Decarbonisation via Innovative Chemical Technologies

A city state, an industrial hub

- Area: 734 km^2 (176th)
- Population: 5.9 million (113rd)
- Population density: 7,804/km^2 (2nd)
- GDP: $497 billion (32nd)
- GPD per capita: $87,884 (5th)
- CO_2 emission: 53.7 $MtCO_{2e}$ (126th, 2018)
- CO_2 emission per capita: 8.1 tCO_2/capita (27th, 2018)
- Net zero targets by 2050
- Peak before 2030

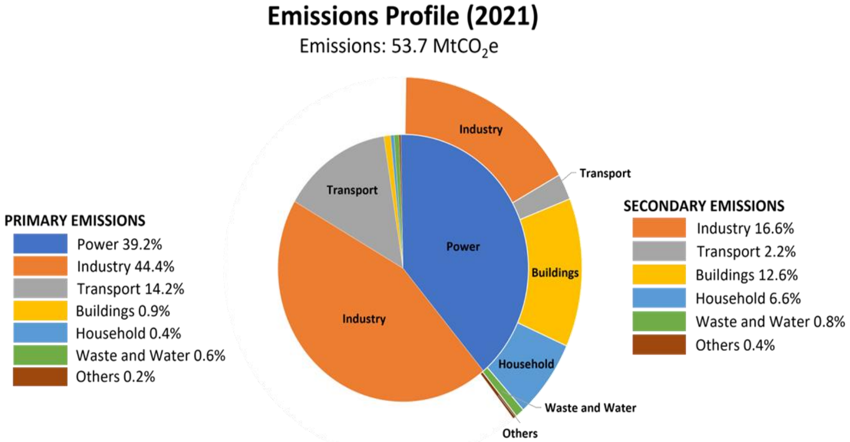


Image from: NCCS

- Major operations from over 100 global chemical firms
- 8th largest exporter of chemicals in 2019
- S$81bil output by energy and chemical industry
- 1.5mil barrels of refined oil per day
- More than 27,000 employment by chemical industry
- 60% of Singapore’s primary and secondary emissions
- 3% of Singapore’s GDP

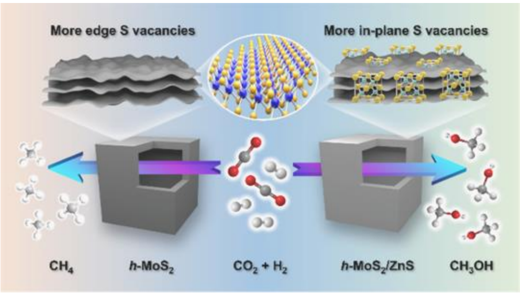
Decarbonising chemical manufacturing

eCO2EP A Chemical Energy Storage Technology

C4T Cambridge Centre for Carbon Reduction in Chemical Technology

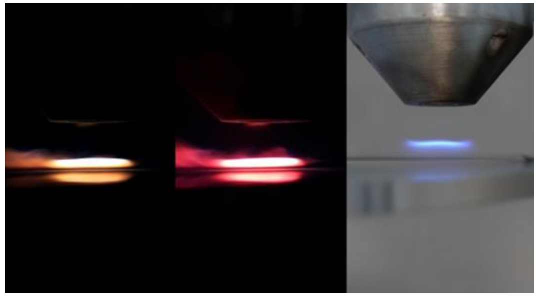
Ample

Better catalysts

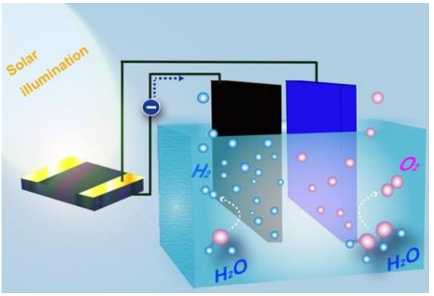


ACS Catal. 12, 16, 9872 (2022)

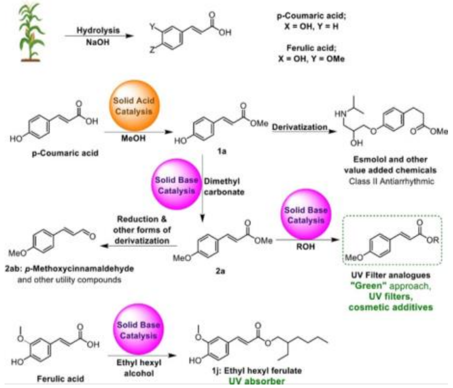
Advanced material manufacturing



New reactor concepts



Green synthetic routes



ChemSusChem. 22, 1586 (2022)

CO_2 capture and utilisation

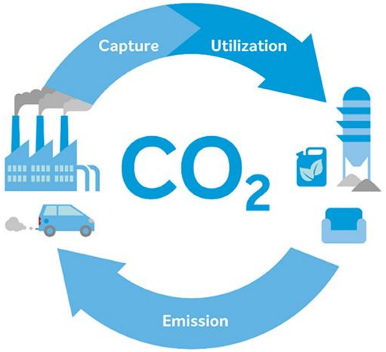


Image: Front. Climate, 4, 841907 (2022)

Electrification of industry

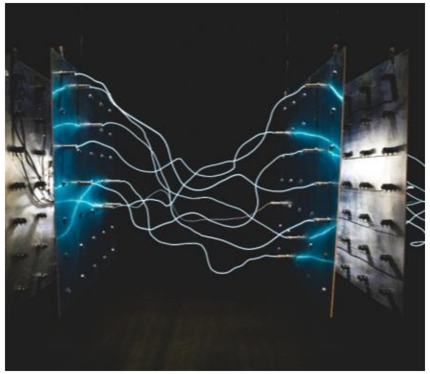


Image: renewablematter.eu

Emission avoidance

Image: cummins.com

Hydrogen economy

Image: Backwoods

IRP1: Multi-scale studies of catalytic and adsorption technologies

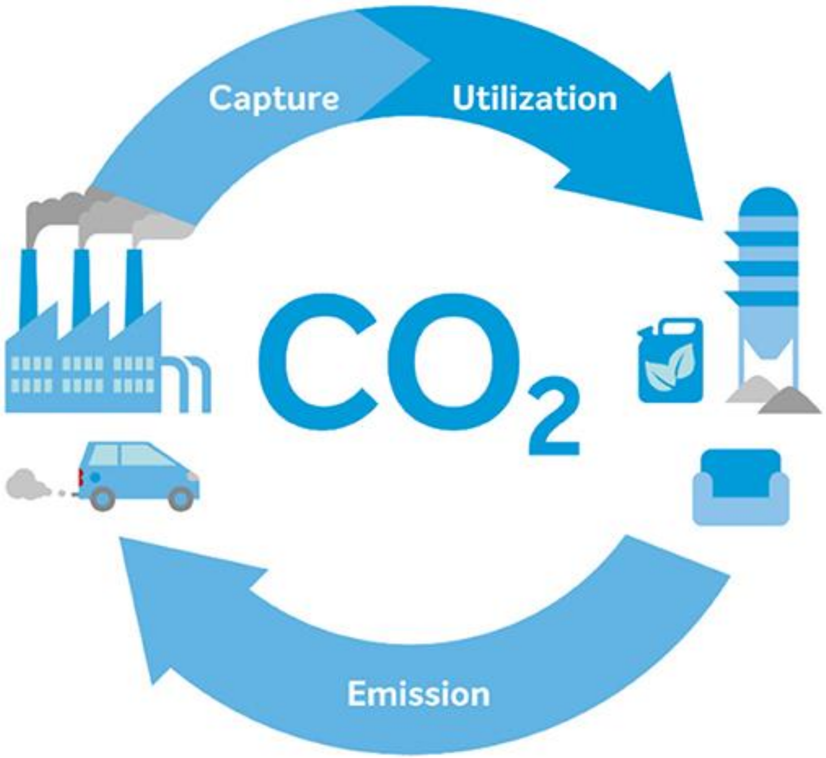
IRP1: Sustainable reaction engineering for carbon neutral industry

IRP2: Electrochemical multi-scale science, engineering and technology

IRP2: Electrosynthetic pathways for advanced low-carbon chemical manufacturing

IRP3: Carbon abatement in the petroleum refining industry: a control and optimisation research network

IRP3: Combustion for cleaner fuels and better catalysts

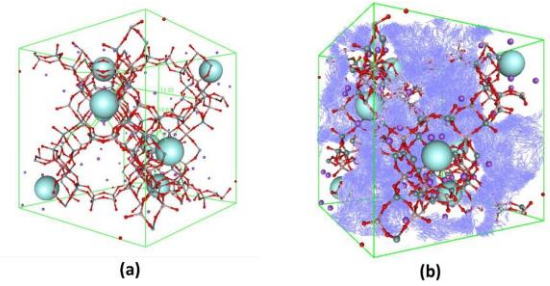


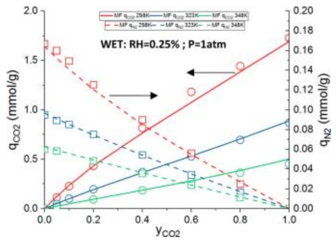
CO_2 capture and utilisation

Carbon capture technologies

Physical adsorption on molecular sieves and silica gel

Simulating CO_2, moisture and nitrogen adsorption in porous adsorbents

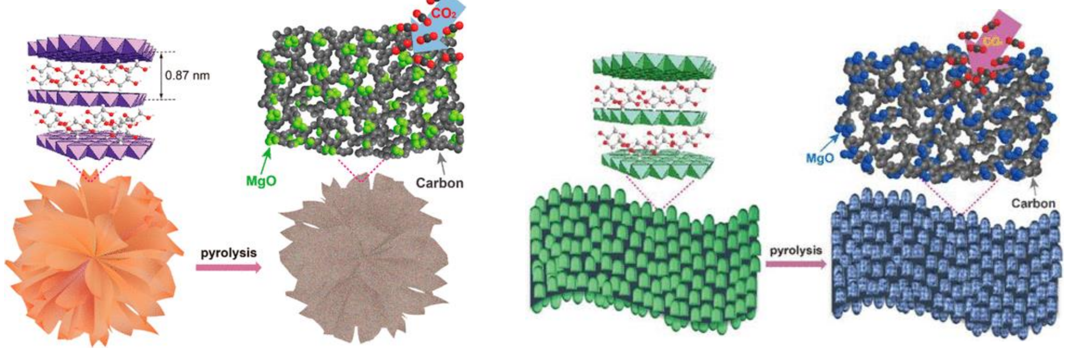




Ind. Eng. Chem. Res. 58, 42, 19611–19622 (2019); J. Phys. Chem. C. 122, 22, 11832–11847 (2018); Micropor. Mesopor. Mat., 261, 181-197 (2018); Chem. Eng. Sci., 227, 115890 (2020).

Chemical adsorption on novel materials

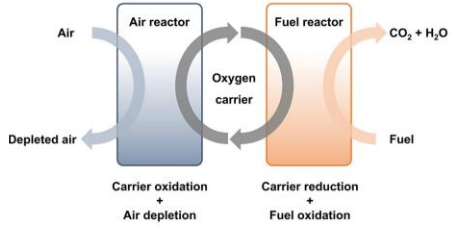
MgO/C nanocomposites for CO_2 capture at ambient temperatures

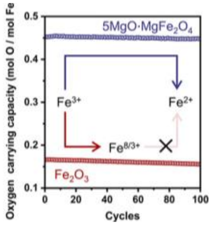


J. Mater. Chem. A, 10, 1682-1705 (2022), Environ. Sci. Technol. 51, 21, 12998–13007 (2017); ACS Appl. Mater. Interfaces, 9, 11, 9592–9602 (2017)

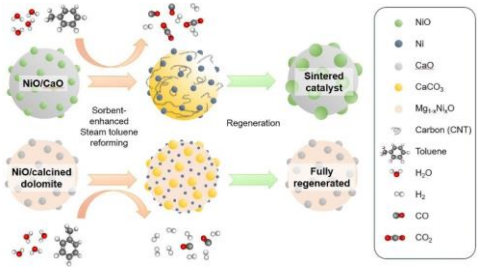
Chemical looping technology

Chemical looping combustion for energy generation with inherent CO_2 capture



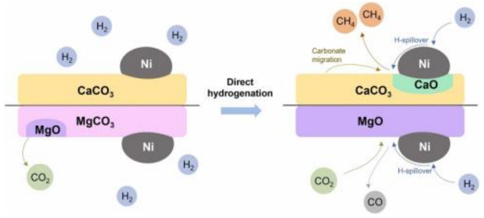


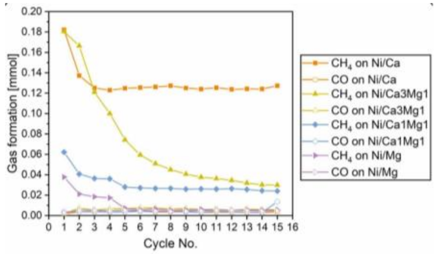
Chemical looping reforming for hydrogen generation with inherent CO_2 capture



ACS Catal., 8, 3, 1748–1756 (2018); ACS Sustainable Chem. Eng. 10, 22, 7242–7252 (2022); Chem. Eng. J. 425, 131522 (2021); Appl. Energ., 236, 635-647 (2019); Fuel Process. Technol., 228, 107169 (2022); Energ. Conv. and Manag., 244, 114455 (2021)

Reactive CO_2 capture on dual functional materials



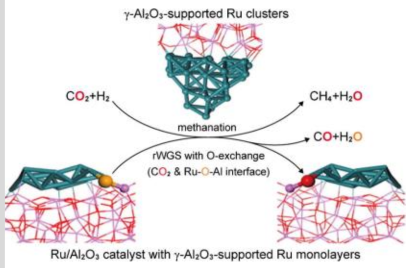


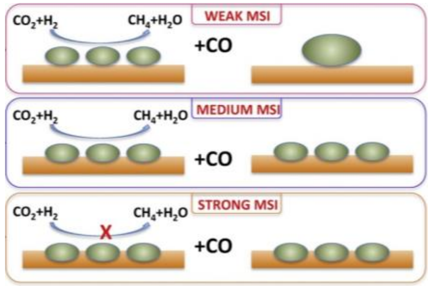
Appl. Catal. B., 338, 123053 (2023)

Conversion of captured CO_2

CO_2 methanation

Insights into interfacial catalysis and metal-support interaction

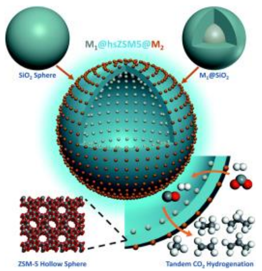


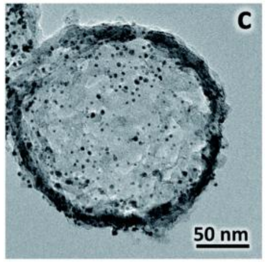


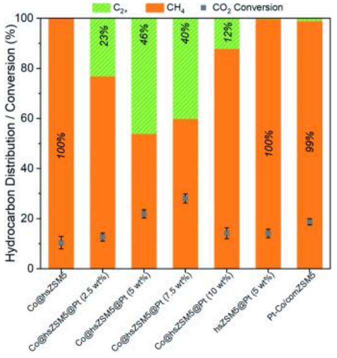
Appl. Catal. B., 237, 504-512 (2018); J. Catal., 367, 194-205 (2018);
Appl. Catal. B., 196, 108-116 (2016)

CO_2 to C_{2+} products

hollow spherical Co@hsZSM5@metal dual-layer nanocatalysts for tandem CO_2 hydrogenation to increase C_{2+} hydrocarbon selectivity



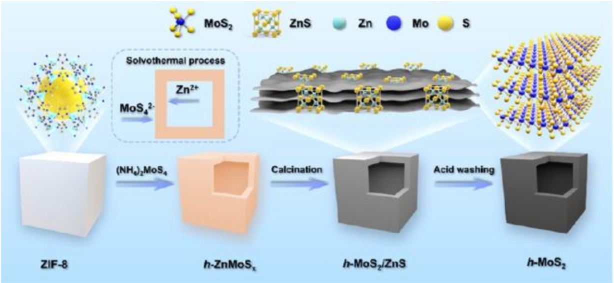




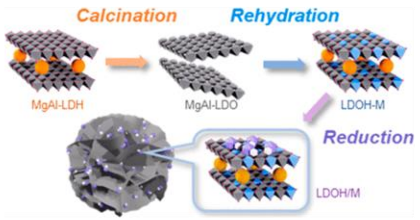
J. Mater. Chem. A, 8, 12757-12766 (2020)

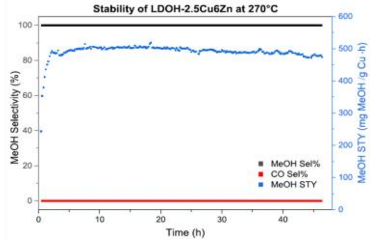
CO_2 to methanol

Hollow MoS_2 nanoboxes with S-vacancies

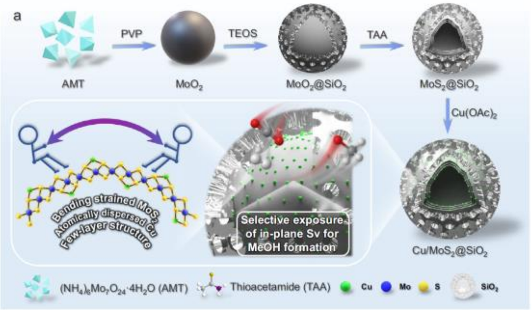


Cu–Zn prepared from LDH precursors

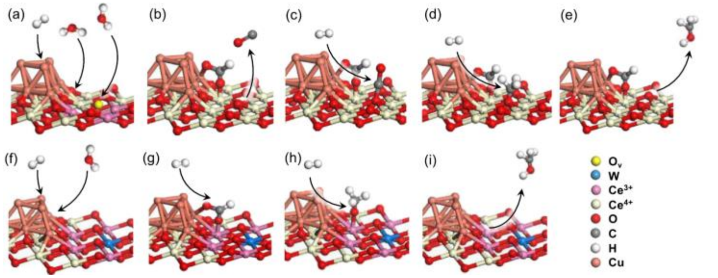




mSiO_2-Encapsulated MoS_2 Catalysts with Fullerene-Like Structure and Atomic Copper ($Cu/MoS_2@SiO_2$).



Altering reaction pathways on Cu/CeO_2 and $Cu/CeW_{0.25}O_x$

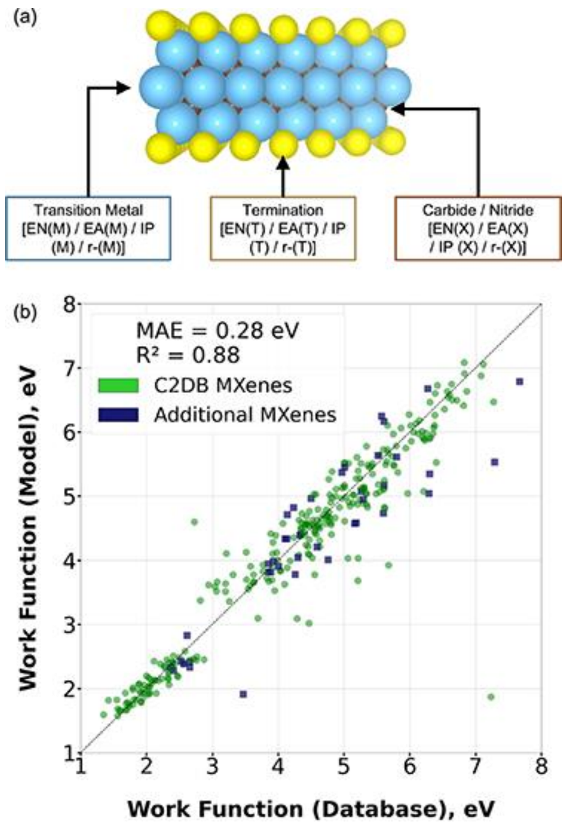


Nat. Comm. 14, 5872 (2023); ACS Sustainable Chem. Eng., 11, 22, 8326–8336 (2023); Ind. Eng. Chem. Res., 62, 4, 1877–1890 (2023); ACS Appl. Energy Mater. 6, 2, 782–794 (2023); Appl. Catal. B., 306, 121098 (2022); ACS Catal., 12, 16, 9872–9886 (2022); ACS Catal. 12, 10, 5750–5765 (2022); Adv. Funct. Mater. 31, 47, 2102896 (2021)

Computational insights

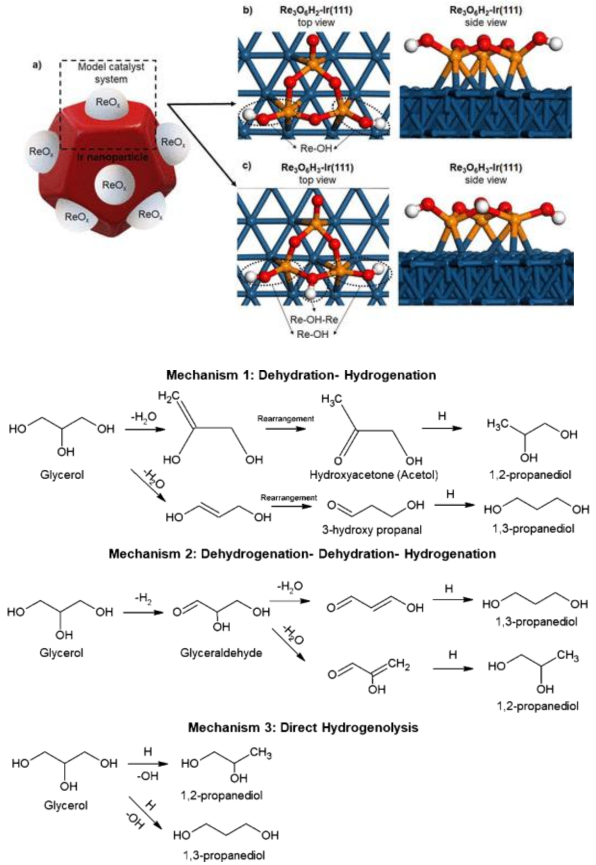
Machine learning

Prediction of physio-chemical properties of catalysts



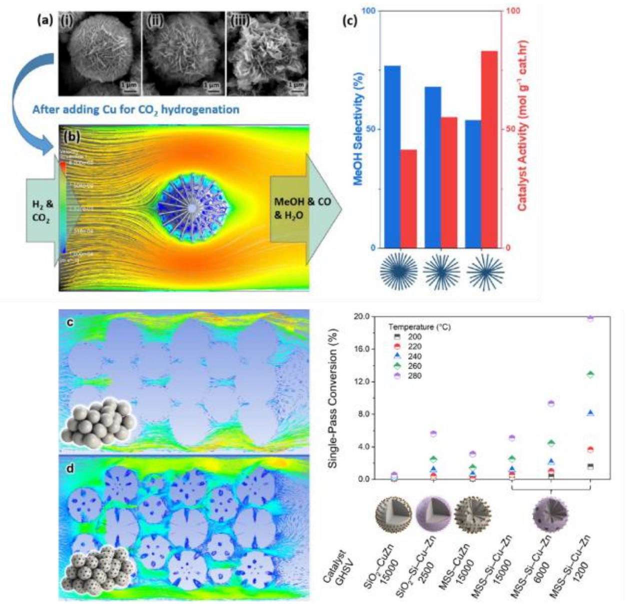
Density functional theory

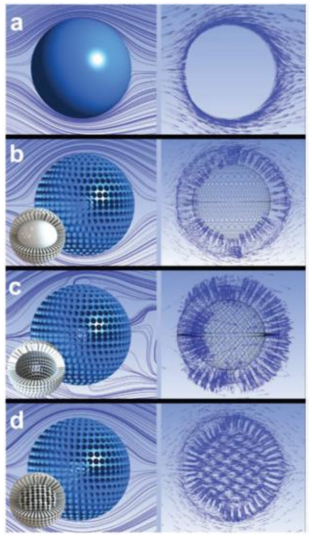
Computational insights into reaction mechanisms, complemented by experiments



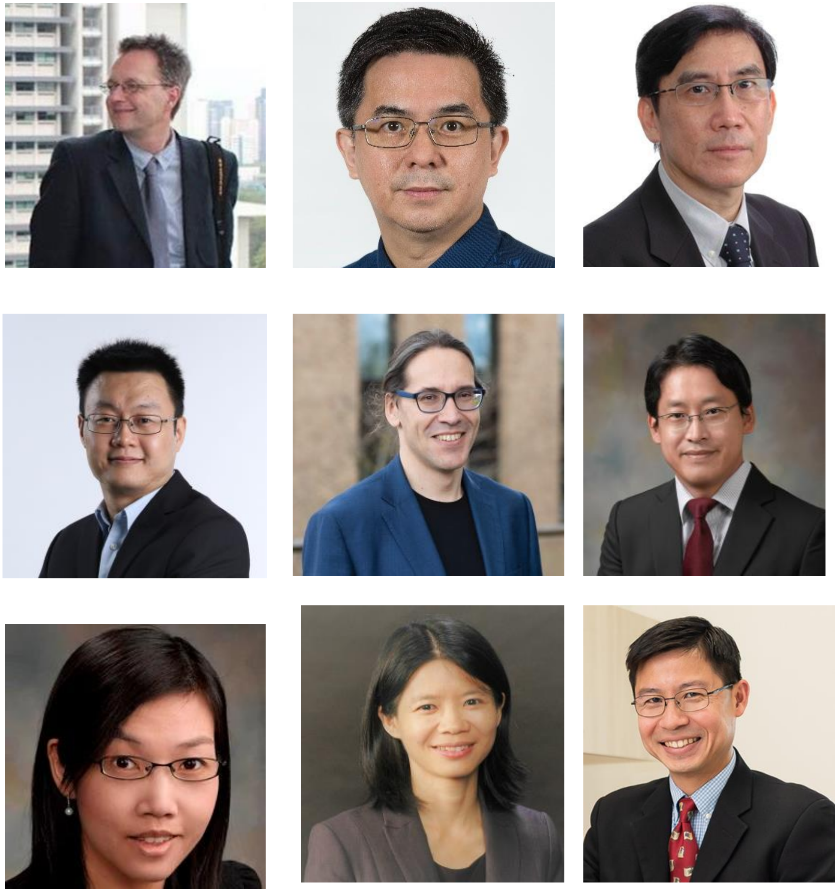
Computational fluid dynamics

Computational fluid dynamics (CFD) insights into CO_2 hydrogenation catalysts





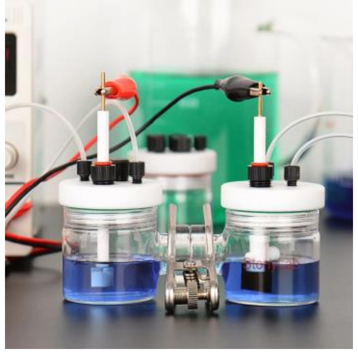
J. Phys. Energy, 5, 034005 (2023); *React. Chem. Eng.*, 4, 165-206 (2019); *ACS Catal.*, 9, 1, 485–503 (2019)

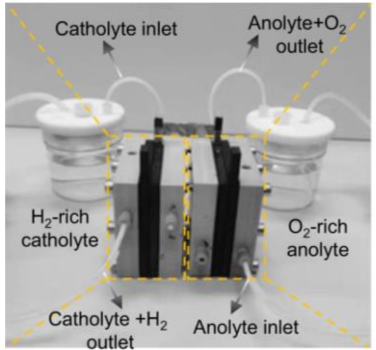


Electrification of chemical industry

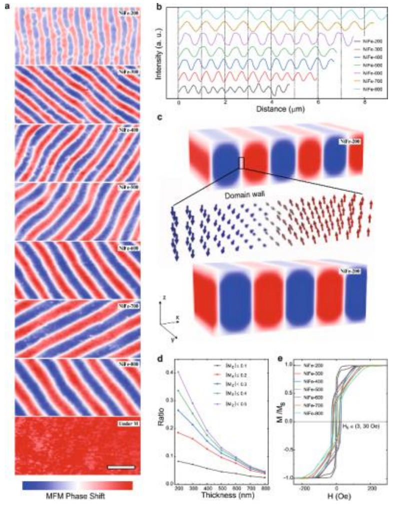
Green hydrogen from water electrolysis

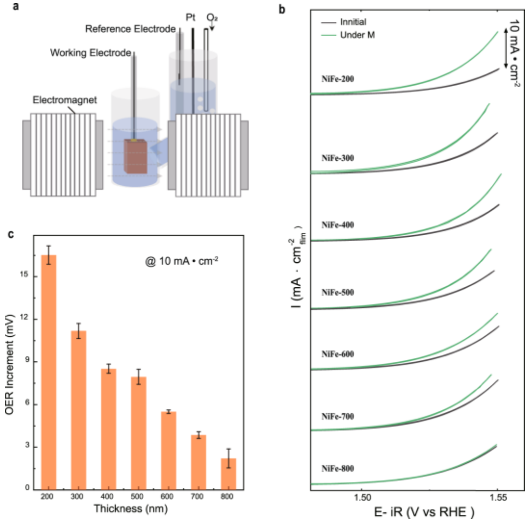
Cathode (HER):	$2H_2O(l) + 2e^- \rightarrow$	$H_2(g) + 2OH^-(aq)$
Anode (OER):	$4OH^-(aq) \rightarrow$	$O_2(g) + 2H_2O(l) + 4e^-$





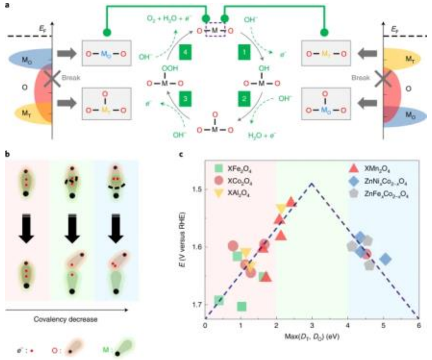
Magnetisation-enhanced OER

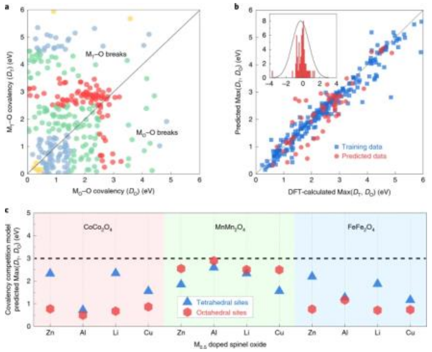




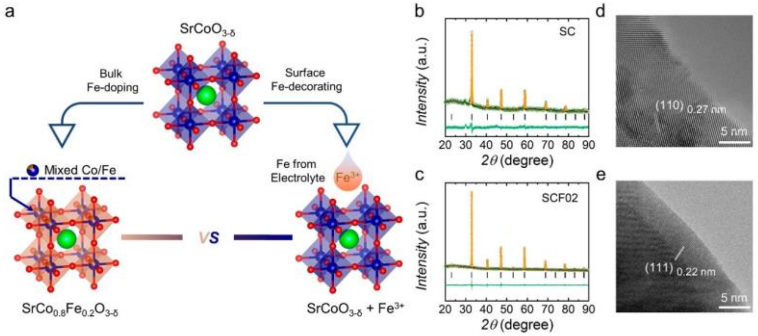
Understanding active sites

Relationship between covalency and OER activity of spinel oxides

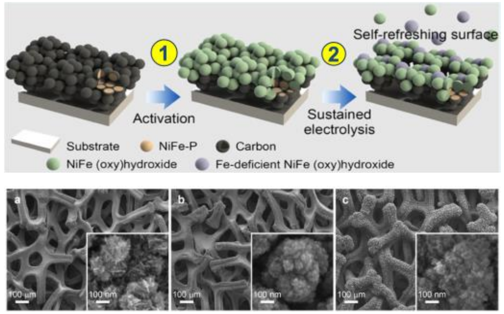




Surface reconstruction of perovskite OER catalysts



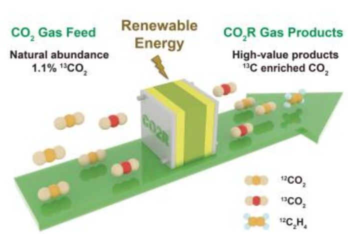
Evolution of (NiFe)OOH in high current densities

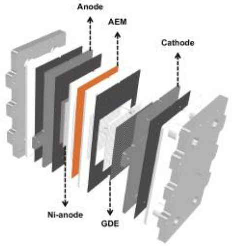


JACS Au 1, 1, 108–115 (2021); Nat. Comm. 12, 3634 (2021); Nat. Comm. 10, 572 (2019); Chem. Mater. 30, 19, 6839–6848 (2018); J. Am. Chem. Soc. 142, 17, 7765–7775 (2020); ACS Appl. Energy Mater. 6, 4, 2320–2332 (2023); Nat. Comm. 14, 2482 (2023); Nat. Comm. 14, 2467 (2023); Adv. Mater. 35, 2 2207041 (2023); ACS Nano 16, 11, 17572–17592 (2022); Nat. Comm. 13, 5510 (2022); Sci. Adv. 7, 50, eabk1788 (2021); Angew. Chem. Int. Ed. 60, 49, 25884 (2021); Nat. Comm. 12, 2608 (2021); Nat. Catal. 3, 554–563 (2020)

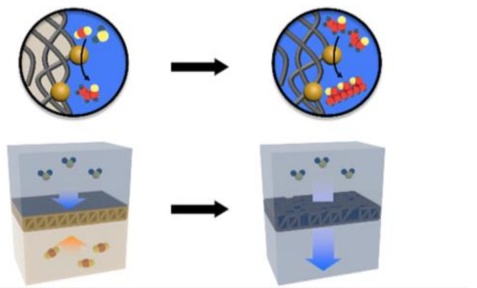
Electrochemical CO_2 reduction

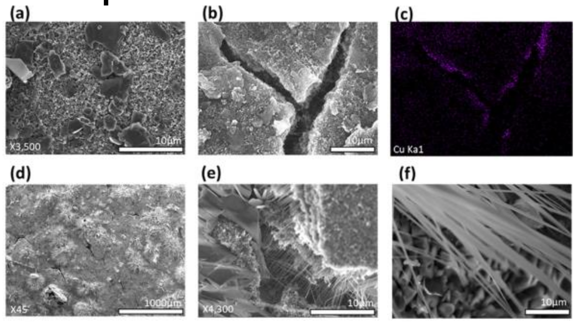
Table-top chemical factory





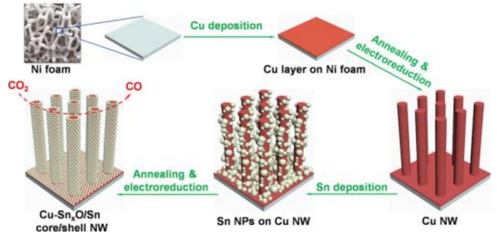
Electrode design and optimisation



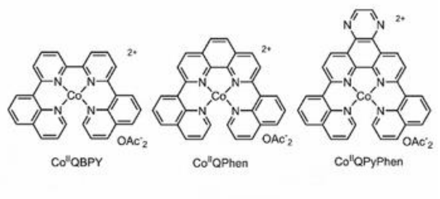


Electrocatalysts for enhanced efficiency and selectivity

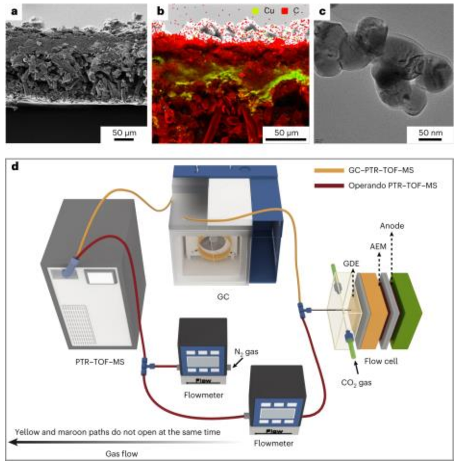
Cu-based catalysts

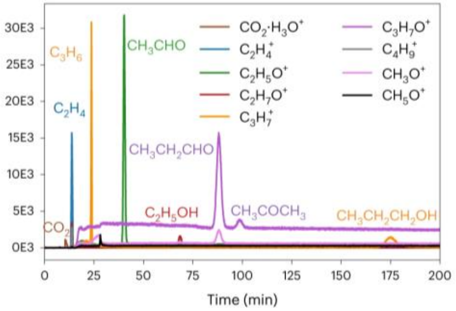


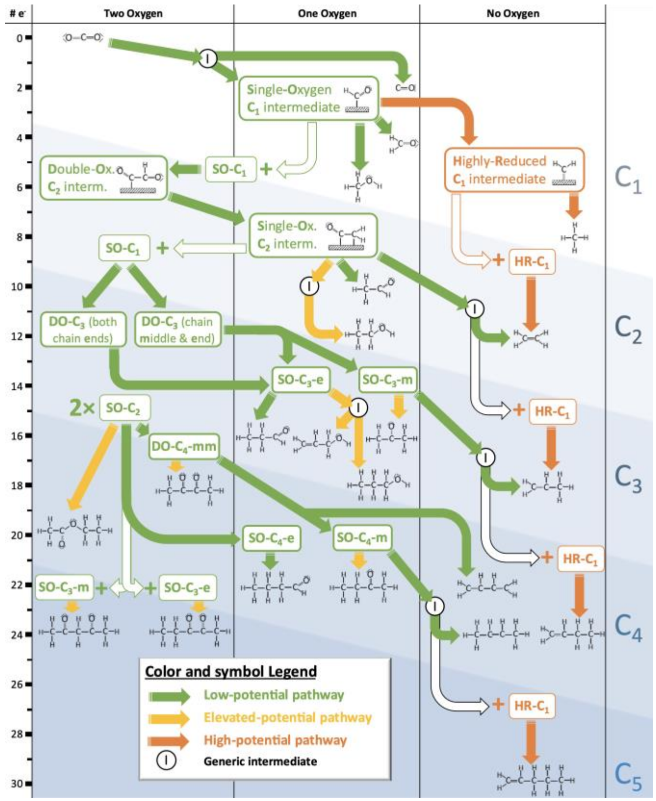
Molecular/complex catalysts



Mechanistic investigations







Nat. Catal. 5, 1169–1179 (2022); ACS Catal. 11, 18, 11416–11428 (2021); Science, 360, 6390, 707-708 (2018); ACS Energy Lett. 7, 2, 599–601 (2022); Small, 19, 41, 2301379 (2023); ChemSusChem, 14, 9, 2126 (2021); Small Structures, 2, 11, 2100093 (2021); Adv. Funct. Mater. 12, 34, 2202108 (2022); Angew. Chem. Int. Ed. 59, 39, 17104 (2020); Angew. Chem. Int. Ed. 58, 38, 13532 (2019); Energy Environ. Sci., 13, 374-403 (2020); Adv. Energ. Mater. 9, 3, 1803151 (2019); Adv. Energ. Mater. 9, 24, 1900090 (2019); Electrochem. Commun., 64, 69-73 (2016)

Electrosynthesis of chemicals

H_2O_2 synthesis

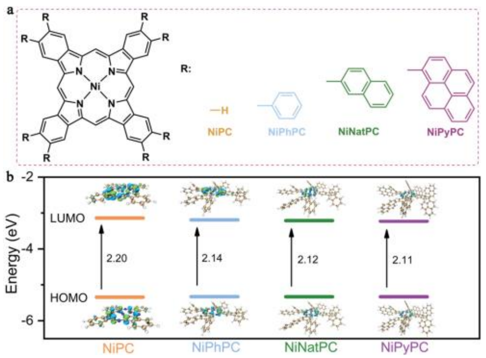
Oxygen reduction

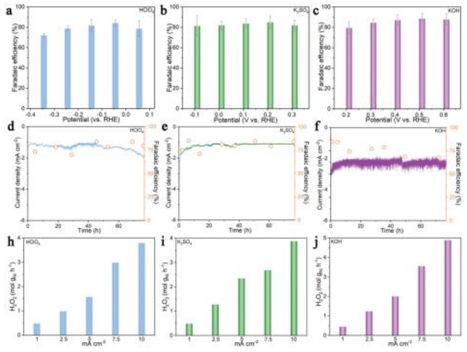
$$O_2 + 2\left(H^+ + e^-\right) \rightarrow\ *OOH + \left(H^+ + e^-\right) \rightarrow H_2O_2\ E^0 = 0.7\ \mathrm{V}$$

Water oxidation

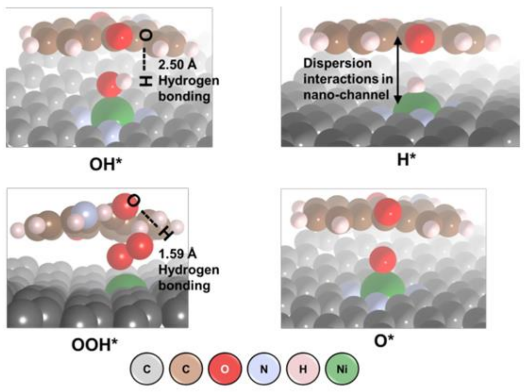
$$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^- \quad E^\circ = +1.76\ \mathrm{V}$$

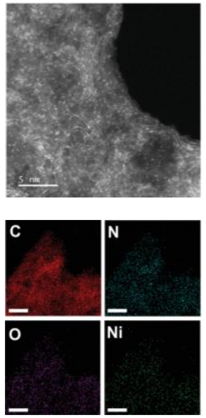
Conjugated nickel phthalocyanine derivatives as heterogeneous electrocatalysts

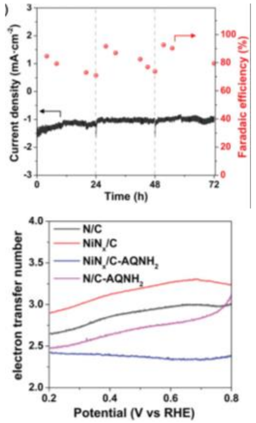




Aminoanthraquinone confined isolated NiN_x sites



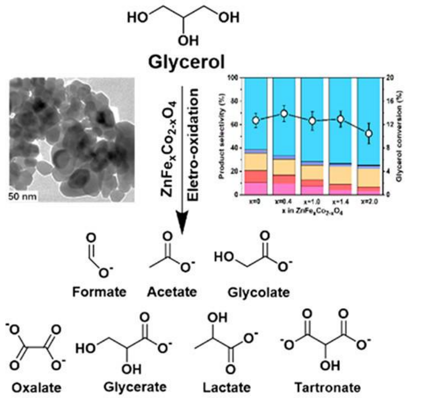




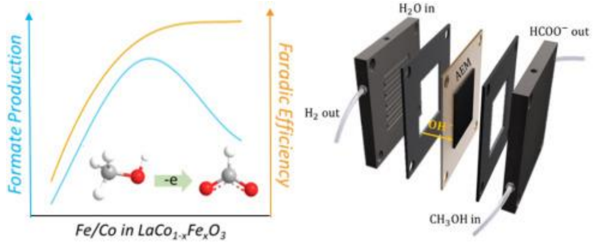
Adv. Mater. 34, 25, 2104891 (2022); Adv. Mater. 2306336 (2023); Adv. Energ. Mater., 8, 31, 1801909 (2018)

Electro-oxidation reactions

Glycerol oxidation to value-added products



Methanol oxidation to formate



Nitrogen oxidation to nitrates

$$\text{Step 1}:\ * + N_2 + OH^- \rightarrow {}^*NNOH + e^- \qquad (2)$$

$$\text{Step 2}:\ * + {}^*NNOH + OH^- \rightarrow {}^*N + {}^*NO + H_2O + e^- \qquad (3)$$

$$\text{Step 3}:\ {}^*NO + OH^- \rightarrow {}^*NOOH + e^- \qquad (4)$$

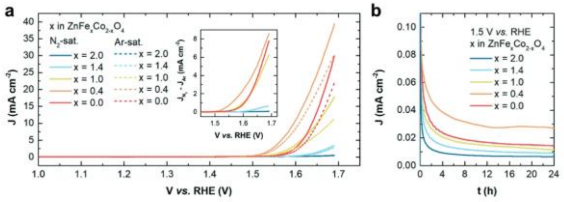
$$\text{Step 4}:\ {}^*NOOH + OH^- \rightarrow {}^*NOO + H_2O + e^- \qquad (5)$$

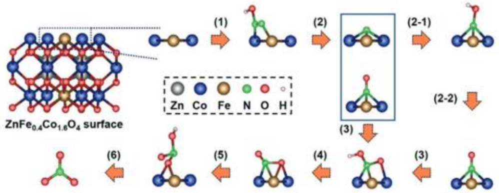
$$\text{Step 5}:\ {}^*NOO + OH^- \rightarrow {}^*NOOOH + e^- \qquad (6)$$

$$\text{Step 6}:\ {}^*NOOOH + OH^- \rightarrow NO_3^- + H_2O \qquad (7)$$

$$\text{Step 2-1}:\ {}^*N + OH^- \rightarrow {}^*NOH + e^- \qquad (8)$$

$$\text{Step 2-2}:\ {}^*NOH + OH^- \rightarrow {}^*NO + H_2O + e^- \qquad (9)$$





ACS Appl. Mater. Interfaces 14, 12, 14293–14301 (2022); eScience, 2, 1, 87-94 (2022); Angew. Chem. Int. Ed. 59, 24, 9418 (2020); Electrochimica Acta, 180, 1059-1067 (2015)

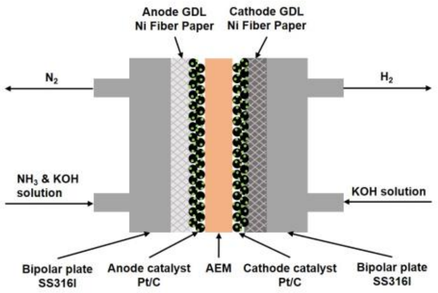
Electro-cracking of ammonia

Anode: $2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^-$

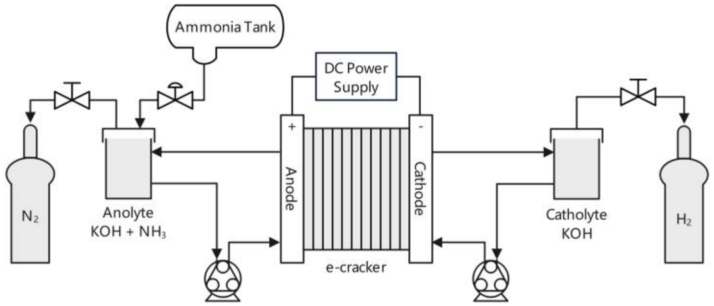
Cathode: $H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Overall: $2NH_3 \rightarrow N_2 + 3H_2$

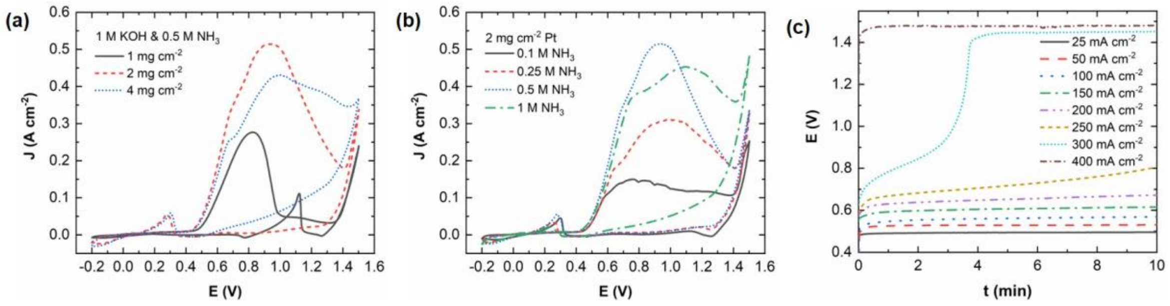
MEA electrolyser



Electrolyser stack

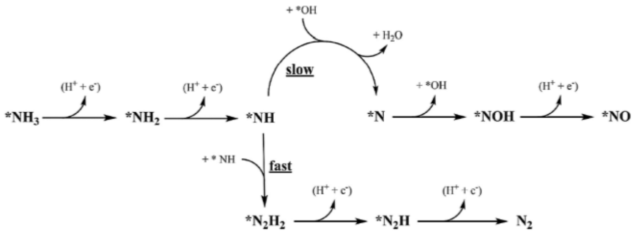


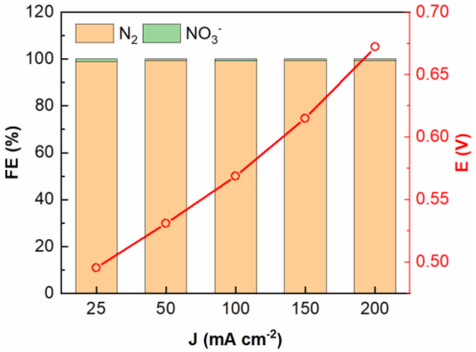
AOE on Pt in MEA elecctrolyser



- Ambient pressure and temperature operations
- 2 mg cm^{-2} is the best loading;
- 0.5 M is the optimal ammonia concentration.
- A stable cell voltage of 0.67 V achieved at 200 mA cm^{-2}.

AOR byproducts



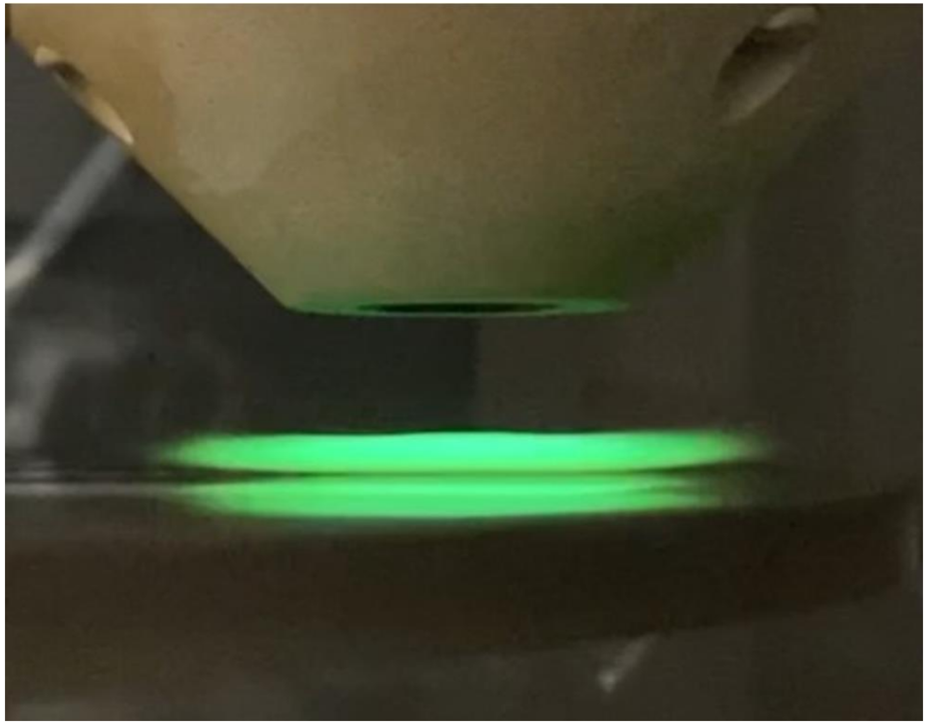


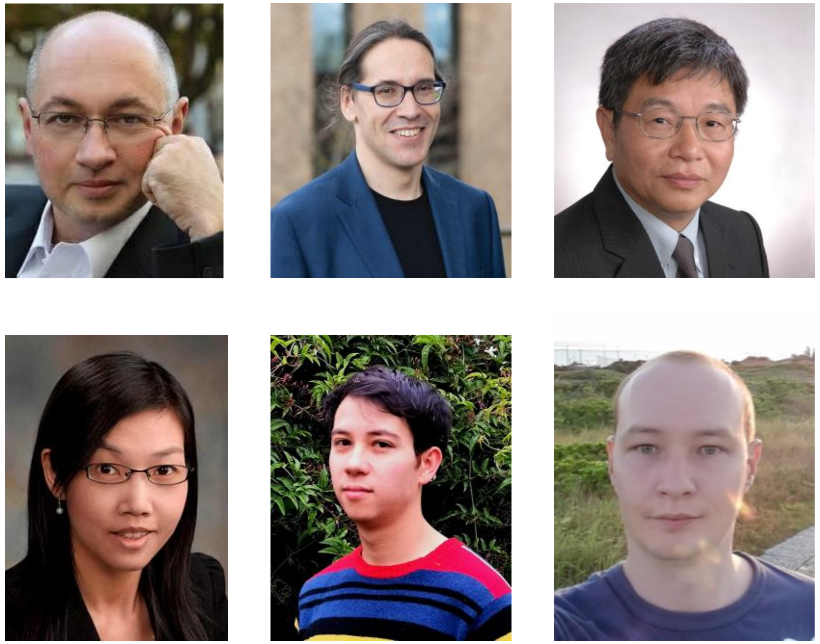
Cost of green hydrogen production

Calculated based on the retail electricity price in Singapore (27.43 cents per kWh)

Reactant	**Reactions**	***E⁰* (V vs. RHE)**	**U_{EC} @ 0.2 A cm^{-2} (V)**	**W_e @0.2 A cm^{-2} (kWh / kg H_2)**	**Electricity cost (SGD / kg H_2)***
H_2O	$2H_2O \rightarrow 2H_2 + O_2$	1.23	1.6Q	42.9	11.8
NH_3	$2NH_3 \rightarrow N_2 + 3H_2$	0.06	0.67	18.0	4.9

Singapore Patent Application # 10202301326Y; *Adv. Mater. 2019, 31, 1805173*; *J. Catal. 2018, 359, 82; Electrochim. Acta 2011, 56, 8085.*

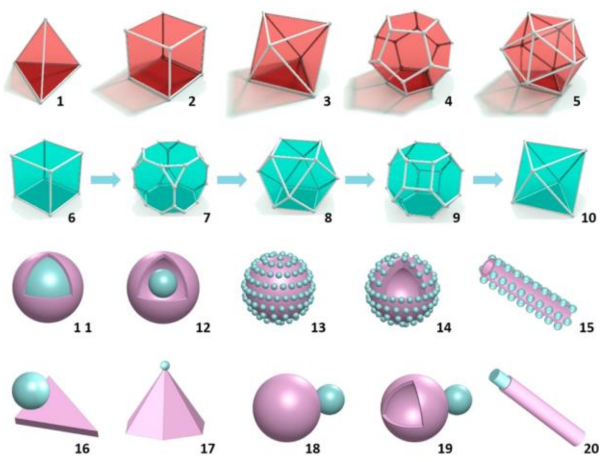


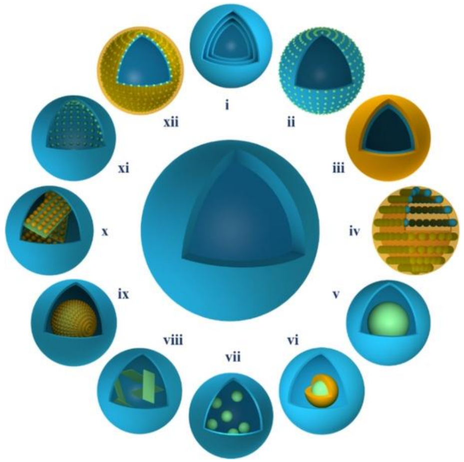


Design, synthesis and bulk production of functional materials

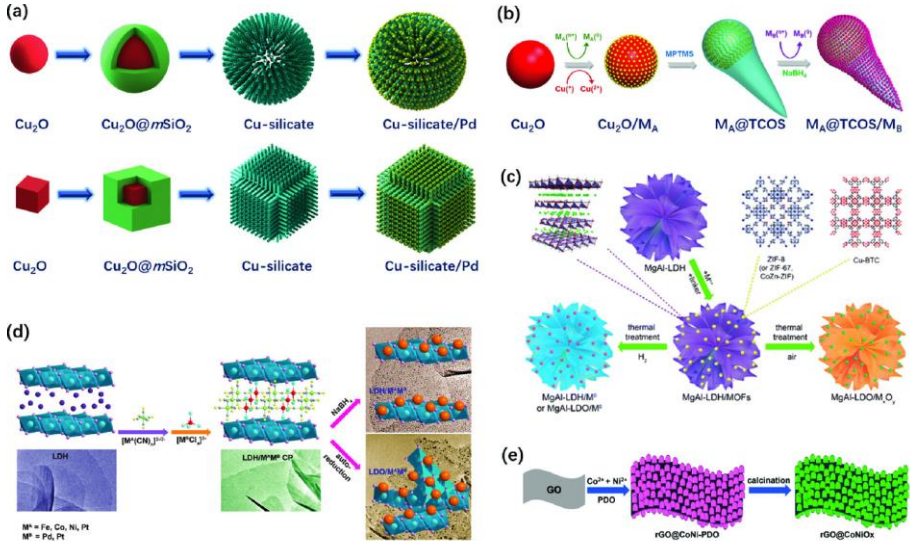
Nanostructured materials for catalysis, energy storage and CO_2 capture

Precise morphology control

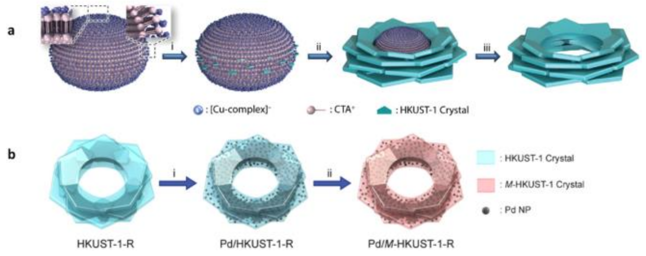


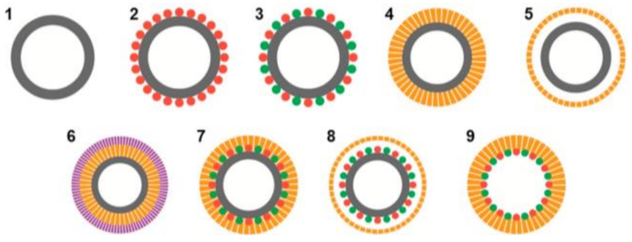


Hierarchical nanocatalysts

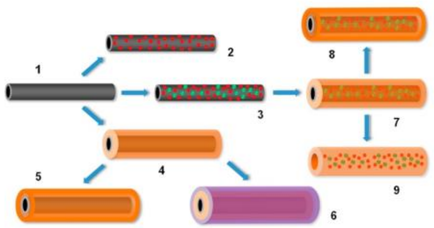


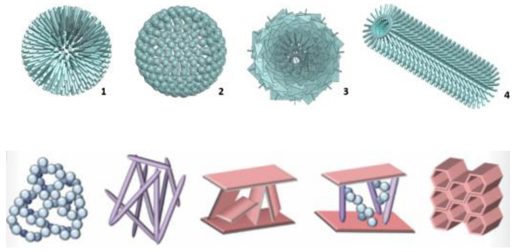
Templated catalytic nanostructures





Self-assembly of low dimensional materials



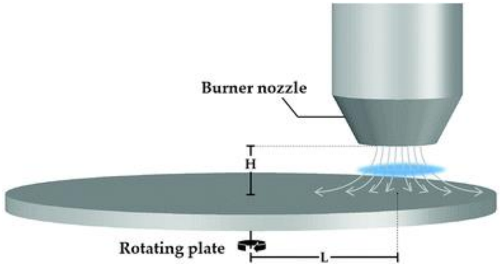


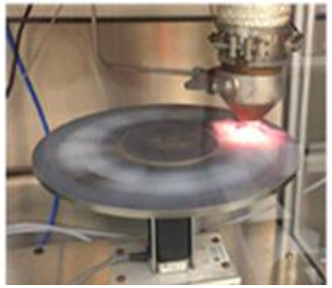
J. Am. Chem. Soc. 142, 32, 13823–13832 (2020); ACS Catal. 12, 16, 9872–9886 (2022); Nano Mater. Sci., 5, 3, 293-311 (2023); ACS Appl. Mater. Interfaces, 11, 26, 23180–23191 (2019); ACS Appl. Mater. Interfaces, 11, 16, 14774–14785 (2019); ACS Sustainable Chem. Eng., 7, 6, 5953–5962 (2019); Adv. Funct. Mater. 29, 39, (2019); Chem. Mater. 31, 14, 5320–5330 (2019); ACS Appl. Mater. Interfaces, 11, 50, 46825–46838 (2019); ChemCatChem, 12, 21, 5303-5311 (2020); ACS Appl. Mater. Interfaces 12, 30, 33827–33837 (2020); J. Mater. Chem. A, 8, 17266-17275 (2020); ACS Appl. Mater. Interfaces 12, 20, 23060–23075 (2020); Matter, 3, 2, 332-334, (2020); Particle, 37, 6, 2000101 (2020); ACS Appl. Nano Mater. 4, 10, 10886–10901 (2021);

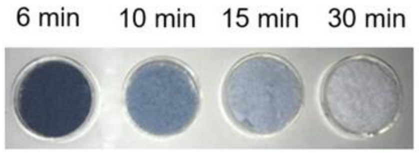
Flame synthesis of nanomaterials

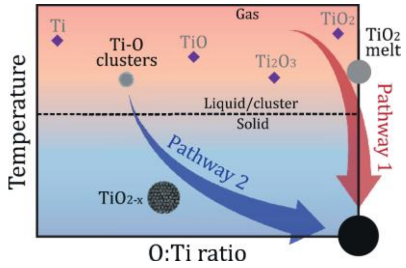
Application in photocatalysts

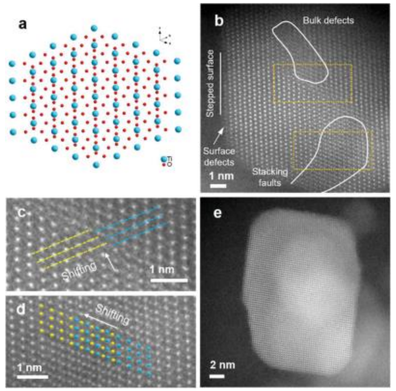
Synthesis of defect-rich TiO_2



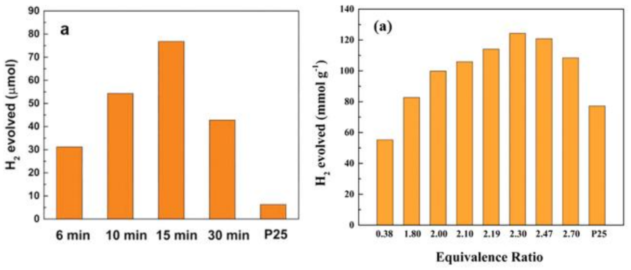








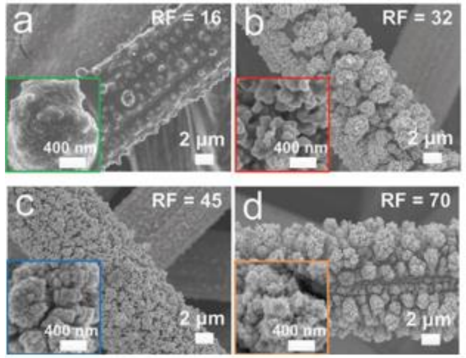
Performance in photocatalytic water splitting

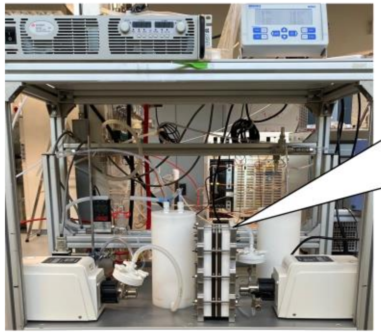


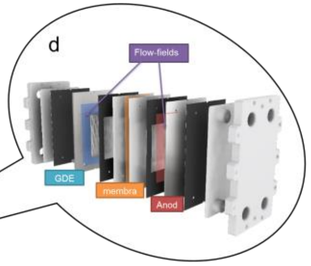
ACS Sustainable Chem. Eng. 6, 11, 14470–14479 (2018); Small, 5, 2, 2000928 (2021); Chem. Eng. Sci., 265, 118155 (2023); Combust Flame, 226, 347-361 (2021)

Application in catalysts for electrochemical carbon dioxide reduction

Flame aerosol synthesis of CuO electrodes (GDE) for direct deposition onto the catalyst substrate without further purification or ink preparation.

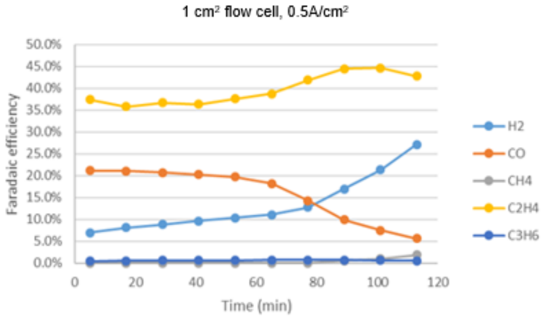


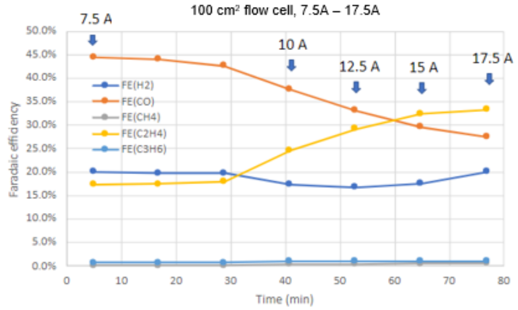




- Increase active GDE area to **100cm²**.
- Increased operating current up to a maximum of **100A**.

Test of GDE in flow electrodes at different current densities and electrode areas.



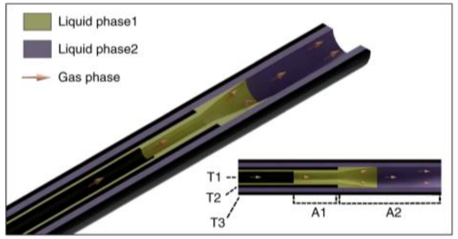


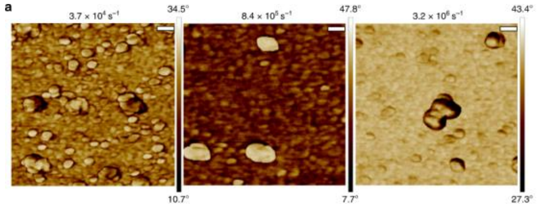
Adv Funct Materials, 32, 36 (2022)

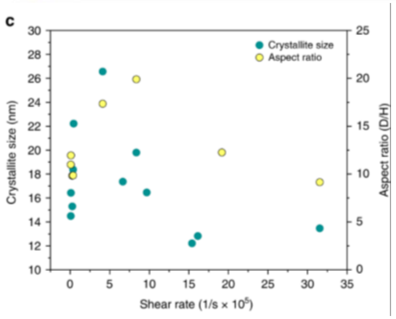
Nanomaterials synthesis in flow

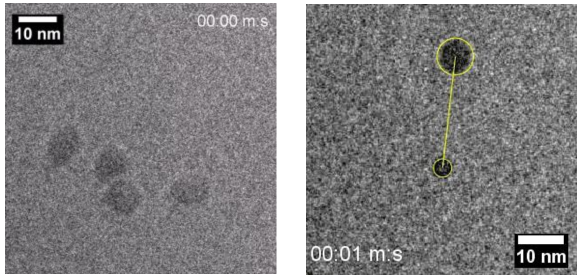
Control particle size through shear

Case study for synthesis of layered double hydroxides (LHD)

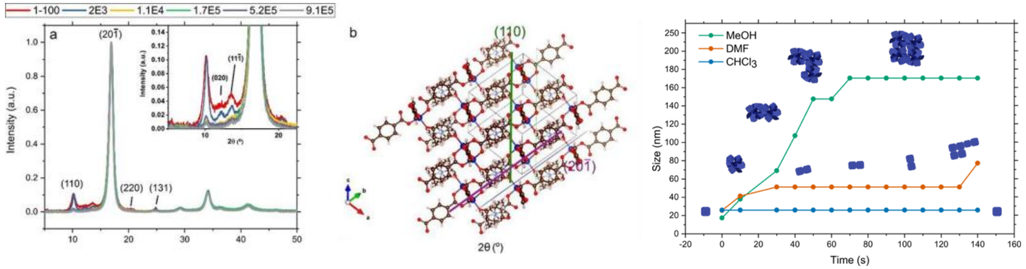






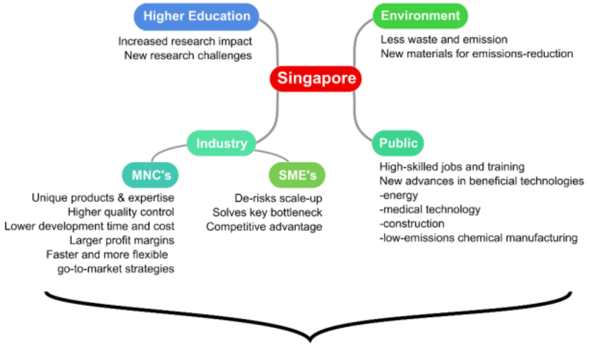


Case study for synthesis of two-dimensional metal organic frameworks (2D MOFs)



Chem. Eng. J. 426, 131345 (2021); Advanced Nanomaterials, 29-59 (2019); Chem. Eng. J., 388, 124133 (2020); J. Phys. Chem. C, 125, 41, 22837–22847 (2021); US Patent App. 16/966,511; Nat. Comm., 9, 4913 (2018)

Accelerated Manufacturing Platform for Engineered Nanomaterials (AMPLE)



Singapore

Higher Education
Increased research impact
New research challenges

Environment
Less waste and emission
New materials for emissions-reduction

Industry

MNC's
Unique products & expertise
Higher quality control
Lower development time and cost
Larger profit margins
Faster and more flexible go-to-market strategies

SME's
De-risks scale-up
Solves key bottleneck
Competitive advantage

Public
High-skilled jobs and training
New advances in beneficial technologies
-energy
-medical technology
-construction
-low-emissions chemical manufacturing

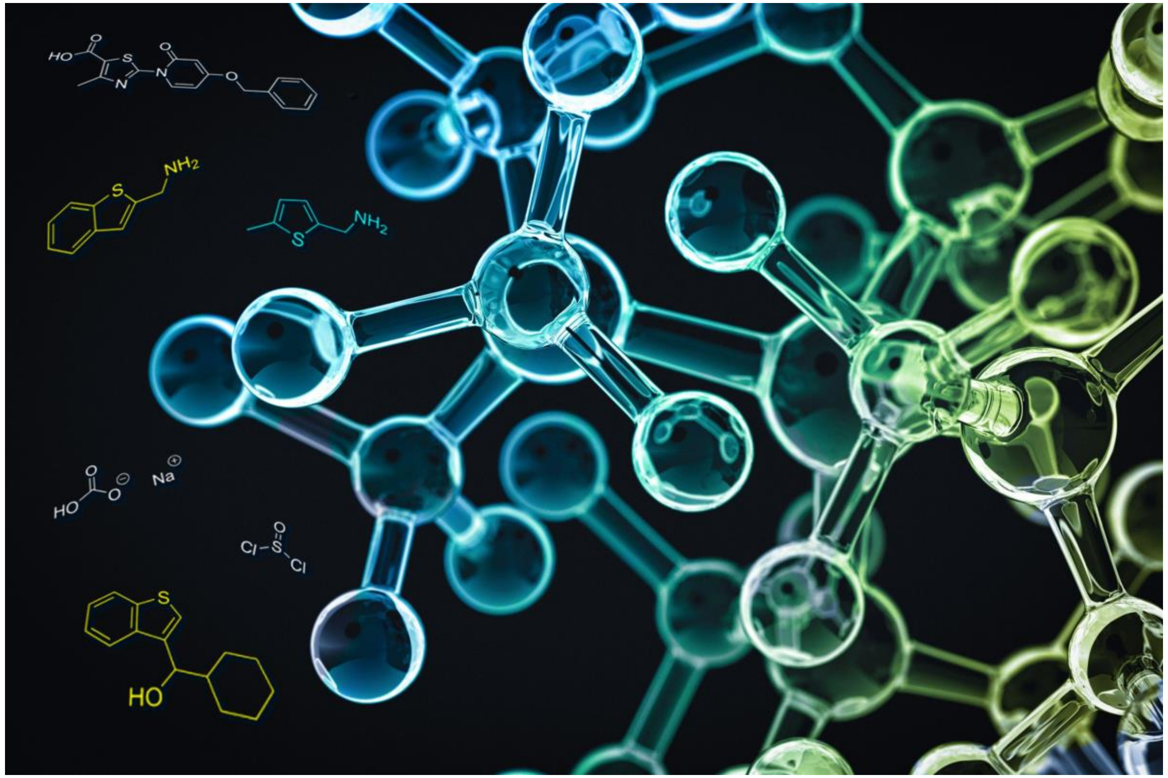
Benefits

- Nanomaterial ecosystem acceleration
- New jobs and training for high skilled labour
- Competitive advantage in materials industries
- More sustainable chemical and materials manufacturing practices
- Heightened impact from research institutes and higher education
- Reduced need on foriegn sources for new materials
- Puts SG at forefront of industry 4.0 principles in materials manufacturing

NRF SINGAPORE

UNIVERSITY OF CAMBRIDGE enterprise

Chem. Eng. J., 426, 131345 (2021)

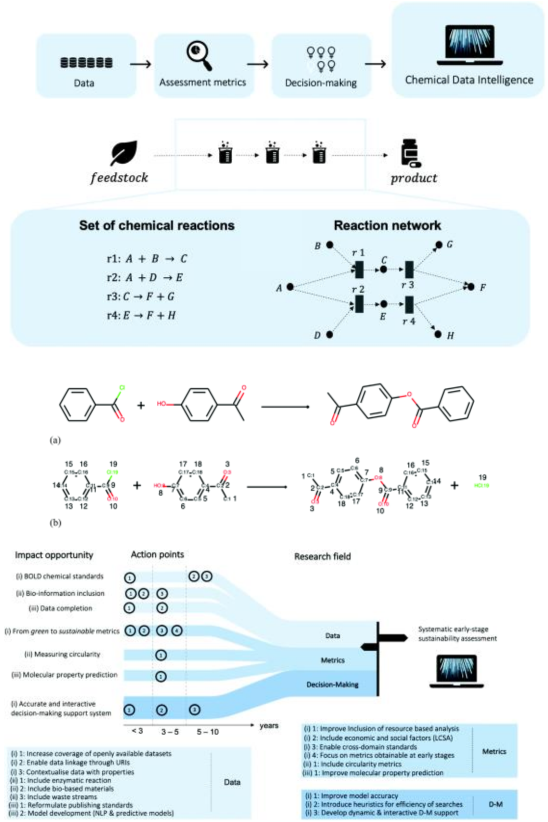


New synthetic pathways and processes engineering

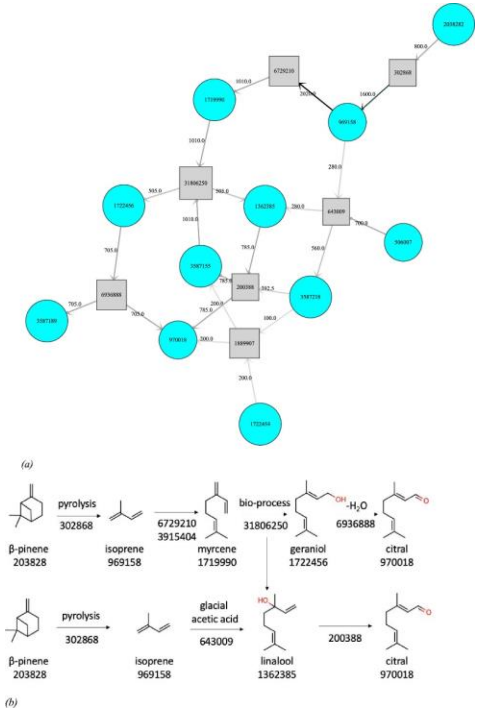
Green chemical synthesis pathways empowered by machine learning and data science

Digitalise and automate design of chemical synthesis

Accelerate sustainable chemistry development
by chemical data intelligence



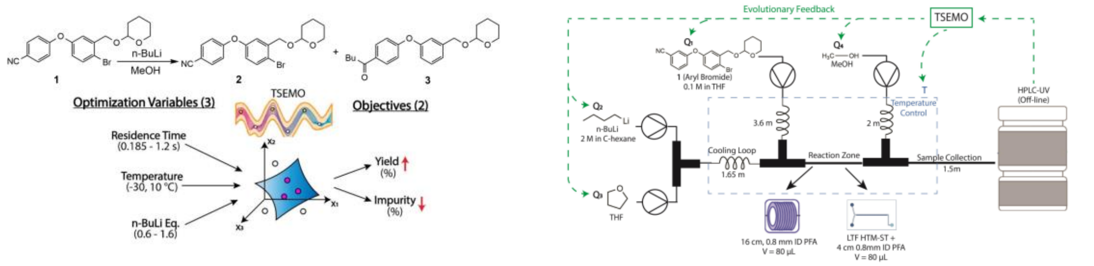
Case study of producing citral from β-pinene, powered by Reaxys.

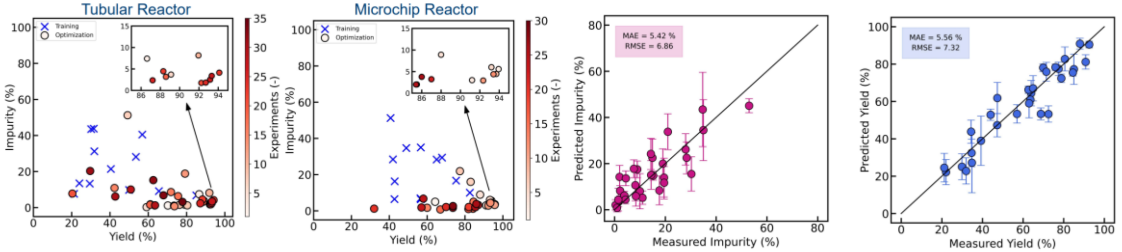


Chem. Eng. Sci., 247, 116938 (2022); ACS Eng. Au, 2, 4, 333–349 (2022); Chem. Sci., 10, 6697-6706 (2019); Curr. Opin. Chem. Eng., 26, 148-156 (2019); React. Chem. Eng., 4, 1969-1981 (2019); Chem. Soc. Rev., 50, 12013-12036 (2021)

Machine learning-enabled process optimisation for pharmaceutical process innovation (funded by PIPS)

Cased study on lithium-halogen exchange reactions





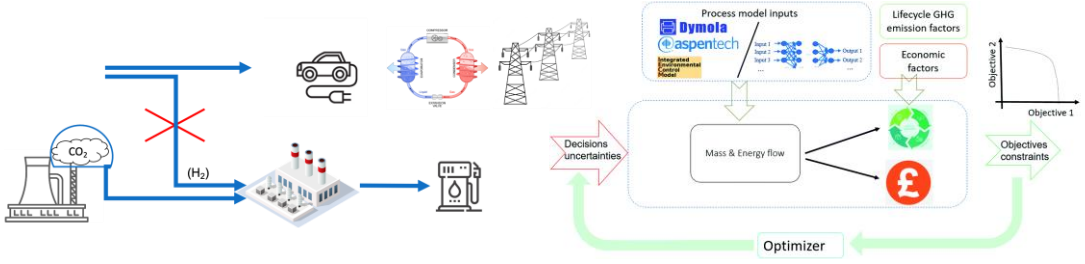
- Yield maximised
- Impurity minimised
- Pareto front identified within 50 experiments
- Applicable to two reactor configurations

Chemistry-Methods 1.1, 71-77 (2021)

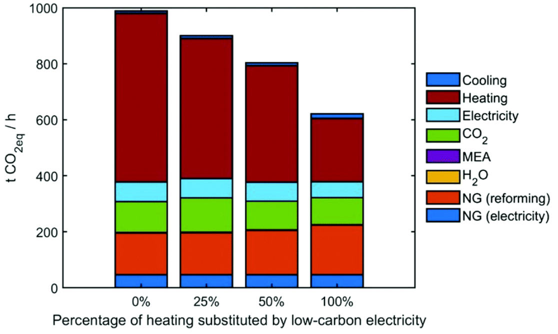
Empowering a low carbon future

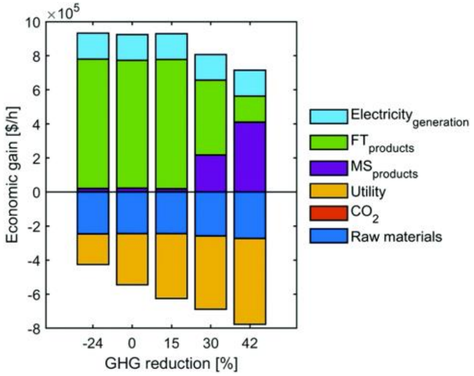
Deploying carbon capture and utilization for industrial park

Simulating a low-carbon energy supply by CCU without renewable electricity or H_2



CCU alone could partially decarbonise the industrial park.
Heating is a significant contributor to GHG emissions.

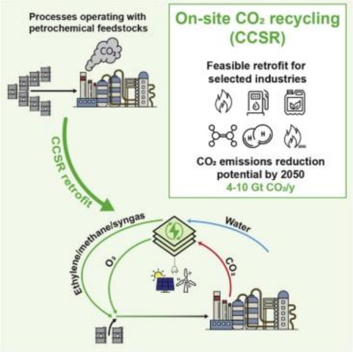


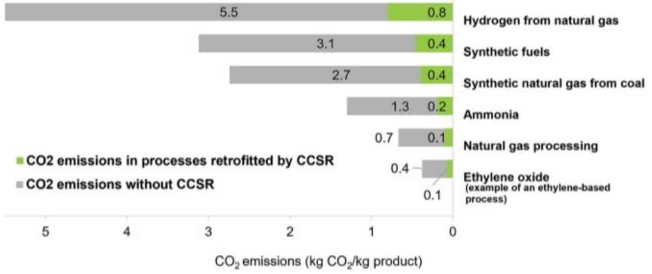


Front. Chem., 7. (2019); *Energy Environ. Sci*., 15, 2139 (2022); *PNAS*, 116, 11187 (2019); *AIChE J*., e17616 (2022).

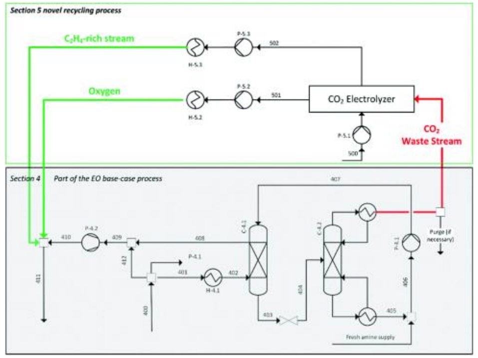
Chemical manufacturing using green electrons

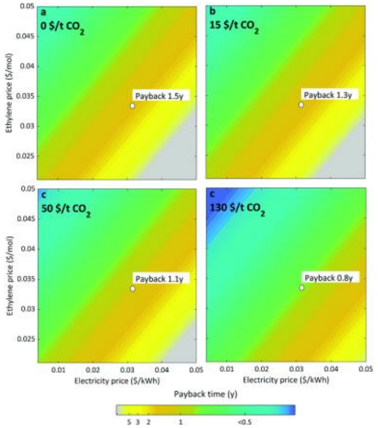
Carbon capture on-site recycling integrated with electrochemical reduction of CO_2





Case study for ethylene oxide production at industrial scales: both cost and CO_2 emissions are reduced.

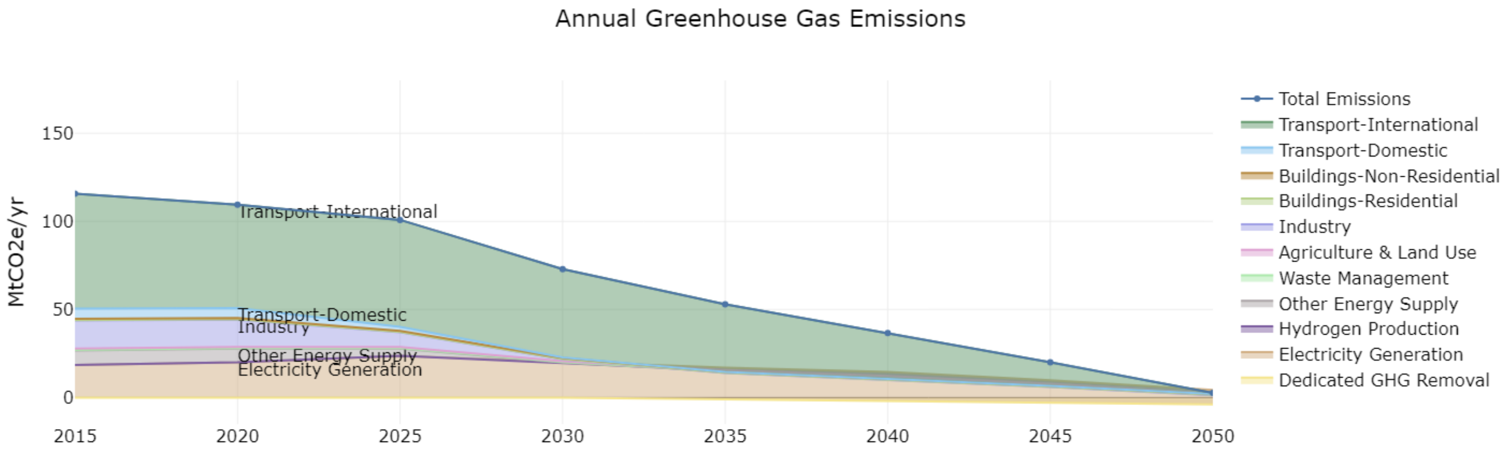


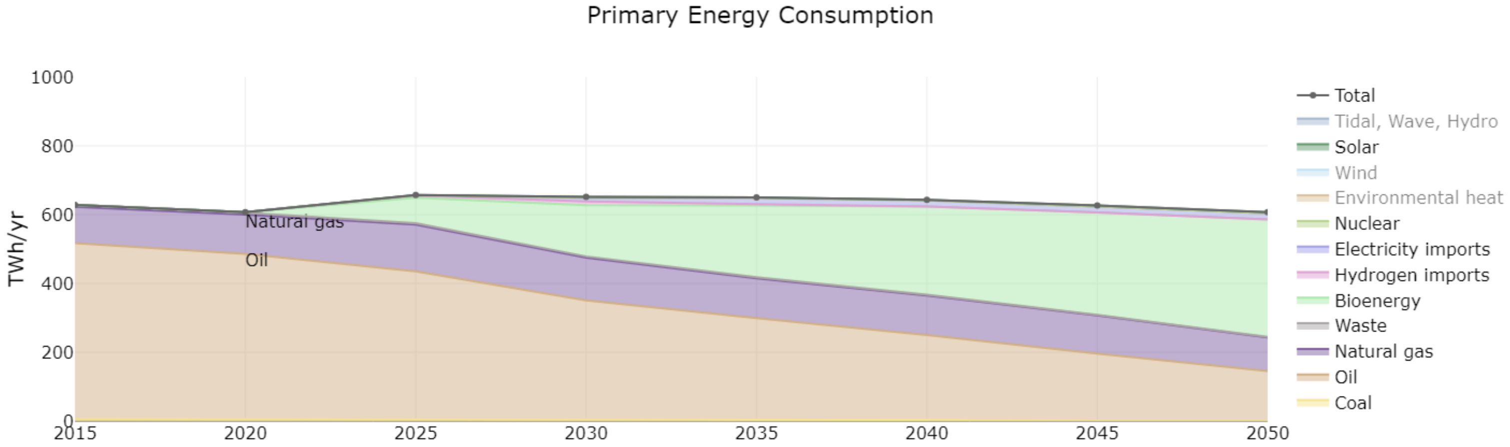


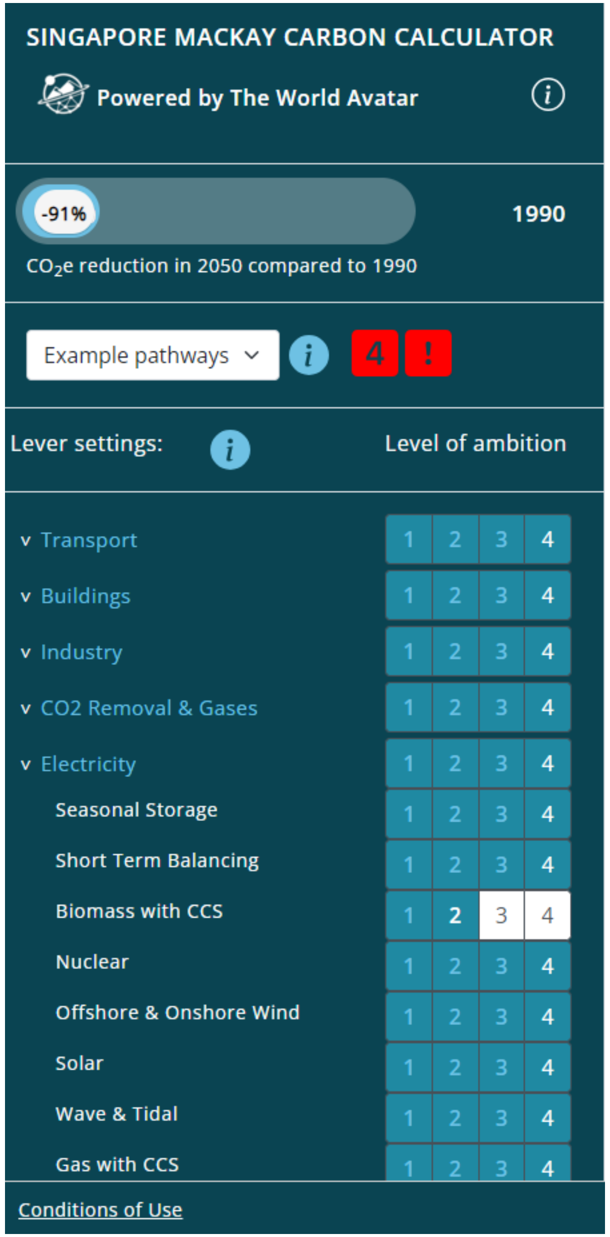
STAR Protocols, 2, 4, 100889 (2021); iScience, 24, 6, 102514 (2021); Energy Environ. Sci., 14, 1530-1543 (2021)

MacKay calculator for Singapore

http://137.132.22.164:45432/







SINGAPORE MACKAY CARBON CALCULATOR

Powered by The World Avatar

-91% 1990

CO$_2$e reduction in 2050 compared to 1990

Lever settings: Level of ambition

v Transport	1	2	3	4
v Buildings	1	2	3	4
v Industry	1	2	3	4
v CO2 Removal & Gases	1	2	3	4
v Electricity	1	2	3	4
Seasonal Storage	1	2	3	4
Short Term Balancing	1	2	3	4
Biomass with CCS	1	2	3	4
Nuclear	1	2	3	4
Offshore & Onshore Wind	1	2	3	4
Solar	1	2	3	4
Wave & Tidal	1	2	3	4
Gas with CCS	1	2	3	4

Conditions of Use

NATIONAL RESEARCH FOUNDATION
PRIME MINISTER'S OFFICE
SINGAPORE

This project is funded by the
National Research Foundation (NRF),
Prime Minister's Office, Singapore under its
Campus for Research Excellence and
Technological Enterprise (CREATE)
programme.