Mechanochemical reaction involving bilayer cationic MOF-occluded S-doped $Mo_2Ti_2C_3$ MXene and silver hybrid bromide for enhanced oxygen reduction electrocatalysis

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VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE

Introduction

Synthesis of new types of heterostructures is an important topic in modern materials chemistry and functional interfaces.[1,2] The aim of the study was to explore new kind of quadruple composite material derived from microporous hybrid halide (HH-1), $[Co(phen)_3]_2[Ag_4Br_8]\cdot 2DMSO\cdot 3H_2O$ (where *phen* denotes *o*-phenanthroline and DMSO denotes dimethyl sulfoxide), $Mo_2Ti_2C_3$@S MXene and a new cationic 2D Metal-Organic Framework, UCT-1, of a bilayer structure, $[Co_2(ISOH)_2(pim)][NO_3]_2\cdot 5H_2O$ [where *ISOH* denotes isophthalic dihydrazide, *pim* denotes pimelate (C_7 dicarboxylate)]. We tested the obtained composite in reaction of electrocatalytic oxygen reduction, revealing its enhanced properties.

Synthesis

MXene

$$Mo_2Ti_2AlC_3 + 3HF \Rightarrow Mo_2Ti_2C_3 + AlF_3 + 3/2\ H_2$$

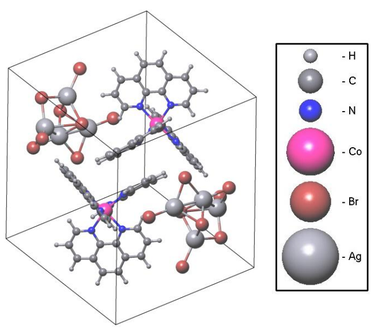
Sulfurization of MXene

$$Mo_2Ti_2C_3 + S \Rightarrow Mo_2Ti_2C_3@S\ (500\ ^oC,\ 25\ h)$$

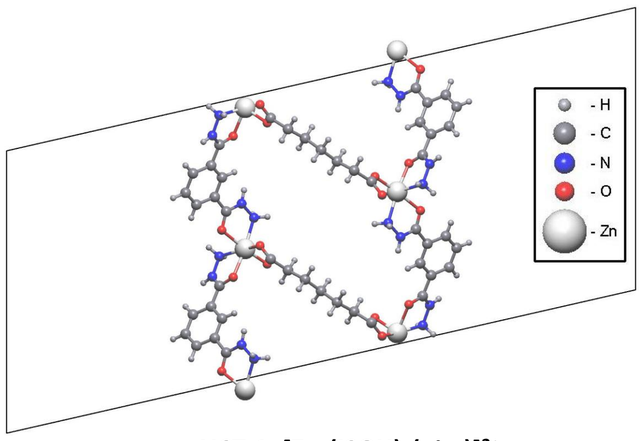
Stepwise Synthesis of the composite (at RT in H_2O)

$$Mo_2Ti_2C_3@S + H_2iso + H_2pim + Co(NO_3)_2 + K_2CO_3 \Rightarrow Mo_2Ti_2C_3@S@UCT\text{-}1 + 2KNO_3 + H_2O + CO_2$$

X-ray Crystal Structures

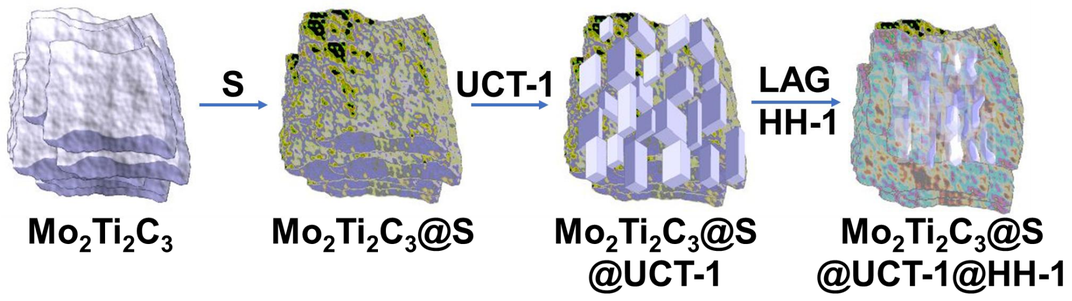


HH-1: $[Co(phen)_3]_2[Ag_4Br_8]$
CCDC-2525327



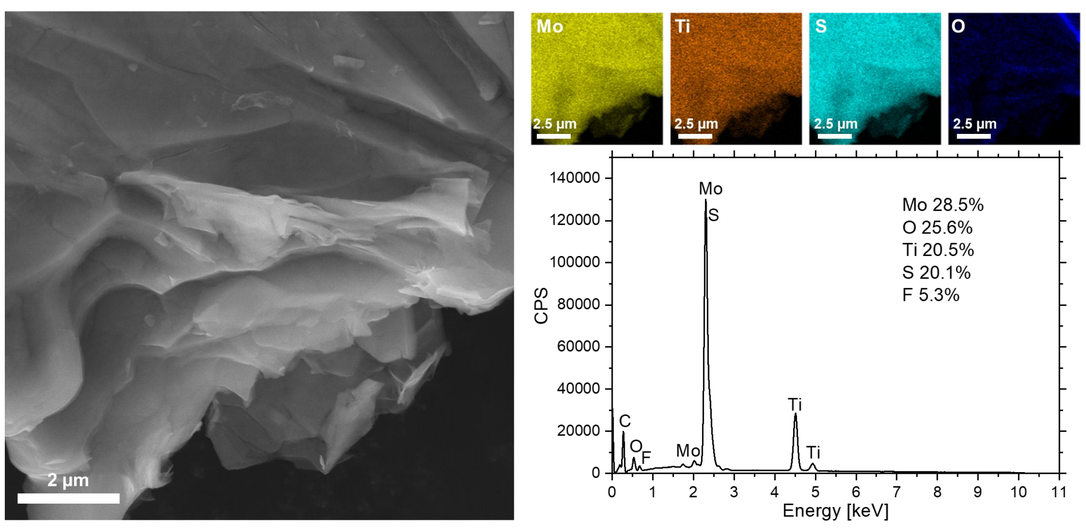
UCT-1: $[Zn_2(ISOH)_2(pim)]^{2+}$
CCDC-2525326

Preparation of the electrocatalyst

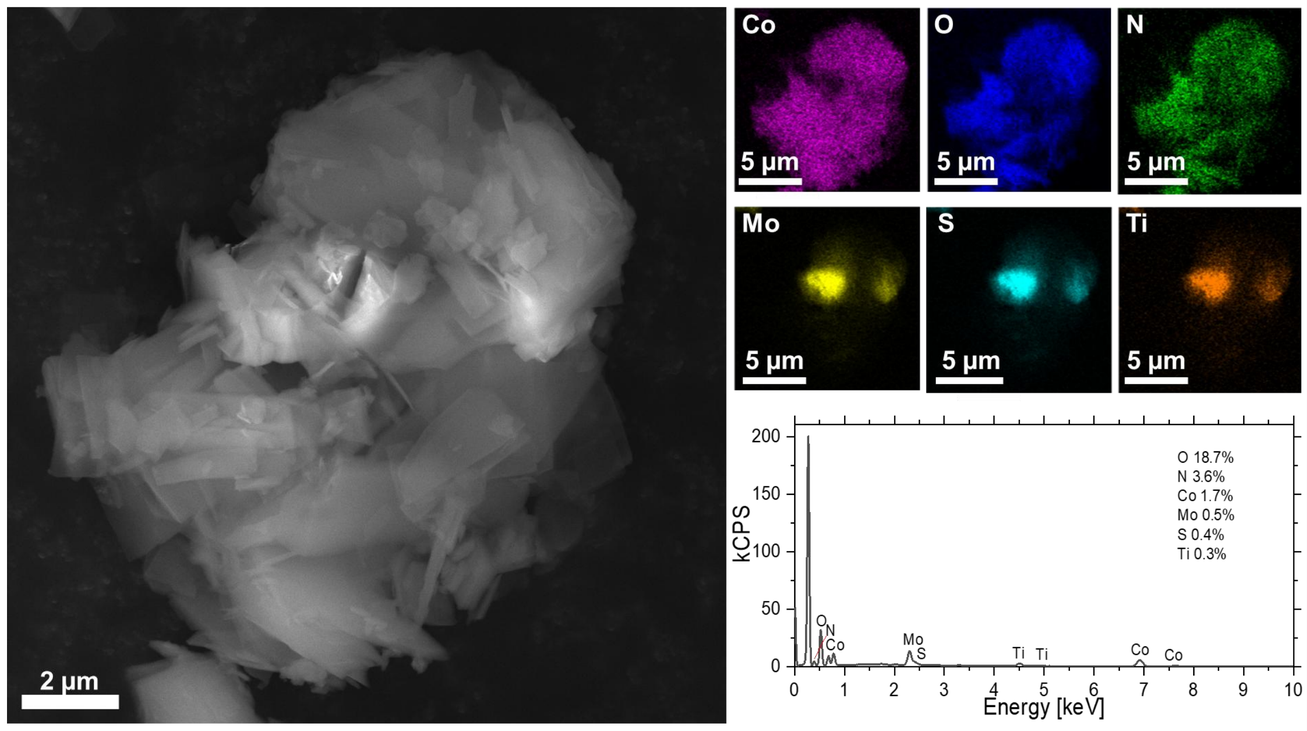


*LAG denotes liquid assisted grinding

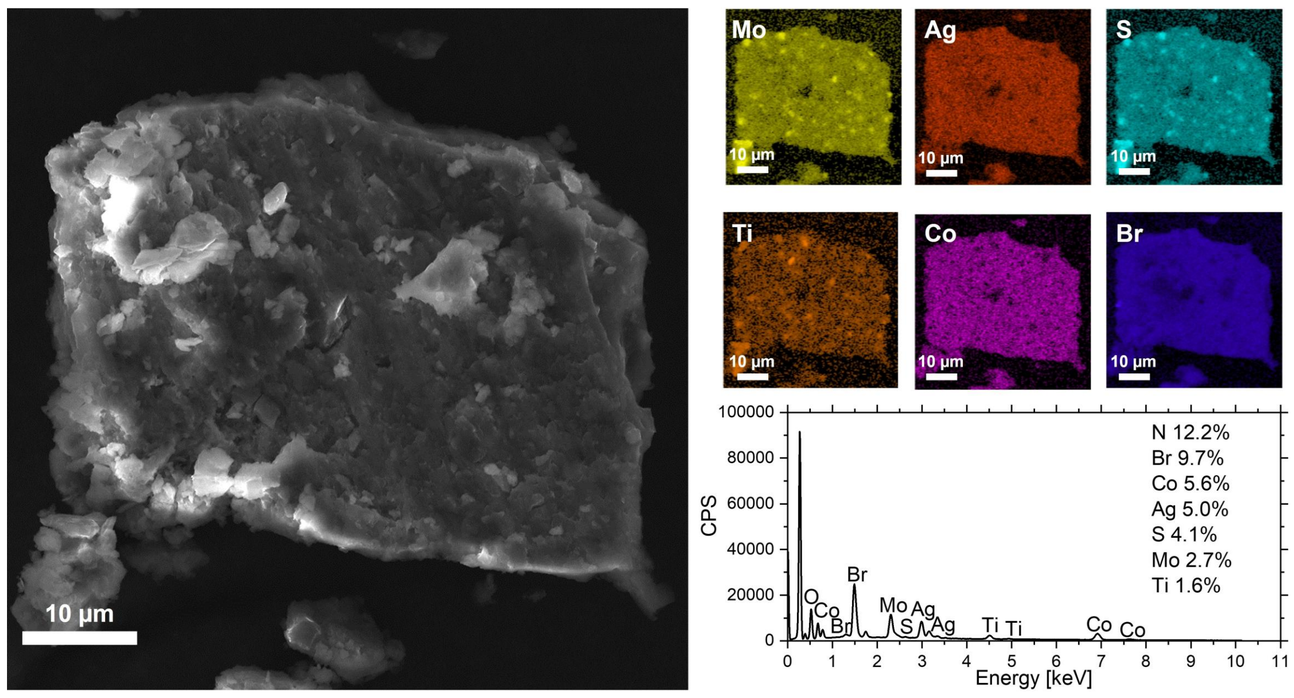
Characterisation of morphology – SEM/EDX of MXene@S



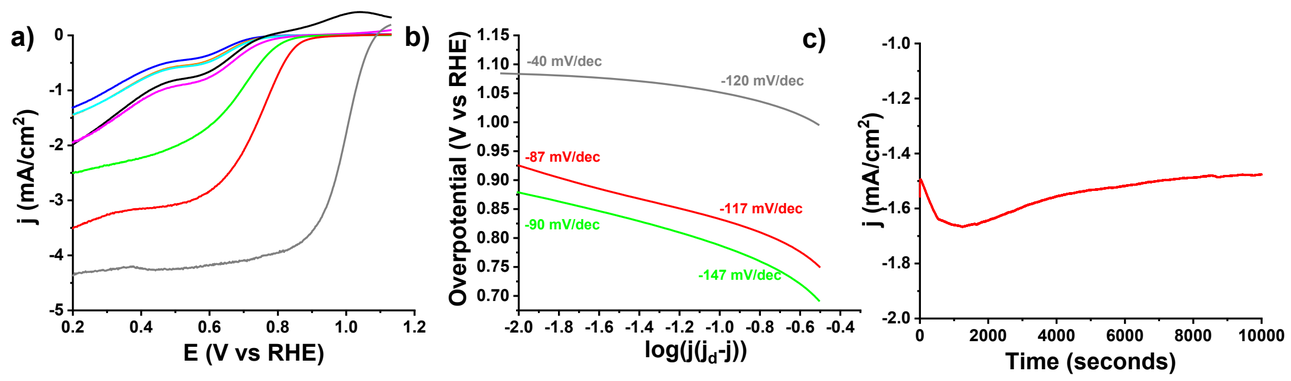
Characterisation of morphology – SEM/EDX of MXene@S@UCT-1



Characterisation of morphology – SEM/EDX of MXene@S@UCT-1@HH-1



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	Half-wave Potential	j_d	J_K	Tafel slope	R_{ct}	ECSA
	(V vs RHE)	(V vs RHE)	(mA cm^{-2})	(mA cm^{-2})	(mV dec^{-1})	(Ω)	(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	—

References

[1] Miller, Aaron M., and David C. Johnson. "Challenges in synthesis of heterostructures." *Journal of Materials Chemistry C* 10, no. 17 (2022): 6546-6562.

[2] Zojer, E. (2024). Electrostatically designing materials and interfaces. *Advanced Materials*, *36*(40), 2406178.

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