Plasma Catalysis: Opportunities and Challenges in Gas Conversion

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Outline

I. Introduction

II. Plasma catalysis for ammonia synthesis

III. Plasma catalysis for the conversion of C1 molecules

IV. Summary

Global Challenges and Opportunities

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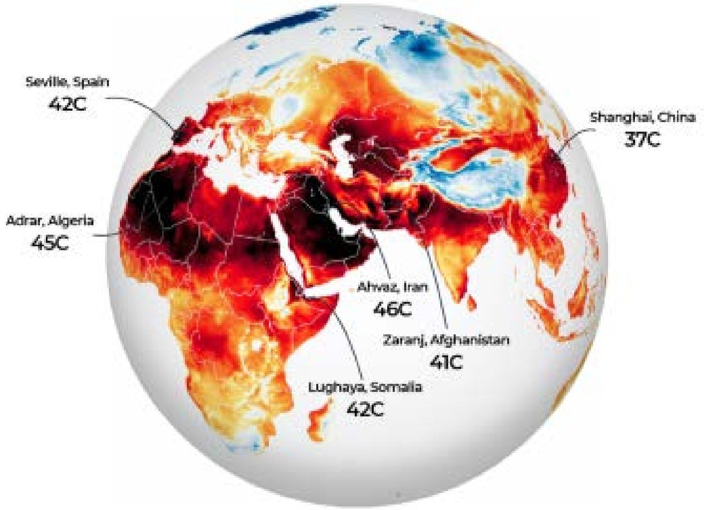
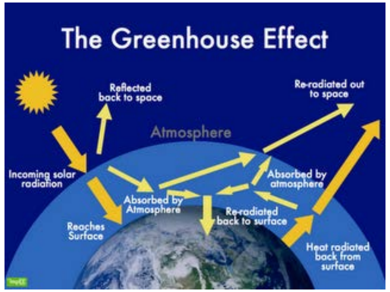
Global Warming & Climate Change

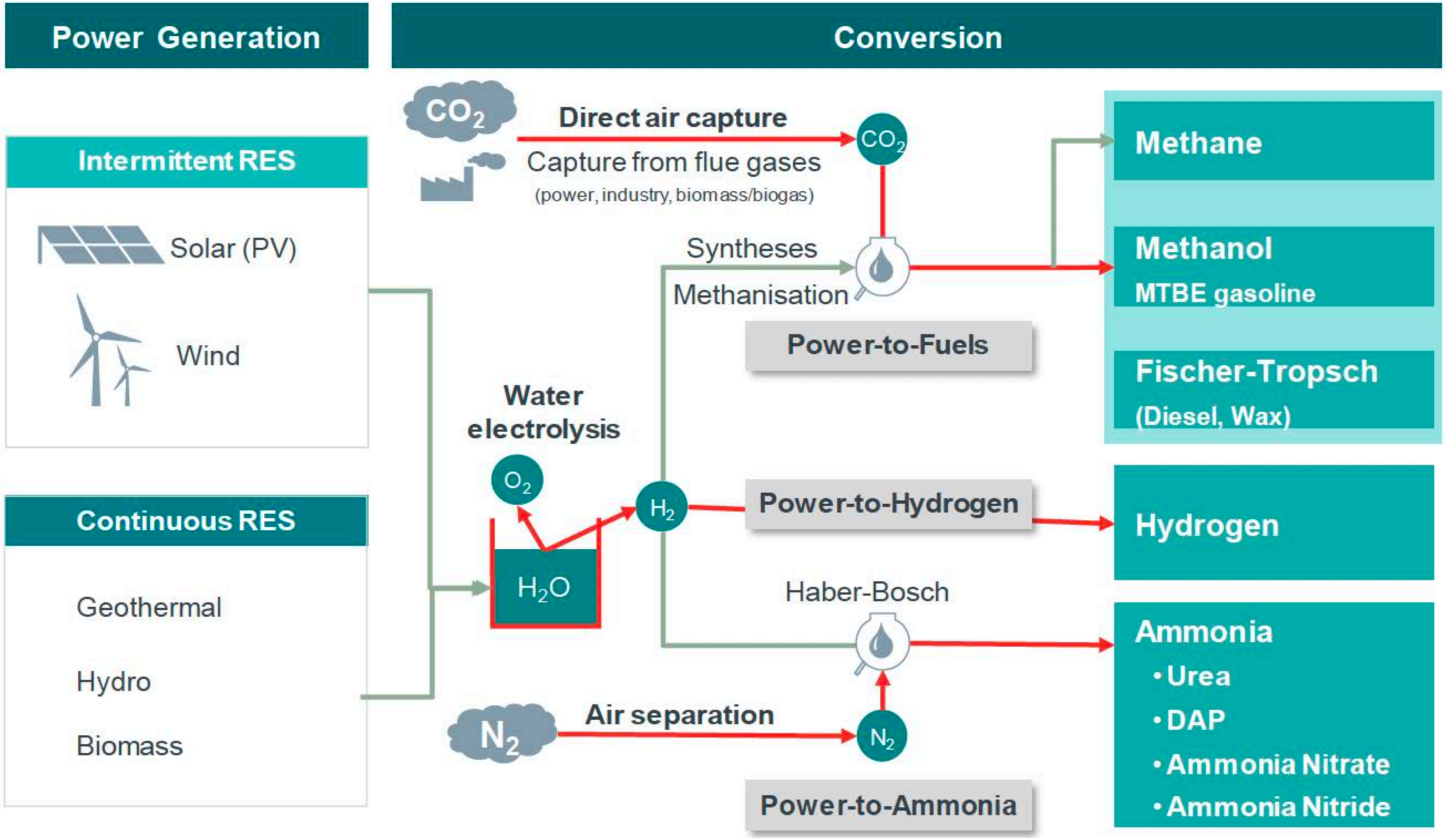




Net Zero Strategy

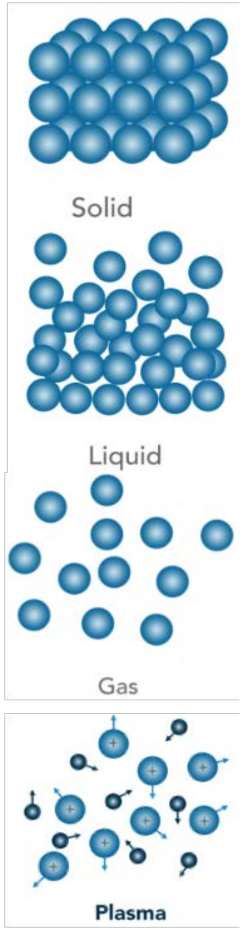
- Energy related **CO_2 emissions** continue to rise, reaching 363 Gt in 2021 (IEA).
- **Decarbonisation** of all sectors of the economy is critical to achieving net zero.
- **Electrification** can speed up the decarbonisation process.
- The IPCC's special report revealed the true extent of the climate crisis, placing an urgent emphasis on science and innovation.
- **We need action now!**

Power-to-X (PtX)
Carbon-neutral fuels and chemicals



Source: World Energy Council 2018

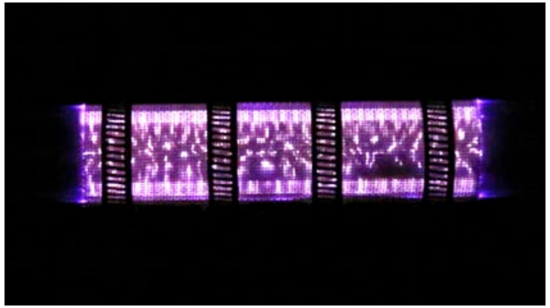
Non-thermal plasma (NTP) technology



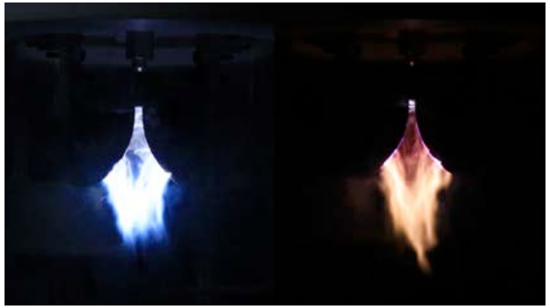
- Operation under ambient conditions
- Enhanced process intensification
- Instant switch on/off
- Modular & scalable
- Flexible electrification

Decentralised, modular and on-demand production of fuels and chemicals using intermittent RES

Dielectric barrier discharge



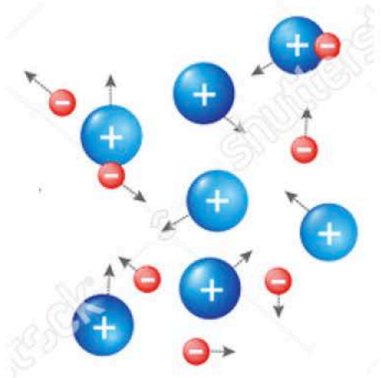
Gliding arc



Plasma Catalysis (Multidisciplinary)
Combination of plasma and catalysis

Plasma → Plasma Catalysis ← Catalysis

Plasma

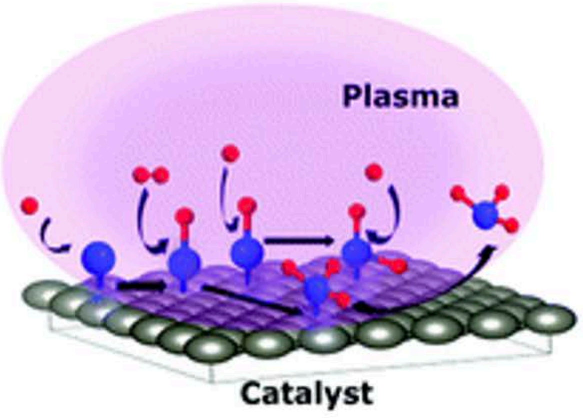


- Highly reactive
- Poor selectivity

Gas-phase reactions

Reactor design/plasma properties

Plasma Catalysis

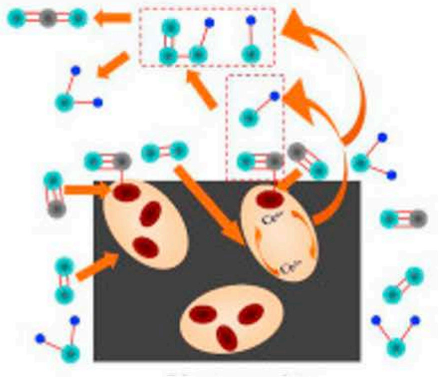


- Synergistic effect

Gas-phase/Surface reactions

Plasma-catalyst interaction/Reactions

Catalysis



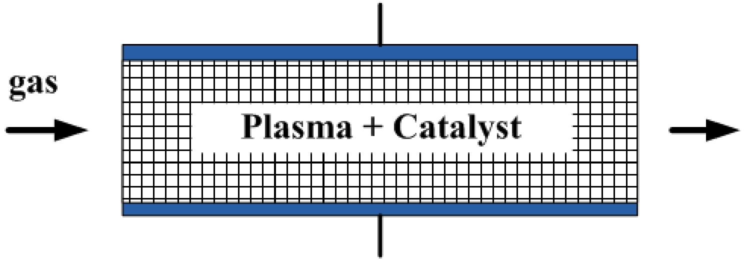
- Highly selective
- Activation barrier

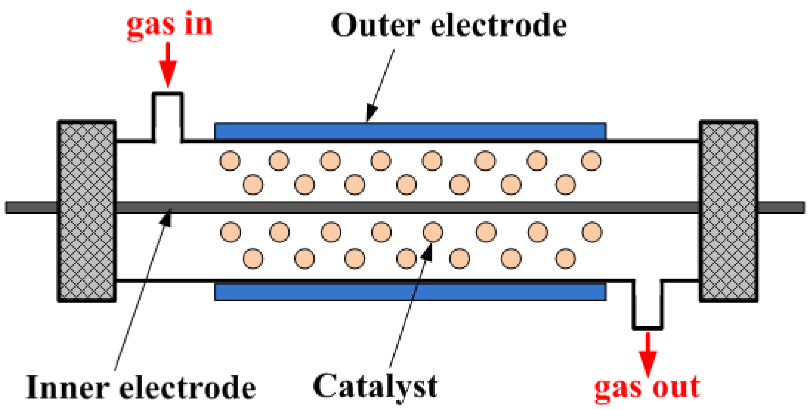
Surface reactions

Catalyst design/catalyst properties

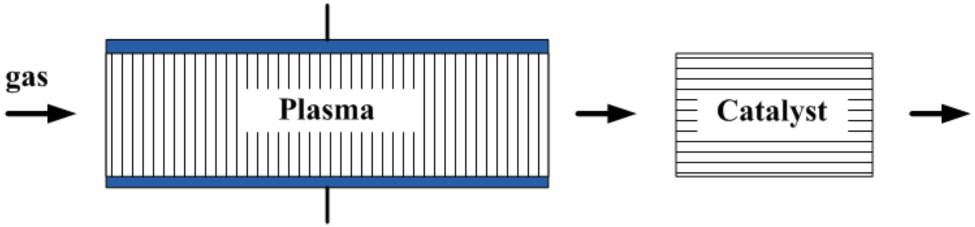
Plasma catalysis configurations

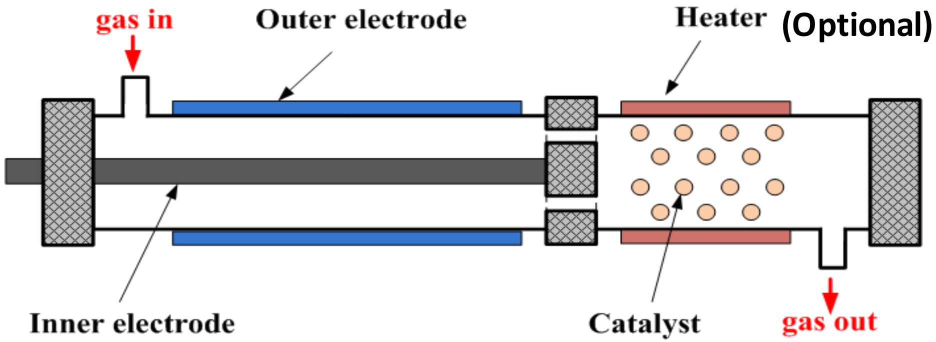
Single-stage (In-plasma catalysis)



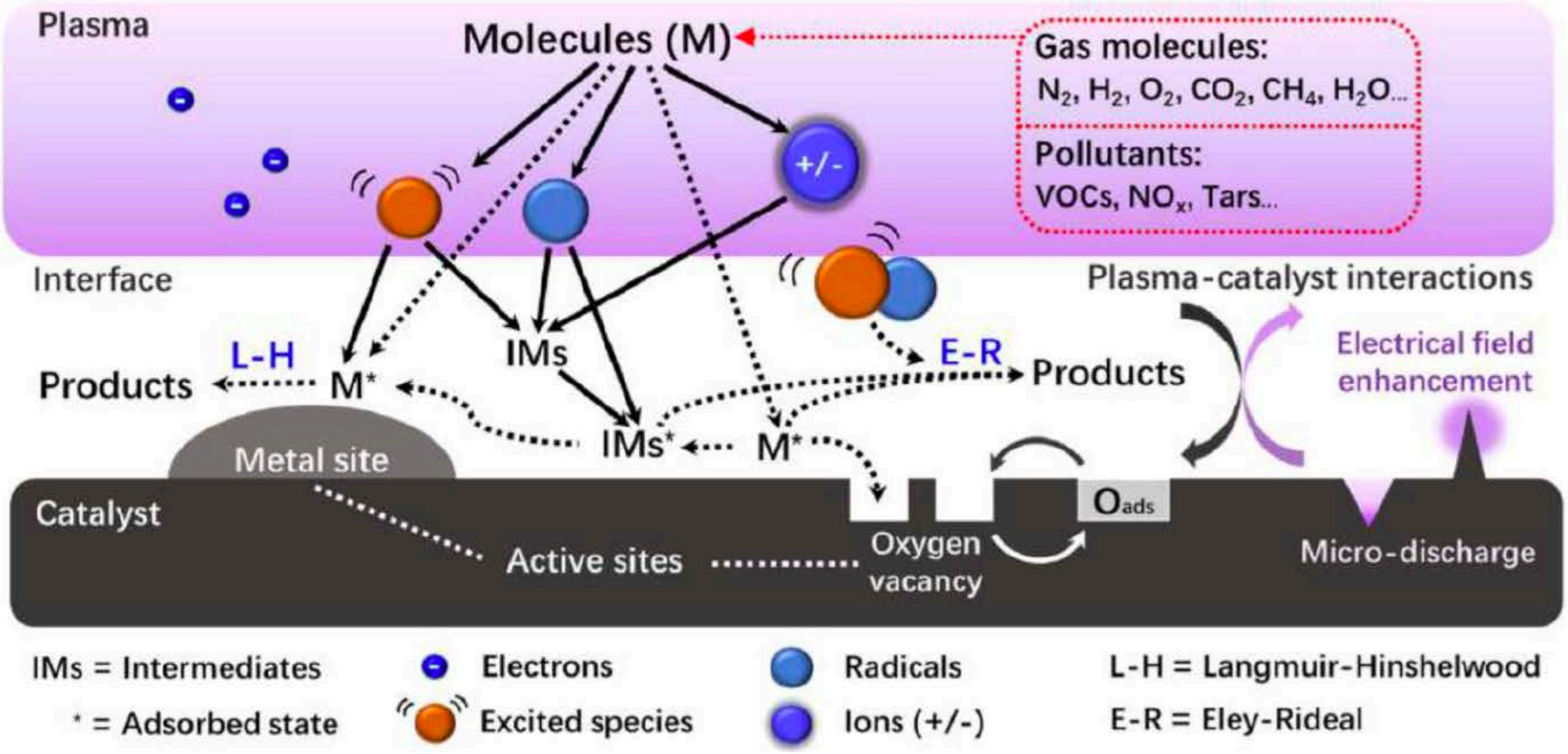


Two-stage (Post-plasma catalysis)





Plasma surface interactions & mechanisms



Bogaerts et al., *J. Phys. D: Appl. Phys.* 2020, 53, 443001 (**Plasma Catalysis Roadmap**)

Chemical reactions using plasma catalysis

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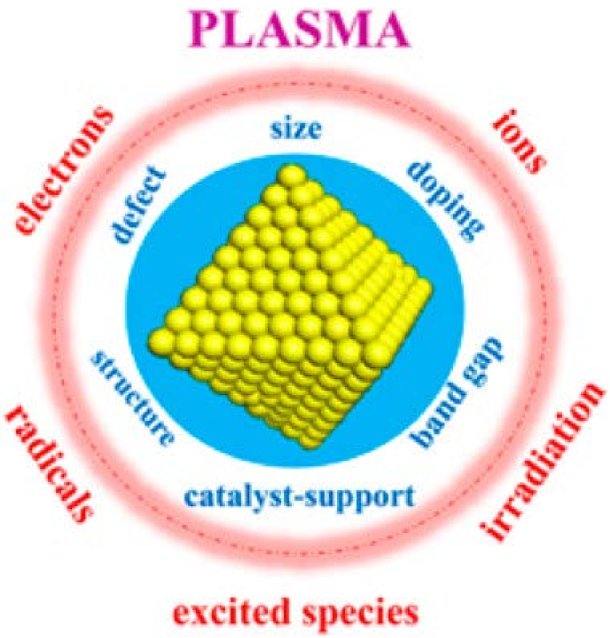
Process	Reactants	Target products
CO_2 conversion	CO_2	CO
	CO_2/H_2	CO
	CO_2/H_2	CH_4
	CO_2/H_2	Liquid fuels
	CO_2/H_2O	Syngas
	CO_2/CH_4	(see below)
	CO_2/C_2H_6	Liquid fuels
CH_4 conversion	CH_4	H_2
	CH_4	Olefins
	CH_4/CO_2	Syngas
	CH_4/CO_2	Olefins
	CH_4/CO_2	Liquid fuels
	CH_4/O_2	Syngas
	CH_4/O_2	Methanol
	CH_4/H_2O	Syngas
	$CH_4/CO_2/H_2O$	Syngas
VOC oxidation	Nonhalogenated VOCs/air	CO_2/H_2O
	Halogenated VOCs/air	CO_2/H_2O/HCl or HF
Odour control	Odour/air	Haress compounds
NH_3 synthesis	N_2/H_2	NH_3
NO_x synthesis	N_2/O_2 or air	NO/NO_2
NO_x removal	Reduction of NO_x by hydrocarbons	N_2
	Reduction of NO_x by NH_3	N_2
	NO_x oxidation	NO_2
Tar reforming	Tar	Syngas
Water gas shift reaction	CO/H_2O	CO_2/H_2
Methanol conversion	$MeOH/H_2O$	H_2
Ethanol conversion	$EtOH/H_2O$	H_2

Bogaerts et al., *J. Phys. D: Appl. Phys.* 2020, 53, 443001

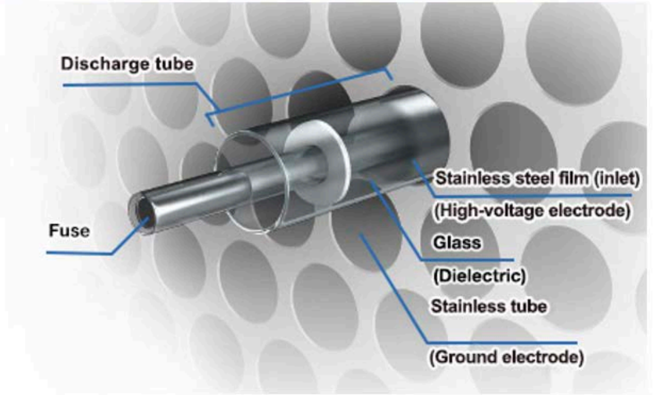
Plasma catalysis has also been extended for the synthesis and modification of catalysts.



Wang et al., *ACS Catal.* 2018, 8, 2093-2110

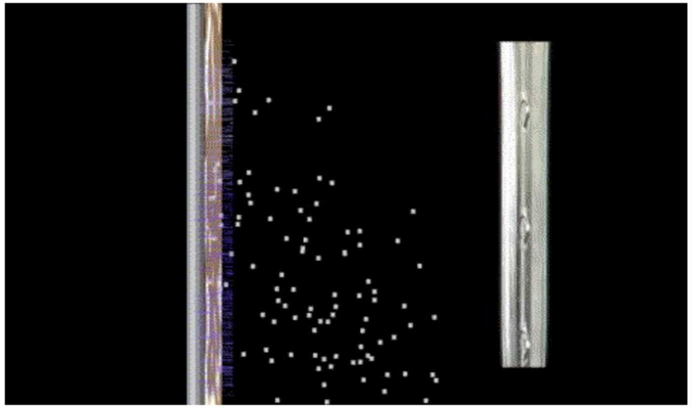
Success stories for industrial-scale development

Plasma ozone generator



- 120 kg O_3/h (Source: Toshiba, Japan)
- Montreal, largest ozone project (45 MW)

Plasma $DeNO_x$/$DeSO_x$



1 MW, 250,000 m^3/h flue gas (Source: TEAMS, China)

Ammonia synthesis: Haber Bosch process

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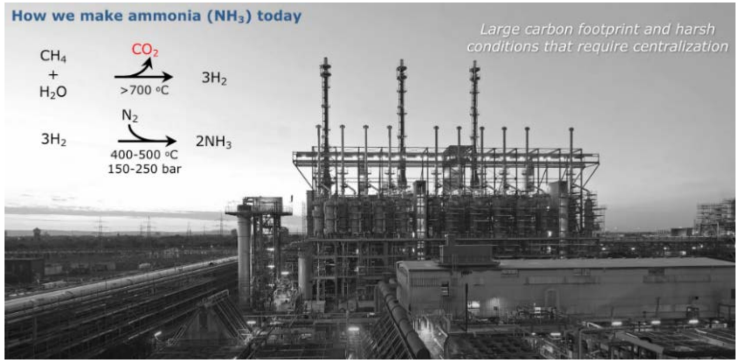
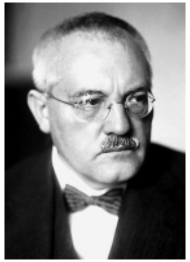


Sustainable, green and decentralised N_2 fixation under mild conditions

Fritz Haber

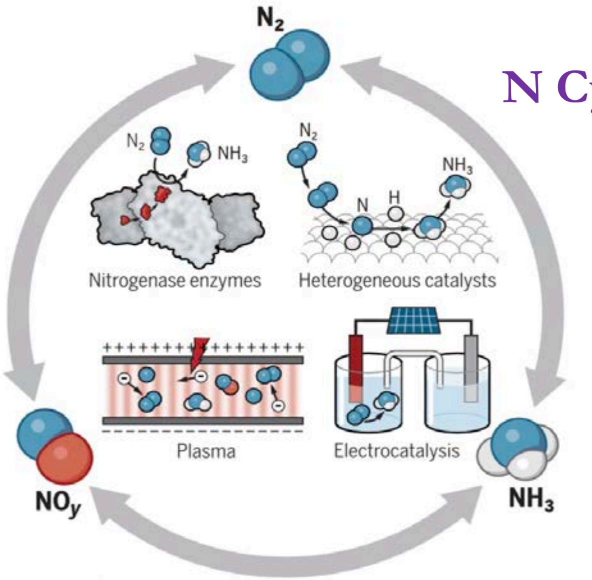


Carl Bosch

"The most important invention of the 20th century (Nature 29 (415), 1999) as it detonated the population explosion."

- 450 - 500 °C and 150-250 bar
- ~2% of global energy supply
- 1.5-2% of global CO_2 emission

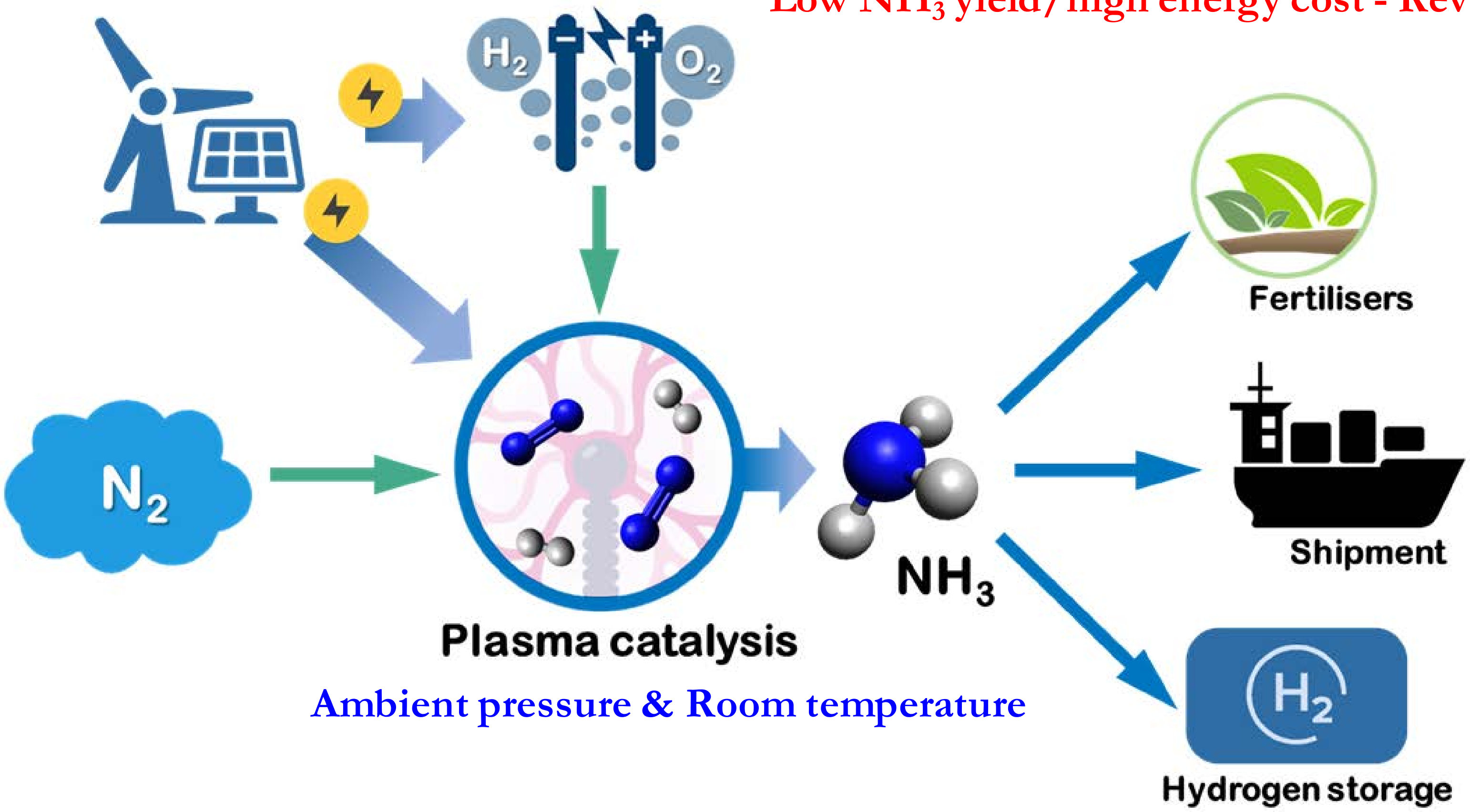
N Cycle



Chen et al., *Science* 2018, 360, 873

Plasma-catalytic ammonia synthesis from N_2 and H_2

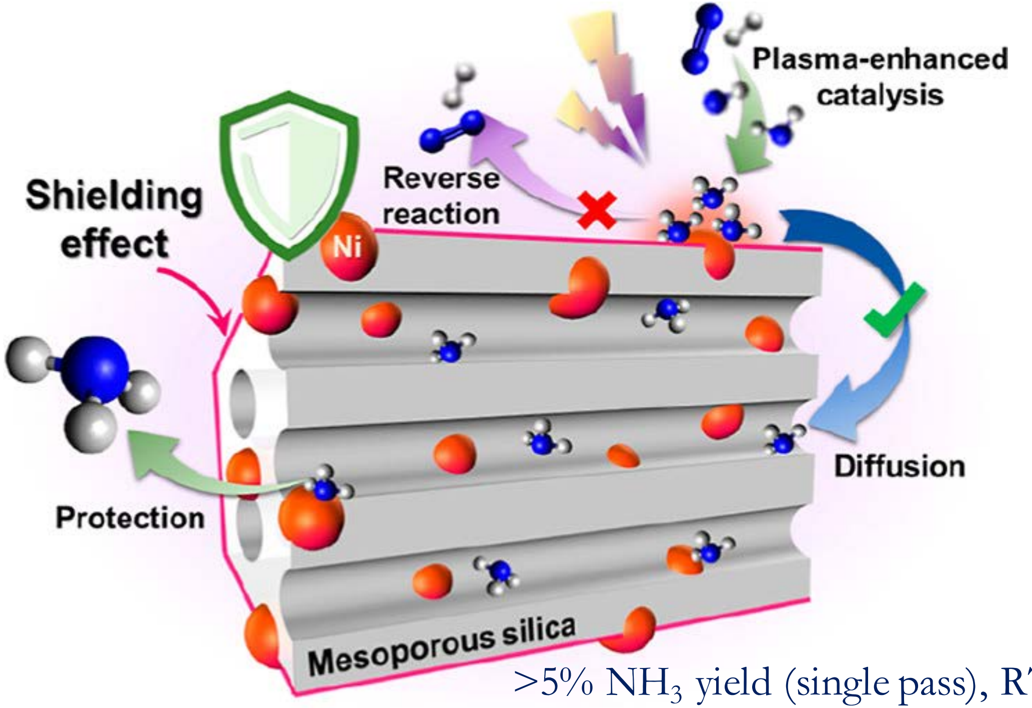
Low NH_3 yield/high energy cost - Reverse reaction



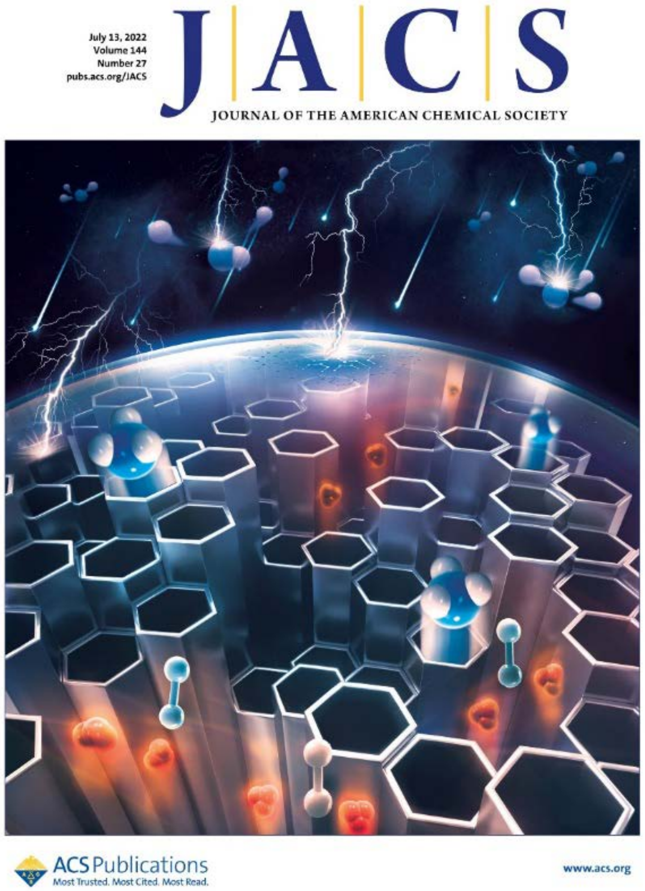
Ambient pressure & Room temperature

Plasma-catalytic ammonia synthesis

"Shielding Protection"
Catalyst Design Strategy

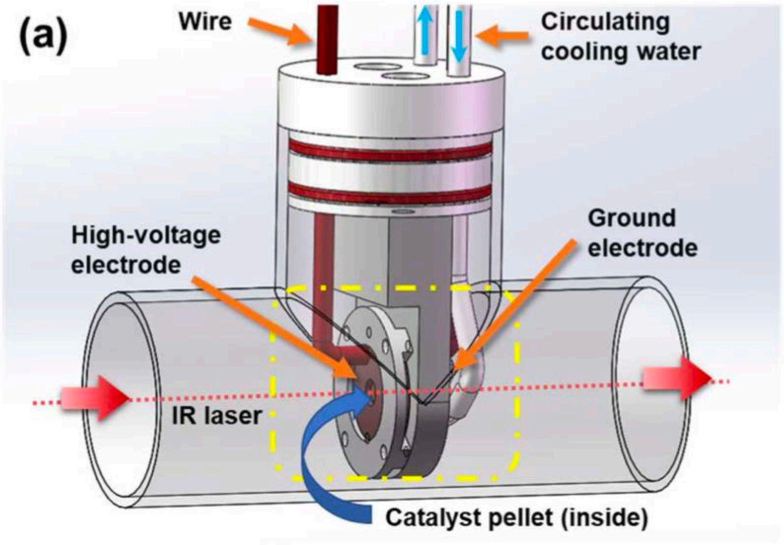


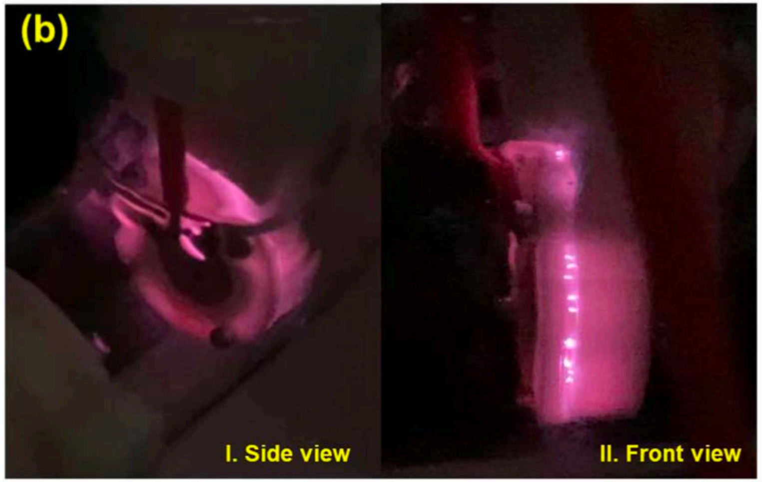
>5% NH_3 yield (single pass), RT/1 bar

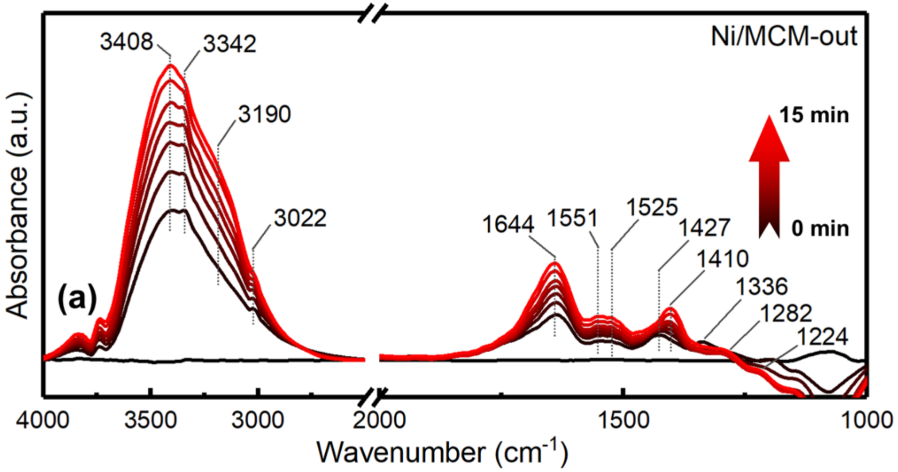


Wang et al., *J. Am. Chem. Soc.* 2022, 144, 12020-12031

In situ DBD/FTIR analysis







- Plasma can be formed on catalyst surfaces.
- Demonstrated its suitability for different plasma catalytic reactions (NH_3 synthesis, toluene reforming, CO_2 hydrogenation, DRM)

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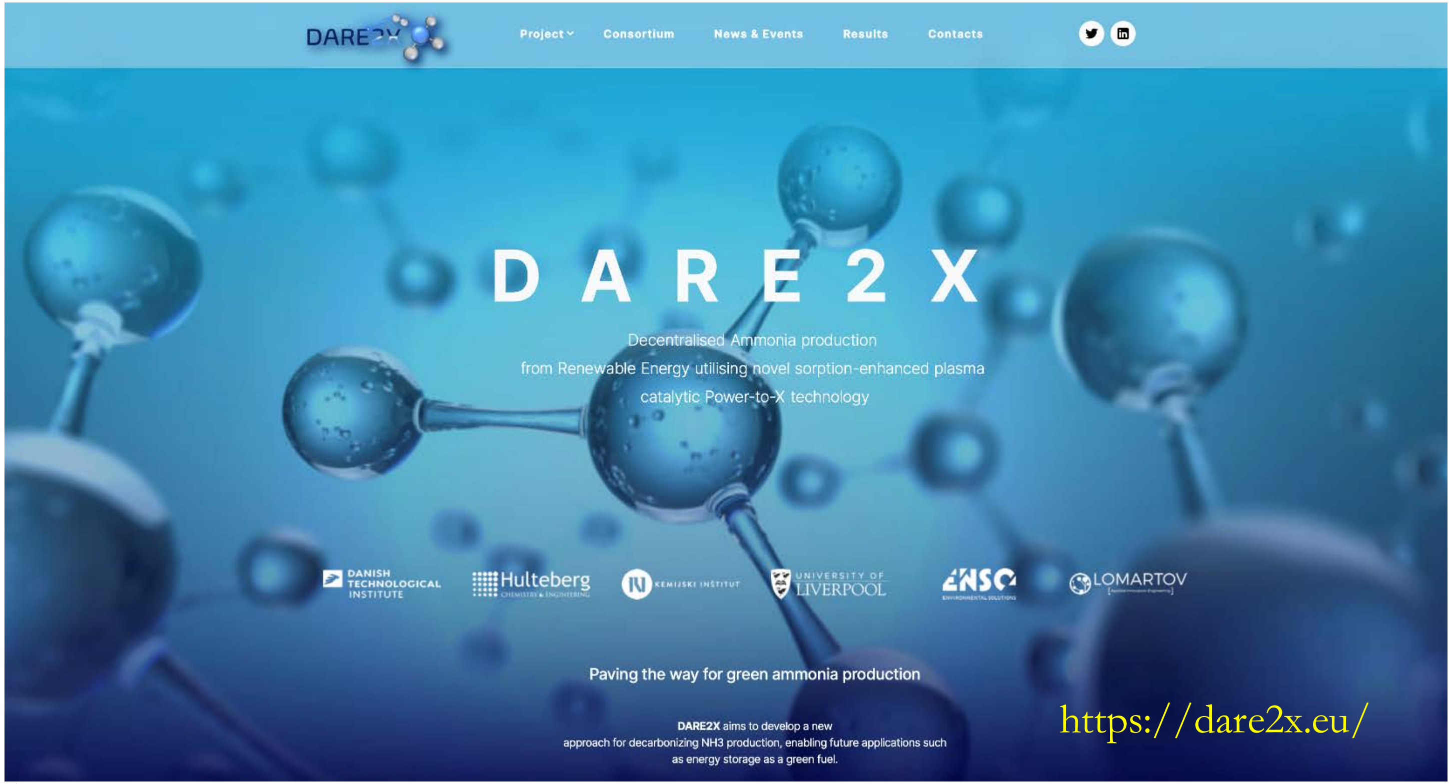
Decentralised Ammonia production from Renewable Energy utilising novel sorption-enhanced plasma catalytic Power-to-X technology (Horizon Europe)



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CO_2 conversion routes

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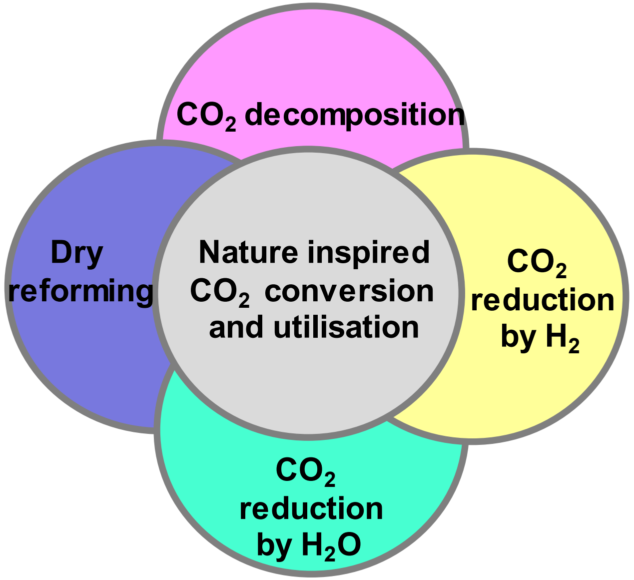

The chemical transformation of CO_2 into useful feedstock chemicals and fuels will become a key element of sustainable low-carbon economy in chemical and energy industry.

—*The Science and Technology Roadmap on Catalysis for Europe*

Routes for chemical transformation of CO_2

- ❑ CO_2 Splitting — $CO_2 \rightarrow$ CO + ½ O_2
- ❑ CO_2 Reduction with water — $CO_2 + H_2O \rightarrow$ syngas, methanol…
- ❑ CO_2 hydrogenation — $CO_2 + H_2 \rightarrow$ CO, CH_4, methanol, …
- ❑ Dry reforming of CH_4 — $CO_2 + CH_4 \rightarrow$ syngas, C2-C4, oxygenates…

Plasma catalysis for CO_2 splitting

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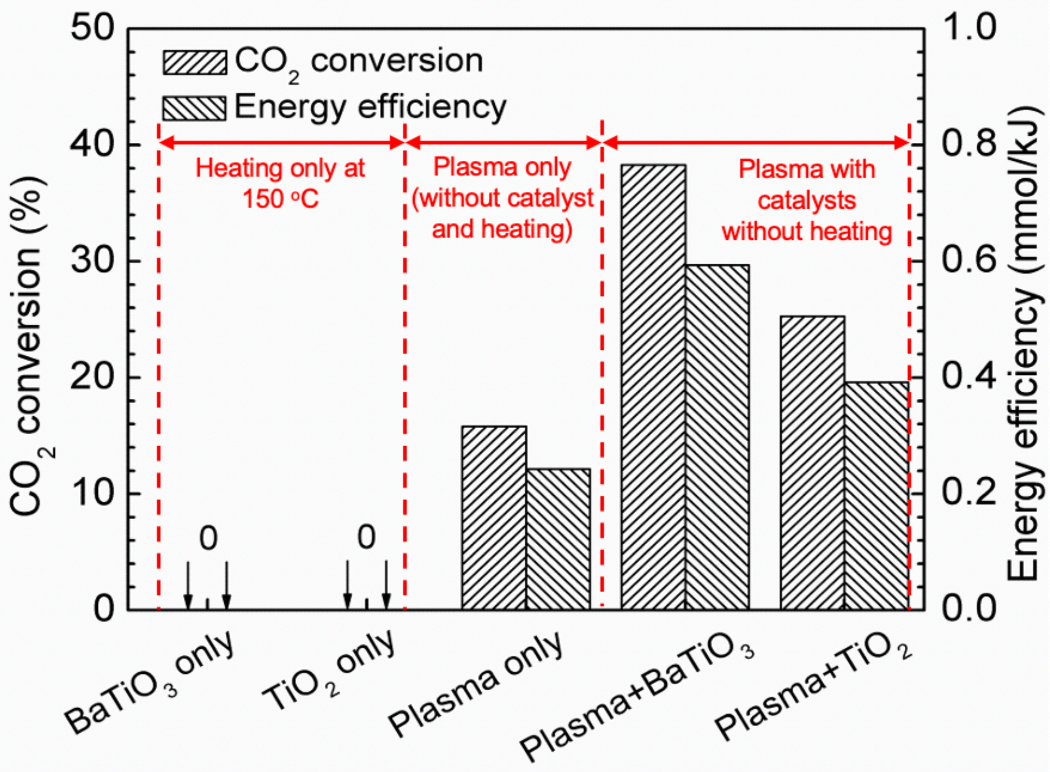

- ❑ Plasma + catalysis > Plasma alone + catalysis alone (**Synergistic effect**)
- ❑ **(Photo)catalytic effect**
  - ✓ - Electron-hole ($e^- – h^+$) pairs
  - ✓ - oxygen vacancies

(1) UV from plasma (minor)

$$TiO_2 + h\nu \rightarrow e^- + h^+$$

$$BaTiO_3 + h\nu \rightarrow e^- + h^+$$

(2) Electrons from plasma

$$TiO_2 + e^- (> 3.2\ eV) \rightarrow h^+ + e^-$$

$$BaTiO_3 + e^- (> 3.0\ eV) \rightarrow h^+ + e^-$$

Demonstration of the **synergistic effect** of plasma-catalysis for the conversion of CO_2 (SEI = 28 kJ/L, 150 °C, 1 atm)

Mei et al., *Appl. Catal. B: Environ.* 2016, 182, 525-532

Plasma catalysis for CO_2 hydrogenation to CO (RWGS)

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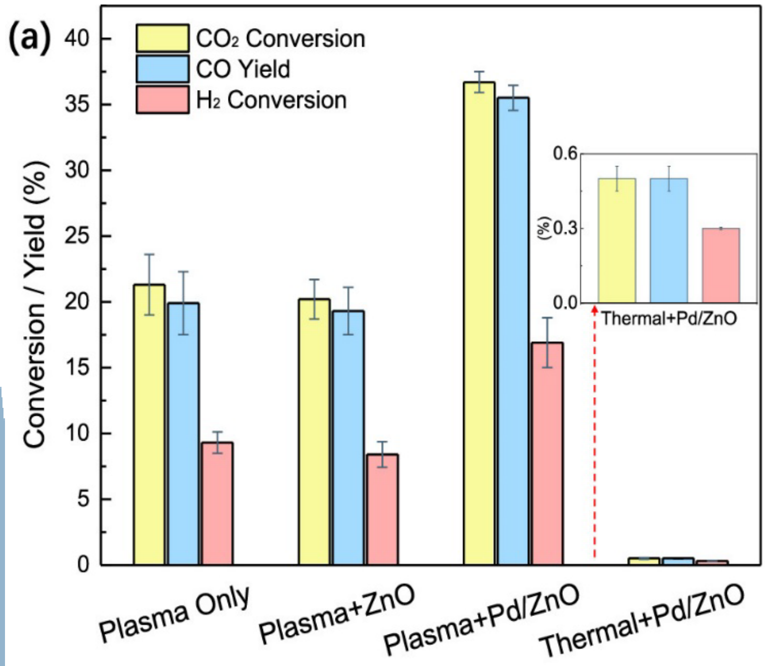
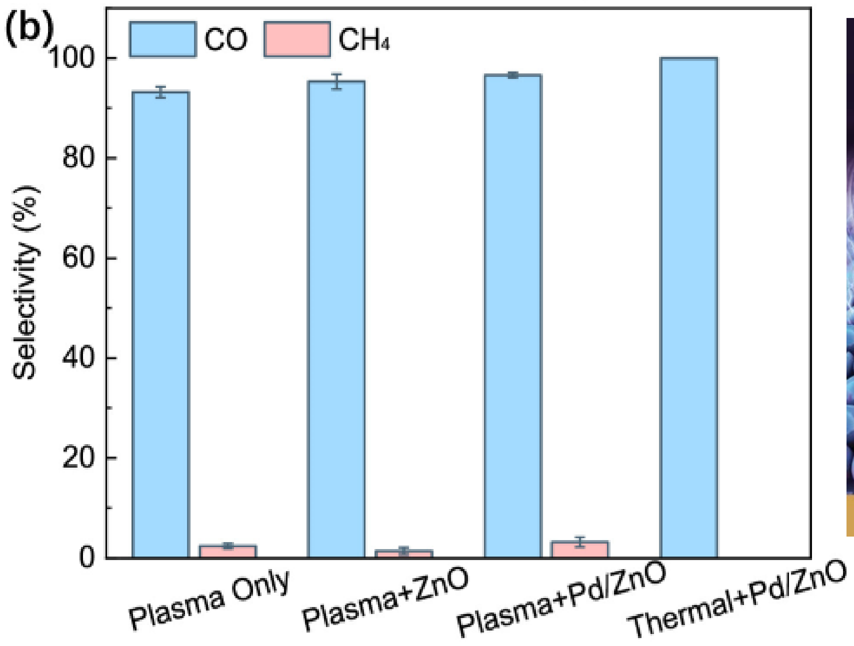
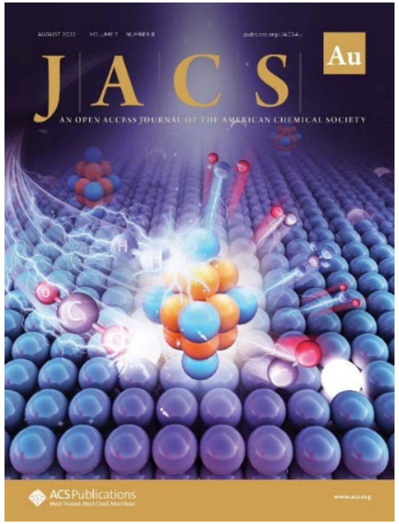


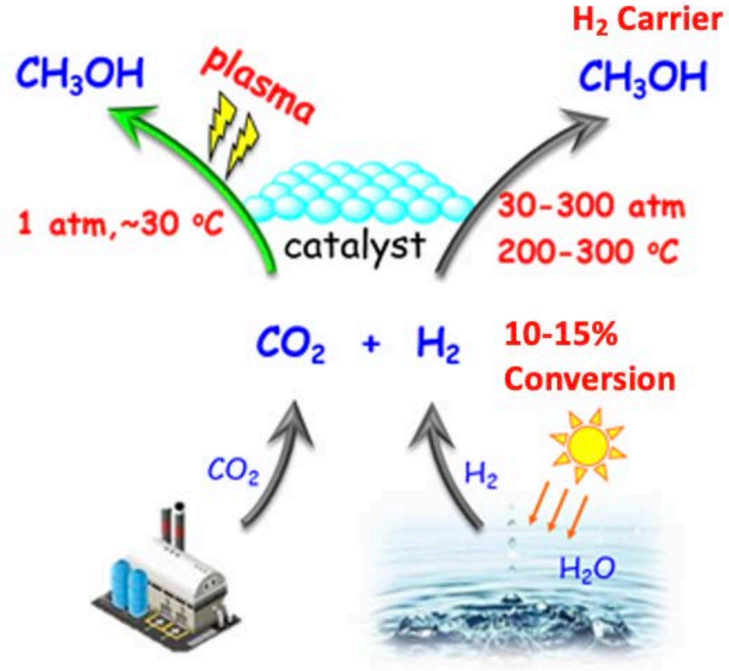




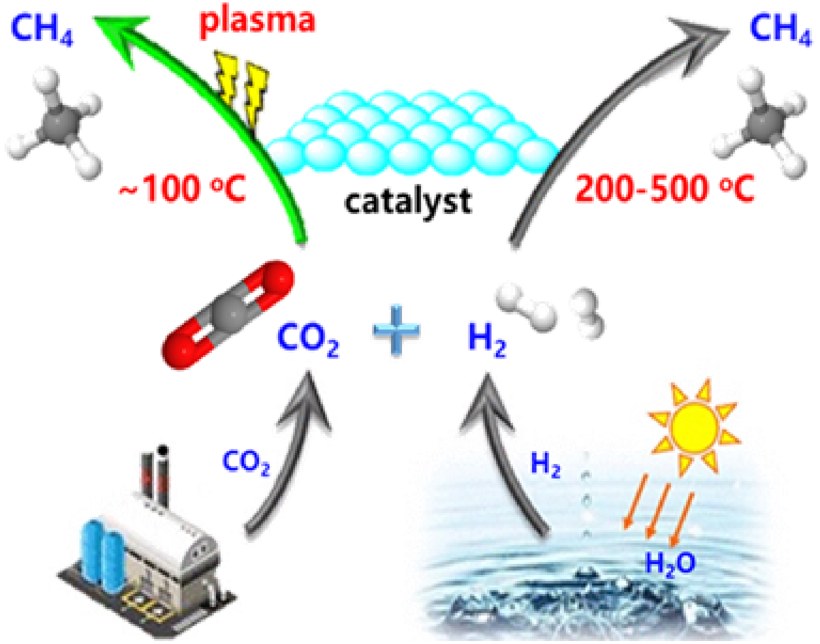
- ❑ Formation of a ZnO_x overlayer/Rich O vacancies
- ❑ Strong metal support interaction (SMSI)/H_2 activation by Pd NPs

Sun et al., ***JACS Au***, 2022, 2, 1800-1810 (Supplementary Cover)

Plasma catalysis for CO_2 hydrogenation



CO_2 to Methanol



CO_2 to Methane

Wang et al., *ACS Catal.* 2018, 8, 90-100

Plasma catalysis for biogas conversion into liquid fuels and chemicals

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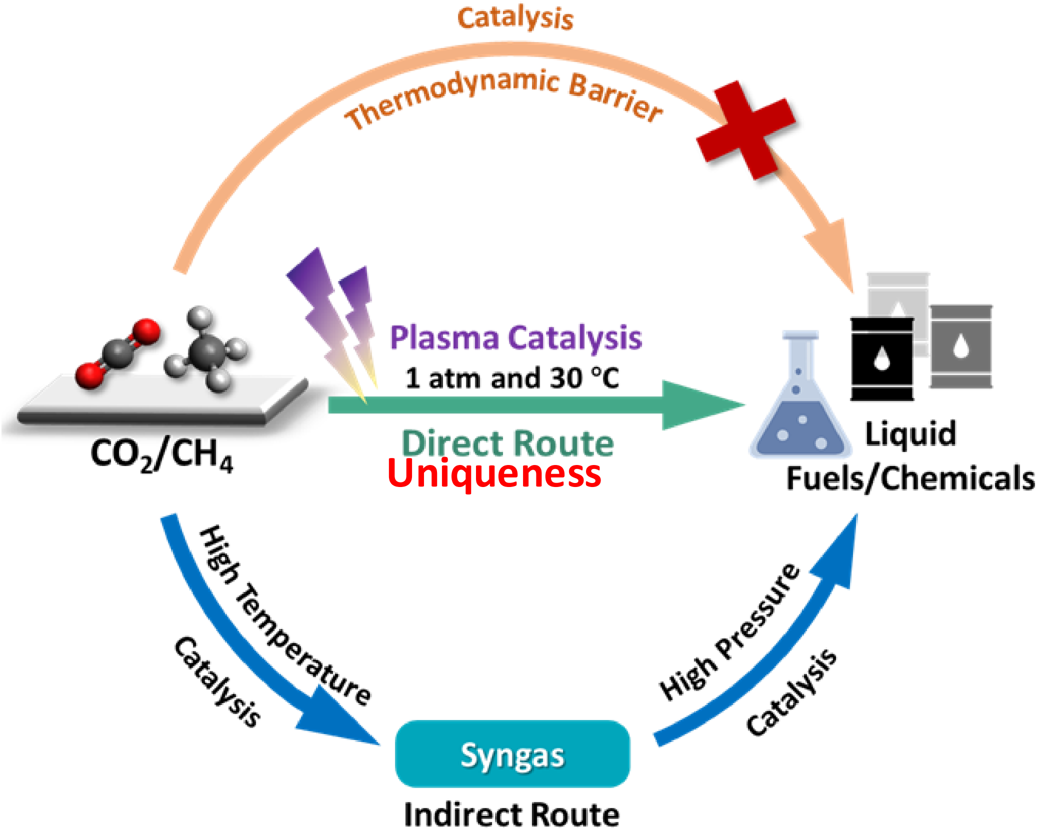
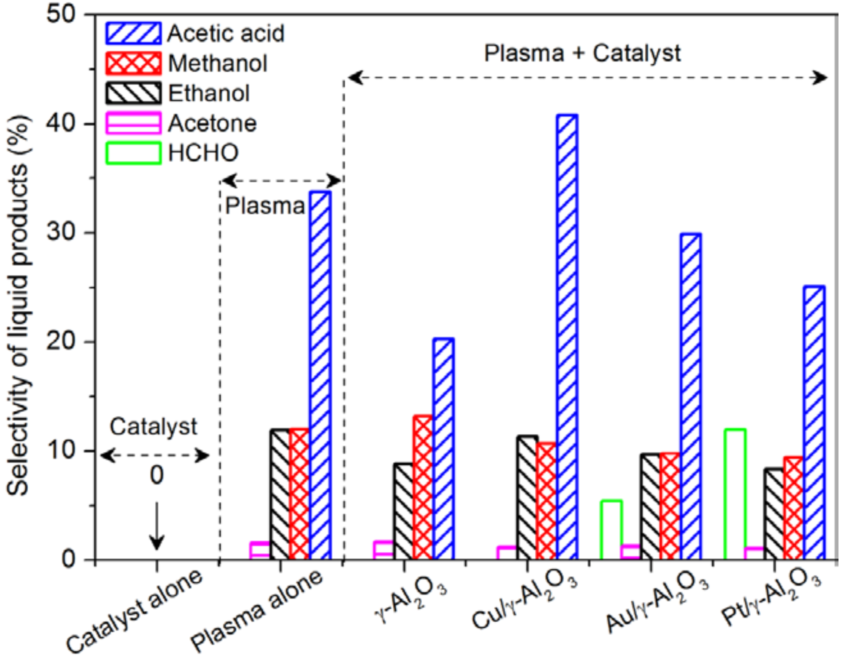
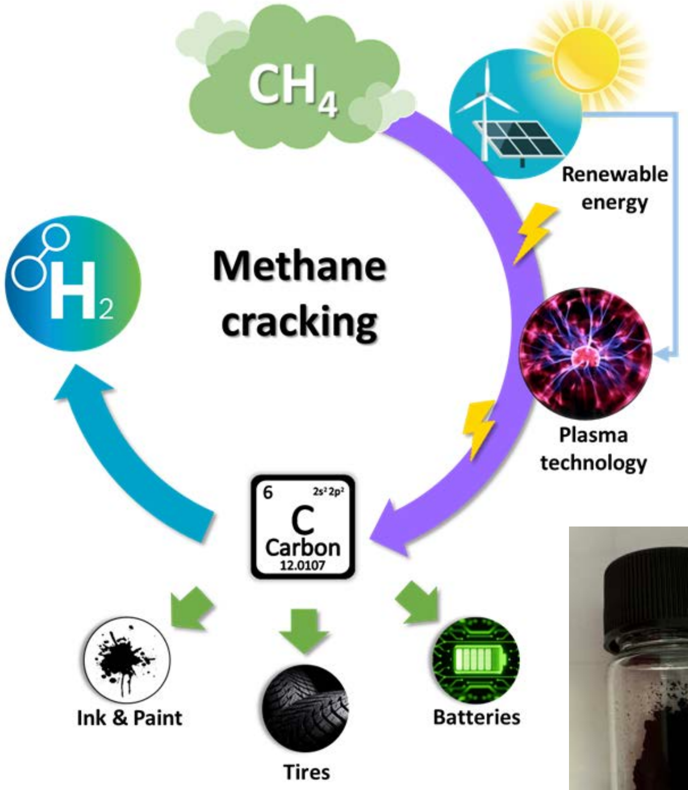


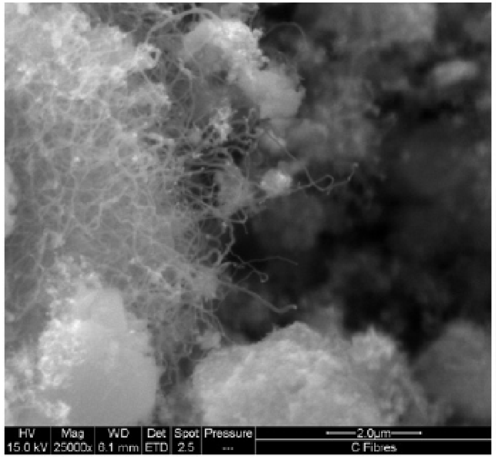


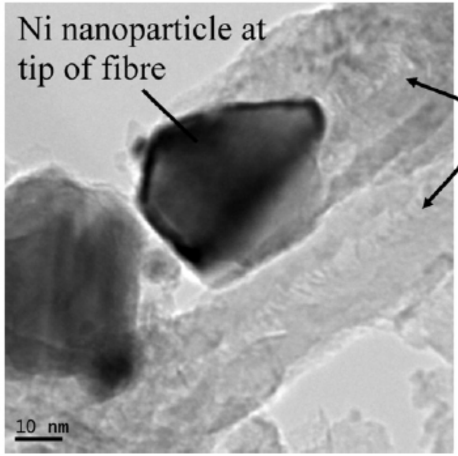
Wang et al., *Angew. Chem. Int. Ed.* 2017, 56, 13679-13683

Plasma methane cracking to hydrogen and value-added carbon materials



			Direct CO_2 emissions in kg CO_2/kg hydrogen	Minimum energy demand in kJ/mol hydrogen*
State-of-the-art	Steam reforming of natural gas	$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	8.85	27
Option 1	Water electrolysis	$2H_2O \rightarrow 2H_2 + O_2$	0	286
Option 2	Methane pyrolysis	$CH_4 \rightarrow 2H_2 + C$	0	37





carbon nanofibres

Gallon et al., *Appl. Catal. B: Environ.* 2011, 106, 616

Plasma Catalysis

Promising but Challenging

- **Energy efficiency/Energy consumption**

Require improvement, except CH_4 to H_2/carbon (>80%), CO_2 methanation (>70%)

- **Catalyst design & selectivity**

Catalysts work in thermal catalysis might not work in plasma catalysis

Typically lower than thermal catalysis, except RWGS (99% CO), CO_2 to CH_4 (99%)

New dimensions introduced in plasma catalysis (e.g., electric field, excited species, etc)

- **Reactor design**

Critical! determine plasma properties, reaction temperatures, plasma-catalyst interactions, etc

- **Reaction mechanism**

More complicated – advanced diagnostics/in situ characterisation/plasma catalysis modelling

- **Scalability & Commercialisation potential**

Successful examples: Gas cleaning (deNOx, ozone generator, etc)

Plasma catalysis - a promising route for decentralised production of sustainable fuels and chemicals

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IOP Publishing
Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 53 (2020) 443001 (51pp)
https://doi.org/10.1088/1361-6463/ab9048

Roadmap

The 2020 plasma catalysis roadmap

Annemie Bogaerts[1], Xin Tu[2], J Christopher Whitehead[3], Gabriele Centi[4,5], Leon Lefferts[6], Olivier Guaitella[7], Federico Azzolina-Jury[8], Hyun-Ha Kim[9], Anthony B Murphy[10], William F Schneider[11], Tomohiro Nozaki[12], Jason C Hicks[11], Antoine Rousseau[7], Frederic Thevenet[13], Ahmed Khacef[14] and Maria Carreon[15]

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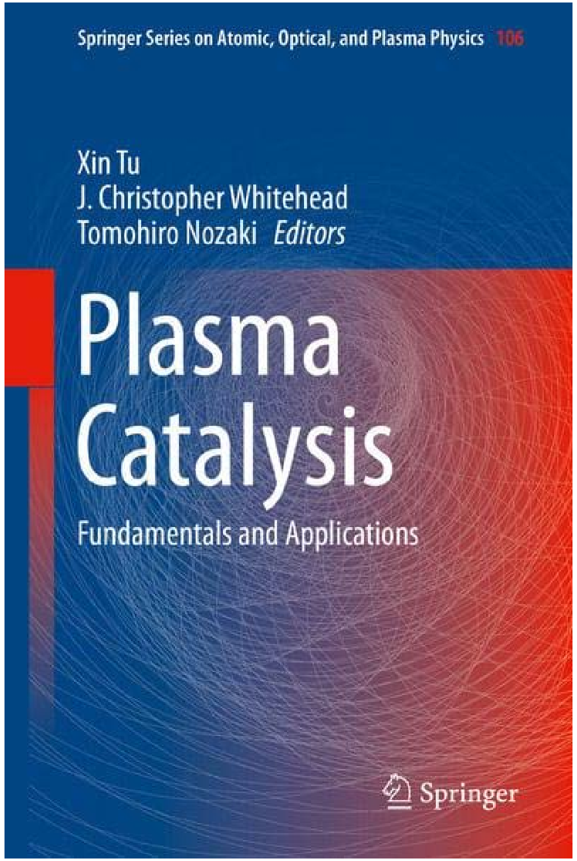

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