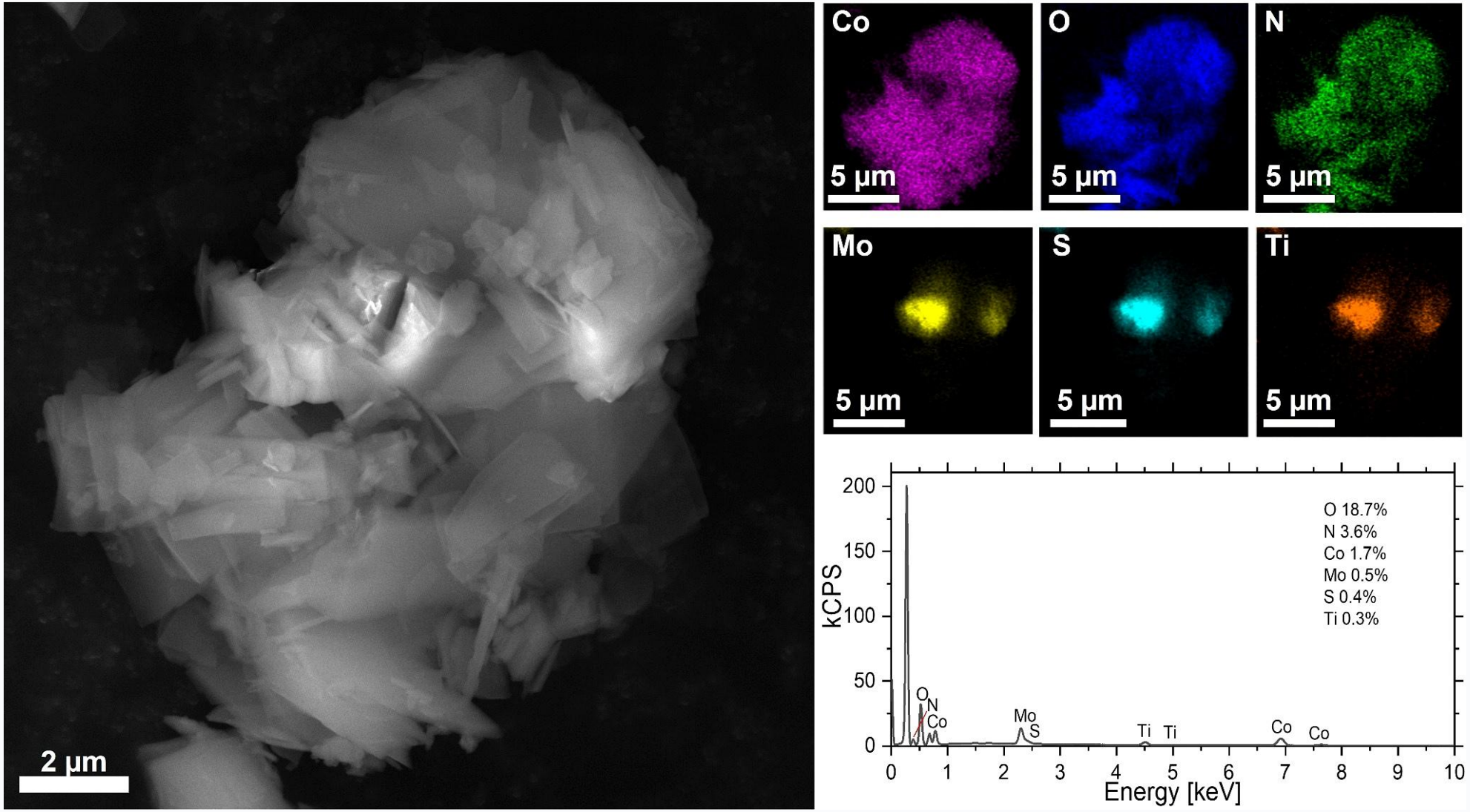

**Enhanced/rebalanced scheme: sulfur coating → UCT-1 growth → LAG HH-1 transfer → final hybrid interface**

# S-doped $Mo_2Ti_2C_3$ MXene: sheet morphology

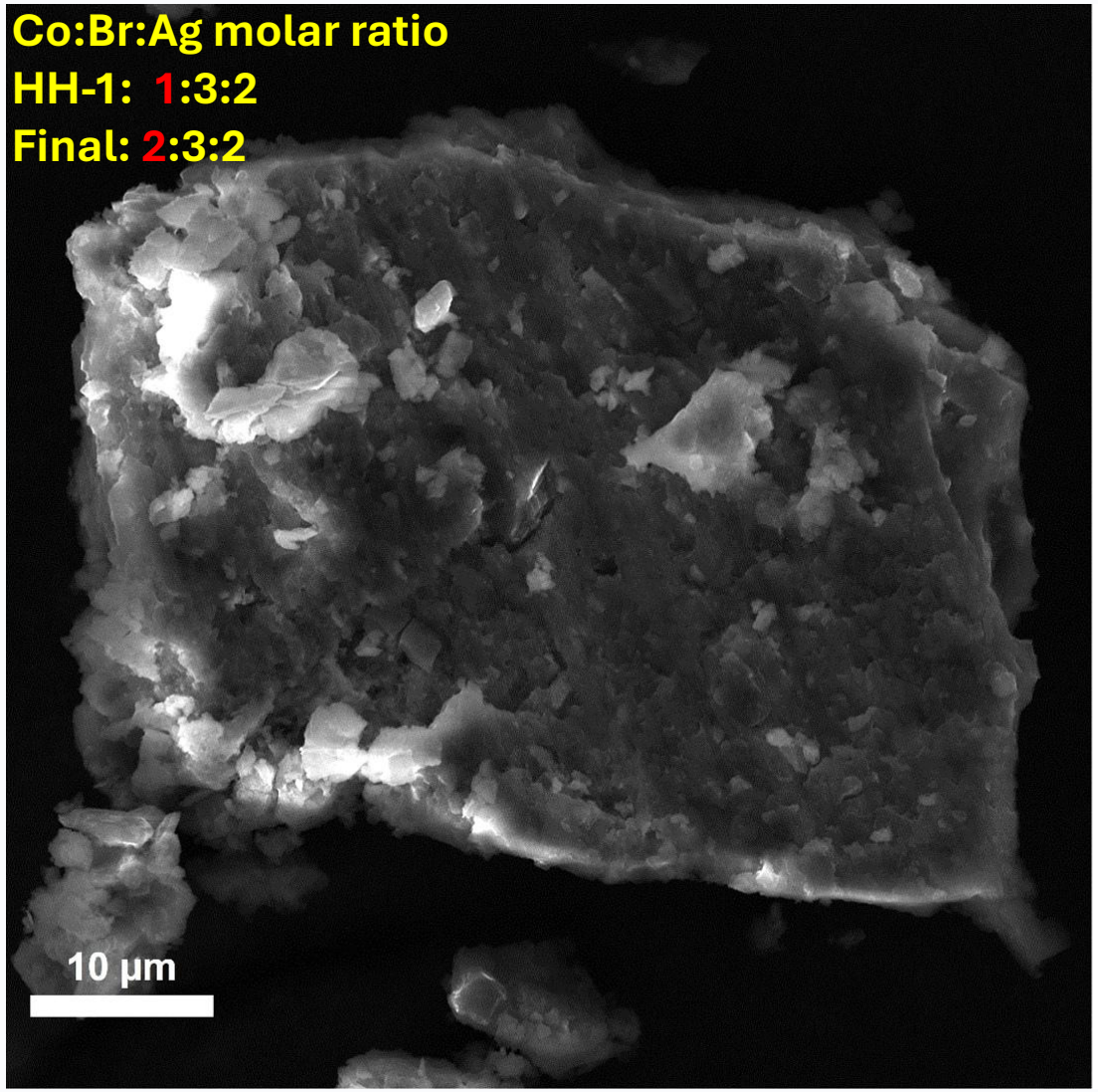


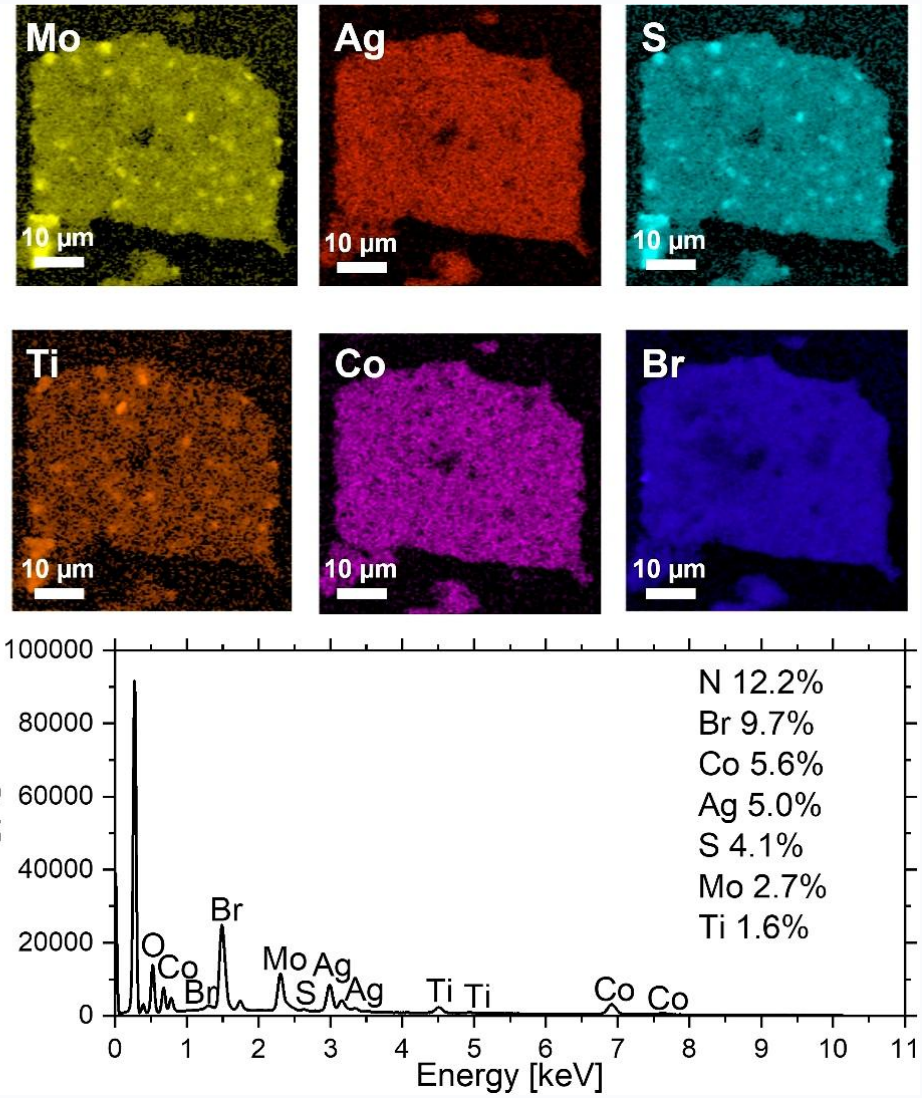



# MOF-decorated S-MXene

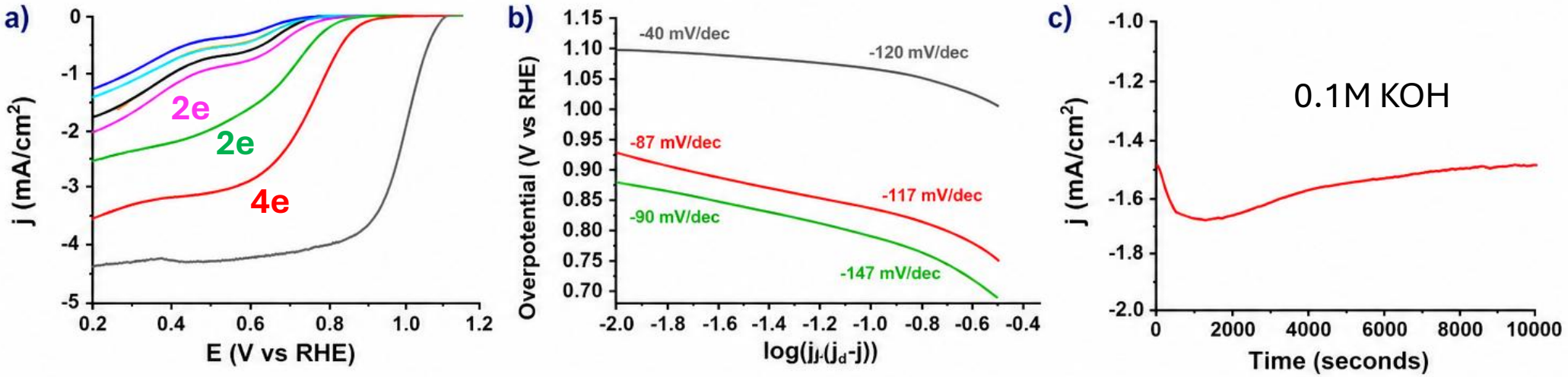


# Final composite: hybrid halide + MXene + MOF-related elements after grinding



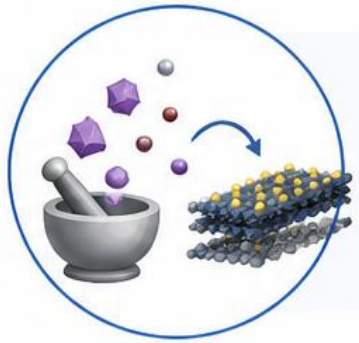
# Electrocatalytic properties in oxygen reduction reaction



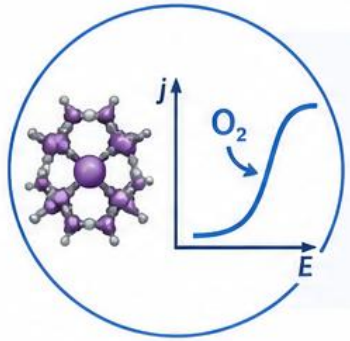

(a) iR-corrected ORR polarization curves obtained at 1600 rpm and Nyquist plots, respectively, for MXene@S@UCT-1@HH-1 (red), MXene (black), UCT-1 (orange), MXene@S (pink), MXene@UCT-1 (blue), MXene@S@UCT-1 (cyan), HH-1 (green) and Pt/C (grey). (b) Tafel plots for MXene@S@UCT-1@HH-1 (red), HH-1 (green) and Pt/C (grey). (c) Chronoamperometric response at 0.74 V (versus RHE) for 10 000 s, respectively, for MXene@S@UCT-1@HH-1.

| Material | Onset Potential (V vs RHE) | Half-wave Potential (V vs RHE) | $j_d$ (mA cm$^{-2}$) | $J_k$ (mA cm$^{-2}$) | Tafel slope (mV dec$^{-1}$) | $R_{ct}$ (Ω) | ECSA (cm$^2$) |
|---|---|---|---|---|---|---|---|
| MXene@S@UCT-1@HH-1 | 0.86 | 0.75 | -3.15 | 2.36 | -87 / -117 | 741 | 2.05 |
| UCT-1 | 0.71 | 0.67 | -0.79 | 0.34 | -104 | 1321 | 0.49 |
| MXene | 0.73 | 0.69 | -1.08 | 0.45 | -100 | 1382 | 0.25 |
| MXene@S | 0.76 | 0.70 | -1.17 | 0.63 | -116 | 1113 | 0.62 |
| MXene@S@UCT-1 | 0.71 | 0.68 | -0.81 | 0.43 | -117 | 1454 | 0.55 |
| MXene@UCT-1 | 0.70 | 0.67 | -0.68 | 0.21 | -101 | 1339 | 0.33 |
| HH-1 | 0.81 | 0.70 | -2.24 | 1.34 | -90 / -147 | 795 | 1.13 |
| Pt/C | 1.08 | 1.01 | -4.24 | — | -40 / -120 | 570 | — |

# CONCLUSIONS



**Tribochemical mass transfer** was discovered, with crucial role of **hybrid halide**.




The **new interfaces** will be candidates for study of **vital electrochemical reactions**.



The catalysts generated in **mechanochemical way**, show **promising stabilities** in aqueous conditions.

# ACKNOWLEDGEMENT

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