Catalysis in AOPs: from lab to market implementation

Carbon-based Catalysts for AOPs

Laboratóriodecatáliseemateriais

LABORATÓRIO ASSOCIADO

LSRE Laboratory of separation and reaction engineering

Laboratóriodecatáliseemateriais lcm

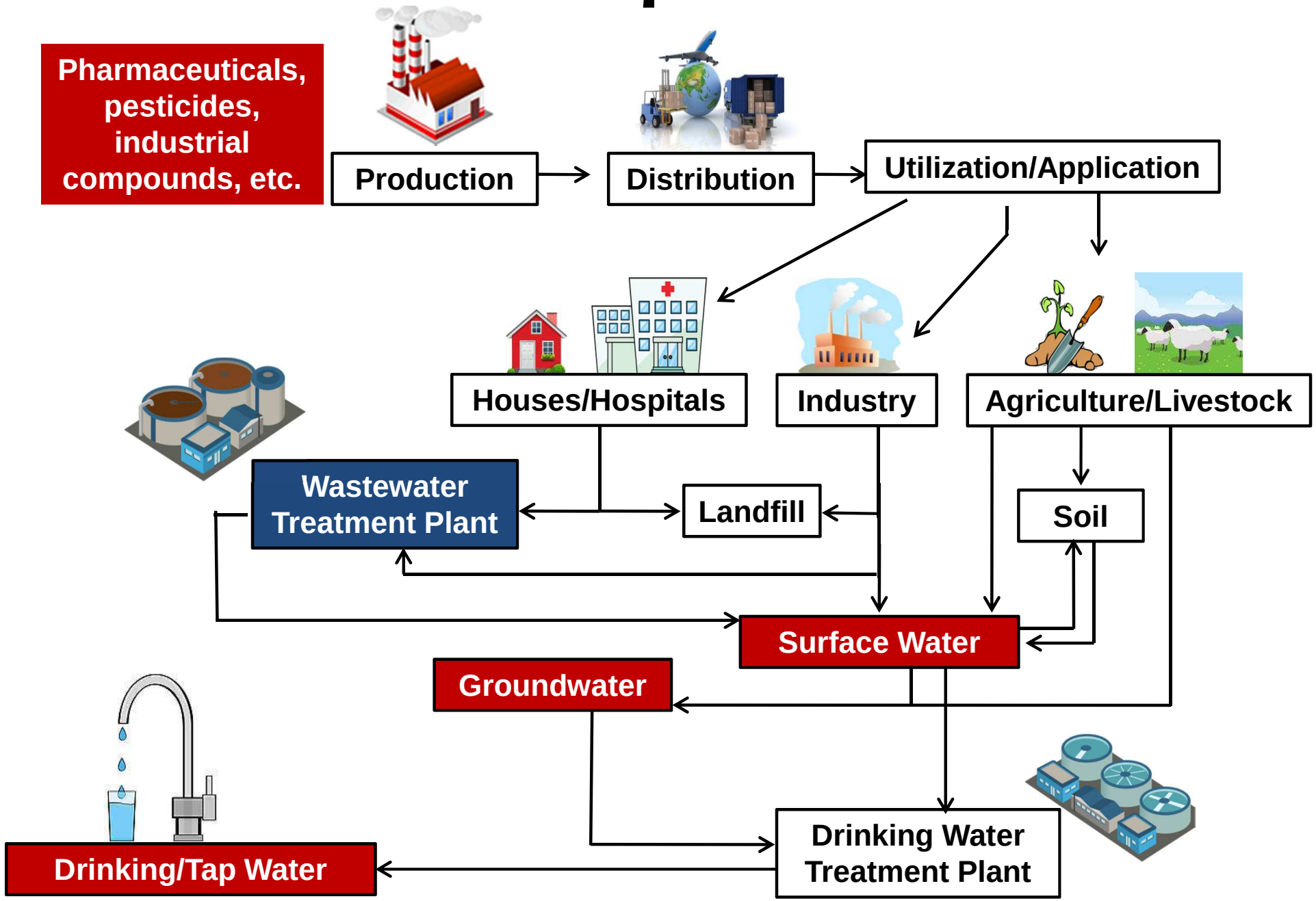
U.PORTO

FEUP FACULDADE DE ENGENHARIA UNIVERSIDADE DO PORTO

Adrián M.T. Silva
adrian@fe.up.pt

Rua Dr. Roberto Frias, 4200-465 Porto

Overview of the problematic



Public health & environmental concerns

Overview of the problematic

Directive 2013/39/EU

Updates the water framework policy: identify **priority substances**/groups of substances…

…and the need to develop **new water treatment technologies**.

Commission Decision 2015/495/EU

First watch list of 10 substances for EU-wide monitoring in the field of water policy.

Public health & environmental concerns

Ribeiro et al., Environ. Int. 75 (2015) 33

Advanced Oxidation Processes

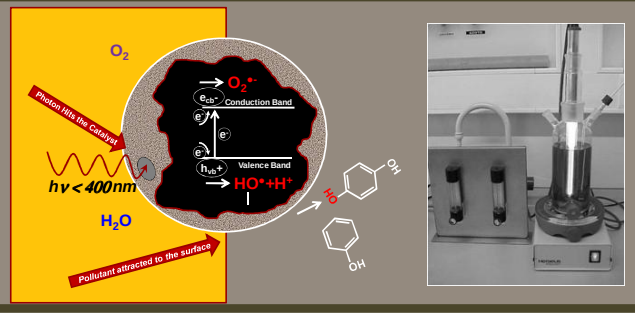
Challenges

Ozonation

TOC reduction

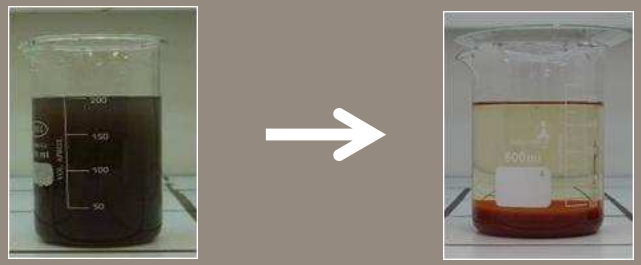
Photocatalysis

Promote Vis-activity



Fenton process

Avoid sludge



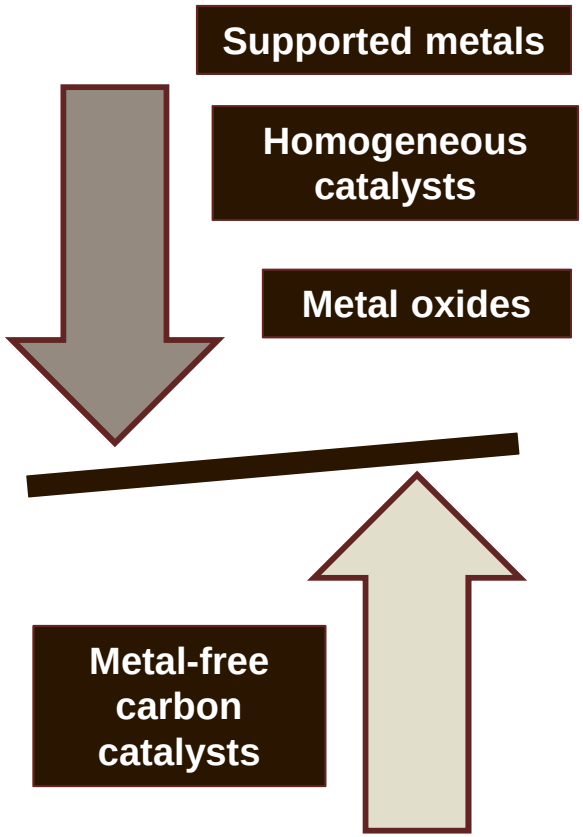
Wet air oxidation

Reduce T & P

Answer: heterogeneous catalysts

Advanced Oxidation Processes

Why Carbon Materials?



Carbon materials as catalysts should be considered today as a cost/environmental option for the future:

- Carbon materials are stable **in both acidic and alkaline** conditions.

- Carbon materials without added metals can be used as **highly active catalysts**.

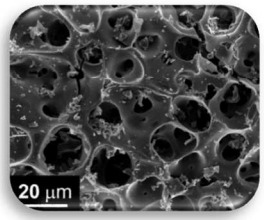
- **Leaching and/or over-oxidation** are often observed when using catalysts based on **metals**.

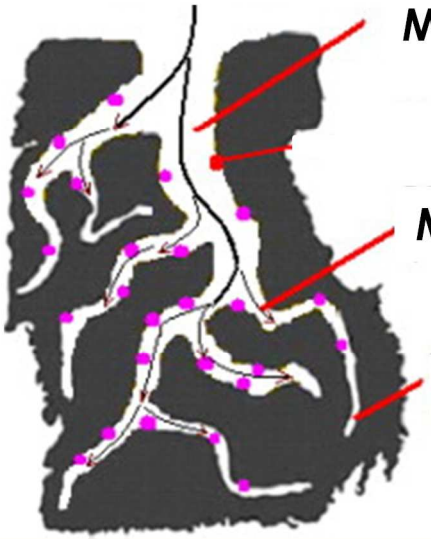
- Technical **disadvantages of homogeneous catalysts** are well known: secondary source of pollution / separation step required.

Best Textural Properties?

Meso- and macropores

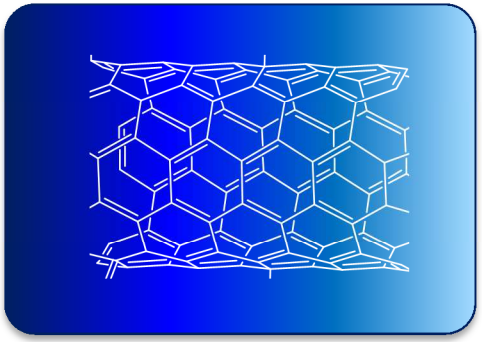
Activated Carbons





Micropores

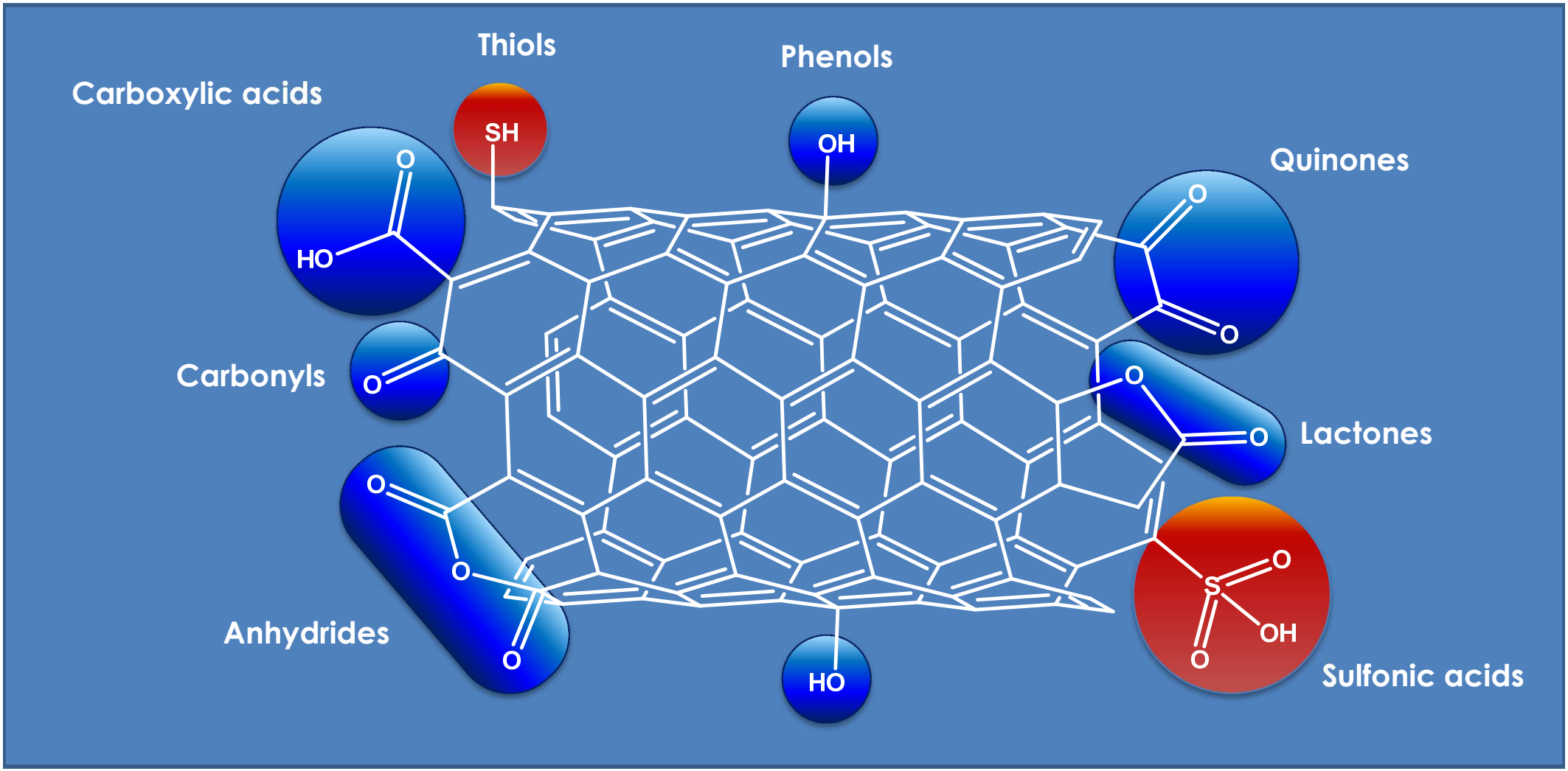
Why carbon nanotubes?



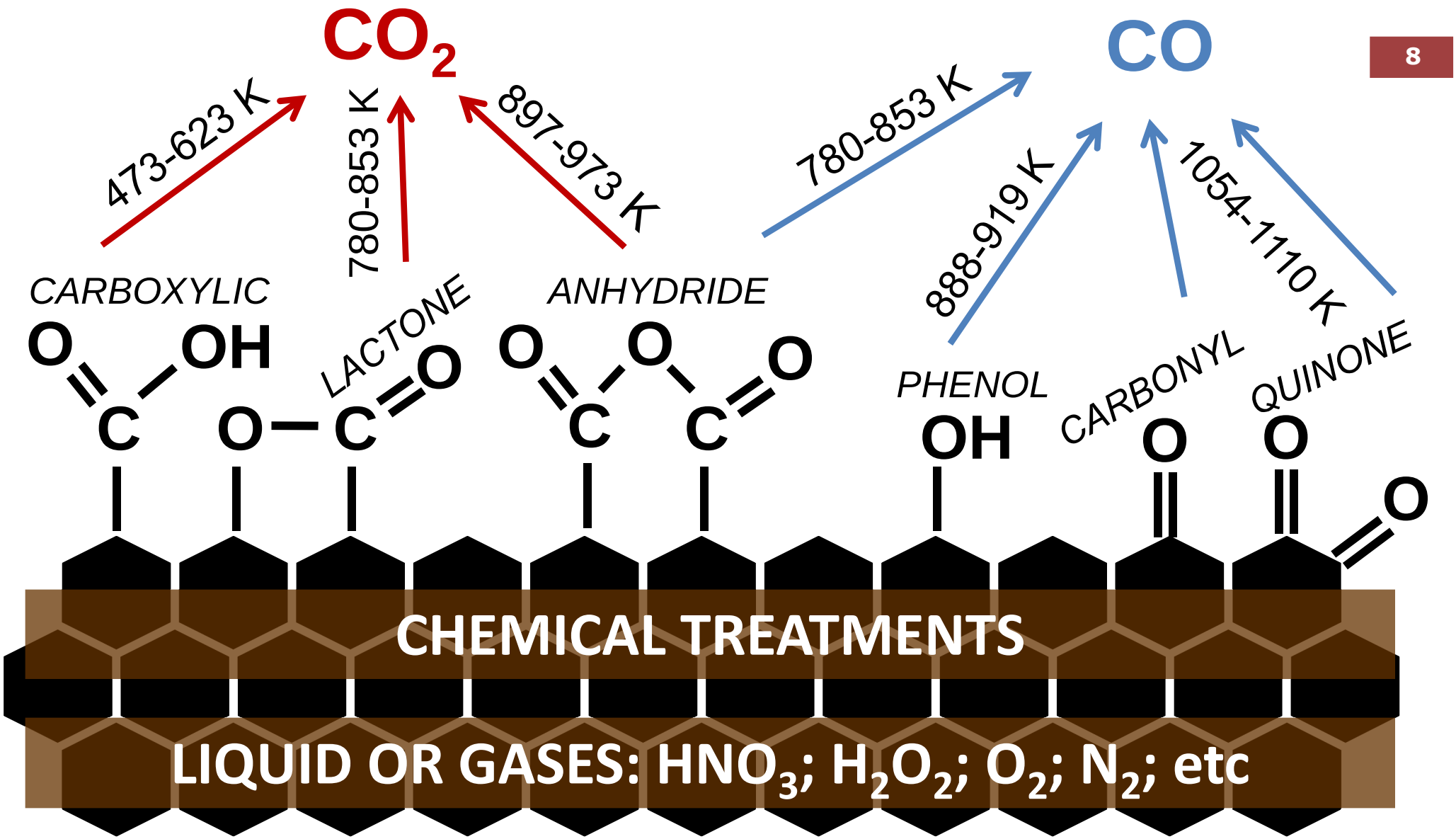
Carbon Nanotubes

The **nonporous nature** of carbon nanotubes **eliminates the mass transfer resistance** related to diffusion into pore structures, thus allowing easy desorbability.

What about Chemical Properties?

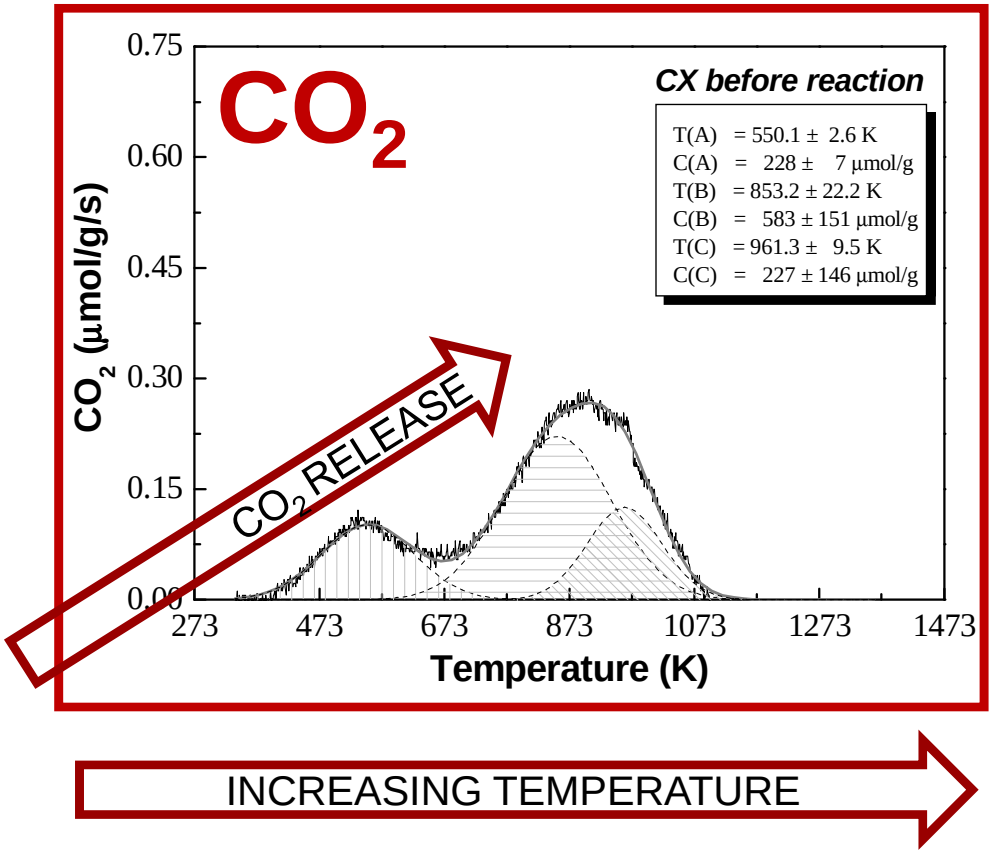


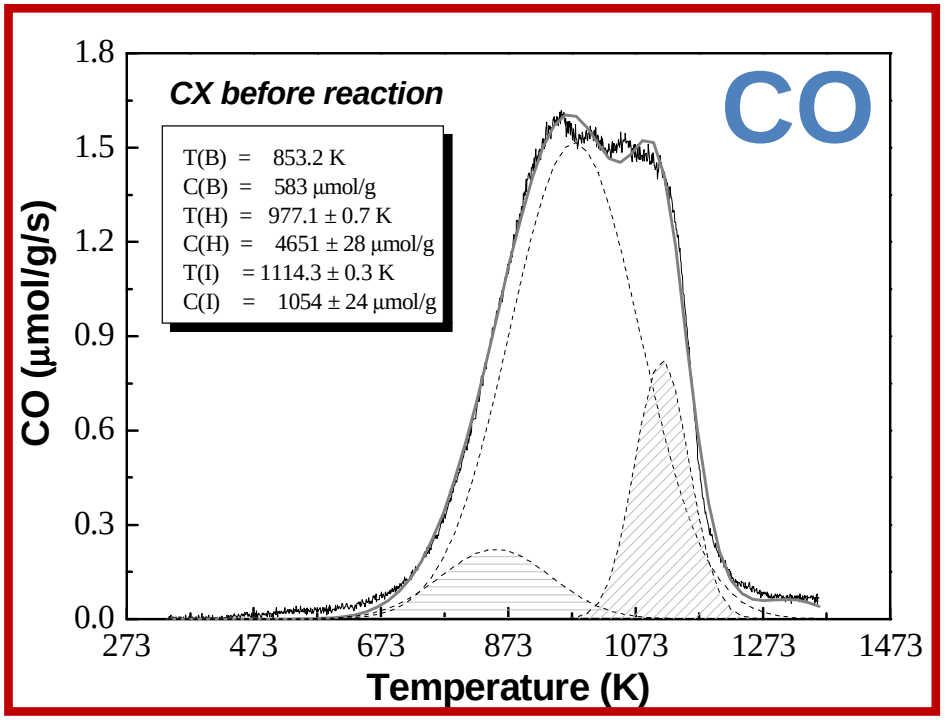
What about Chemical Properties?



CARBON MATERIAL

What about Chemical Properties?

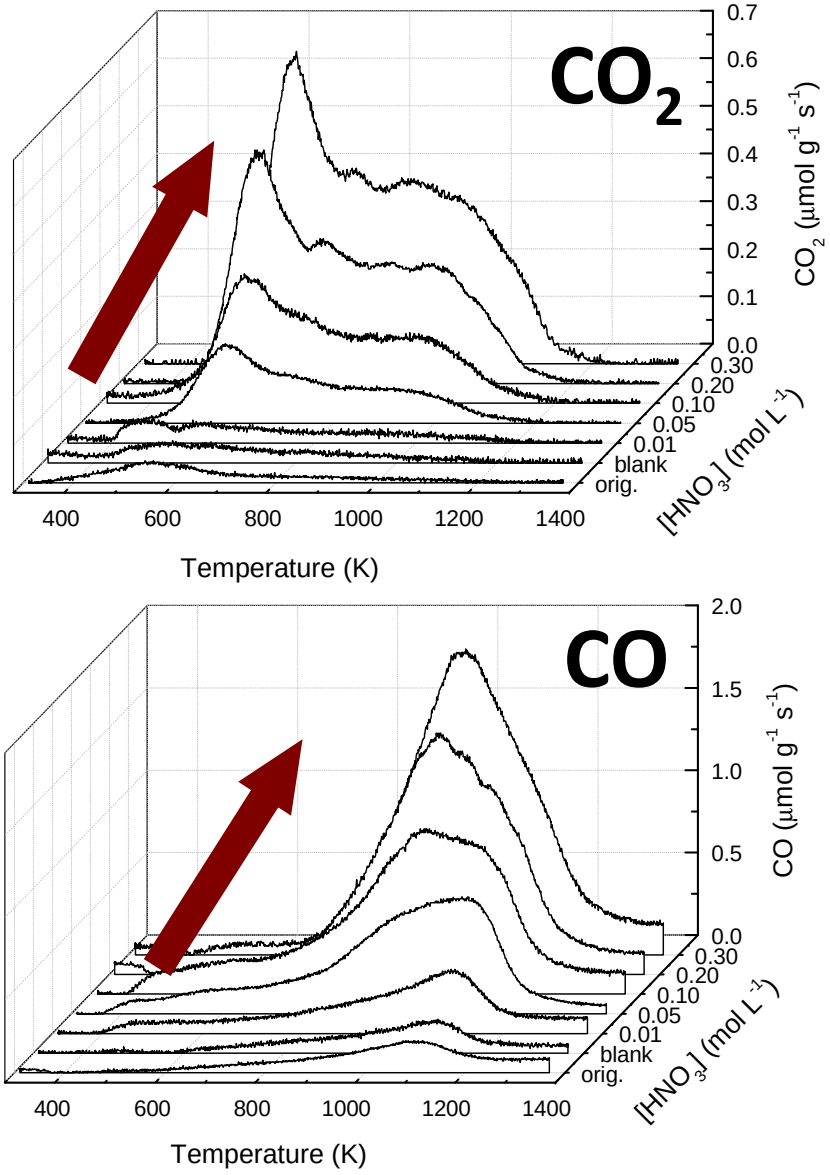


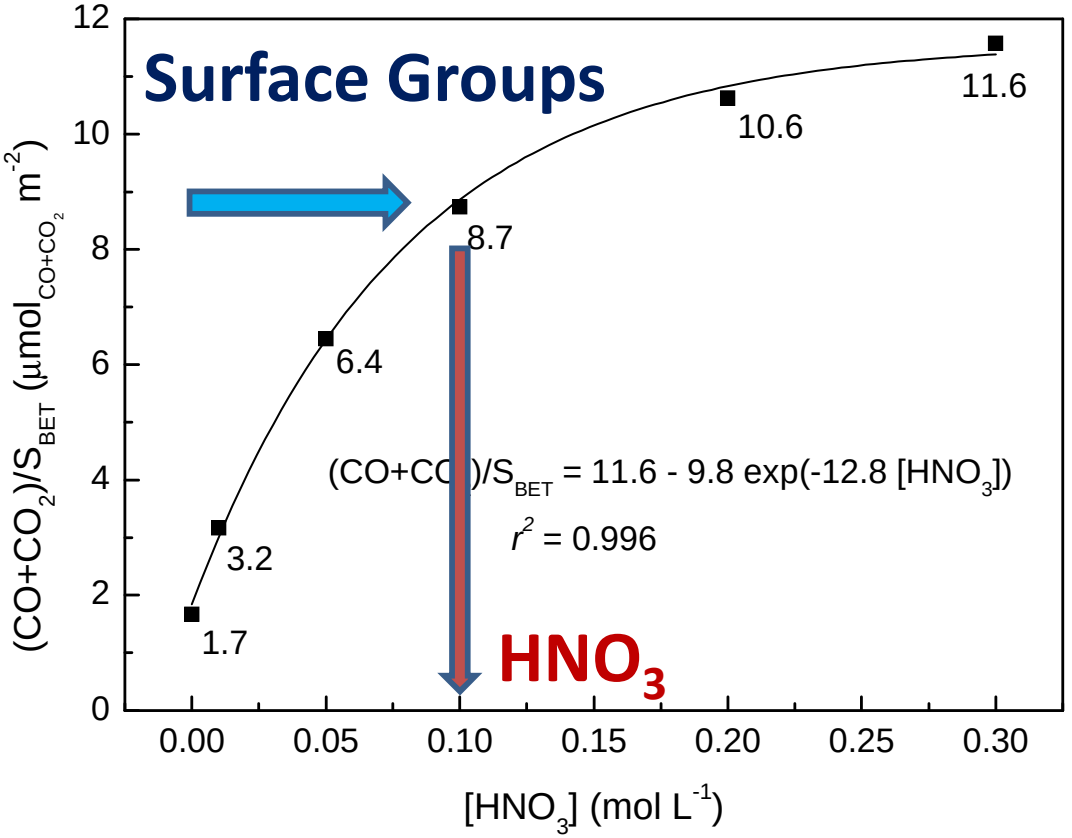


INCREASING TEMPERATURE

What about Chemical Properties?

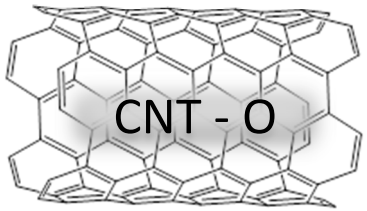
Controlled Functionalization





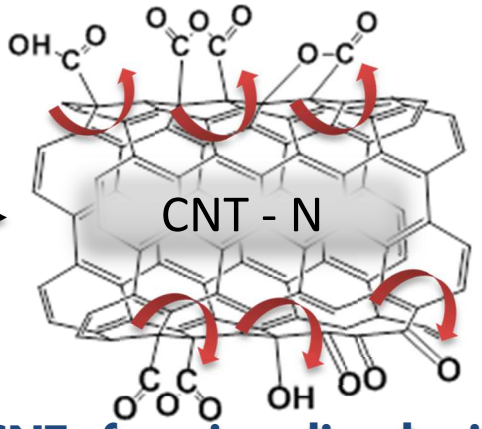
Silva et al., Carbon 47 (2009) 1670

What about Chemical Properties?



HNO_3

Boiling Temp



CNTs functionalized with O-containing groups

Thermal

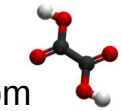
Treatments

- CNT – N200
- CNT – N400
- CNT – N600

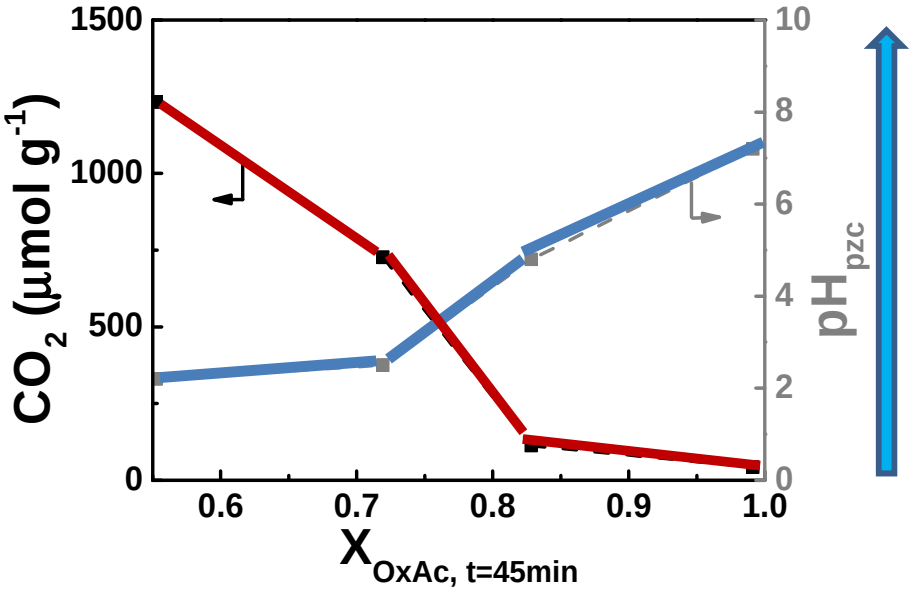
	O	N	N200	N400	N600
[CO] ($\mu mol\ g^{-1}\ s^{-1}$)	187	1852	1308	1205	826
[CO_2] ($\mu mol\ g^{-1}\ s^{-1}$)	33	1233	727	113	43
pH_{pzc}	6.8	2.2	2.5	4.8	7.2

Catalytic Wet Air Oxidation

Oxalic acid



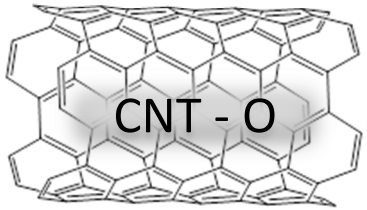
[OxAc] = 1000 ppm
T = 140ºC
P = 40 bar (7 bar O_2)



Rocha et al., Appl. Catal. B. 147 (2014) 314

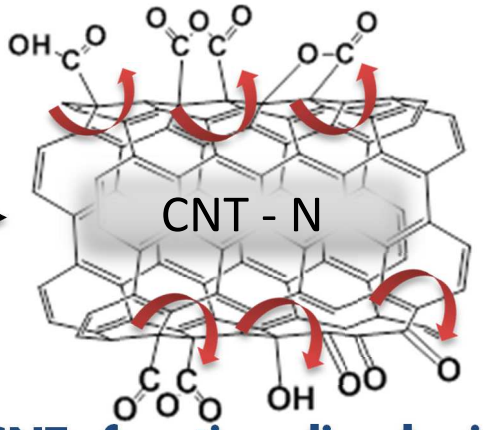
What about Chemical Properties?

MWCNTs / Nanocyl™



HNO_3

Boiling Temp



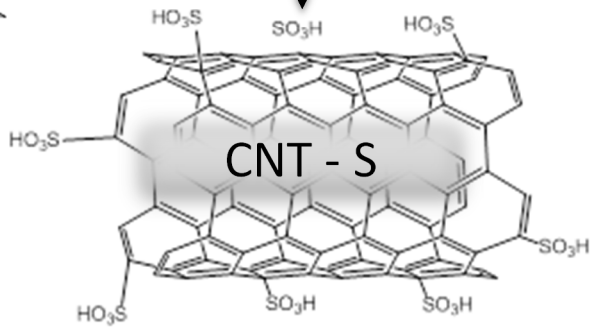
CNTs functionalized with O-containing groups

Thermal

Treatments

- CNT – N200
- CNT – N400
- CNT – N600

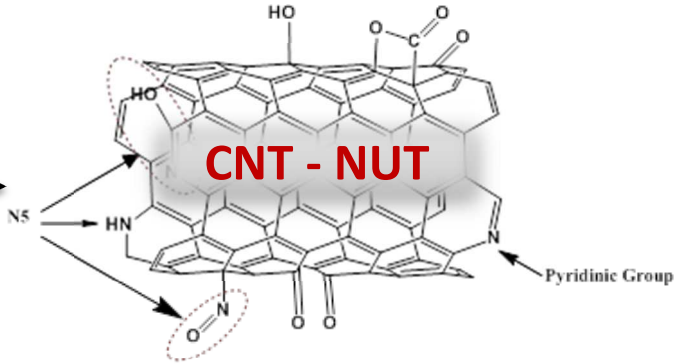
H_2SO_4



CNTs functionalized with Sulfonic groups

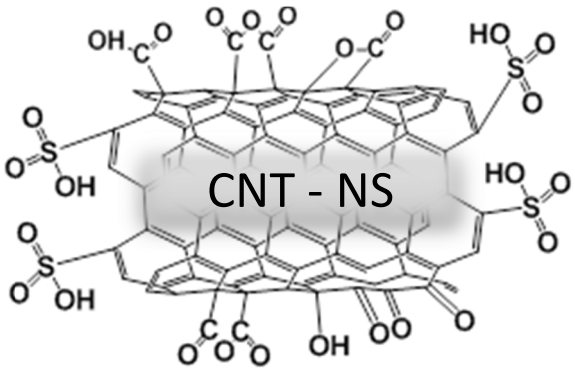
Urea; 200 °C

Thermal Treatment (N_2; 600 °C)



CNTs functionalized with N-containing surface groups

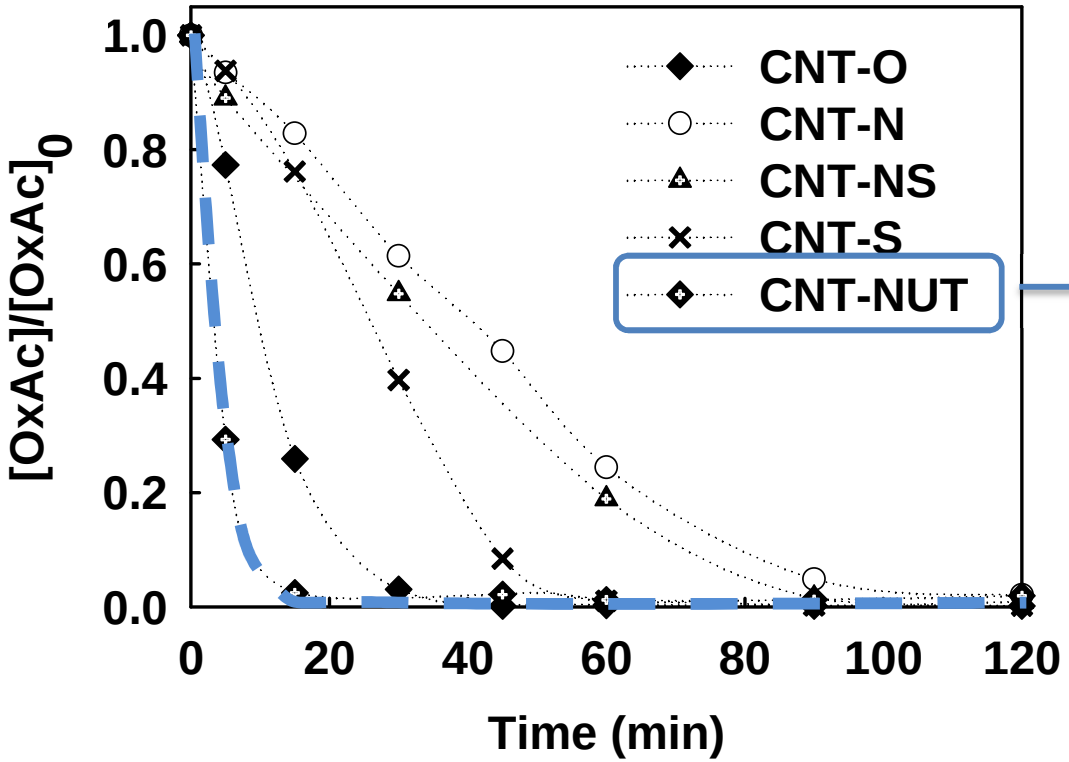
H_2SO_4 / HNO_3



CNTs functionalized with O- and S-containing groups

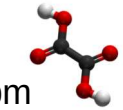
Rocha et al., Appl. Catal. B. 147 (2014) 314

What about Chemical Properties?



Catalytic Wet Air Oxidation

Oxalic acid



[OxAc] = 1000 ppm
T = 140ºC
P = 40 bar (7 bar O_2)

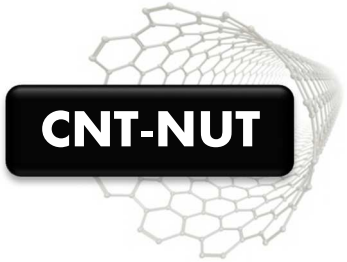
Highest activity

Highest pH_{PZC} = 7.3

Absence of acidic O-containing groups

Presence of N-containing groups

Delocalised π electrons in CNTs increase with N-dopant and play a key role in the reactions occurring in AOPs.



XPS **N (% wt.) = 0.69**

N5 → Pyrrolic –N groups

N6 → Pyridinic –N groups

What about Chemical Properties?

Highest activity

Basicity (or neutral)

Absence of acidic O-containing groups

Presence of N-containing groups

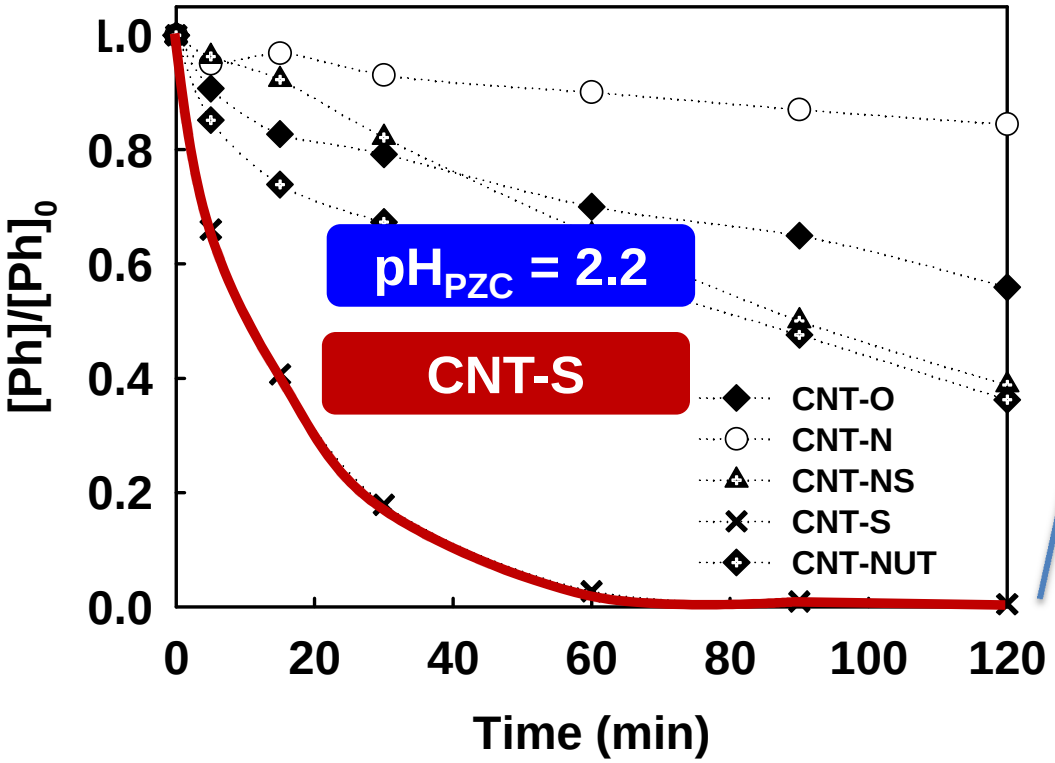
BUT is not always the case

What about Chemical Properties?

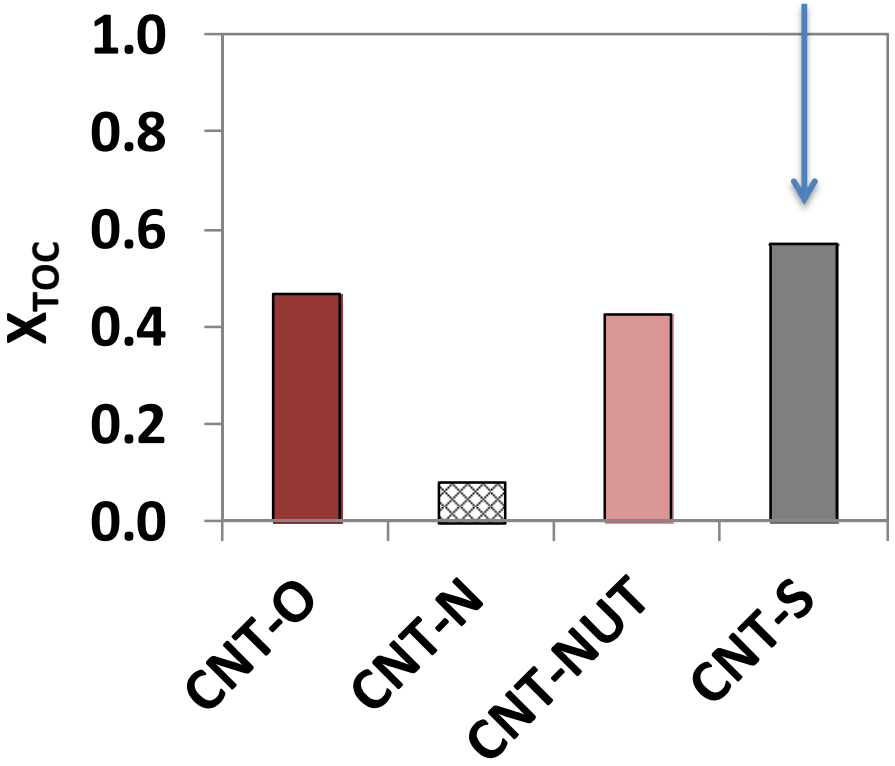
Phenol

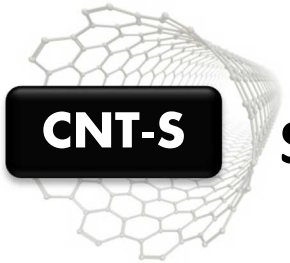
Catalytic Wet Air Oxidation

[Phenol] = 75 ppm
T = 160ºC
P = 40 bar (7 bar O_2)



Very high activity





XPS

S (% wt.) = 1.15

Sulfonic Groups

BUT is not always the case

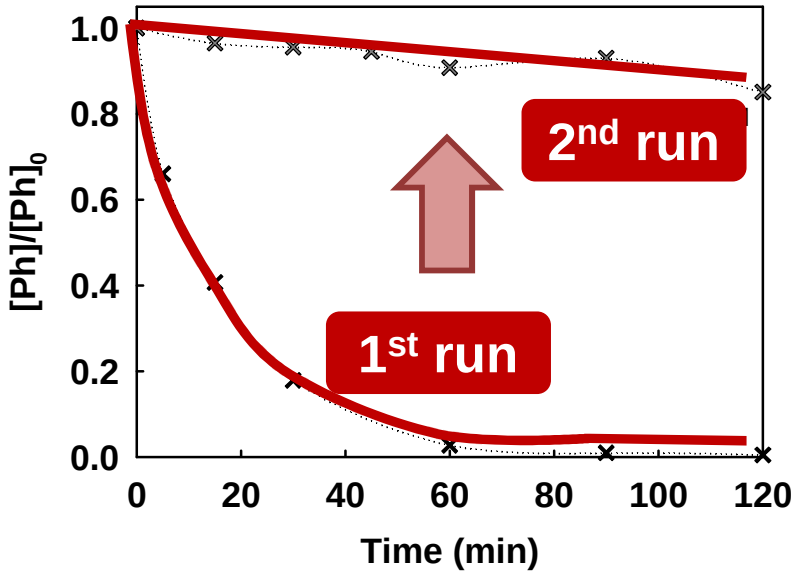
What about Chemical Properties?

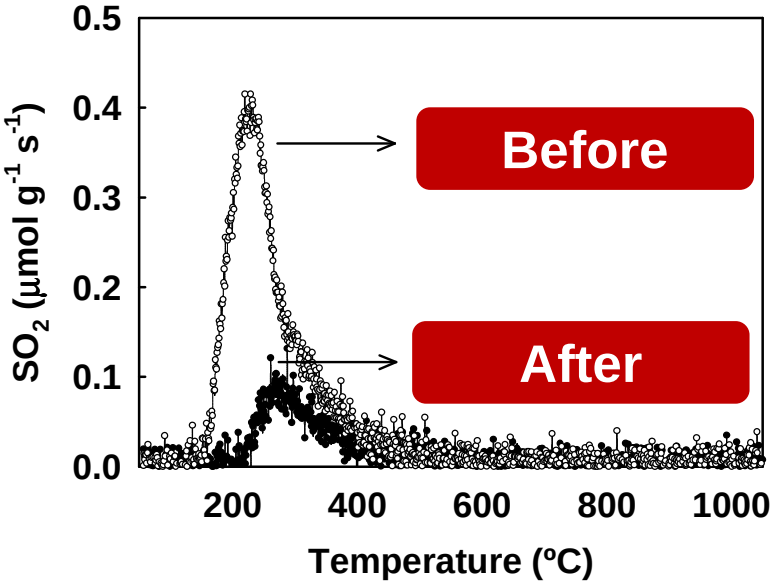
Phenol

Catalytic Wet Air Oxidation

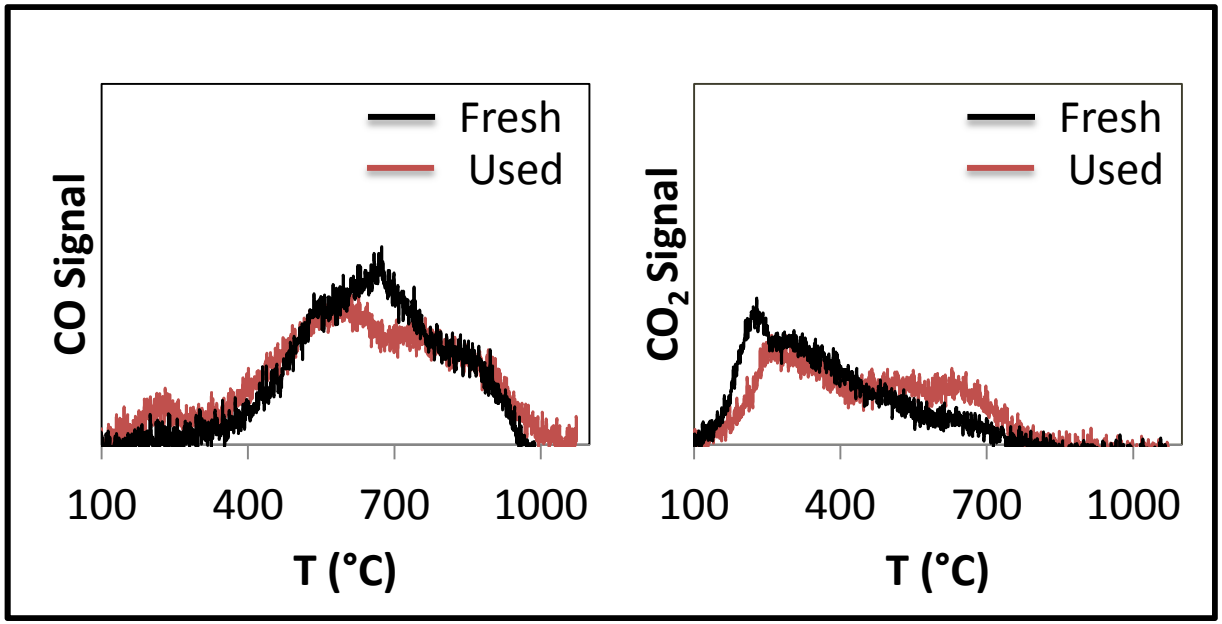
[Phenol] = 75 ppm
T = 160ºC
P = 40 bar (7 bar O_2)

Cyclic Experiment





TPD



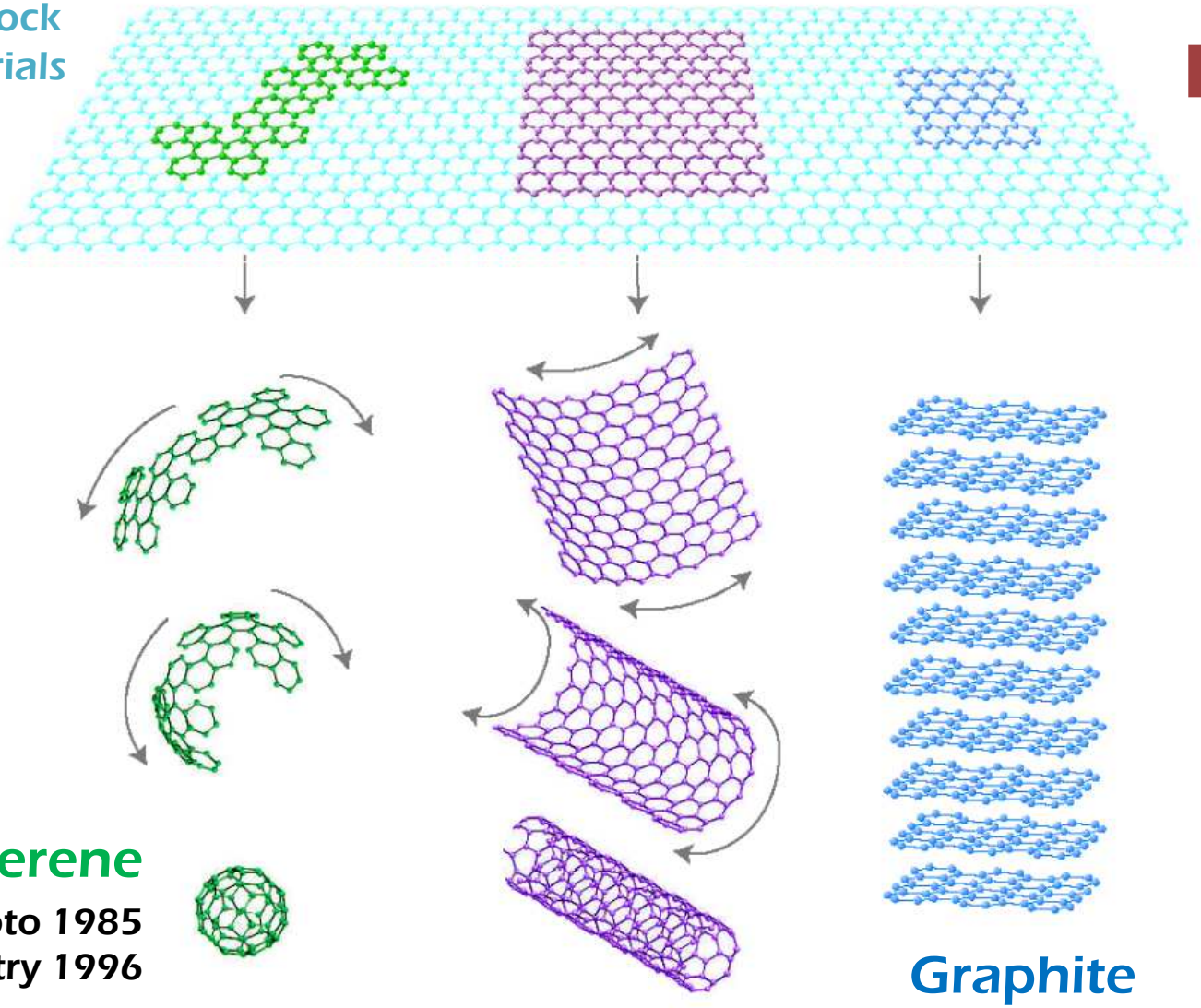
S- RADICALS MAY BE INVOLVED

Operating conditions, as high temperature (160 °C) can promote radicals formation

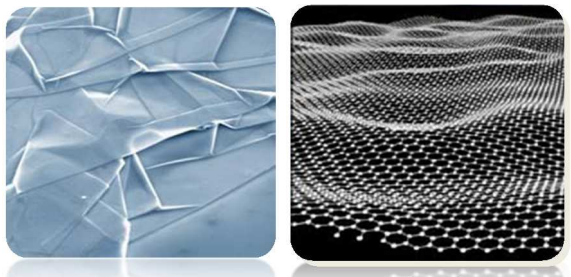
Rocha et al., Appl. Catal. B. 147 (2014) 314

Graphene

basic building block
for carbon materials



isolated and Identified by
A. Geim & K. Novoselov 2004
Nobel Prize in Physics 2010



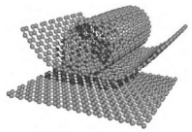
experimentally sought long
before by H.P. Boehm et al. 1962
Fifth Conference on Carbon

*Theoretical surface area of an individual **graphene** sheet is ca.*
2600 m^2 g^{-1}

Fullerene

H.W. Kroto 1985
Nobel Prize in Chemistry 1996

Carbon Nanotubes



Multi-walled 1991 ?
Single-walled 1993 ?

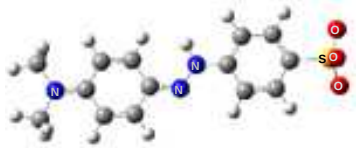
Graphite

mineral known for
thousands of years

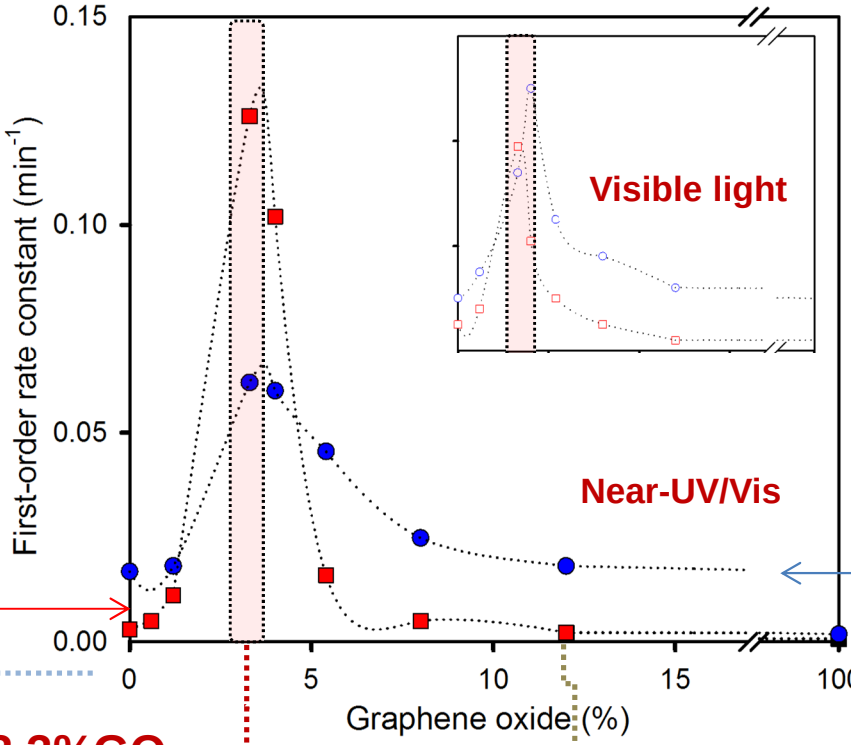
Geim and Novoselov, Nat Mater 6 (2007) 183-191.

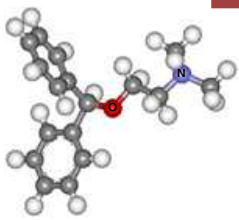
Reduced graphene oxide -TiO_2

Photocatalysis



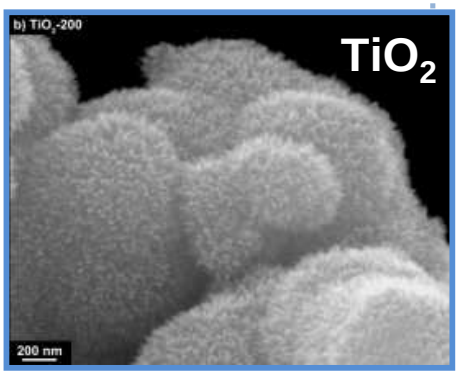
Azo-dye
Methyl Orange

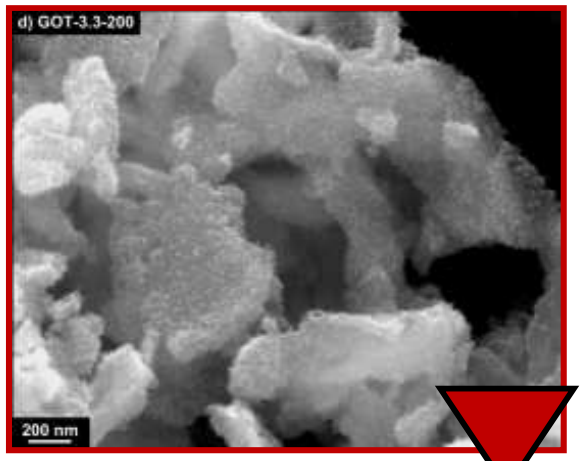


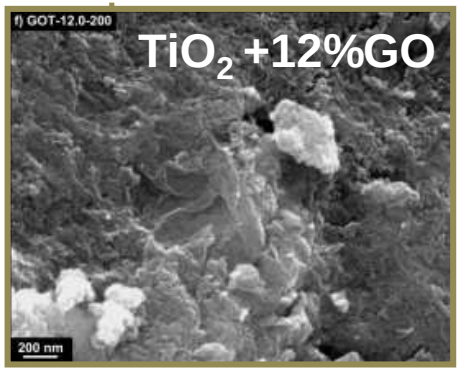


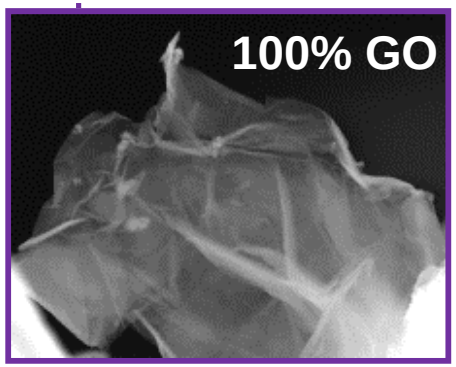
Pharmaceutical
Diphenhydramine

TiO_2 +3.3%GO









Optimal assembly and interfacial coupling of the TiO_2 nanoparticles over the GO sheets

Pastrana-Martínez et al., Appl. Catal. B. 123-124 (2012) 241

From lab...

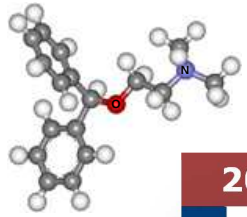
... to market implementation

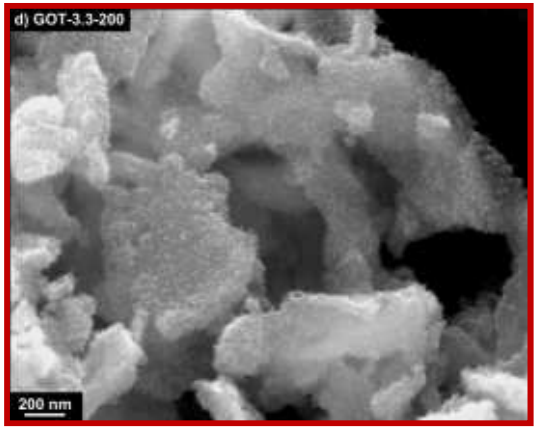
Catalysts should be immobilized on proper supports

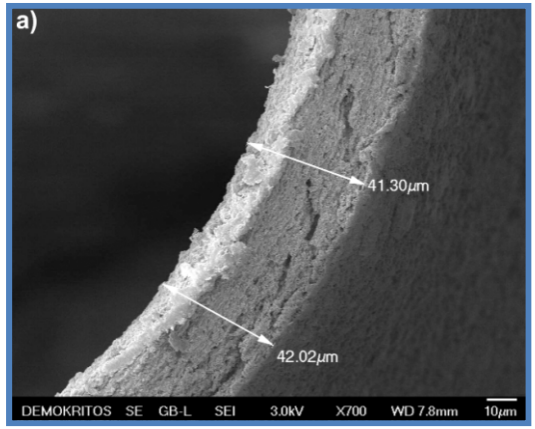
… to market implementation

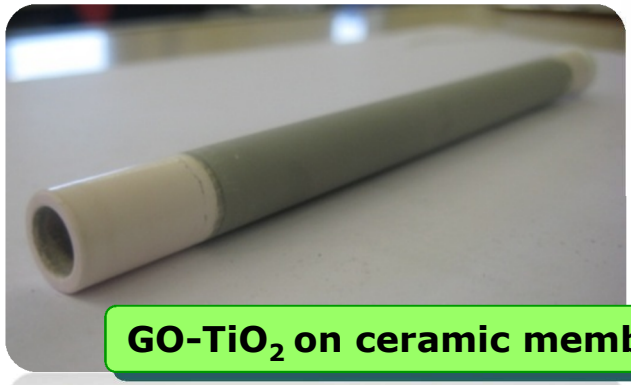
Pastrana-Martínez et al., Appl. Catal. B. 142-143 (2013) 101

Pharmaceutical
Diphenhydramine



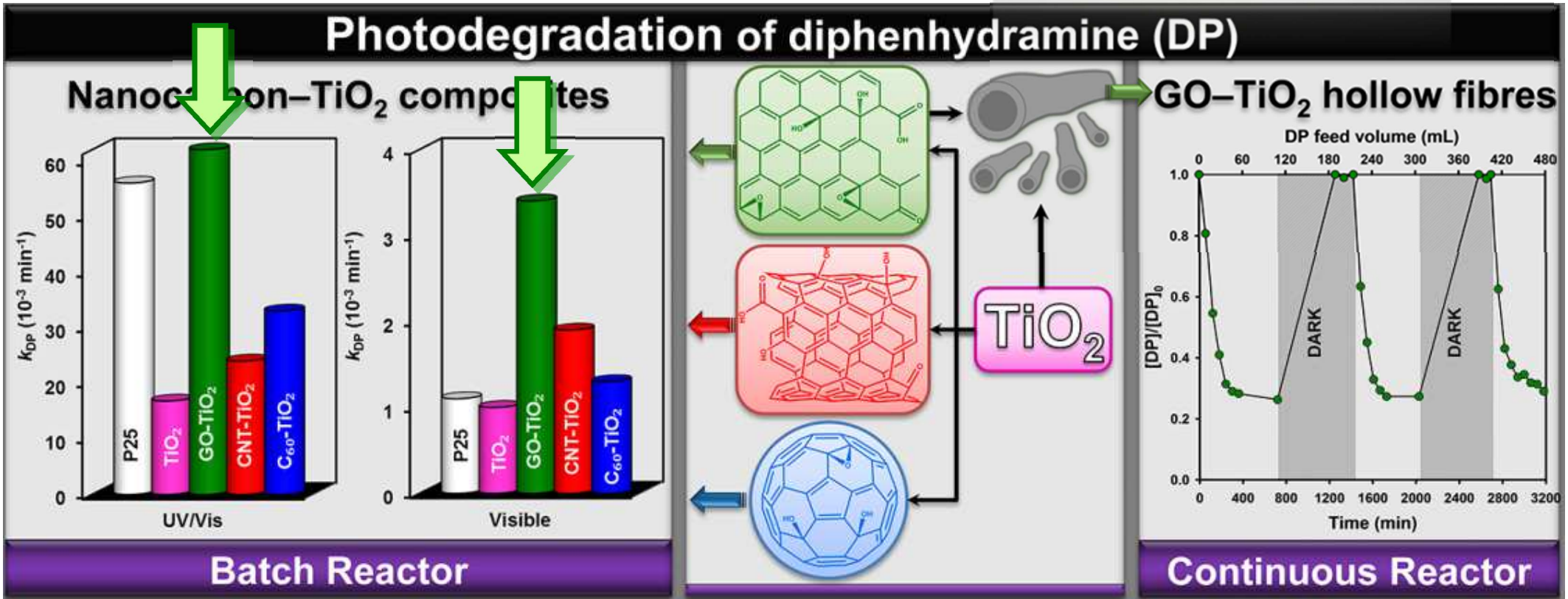






GO-TiO_2 on ceramic membrane

Photodegradation of diphenhydramine (DP)



... to market implementation

adventech®
advanced environmental technologies

History -2006

*Business Plan of "**ASITech**" project : won the 2nd place in a contest for creation of enterprises with technological base supported by "OPEN - Business Specific Opportunities" and that was also selected in another contest promoted by IAPMEI (FINICIA programme).*

… to market implementation

adventech®
advanced environmental technologies

History - 2007

Presentations of ASITech project and meetings with investors.

The most difficult decision to start (capital needed):
- Rapid company growth (5 % of the company).
- Slow /modest growth (100 % of the company).

Application to a national program : ***Adventech***

... to market implementation

adventech®
advanced environmental technologies

History - 2008

- Adventech created in April 2008.

Customized Industrial Wastewater Treatment Plants
Wastewater Reuse Plants
Industrial Waste Gases Treatment Plants

History - 2015

Advanced Oxidation Processes:
Fenton Process, (Catalytic) Ozonation, Wet Air Oxidation, (Photocatalysis)

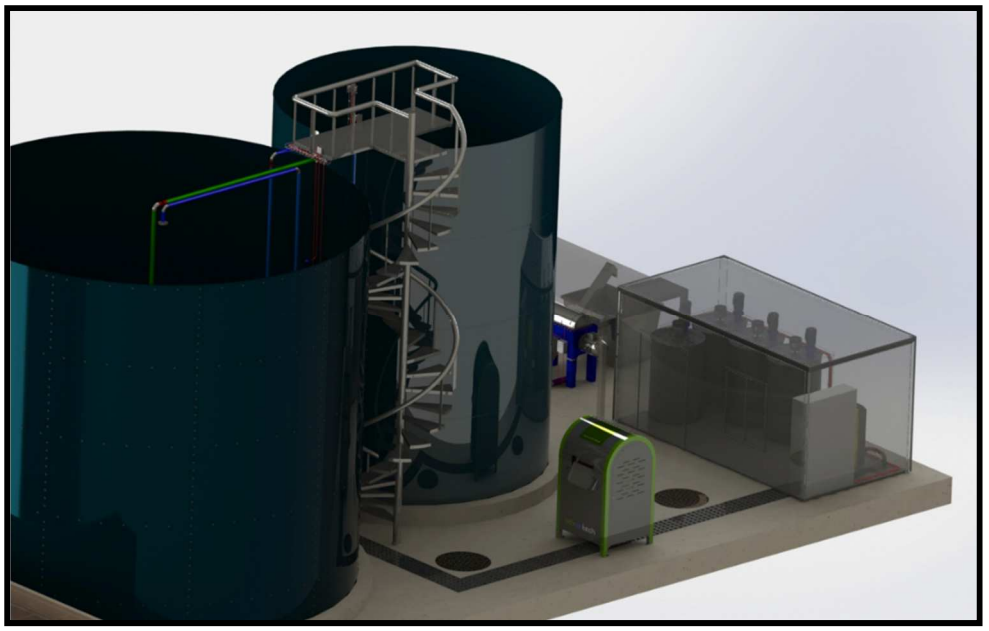
Separation Processes:
Coagulation/flocculation, Flotation, Membranes, Activated Carbon

Biological Processes:
Anaerobic, traditional activated sludge, SBR, MBR, MBBR

... to market implementation

How Adventech Works

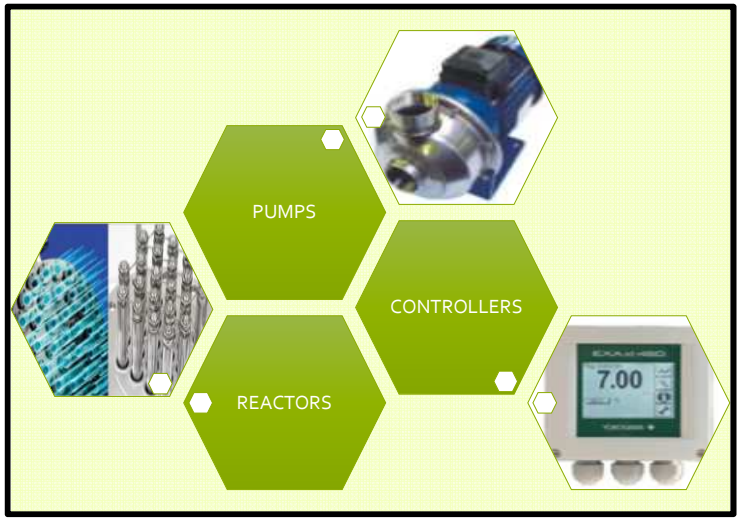
1. *The costumer has a specific problem.*
2. *Samples are collected.*
3. *Regulations and needs are identified.*
4. *R&D is performed at Adventech Lab.*
5. *Best solution is selected at lab scale.*
6. *Technical 2D project.*
7. *Technical 3D project.*



... to market implementation

How Adventech Works

8. Equipments are selected.



9. The technical/investment proposal is presented to the costumer.

10. In case of agreement, the global solution is provided to the costumer.

Winery
Olive Oil
Metalworking
Detergents industry
Pharmaceutical
Tomato
Detergents industry
Cheese
Shipbuilding industry
Landfill
Ceramic
Resins and paints
Chips
others.

… to market implementation

Success Stories

WINERY WASTEWATER
7 -150 m³/day

… to market implementation

Success Stories

OLIVE MILL
WW 30 m³/day

ELDERBERRY
WW 5 m³/day

… to market implementation

Success Stories

FISH & MEAT WW 30 m³/day

COSMETIC & DETERGENTS WW 40 m³/day

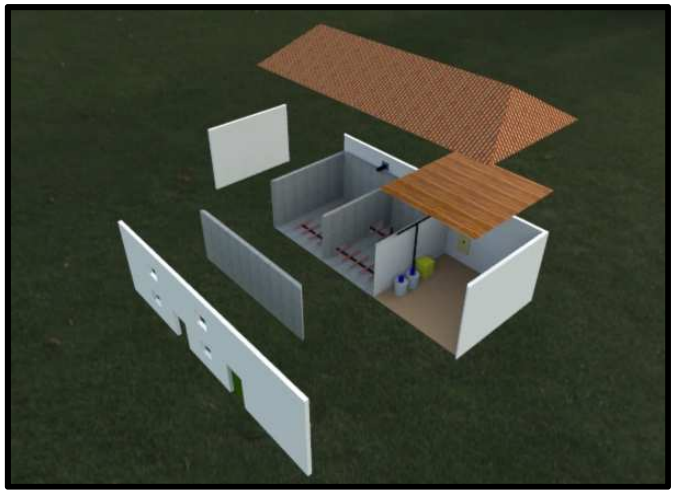
SHIPBUILDING WW REUSE 36 m³/day

… to market implementation

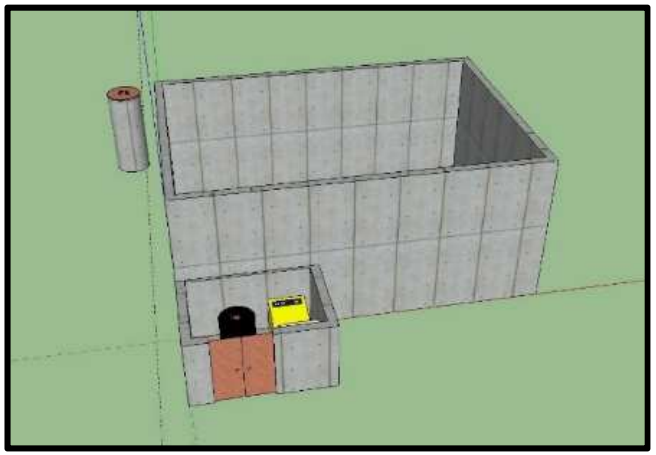
Success Stories

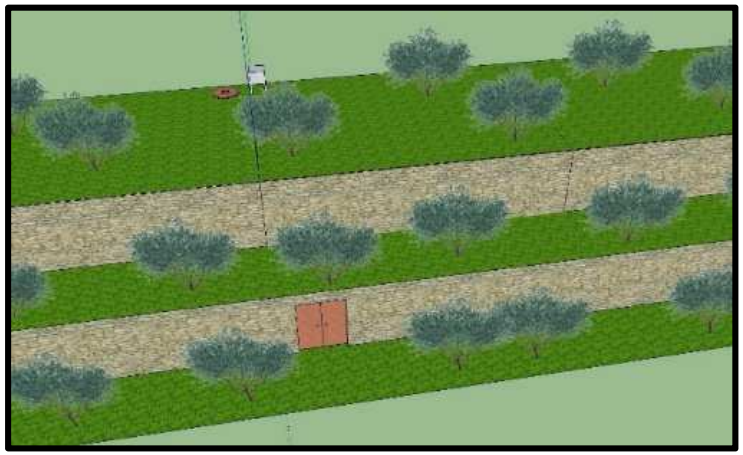
*Building **Hidden** WWTPs*

Inside an old house



Underground





… to market implementation

Success Stories

*Recovering **Old Structures** as WWTPs*

Old production tanks

Old winery “balloons”

… to market implementation

Success Stories

... to market implementation

adventech®
advanced environmental technologies

Centro Empresarial e Tecnológico
3700-121 São João da Madeira, Portugal

http://www.adventech-group.com || info@adventech-group.com

FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA EDUCAÇÃO E CIÊNCIA

IF INVESTIGADOR FCT

POPH PROGRAMA OPERACIONAL POTENCIAL HUMANO

NEPCAT

ON.2 O NOVO NORTE
PROGRAMA OPERACIONAL REGIONAL DO NORTE

COMPETE
PROGRAMA OPERACIONAL FACTORES DE COMPETITIVIDADE

QREN QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
PORTUGAL 2007-2013

SEVENTH FRAMEWORK PROGRAMME

UNIÃO EUROPEIA
FEDER

LABORATÓRIO ASSOCIADO
LSRE LABORATORY OF SEPARATION AND REACTION ENGINEERING
Laboratório de catálise e materiais lcm

U.PORTO
FEUP FACULDADE DE ENGENHARIA
UNIVERSIDADE DO PORTO

Laboratóriodecatáliseemateriais

Grazie mille.

Adrián M.T. Silva
adrian@fe.up.pt