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Carbon nanostructures decorated with Cerium Oxide as multi-functional electrocatalysts for CO_2 conversion

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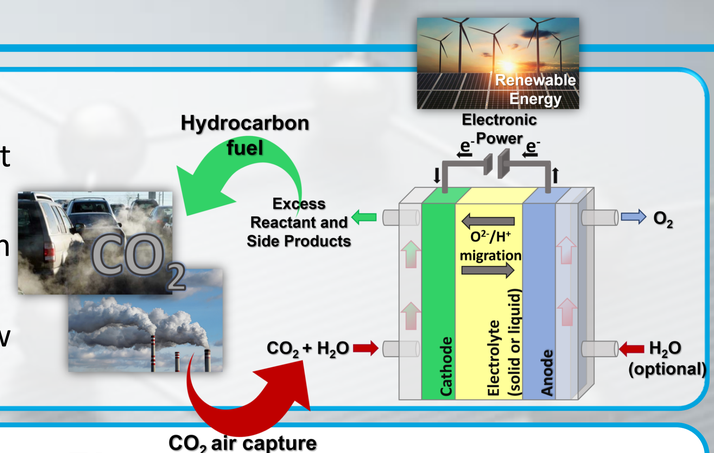
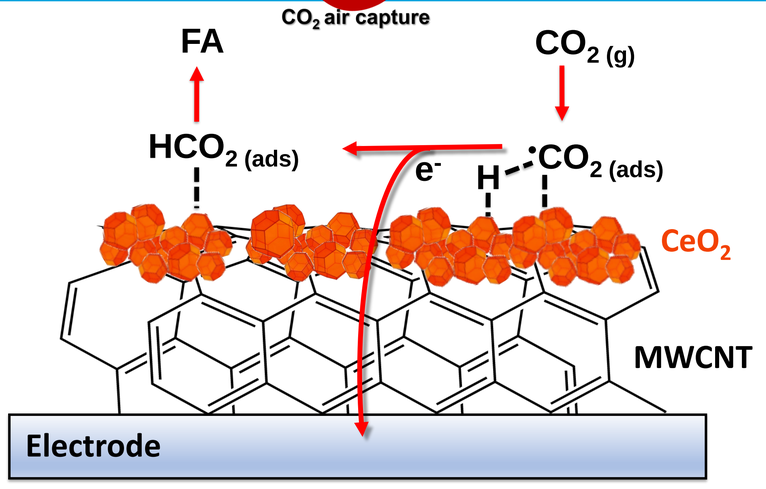
Introduction

- Due to the alarming problem of global warming and climate changes, recently the research has focused on the development of new materials and technology capable of capturing and converting CO_2 into useful products.[1]
- In this work we present a **new design of electrocatalysts** able to reduce CO_2 in a selective and efficient way: the combination of different building blocks in a single nanostructure increase the selectivity
- Combining the unique physico-chemical properties of functionalized MWCNTs and cerium oxide (CeO_2), we demonstrate how to selectively control the production of **formic acid** (FA) in aqueous solutions.[2]



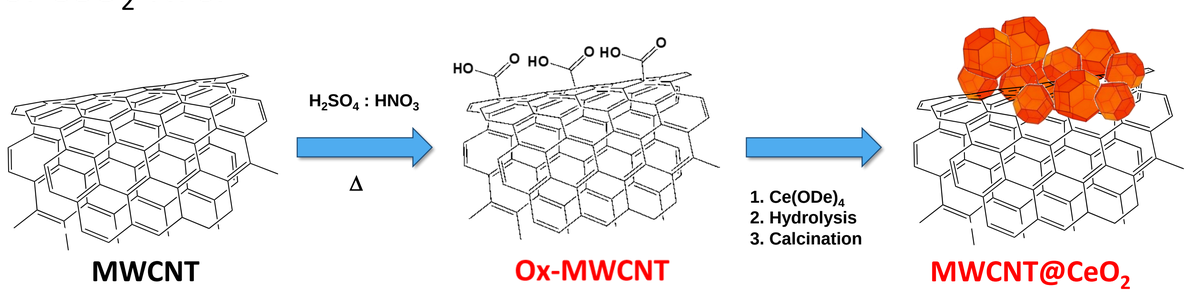
MWCNTs decorated with CeO_2 nanoparticles

- The catalytic activity of CeO_2 depend on **reversible $Ce^{3+/4+}$ redox pair** and release or storage of oxygen atoms. The formation of **oxygen vacancies** in reduced CeO_2 promotes CO_2 binding and activation by Ce^{3+} sites.[3]
- The **nano-dimensions** of CeO_2 determine redox proprieties and oxygen vacancies formation.
- The MWCNTs **counteract** the insulating effect of oxide shell and **promote** the generation of Ce^{3+} sites, thank to great **surface area** and **electrical conductivity**.



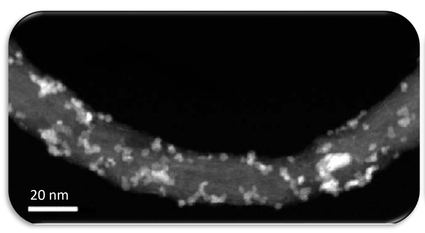
Synthesis

The oxidation of MWCNTs with H_2SO_4/HNO_3 forms oxygenated groups on MWCNTs surface that allow the anchoring of $Ce(ODe)_4$. The Ce precursor hydrolysis forms amorphous CeO_2 islands, while the calcination at 250°C leads to the crystallization of CeO_2-NPs.

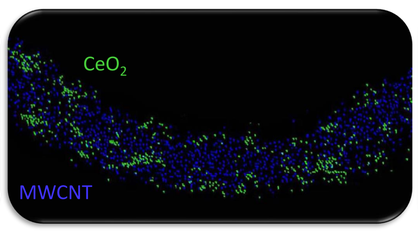


Morphology of MWCNTs@CeO_2

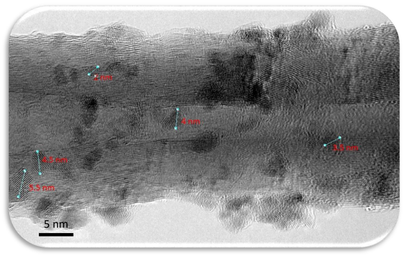
The MWCNTs have diameter in the range 20-30 nm, while the mean size of CeO_2 NPs is 2.8±0.5 nm, with *fcc* structure.



STEM-HAADF of a typical MWCNT@CeO_2



Energy-dispersive X-ray map highlighting the element distribution of CeO_2 (green) and the structure of MWCNT



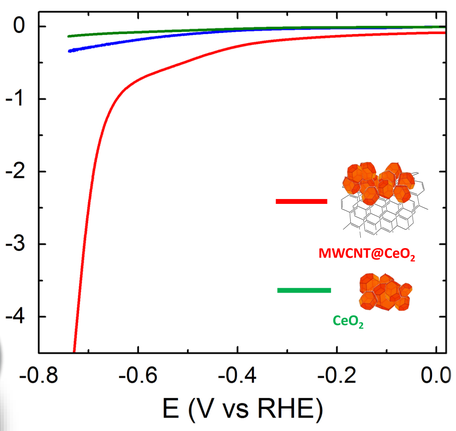
HRTEM of MWCNT@CeO_2

CO_2RR performances

- The electrocatalyst **MWCNT@CeO_2** shows a **higher cathodic current** than alone CeO_2 NPs. The catalytic activity derive from **combination** and **interaction** of CeO_2 NPs with MWCNTs.
- Presence of only two CO_2RR products: **hydrogen** an **formic acid** → **high selectivity**
- The FE for formic acid is almost 60 % at -0.22 V vs RHE, near to standard potential.

CA for MWCNT@CeO_2 at different overpotentials

The Faradic Efficiency for FA (red) and H_2 (blue) production

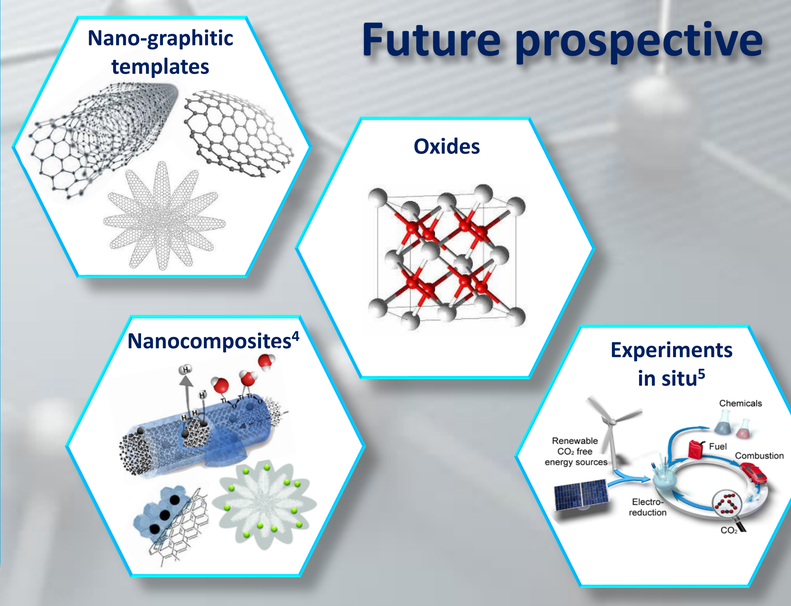


LSV for MWCNT@CeO_2 (red line), the bare GC electrode (blue line) and CeO_2 NPs (green line) in a CO_2-satured solution. Scan rate: 2 mV s^{-1} in HNO_3 0.1 M.

Conclusions

- The catalytic activity originates from **interaction** between MWCNTs and CeO_2 NPs.
- The electrocatalyst **MWCNT@CeO_2** has a high selectivity in CO_2RR process.

Future prospective



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