



# 3DOM Ceria Ecoceramics from Sustainable Cork Templates for Solar Thermochemical CO<sub>2</sub> Splitting

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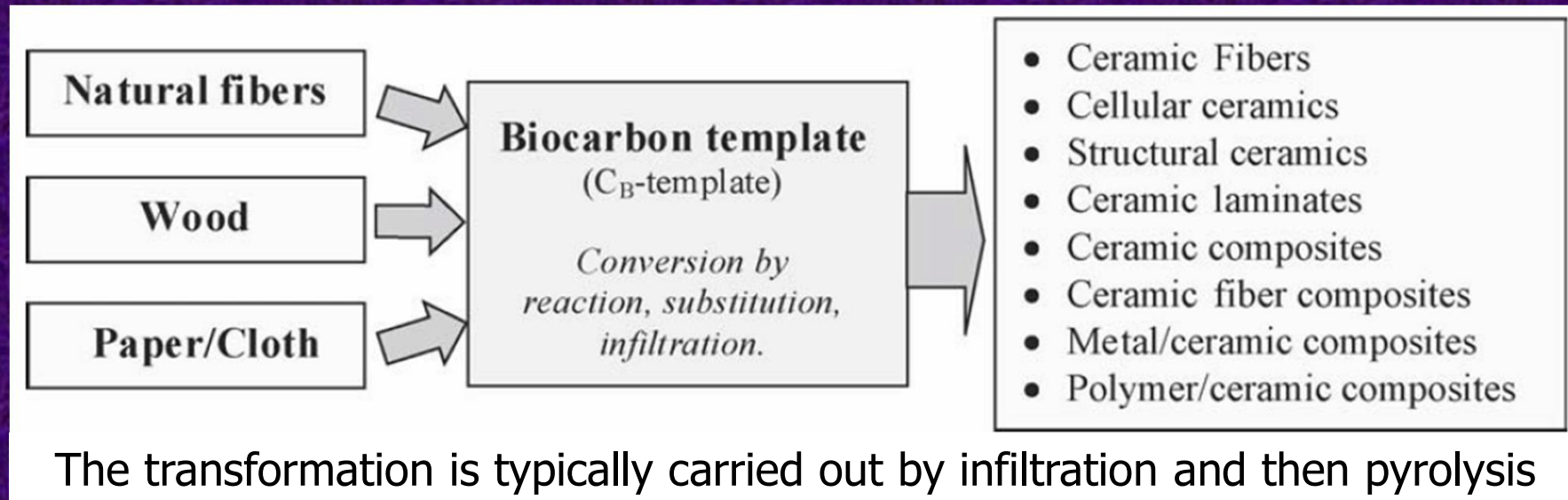
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# What are Ecoceramics?

- The name "Ecoceramics" - environmentally conscious ceramics – was invented by M. Singh at NASA in 2003
- A new class of Materials which can be fabricated from sustainable sources such as wood and wood wastes
- Aim is to create ceramics with the cellular microstructure of wood - "**biomimetic**" or "**biomorphic**" material (copying nature)

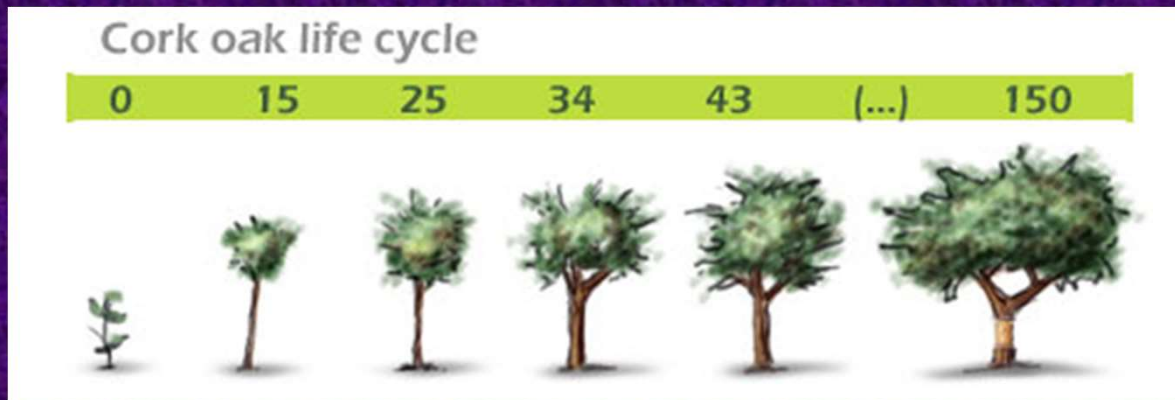


- We are the first to make Ecoceramics from cork templates

# Cork is the Bark of a Slow Growing Oak (*Quercus Suber*) from the Mediterranean

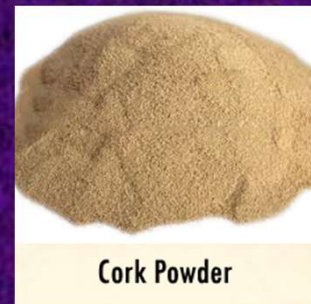
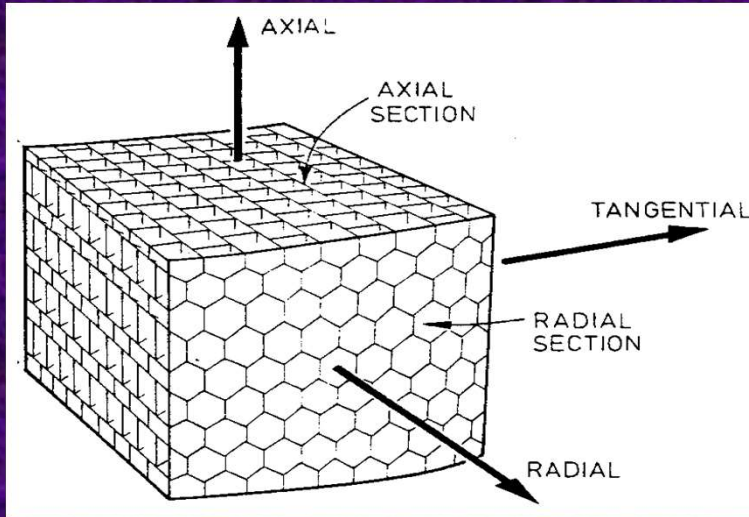


50% of all cork comes from Portugal

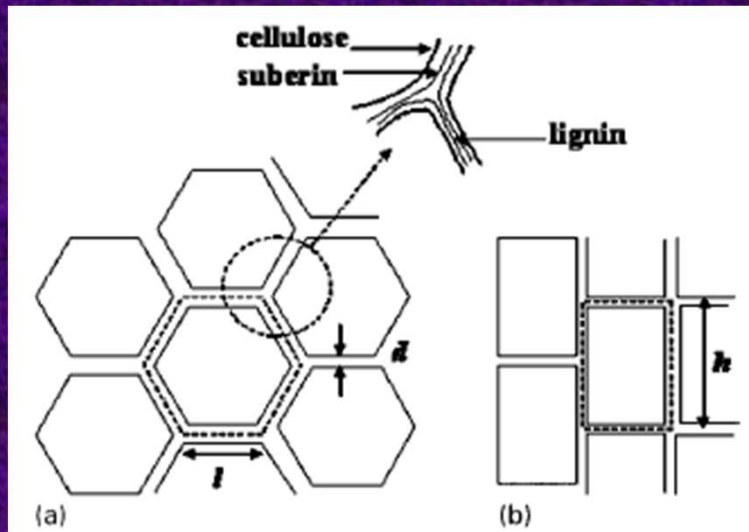


Bark is harvested every 9-13 years, but tree lives on unharmed as carbon sink for >200 years

# Cork is a Renewable Portuguese Resource, with a Natural 3-DOM Microstructure

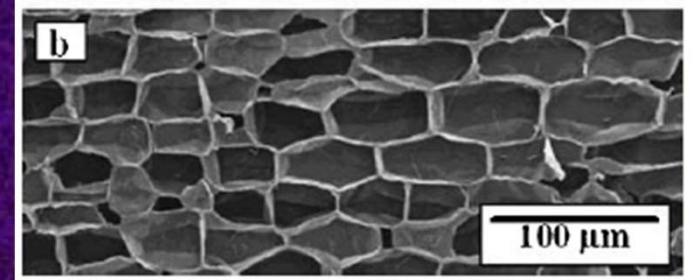
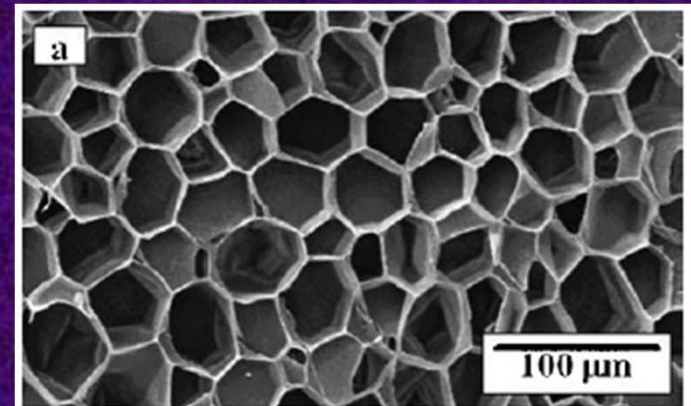


~50,000 t per year of waste cork powder & granules are generated by the cork industry – currently most is burnt to generate energy



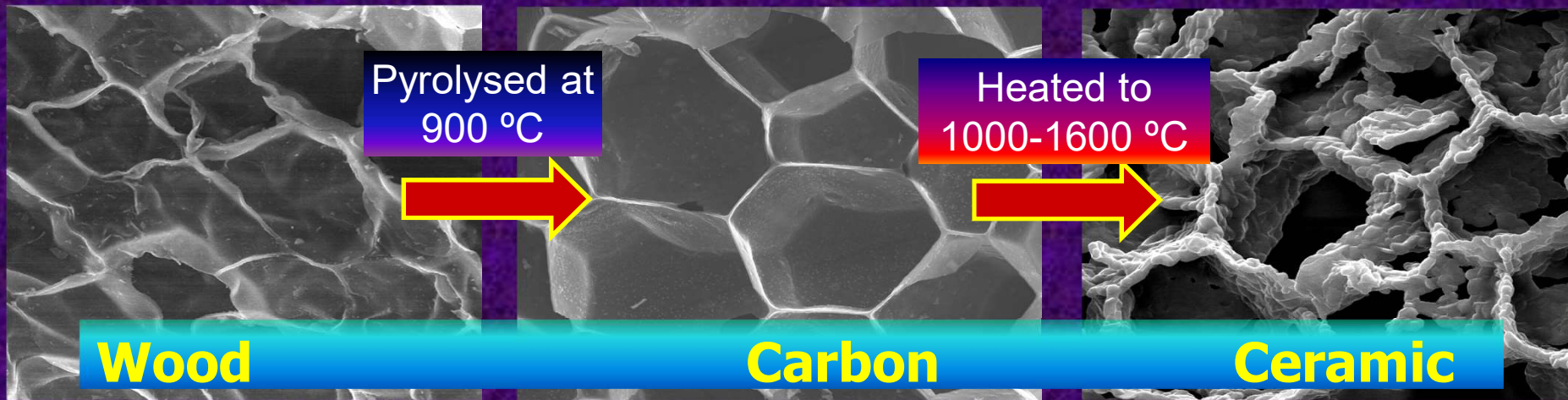
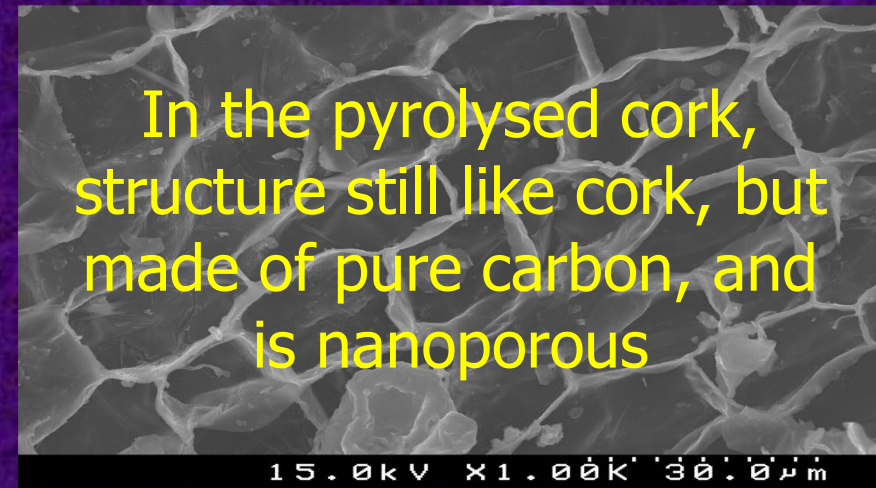
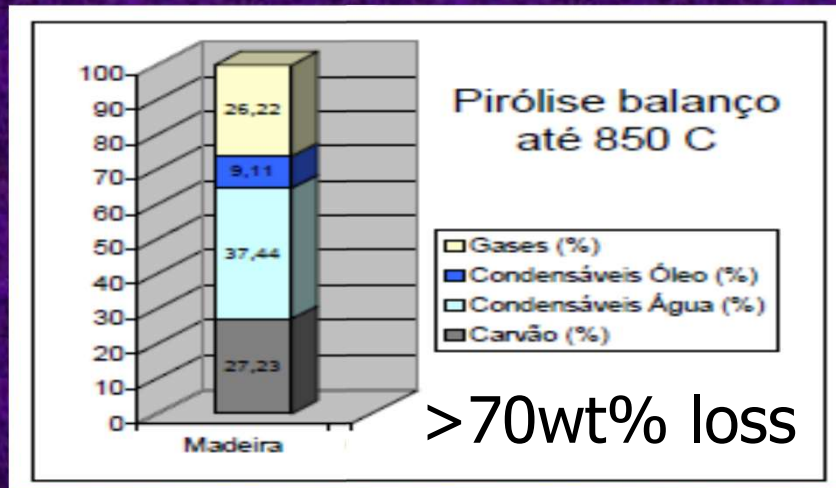
a) Hexagonal Radial section

b) Rectangular Tangential or Axial section

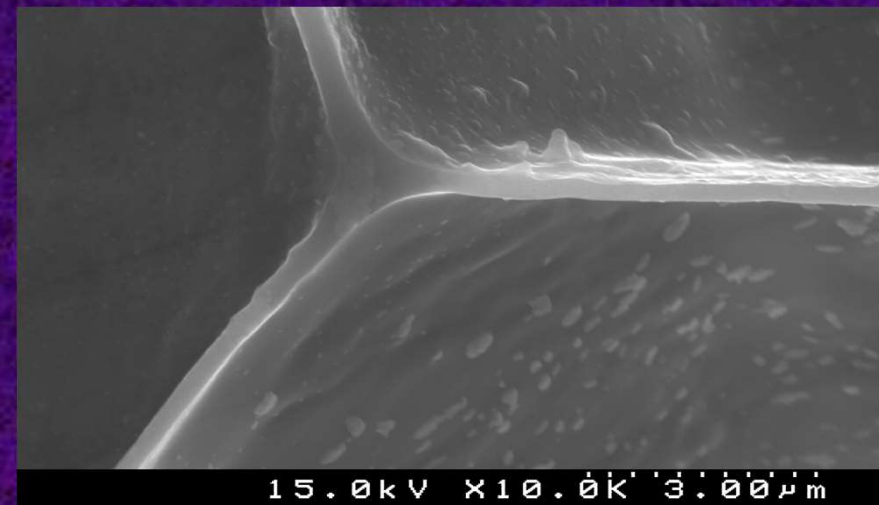
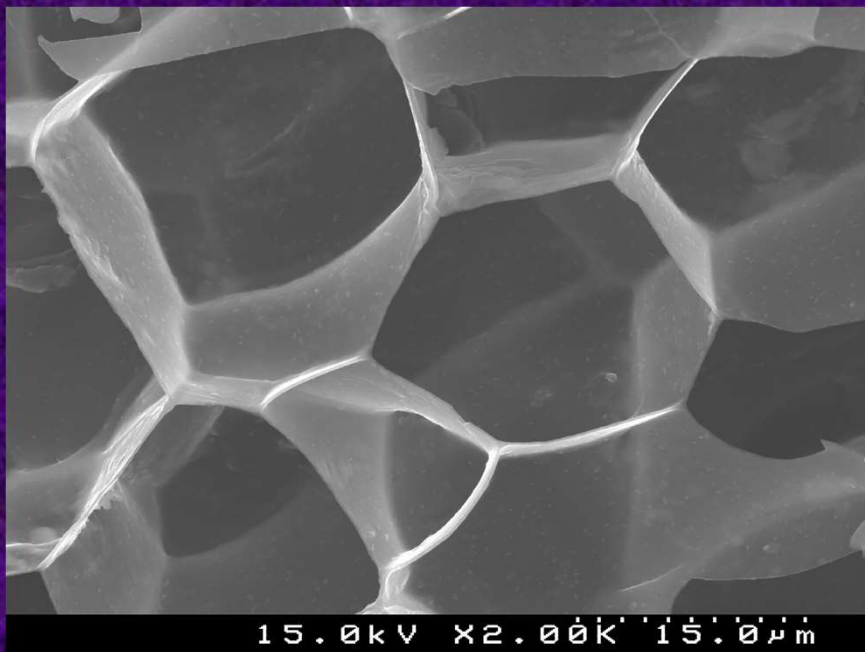
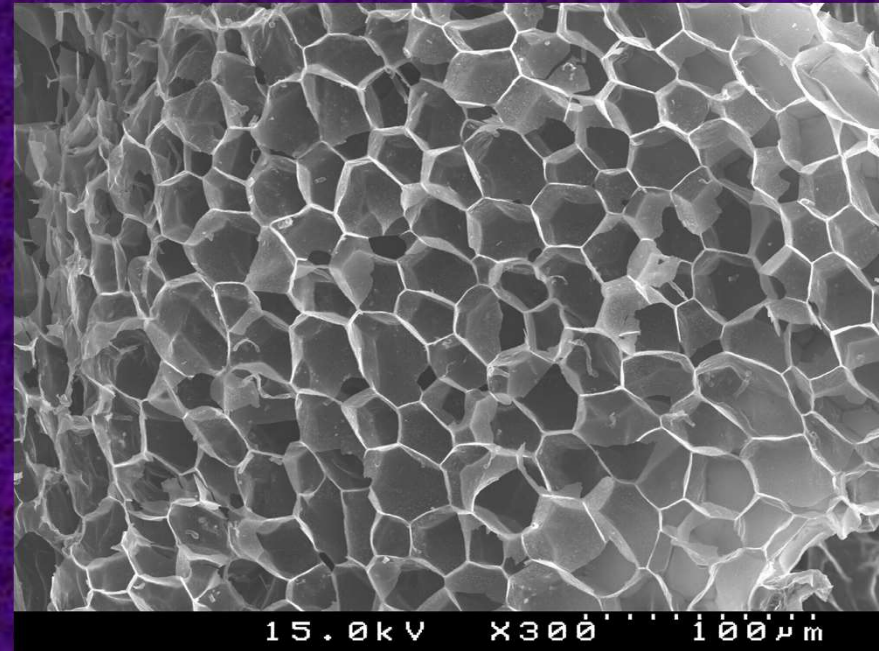
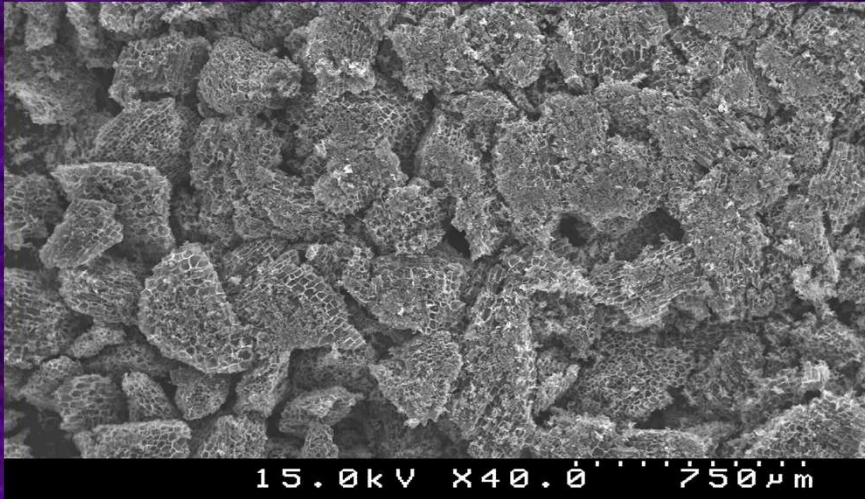


# Pyrolysed Cork → Carbon → Ceramic

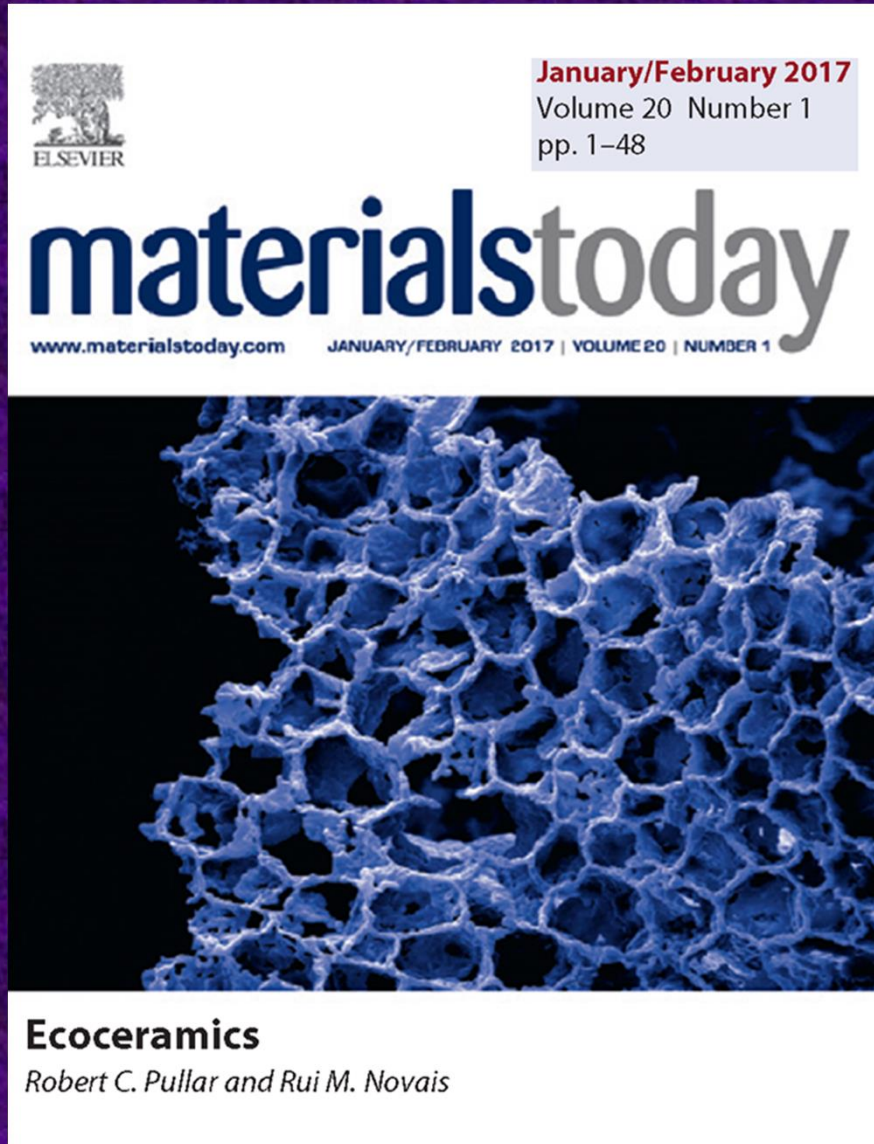
- Graphite furnace at 900 °C in Ar or N<sub>2</sub> cork → carbon
- Then the carbon matrix is infiltrated with precursor solution & heated in air to burn out carbon and form the ceramic



# SEM Images of Pyrolysed Waste Cork Powder (now nanoporous carbon)

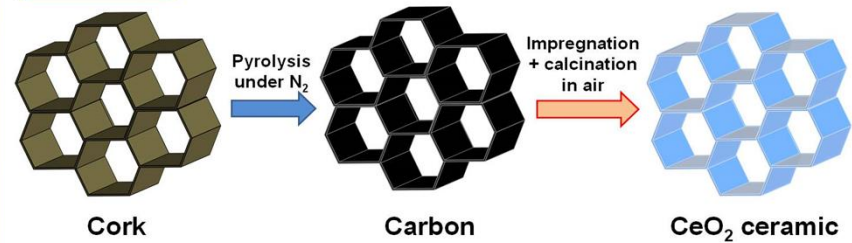


# Our Ecoceramics were on the Cover of *Materials Today* (Vol 20, Jan 2017, p. 45-46)



## Concept

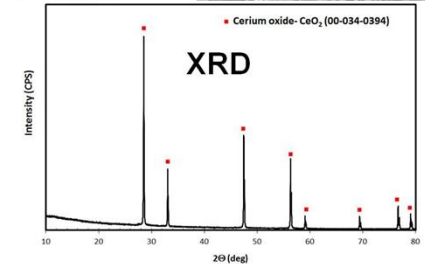
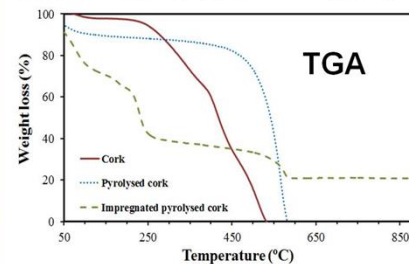
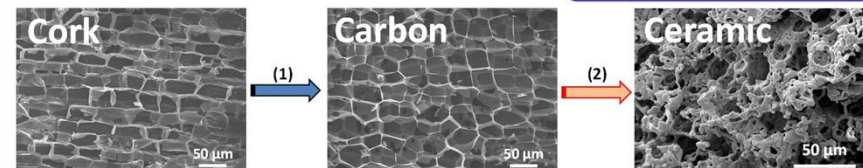
Now we are making CeO<sub>2</sub>



## Processing



## Characterisation

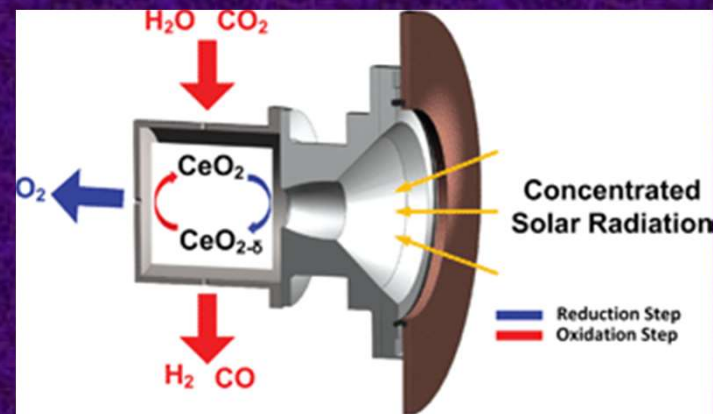
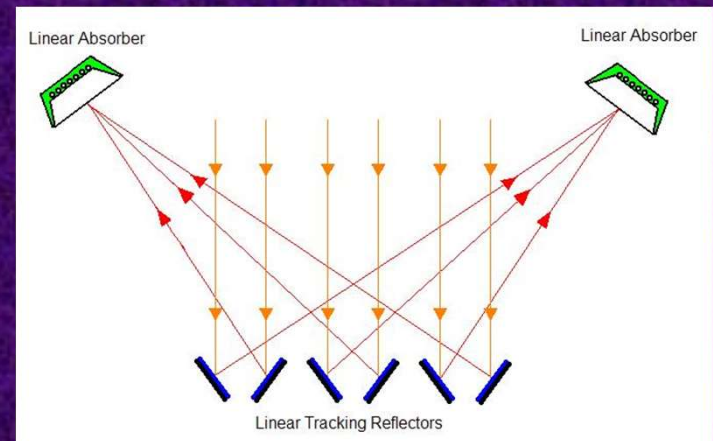


# Looking at Applications in Renewable Energy and Hydrogen Generation

Direct concentrated solar energy – a beam of sunlight, NOT photovoltaics

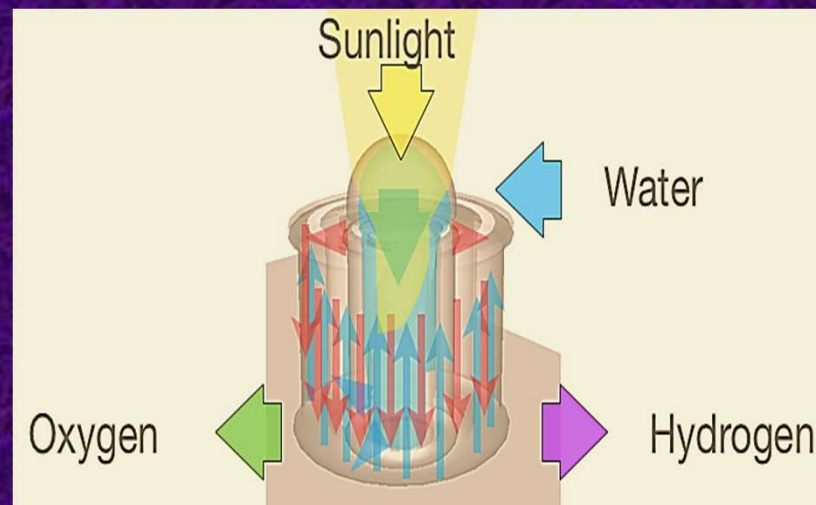
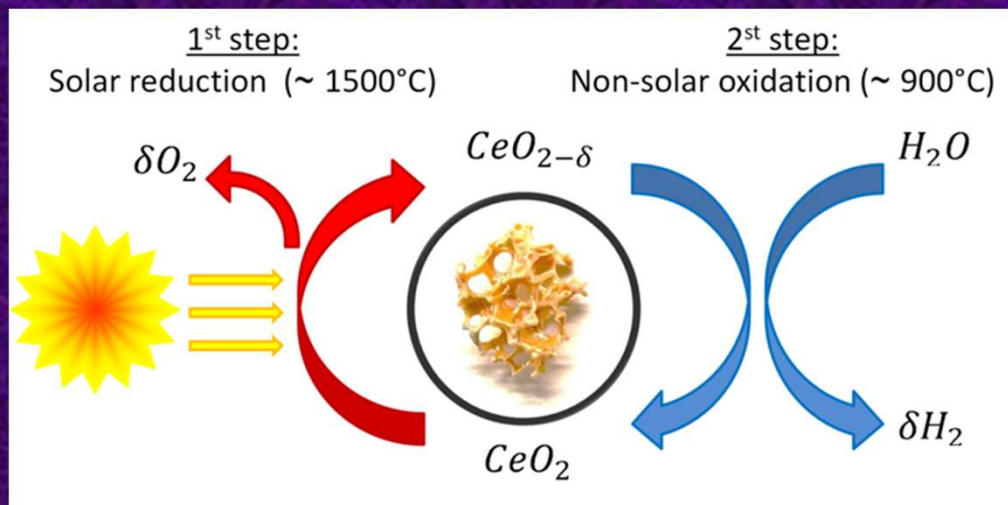
**ThermoChemical Fuel Production (TCFP)**  
to split water or  $\text{CO}_2$  on ceria at  $1500\text{ }^\circ\text{C}$

## Direct Concentrated Solar Energy Plant



# Why Cork based $\text{CeO}_2$ Ecoceramics could be Good for TCFP Water & $\text{CO}_2$ Splitting

Two-step redox thermochemical cycle, requires temperatures up to  $1500\text{ }^\circ\text{C}$  (thermolysis), so needs a high temp ceramic ( $\text{CeO}_2$ )



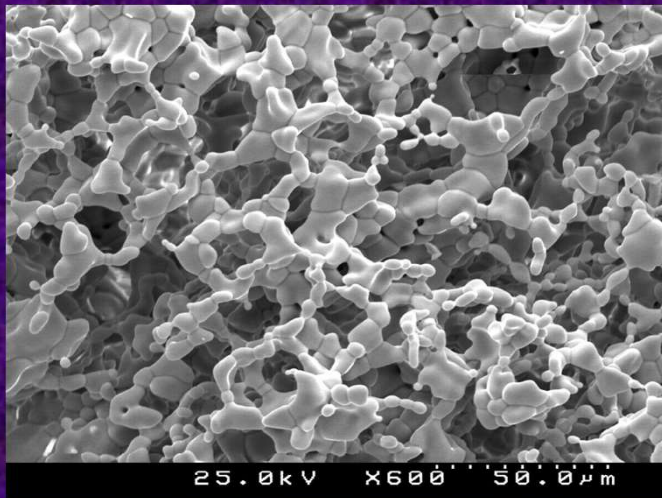
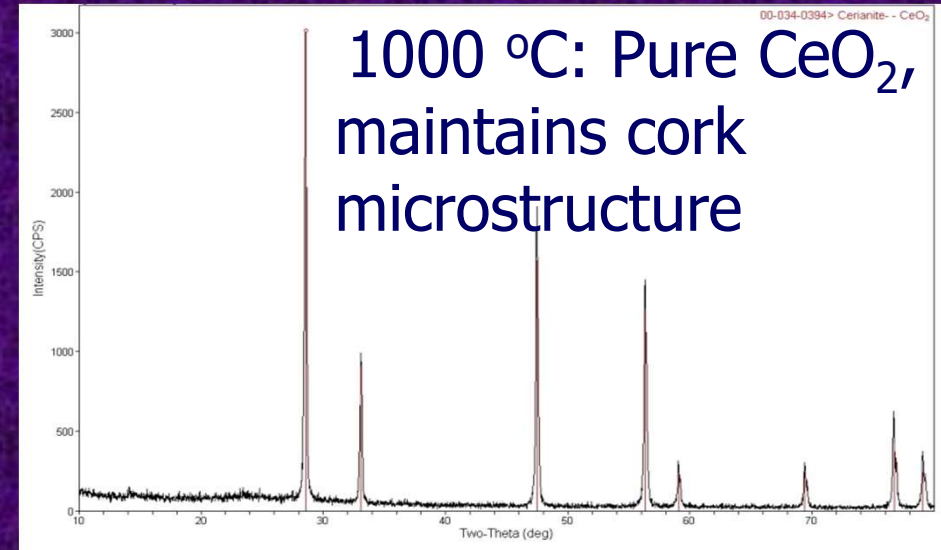
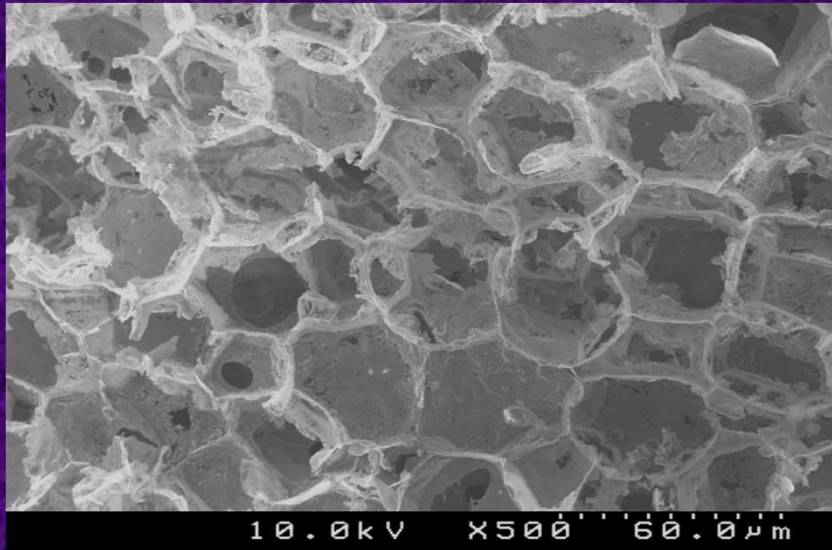
Non-stoichiometric ceria combines excellent reactivity (high  $\text{O}_2$ -ion conductivity) and good cyclability (high-temp stability)

**However**, currently low  $\text{H}_2$  &  $\text{CO}$  yields – very inefficient process

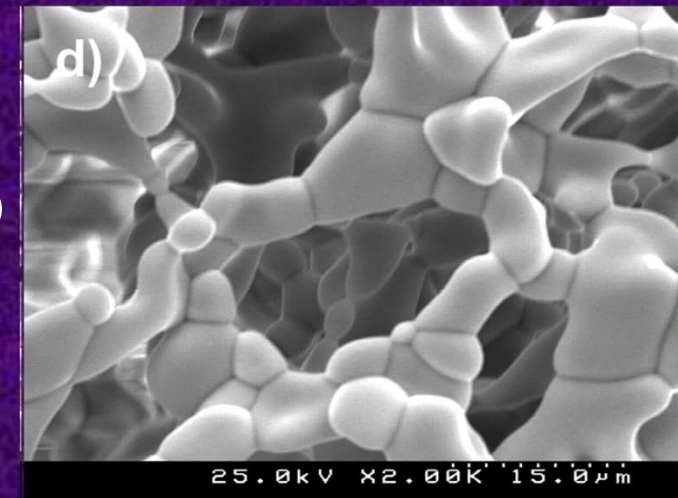
Reaction kinetics would be enhanced using 3-DOM  $\text{CeO}_2$

**Cork could be an ideal biomimetic and sustainable template**

# Waste Cork-based Ceria Ecoceramics heated to 1000 °C and 1600 °C

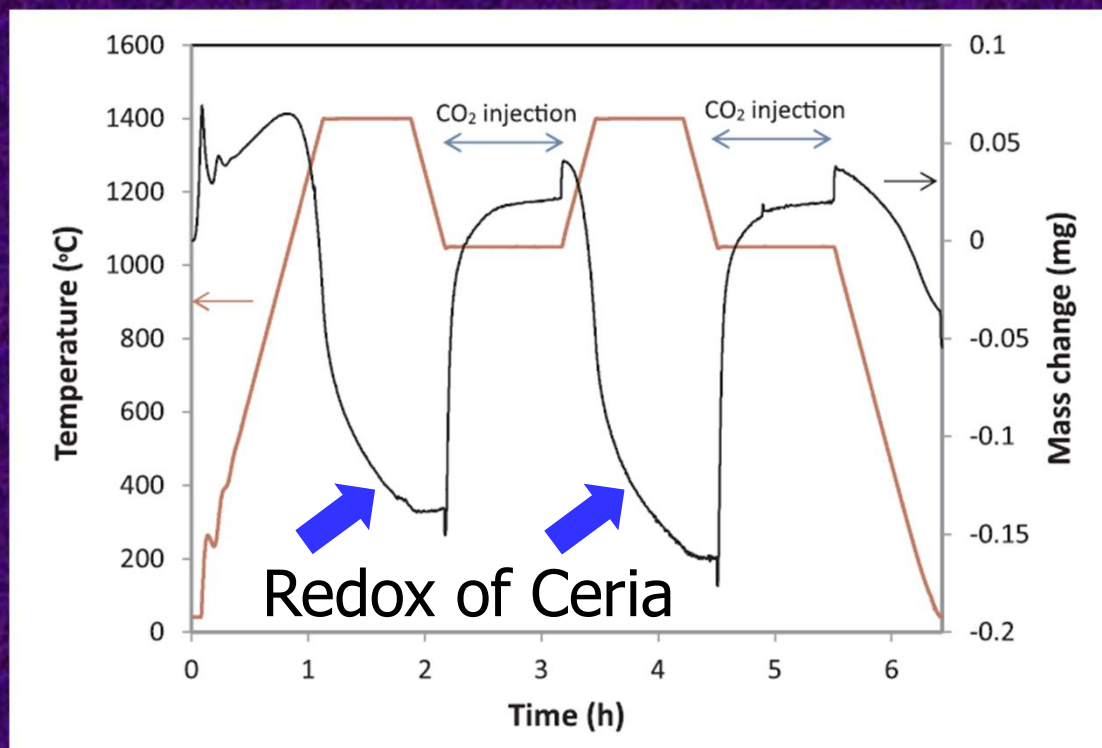
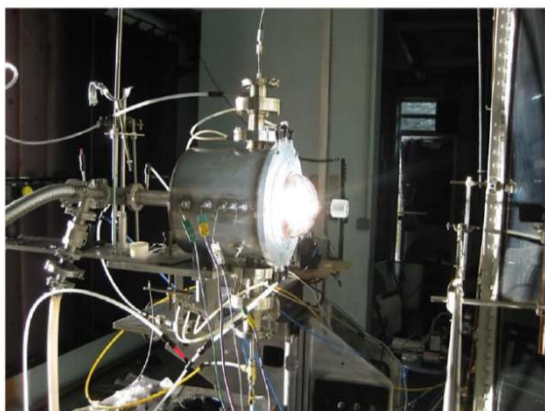
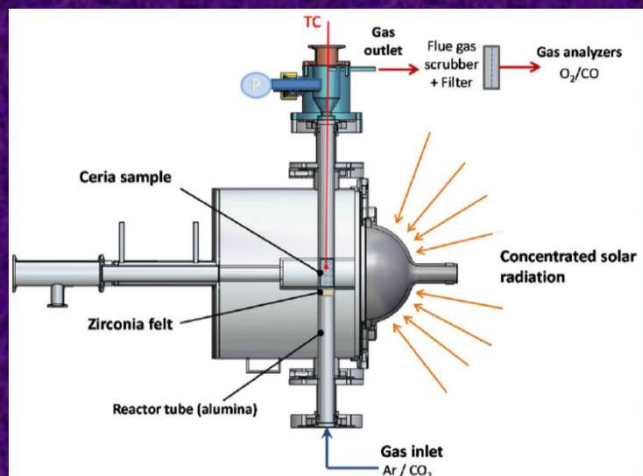


**1600 °C:**  
Grains have  
grown greatly up  
to 10 µm, cork  
structure  
damaged but  
porosity greater



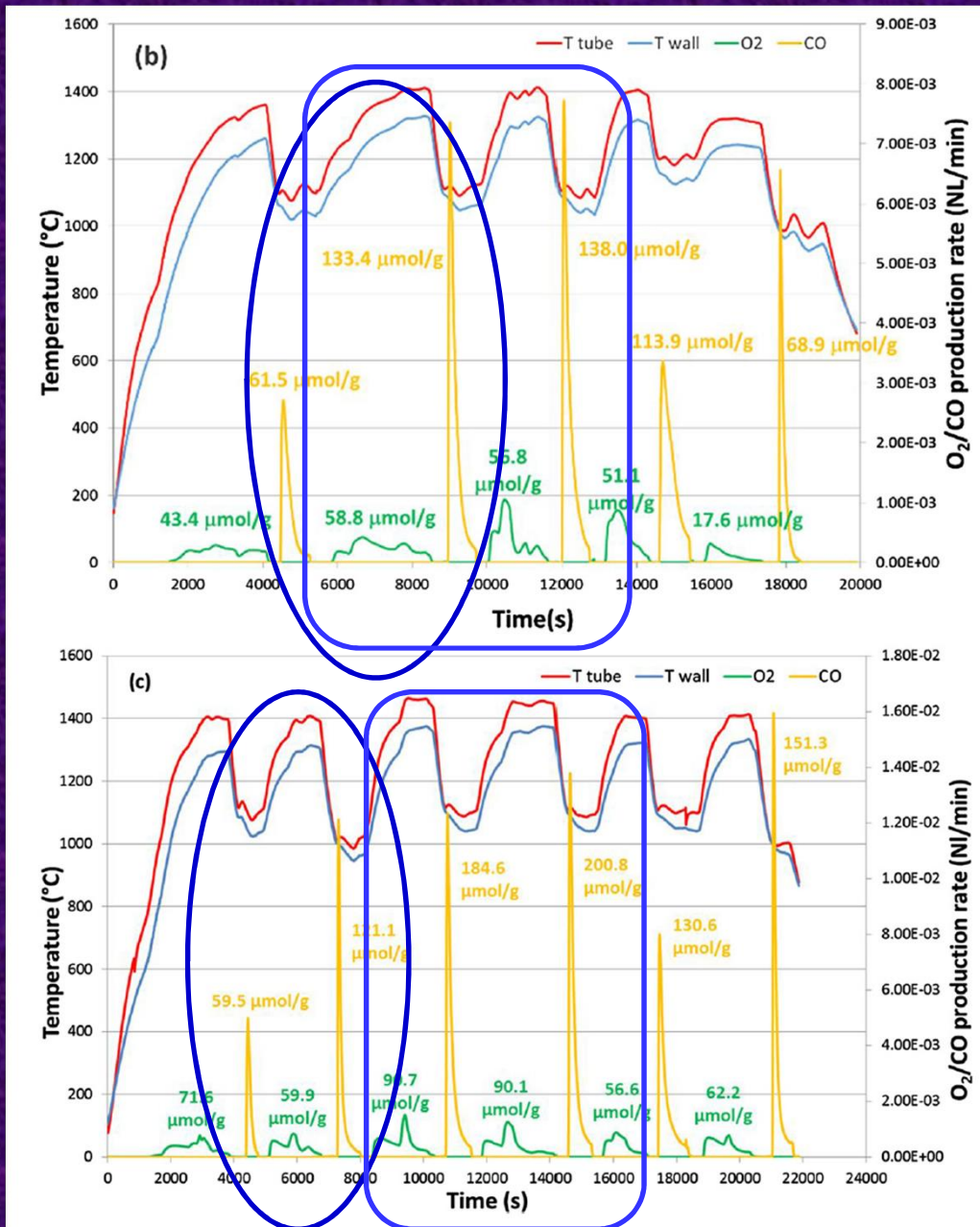
# Solid–Gas Thermochemical Reactions to Split $\text{CO}_2 \rightarrow \text{CO} + \text{O}_2$ (for syngas)

- Using a solar chemical reactor mounted on a medium size solar furnace (MSSF) facility at CNRS-PROMES – 2 m diameter parabolic dish concentrator, 15 mm diameter cavity receiver



Two steps –  $\text{CO}_2$  split at 1050 °C, ceria reduced at 1400 °C, all in solar reactor

# CO<sub>2</sub> Splitting with CeO<sub>2</sub> Cork Ecoceramics



Top (b) = 750 w / m<sup>2</sup>

Bottom (c) = 1000 w / m<sup>2</sup>

**Yellow** = CO production in oxidation step @ 1050 °C

**Green** = O<sub>2</sub> production in reduction step @ ~1400 °C

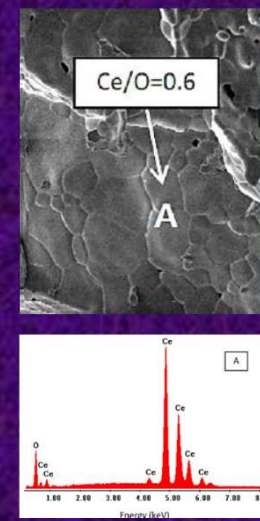
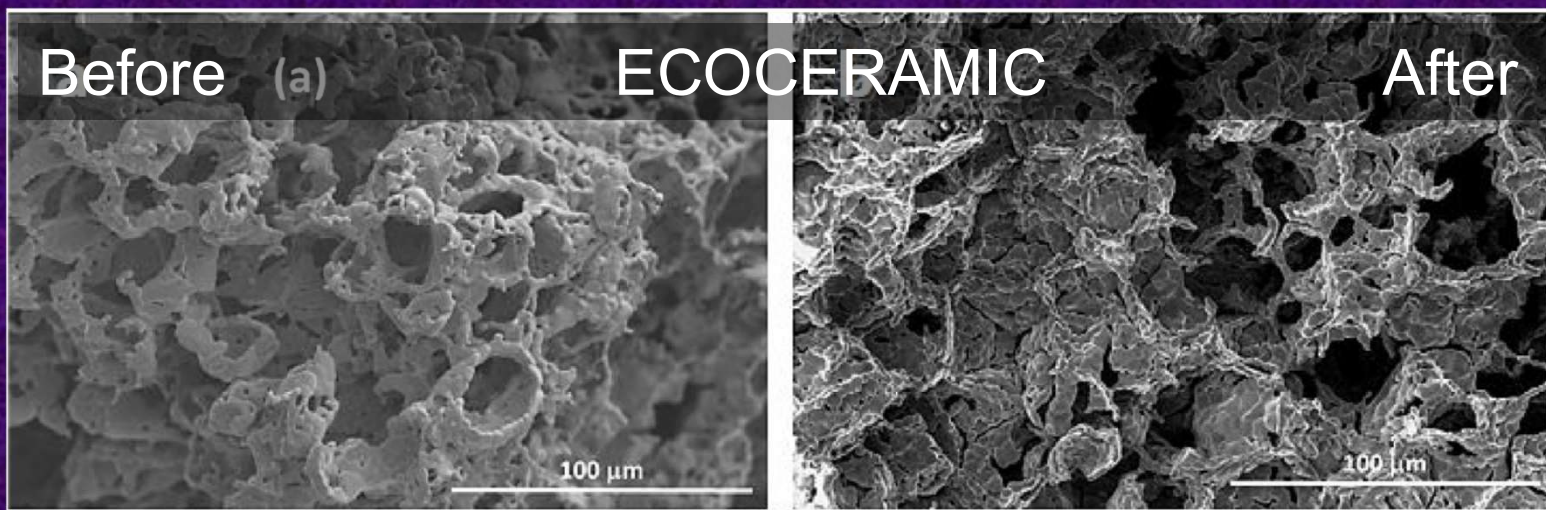
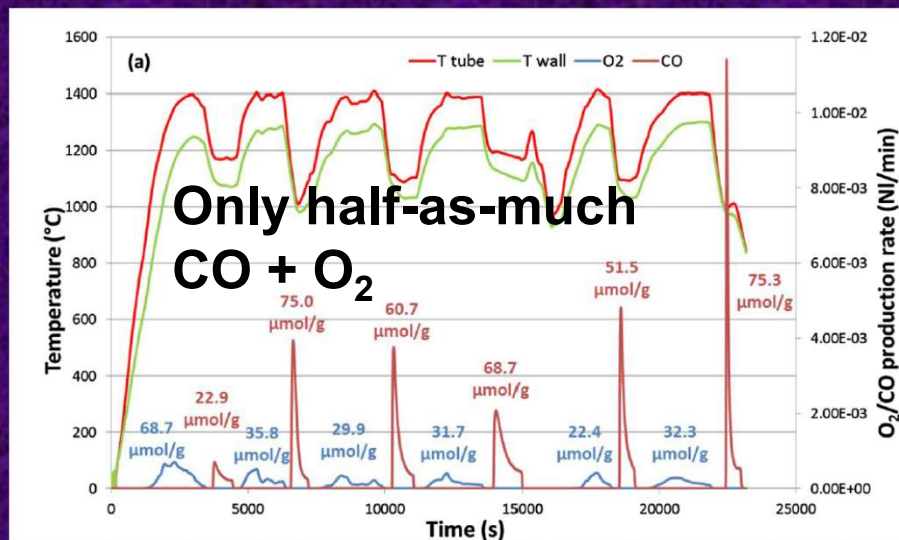
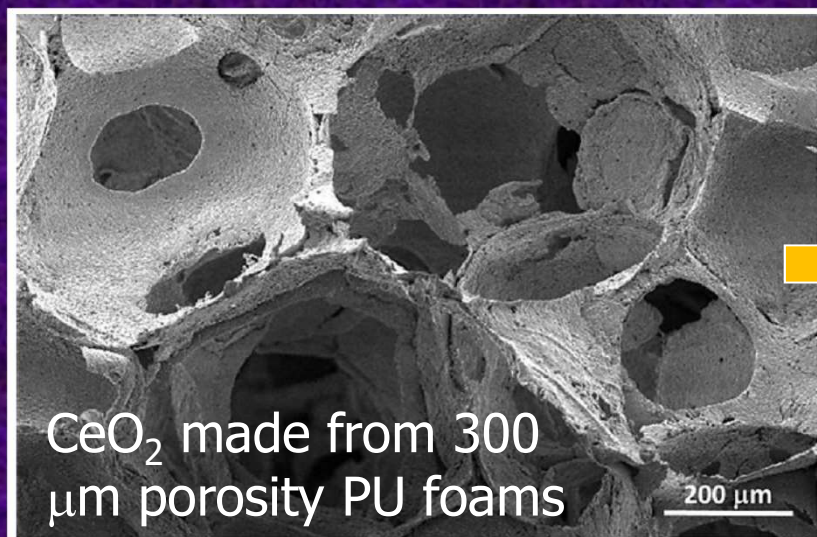
Very repeatable cycling

Produced ~**130 μmol/g CO** and ~**60 μmol/g O<sub>2</sub>** with reduction at 1400 °C

~**200 μmol/g CO** and ~**90 μmol/g O<sub>2</sub>** with 1450 °C

CO production rate 3 x more than other reported cerias

# CeO<sub>2</sub> Ecoceramics twice as good as CeO<sub>2</sub> Foams made from Non-Sustainable PU Templates



After 6 cycles cork structure mostly maintained, evidence of CeO<sub>2-δ</sub>





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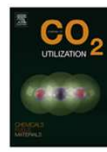
<https://doi.org/10.1016/j.jcou.2018.06.015>  
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Solar thermochemical CO<sub>2</sub> splitting using cork-templated ceria ecoceramics

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