PIONEER PLASMA CATALYSIS $CO_2$ RECYCLING — icb INSTITUTO DE CARBOQUIMICA — CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

785. WE-Heraeus-Seminar Non-Thermal Plasmas for Sustainable Chemistry

# Physicochemical and electrical characterization of $CeO_2$-based nanostructured catalysts for plasma-assisted $CO_2$ methanation in a DBD reactor


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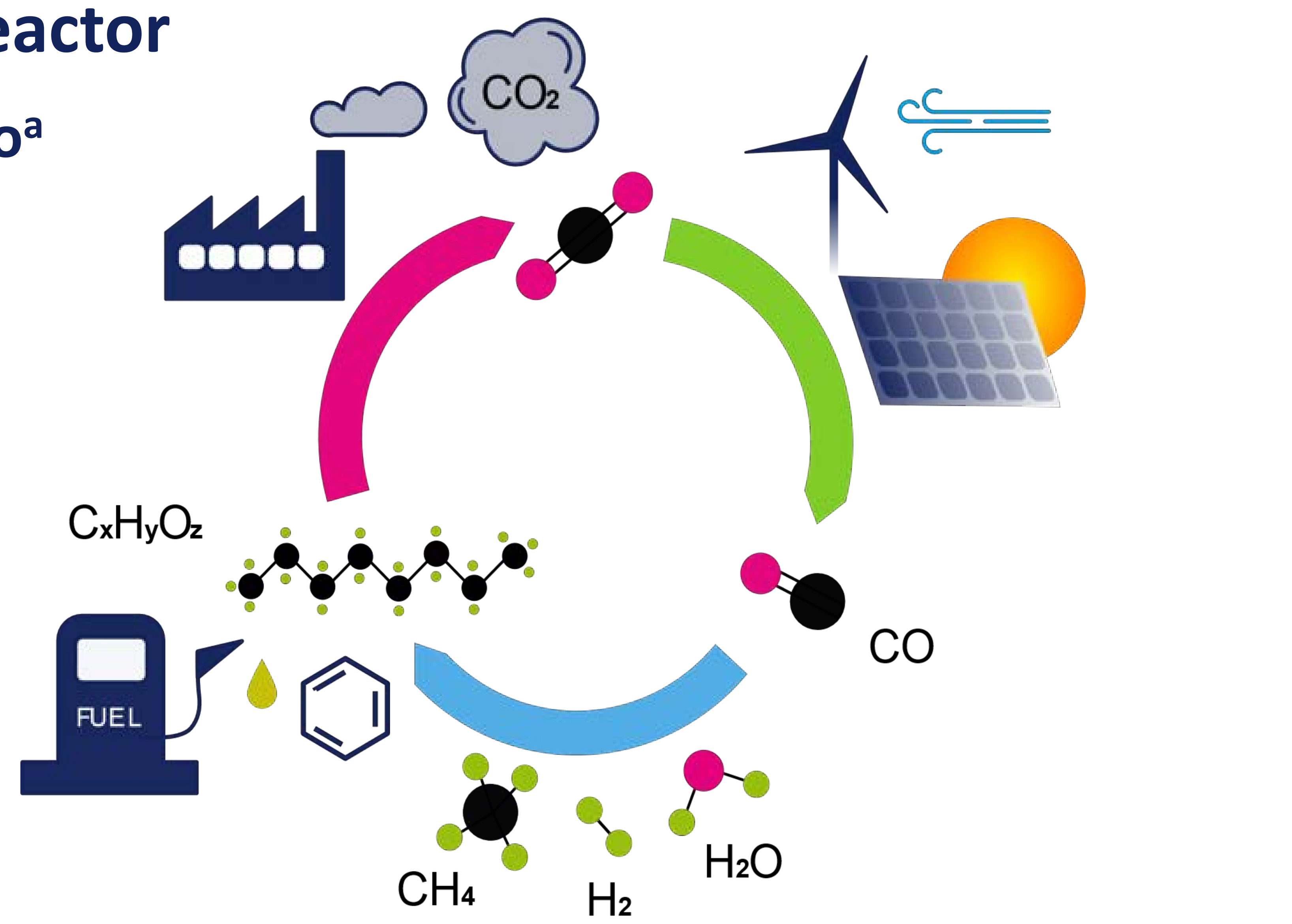
The use of $CO_2$ has great potential to complement greenhouse emission reduction strategies and to establish a sustainable and circular economy that exploits $CO_2$ not as an emission but as a carbon reservoir to produce value-added compounds. Innovative technologies such as non-thermal plasmas are being explored for $CO_2$ activation and reduction.
The combination of plasma and catalysis for the conversion of $CO_2$ allows the direct application of renewable electricity in an efficient way. Its application in the catalytic methanation of $CO_2$ takes advantage of the synergy between the ionized species in the plasma and their contact with the catalytic material to favour the reaction.




Closed carbon cycle: $CO_2$ capture and utilization using renewable energy sources to produce chemicals and fuels.
Credits: Carolina Garcia

## Preparation of nanostructured Ni/$CeO_2$ catalysts:

Hydrothermal synthesis for $CeO_2$ supports

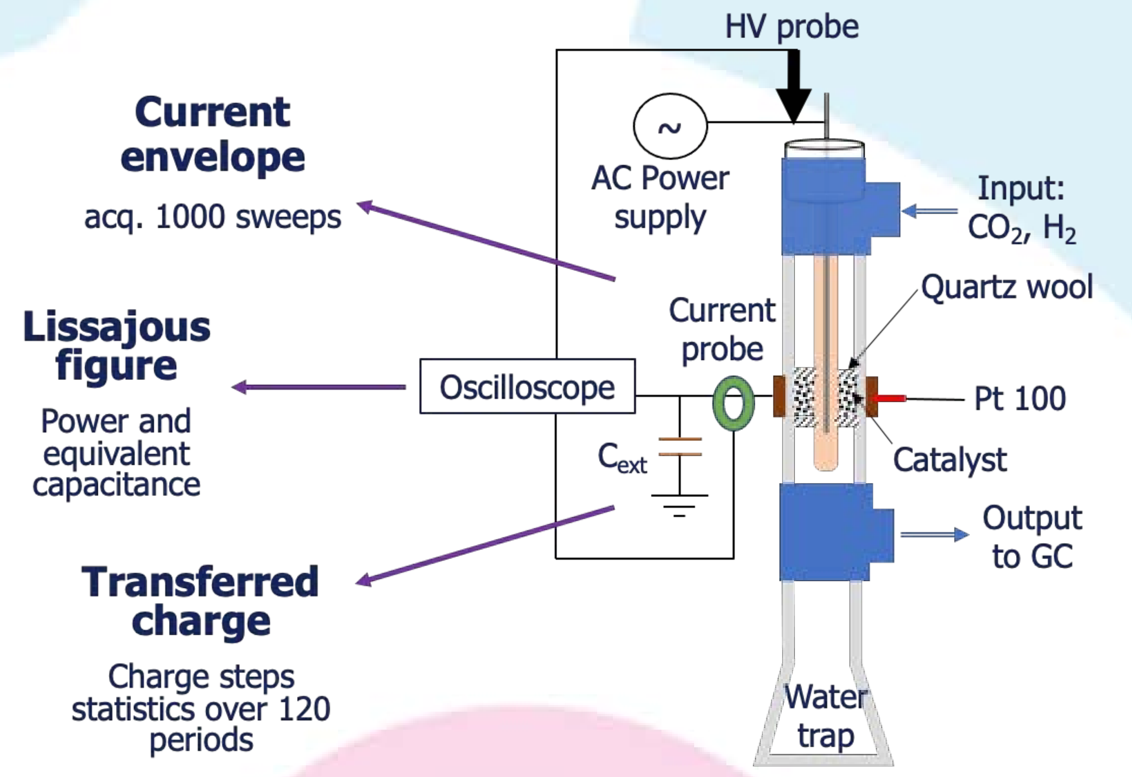
15 %wt. Ni wet impregnation

Reduction at 600 °C

## Physicochemical characterization

| | |
|---|---|
| SEM | Morphology |
| $N_2$ physisorption | Surface area |
| XRD | Crystal phases and crystallite size |
| $CO_2$-TPD | Surface basic sites |

## DBD reactor and electrical characterization

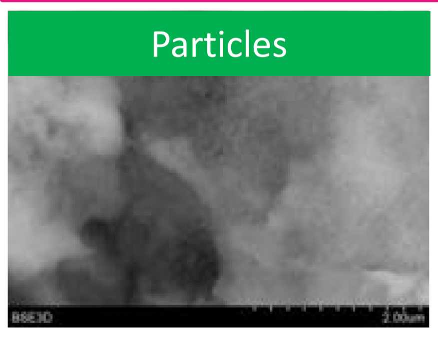



Schematics of the DBD set-up

Non-thermal Plasma Dielectric Barrier Discharge (DBD) Reactor
- AC sinusoidal signal, frequency 12.3 kHz and high voltage 20-30 kV
- $CO_2/H_2$ gas mixture 1:4, total flow 100 mL/min, WHSV 30000 mL/$hg_{cat}$
- Packed bed with powdered catalysts size 25-200 µm
- SEI 1.6-1.9 J/L

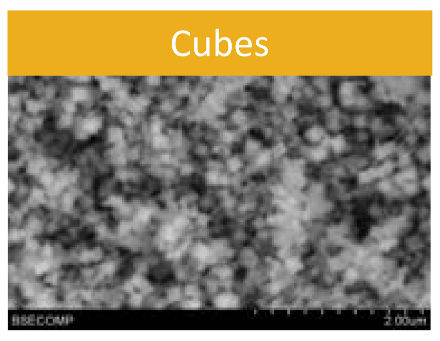
## Catalysts morphology

Particles

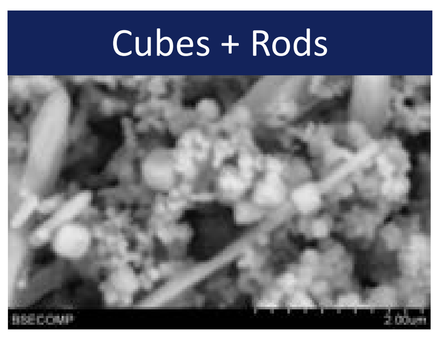


Needles

Cubes



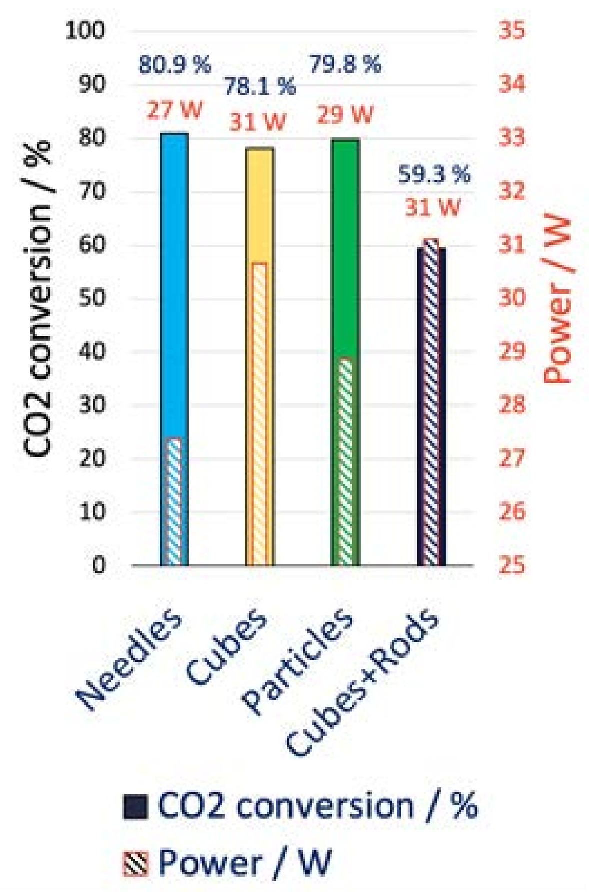
Cubes + Rods



## Catalysts physicochemical properties

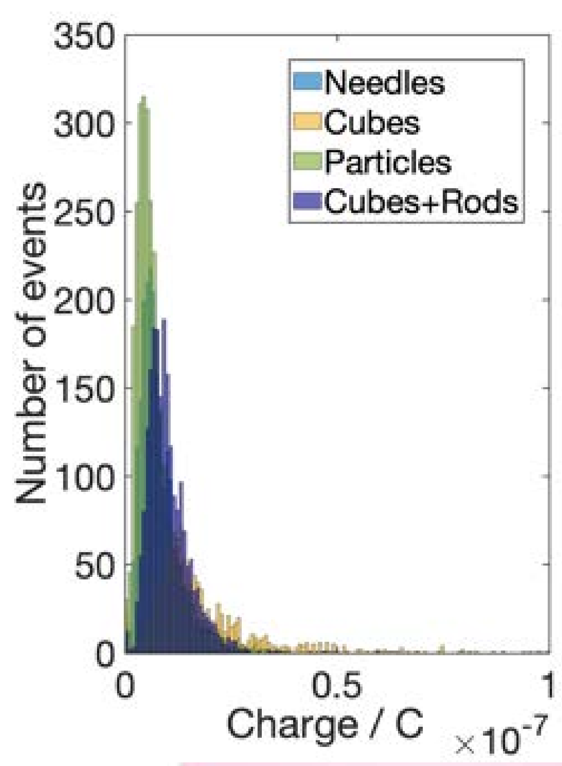
| | |
|---|---|
| Surface area | 70 m²/g |
| Ni crystallite size | 29 nm |
| Intermediate basic sites | 115 $\mu mol_{CO2}/g_{cat}$ |
| Surface area | 44 m²/g |
| Ni crystallite size | 18 nm |
| Intermediate basic sites | 71 $\mu mol_{CO2}/g_{cat}$ |
| Surface area | 33 m²/g |
| Ni crystallite size | 22 nm |
| Intermediate basic sites | 112 $\mu mol_{CO2}/g_{cat}$ |
| Surface area | 8 m²/g |
| Ni cystallite size | 30 nm |
| Intermediate basic sites | 6 $\mu mol_{CO2}/g_{cat}$ |

## $CO_2$ conversion and injected power



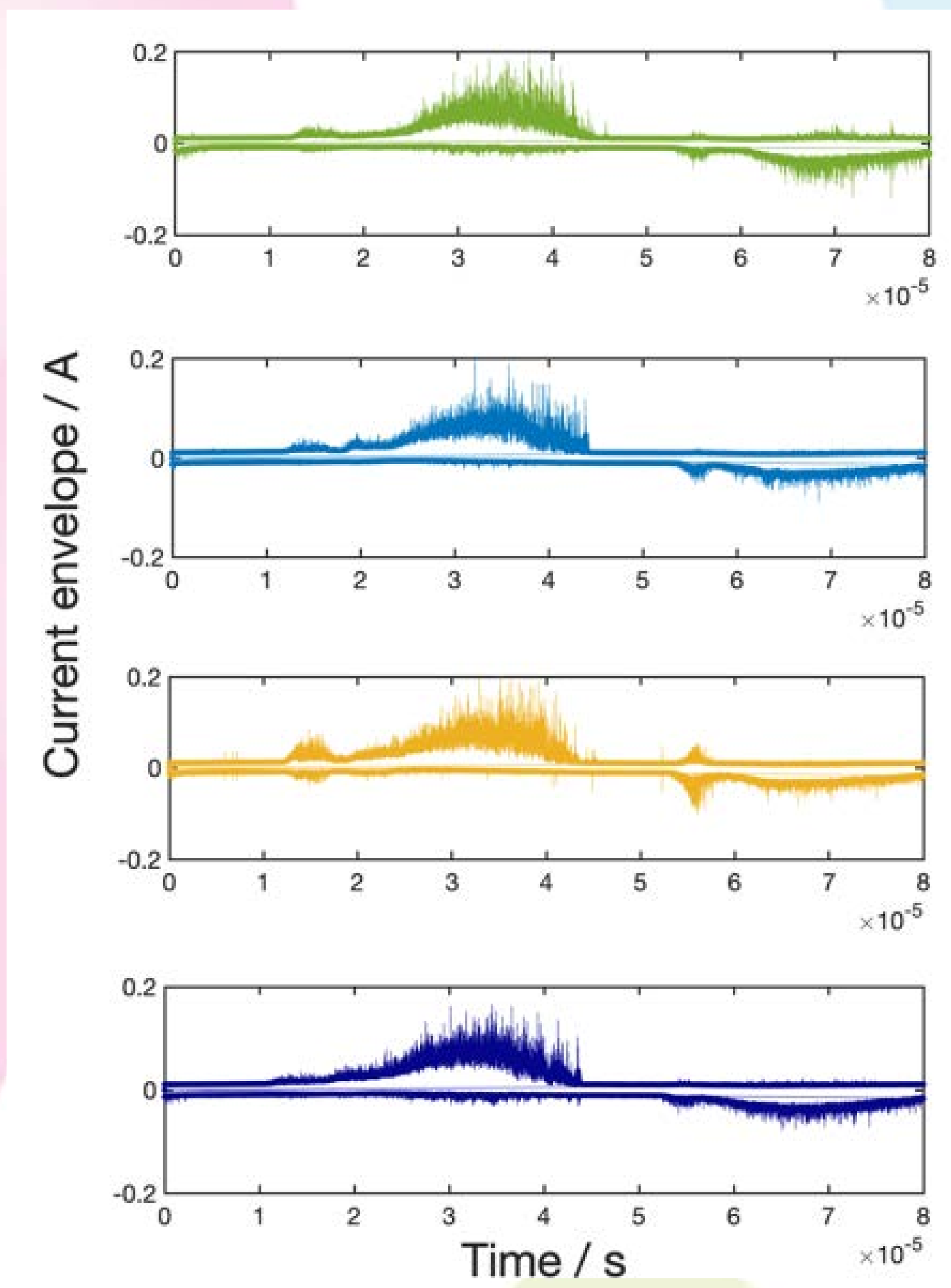

| | $C_{equivalent}$ (pF) |
|---|---|
| Particles | 14.5 |
| Needles | 12.9 |
| Cubes | 15.1 |
| Cubes+Rods | 16.3 |

## Charge steps statistics




| | $Q_{half\ cycle}$ ($10^{-7}$ C) |
|---|---|
| Particles | 1.8 |
| Needles | 1.6 |
| Cubes | 2.1 |
| Cubes+Rods | 1.8 |

## Current envelope




- A clear **relation between physicochemical properties and the activity** in plasma-assisted $CO_2$ methanation is established: the material with the largest structures, low surface area and poor basicity does not reach high conversion above 70 % at ~30 W.
- **Different charge transfer behaviours** are observed with different packing materials.
- For materials with similar physicochemical properties: **low $C_{equivalent}$** is linked with **low $Q_{half\ cycle}$** and with an **enhanced efficiency** of the catalysts (this is the case of the catalyst with needles morphology with 80.9 % conversion at 27 W).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