# PRODUCTION OF ORGANIC MOLECULES FROM $CO_2$ AND $H_2O$ BY PHOTOCATALYSIS IN NANO-OXIDES (PROJECT 31)

**Prof. Dr. Douglas Gouvêa**
Department of Metallurgical and Materials Engineering
Polytechnic School
University of São Paulo, Brazil

Research Centre for Gas Innovation
cleaner energy for a sustainable future

V WORKSHOP RCGI 21-22 Aug 2018

# Scope

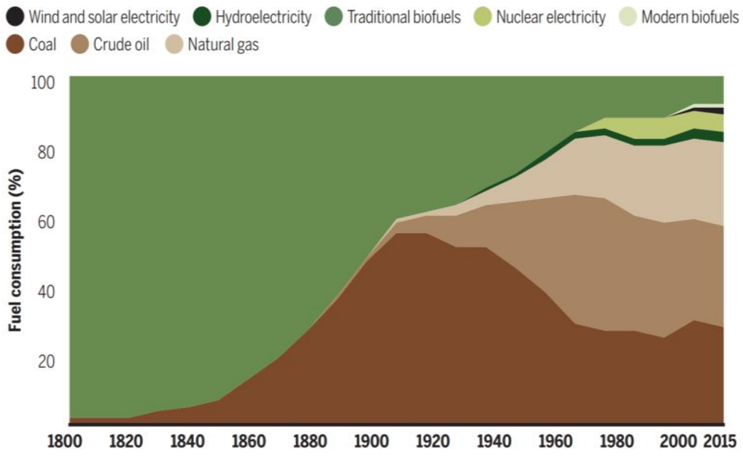
- The scope of the proposal concerns the manufacture and characterization of nano-oxides to promote ideal conditions to synthetize organic molecules from $CO_2$ and $H_2O$ by photocatalytic reactions (artificial photosynthesis - AP).
  - Type of semiconductor oxide, surface composition and particle size of nano-oxides play a key role in creating the conditions for absorption of light radiation, adsorption and reactions of $H_2O$ and $CO_2$ molecules to produce organic molecules.
- The physico-chemistry of interfaces (surfaces and grain boundaries) of nano-oxides can be controlled by segregation of additives which has a strong role in the particle size stabilization and electrical transport. However, the bandwidth and its defects are controlled by the composition of the semiconductor´s bulk, which in turn controls the absorption of light.

# Team

- Prof. Douglas Gouvêa (EPUSP)
- Prof. Guilherme F. B. Lenz e Silva (EPUSP)
- Prof. Ricardo Hauch Ribeiro de Castro (UC Davis)
- Andre Luiz da Silva (EPUSP – Postdoc)
- Lorena Batista Caliman (EPUSP – Postdoc)
- Gustavo M. Fortes (EPUSP – PhD Student)
- Cátia Alexandra Podence Alves (EPUSP – PhD student)
- Henry Gandelman (EPUSP – Master Student)
- Matheus Horstmann Fernandes (EPUSP – IC PIBIQ)

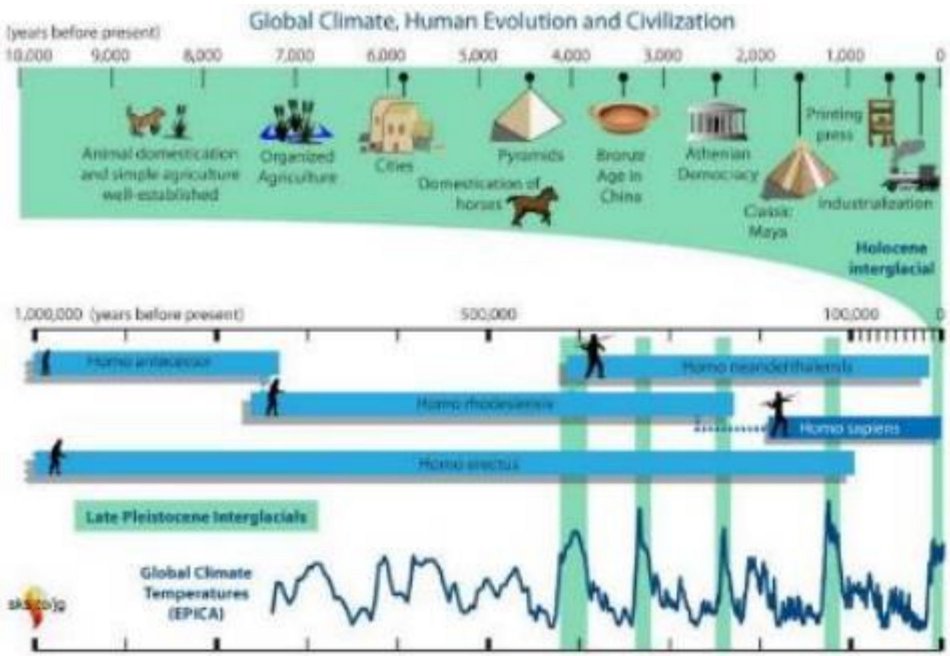
# World Energy Matrix

- The world energy matrix is largely dominated by the traditional biofuels as coal, crude oil and natural gas.
- The $CO_2$ emission due to the natural gas and crude oil flaring remains a problem.
- A possible solution could be to use $CO_2$ as a raw material to create fuels or chemical precursors imitating the nature.




P. Voosen, "THE REALIST Vaclav Smil looks to history for the future of energy. What he sees is sobering," *Science*, 359[6382] 1320-24 (2018).

# Global Climate



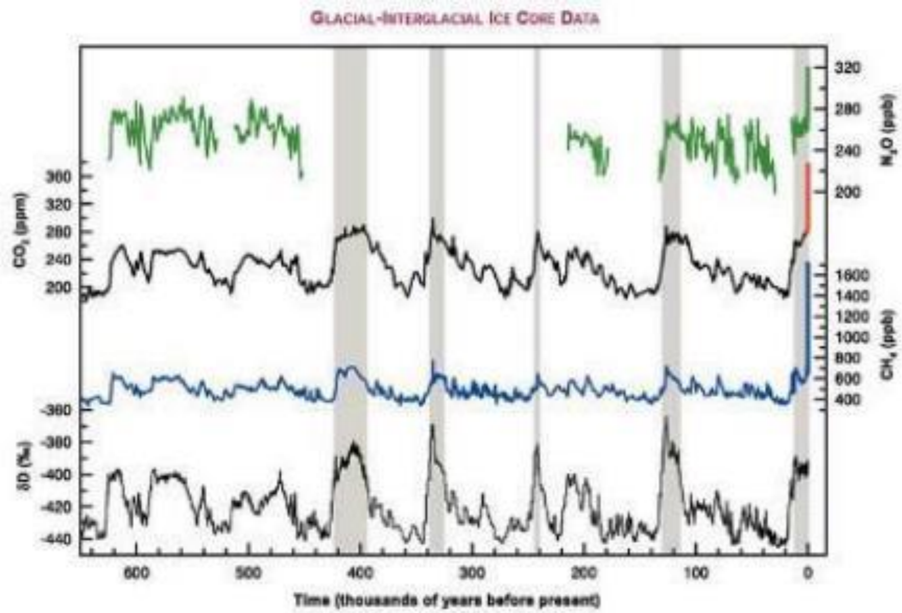
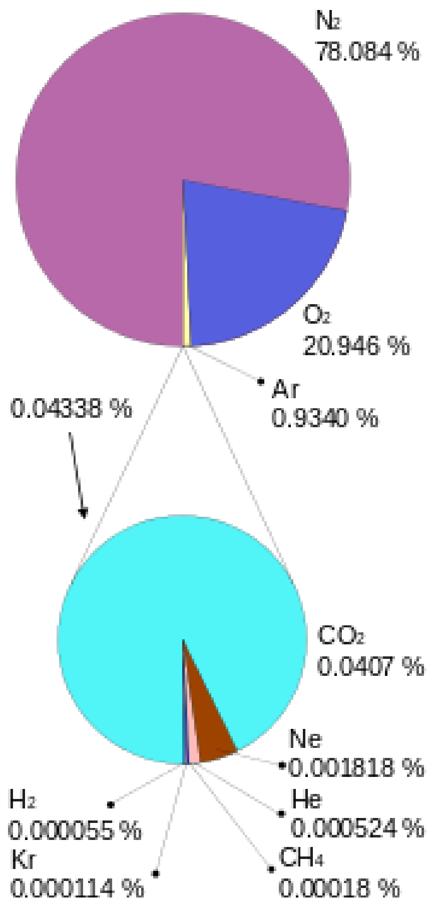




Figure TS.1. Variations of deuterium (δD) in antarctic ice, which is a proxy for local temperature, and the atmospheric concentrations of the greenhouse gases carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) in air trapped within the ice cores and from recent atmospheric measurements. Data cover 650,000 years and the shaded bands indicate current and previous interglacial warm periods. (Adapted from Figure 6.3)

***Better to be safe than sorry !***

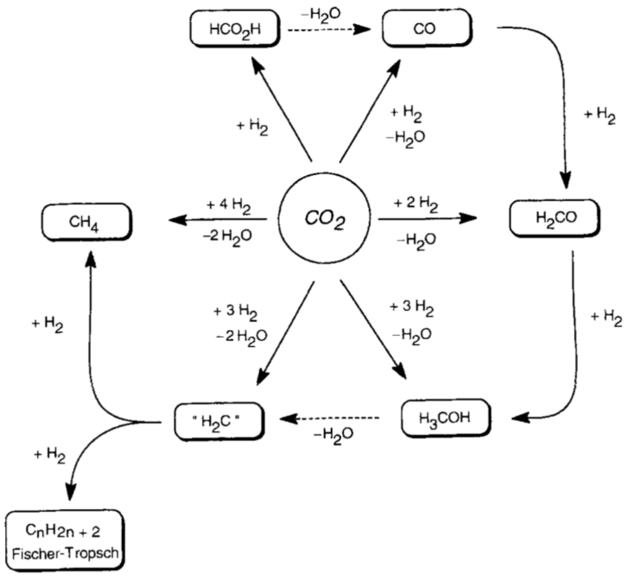
https://www.co2.earth/ 05/11/2018

# $CO_2$ as a raw material





https://www.co2.earth/




Scheme 1. Reduction of $CO_2$ as a source for industrially important products.

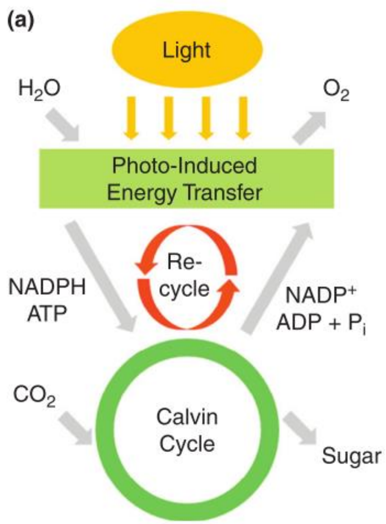
W. Leitner, **Carbon-Dioxide as a Raw-Material - the Synthesis of Formic-Acid and Its Derivatives from $CO_2$**, Angew Chem Int Edit 34(20) (1995) 2207-2221.

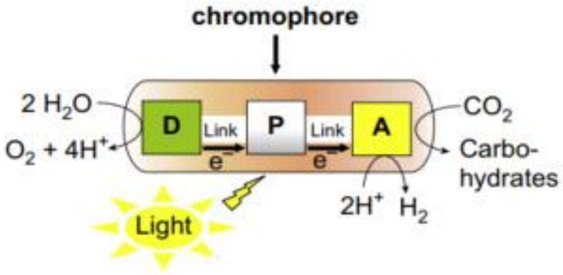
According to the American National Center for Atmospheric Research, "The total mean mass of the atmosphere is $5.1480 \times 10^{18}$ kg.

with 0.04 % of $CO_2$ = **$2.1 \times 10^{12}$ tones**

# Photosynthesis

- The process by which green plants and some other organisms use sunlight to synthesize foods from carbon dioxide and water. Photosynthesis in plants generally involves the green pigment chlorophyll and generates oxygen as a byproduct.



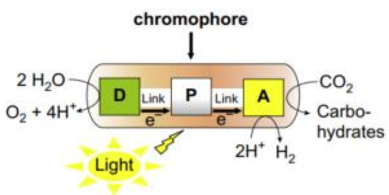



# Five possible processes to reproduce organic fuel by Artificial Photosynthesis (AP)

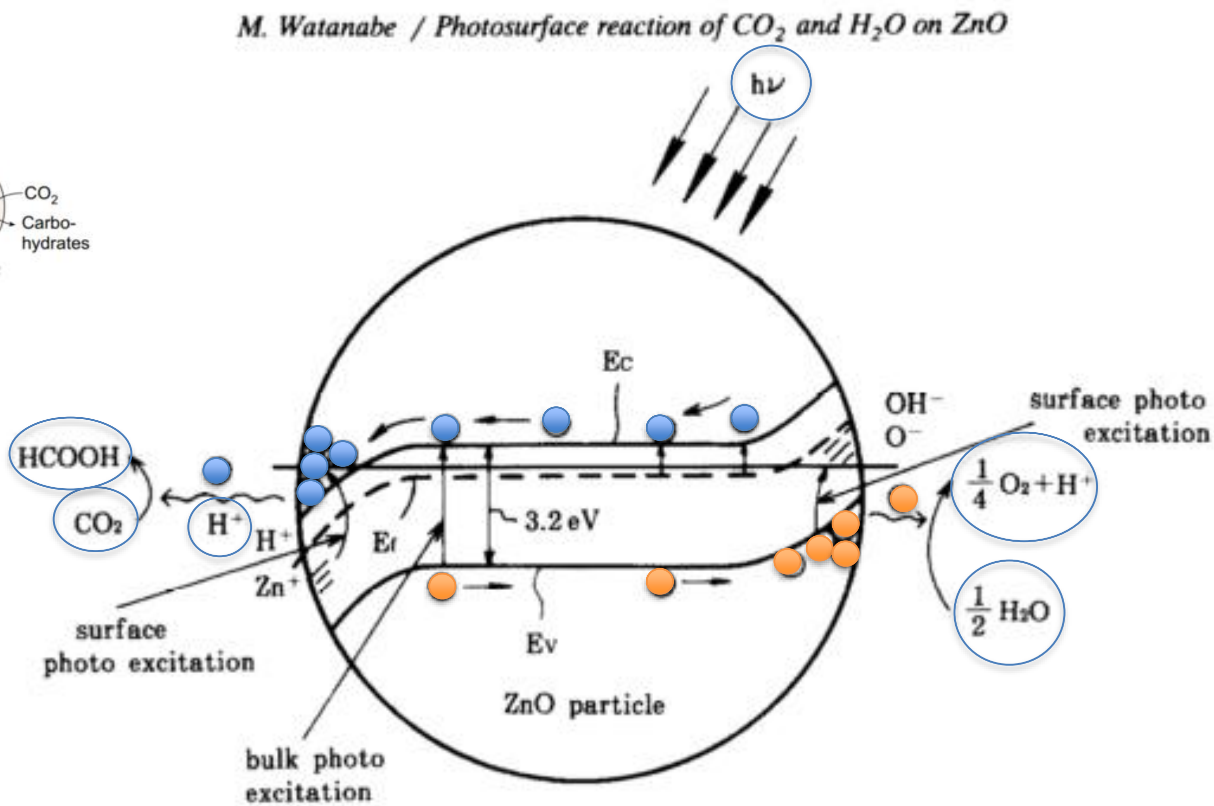
- gene modified microorganisms,
- hybrid systems immobilizing enzymes on electrodes,
- metal organic molecules,
- **photochemically/catalytically active surfaces of semiconductor particles** and
- photoelectrochemical/photoelectrocatalytic devices using semiconductors equipped with catalysts.


  - R. Bruno, "***Artificial photosynthesis***," pp. xii, 248 pages First edition. ed. Elsevier/Academic Press is an imprint of Elsevier: Amsterdam, (2016).
  - S. Fiechter, "***Artificial Photosynthesis - An Inorganic Approach***," pp. xii, 248 pages. in Advances in Botanical Research - Artificial photosynthesis. Edited by R. Bruno. Elsevier/Academic Press is an imprint of Elsevier, Amsterdam, 2016.

# nano ZnO - Artificial Photosynthesis




Formic Acid



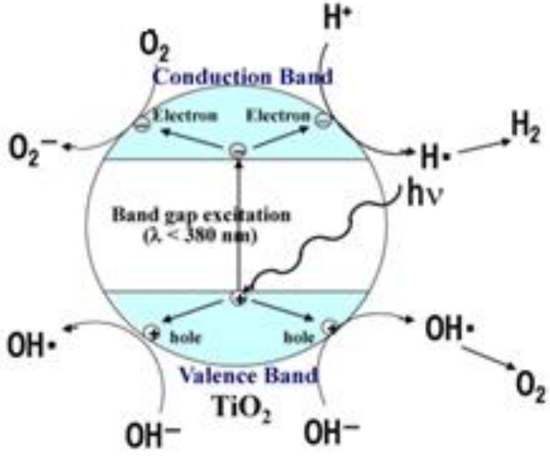

M. Watanabe, "Photosynthesis of Methanol and Methane from $CO_2$ and $H_2O$ Molecules on a ZnO Surface," Surface Science, 279[3] L236-L42 (1992).

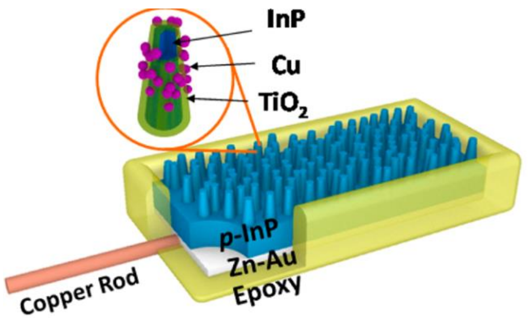
# $TiO_2$ - Photocatalysis

- $TiO_2$ is a very interesting semiconductor ($E_g$ = 3.0 eV) for AP because the high reactivity with water.
- Very efficient for water splitting.

$$H_2O \xrightarrow{TiO_2 + light} O_2 + H_2$$

- For AP, $TiO_2$ have been only used in composite materials.
- Used for purification of water and air and self-cleaning surfaces.



# $\alpha$-$Fe_2O_3$ as a photocatalytic

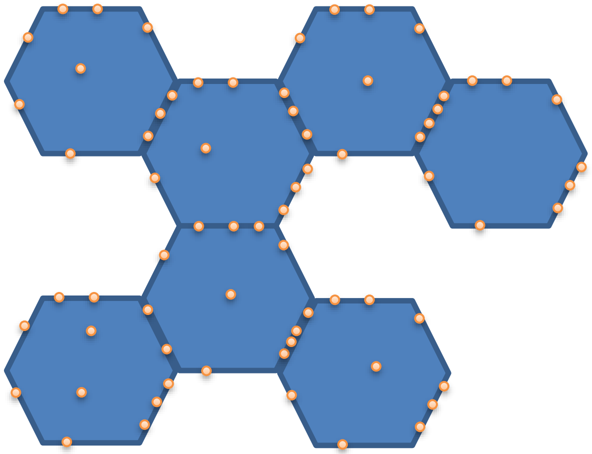
- $\alpha$-$Fe_2O_3$ has an advantage over the other conventional materials like $TiO_2$ and ZnO in using solar energy for photocatalytic applications due to its lower band gap ~2.2 eV.
  - As a result of which $\alpha$-$Fe_2O_3$ is capable of absorbing a large portion of the visible solar spectrum (absorbance edge ~600 nm).
- Also its good chemical stability in aqueous medium, one of the cheapest semiconductor materials available, abundance and nontoxic nature makes it a promising material for water splitting applications.

# Materials used in the artificial photosynthesis

- A literature survey reveals 1625 papers published with the word "artificial photosynthesis" in the title, abstract or keyword (Scopus, April, 11, 2018).
- The search within the results showed:
  - 598 (37%) papers referred to nanoparticles,
  - 324 $TiO_2$,
  - 48 ZnO and
  - 55 used $Fe_2O_3$
- For water splitting there are two main groups of elements that can act as active cation components:
  - $Ti^{4+}$, $Zr^{4+}$, $Nb^{5+}$, $Ta^{5+}$, $W^{6+}$, and $Ce^{4+}$ photocatalysts based on transition-metal cations with empty 'd' orbitals
  - $Ga^{3+}$, $In^{3+}$, $Ge^{4+}$, $Sn^{4+}$, and $Sb^{5+}$ transition-metal cations with empty 'd' orbitals
- For photocatalytic conversion of carbon dioxide:
  - 1978 for $SrTiO_3$ by Hemminger [Chemical Physics Letters 57(1) (1978) 100-104]
  - 1979 for ZnO, CdS, GaP, SiC, $BiWO_6$ on 1979 by Inoue [Nature 277(5698) (1979) 637-638].

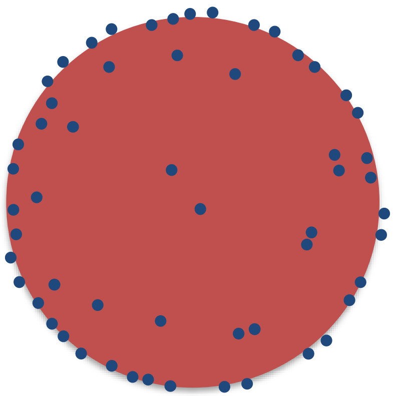
# Artificial Photosynthesis with Nanoxides

- Main concepts:
  - Semiconductor (bulk)
    - Light absorption (bandgap x kT)
    - e/h generation (intrinsic and extrinsic)
    - e/h recombination time
  - Nanoparticles
    - Particle size stability (high SSA)
  - Interfaces
    - Composition (surfaces and grain boundaries)
      - Segregation of additives
    - Charge mobility (e/h) inter-particles
    - Adsorption and reaction (charge transfer)
      - $CO_2$
      - $H_2O$



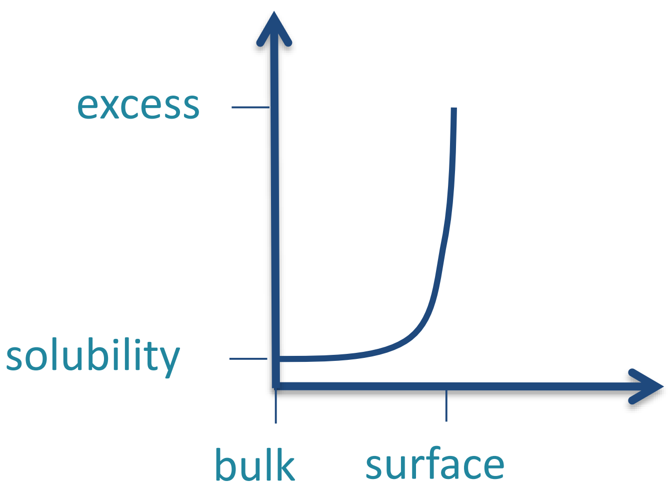
# SURFACE EXCESS - $\Gamma$
# SEGREGATION, ADSORPTION AND SURFACE ENERGY

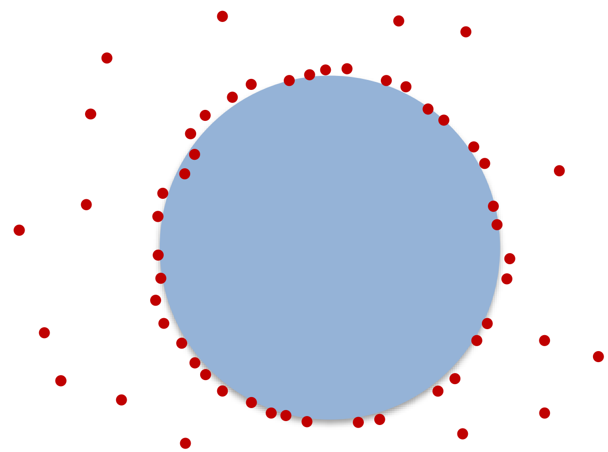
Segregation



$$\Gamma = \frac{n}{surface} \; (mol/m^2)$$

$$\sigma = \sigma_0 - \Gamma \Delta H_{ads}$$



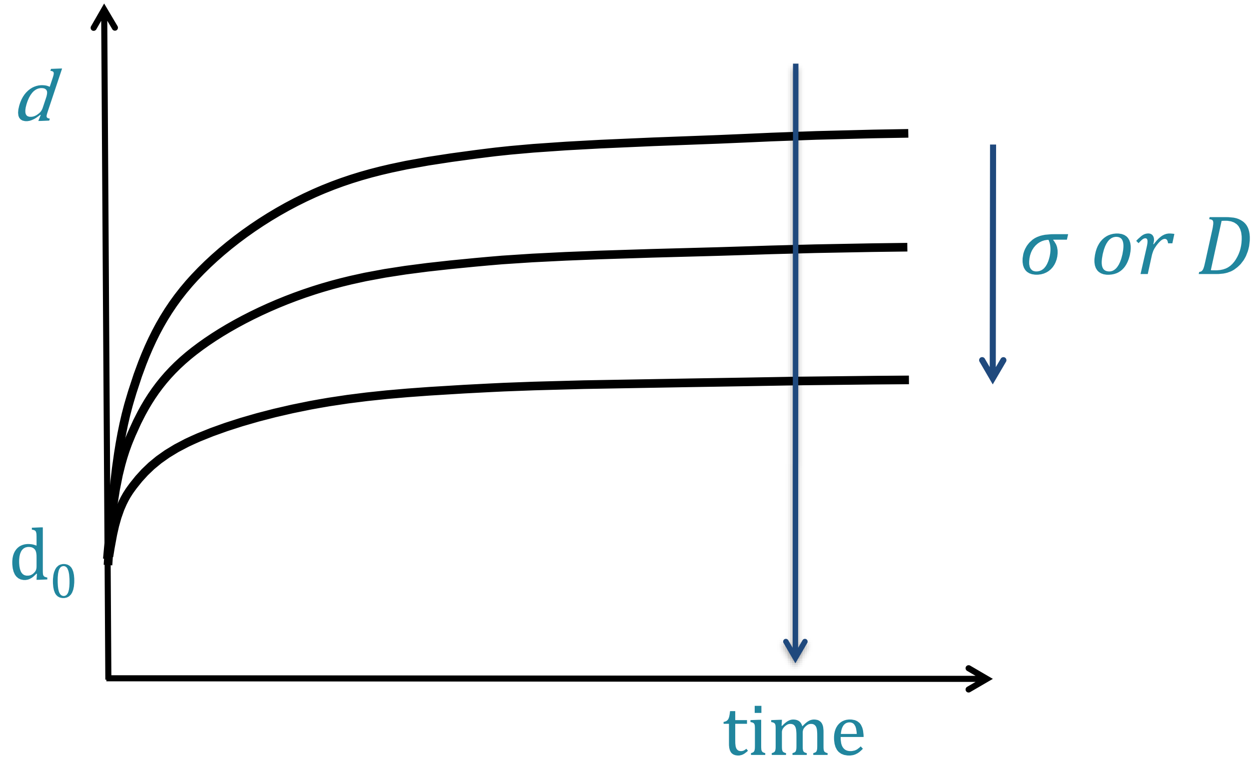
Adsorption

R.H.R. Castro and D. Gouvêa
Sintering and Nanostability: The Thermodynamic Perspective
**(Feature Paper)** J. Am. Ceram. Soc. 99(4) (2016) 1105-1121.

# Surface excess and particle size

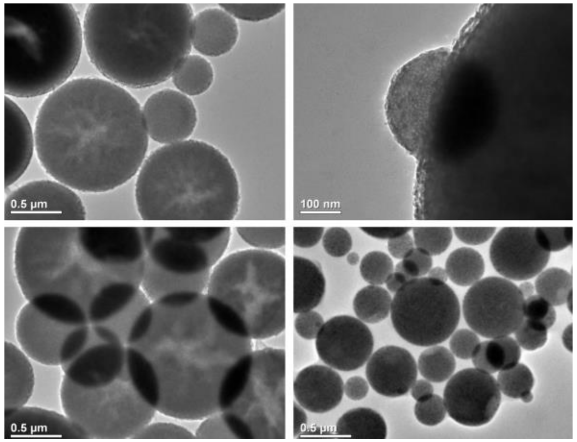
$$d^n - d_0^n = K\,\sigma\,D\,t$$

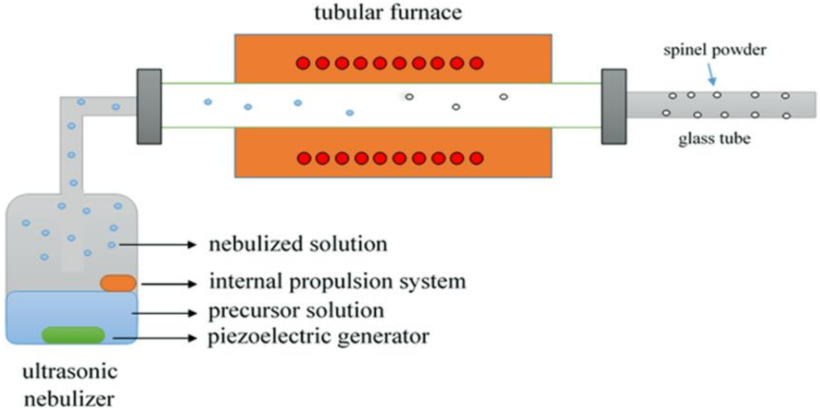
$$\sigma = \sigma_0 - \Gamma \Delta H_{seg/ads}$$



# Nanoparticle Synthesis

- Pechini method:
  - synthesis method consists in the complexation of the metal cations in a polymeric chain formed by citric acid and ethylene glycol (temperatures 70 to 120°C);
  - easy to make polycrystalline thin films
- Ultrasonic Spray Pyrolysis:
  - aqueous solution of cations is ultrasonic nebulized into a tubular furnace
- Precipitation in ethanol:
  - Avoid amphoteric effects on solubility
- Sol-gel of Alkoxides :
  - Direct mixtures of nanohydroxides during precipitation



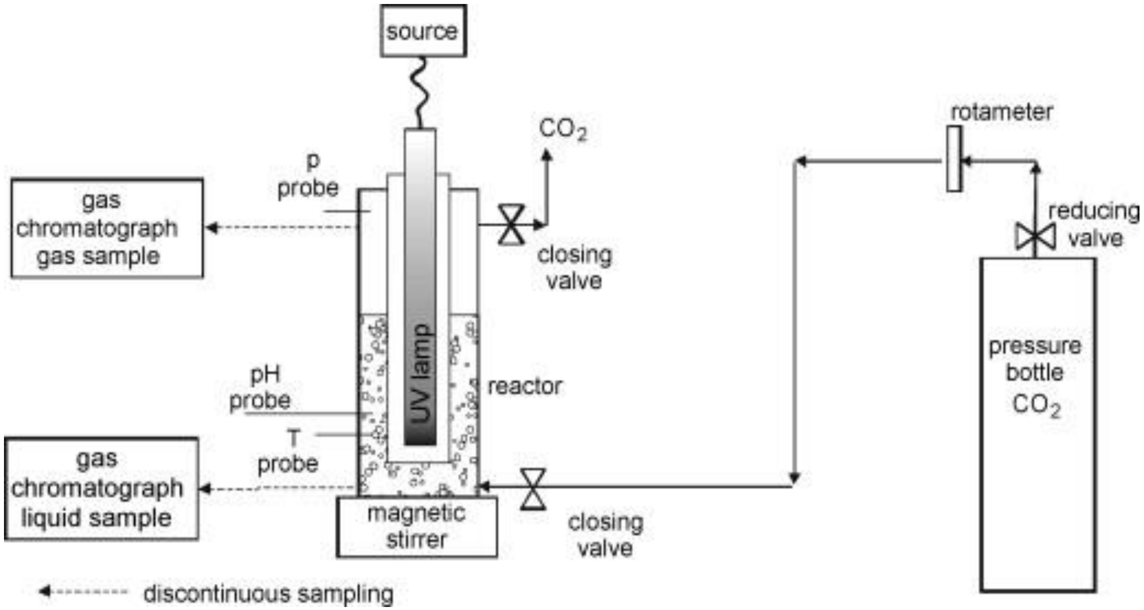




Gouvêa et al. , "Synthesis of Ca-doped spinel by Ultrasonic Spray Pyrolysis," *Materials Letters*, 171 232-35 (2016)

# Characterization

- FTIR – DRIFT (T and P)
- XRD – Rietveld Method
- Gas adsorption ($N_2$, $H_2O$, $CO_2$)
- XRF
- XPS
- Gas Chromatography
- Mass Spectrometry
- Electrical conductivity
- Photoluminescence (PL)

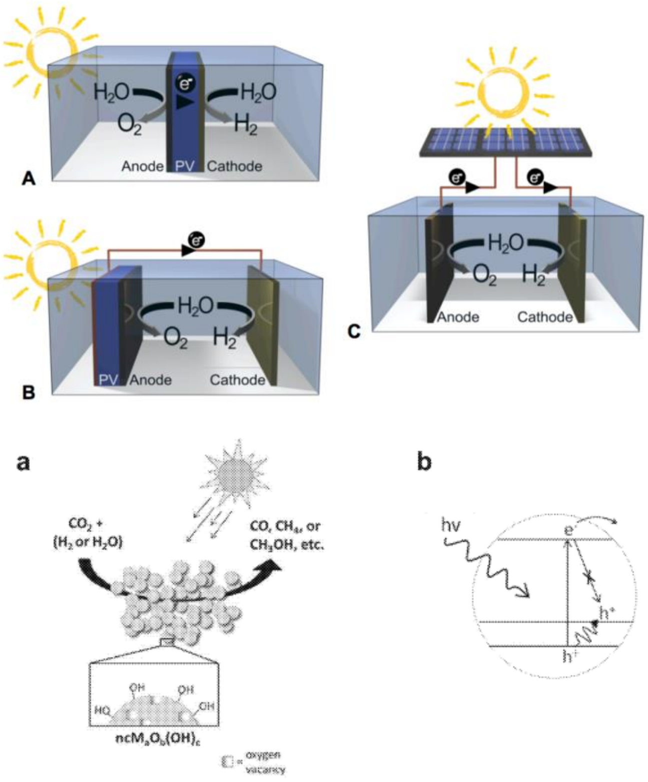
# Apparatus for Artificial Photosynthesis




K. Kočí, L. Obalová, L. Matějová, D. Plachá, Z. Lacný, J. Jirkovský, and O. Šolcová,
Effect of $TiO_2$ particle size on the photocatalytic reduction of $CO_2$ Applied Catalysis B: Environmental, 89[3] 494-502 (2009)

# Patents on Artificial Photosynthesis

- The inventions relates process for storing solar energy in organic compounds containing carbon and hydrogen, and more particularly to such a process wherein a form of solar energy is used to activate water.
- Most of the patents consider AF as only water splitting !!!
- More concepts than products.
- Bio-systems (alga and/or bacteria)
- A large number in Chinese.




US 9,764,959 B2 sep. 19, 2017
Nanostructured metal oxide composition for applied photocatalysis

# *Technology Readiness Levels* (TRL)

| Table B-2 TRLs defined in API 17N | |
|---|---|
| **TRL** | **API 17N** |
| 0 | **Unproven Concept**<br>Basic R&D, paper concept |
| 1 | **Proven Concept**<br>Proof of concept as a paper study or R&D experiments |
| 2 | **Validated Concept**<br>Experimental proof of concept using physical model tests |
| 3 | **Prototype Tested**<br>System function, performance and reliability tested |
| 4 | **Environment Tested**<br>Pre-production system environment tested |
| 5 | **System Tested**<br>Production system interface tested |
| 6 | **System Installed**<br>Production system installed and tested |
| 7 | **Field Proven**<br>Production system field proven |

Research Centre for Gas Innovation

cleaner energy for a sustainable future

# THANK YOU

facebook.com/GasInnovation

twitter.com/rcgipage

www.usp.br/rcgi