Introduction to CO_2 reduction

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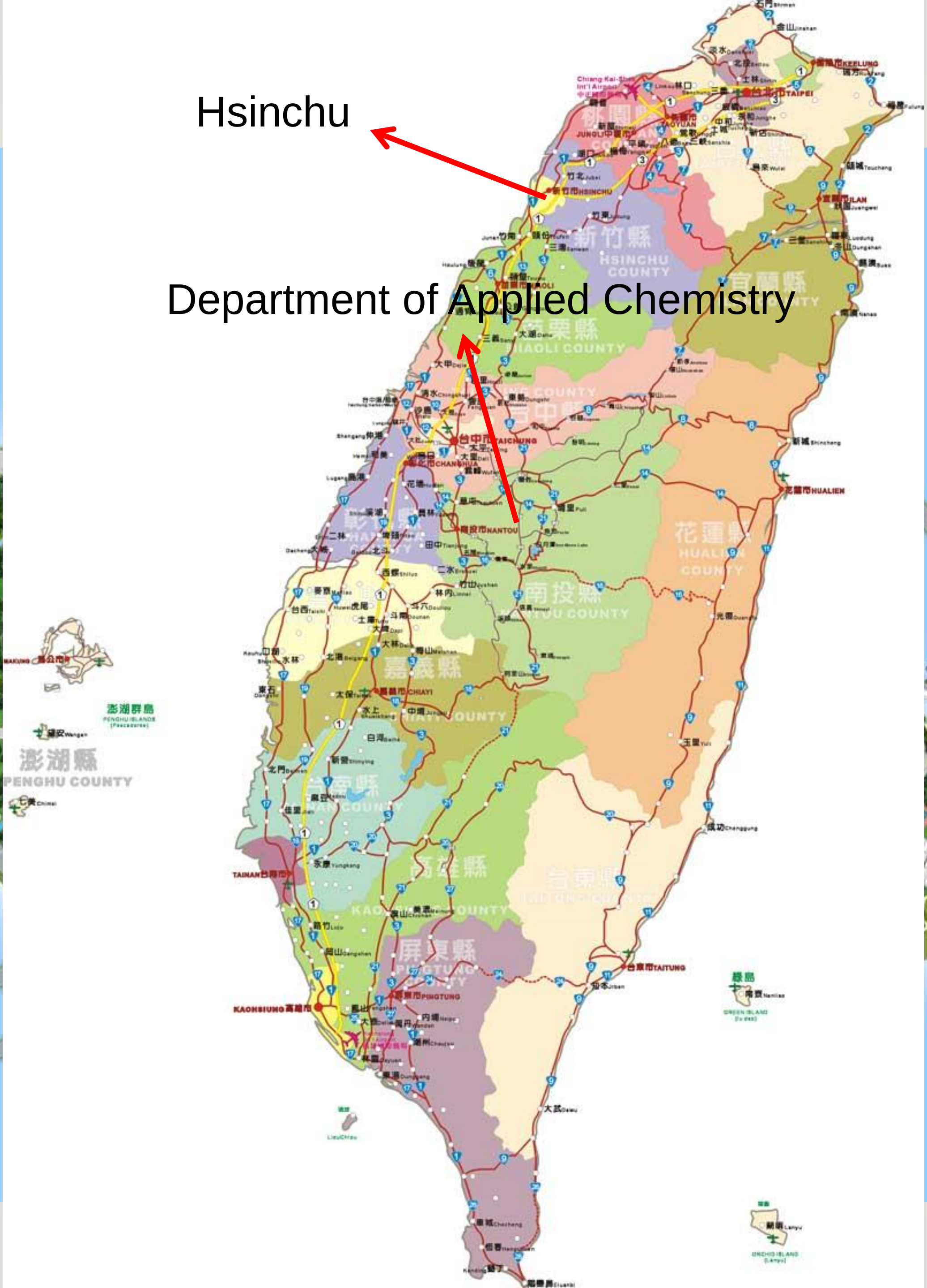
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Summary of the Lectures

Solar Cells and Photocatalysis

Lecture 1: Introduction to CO_2 Reduction

Lecture 2: Photocatalysis 1 – Introduction

Lecture 3: Photocatalysis 2 – Photocatalysts

Lecture 4: Photocatalysis 3 – Heterojunctions

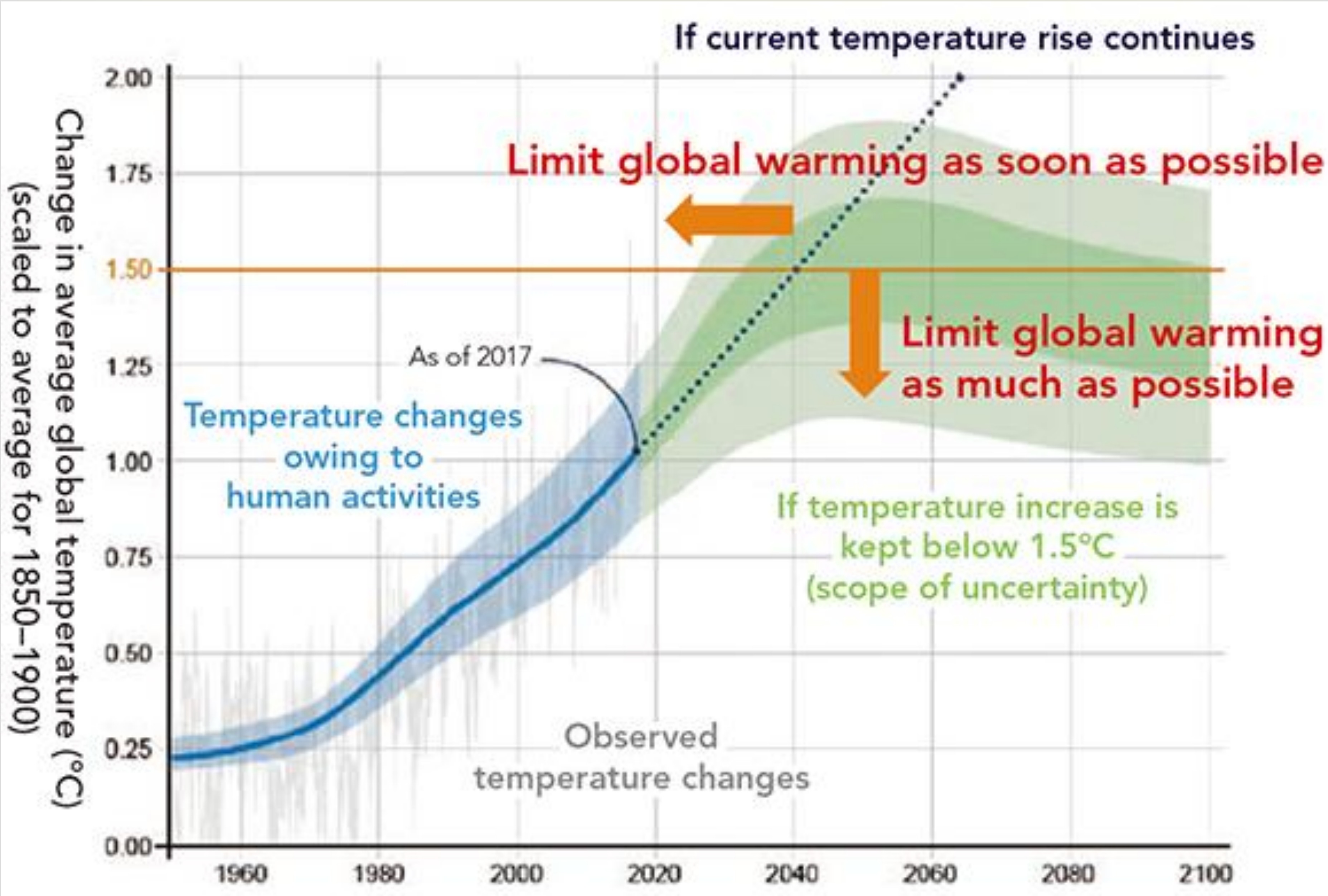
Lecture 5: Photocatalysis 4 – Halide Perovskites

Lecture 6: Solar Cells 1 – From DSSC to PSSC

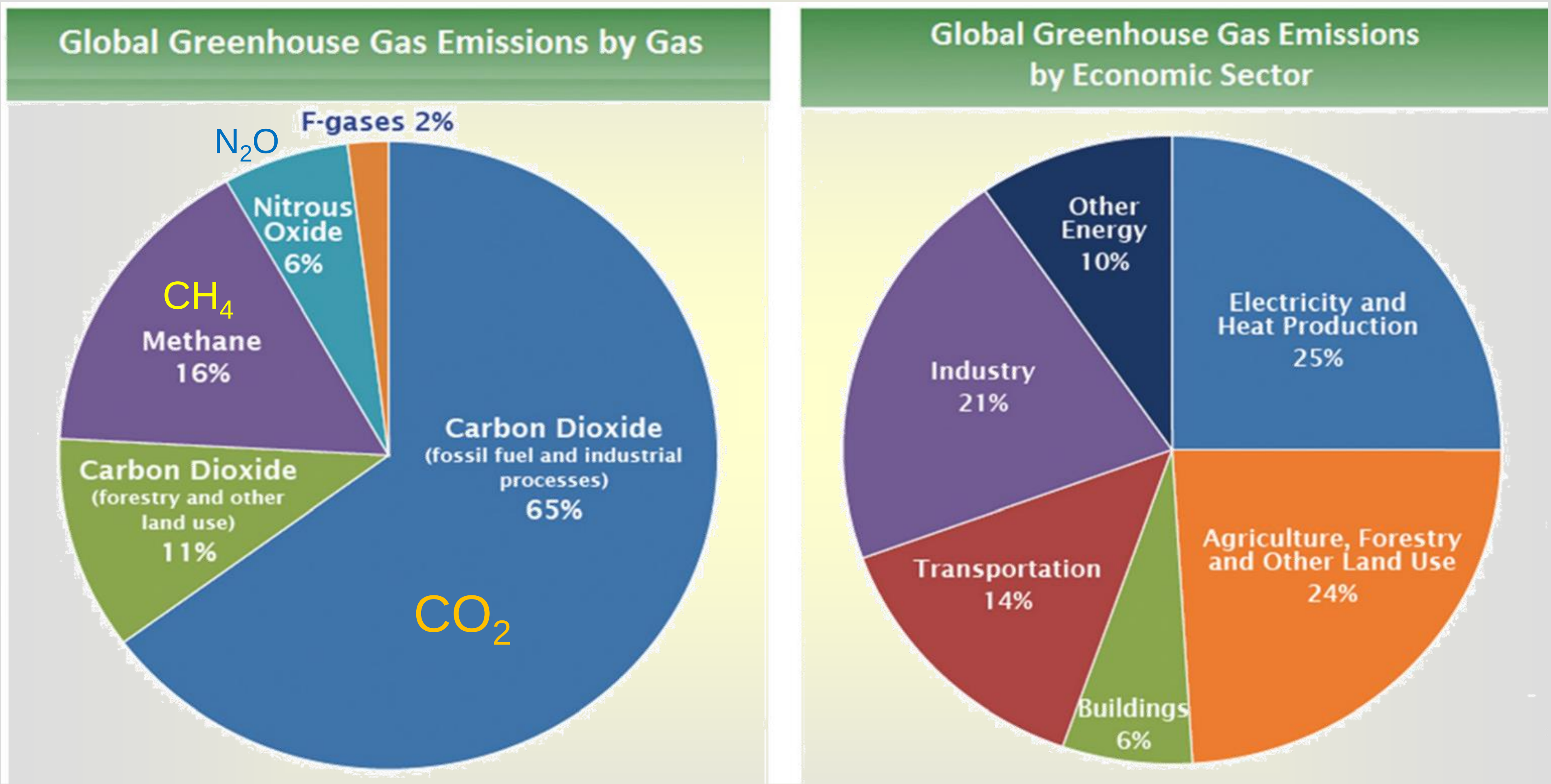
Lecture 7: Solar Cells 2 – Lead Perovskite Solar Cells

Lecture 8: Solar Cells 3 – Lead-free perovskite solar Cells (seminar speech)

The Issue of Global Warming



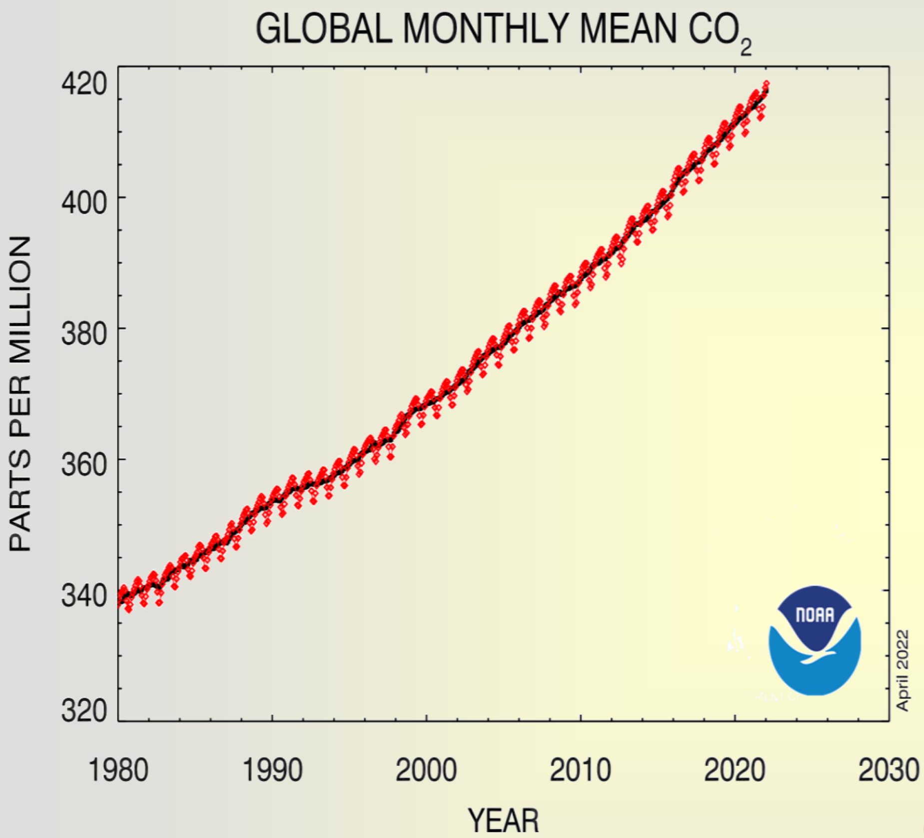
Global Greenhouse Gas Emissions

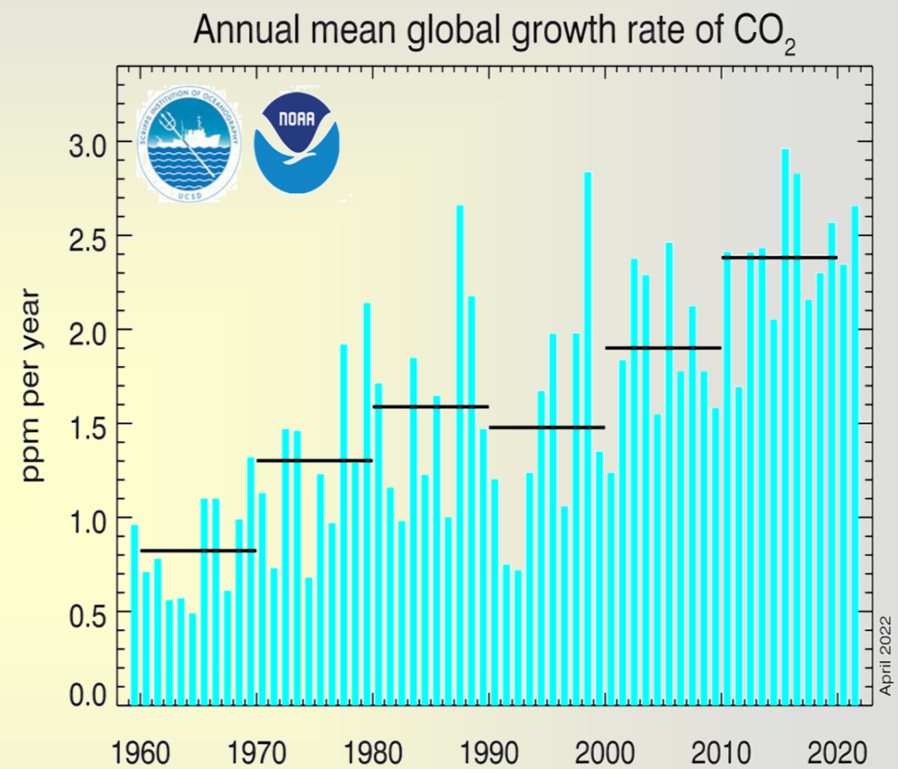


Global greenhouse gas (GHG) emission produced by human activities and categorized on the basis of the economic sectors that lead to their production.

* IPCC, 2014, Climate Change 2014: Mitigation of Climate Change, Cambridge University Press, United Kingdom and New York, NY, USA, 2014.

Global Growth Rate of CO_2

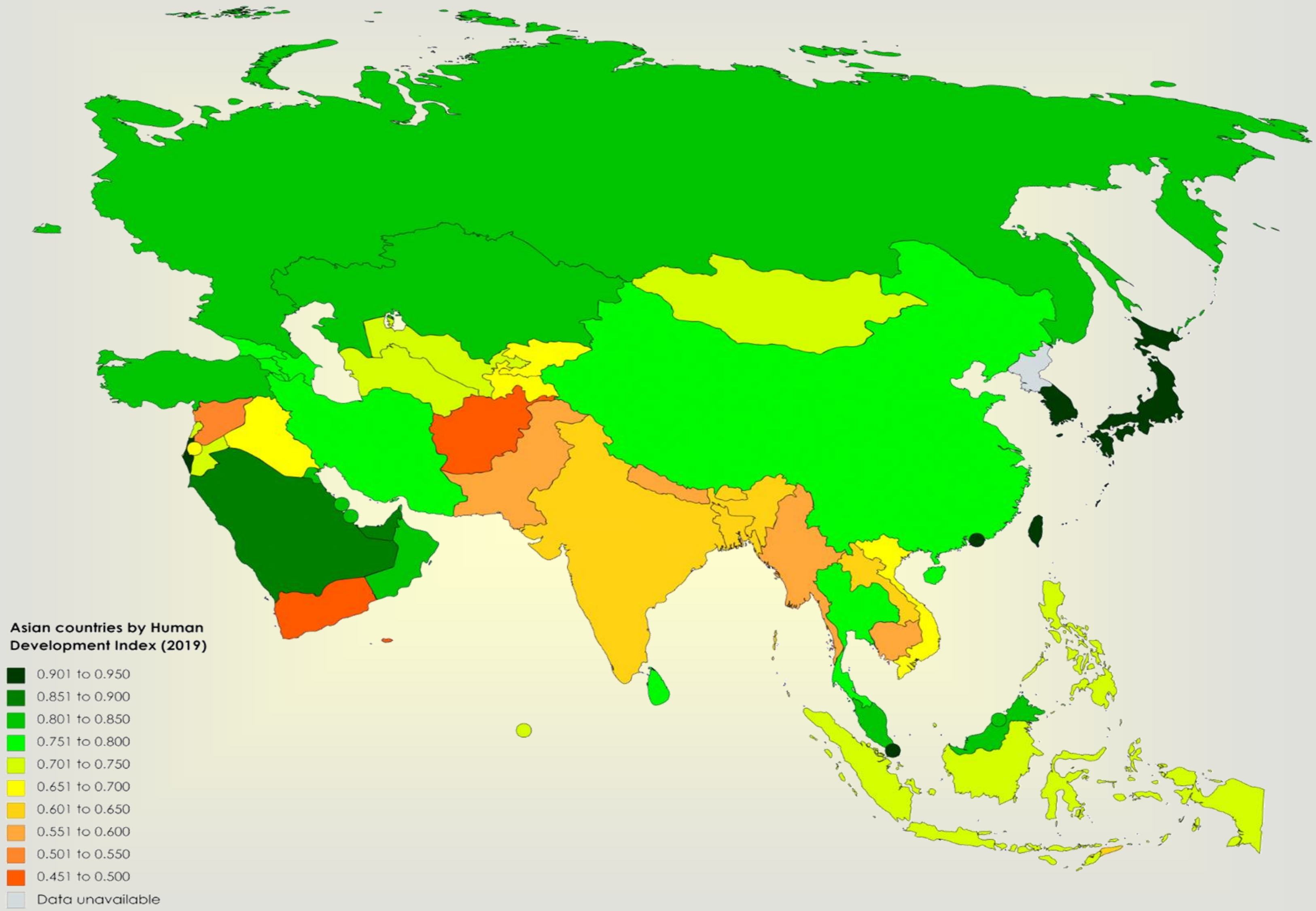




CO2 data: This graph shows annual mean carbon dioxide growth rates, based on globally averaged marine surface data, since the start of systematic monitoring in 1959. The horizontal lines indicate the decadal averages of the growth rate. (NOAA Global Monitoring Laboratory)

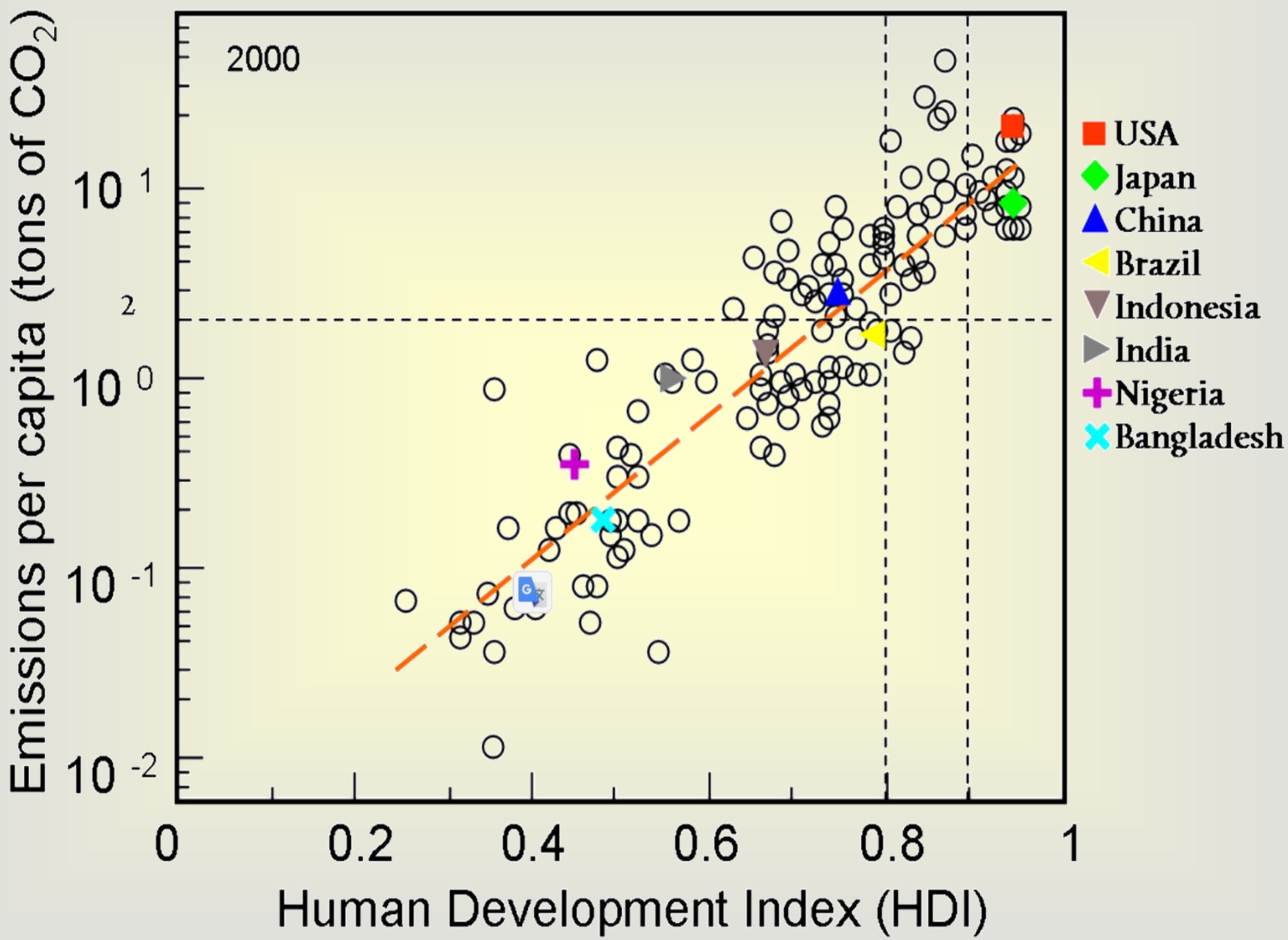
Adopted from the website of National Ocean and Atmospheric Administration (NOAA).
https://www.noaa.gov/news-release/increase-in-atmospheric-methane-set-another-record-during-2021

Human Development Index (HDI) in Asia



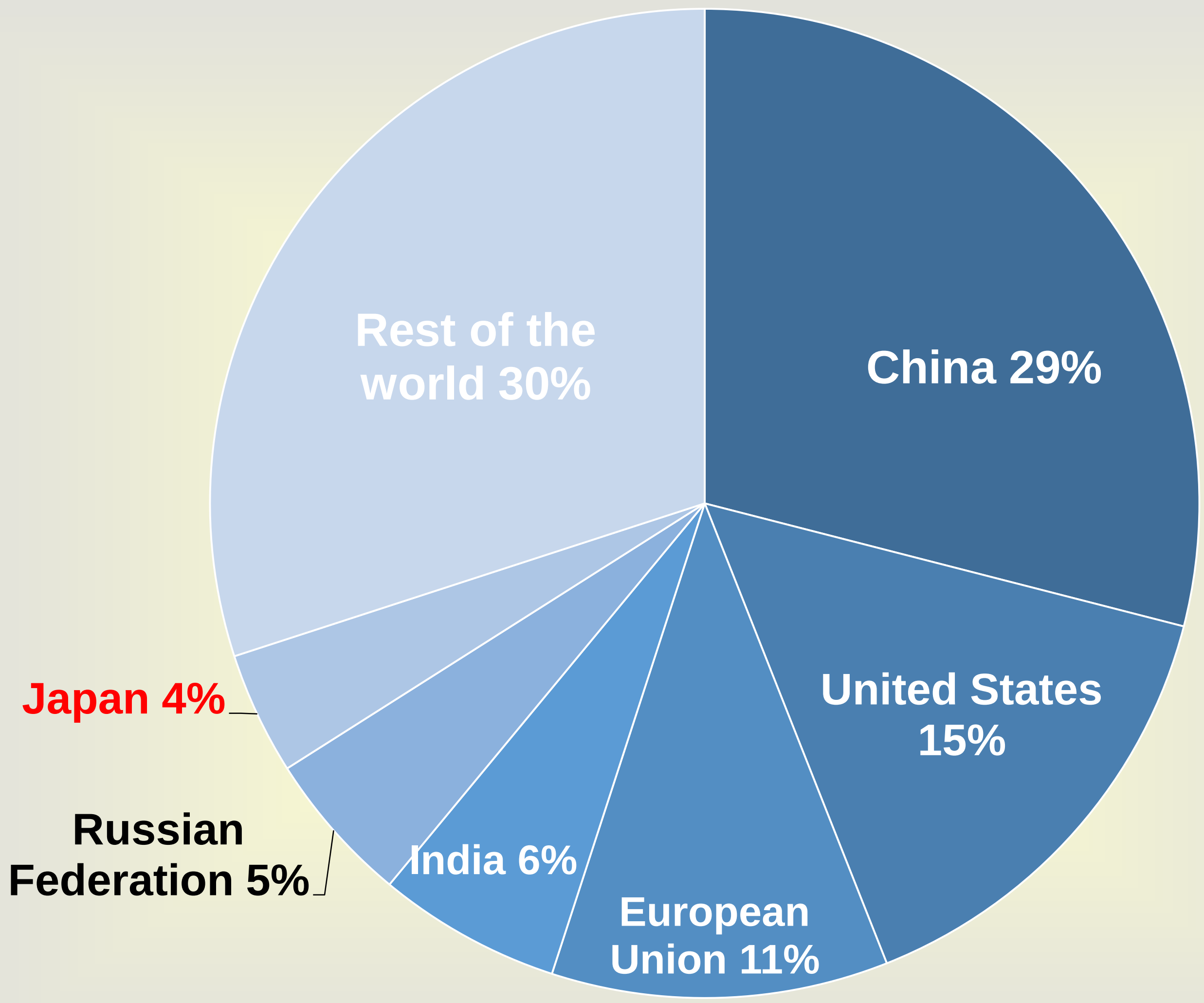
World map of countries by Human Development Index (HDI) categories in increments of 0.050 (based on 2019 data, published in 2020).

Correlation between HDI & CO_2 emissions



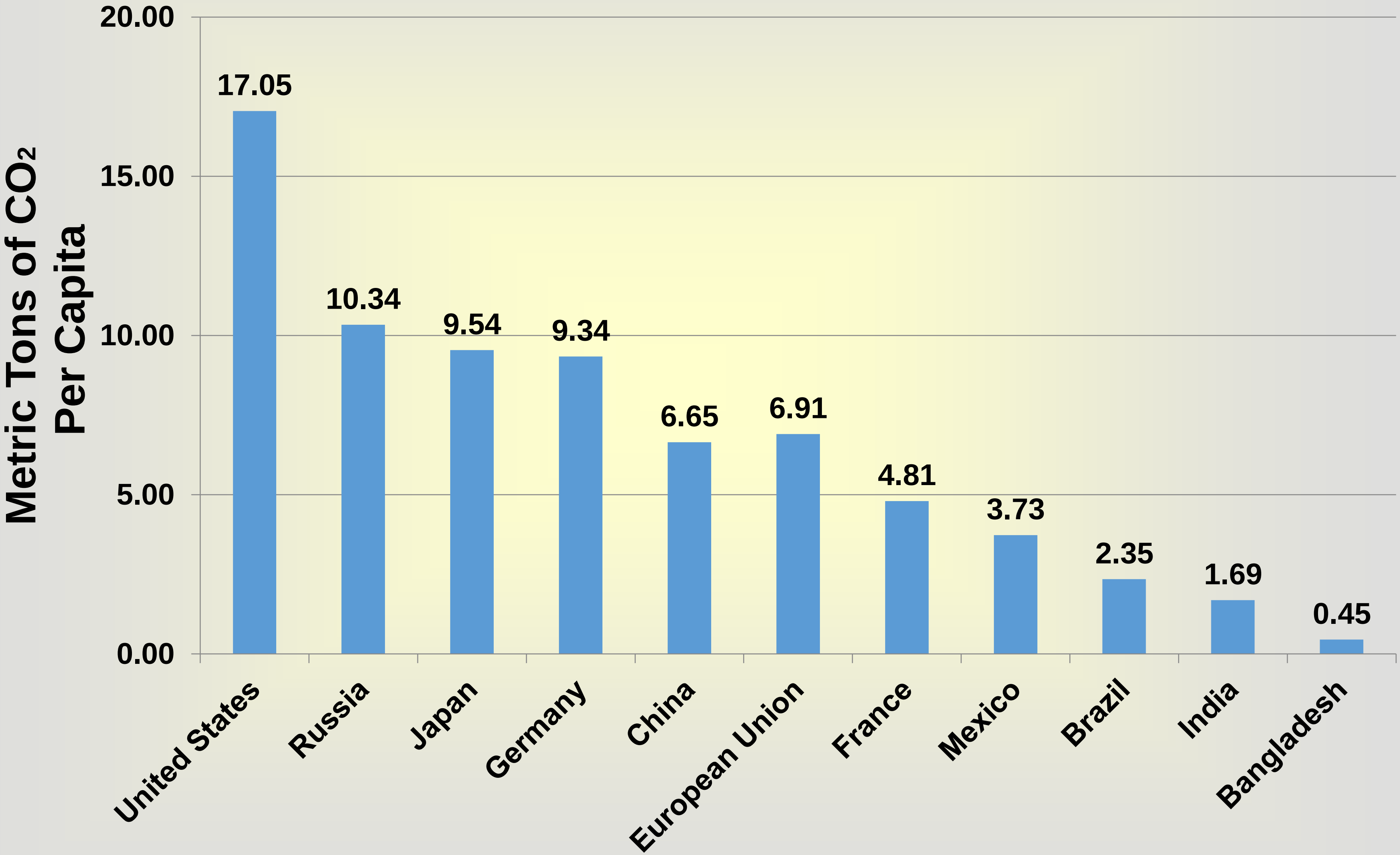
Correlations between HDI and CO_2 per capita emissions in the year 2000

Percentages of Global CO_2 Emissions by Country/Region



Source: Jos G.J. Olivier et al., European Commission's Joint Research Centre, 2014 "Trends in global CO_2 emissions: 2014 Report" http://edgar.jrc.ec.europa.eu/news_docs/jrc-2014-trends-in-global-co2-emissions-2014-report-93171.pdf

Per-Capita CO_2 emissions, by Country



Source: British Petroleum, Energy charting tool 2015.

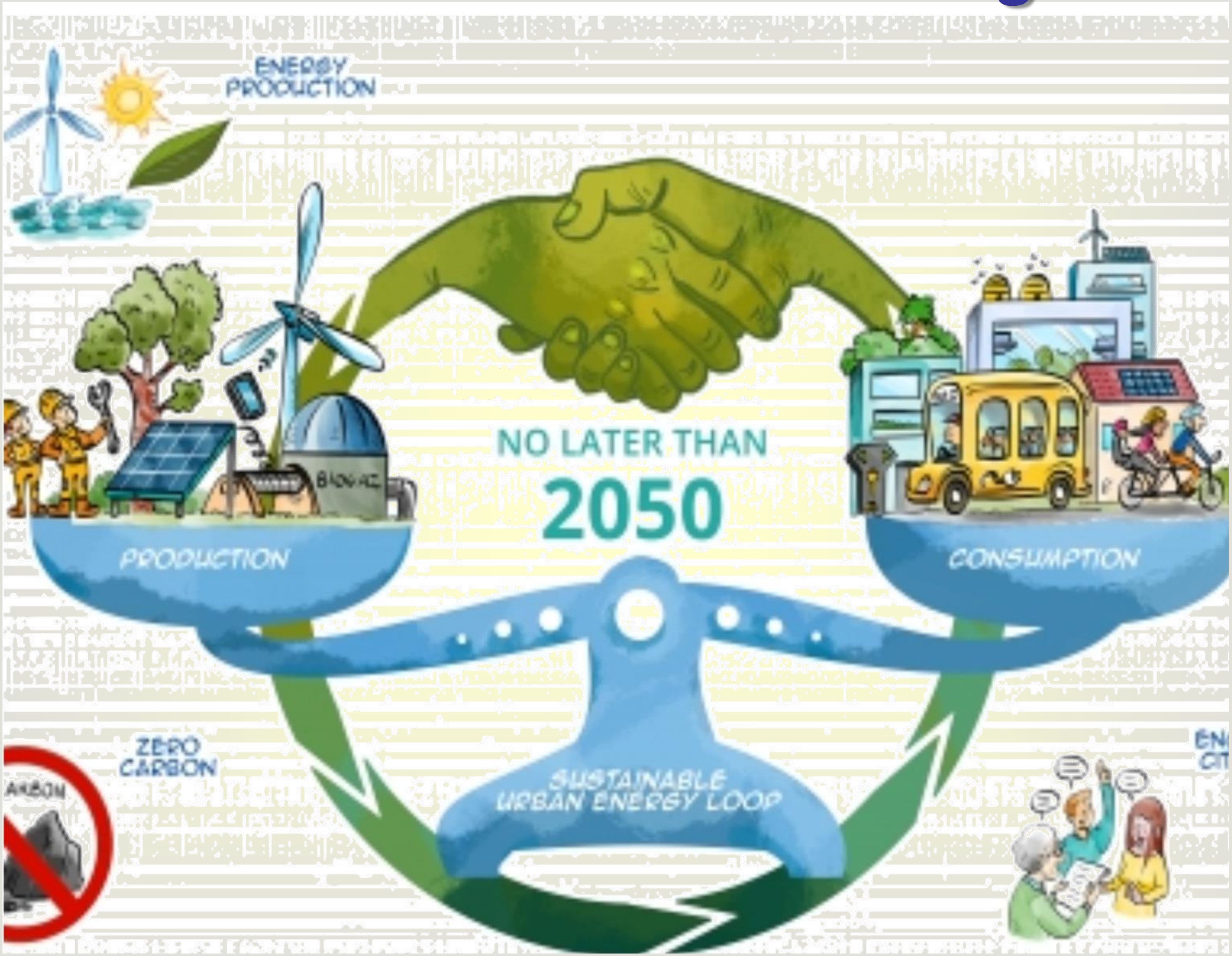
NET Zero Carbon Generation

What is the Paris Agreement 2015?

- ❑ Address climate change and its negative impacts.
- ❑ **Included commitments from all major emitting countries.**
- ❑ **Provided a pathway for developed nations to assist developing nations in their climate mitigation and adaptation efforts.**
- ❑ **Aims:**
- ❖ **Reduce global greenhouse gas emissions.**
- ❖ **Limit the global temperature increase in this century to 2 degrees Celsius above preindustrial levels.**
- ❖ **Cut climate pollution of countries and to strengthen commitments over time.**

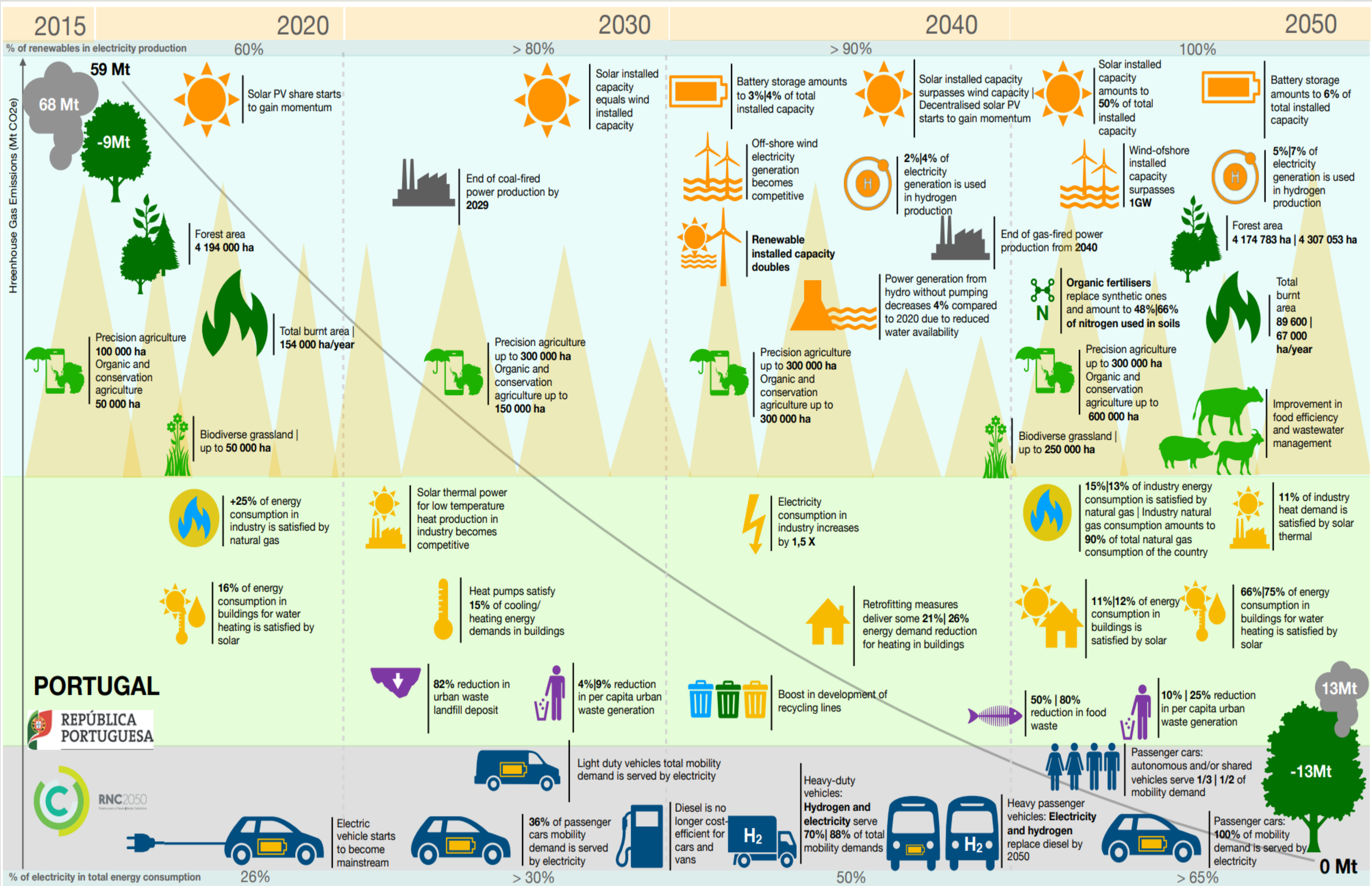
International leaders stand together at the gathering of COP21 in 2015.

NET Zero Carbon Generation Agreement



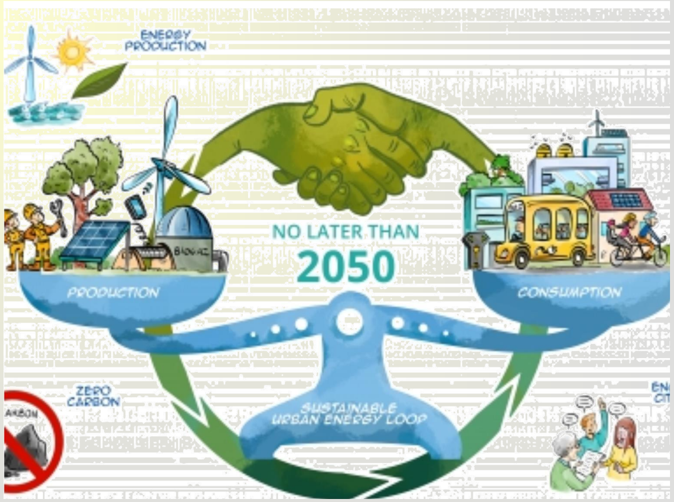
Removing the greenhouse CO_2 gas from the earth's atmosphere is known as Negative emissions technologies (NET).

Strategy to Meet Net Zero Carbon by 2050

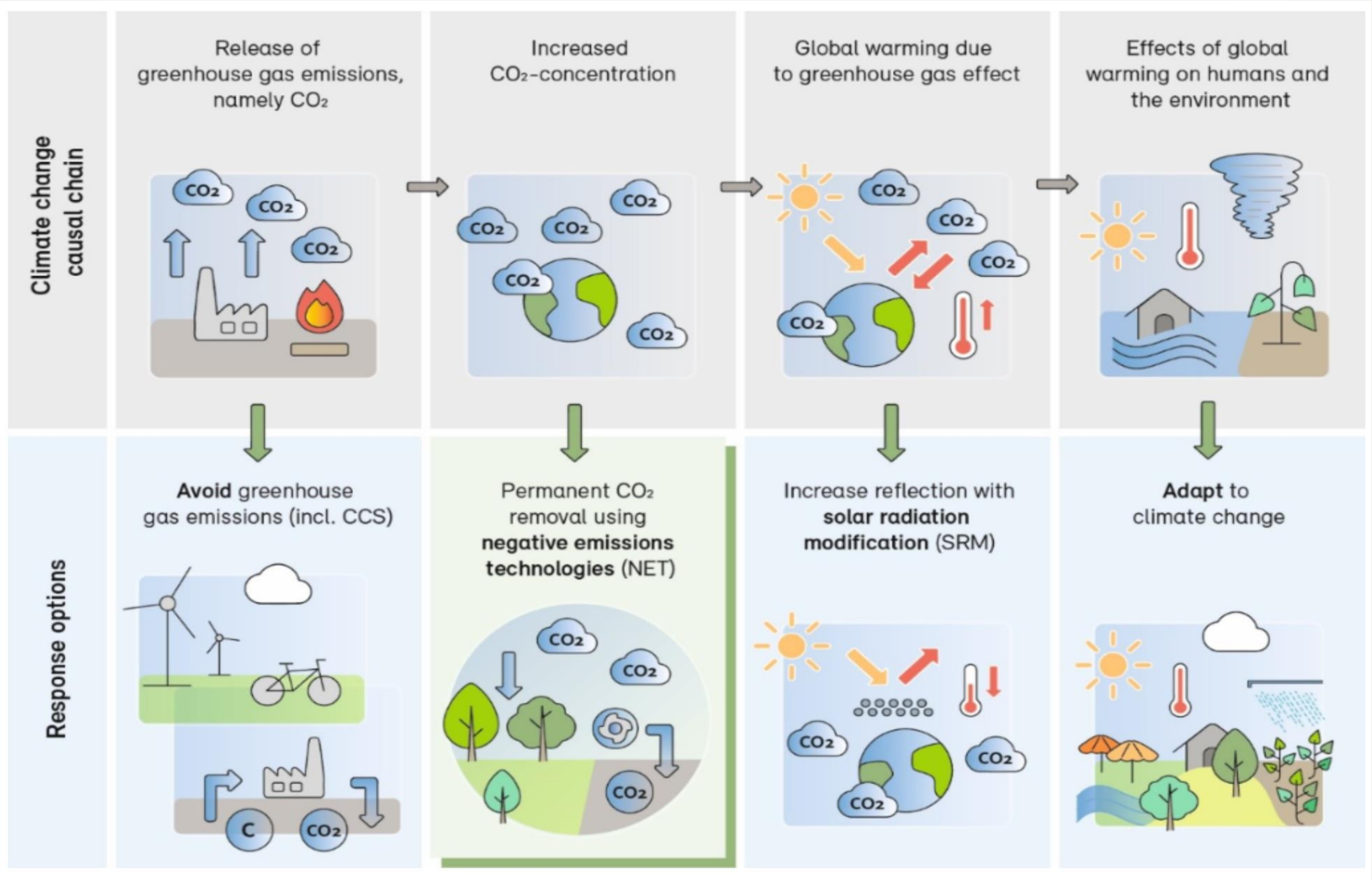


Strategy to Meet Net Zero Carbon by 2050

- Long term plan to reduce GHG emissions year on year
- Displace fossil fuels with ‘green’ electricity
- Consider new and future technologies
- Reduce GHG emission as low as practicable
- Offset remaining GHG emissions



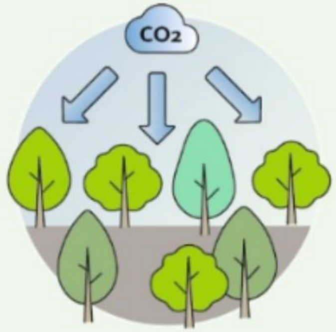
Human Response along the Climate Change Causal Chain



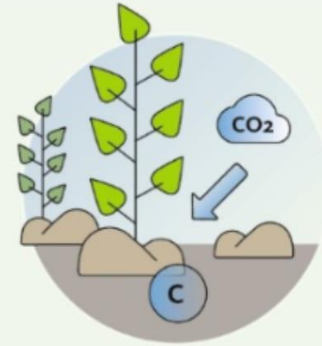
Source: FOEN illustration based on Jan C. Minx et. al., 2018.

Possible Approaches for Removing CO_2 Emissions

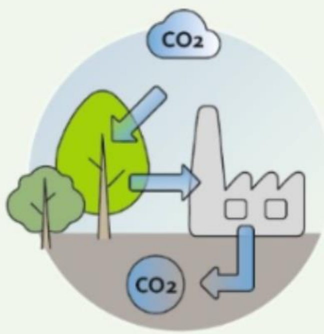
Afforestation, reforestation, forest management and wood utilisation
Trees remove CO_2 from the air as they grow. The CO_2 can be stored in trees, soil and wood products.



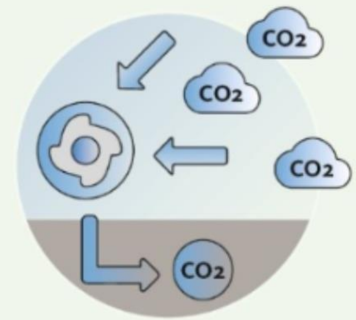
Soil management (incl. biochar)
The introduction of carbon (C) into soils, e.g. through crop residues or vegetable carbon, can accumulate C in the soil.



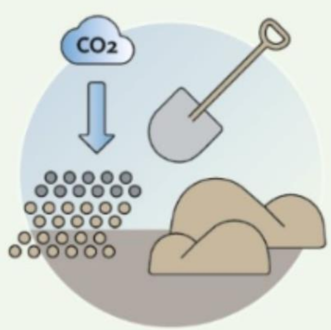
Bioenergy with carbon capture and storage (BECCS)
Plants convert CO_2 into biomass, which provides energy. CO_2 is captured and stored underground.



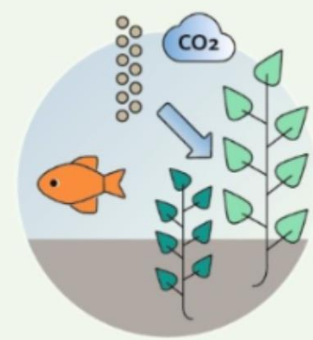
Direct air capture carbon capture and storage (DACCS)
CO_2 is extracted from the ambient air by chemical processes and stored underground.



Enhanced weathering
Crushed minerals bind CO_2 chemically and can then be stored in products, in the soil or in the sea.

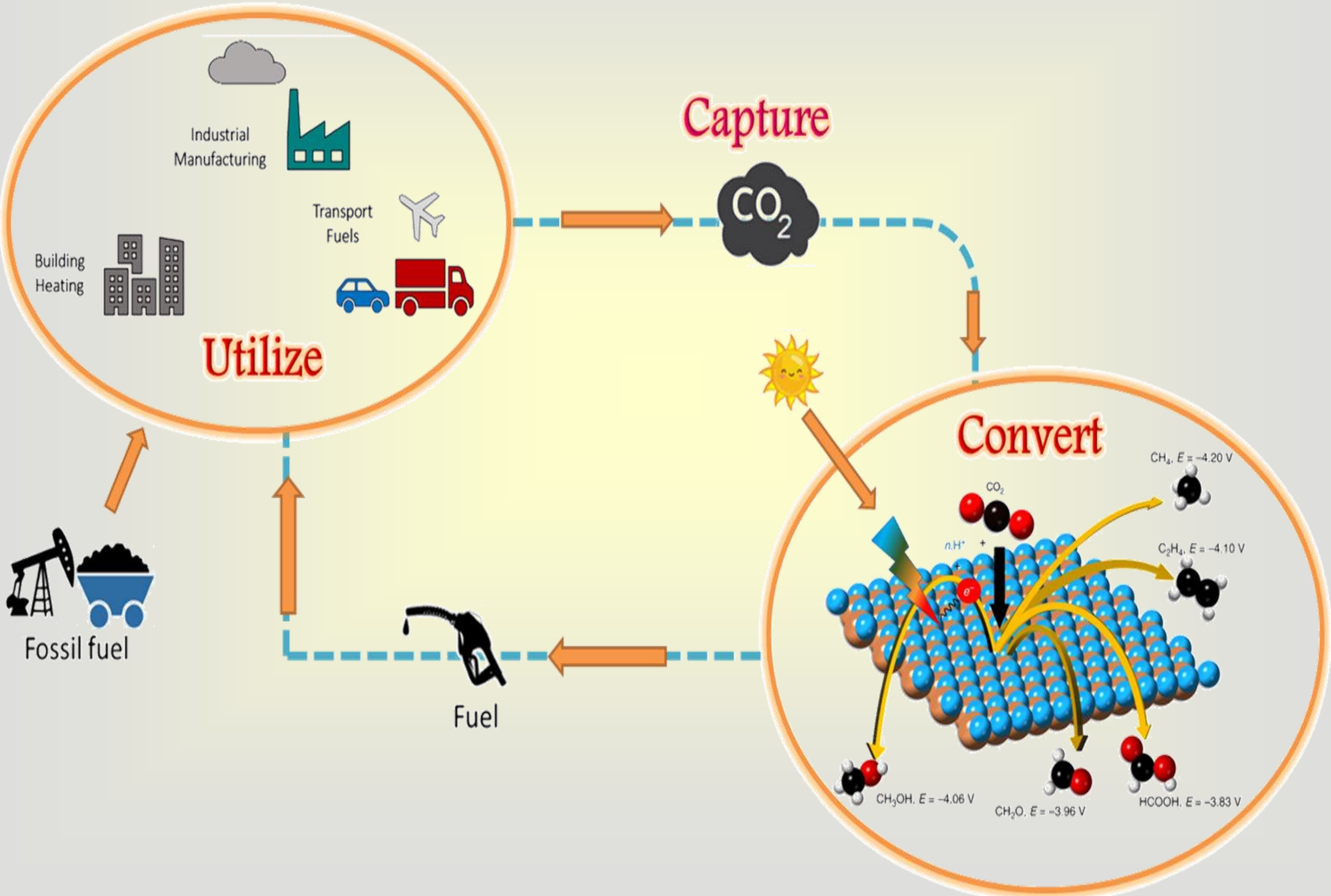


Ocean fertilisation
Iron or other nutrients are added to the ocean to increase the absorption of CO_2 by algae.



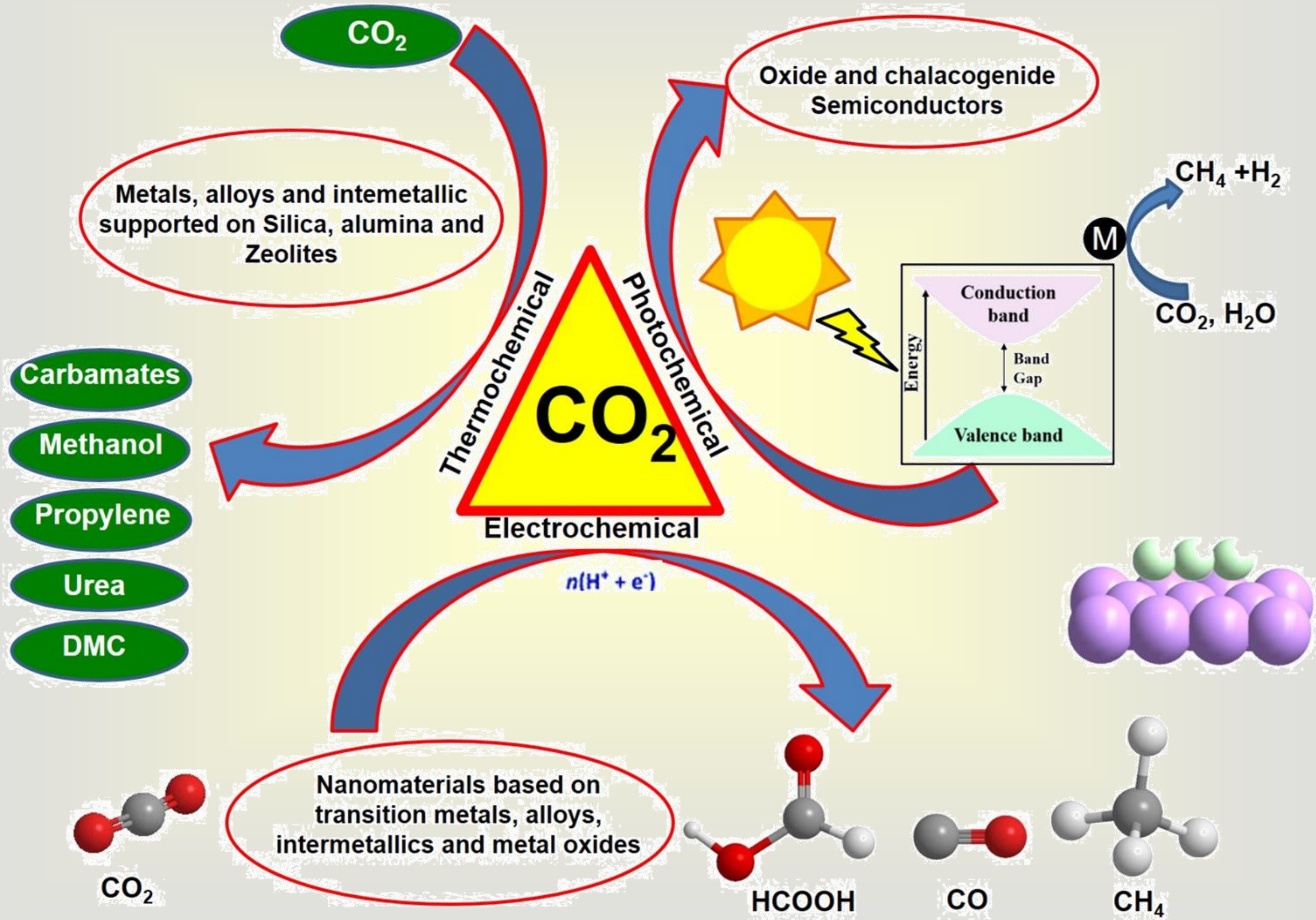
Source: FOEN illustration based on Jan C. Minx et. al., 2018.

Carbon Dioxide Cycle for Scientists



Strategies for CO_2 Reduction

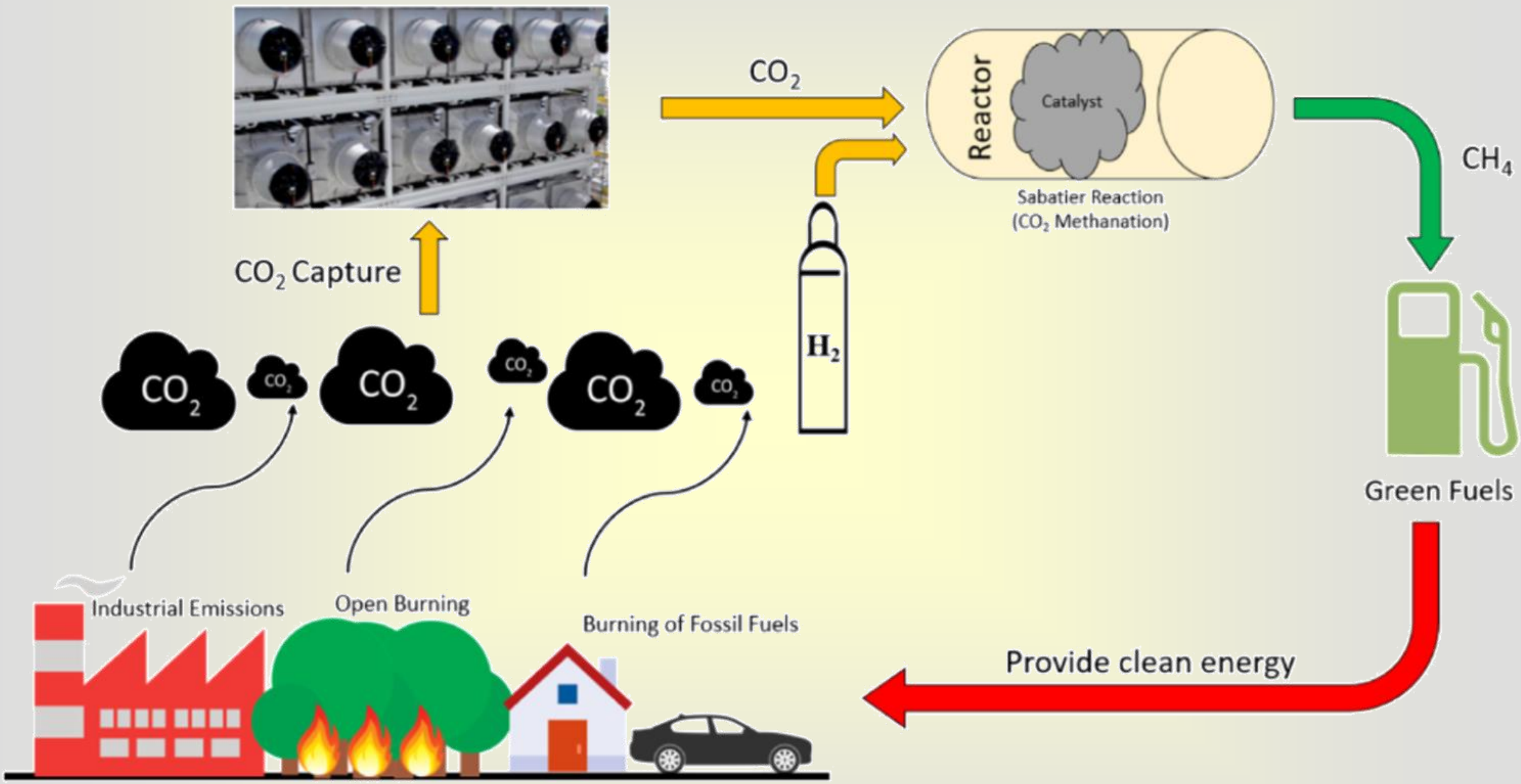
Different Approaches of CO_2 Reduction



ACS Energy Lett. 3 (7), 2018, 1557–1561

Thermocatalytic CO_2 Reduction

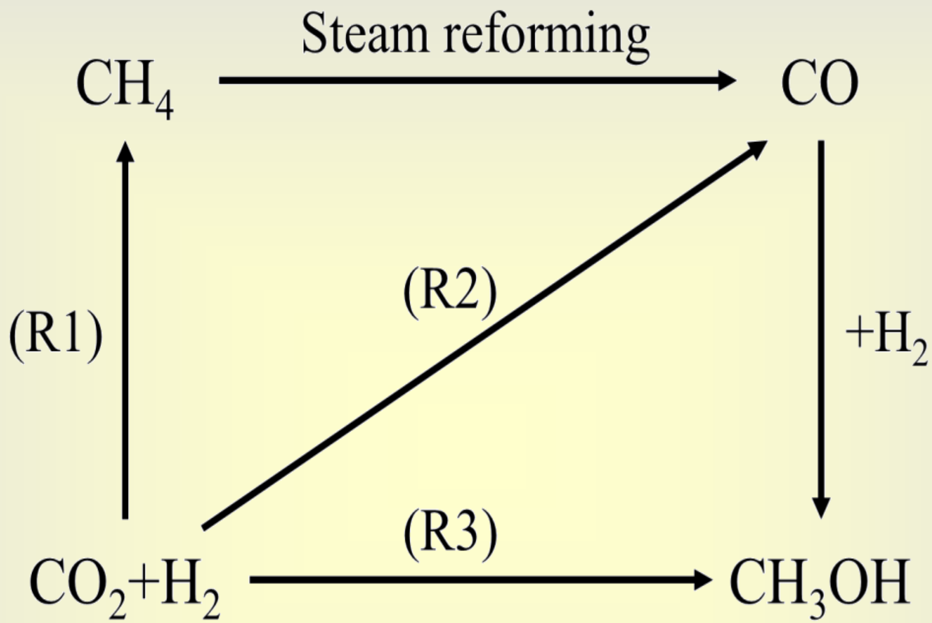
Thermochemical CO_2 Reduction



The capture and recycling of CO_2 into green fuels and energy using Thermochemical process.

Journal of Environmental Chemical Engineering 9 (4), 2021, 105460.

Thermochemical CO_2 Reduction



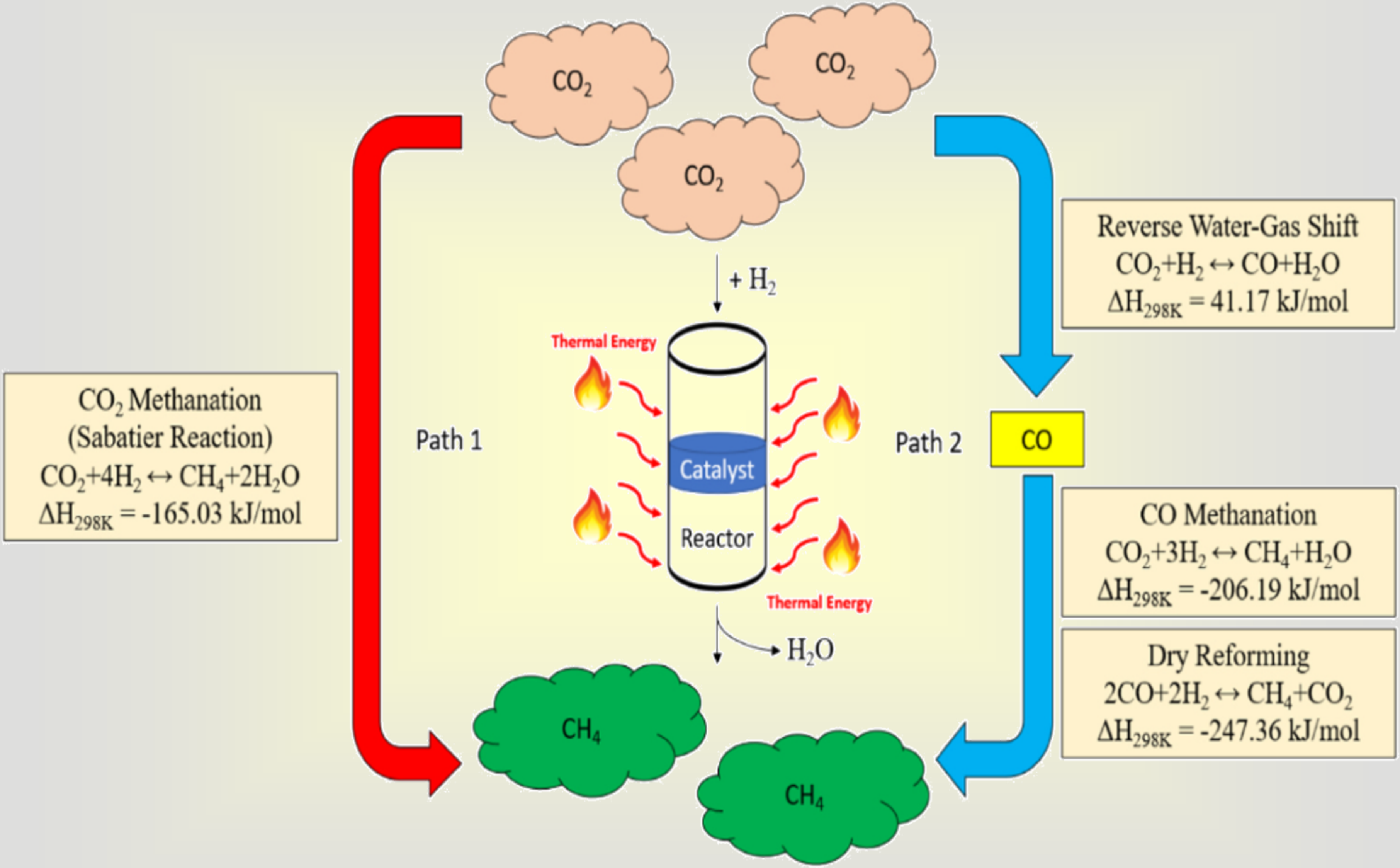
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \quad \Delta H_{298K} = -252.9 \text{ kJ/mol}^{4} \qquad (R1)$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H_{298K} = 41.2 \text{ kJ/mol}^{4} \qquad (R2)$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O, \quad \Delta H_{298K} = -49.5 \text{ kJ/mol}^{4} \qquad (R3)$$

L. Wang, Y. Yi, H. Guo, and X. Tu, Atmospheric Pressure and Room Temperature Synthesis of Methanol through Plasma-Catalytic Hydrogenation of CO_2, ACS Catal., 8(1), 2018, 90–100.

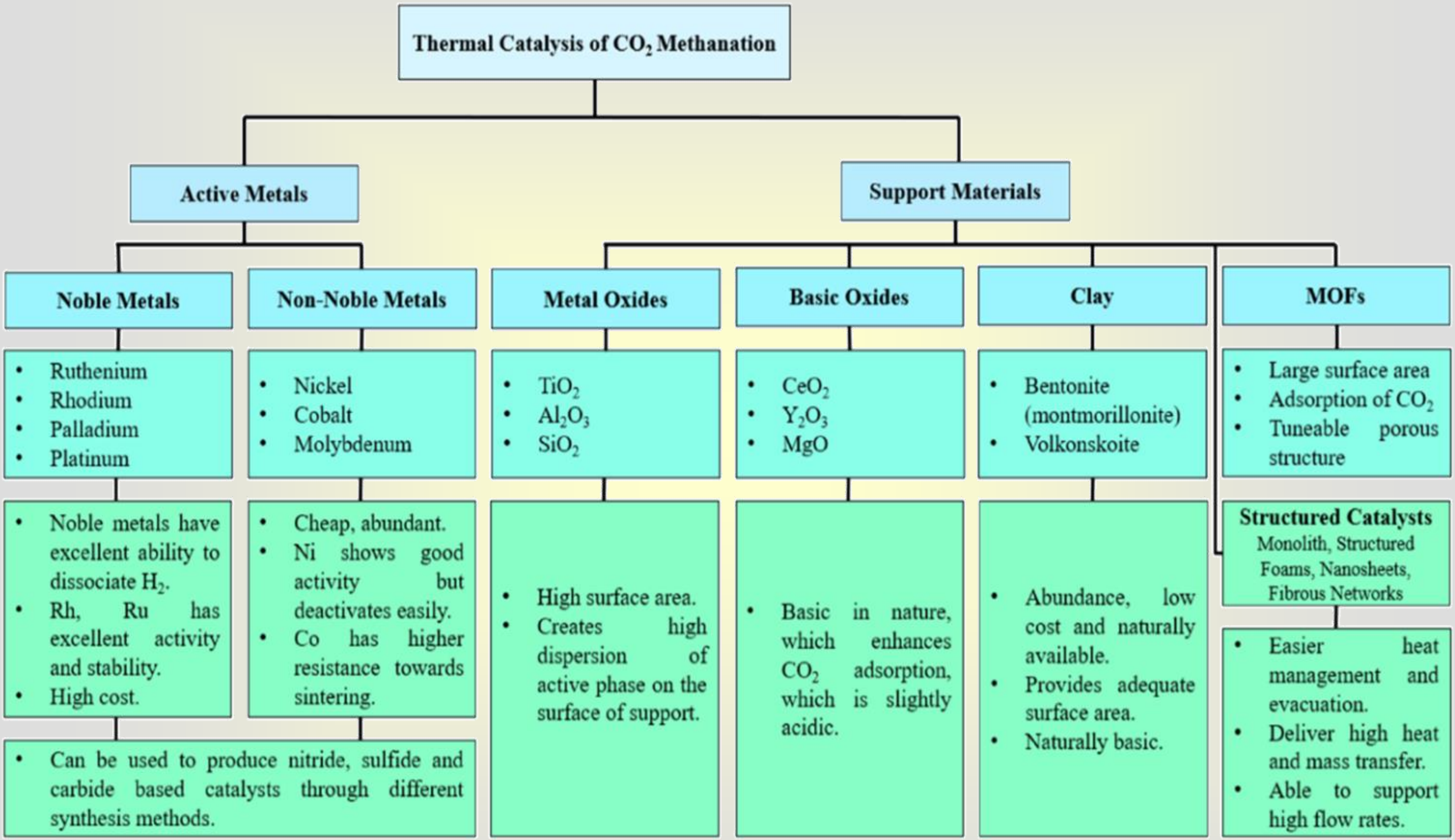
Thermochemical CO2 Reduction



Possible pathways for the CO_2 conversion to CH_4.

Journal of Environmental Chemical Engineering 9 (4), 2021, 105460.

Thermochemical CO2 Reduction

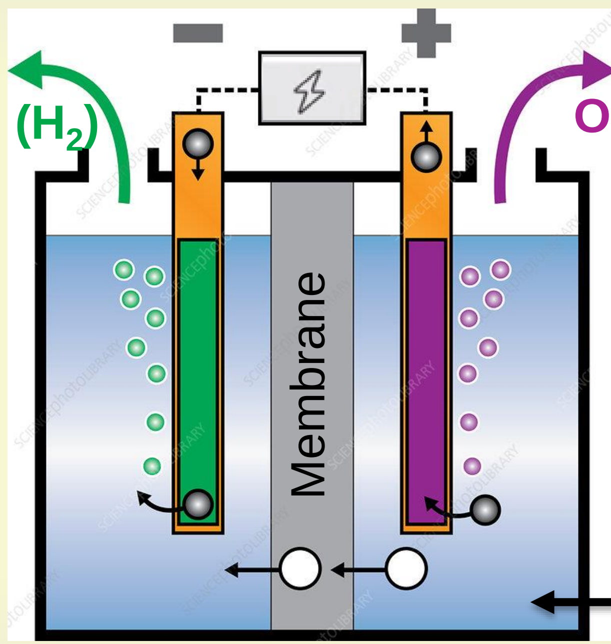


Journal of Environmental Chemical Engineering 9 (4), 2021, 105460.

Electrocatalytic CO_2 Reduction

Electrolysis Process

- Water can break into H_2 and O_2 gas by external power supply.



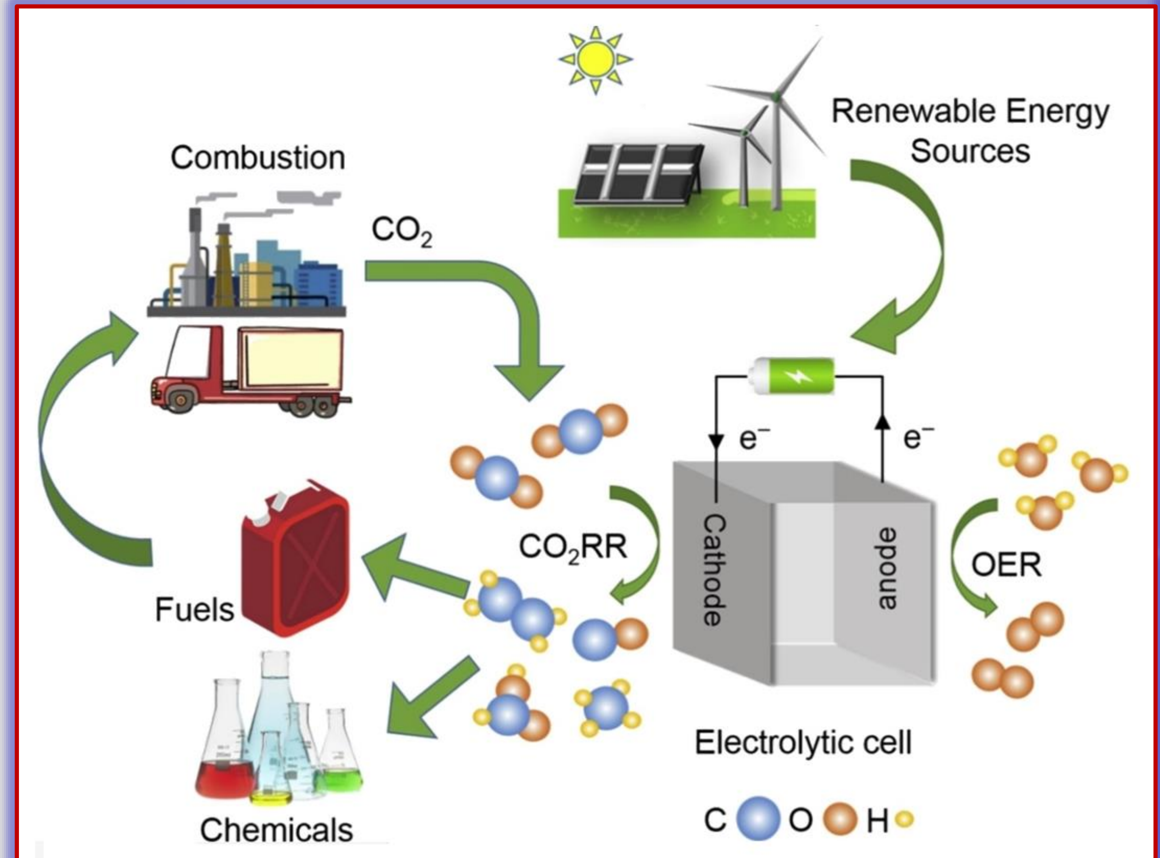
$4H^+ + 4e^- \rightarrow 2H_2$
(Cathode reduction)

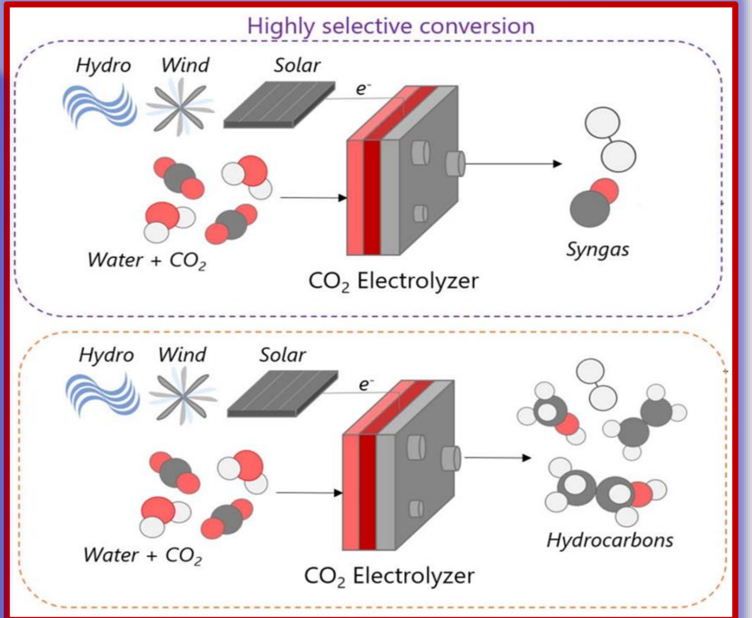
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
(Anode reaction)

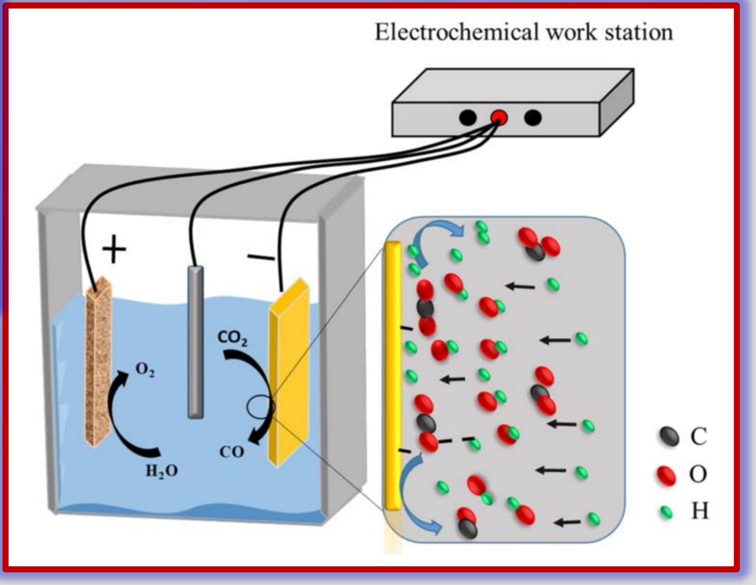
$2H_2O$ + electricity $\rightarrow 2H_2 + O_2$

- But it is an energy intensive process.

Electrochemical CO_2 Reduction

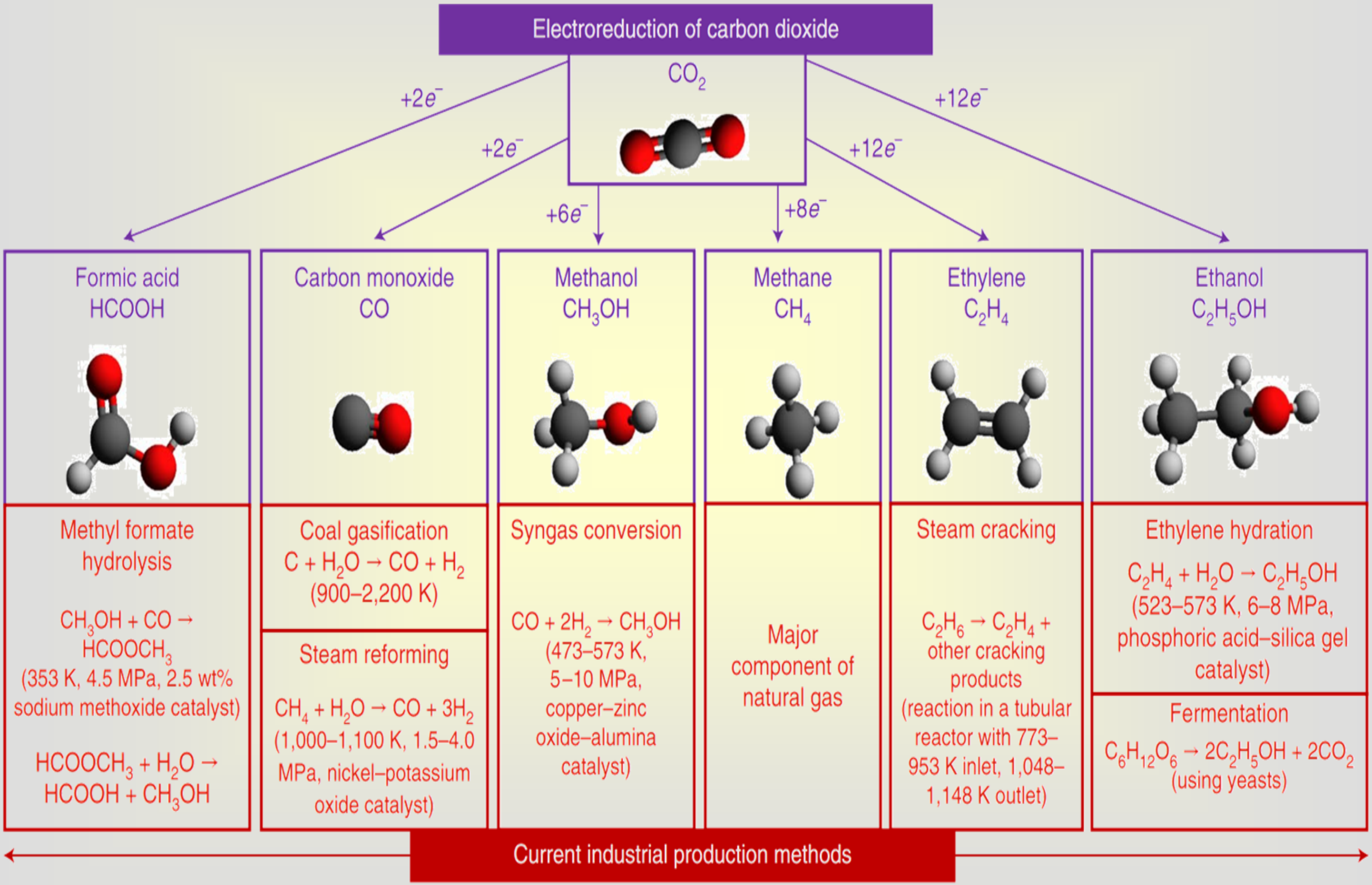






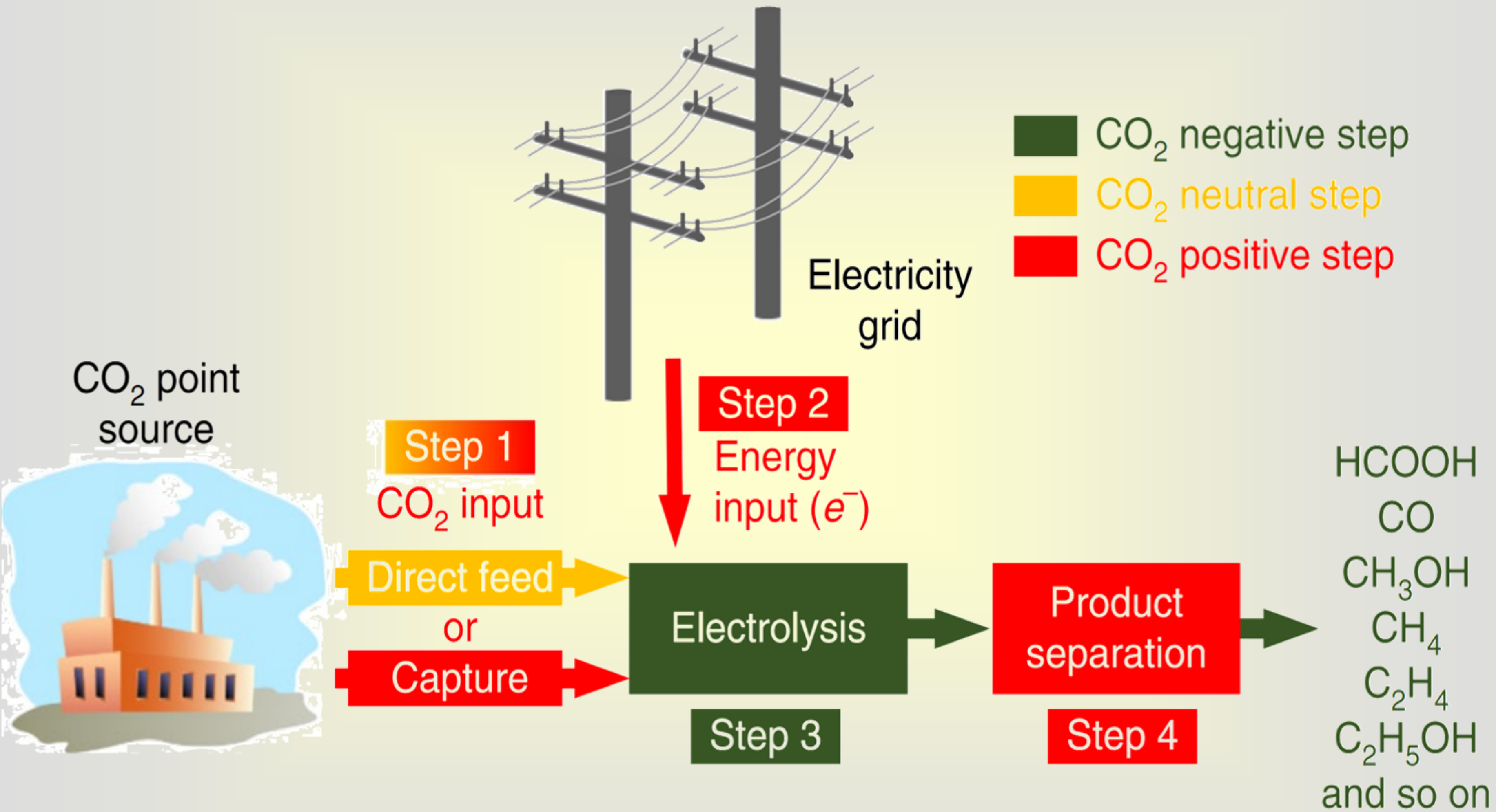
- Journal of CO2 Utilization 35, 2020, 90-105.
- Science 364, 350, 2019.
- SN Applied Sciences 3, 812, 2021.

Current Industrial CO2 Electroreduction Products



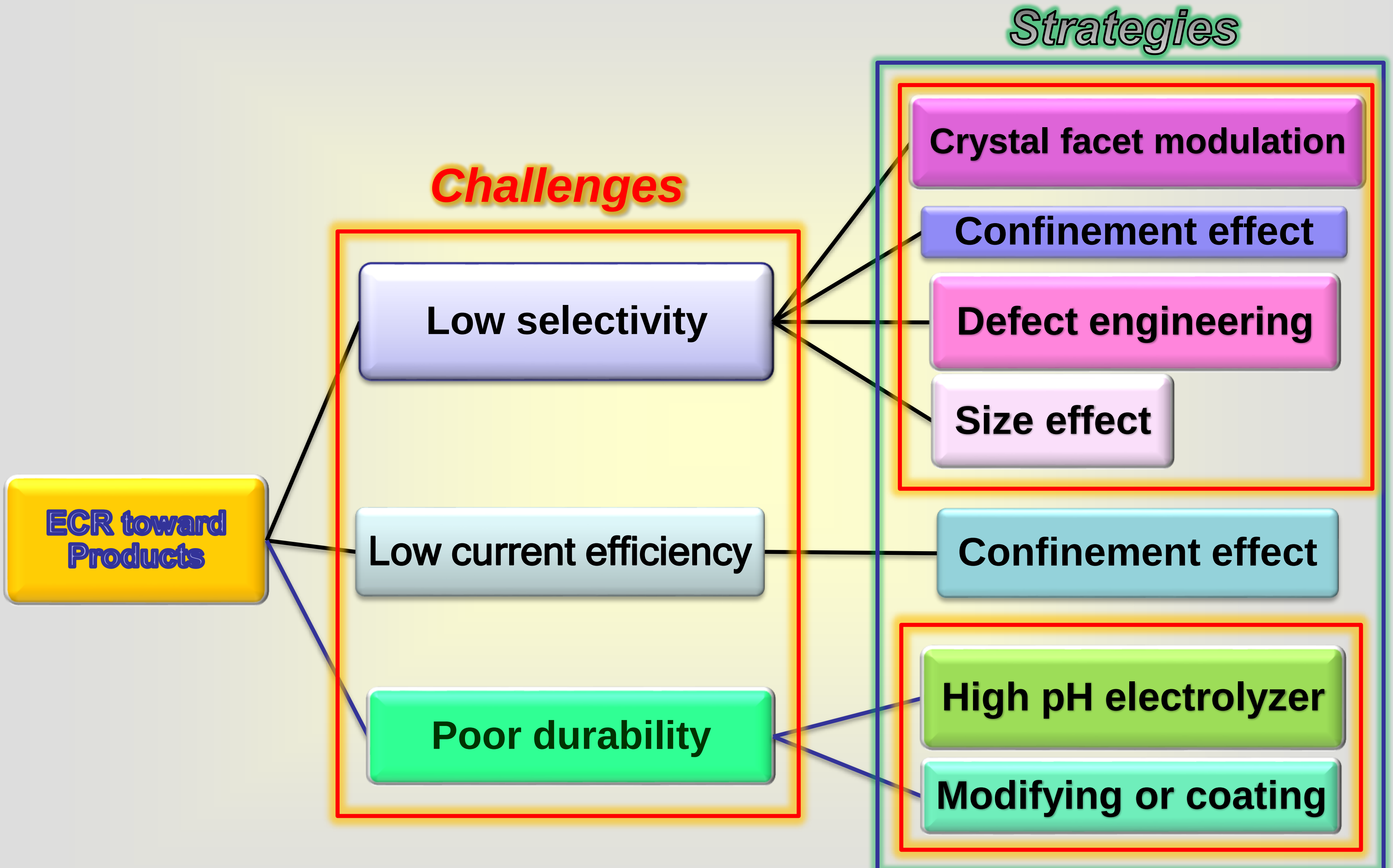
Nature Energy, 4, 2019, 466–474.

Industrial Implementation Steps of CO_2 Reaction



Nature Energy, 4, 2019, 466–474.

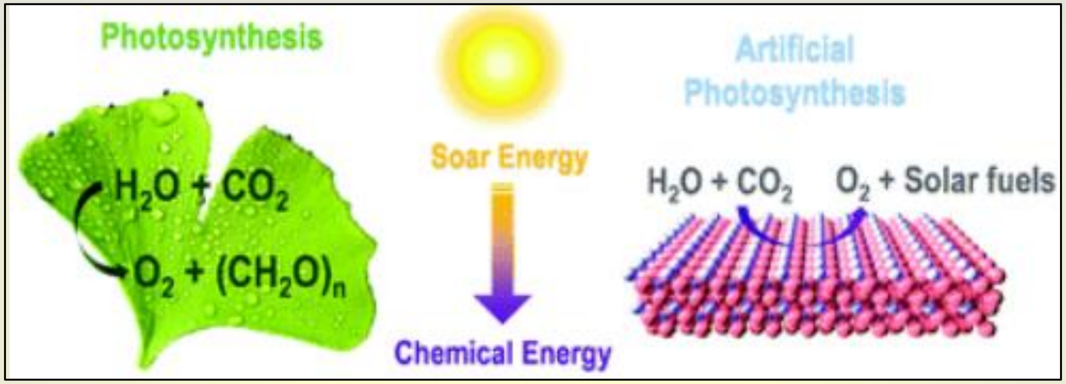
Electrochemical CO_2 Reduction

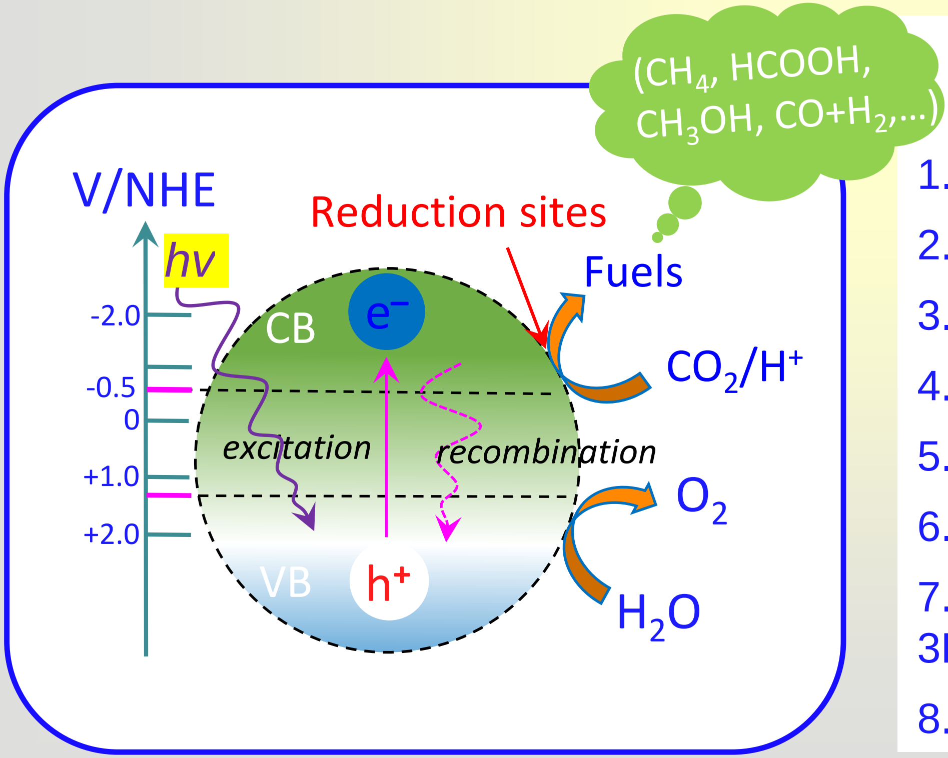


Acta Phys. -Chim. Sin. 2020, 36 (1), 1906085

Photocatalytic CO_2 Reduction

Photochemical CO_2 Reduction



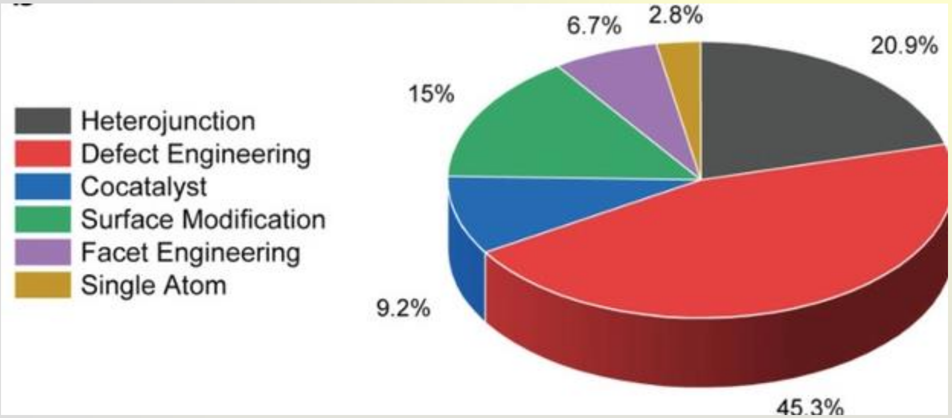


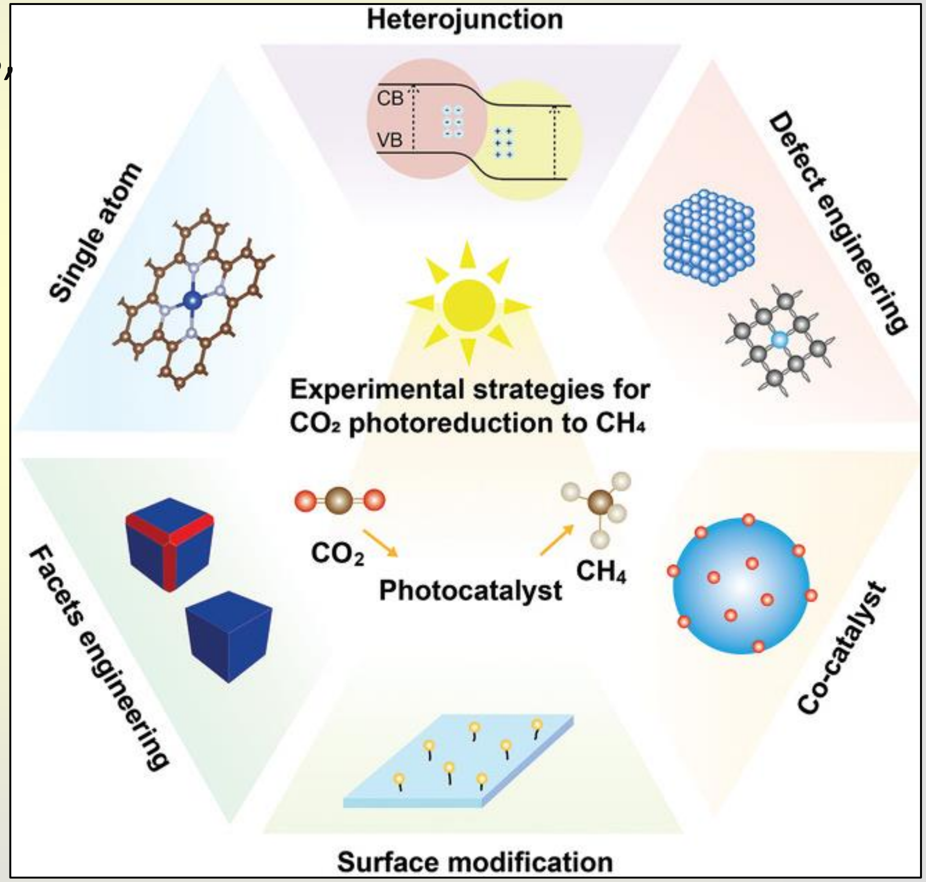
Reactions	V/NHE at pH 7
1. $CO_2 + e^- \rightarrow CO_2^-$	-1.90
2. $CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
3. $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
4. $CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48
5. $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
6. $CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24
7. $CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	-0.33
8. $2H^+ + 2e^- \rightarrow H_2$	-0.41

Photocatalytic CO_2 reduction

Key features

- Higher reduction potential is required,
- Multiple photoelectrons transfer process,
- Catalytically active sites,
- Intermediate adsorption/desorption process,
- Water oxidation is a rate limiting step.





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Thanks