CO_2 and Plastic Waste Utilization in the Context of Climate Change Mitigation

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By high speed train …

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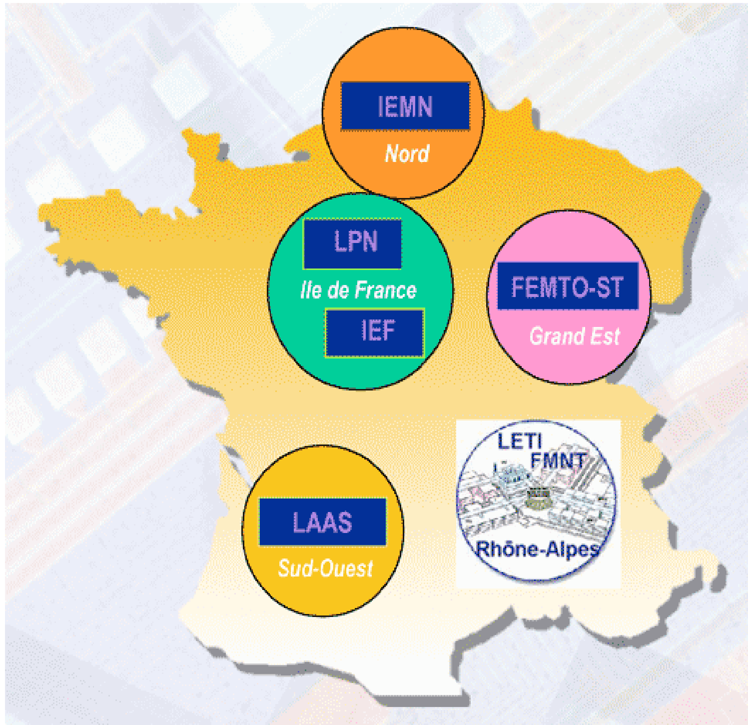
520 chercheurs, ingénieurs, techniciens, thésards



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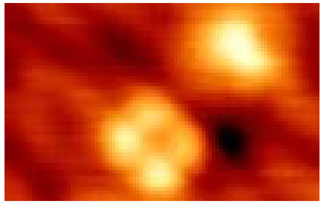
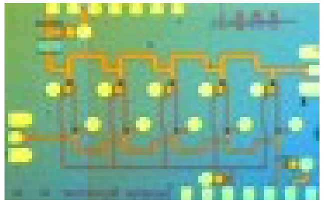
The research carried out can be divided into six major scientific areas (24 research groups)

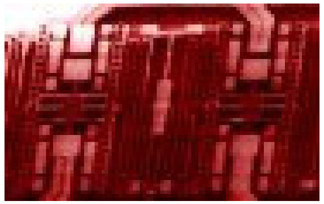


Materials and Nanostructures

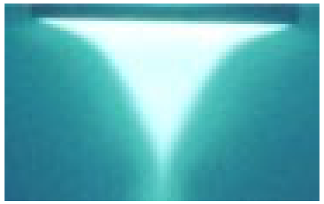
Micro- and Nano-systems



Micro Nano Opto Electronics



Telecommunication circuits and systems



Acoustics

Instrumentation

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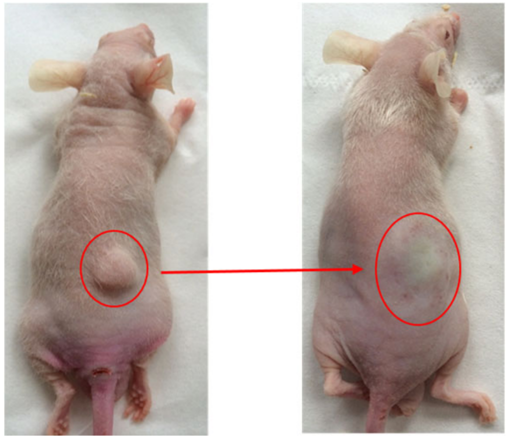
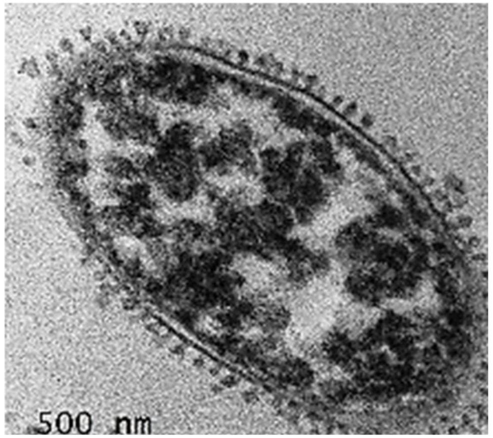
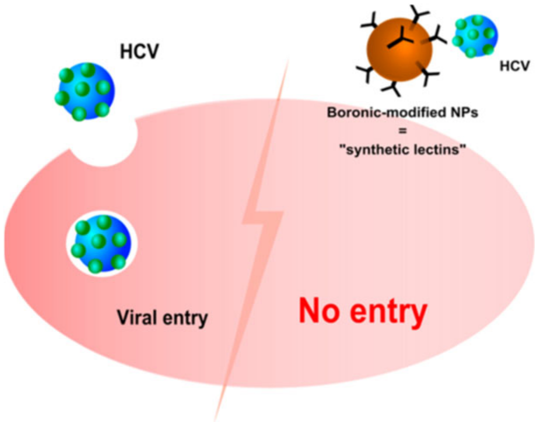
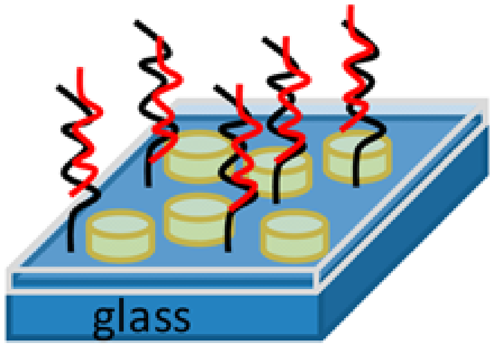


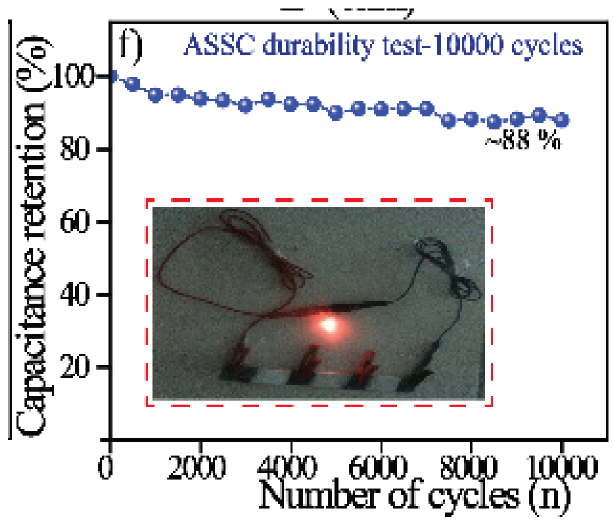




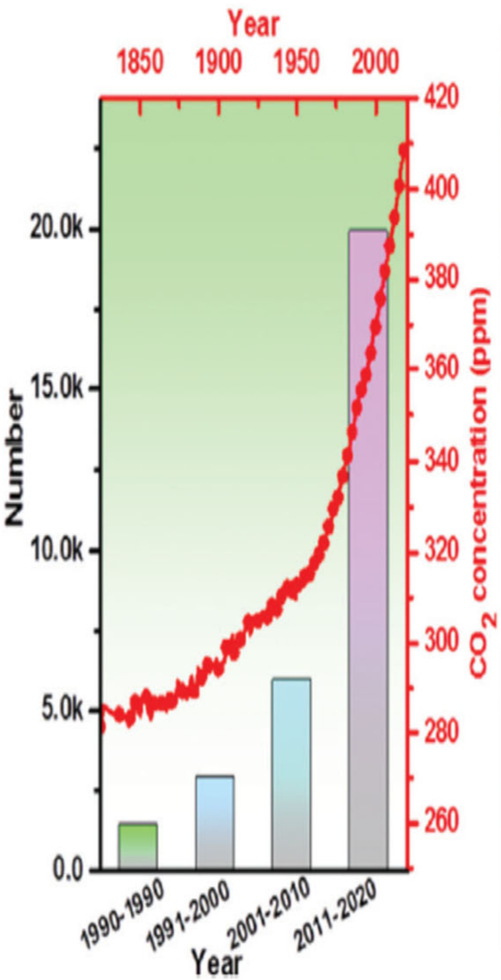
The main projects are:

- **Synthesis of nanostructured materials (nanoparticles, nanowires, nanorods,….) for drug delivery, fighting antibacterial resistance, antivirals, anti-fungal, as potent adjuvants,….**
- **Controlled surface chemistry for specific immobilization of biological molecules**
- **Biomolecule analysis (DIOS-MS)**
- **Label-free detection of biomolecular interactions (SPR, LSPR, electrochemical)**
- **Environmental remediation (photocatalysis, AOPs, adsorption), CO_2 photoreduction**
- **Energy storage (supercapacitors)**
- **Clean energy (water splitting)**





Some facts on CO_2



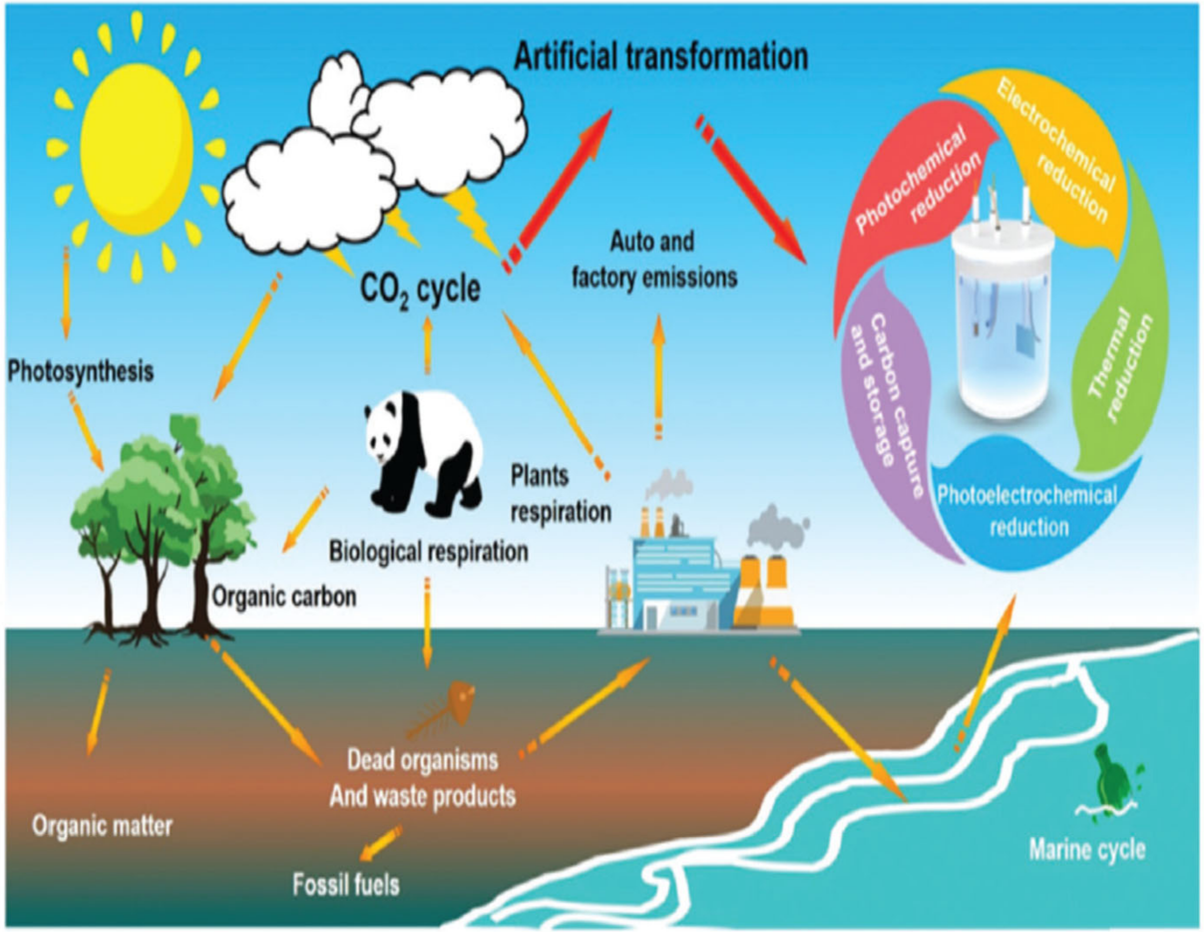


Fig. 1 Surface average atmospheric CO_2 concentration (ppm) and statistics on the numbers of publications related to CO_2 reduction in the last few decades. (Data obtained from Web of Science, collected May 10, 2020) (left). Diagrammatic illustration of the carbon cycle (right).

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Chem. Soc. Rev., 2021, 50, 4993-5061

Climate Change

Climate change occurs when changes in Earth's climate system result in new weather patterns that last for at least a few decades, and maybe for millions of years.
The climate system is comprised of five interacting parts, the atmosphere (air), hydrosphere (water), cryosphere (ice and permafrost), biosphere (living things), and lithosphere (earth's crust and upper mantle).

The climate system receives nearly all of its energy from the sun, with a relatively tiny amount from earth's interior. The climate system also gives off energy to outer space. The balance of incoming and outgoing energy, and the passage of the energy through the climate system, determines Earth's energy budget.

When the incoming energy is greater than the outgoing energy, earth's energy budget is positive and the climate system is warming. If more energy goes out, the energy budget is negative and earth experiences cooling. Oh joy. How do we arrange for that?

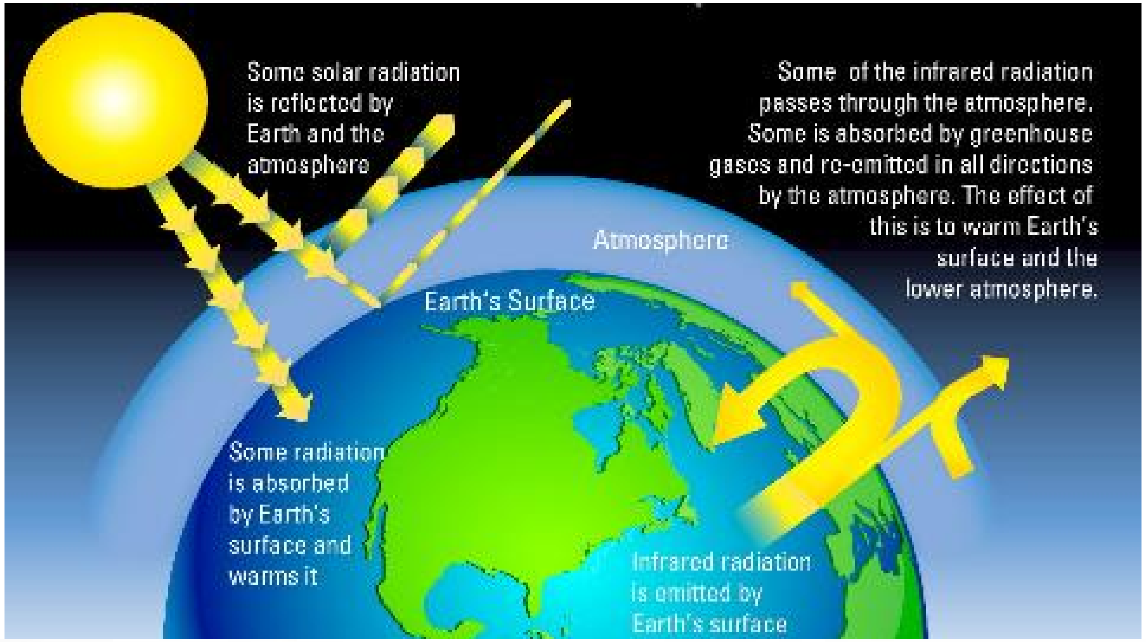
Climate Change

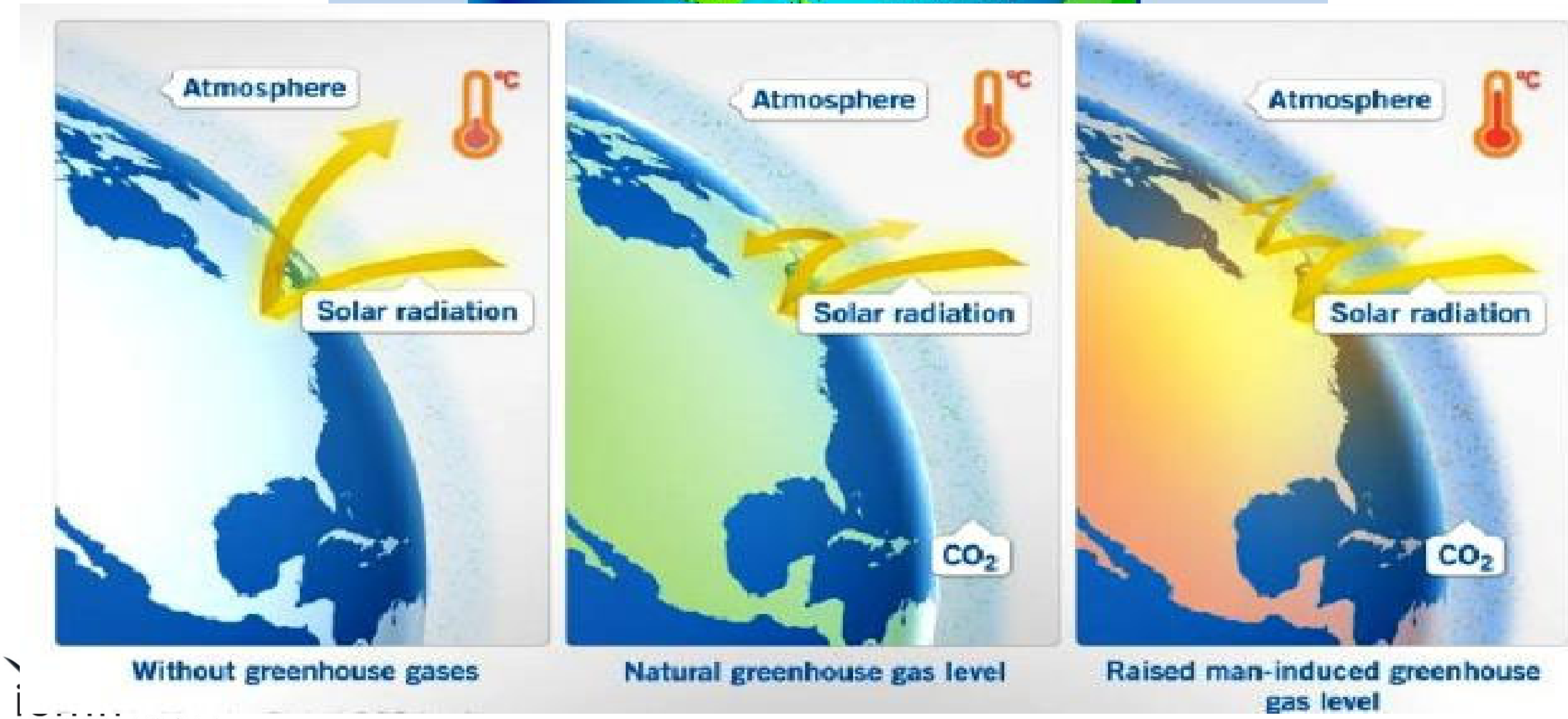
TOO MUCH CO_2

Carbon dioxide (CO_2) is essential to life on Earth, but too much in the atmosphere is a bad thing where greenhouse gases prevent the sun's heat from escaping back into space, keeping the Earth warmer than is comfortable for plants and animals to survive - hence changing our climate.

CO_2 naturally moves into and out of the atmosphere. For example, plants take up and use CO_2 to produce energy, and animals breathe out CO_2 made from using energy. The greatly increased amount of CO_2 in the atmosphere resulting from human invention and industrialization, is causing the Earth's temperature to rise rapidly.

The IPCC's (Intergovernmental Panel on Climate Change) Special Report of 1.5 Degrees (October 2018), reinforced the fact that a 1.5 degree world cannot be reached without deployment of all clean technologies. This is one of the major challenges facing mankind at this time.





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http://www.change-climate.com/Climate_Change.htm

Overview of the Basic Chemistry and Biology of CO_2

- **CO_2 is a colorless, odorless and tasteless gas with a density of about 60% than that of dry air.**

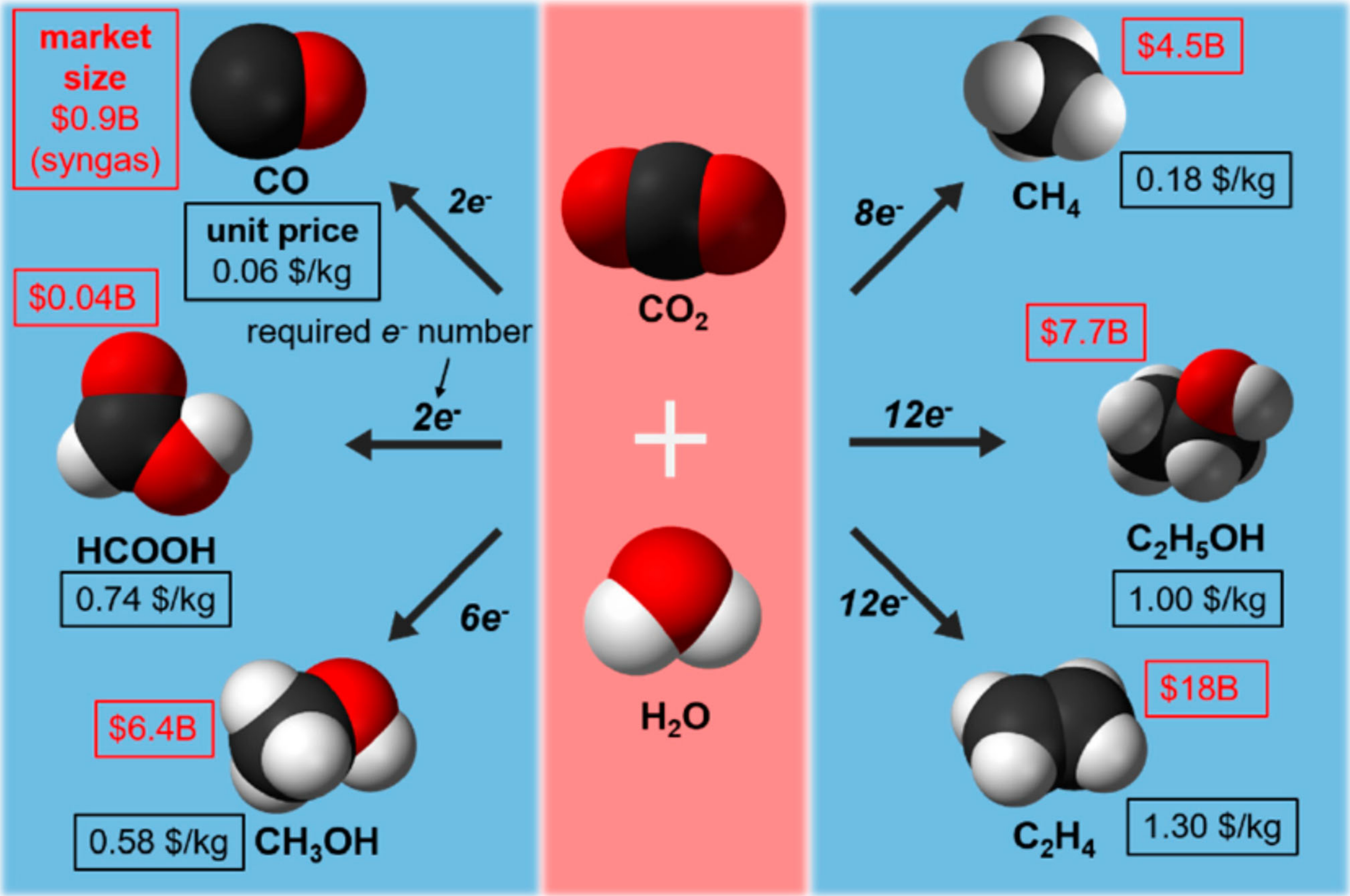
- **CO_2 is an extremely stable molecule. Its C=O bond has a dissociation energy of ~ 750 kJ mol^{-1}, much higher than other chemical bonds such as C-H (~ 430 kJ mol^{-1}) and C-C (~ 336 kJ mol^{-1}).**

- **Carbon in CO_2 is in its highest oxidation state (+4). Therefore, CO_2 reduction will lead to a large variety of products with different carbon oxidation states (CO, CH_4, CH_3OH, HCOOH).**

- **Applications:**

Food industry (food additive for acidity regulating), carbonated soft drinks, supercritical CO_2 as solvent, agriculture to conduct photosynthesis…)

Complexity of CO_2 Reduction Reaction – Final products



Catalysts 2019, 9, 224

Major Sources of CO_2 emissions

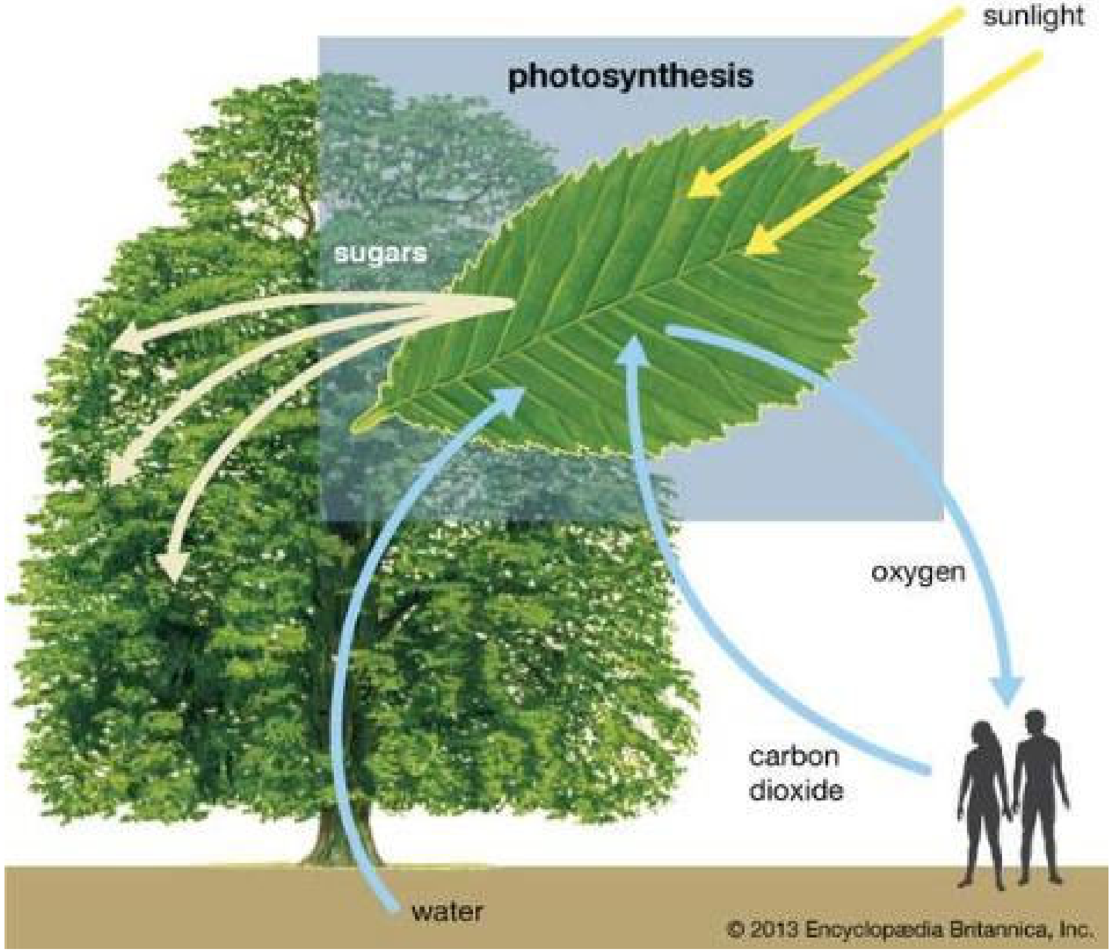
Source	Global CO_2 emission [Mt per year]	CO_2 purity [vol%]
Coal	14 200	12–15
Natural gas	6320	3–5
Refineries	850	3–13
Cement production	2000	14–33
Ethylene production	260	12
Iron and steel production	1000	15
Natural gas production	50	5–70
Ammonia production	150	100

- **Its current concentration in atmosphere is about 417 ppm (0.04%), as compared to pre-industrial levels of 280 ppm. https://www.CO2.earth/daily-CO2, and will reach 500 ppm by 2045.**

- **As a consequence, this may cause the Greenland and Antarctic ice sheets to melt, resulting in sea levels rising and extinction of about 24% of plant and animal species, and disappearance of some countries and islands.**

ChemSusChem, 2017, 10(6), 1036–1038.

Overview of the Basic Chemistry and Biology of CO_2

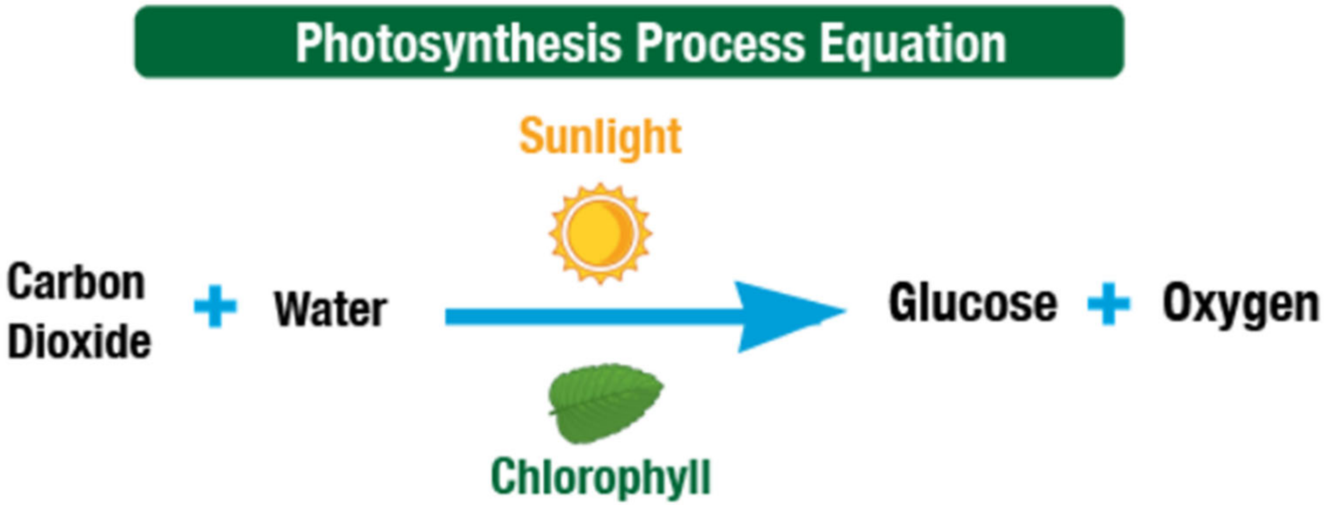


Photosynthesis, the process by which green plants and certain other organisms (algae, bacteria) transform light energy into chemical energy. During photosynthesis in green plants, light energy is captured and used to convert water, carbon dioxide, and minerals into oxygen and energy-rich organic compounds.

The process of photosynthesis

Photosynthesis is the process by which green plants, algae, and some bacteria convert light energy into chemical energy. It mainly occurs in the chloroplasts of plant cells. During photosynthesis, plants take in carbon dioxide from the air and water from the soil. Using sunlight, they transform these into glucose (a sugar) and oxygen. This process is essential for producing food and oxygen, supporting life on Earth.

The overall reaction can be summarised as:



https://www.monash.edu/student-academic-success/biology/photosynthesis/the-process-of-photosynthesis

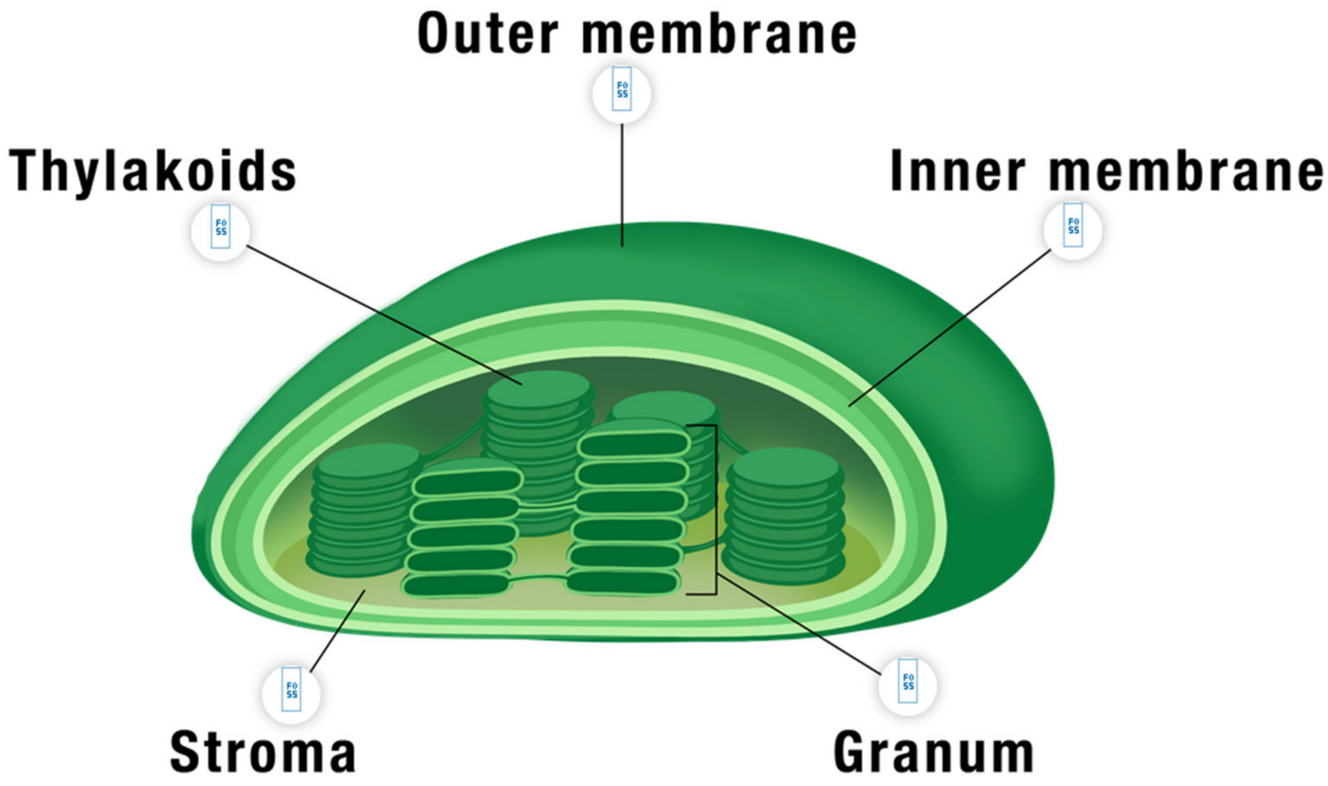
The chloroplast

The chloroplast is the key organelle responsible for photosynthesis.

Chloroplasts are double-membraned organelles found in plant cells and some algae, responsible for photosynthesis.

This unique structure allows chloroplasts to efficiently convert light energy into chemical energy through photosynthesis.

Click on the key parts of the chloroplast to find out more about its function.



Chloroplast

https://www.monash.edu/student-academic-success/biology/photosynthesis/the-process-of-photosynthesis

The light-dependent stage of photosynthesis

The first stage of photosynthesis is the light dependent stage.

It involves the capture and conversion of sunlight into chemical energy. This process occurs in the grana of the chloroplast, or more specifically in the thylakoid membranes.

Light is absorbed by the chlorophyll in the thylakoid membranes and the light energy is used to split a water molecule. The released electrons and H^+ ions from the water molecule are absorbed by the energy carrier $NADP^+$, which becomes a loaded electron acceptor known as NADPH.

The energy carrier ADP absorbs the released energy and is converted to ATP.

The oxygen from the split water molecule is released into the atmosphere, or it may be used as an input for cellular respiration in the plant. It is a waste product of this reaction.

https://www.monash.edu/student-academic-success/biology/photosynthesis/the-process-of-photosynthesis

The light-independent stage of photosynthesis

The second stage of photosynthesis is the light-independent stage or Calvin cycle.

Despite its name, the light independent reaction can occur when it is light, however, this stage does not directly rely on sunlight.

The Calvin cycle involves building carbon molecules into energy-rich organic molecules, such as glucose. This process occurs in the stroma of the chloroplast.

Carbon dioxide is absorbed into the Calvin cycle. In the first step of the cycle, the enzyme RuBisCO catalyses a reaction between CO_2 and a molecule called RuBP. RuBP is combined with carbon dioxide to ultimately produce two 3-carbon molecules. Numerous reactions occur during the Calvin cycle until the eventual formation of glucose.

The energy carriers, NADPH and ATP, provide energy for this process to occur. They also assist to regenerate RuBP within the cycle, making it ready to react with the next CO_2 molecule and keep the cycle going. In the Calvin cycle, ATP and NADPH are converted back to ADP +P_i and $NADP^+$, respectively, which can be returned to the light-dependent reactions.

https://www.monash.edu/student-academic-success/biology/photosynthesis/the-process-of-photosynthesis

CO_2 Sequestration by Microalgae

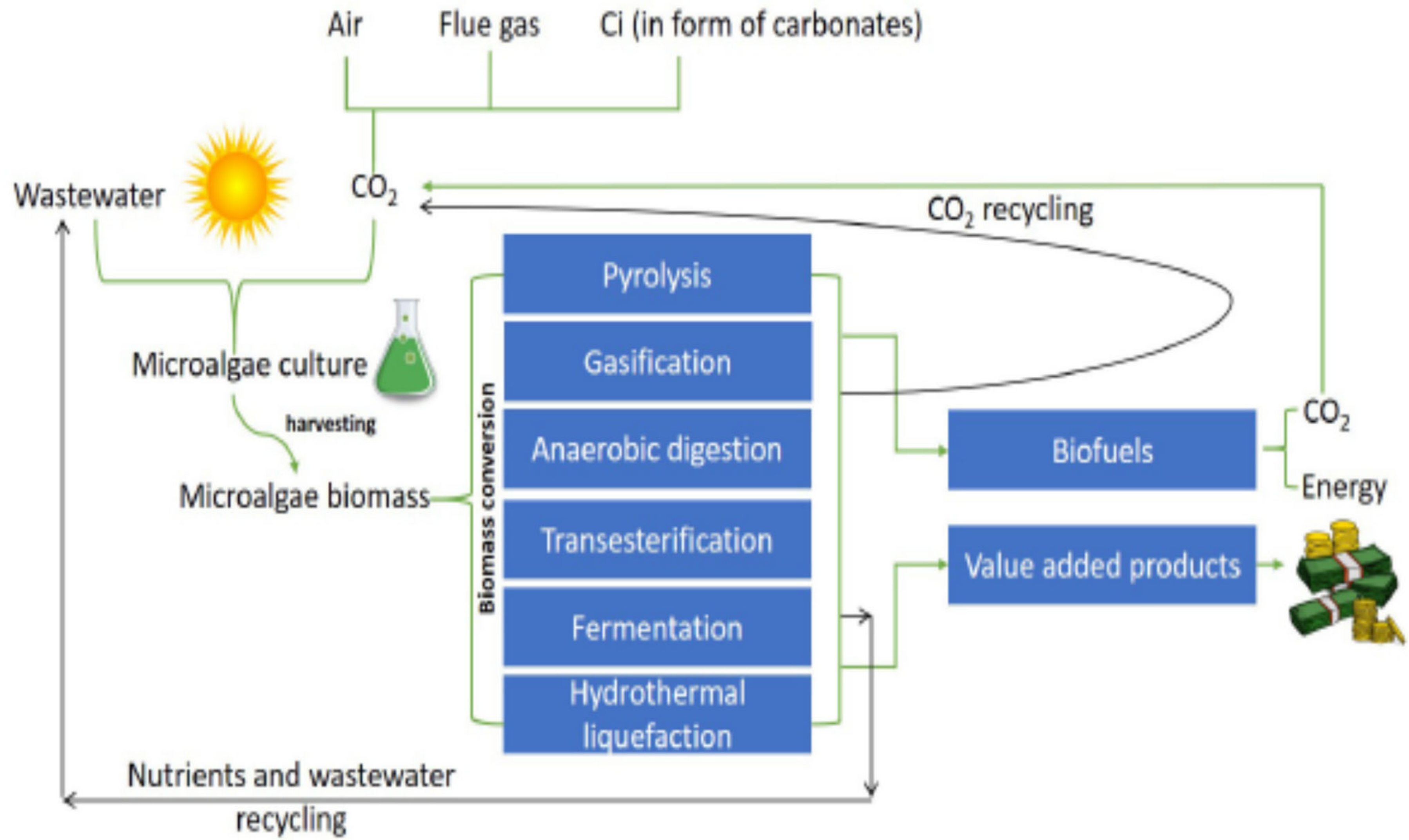
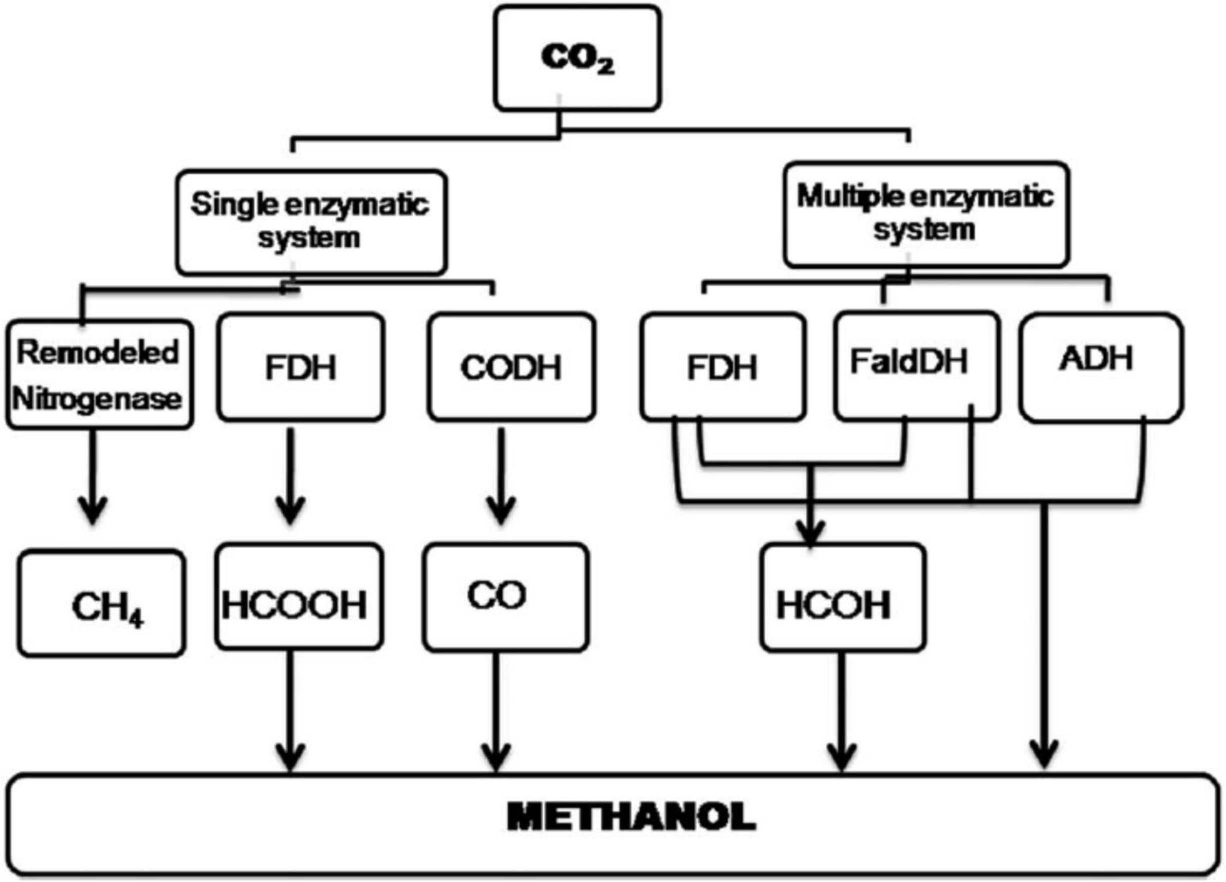


FIGURE 1 | A simplistic representation of microalgal based biorefinery system.

https://www.frontiersin.org/journals/marine-science/articles/10.3389/fmars.2019.00029/full

CO_2 Enzymatic Reduction - Biocatalysis

Formate dehydrogenase (FDH)	CO_2 + NADH ⟷ HCOOH + NAD^+, FDH
Formaldehyde dehydrogenase (FaldDH)	HCOOH/HCOO + NADH ⟷ HCOH + NAD^+, FaldDH
Alcohol dehydrogenase (ADH)	HCOH + NADH ⟷ CH_3OH + NAD^+, ADH



- Highly selective
- NAD+ regeneration
- Enzyme cost
- Stability

RSC Adv., 2016, 6, 44170–44194

CO_2 Capture and Sequestration

Carbon Capture and Storage (CCS) is a technology that can capture up to 90% of the carbon dioxide (CO_2) emissions produced from the use of fossil fuels in electricity generation and industrial processes, preventing the CO_2 from entering the atmosphere.

Carbon, Capture and Storage (CCS) could be a useful technology for tackling climate change if it can be delivered in an affordable way.

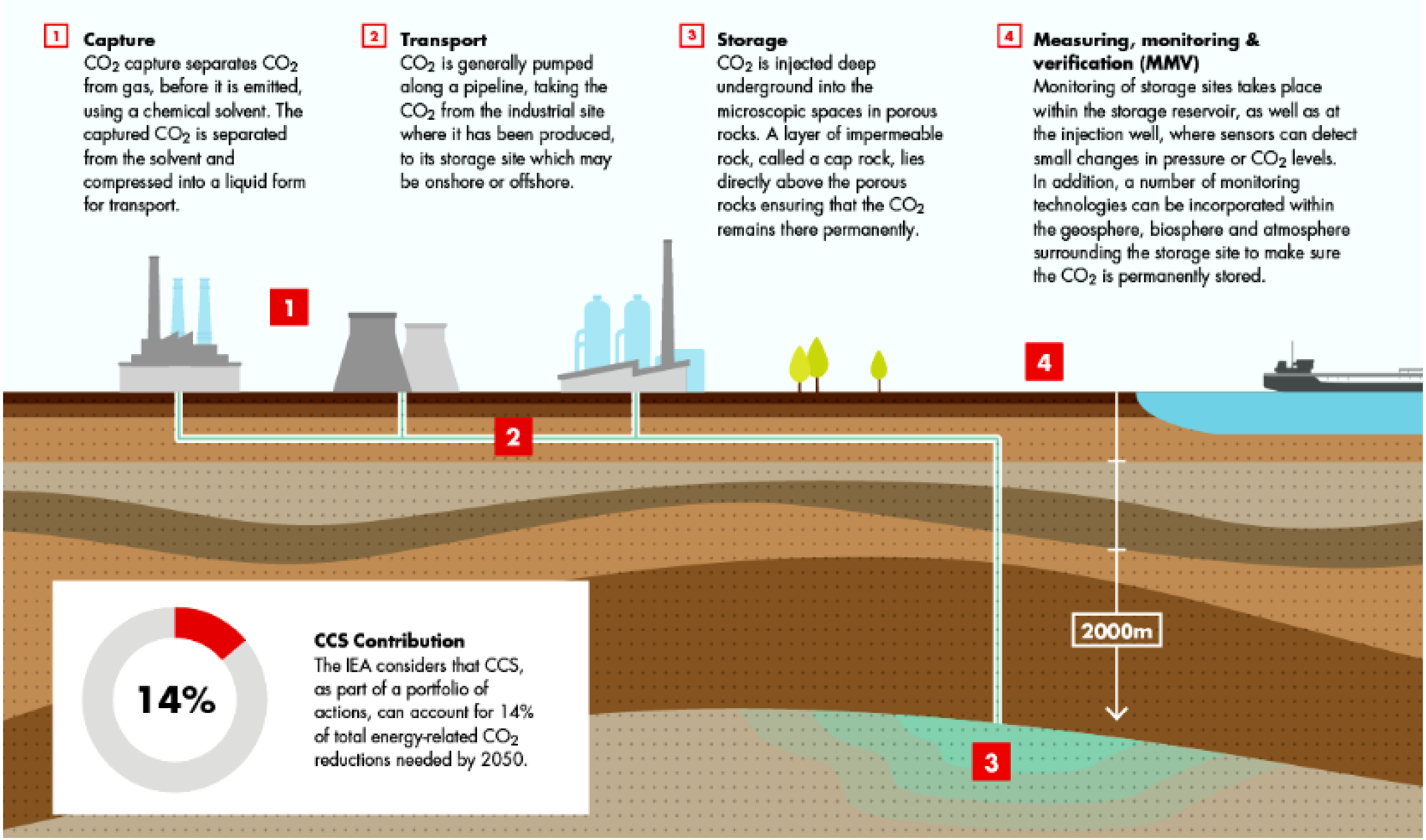
CCS is one of a suite of technologies that will all be required to combat climate change, including renewables, nuclear and energy efficiency. The importance of CCS as one of the tools against global warming is highlighted in a report by the International Energy Agency, which found that CCS could contribute to a 19% reduction in global CO_2 emissions by 2050, and that fighting climate change could cost over 70% more without CCS.

CCS can be applied to fossil fuel-fuelled electricity generating plant, such as coal or gas fired power stations. Fossil fuel plants with CCS have a key role to play in providing a balanced energy supply, which can cope with rapid changes in demand, and intermittency of supply, which nuclear and renewables cannot. CCS will play a key role in the UK to provide secure, affordable, low carbon electricity in the transition to a low-carbon economy.

CCS can also significantly reduce emissions from industry such as cement, steel and chemical industries, and in many instances, is the only currently viable technology to do so. CCS when combined with biomass can result in negative CO_2 emissions. As plants grow, they absorb CO_2 from the atmosphere. When they are burnt to produce power, if the CO_2 is captured and stored there is a net reduction in CO_2 in the atmosphere.

http://www.change-climate.com/Climate_Change.htm

CO_2 Capture and Sequestration



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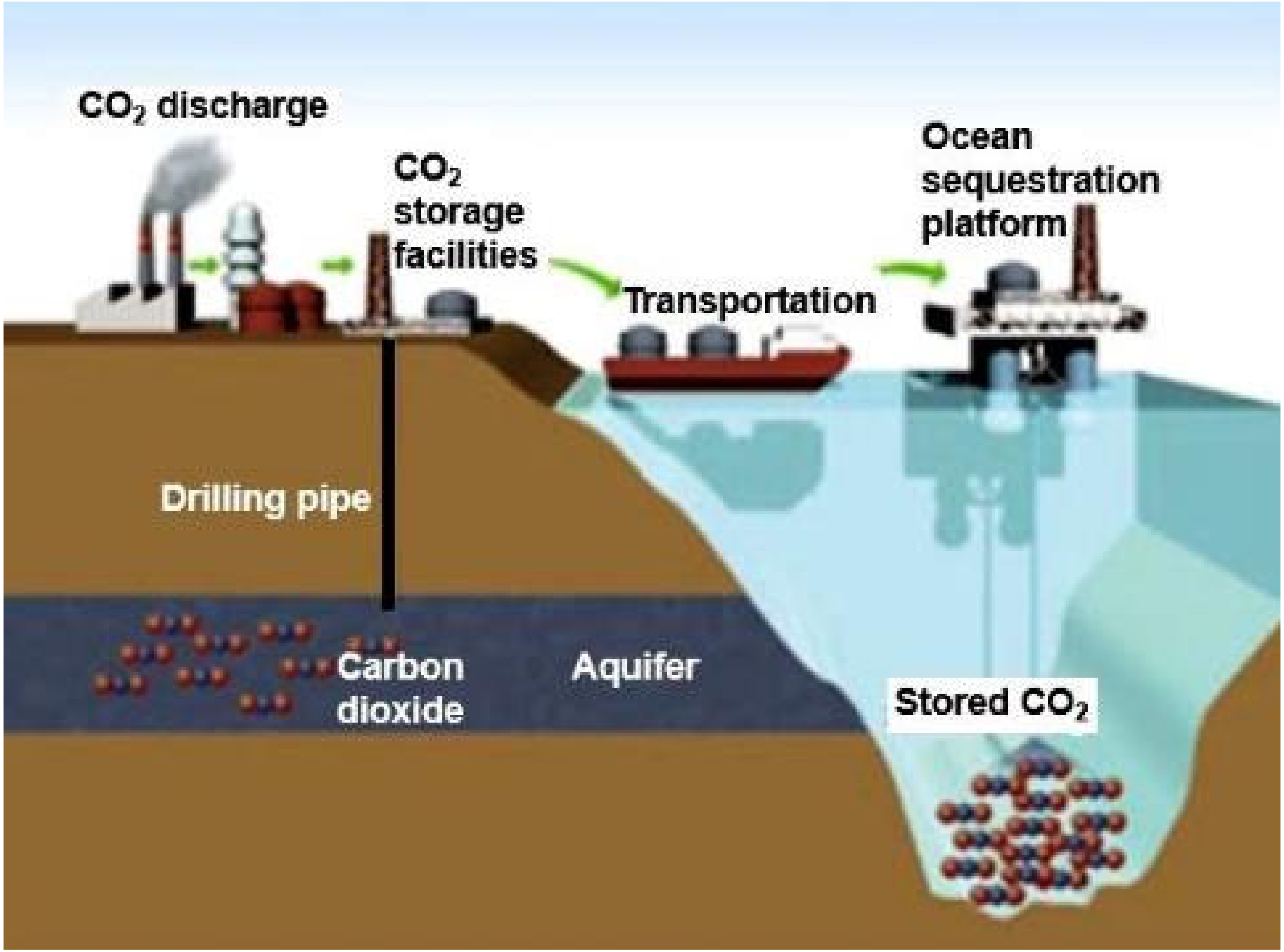
http://www.change-climate.com/Climate_Change.htm

CO_2 sequestration in Oceans



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http://www.change-climate.com/Climate_Change.htm

Complexity of CO_2 Photochemical Reduction

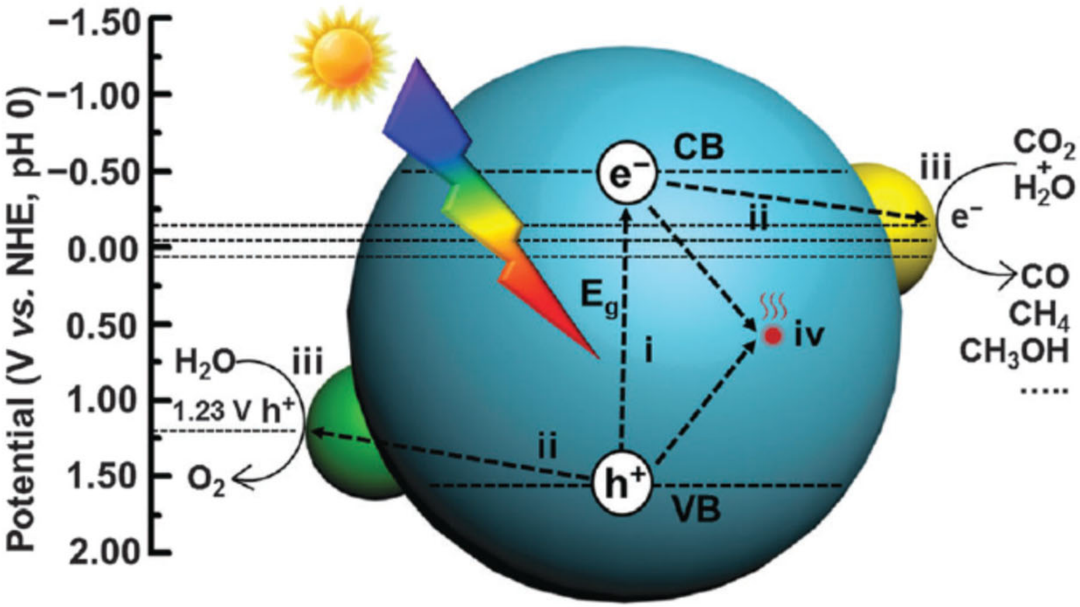
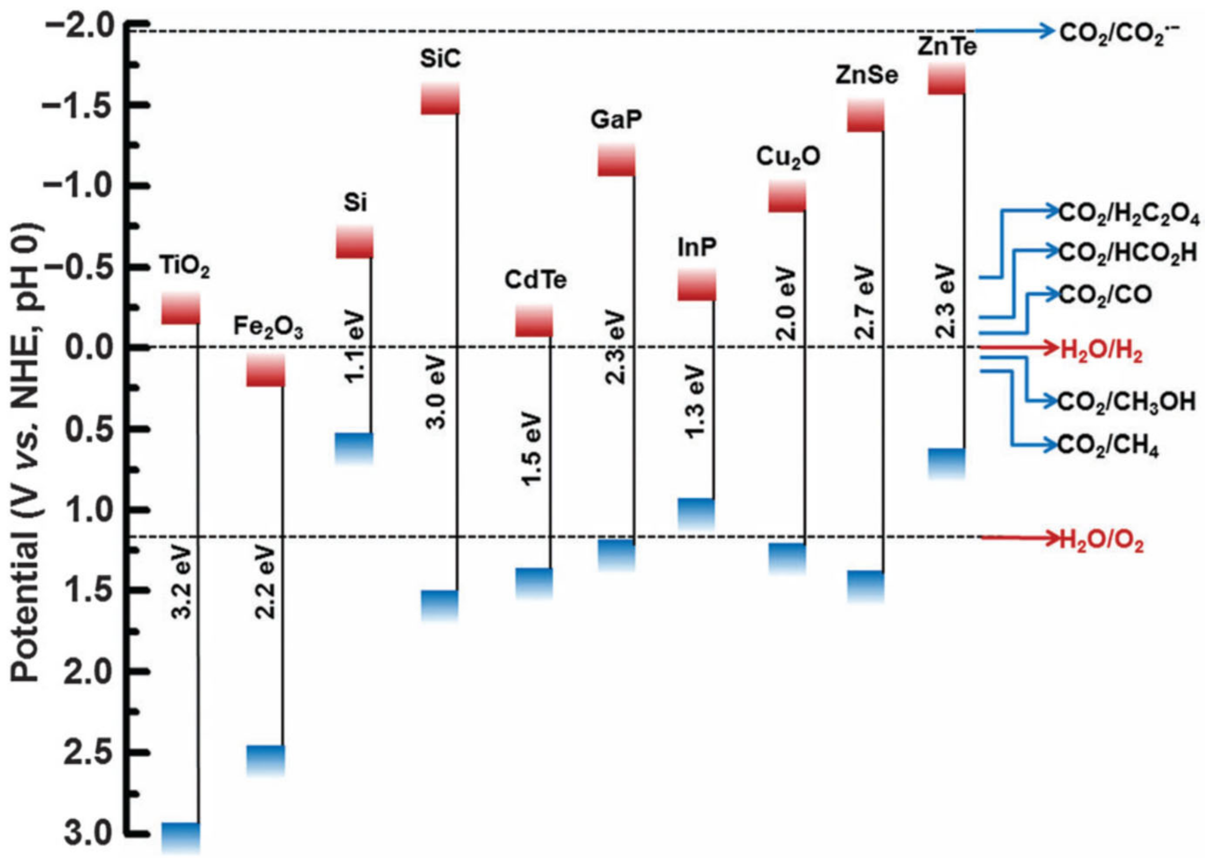


Table 1 The main products of CO_2 and water reduction and the corresponding reduction potentials with reference to NHE at pH 7 in aqueous solution, 25 °C and 1 atm gas pressure[7]

Product	Reaction	E^0 (V *vs.* NHE)	Equation
Hydrogen	$2H_2O + 2e^- \rightarrow 2OH^- + H_2$	−0.41	(1)
Methane	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.24	(2)
Carbon monoxide	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.51	(3)
Methanol	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.39	(4)
Formic acid	$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.58	(5)
Ethane	$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−0.27	(6)
Ethanol	$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.33	(7)
Oxalate	$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.87	(8)

Energy Environ. Sci., 2016, 9, 2177--2196

Complexity of CO_2 Photochemical Reduction



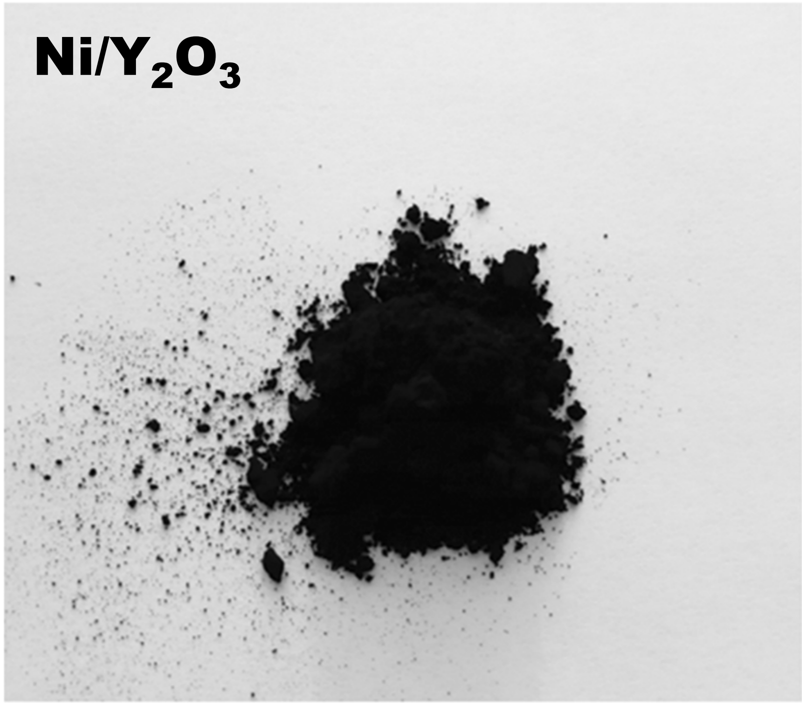
- **The process is overall complex and not selective**
- **Competition with HER**
- **Low energy conversion efficiency**
- **Catalyst dependent process (cost, chemical nature, stability….)**
- **Separation of the products**

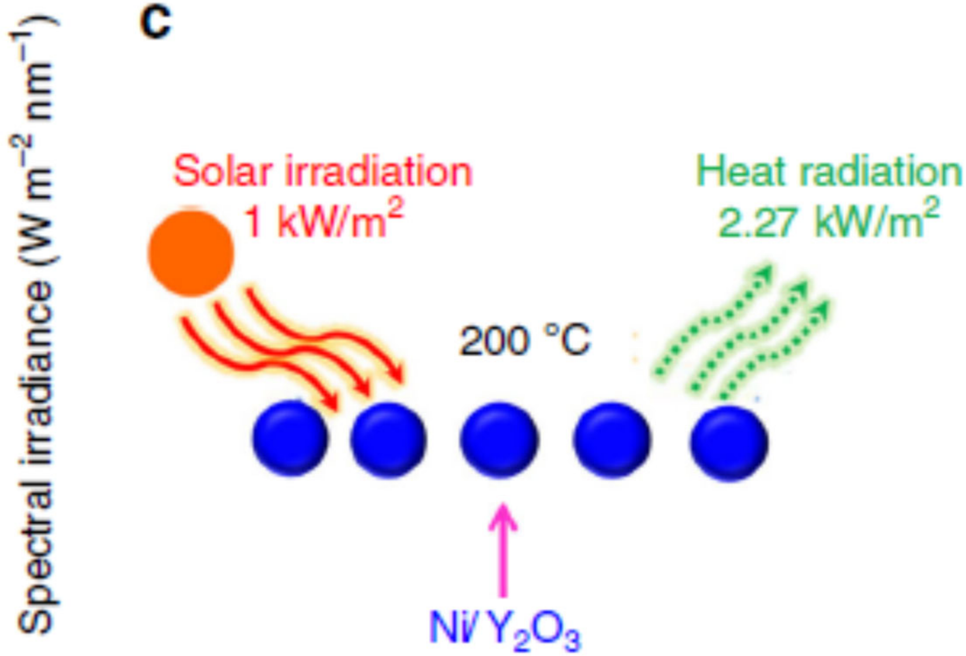
Energy Environ. Sci., 2016, 9, 2177--2196

Plasmon-enhanced (Photothermal) CO_2 Reduction Reaction

Example: CO_2 methanation

Solar-driven CO_2 methanation via a photothermal effect represents a promising strategy to produce CH_4 without secondary energy input.
However, intense light irradiation (more than 10 kWm^{-2}, equal to ten times the standard intensity of solar light) must be provided to heat the catalysts to 200 °C to drive the CO_2 methanation

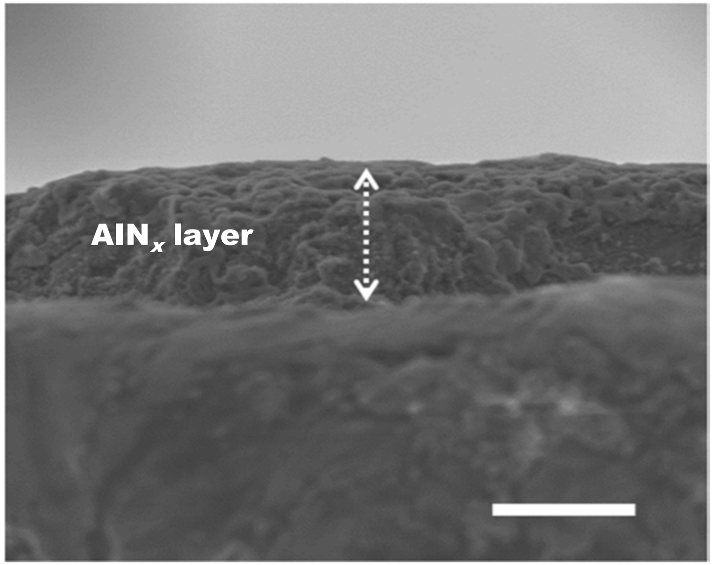


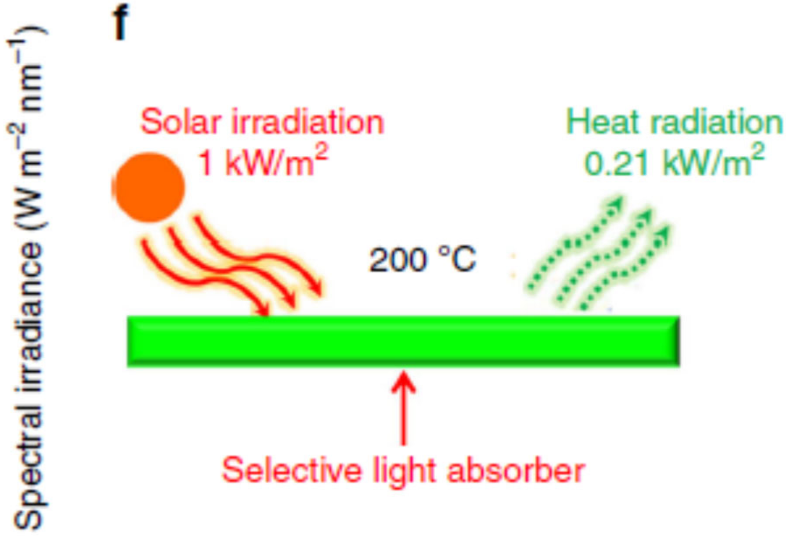


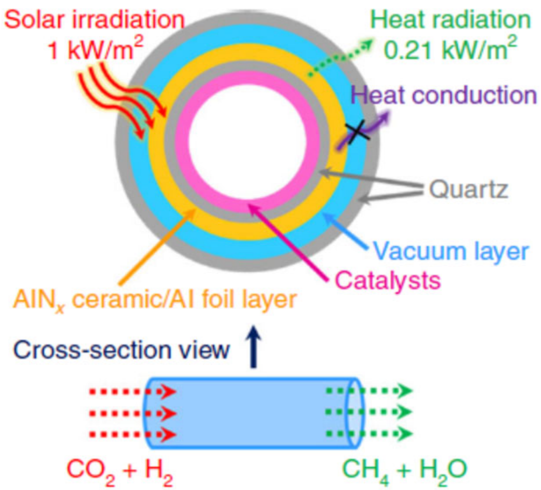
Nature Commun. 2019, 10, 2359

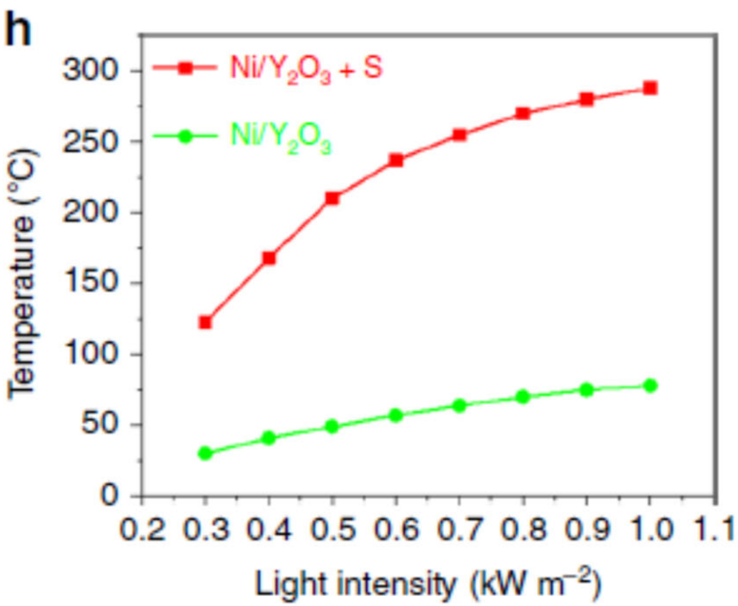
Plasmon-enhanced (Photothermal) CO_2 Reduction Reaction

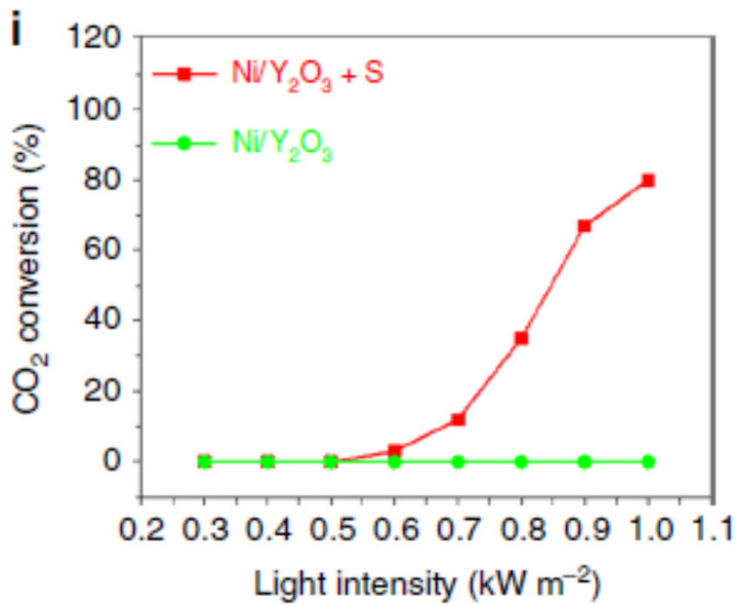
Example: CO_2 methanation











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Nature Commun. 2019, 10, 2359

CO_2 Methanation

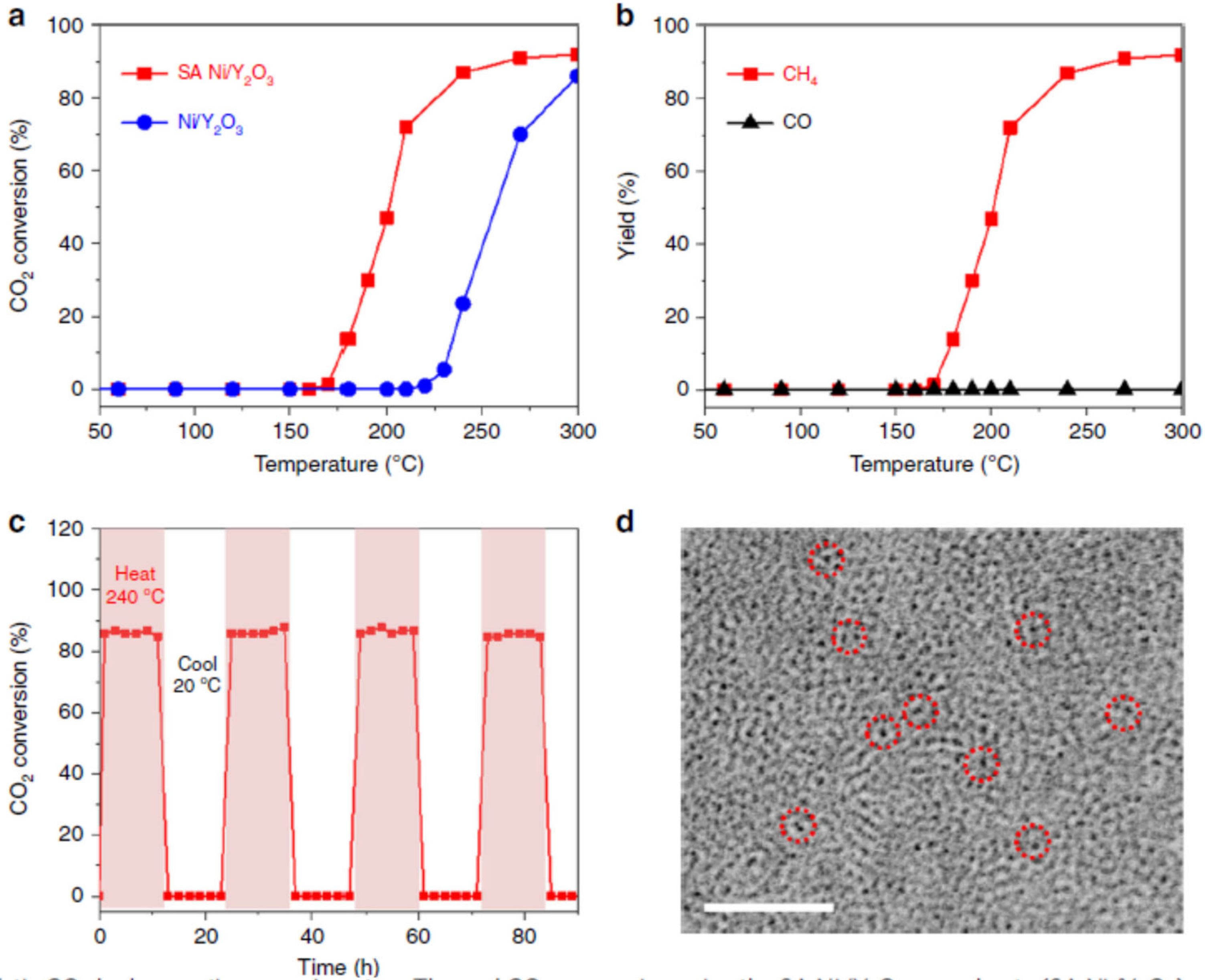
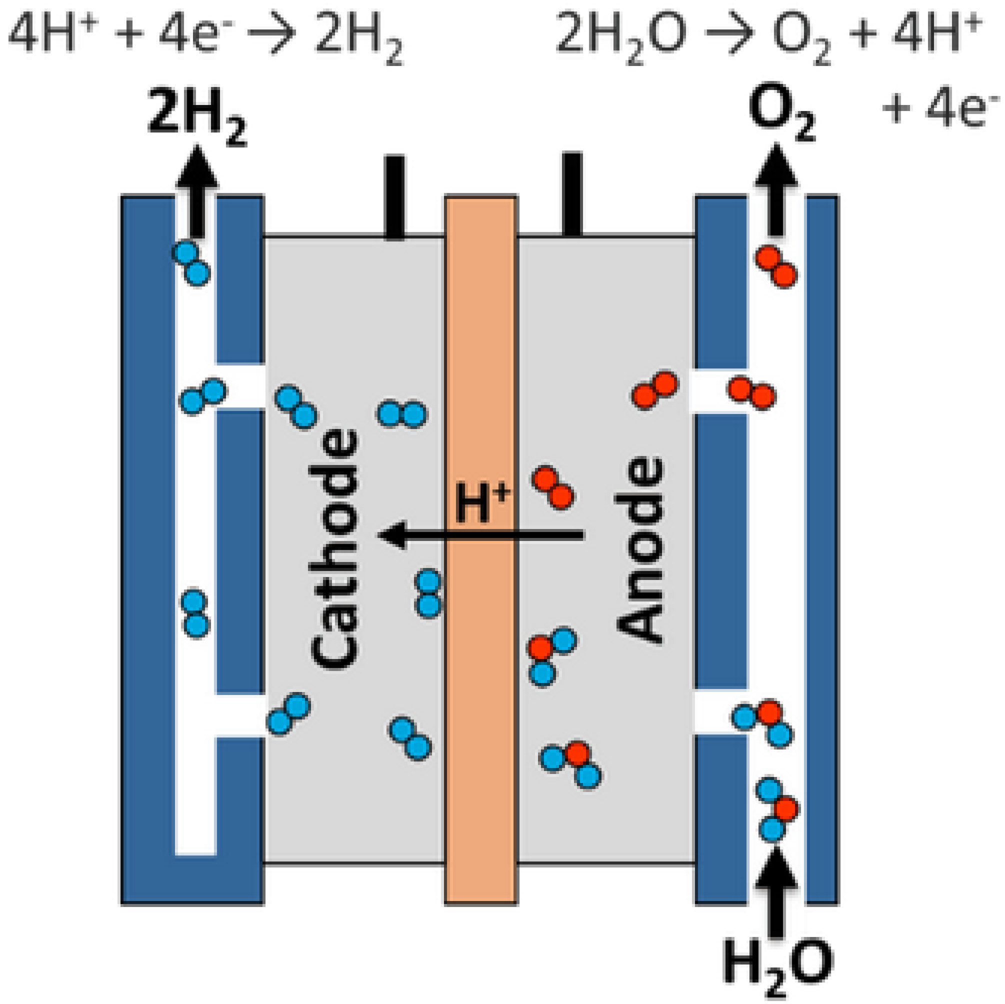


Fig. 4 Thermocatalytic CO_2 hydrogenation experiments. **a** Thermal CO_2 conversion using the SA Ni/Y_2O_3 nanosheets (SA Ni/Y_2O_3) and Ni nanoparticles/Y_2O_3 nanosheets (Ni/Y_2O_3) as a function of temperature. **b** CH_4 and CO yields from the CO_2 hydrogenation over the SA Ni/Y_2O_3 nanosheets as a function of temperature. **c** CO_2 hydrogenation versus reaction time over the SA Ni/Y_2O_3 nanosheets at 240 °C. **d** Aberration-corrected TEM image of the SA Ni/Y_2O_3 nanosheets after the stability test shown in Fig. 4c. Reaction conditions: 100 ml min^{-1} of reaction gas (2.5% CO_2 + 10% H_2 + 87.5% N_2), 100 mg of catalyst. The scale bar in **d** is 2 nm

Nature Commun. 2019, 10, 2359

CO_2 Electrochemical Reduction Reaction

Pt/C

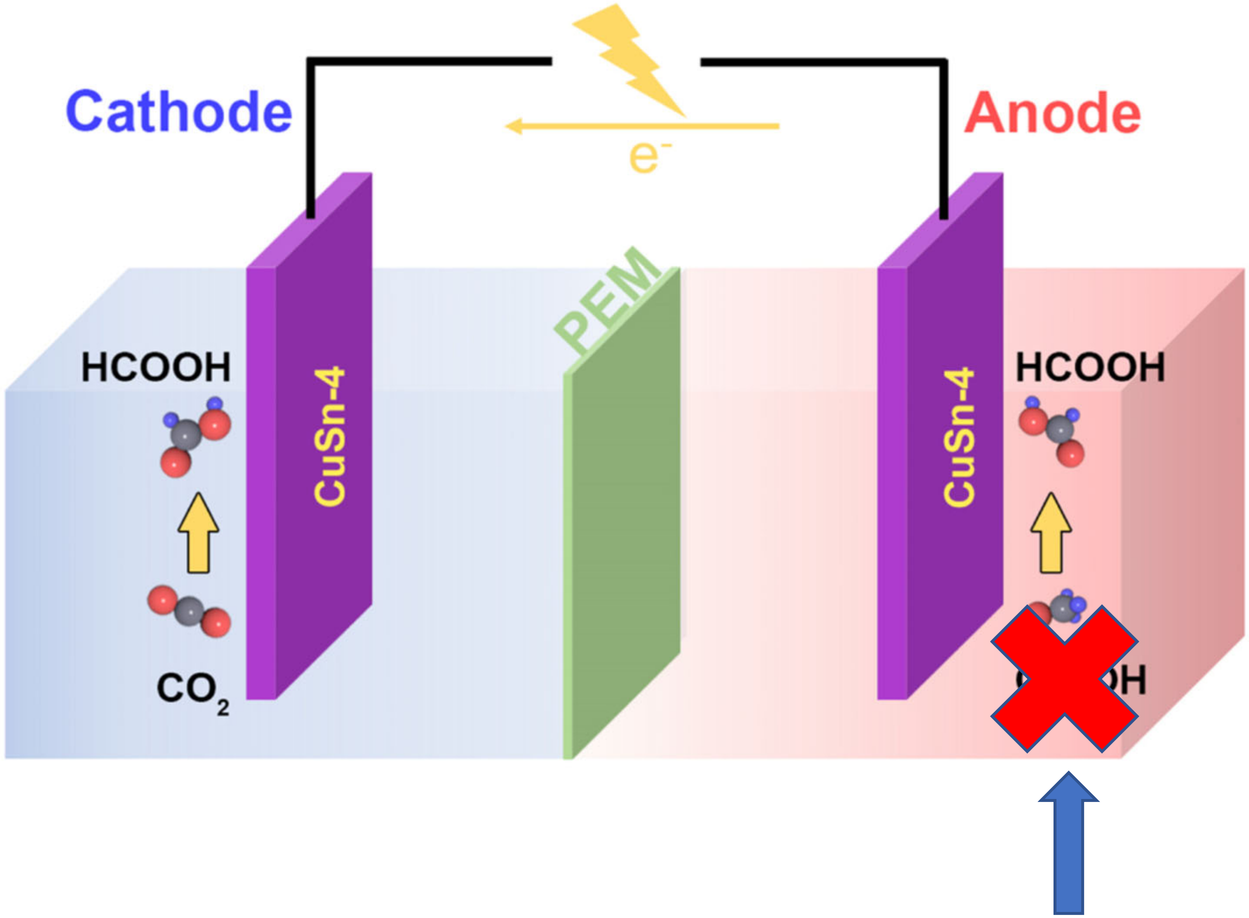


IrO_x/RuO_x

- Expensive
- Scarce
- Lack of bifunctionality

https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis

Concurrence Production of the Same Fuel at Both Cathode and Anode



Precursors from various wastes

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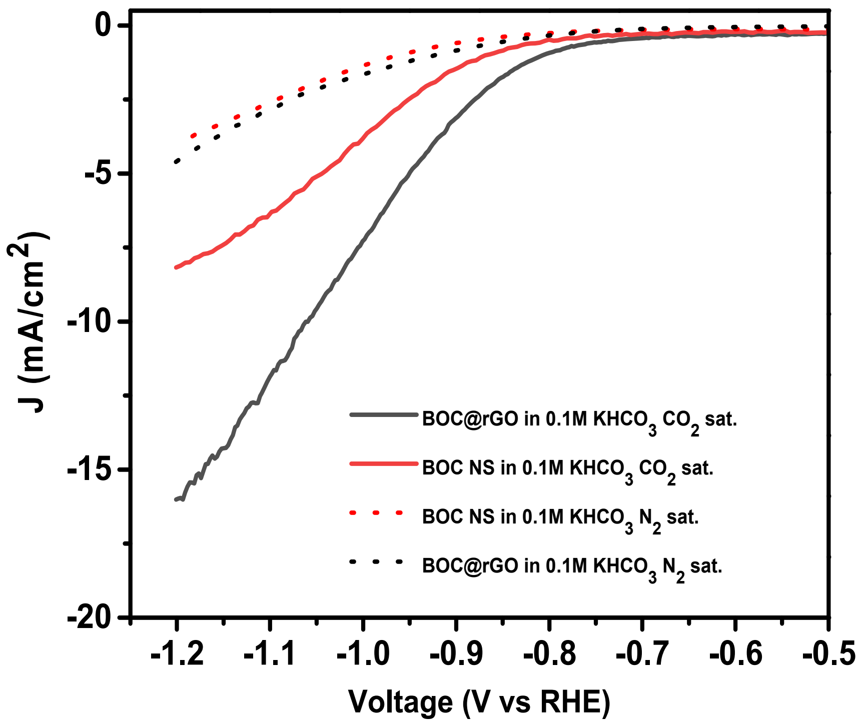
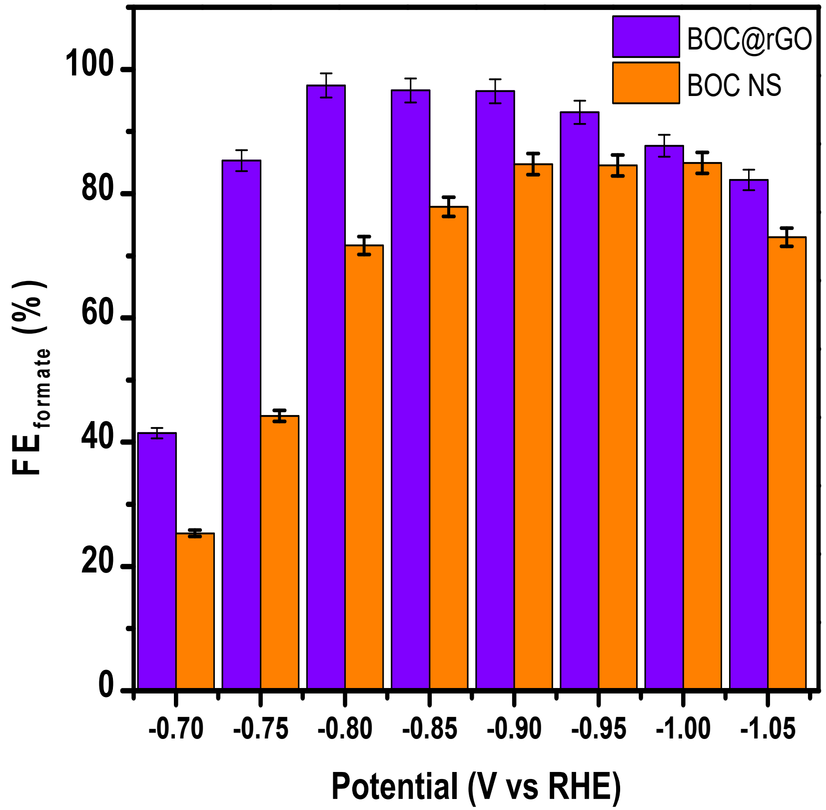
Possible Pathways for CO_2 Electrochemical Reduction Reaction – Selected Standard Potentials of CO_2 in aqueous solutions (V *vs.* SHE) at 1.0 atm and 25°C.

Reaction	E^0/V (*vs.* SHE)	Number
$CO_2 + e^- \rightarrow CO_2^{-\bullet}$	−1.90	1
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	−0.530	2
$CO_2 + 2H_2O + 2e^- \rightarrow CO + 2OH^-$	−1.347	3
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−0.610	4
$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$	−1.491	5
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	−0.480	6
$CO_2 + 3H_2O + 4e^- \rightarrow HCHO + 4OH^-$	−1.311	7
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−0.380	8
$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^-$	−1.225	9
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−0.240	10
$CO_2 + 6H_2O + 8e^- \rightarrow CH_4 + 8OH^-$	−1.072	11
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	−0.200	12
$CO_2 + 2H_2O + 4e^- \rightarrow C + 4OH^-$	−1.040	13
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−0.340	14
$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-$	−1.177	15
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−0.270	16
$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	−0.913	17
$2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$	−1.003	18
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−0.330	19
$2CO_2 + 9H_2O + 12e^- \rightarrow C_2H_5OH + 12OH^-$	−1.157	20
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	−0.320	21
$2H^+ + 2e^- \rightarrow H_2$	−0.420	22

Chem. Soc. Rev., 2021, 50, 4993-5061

Selected electrochemical CO_2 reduction to Formate





BOC@rGO LSV plots in CO_2 sat. solution show an onset potential of -0.64 V vs. RHE, increasing to -16 mA/cm^2 at -1.2V *vs.* RHE. Without CO_2, HER dominates as the cathodic process, with lower current density.

- Faradaic efficiency measurements were calculated using data from ^{1}H NMR and charge obtained from the CPE plots.
- Highest formate FE of 97.4% was achieved at -0.8V *vs.* RHE.

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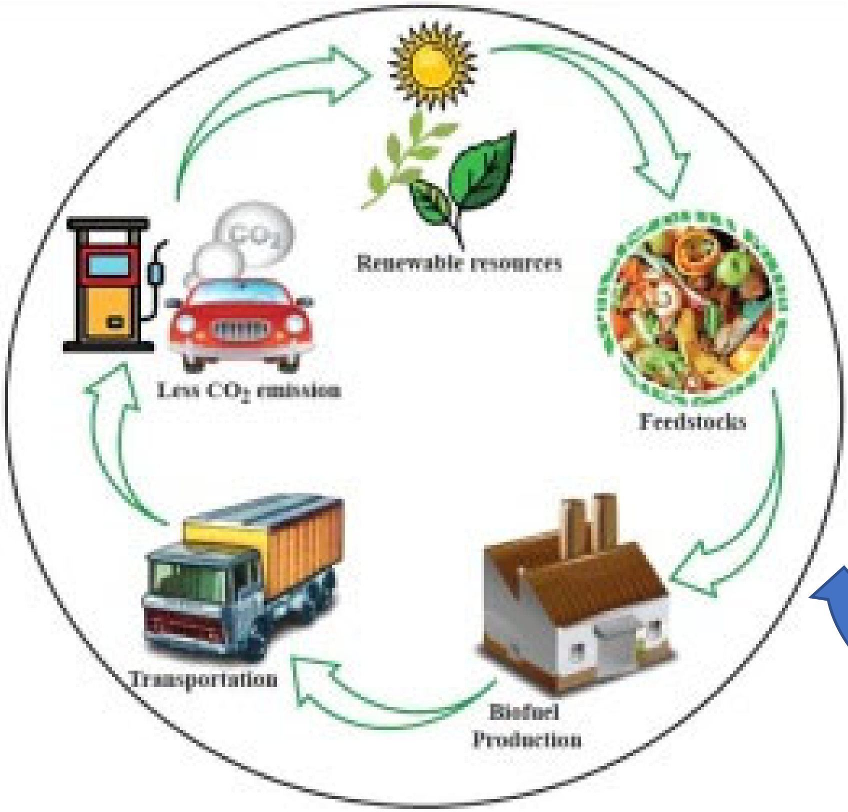
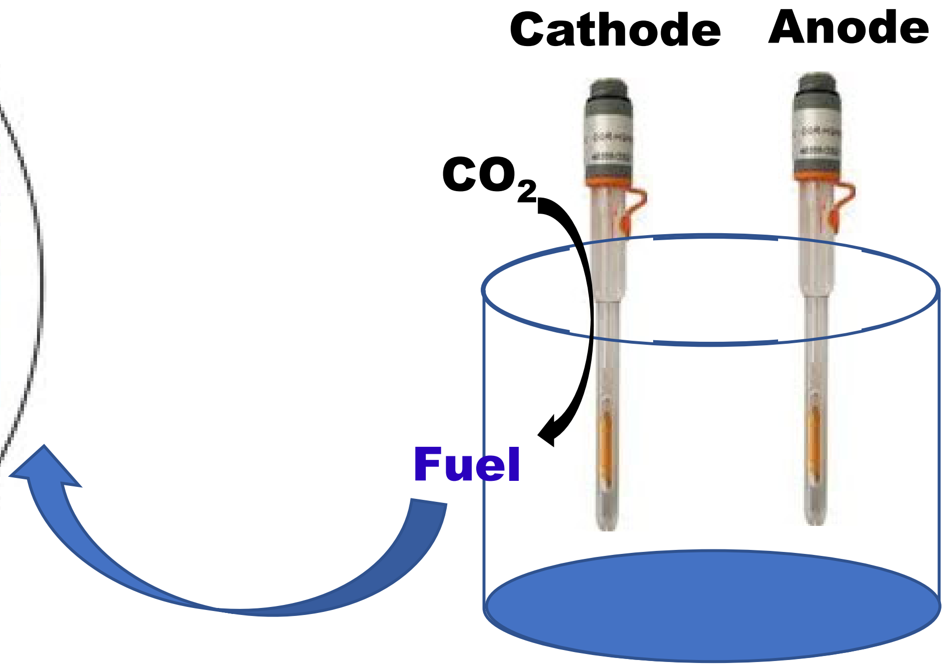
Combination of bio- and electrocatalytic processes



https://www.sciencedirect.com/science/article/pii/S2590174520300428



https://www.origalys.co.uk/origasens-reference-electrode-hg-hgo-c2x19681514

Pros and Cons

CO_2 capture methods
- Membrane separation
- Chemical adsorption
- Physical adsorption

→

Mature technology
High cost and/or large energy consumption
Eventual CO_2 release

CO_2 storage/sequestration
- Geological
- Marine

→

Huge amounts of CO_2 sequestration
Absence of data on impact on land and sea organisms (pH change) and eventual CO_2 release in the atmosphere

CO_2 reduction
- Photochemical
- Electrochemical
- Biological
- Combination of the above techniques

→

Easy to implement
Environmentally friendly techniques
Use of solar energy (photochemical)
Can potentially alleviate both energy crisis and environmental problems
Low efficiencies
High overpotentials (electrochemical)
Competition with HER (electrochemical)
Low product selectivity
High cost (bioelectrocatalysis)

SIX IMPORTANT CHANGES TO COOL THE PLANET

1. TRANSPORT: Phase out polluting vehicles. Government aims to end the sale of new petrol, and diesel vehicles by 2040 but have no infrastructure plan to support such ambition. Marine transport can be carbon neutral.

2. RENEWABLES: Renewable energy should replace carbon-based fuels (coal, oil and gas) in our electricity, heating and transport. Conventional energy exploration companies should consider a phased transition to green alternatives.

3. HOUSING: On site micro or macro generation is the best option, starting with sustainable new homes built of renewable materials that lock carbon and are affordable. Offering planning rights free to encourage eco builds and cut out empire building councils that add significant costs and legal obstacles to hinder progress.

4. AGRICULTURE: We need trees to absorb carbon emissions from a growing population, fossil fueled air travel, and to build new homes. We need to reduce food waste and promote less energy intensive eating habits such as no meat Mondays.

5. INDUSTRY: Factories should be aiming for solar heating and onsite renewable energy generation until the grid is all solar and wind powered.

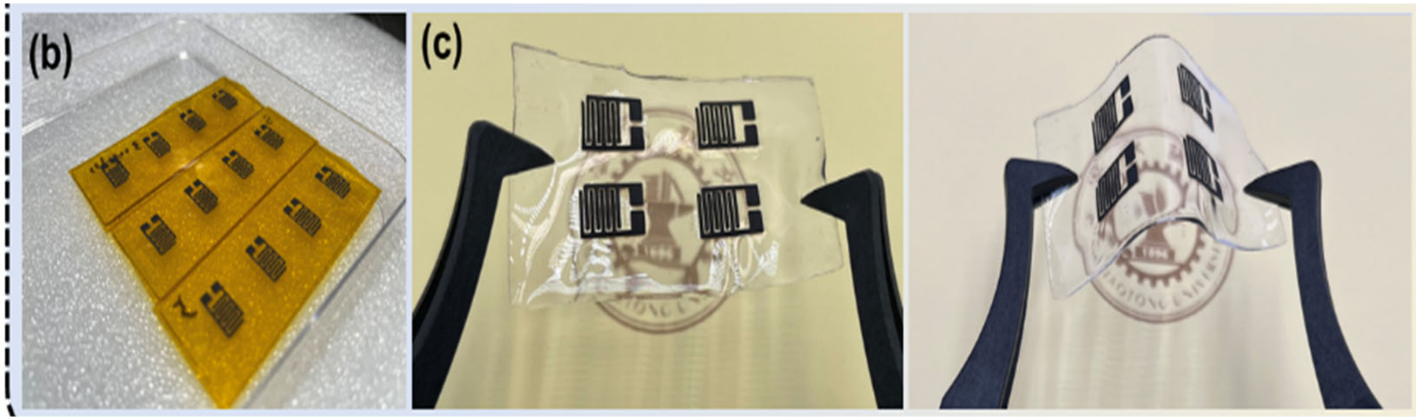
6. POLITICS: National governing bodies need to adopt policies to eliminate administrative wastages, to include scaling down spending on war machines, **increase spend on educating the public and supporting sustainable social policies** that mesh with other cultures. We need an end to local empire building kleptocrats.

WHAT IS A KLEPTOCRAT ?

Kleptocracy is a government with corrupt leaders (kleptocrats) that use their power to exploit the people and natural resources of their own territory in order to extend their personal wealth and political powers. Typically, this system involves embezzlement of funds at the expense of the wider population.

A kleptocracy is a government ruled by corrupt politicians who use their political power to receive kickbacks, bribes, and special favors at the expense of the populace. Kleptocrats may use political leverage to pass laws that enrich them or their constituents and they usually circumvent the rule of law.

Upcycling Commodity Polymers for the Preparation of Added-value Materials and Fuels



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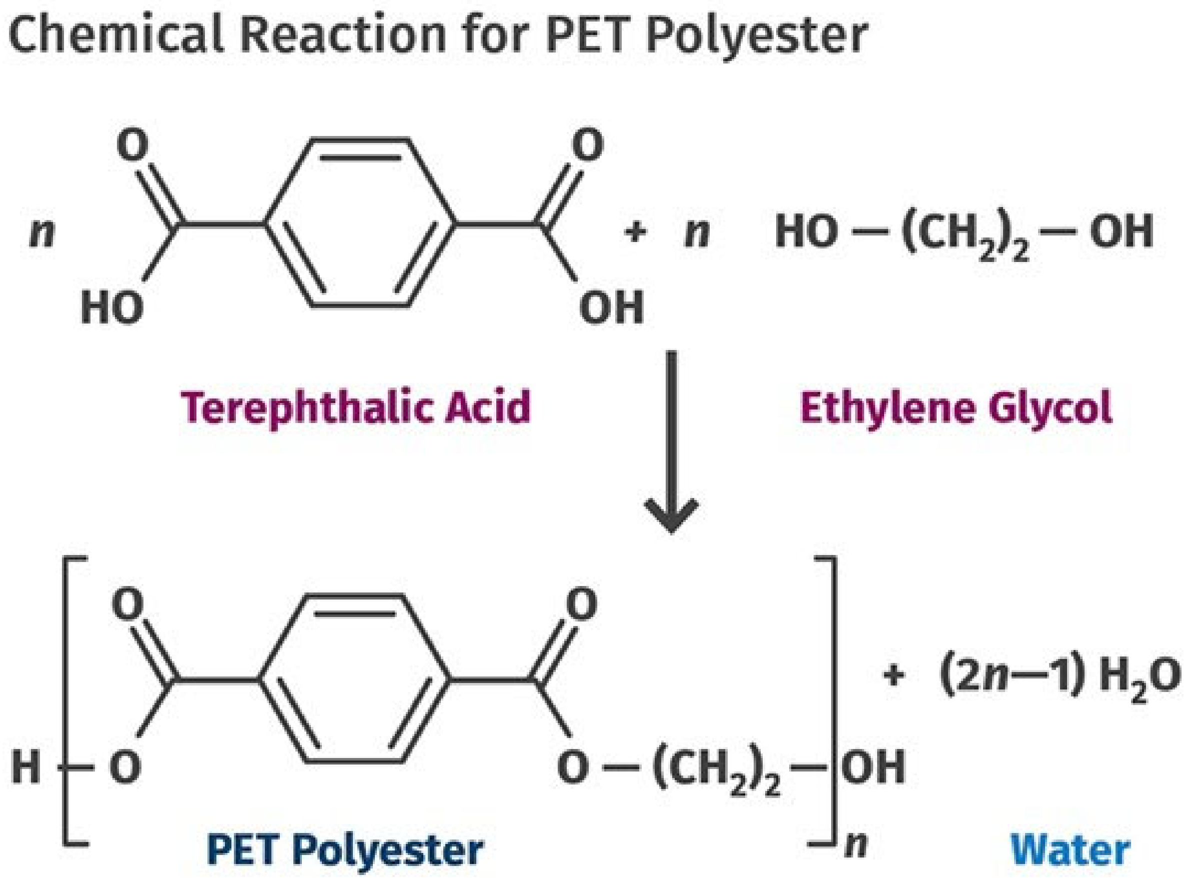
Preparation of Polyethylene terephthalate (PET)



https://men246.wordpress.com/author/men246/

https://www.singh-enterprises.in/product/pet-bottles-transparent/

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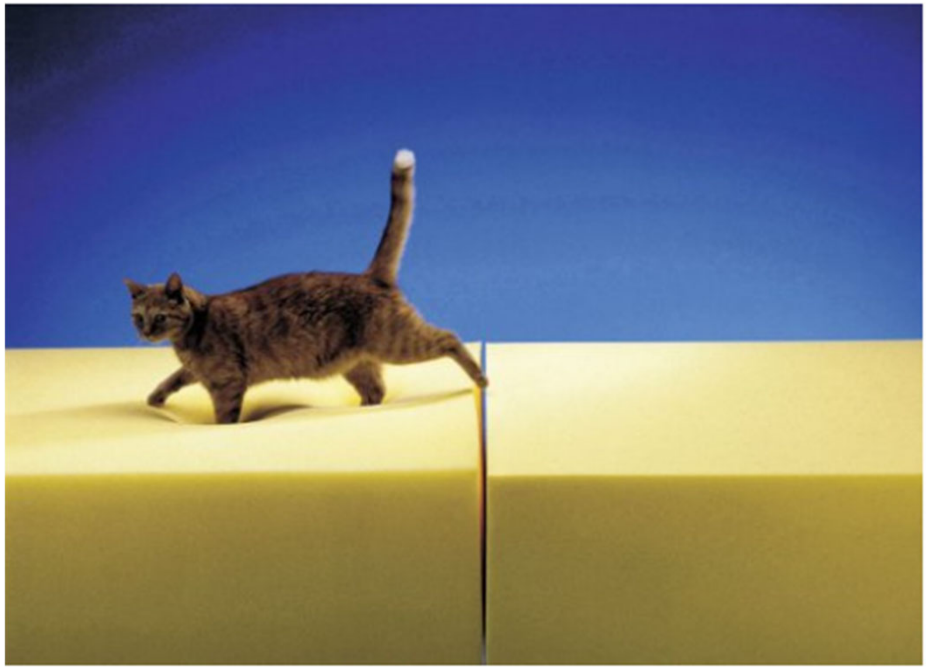
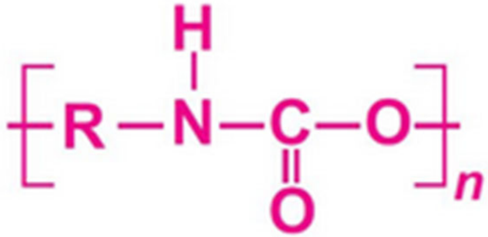
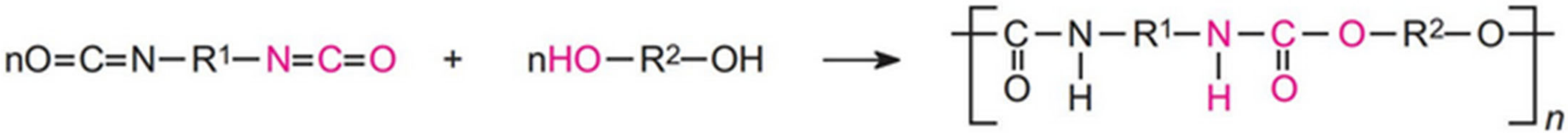
Preparation of Polyurethane (PU)







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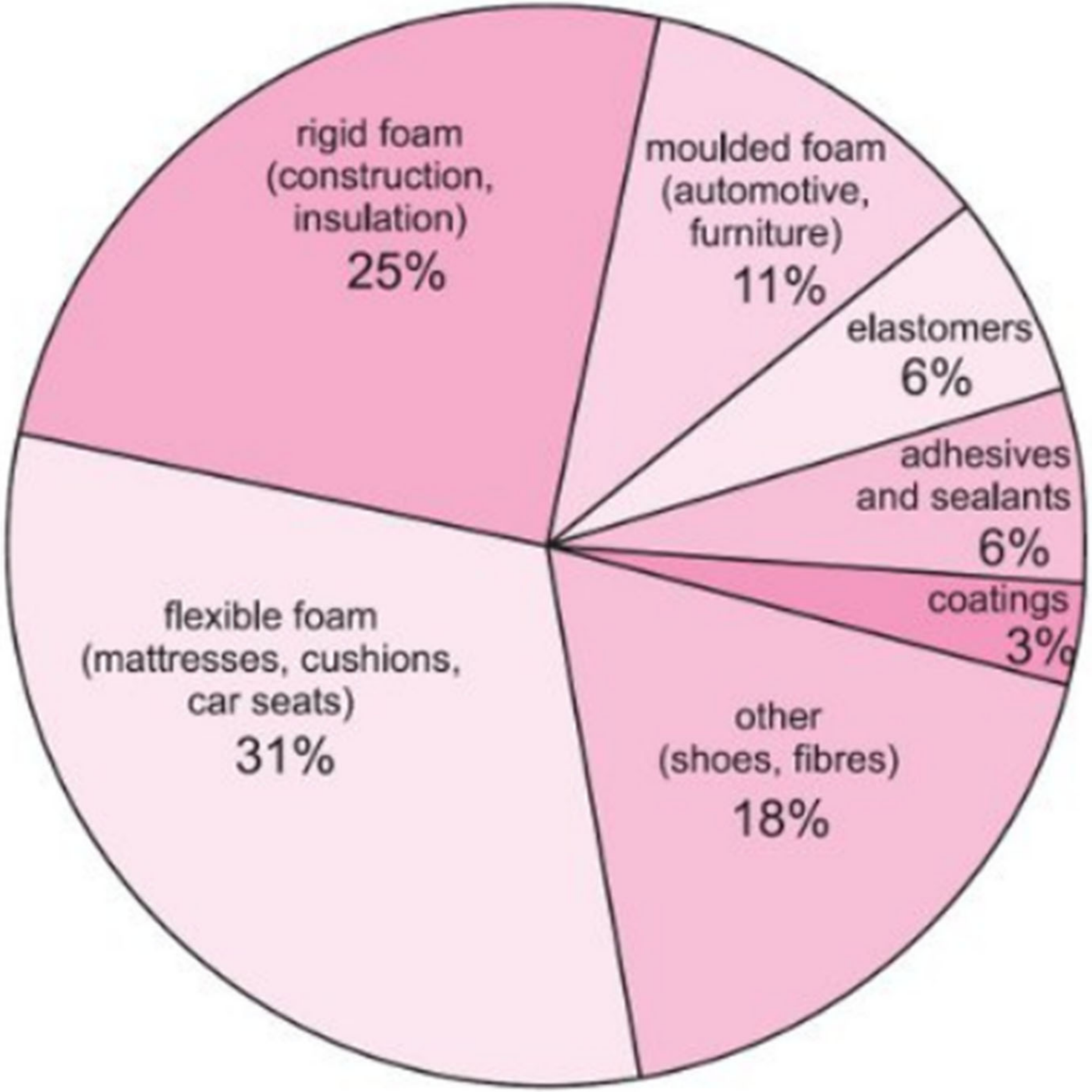
https://www.essentialchemicalindustry.org/polymers/polyurethane.html

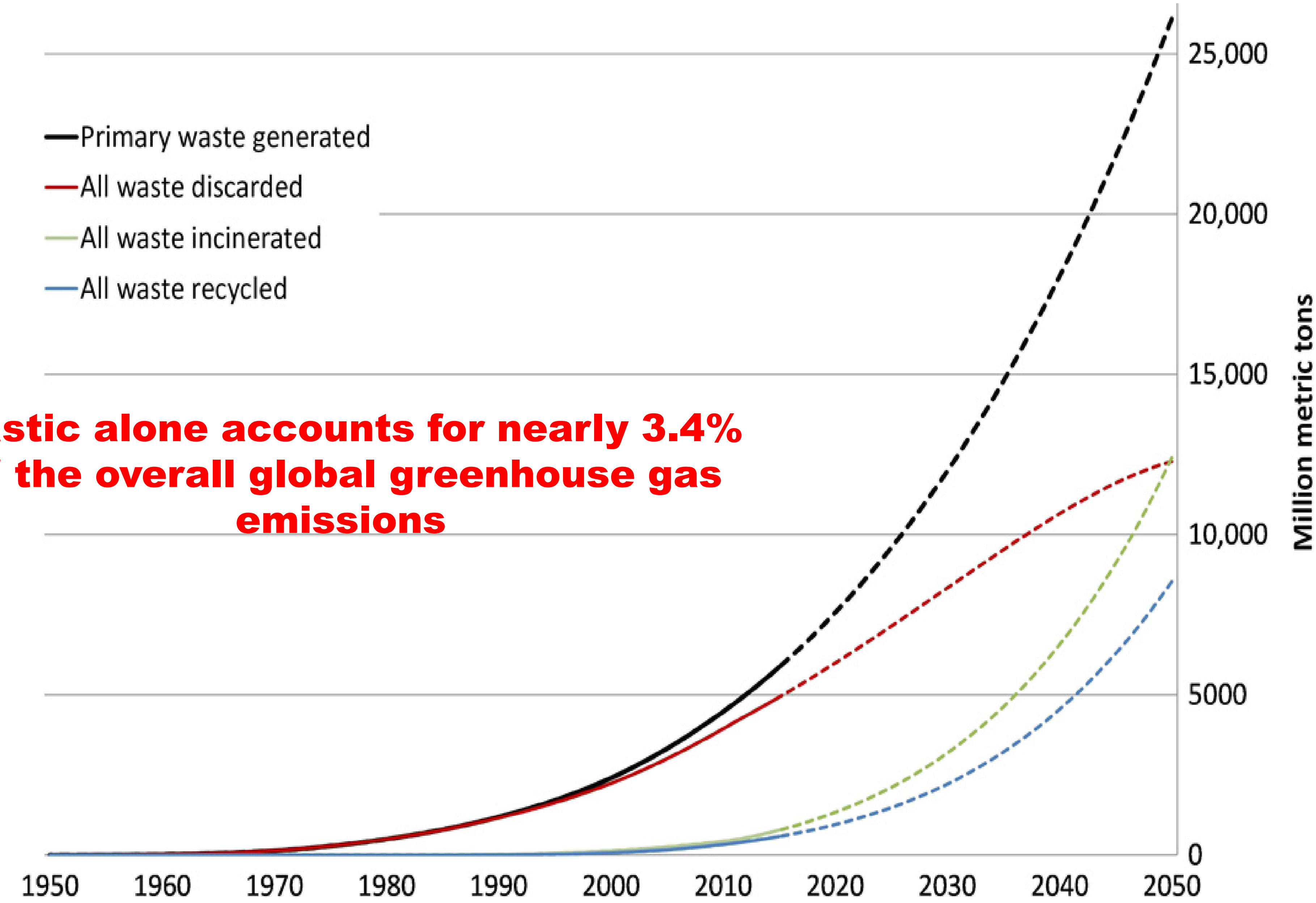
Uses of Polyurethane (PU)



https://www.essentialchemicalindustry.org/polymers/polyurethane.html

Some key facts on plastic waste

plastic alone accounts for nearly 3.4% of the overall global greenhouse gas emissions



Cumulative production and management of plastic waste (measured in million metric tons). The solid lines represent past records spanning from 1950 to 2015, while the dashed lines depict extrapolations of these historical patterns until 2050

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https://www.science.org/doi/10.1126/sciadv.1700782

Plastic Waste Management – Key Facts

• Plastic consumption has **quadrupled** over the past 30 years, driven by growth in emerging markets. Global plastics production doubled from 2000 to 2019 to reach **460 million tonnes**. Plastics account for **3.4% of global greenhouse gas emissions**.

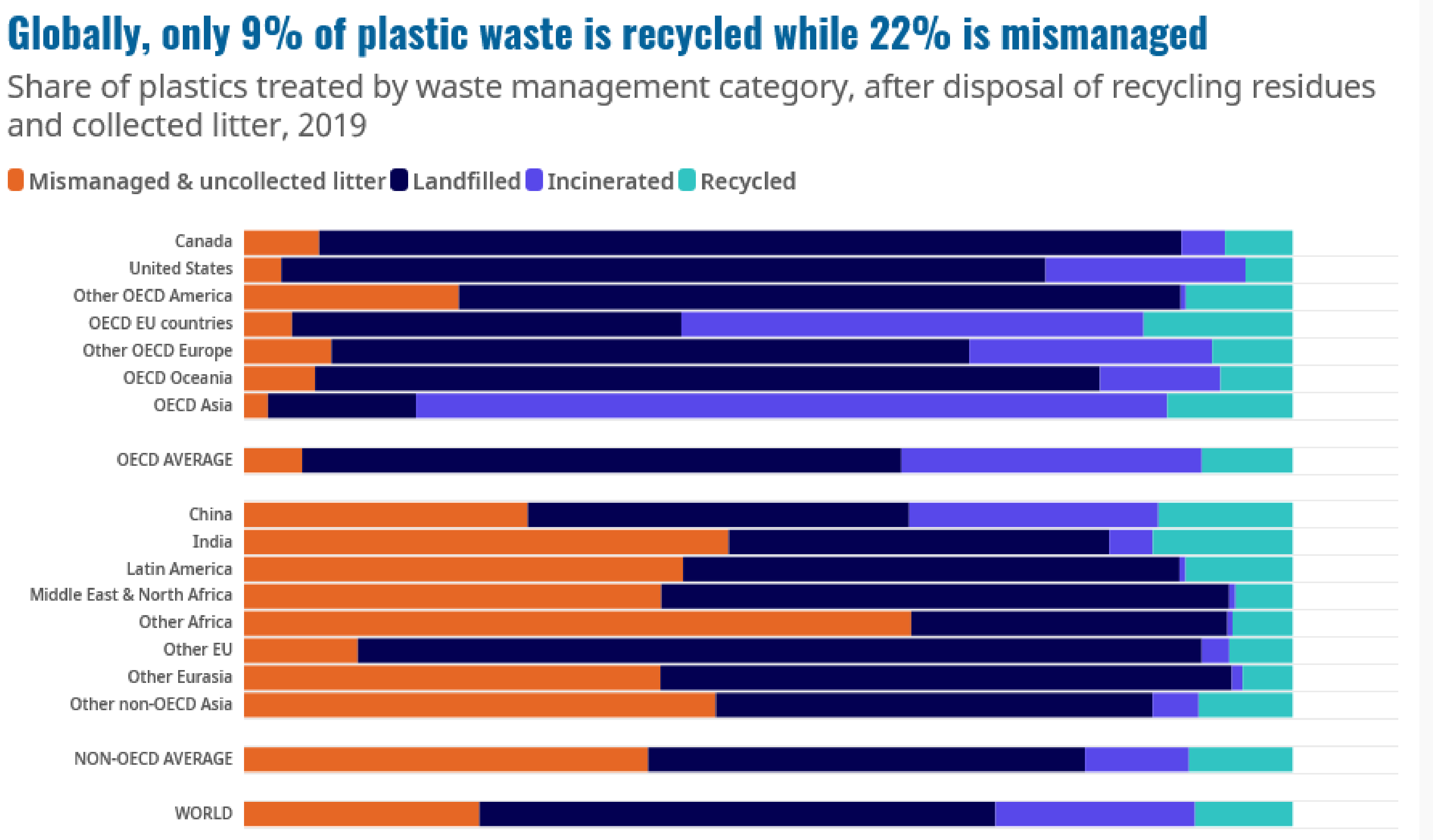
• Global **plastic waste generation** more than **doubled** from 2000 to 2019 to 353 million tons. Nearly two-thirds of plastic waste comes from plastics with lifetimes of **under five years**, with 40% coming from packaging, 12% from consumer goods and 11% from clothing and textiles.

• Only **9% of plastic waste is recycled** (15% is collected for recycling but 40% of that is disposed of as residues). Another **19% is incinerated**, 50% ends up in landfill and **22% evades waste management systems** and goes into uncontrolled **dumpsites**, is burned in open pits or ends up in terrestrial or aquatic environments, especially in poorer countries.

• In 2019, **6.1 million tons (Mt)** of plastic waste **leaked** into **aquatic environments** and 1.7 Mt flowed into oceans. There is now an estimated 30 Mt of plastic waste in seas and oceans, and a further **109 Mt has accumulated in rivers**. The build-up of plastics in rivers implies that leakage into the ocean will continue for decades to come, even if mismanaged plastic waste could be significantly reduced.

Plastic Waste Management – Key Facts

- Considering global value chains and trade in plastics, aligning design approaches and the regulation of chemicals will be key to improving the circularity of plastics. An international approach to waste management should lead to all available sources of financing, including development aid, being mobilized to help low and middle-income countries meet estimated costs of EUR 25 billion a year to improve waste management infrastructure.

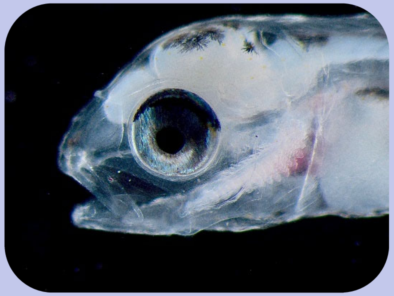


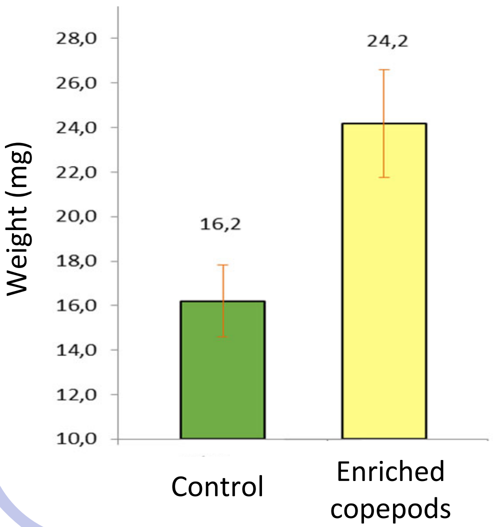
https://www.oecd.org/en/about/news/press-releases/2022/02/plastic-pollution-is-growing-relentlessly-as-waste-management-and-recycling-fall-short.html

BIONAMERIS

FISH FARMING SPECIES

Sea bream *(Sparus aurata)*





50 % growth

15 % survival

15 % length

- 80 % malformations

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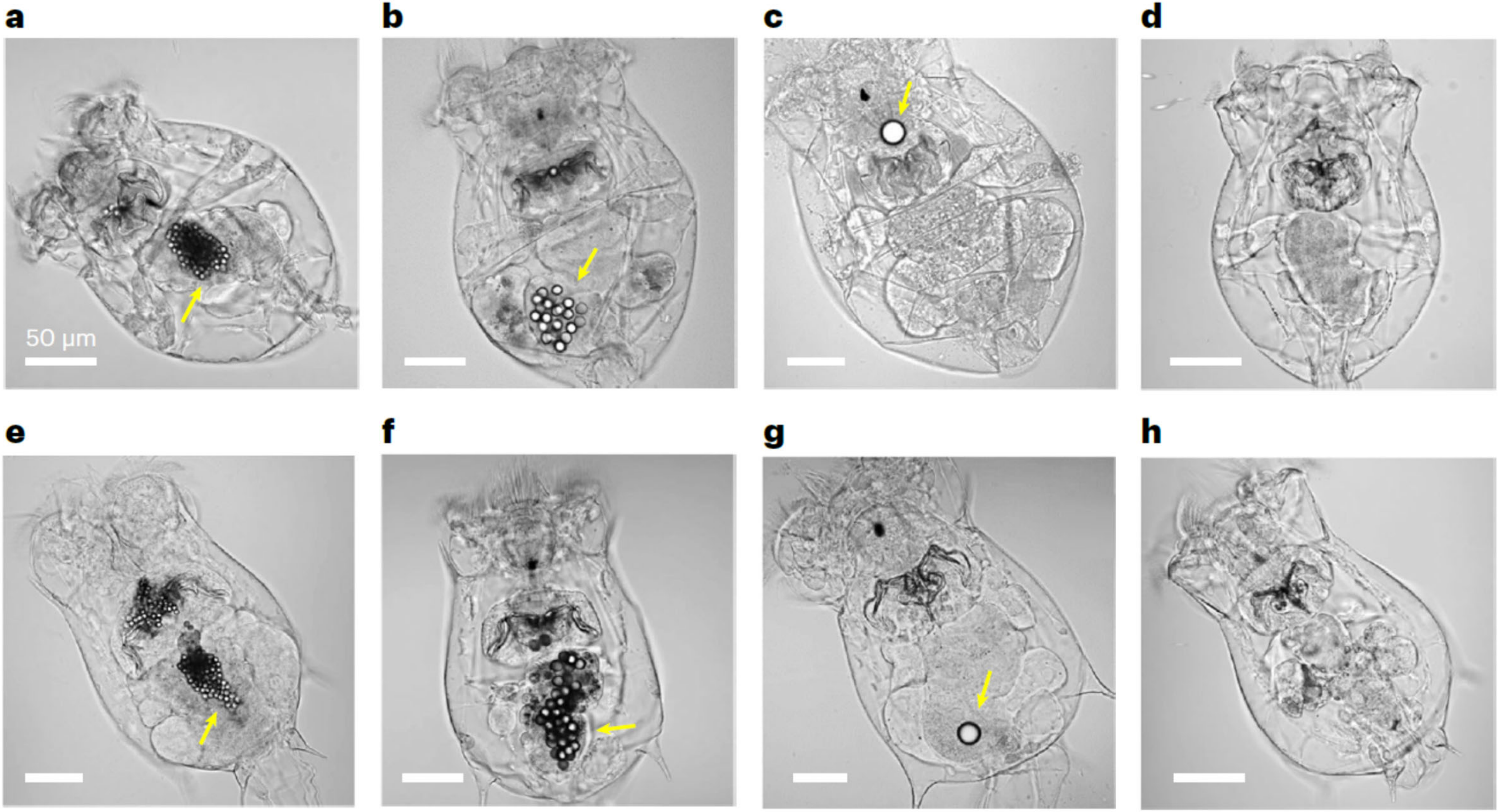
Microplastic fragmentation by rotifers in aquatic ecosystems contributes to global nanoplastic pollution



Ingestion of PS microplastics of different sizes by marine and freshwater rotifers as imaged and counted by optical microscopy. **a–d**, **e–h**, The uptake of microplastics by marine rotifers (a–d) and freshwater rotifers (e–h); the sizes of the exposed PS microplastics were 5 (**a**,**e**), 10 (**b**,**f**), 20 (**c**,**g**) and 30 µm (**d**,**h**). The yellow arrows in **a–c** and **e–g** point to the ingested PS microplastics

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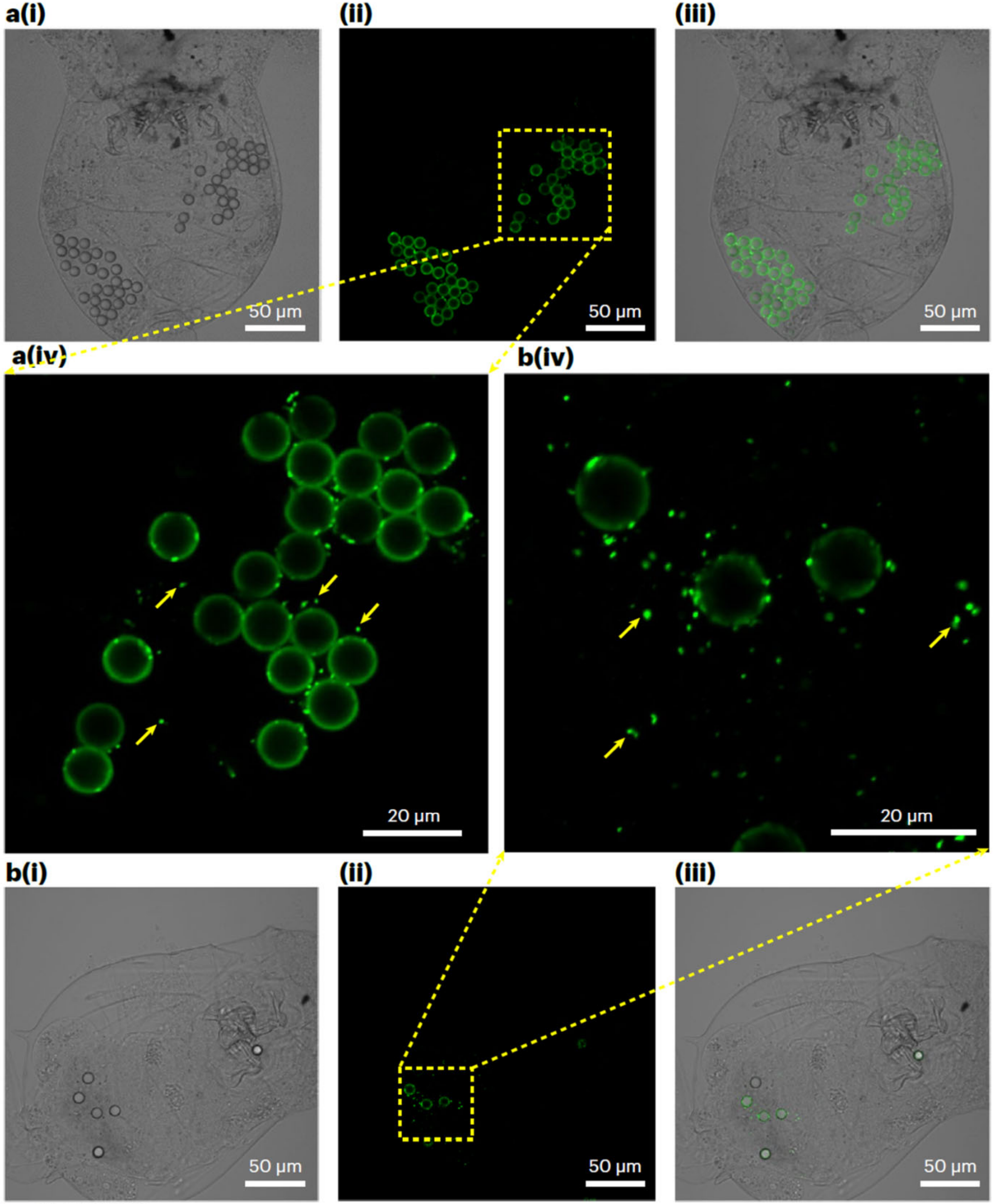
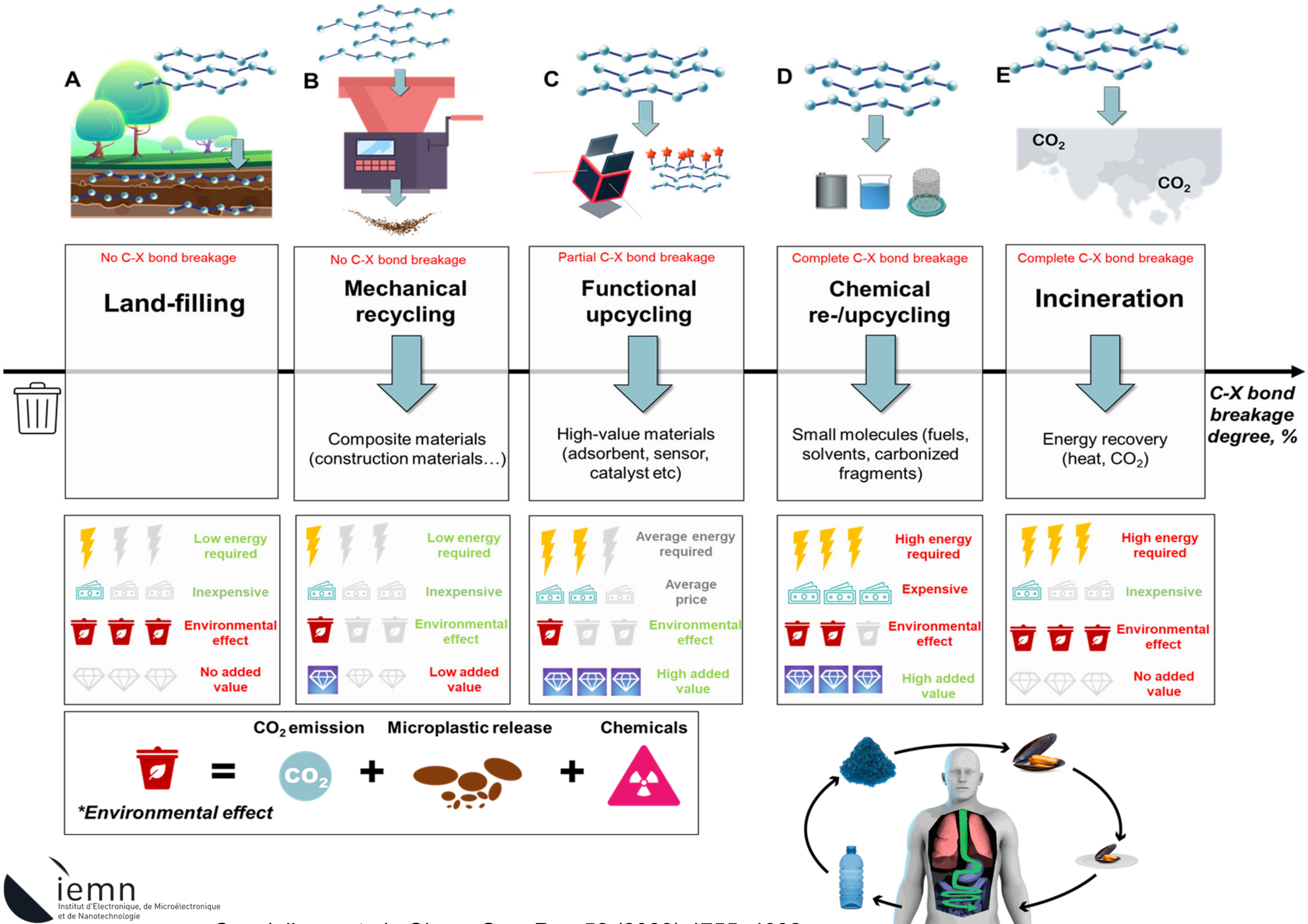
Nature Nanotechnology | Volume 19 | March 2024 | 406–414



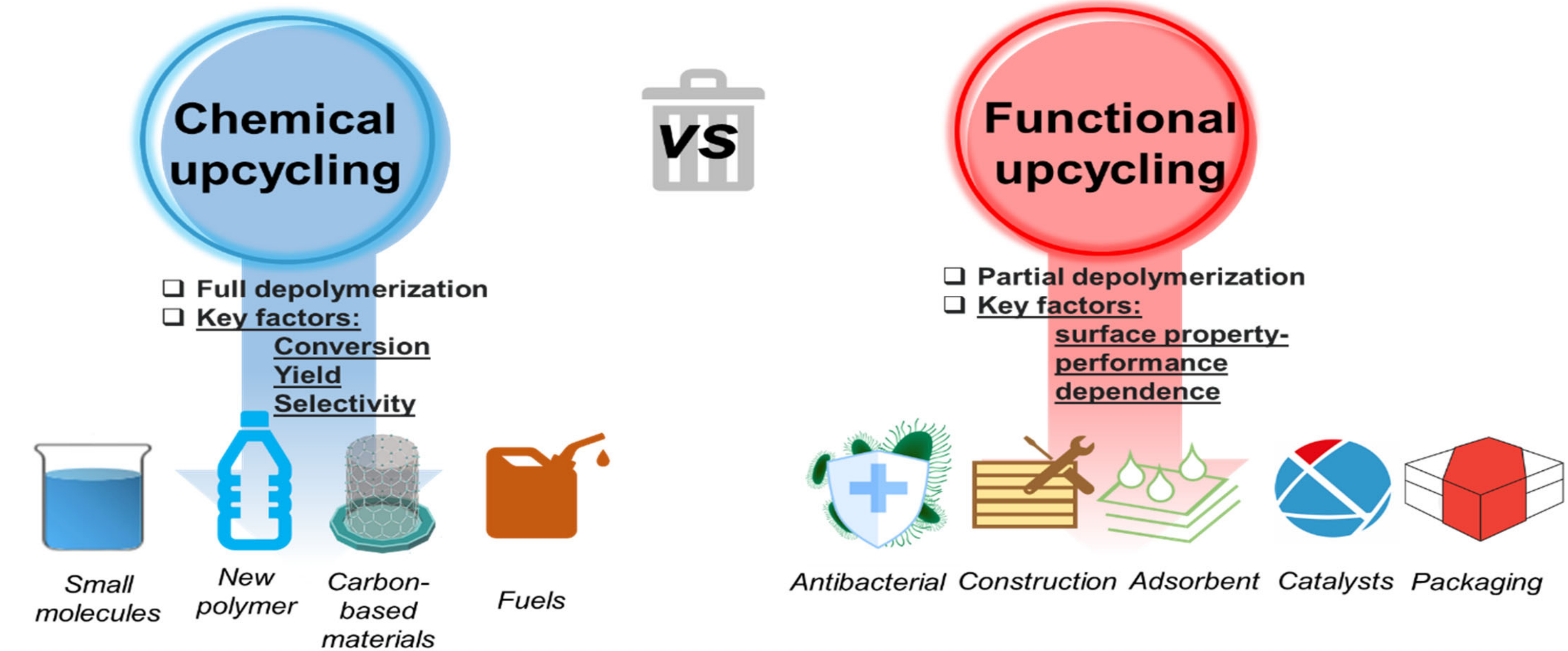
Fragmentation of PS microplastics by marine and freshwater rotifers as imaged by LSCM. **a**, The bright-field image (**i**), image excited from 488 nm (ii) and merged field (iii) of marine rotifers. **b**, The bright field image (i), image excited from 488 nm (ii) and merged field (iii) of freshwater rotifers. a(iv) and b (iv) were enlarged from the square yellow frames in a(ii) and b(ii), respectively.
The yellow arrows indicate the smaller microplastic fragments.

Nature Nanotechnology | Volume 19 | March 2024 | 406–414

Plastic Waste Management



Guselnikova et al., *Chem. Soc. Rev.* 52 (**2023**) 4755–4832



Chemical upcycling

Advantages

- ❑ New molecules are generated
- ❑ Added value is expected to be high
- ❑ Upscaled procedure are reported

Disadvantages

- ❑ High input energy: temperature and/or pressure
- ❑ Complex Met-based (*ex.*, Pd, Ru) catalytic systems are required
- ❑ Aggressive chemical (acids, bases *etc.*) are common
- ❑ Low tolerance to contamination

Functional upcycling

Advantages

- ❑ Control of surface properties: adhesion, wettability *etc.*
- ❑ Could be realized without Met-based catalyst
- ❑ Added value is expected to be high
- ❑ Relative tolerance to contamination
- ❑ Lower input energy: surface functionalization

Disadvantages

- ❑ Risk of microplastic release
- ❑ Aggressive chemical (acids, bases *etc.*) are common
- ❑ Preliminary mechanical recycling could be required

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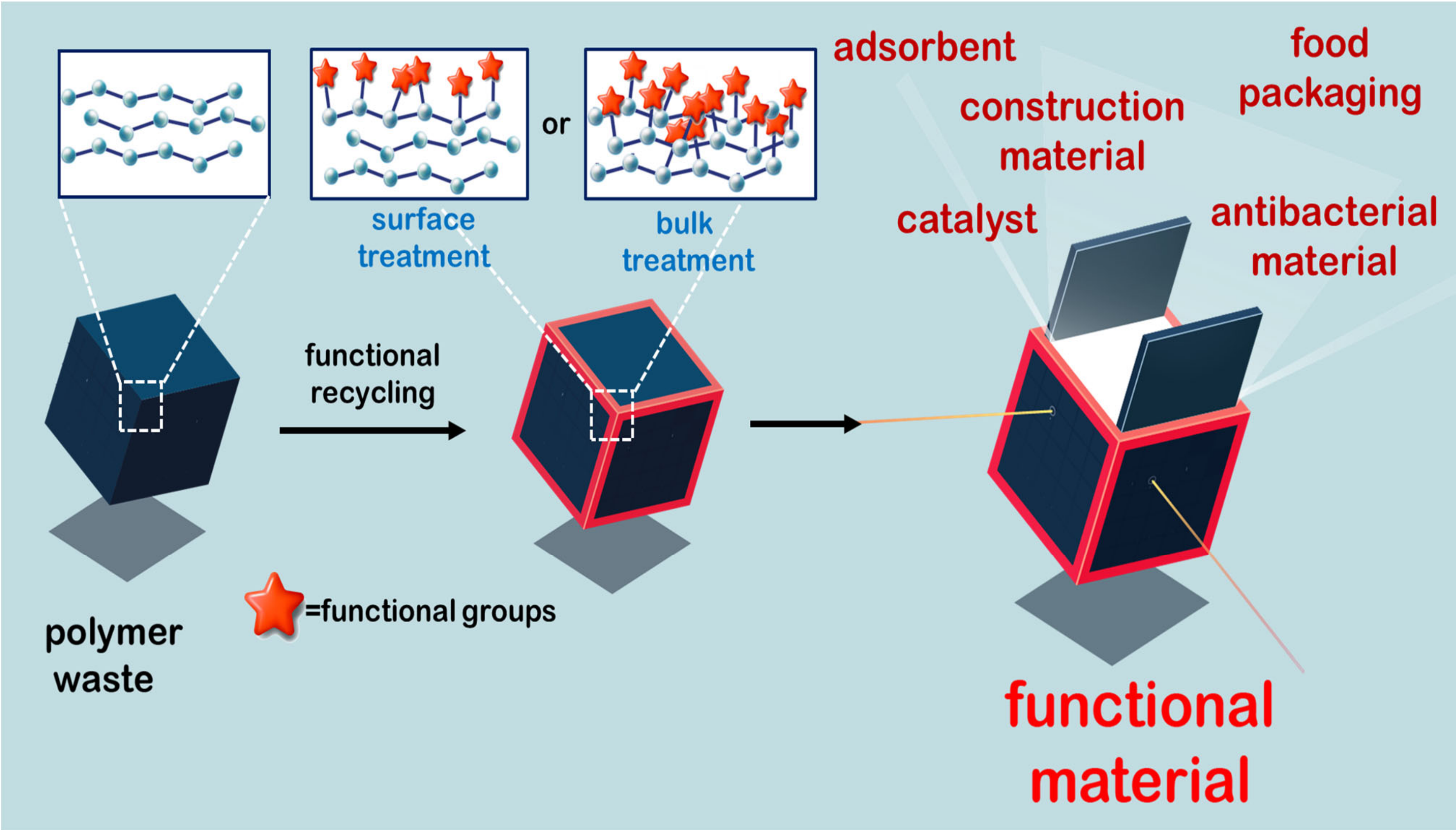
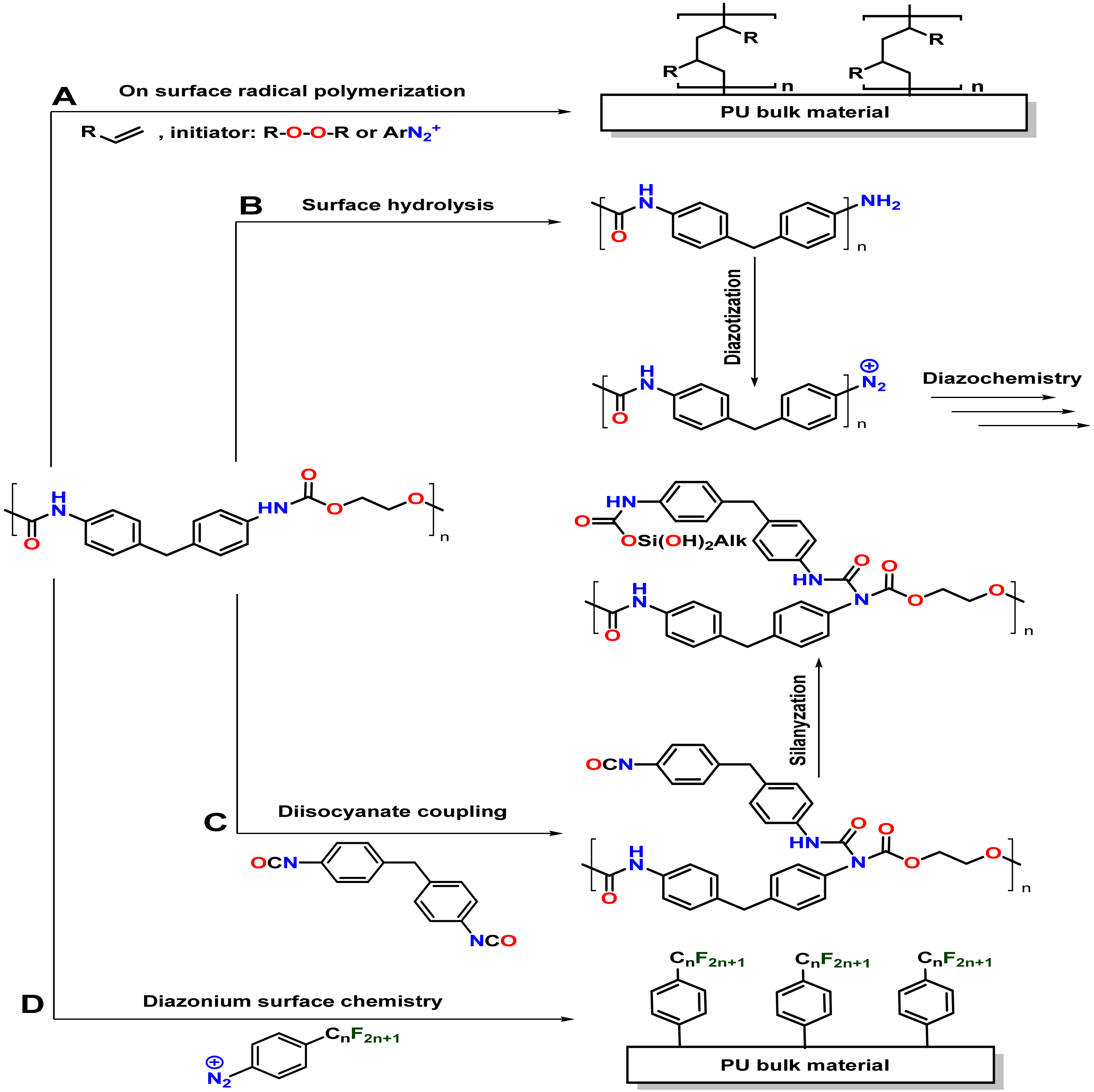
Guselnikova et al., Chem. Soc. Rev. 52 (**2023**) 4755–4832

The general concept of functional upcycling



Guselnikova et al., Chem. Soc. Rev. 52 (**2023**) 4755–4832

Functionalization of PU: (a) – on-surface radical polymerization; (b) – surface hydrolysis followed by diazotization and secondary transformations; (c) – functionalization by diphenyl diisocyanate followed by silanization; (d) – diazonium surface functionalization for surface hydrophobization



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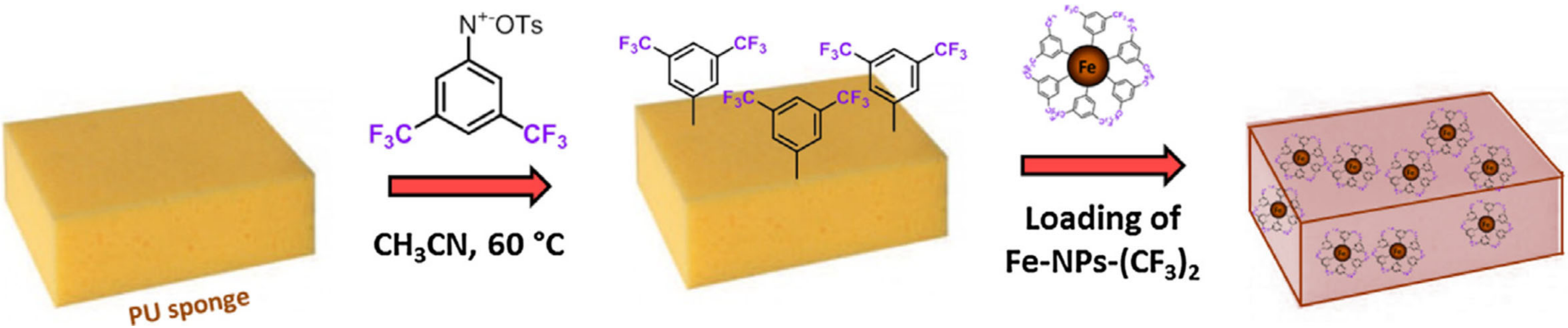
Magnetic polyurethane sponge for efficient oil adsorption and separation of oil from oil-in-water emulsions

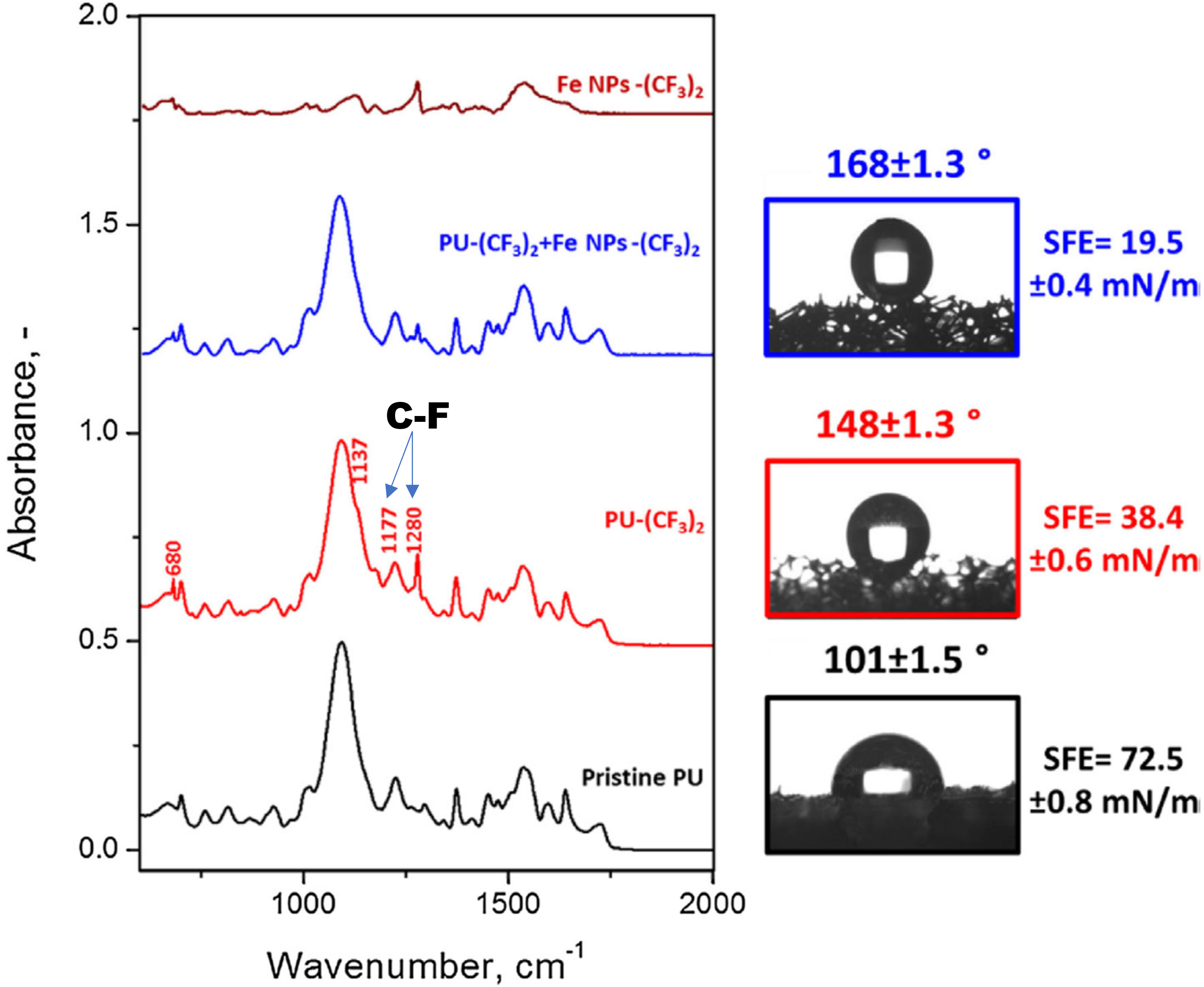
Coll. Olga Guselnikova & Pavel S. Postnikov,
Tomsk Polytechnic University, Russia



Schematic representation of the preparation of FeNPs-$(CF_3)_2$ loaded superhydrophobic PU sponge.

Guselnikova et al., Separation and Purification Technology 240 (2020) 116627

Magnetic polyurethane sponge for efficient oil adsorption and separation of oil from oil-in-water emulsions



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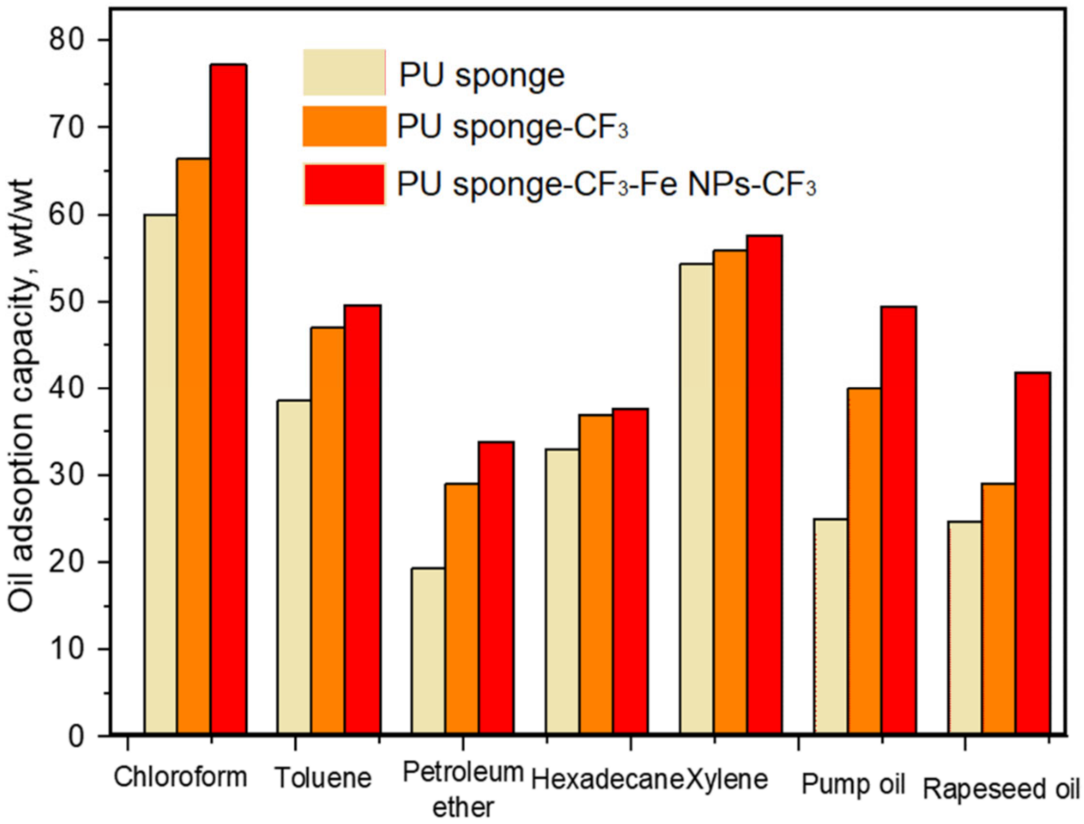
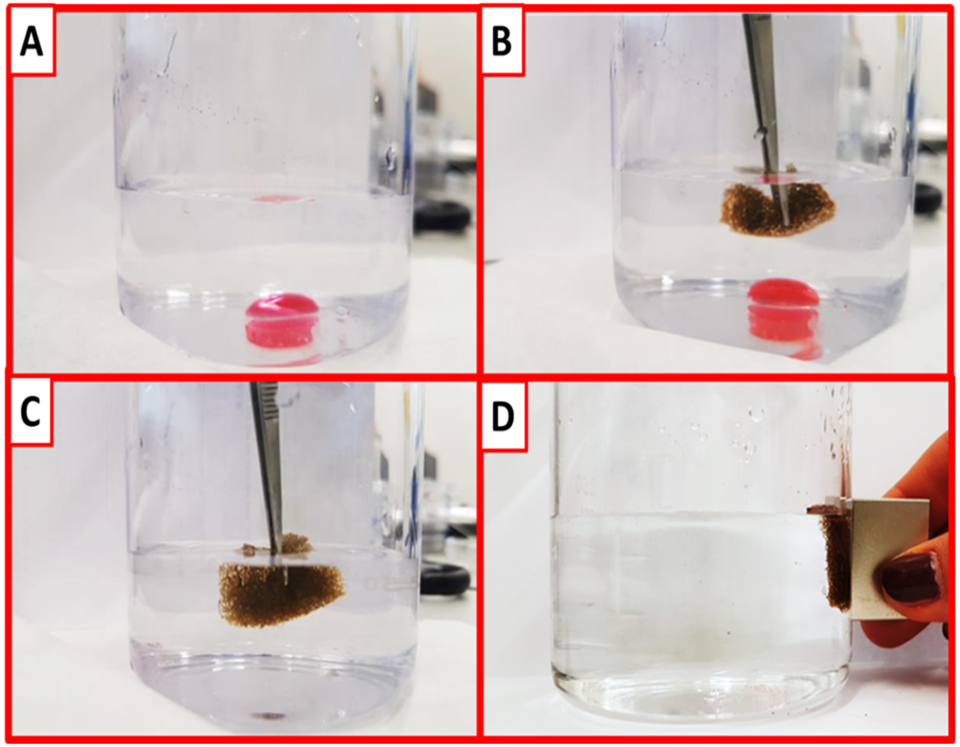


Adsorption capacities of bare PU sponge, functionalized PU-CF_3 sponge, and superhydrophobic FeNPs-$(CF_3)_2$ loaded PU-$(CF_3)_2$ sponge



Removal of chloroform (dyed by Sudan III) by magnetic PU-$(CF_3)_2$-FeNPs-$(CF_3)_2$.

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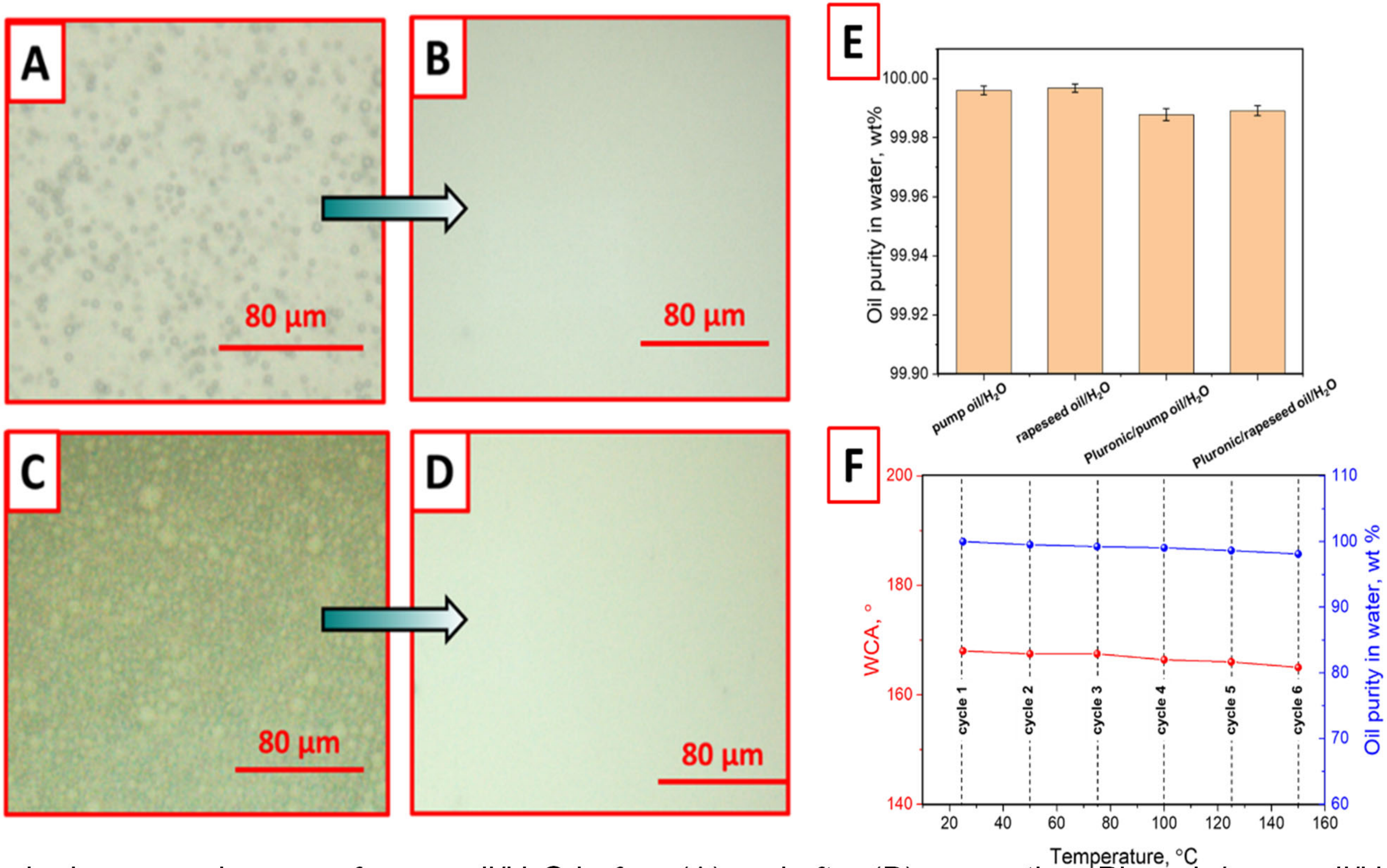
Guselnikova et al., Separation and Purification Technology 240 (2020) 116627

Magnetic polyurethane sponge for efficient oil adsorption and separation of oil from oil-in-water emulsions



Optical microscopy images of pump oil/H_2O before (A) and after (B) separation, Pluronic/pump oil/H_2O before (C) and after (D) separation with magnetic FeNPs-$(CF_3)_2$-PU-$(CF_3)_2$, (E) Oil purity in the filtrate after absorption by PU-$(CF_3)_2$-FeNPs-$(CF_3)_2$ sponge for a selection of emulsions, (F) Thermal stability of PU-$(CF_3)_2$-FeNPs-$(CF_3)_2$ sponge (WCA and oil purity after several separation cycles up to 150 °C)

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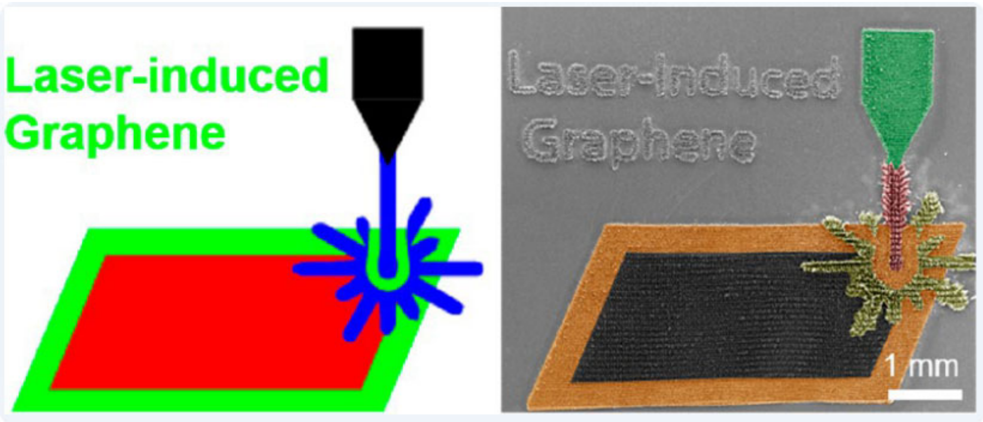
Guselnikova et al., Separation and Purification Technology 240 (2020) 116627

Why is laser-induced graphene (LIG) Technique?

2014: 1st introduction for the direct laser writing method to produce LIG

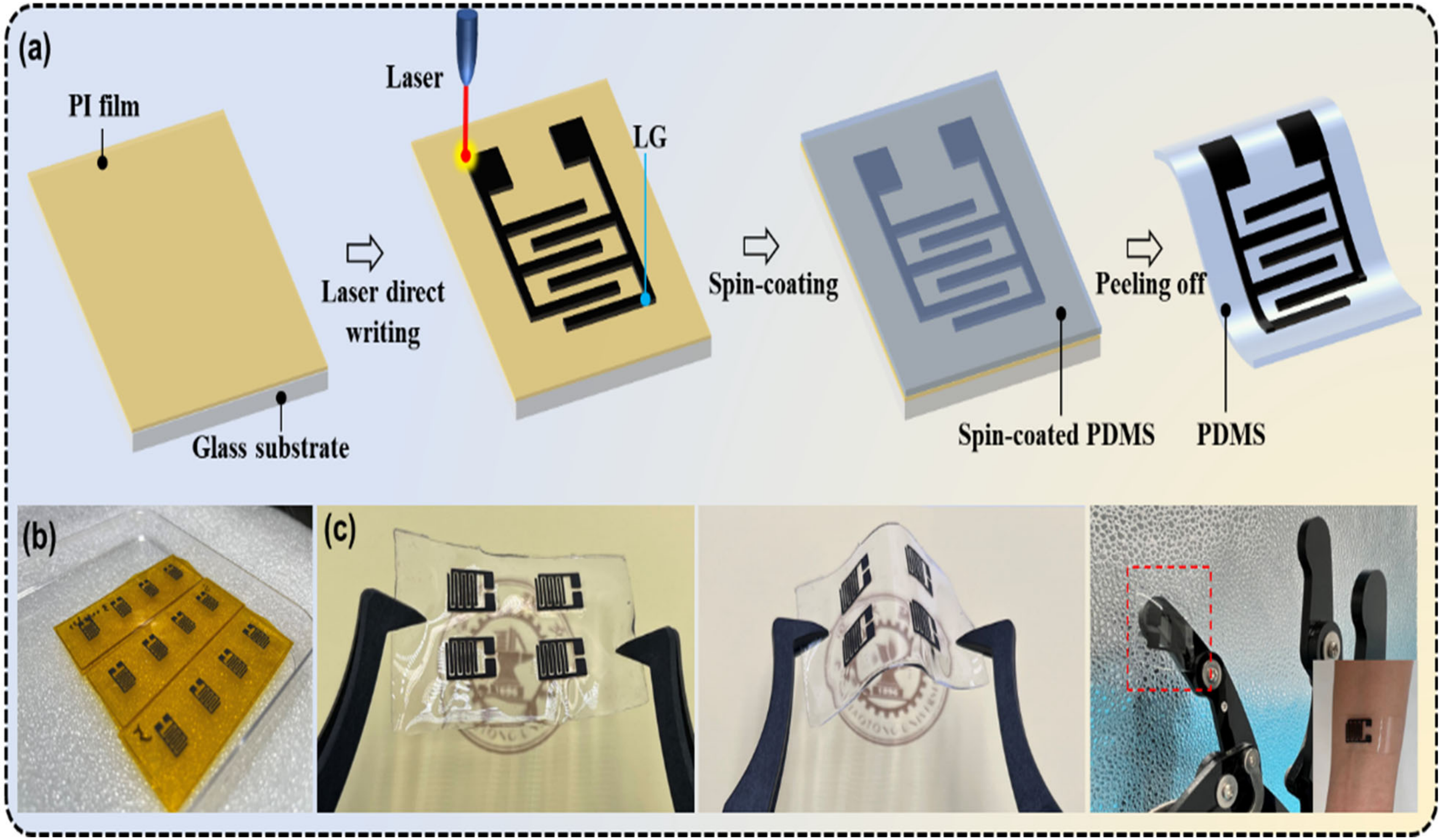


https://cdn.ulsinc.com/assets/pdf/white_papers/5cae7cf83cc4b275c515a982/laser_induced_graphene.pdf

LIG technique offer:

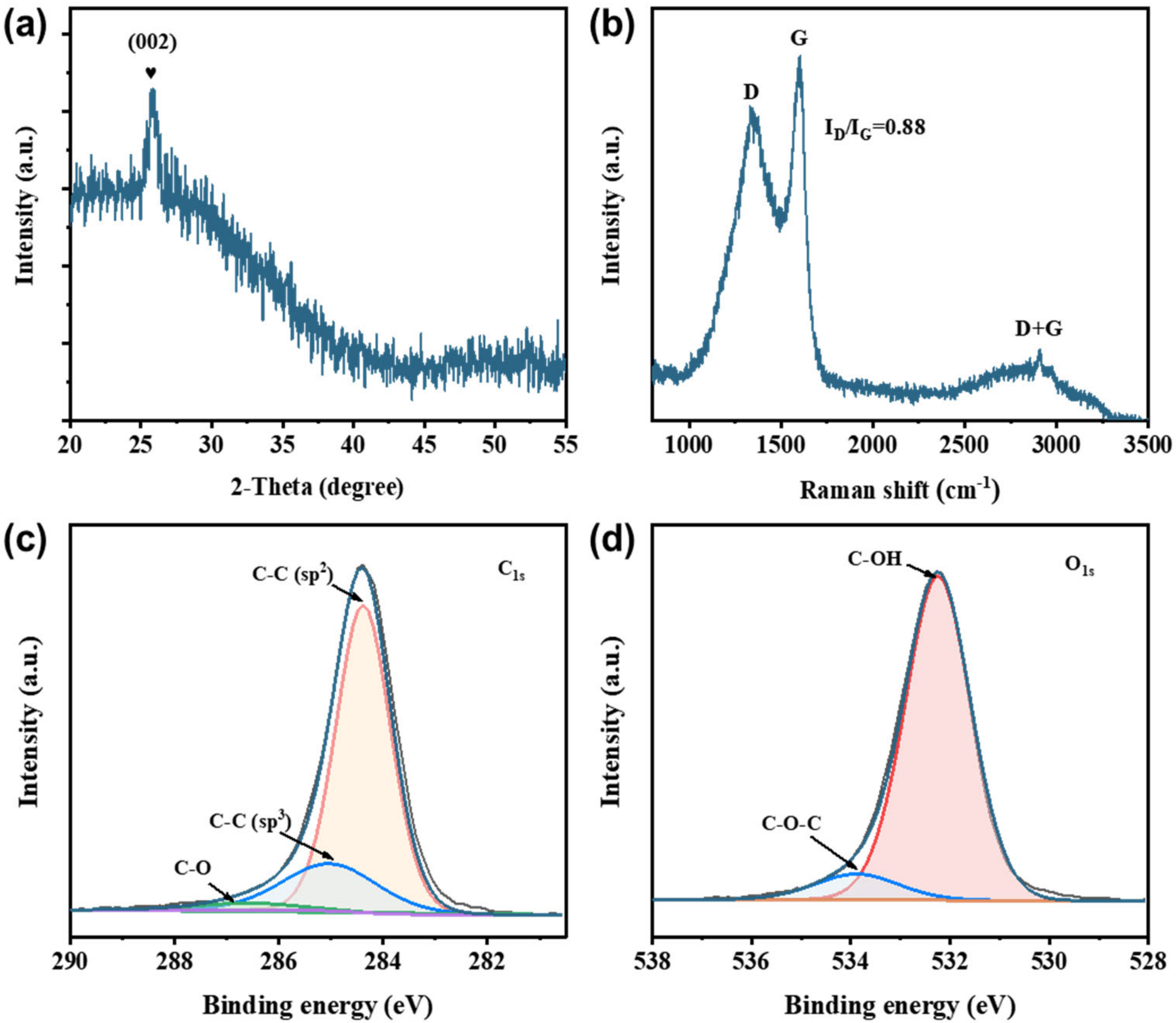
- **Fast**
  - **it achieves both material conversion and electrode patterning in a single step.**
- **Low-Cost**
  - **it does not require high temperatures, solvents and cleanroom conditions.**
- **Tunability**
  - **The laser wavelength, scanning conditions, and substrate material all influence the structure and properties of the resulting LIG.**

Flexible Symmetric Micro-Supercapacitors with Wide Working Voltage Window Assisted by Laser Fabrication and Liquid Crystal Gel Electrolyte



https://www.nature.com/articles/s41378-024-00742-0

Flexible Symmetric Micro-Supercapacitors with Wide Working Voltage Window Assisted by Laser Fabrication and Liquid Crystal Gel Electrolyte



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https://www.nature.com/articles/s41378-024-00742-0

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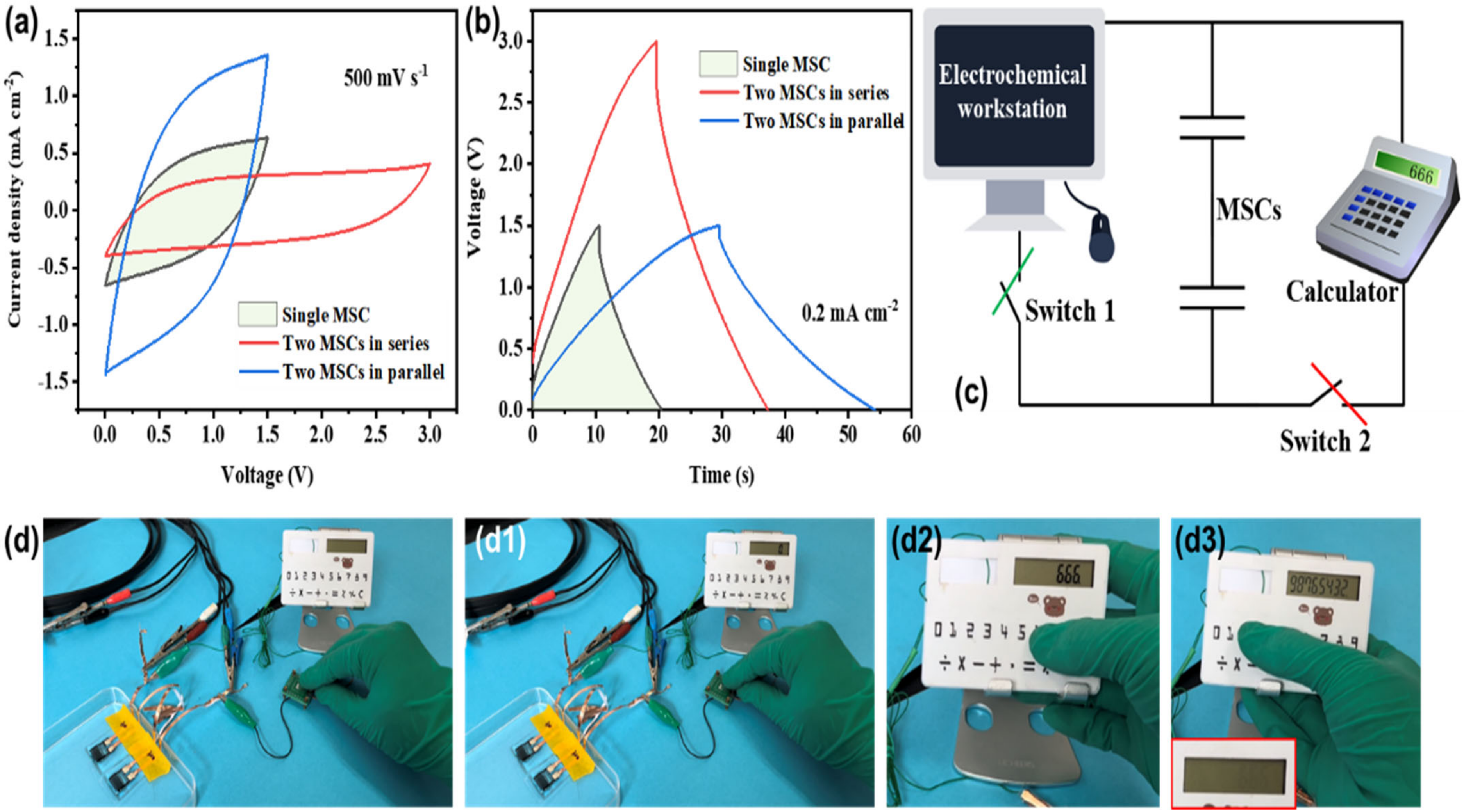

(**a**) CV curves at 500 mV s^{-1} of a single MSC-300, and two MSC-300 connected in series and parallel. (**b**) GCD plots at 0.2 mA cm^{-2} measured with PA-NI LC gel electrolyte. (**c**) Schematic equivalent circuit diagram and (**d**) photographs of the application test system

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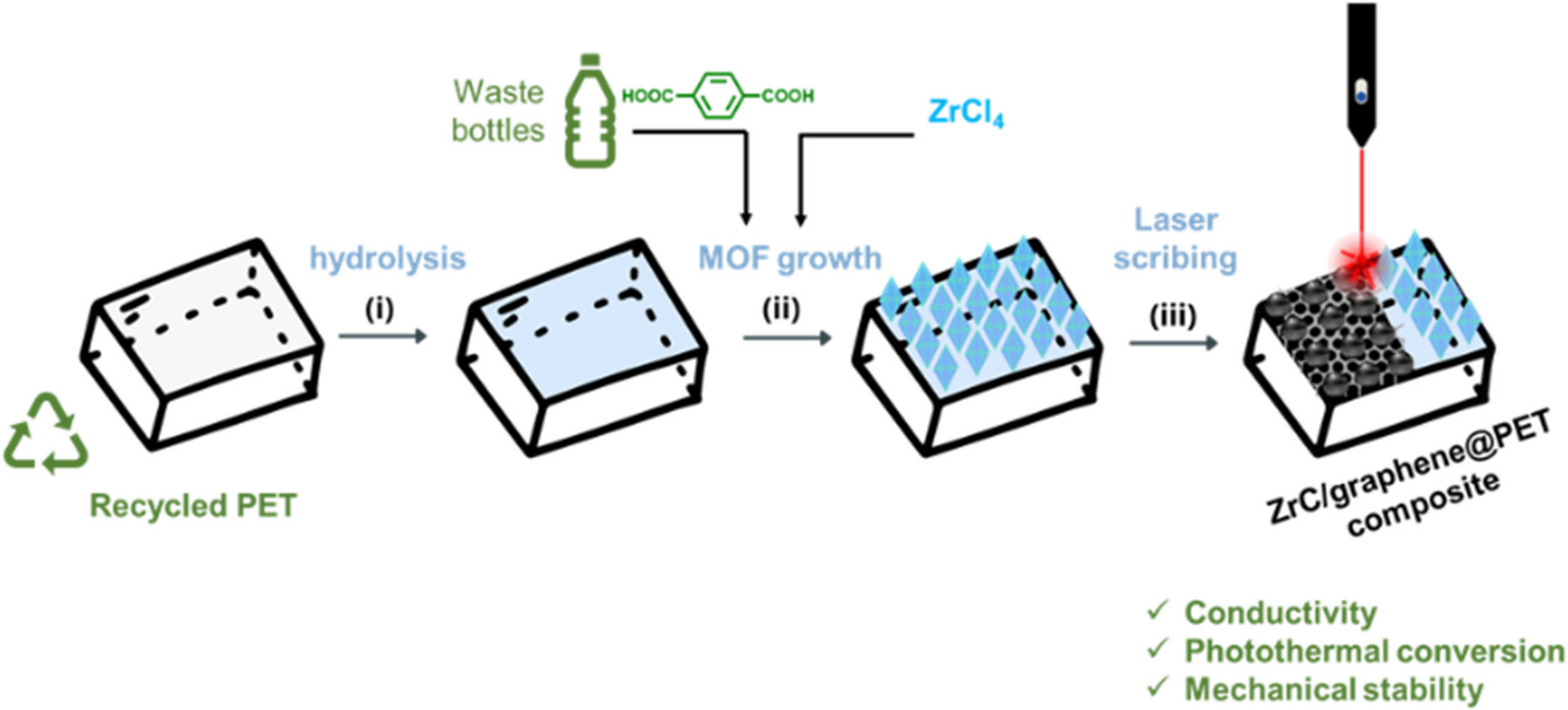
https://www.nature.com/articles/s41378-024-00742-0

Waste PET upcycling to conductive carbon-based composite through laser-assisted carbonization of UiO-66



Strategy for PET@LB-UiO-66 preparation from recycled PET: (i) PET hydrolysis, (ii) UiO-66 PET surface growth from waste PET bottle, and (iii) laser scribing process by 405 nm irradiation.

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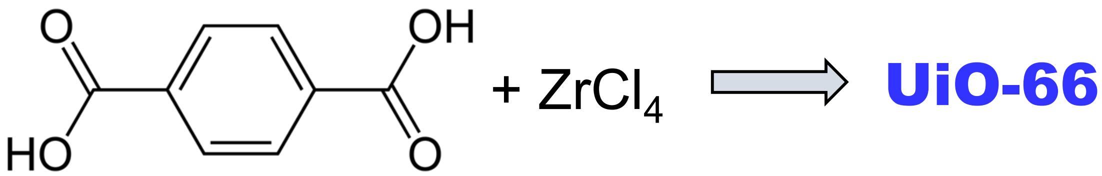
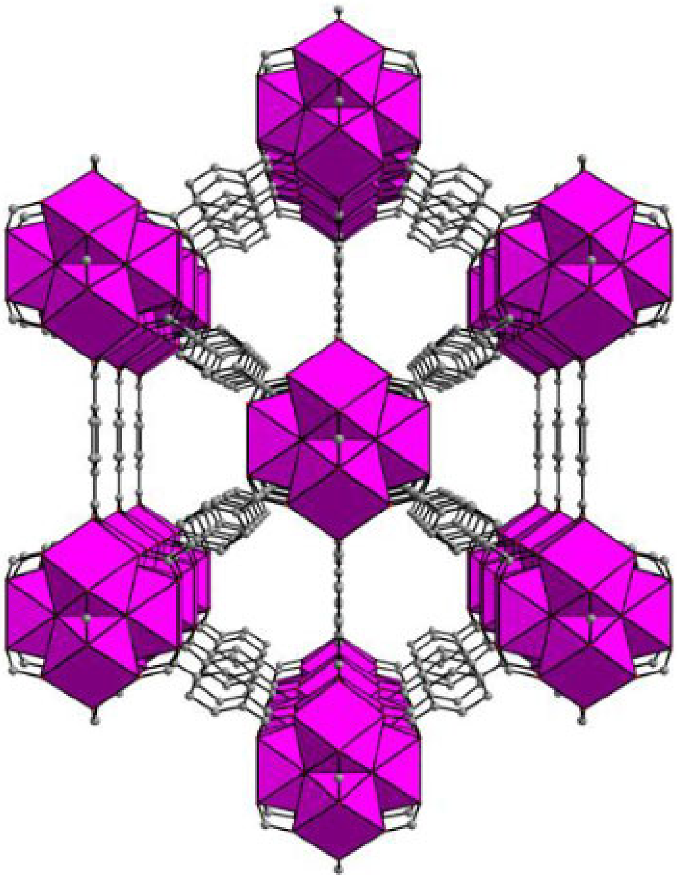
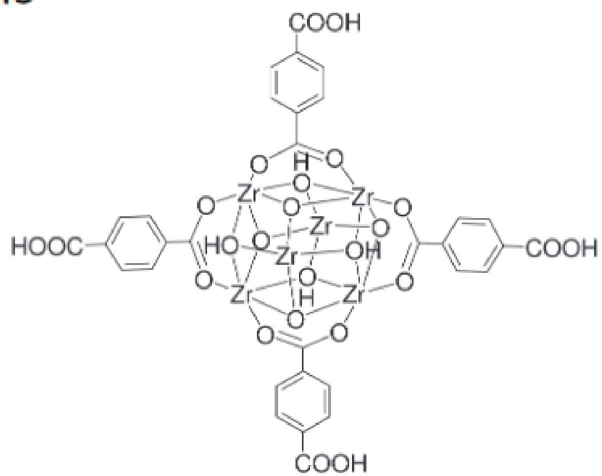
Kogolev et *al.*, J. Mater. Chem. A, 2023, 11, 1108–1115

UiO-66 (Universitetet i Oslo) MOF structure





- Cheap (based on Zr^{4+} and terephthalic acid)
- High porosity
- High thermal stability
- High stability to hydrolysis
- Easy to synthesize
- Extremely versatile



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The Royal Swedish Academy of Sciences has decided to award the Nobel Prize in Chemistry 2025 to

Susumu Kitagawa
Kyoto University, Japan

Richard Robson
University of Melbourne, Australia

Omar M. Yaghi
University of California, Berkeley, USA

“for the development of metal–organic frameworks”

https://www.google.com/se
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wExuAdZwgcFNC0xLjHIB0GA
CAE&sclient=gws-wiz-serp

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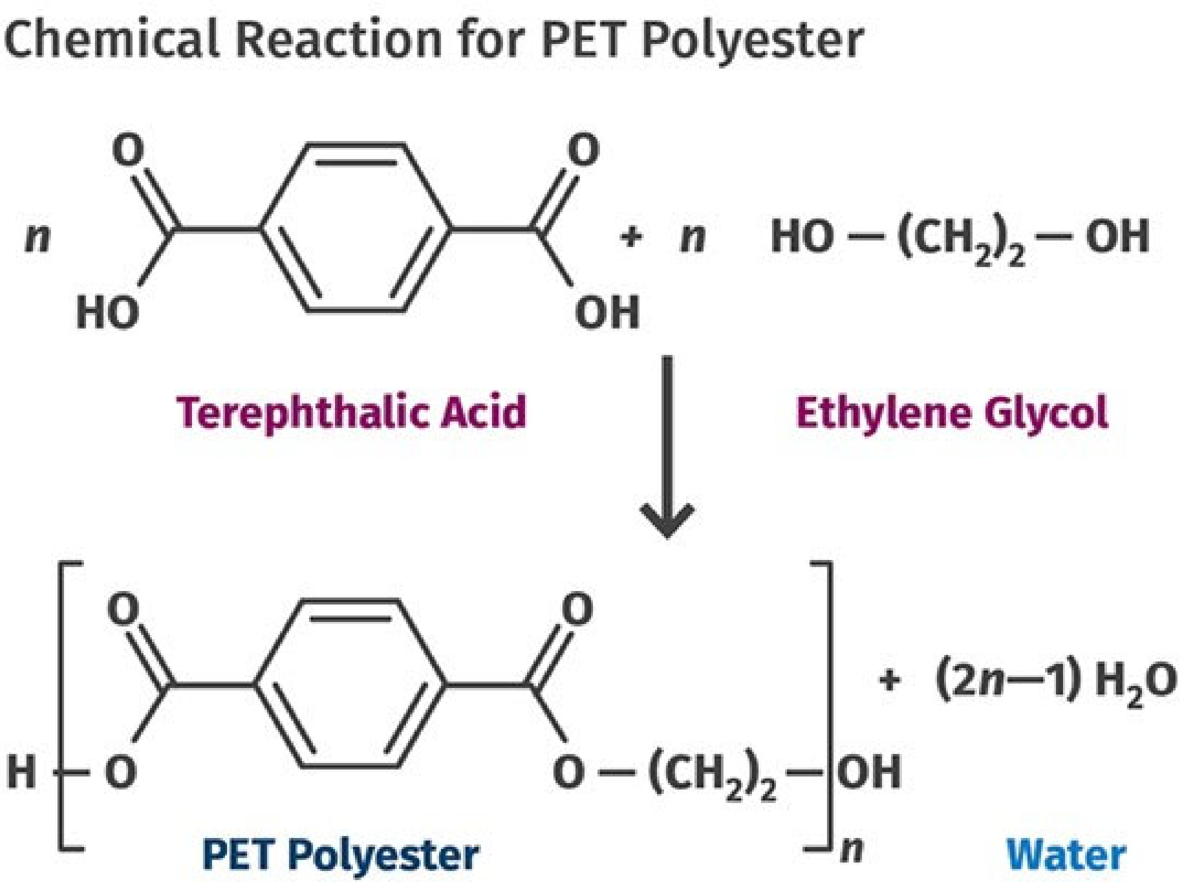
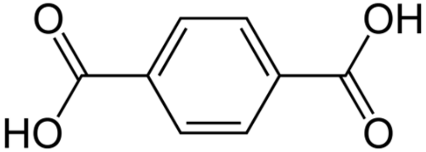
Preparation of Polyethylene terephthalate (PET)



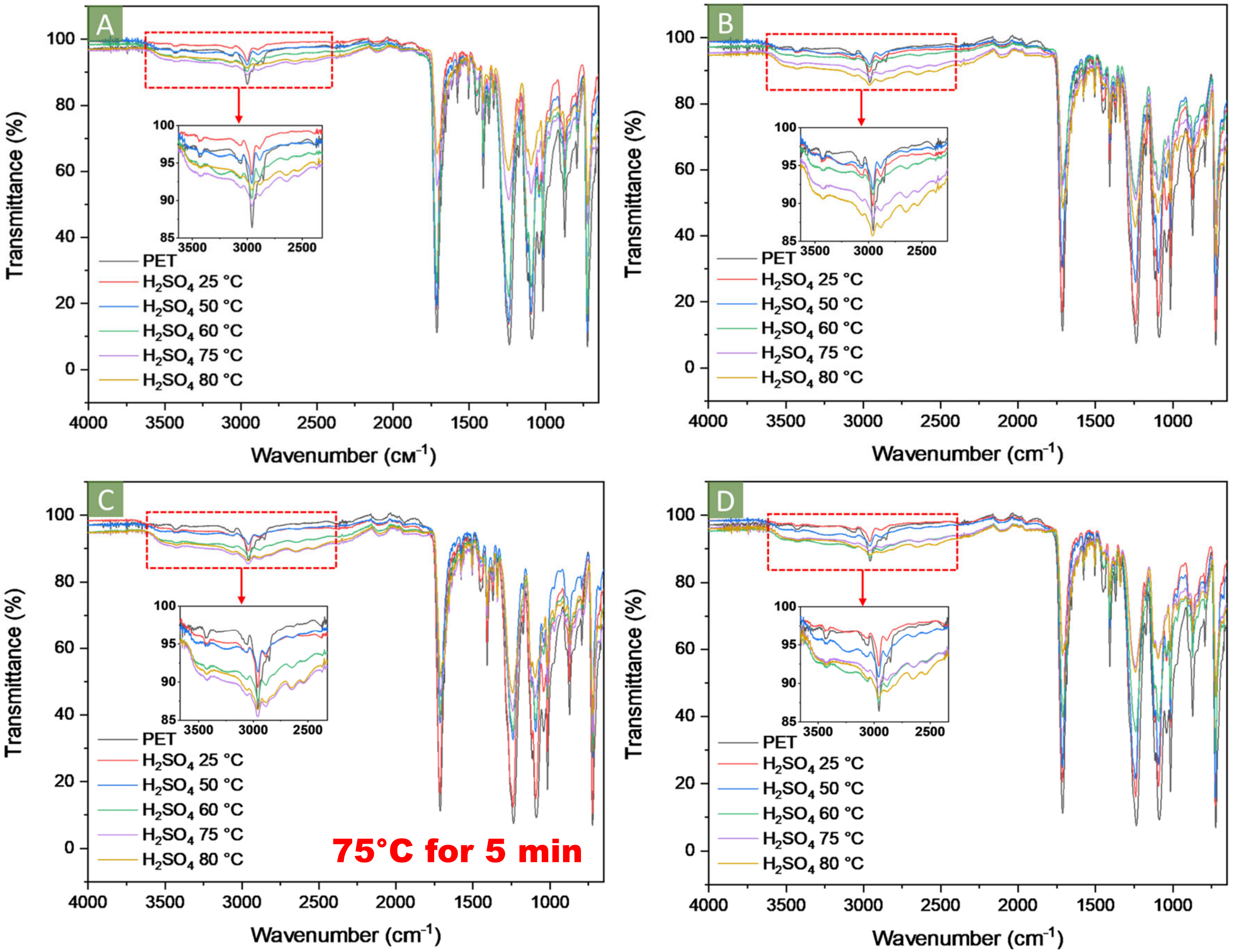
https://www.singh-enterprises.in/product/pet-bottles-transparent/

Hydrolysis of Polyethyleneterephthalate (PET)

$(PET)_n + (2n\text{-}1)H_2O \rightarrow nC_8H_6O_4$ (Terephthalic acid) + $nC_2H_6O_2$ (ethylene glycol)



Waste PET upcycling to conductive carbon-based composite through laser-assisted carbonization of UiO-66



FTIR spectra of pristine and hydrolyzed PET (PET-H) plates using concentrated H_2SO_4 for (A) 1 min, (B) 2.5 min, (C) 5 min, (D) 10 min.

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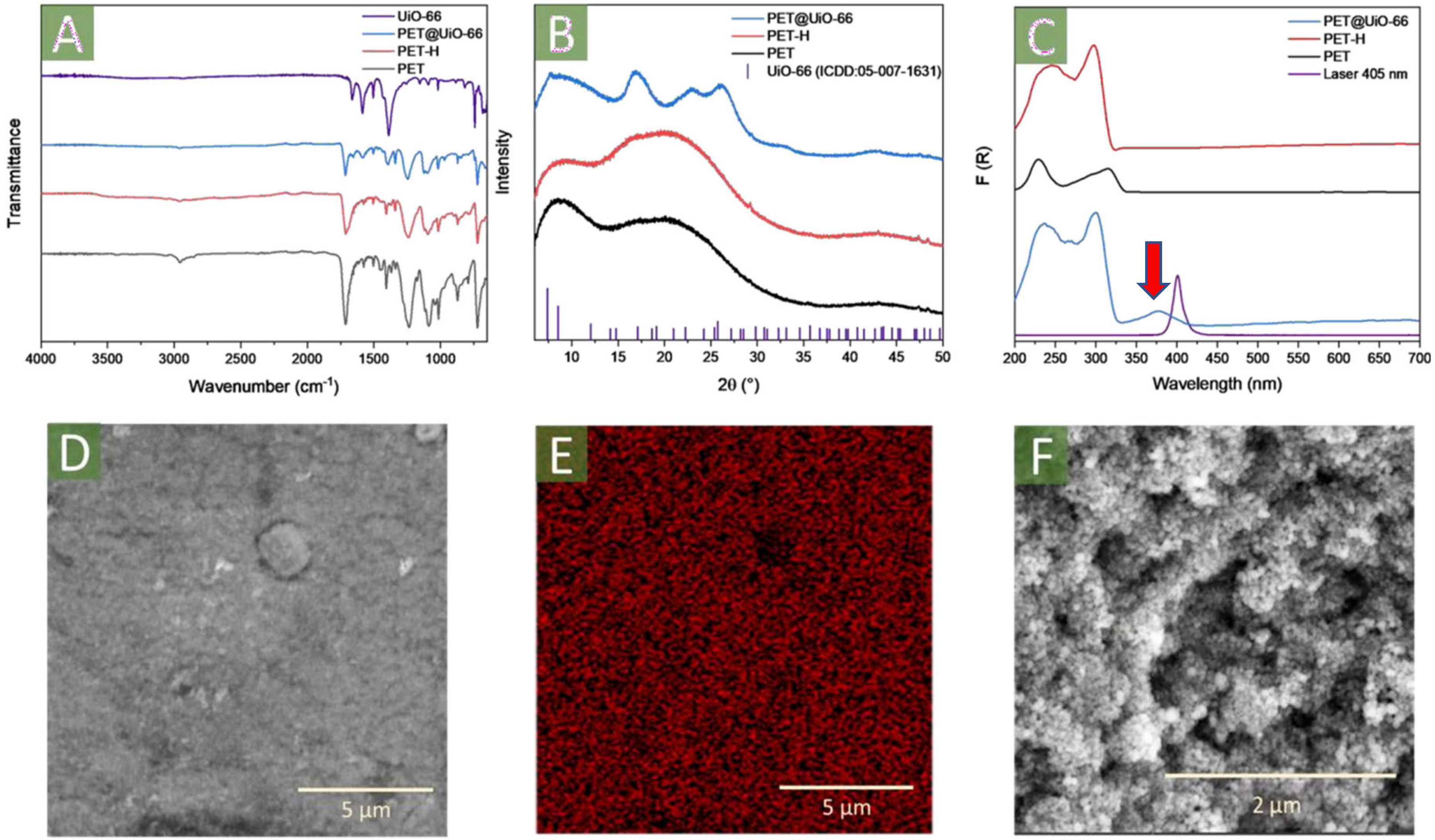
Waste PET upcycling to conductive carbon-based composite through laser-assisted carbonization of UiO-66

UiO-66 at 1584 and 1397 cm^{-1} due to asymmetric and symmetric stretches of COO-Zr bonds



Characterization of PET@UiO-66: (A) FTIR spectra, (B) XRD patterns, (C) UV-vis spectra, (D-E) SEM-EDX map of Zr, and (F) SEM image at higher magnification

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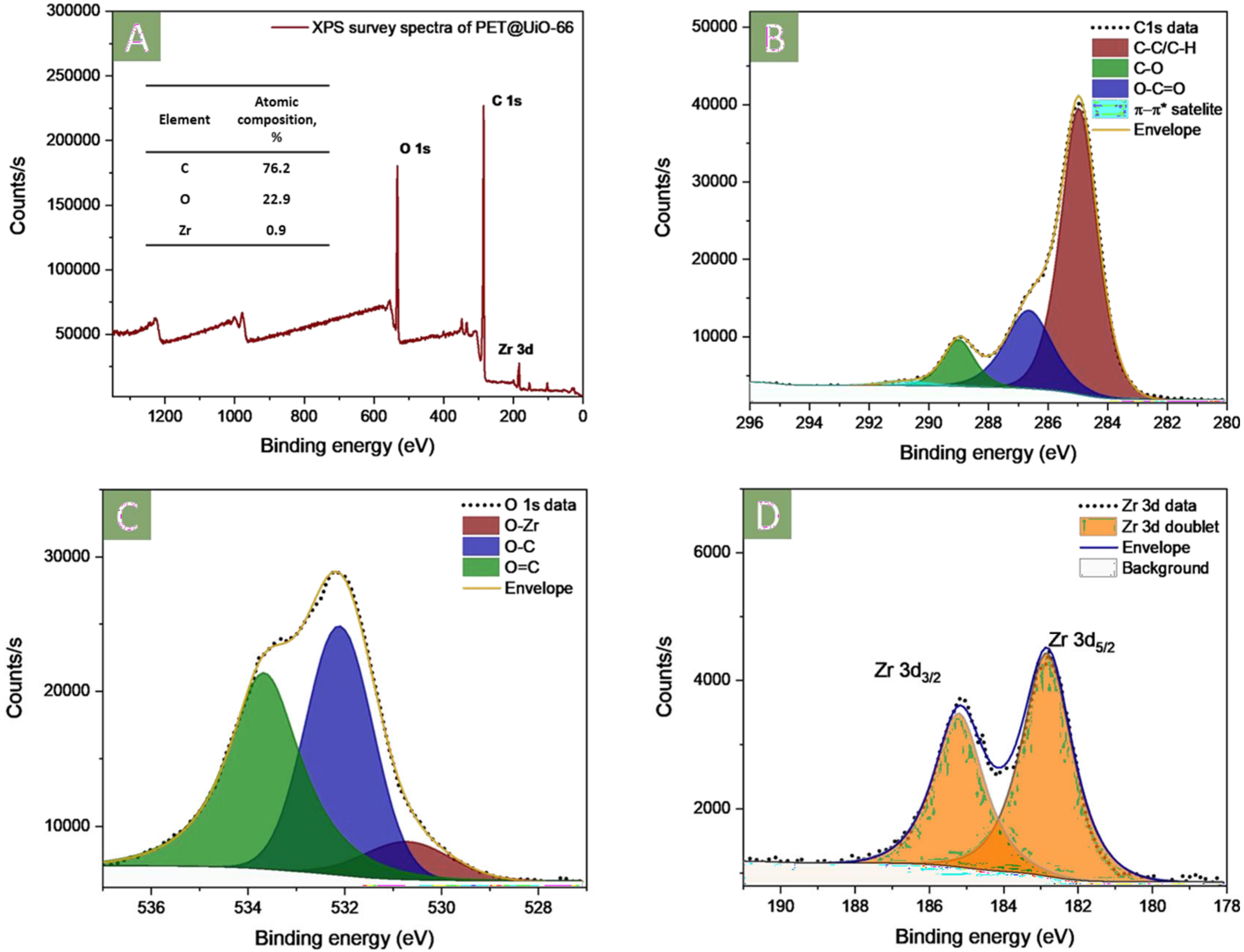
Waste PET upcycling to conducting carbon-based composite through laser-assisted carbonization of UiO-66



Characterization of PET@UiO-66 by XPS: (A) Survey spectrum, (B) C 1s, (C) O 1s, and (D) Zr 3d regions

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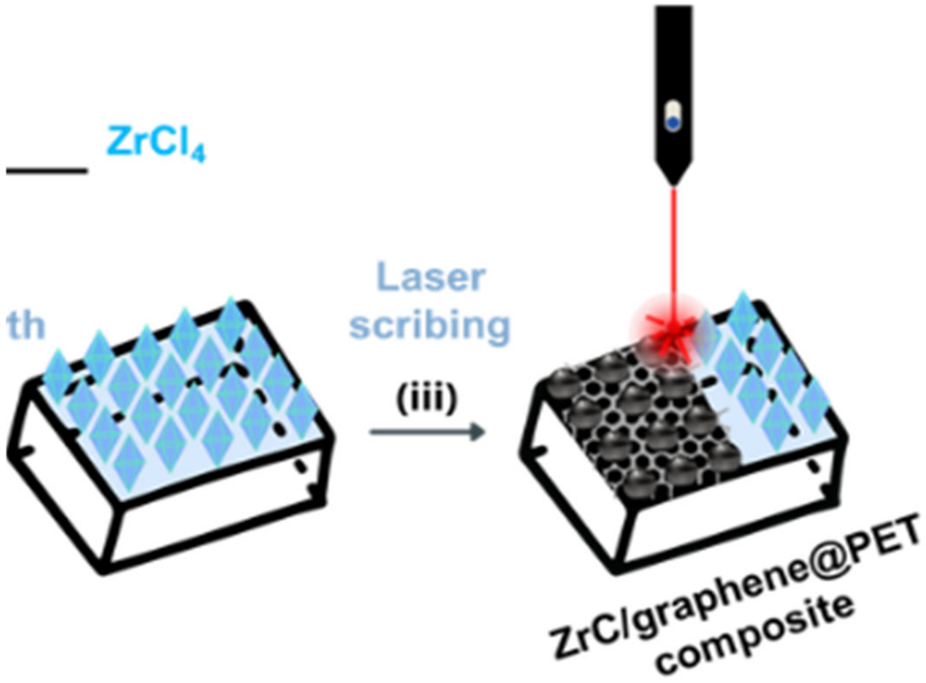
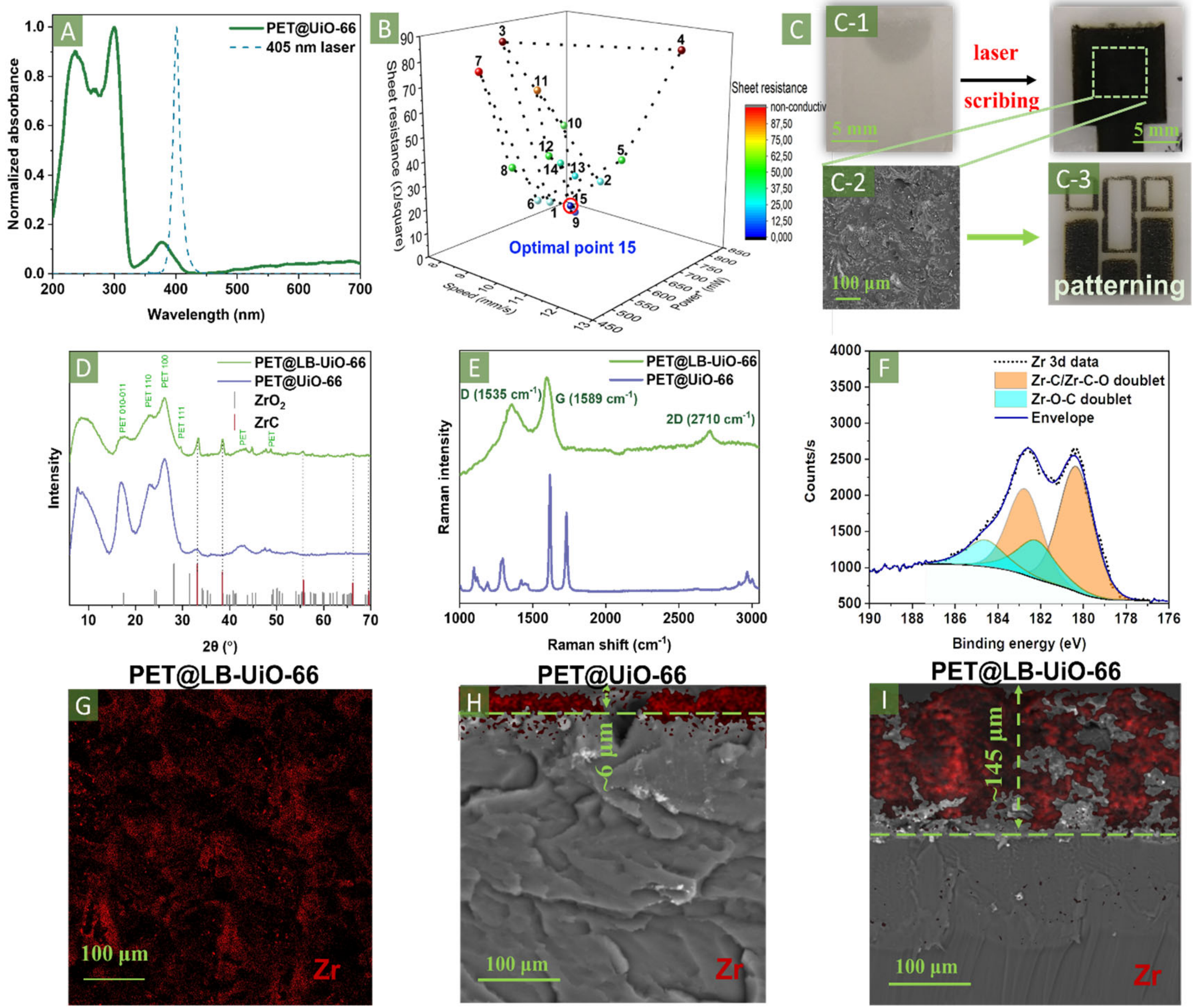
Preparation of PET@LB-UiO-66

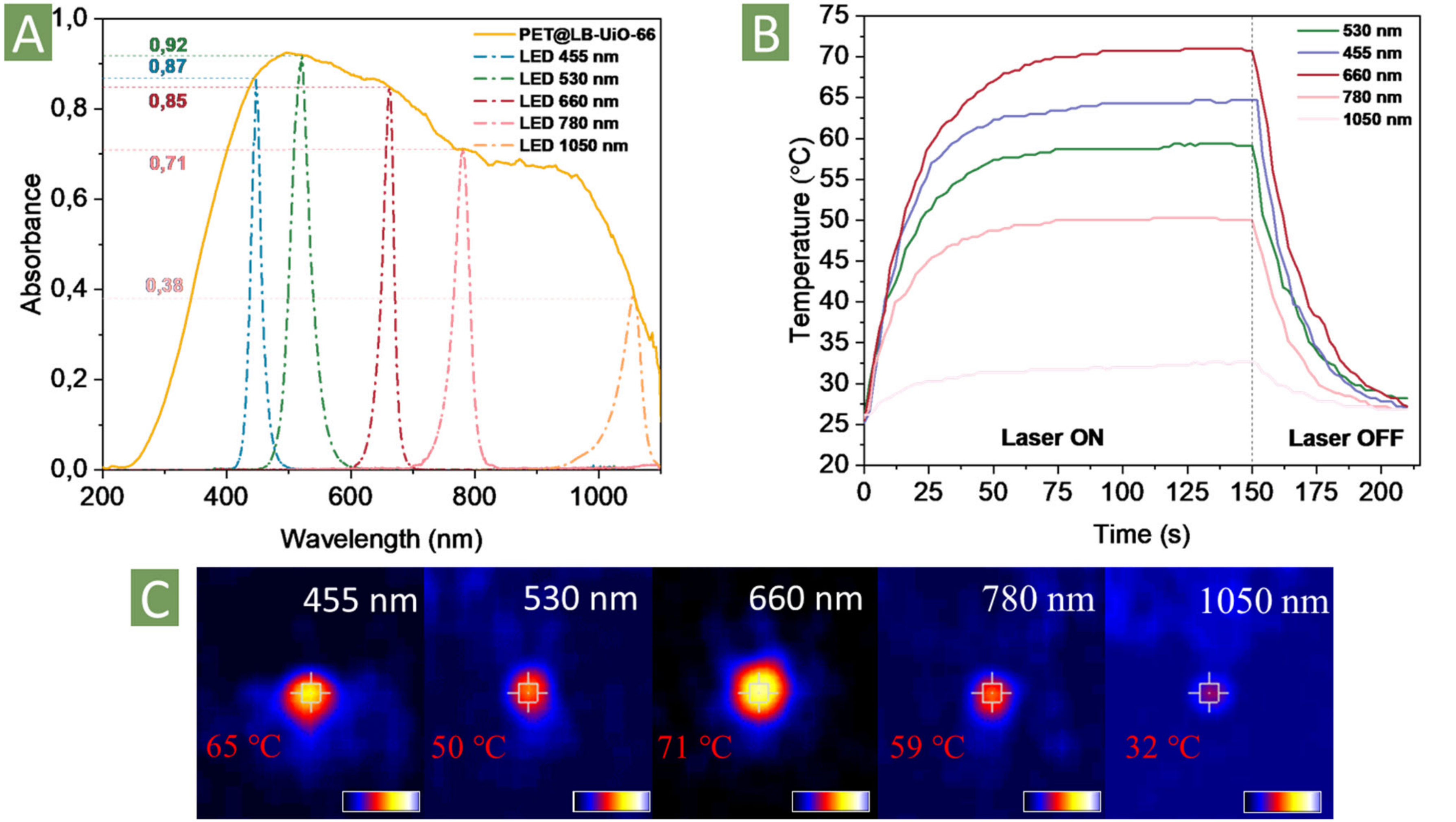


Laser processing was carried out using a pulsed diode laser NEJE DK-8-KZ at a wavelength of 405 nm on the 1 cm^2 PET@UiO-66 area. The laser was operated at a pulse frequency of 1.6 kHz and rated power of ~1.6 W. To carry out the process, the laser beam was focused on the material, and irradiation was carried out when the laser moved along the plate. In our laser control system, the average power was varied by controlling the laser pulse time and frequency. The software allowed us to control two parameters – "P" (power) and "D" (depth). The "P" parameter controlled the pulse duration, while "D" set the pulse frequency (laser beam velocity). **Optimization of the carbonization process** was carried out using the **Nelder-Mead** method by varying parameters "P" and "D" in the software of the laser system. For carbonization of UiO-66 on the surface, the following optimized parameters were subsequently used: 49 % power from nominal (735 mW), 26 % depth (9.0 mm/s).



(A) UV-vis spectrum of PET@UiO-66. (B) Optimization of PET@UiO-66 carbonization by the Nelder-Mead Method; *Nominal laser power. (C) Material images before and after laser treatment, where C-1 is a general view, C-2 – SEM of PET@LB-UiO-66 after treatment under optimal conditions, C-3 – Optical image of the pattern (Logo Tomsk Polytechnic University) prepared by PET@UiO-66 laser scribing. Characterization of PET@LB-UiO-66: (D) XRD patterns, (E) Raman spectra, (F) Zr 3d XPS spectrum, (G) EDX mapping of Zr from image on C-2, cross-sectional SEM-EDX images of (H) PET@UiO-66 and (I) PET@LB-UiO-66.

Waste PET upcycling to conducting carbon-based composite through laser-assisted carbonization of UiO-66



(A) UV-vis spectrum of PET@LB-UiO-66 with spectra of LED sources. (B) Photothermal curves of PET@LB-UiO-66 acquired at 5 different wavelengths. (C) Images taken using a thermal camera during LED irradiation of PET@LB-UiO-66 at 5 different wavelengths.

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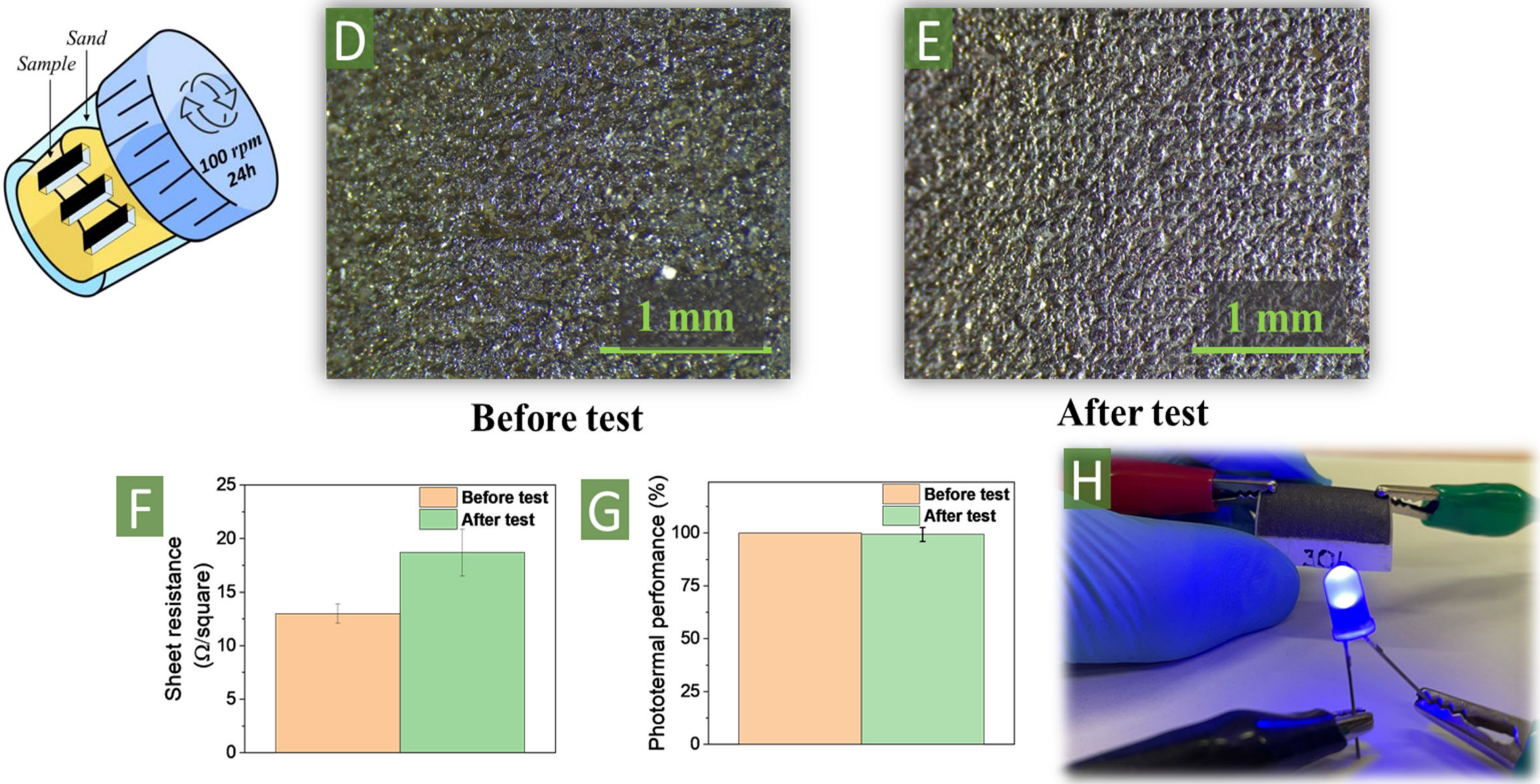
Waste PET upcycling to conducting carbon-based composite through laser-assisted carbonization of UiO-66



Optical microscopic photos: (D) Before mechanical test, (E) after mechanical test. Comparison diagram of (F) sheet resistance and (G) photothermal performance before and after mechanical test. (H) Photo of bent PET@LB-UiO-66 used as conductor to power LED.

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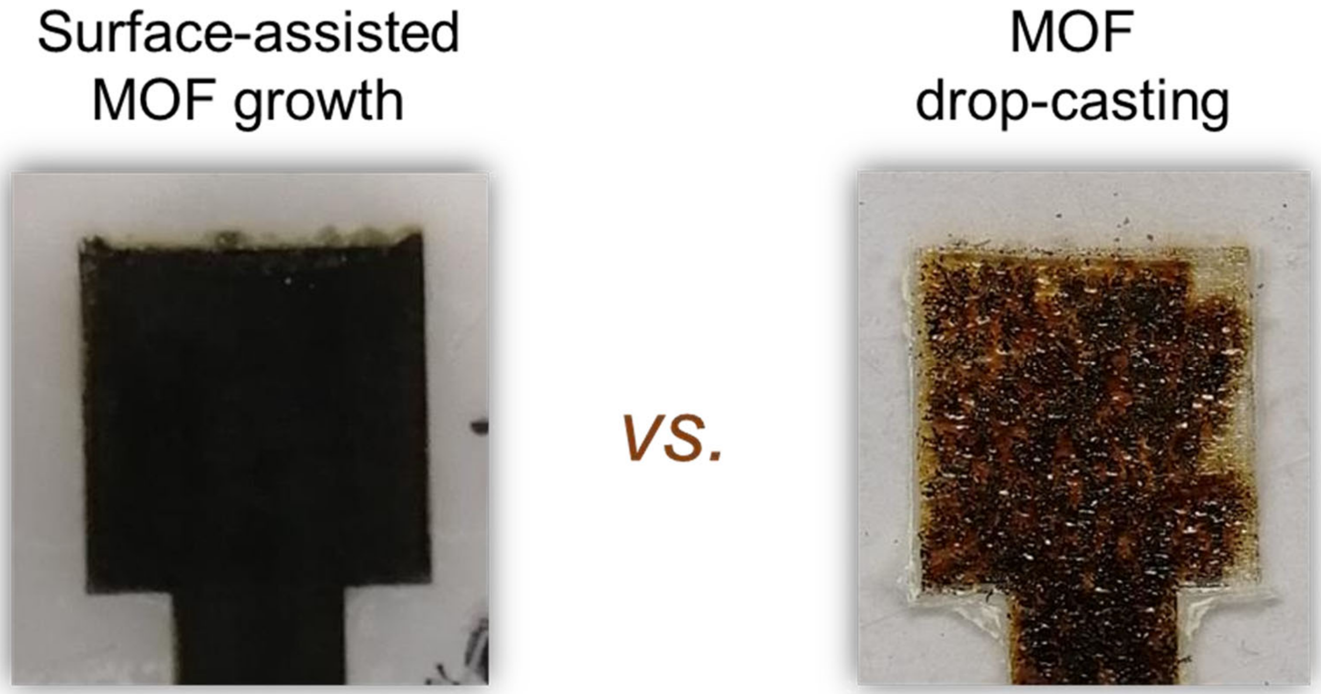
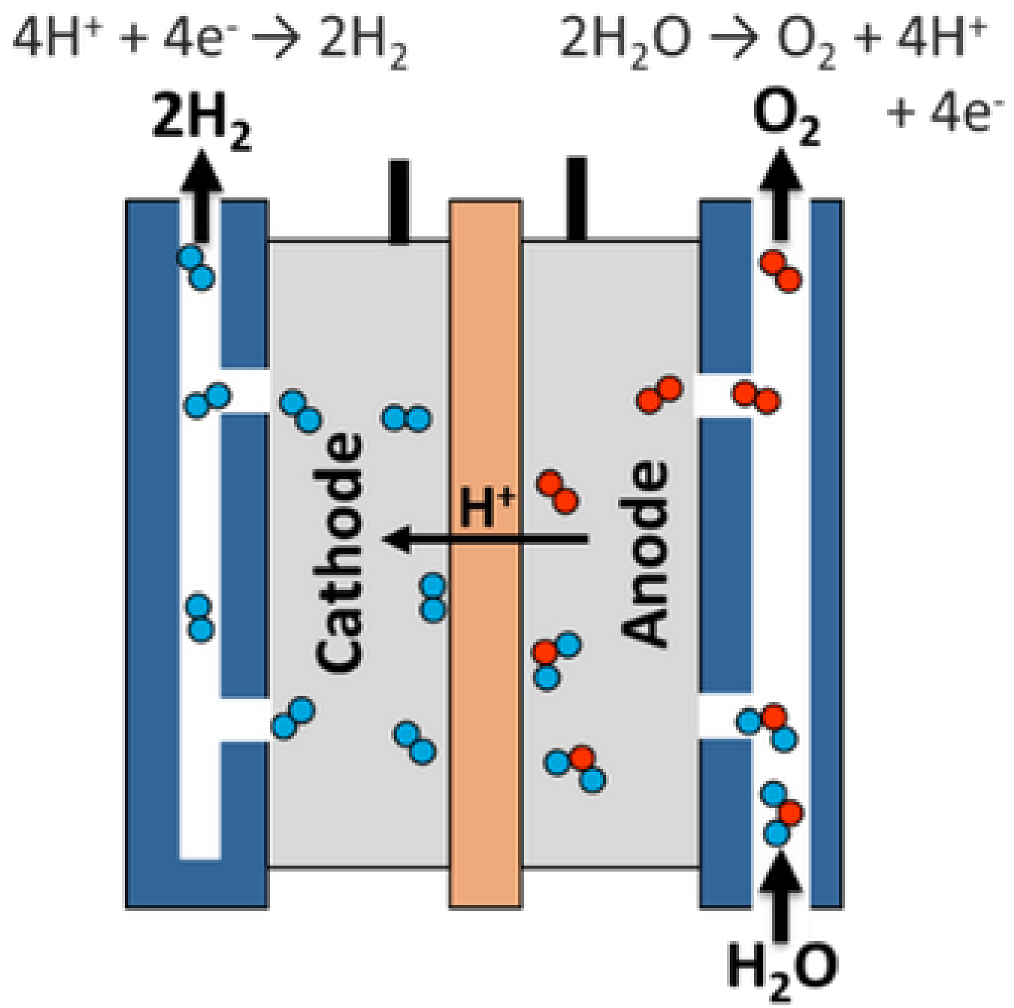
Laser-induced graphitization of drop-casted UiO-66 on PET and pristine PET



Optical microscopic images of materials obtained after laser scribing (A) PET@LB-UiO-66 and (B) drop-casted UiO-66

CO_2 Electrochemical Reduction Reaction

Pt/C

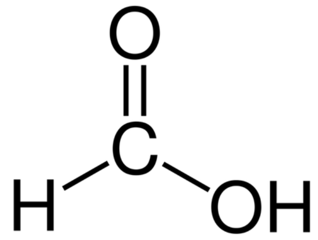


IrOx/RuOx

- Expensive
- Scarce
- Lack of bifunctionality

https://www.energy.gov/eere/fuelcells/hydrogen-production-electrolysis

Industrial Applications of Formic Acid



Formic acid is the simplest carboxylic acid, consisting of a carboxyl group (-COOH) attached to a hydrogen atom. It occurs naturally in insects, plants, and animals, including ants, nettles, and honeybees. However, it is predominantly produced synthetically on an industrial scale.

Formic acid has wide-ranging applications and is frequently used in industries including textile dyeing, leather tanning, and rubber production. Owing to its uses as a preservative, disinfectant, and reducing agent in medicine, formic acid has been a vital topic of many research studies.

Direct formic acid fuel cells (DFAFCs)

How is Formic Acid Produced?

Methanol Carbonylation Process: In this method, methanol reacts with carbon monoxide in the presence of a catalyst, typically rhodium or iodomethane, to produce formic acid.

$$CH_3OH + CO \rightarrow HCOOH$$

This reaction occurs under high pressure (typically 30-50 bar) and around 200°C. The formic acid is then separated from the reaction mixture by distillation.

Methanol Oxidation Process: Here, methanol is oxidized using an appropriate oxidizing agent, such as air or oxygen, in the presence of a catalyst such as copper or silver. The oxidation reaction produces formaldehyde, which is then further oxidized to formic acid.

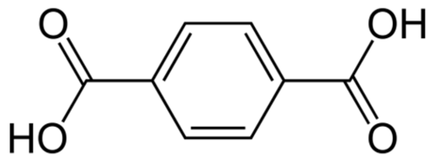
$$2\ CH_3OH + O_2 \rightarrow 2\ HCHO + 2\ H_2O$$

$$2\ HCHO + O_2 \rightarrow 2\ HCOOH$$

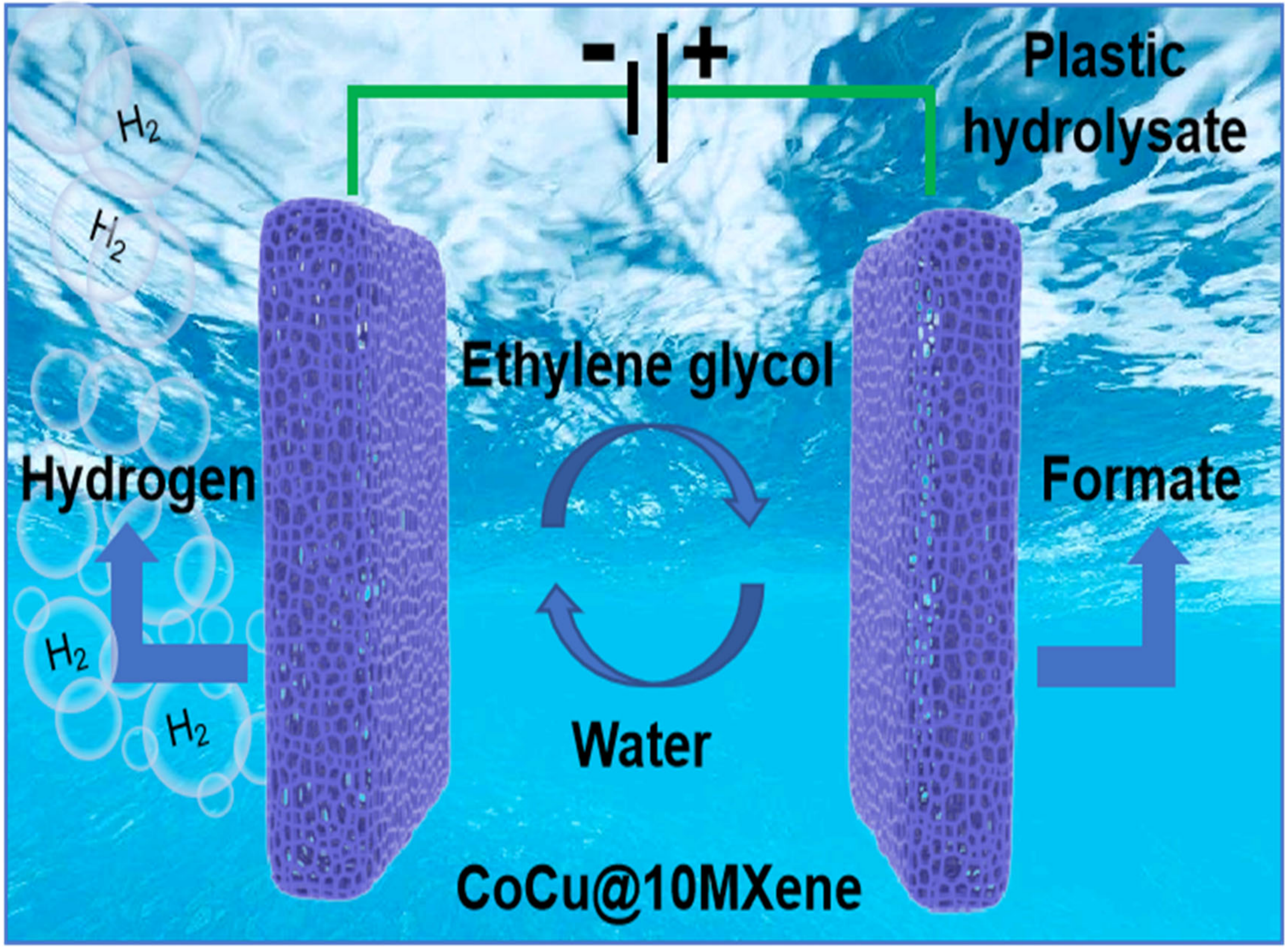
This reaction occurs at around 150-200°C and around 1-2 bar pressure. The formic acid is then separated from the reaction mixture by distillation.

Hydrolysis of Polyethyleneterephthalate (PET)

$(PET)_n + (2n\text{-}1)H_2O \rightarrow nC_8H_6O_4$ (Terephthalic acid) + $nC_2H_6O_2$ (ethylene glycol)



Electrocatalytic Upcycling of Polyethylene Terephthalate to Formic Acid and Hydrogen Fuels Using CoCu/MXene Catalyst



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https://www.sciencedirect.com/science/article/pii/S2095495624008672

Joint Valorization of CO_2 and Polymer Waste

**PhD work of Dr. Sravan Kaliparthi Kumar, Dr. Zhaohui Zhang,
Zhiran Yu, Yunchu Zeng**

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How one can make valuable chemicals/fuels from CO_2, plastic and biomass wastes?

Formate/Formic acid

Formate/Formic acid

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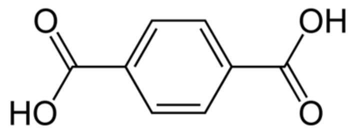
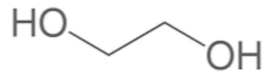
Concurrence Production of the Same Fuel at Both Cathode and Anode

Hydrolysis:

$(PET)_n$ + $(2n\text{-}1)H_2O$ → $nC_8H_6O_4$ (Terephthalic acid, TPA) + $nC_2H_6O_2$ (ethylene glycol, EG)





Anode:

$C_2H_6O_2 + 8OH^- \rightarrow 2HCOO^- + 6H_2O + 6e^-$

Cathode:

$3CO_2 + 3H_2O + 6e^- \rightarrow 3HCOO^- + 3OH^-$

Overall:

$C_2H_6O_2 + 3CO_2 + 5OH^- \rightarrow 5HCOO^- + 3H_2O$

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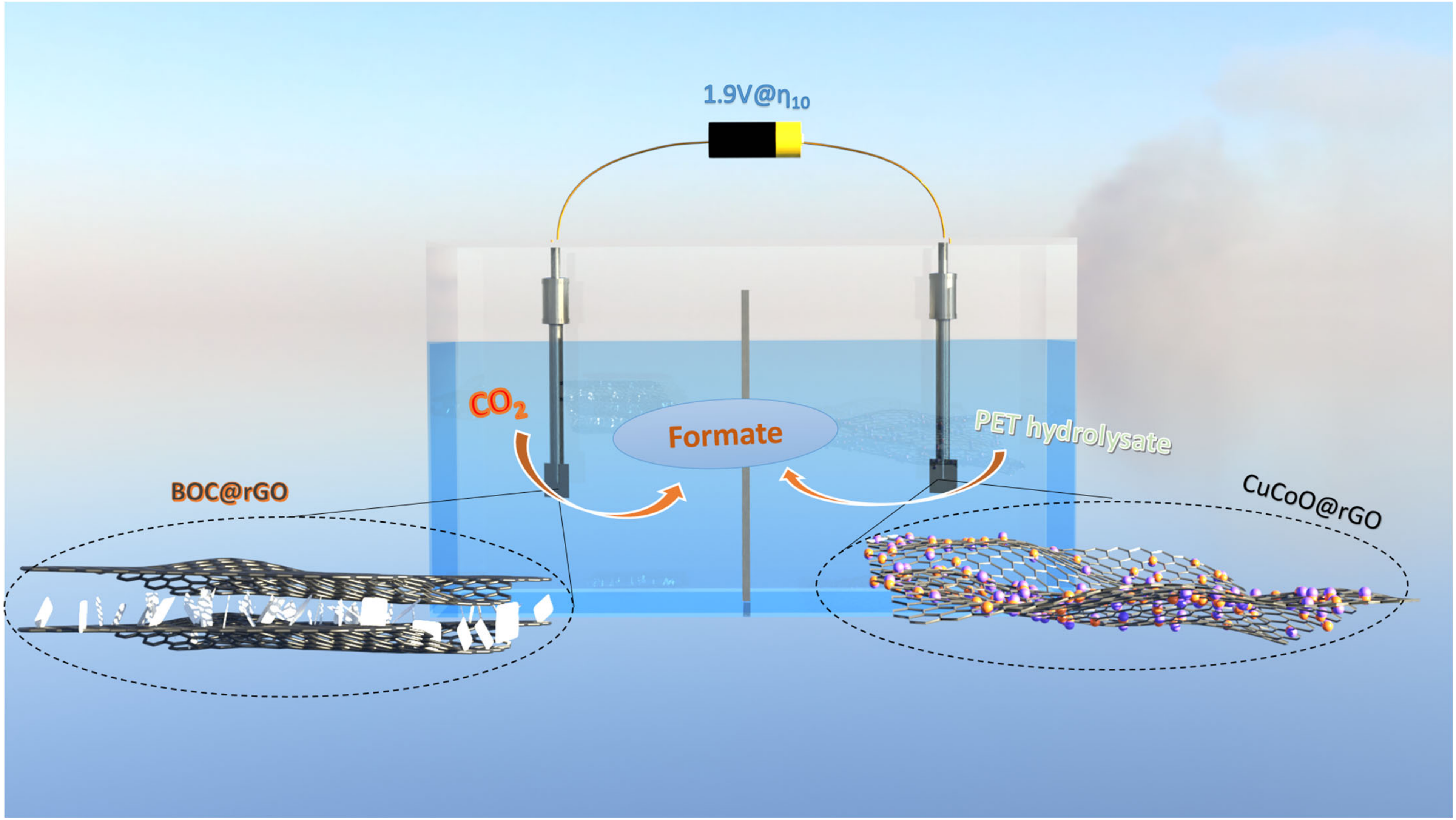
Kumar et al. *Journal of Materials Chemistry A* 11 (**2023**) 26075–26085

Concurrence Production of the Same Fuel (formate) at Both Cathode and Anode



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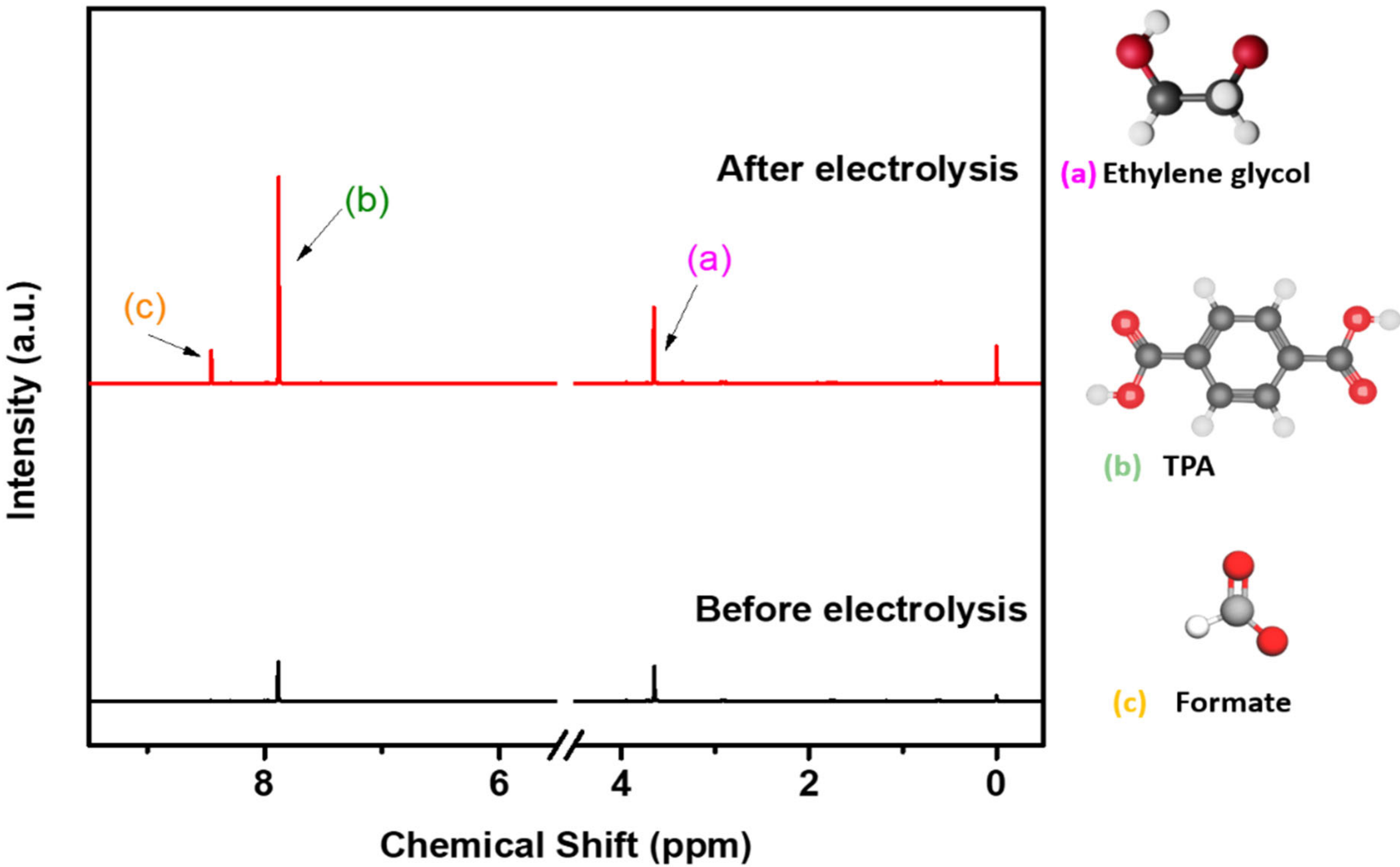
Kumar et al. *Journal of Materials Chemistry A* 11 (**2023**) 26075–26085

^{1}H NMR before and after electrolysis of PET hydrolysate solution using CuCoO@rGO nanocomposite



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Kumar et al. *Journal of Materials Chemistry A* 11 (**2023**) 26075–26085

Conclusion

- **Functional upcycling is a newly-introduced approach for polymer waste management**
- **Many opportunities for the preparation of functional materials**
- **The field will benefit from organic, polymer and surface chemistry approaches**

Open questions

- **The recycled material should have a higher added value than the parent material**
- **The possibility of recycling of the upcycled material**
- **Cost effectiveness**
- **Limit polymer leaching during functionalization**
- **Limit the use of aggressive chemicals**
- **Develop mild functionalization schemes**

Acknowledgment

Indo-French Centre for the Promotion of Advanced Research (IFCPAR), 2019 - 2023
Research Project No. 6005-1 – "Enhanced CO_2 adsorption and its photo-electrochemical Conversion using semiconductor-metal complex hybrids"

Collaborator: Dr. Suman L. Jain, IIP Dehradun

CNRS - AAP 2021 du défi Captage, stockage et valorisation du CO_2 (2021-2022)
Plasmon-enhanced CO_2 Electrochemical Reduction Reaction to Added Value Chemicals

ANR AAPG2023, CES 05 – Une énergie durable, propre, sûre et efficace
Plasmon-Enhanced Hybrid Electrolysis for Sustainable Fuel from Waste

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