PRO AGRO LECTORIUM

Are we safe? Neutralization and Detection of Agrochemicals

Prof. Dr. Elisa S. Orth, Federal University of Paraná, Brazil

UFPR UNIVERSIDADE FEDERAL DO PARANÁ

Grupo de Catálise e Cinética UFPR

Are we safe?

Brazil's Dangerous Use of Pesticides is a Danger to the Whole World

Borders between Mercosur countries have become a hub for trafficking agrochemicals

Beirut explosion: What we know so far

In agricultural giant Brazil, a growing hazard: The illegal trade in pesticides

Brazilians Poisoned by Pesticides Sprayed Near Homes and Schools

Syria : the use of chemical weapons by the regime against its own population constitutes war crimes [fr]

Salisbury still affected by 'trauma' of novichok poisonings five years on, says health chief

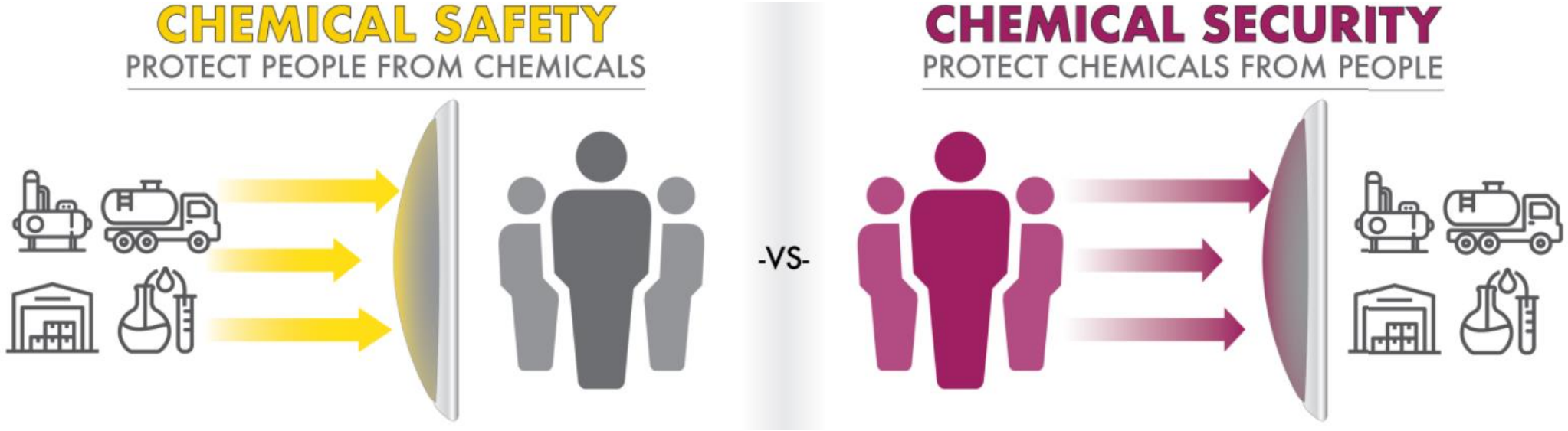
Chemical safety and security?

CAS

> 244 million molecules registered (organic/inorganic)

~ 350 thousand commercialized

~ 1000 toxic (?)



www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

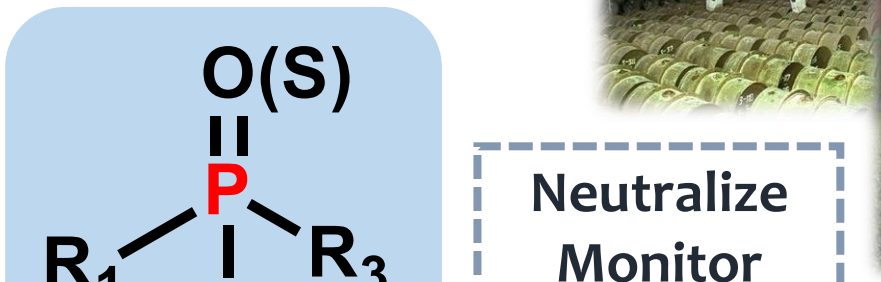
PROBLEMATICS!

Agrochemicals

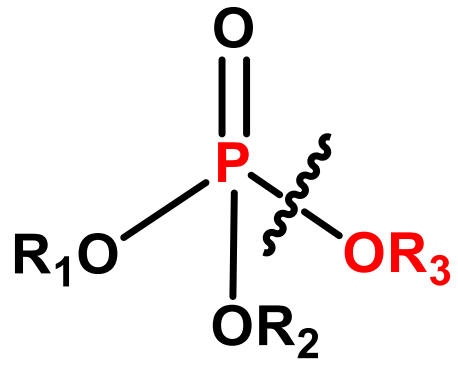
Undesired stockpiles
Allert attack/misuse

Chemical warfare

Organophosphates



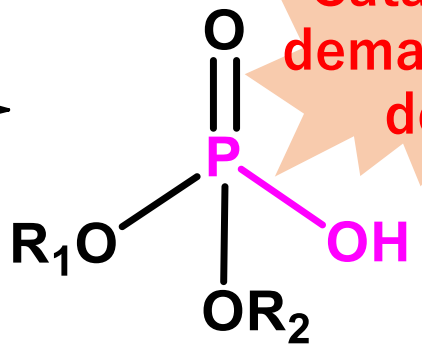
Neutralize
Monitor



Detoxify

Catalysts

Monitor



Catalysts on demand or by-design

STABLE

TOXIC

LESS TOXIC

Neutralization: *eliminate toxicity* ***Cleave P-O***

www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Curitiba

Grupo de Catálise e Cinética UFPR

Group of Catalysis and Kinetics

www.quimica.ufpr.br/elisaorth

Elisa Souza Orth

(elisaorth@ufpr.br)

FEDERAL UNIVERSITY OF PARANÁ

@gcc.ufpr

16 members

Mayara Gonçalves (Pos-doc)
Patricia Soares (Pos-doc)
Regiane Gonzalez (Pos-doc)
Willian Takarada (Dr)
Bruna Ferreira (Dr)
Thiago Santos (Dr)
Amanda Scheuer (Ms)
Gabriel Gomes (Ms)
Mariana Nazareno (Ms)
Mariane Burgo (IC)
Luane Santos (IC)
Ana Lima (IC)
Dayane Lima (IC)
Isabella Nunes (midia)
Lucas Vanzella (midia)
Ester Dores (midia)

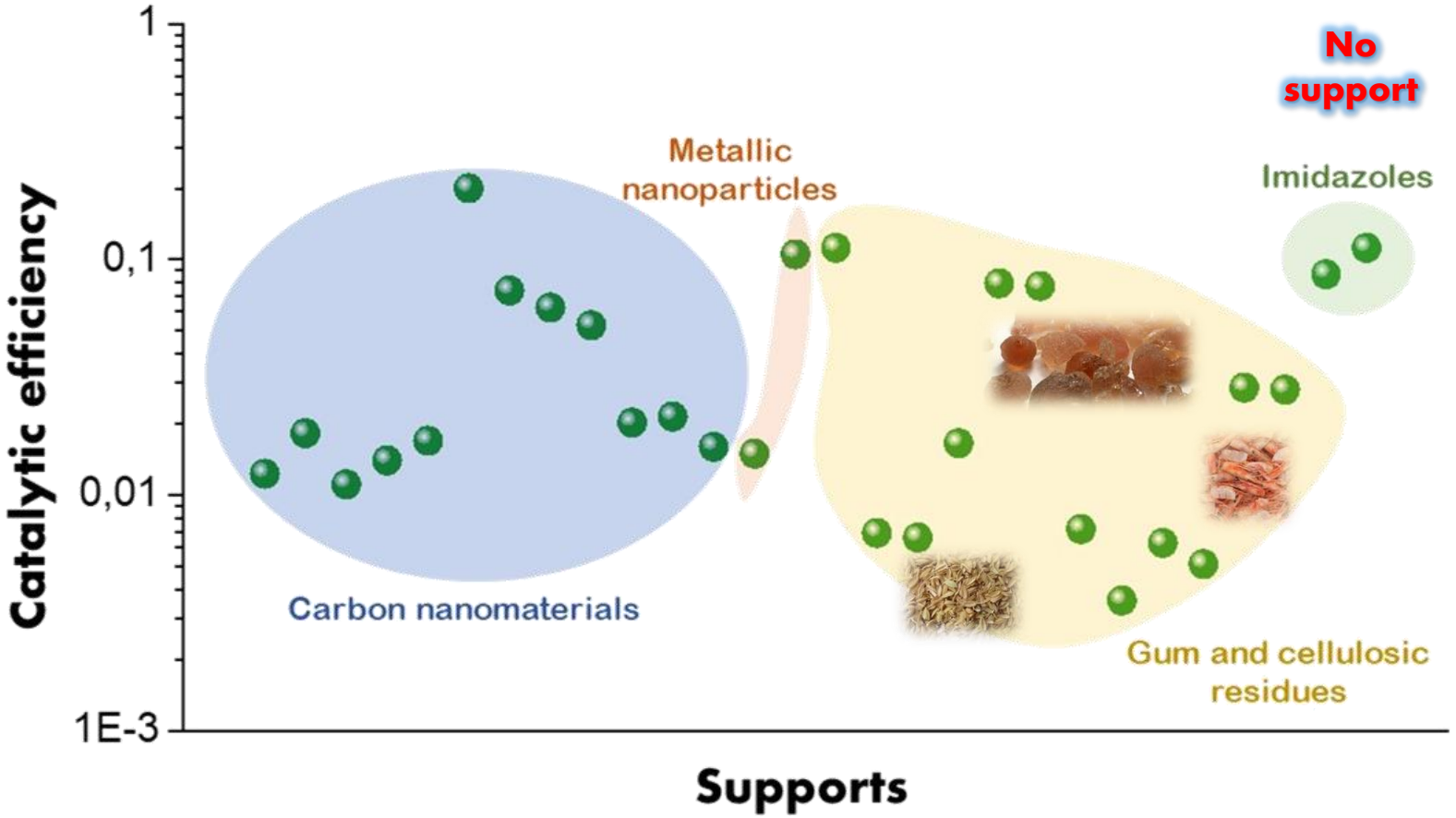
Colaborators herein

Aldo Zarbin- UFPR ; Maria Rocco-UFRJ; Sergio Domingues – UFRJ; Luiz Junior- UFPR; Marcio Bergamini-UFPR; Rilton Freitas – UFPR; Juliana Maurer – UFPR; Christian Wittee-UFPR; Francine Bertella-UFPR; Tue Hassenkam – Dinamarca

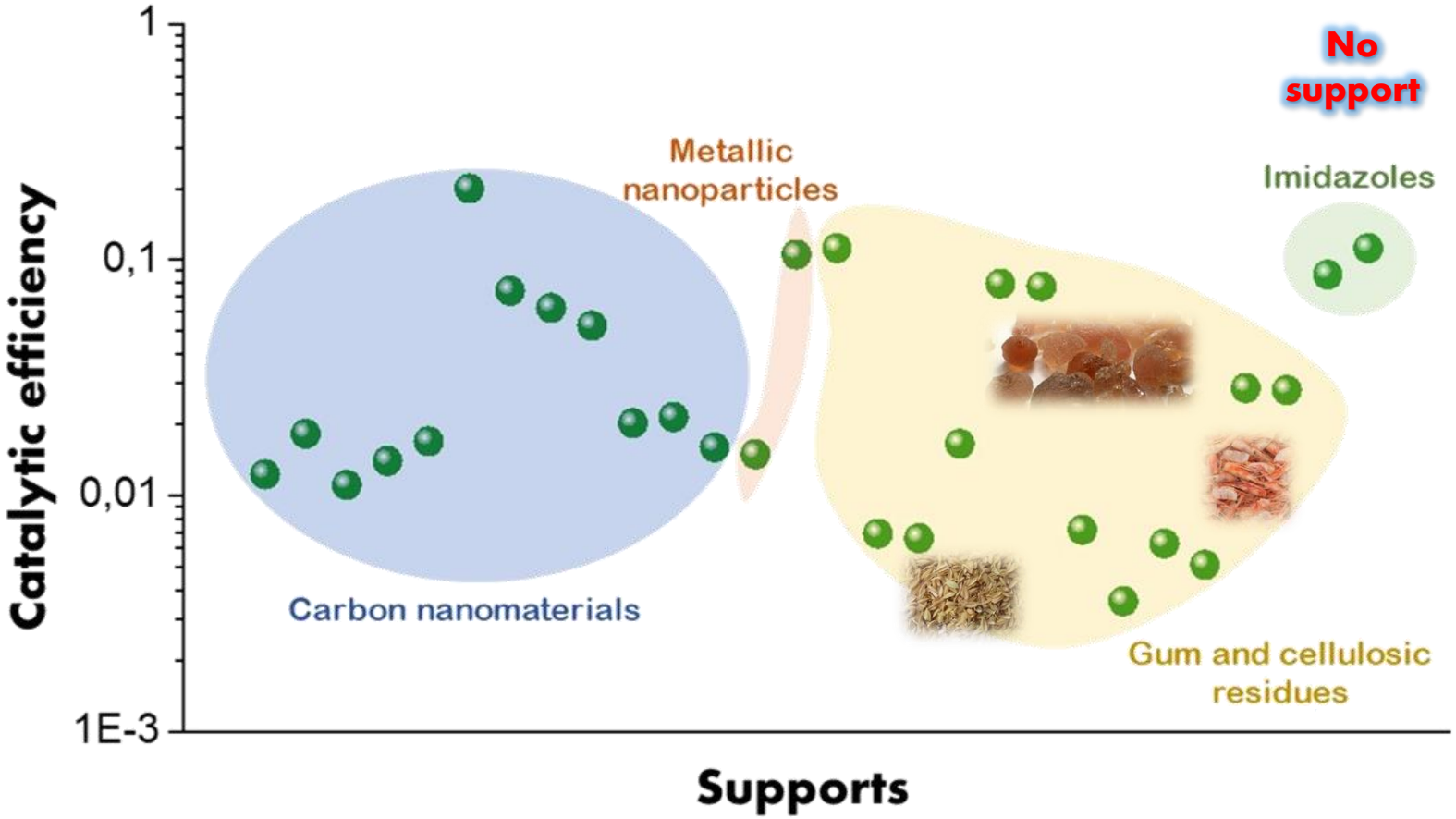
Are we safe? Neutralization and Detection of Agrochemicals

TODAY

1. Nanocatalysts
2. Sustainable catalysts
3. Detection



Are we safe? Neutralization and Detection of Agrochemicals



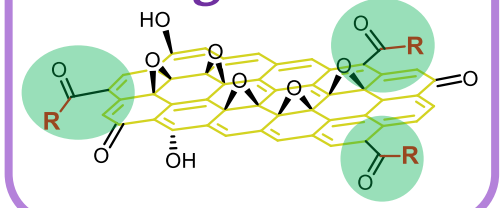
TODAY

1. Nanocatalysts
2. Sustainable catalysts
3. Detection

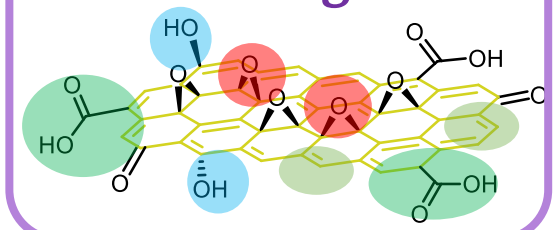
Functionalization: what is good?

Challenge: confirm functionalization

Coverage?



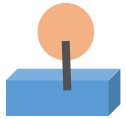
Site targeted?

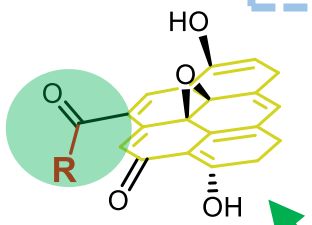


Good?

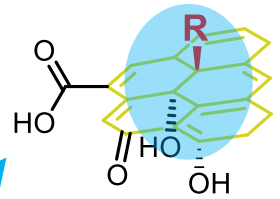
Application -driven

Covalent

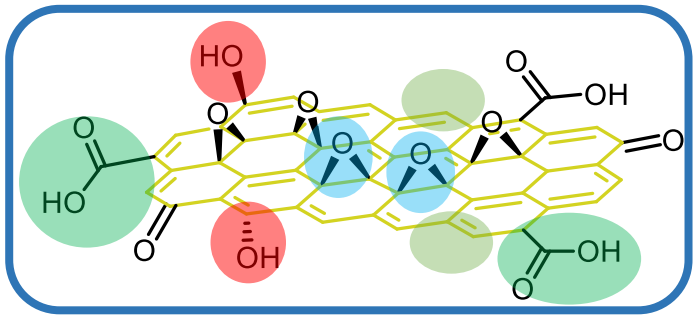




Carboxylic acid



Epoxide



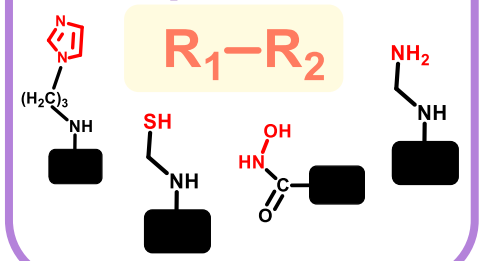
Hydroxyl

Epoxides

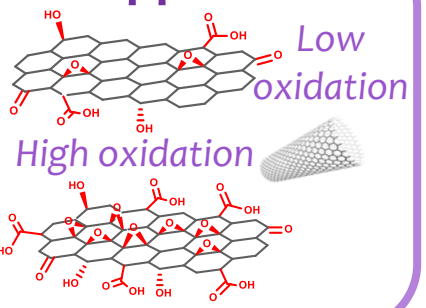
Carboxylic acid

sp2 carbon

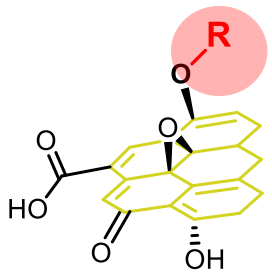
Group anchored?



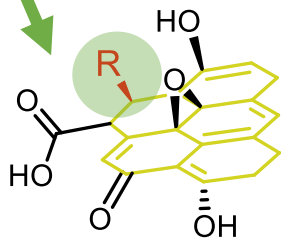
Support?



Hydroxyl



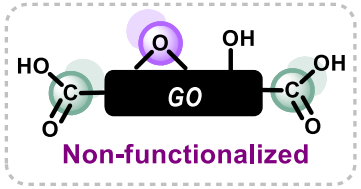
sp2 carbon



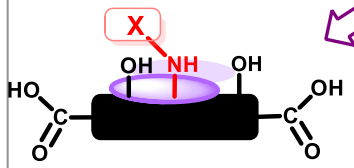
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Nanodesing: strategy?

> 30 nanocatalysts



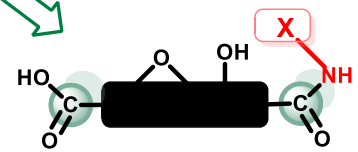
Via epoxide opening



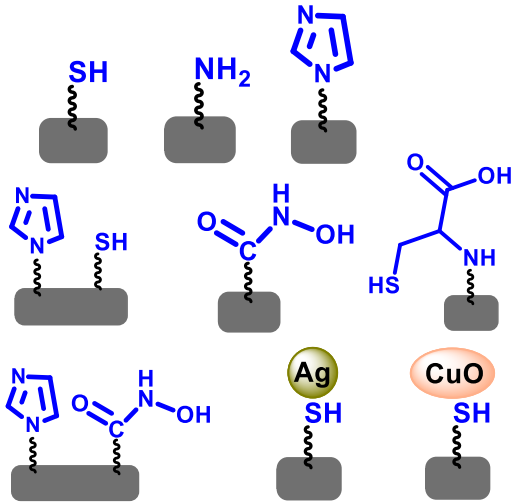
$X-NH_2$

Derivatizing agent

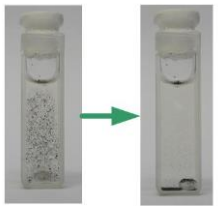
Via amidation with carboxylic acid



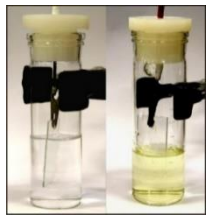
- ✓ ≠ Oxidation degree
- ✓ Mono- Bifunctionalized
- ✓ ***Vary precursor:*** *graphene oxide; crumbled graphene; carbon nanotube; metallic nanoparticles*
- ✓ ***Vary groups:*** *imidazole, thiol, amine, hydroxamate, cysteine, etc*



Powder



Thin film

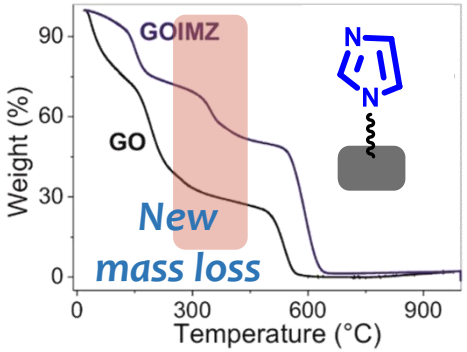


J. Mat. Chem. A 2024; ChemCatChem, 2024. JBCS, 2024, Frontiers Carbon, 2024. Green Chem, 2022. ACS Appl. Nano Mater. 2022; Appl Catal B-Environ, 264, 118496,2020; *J. Cat. 356, 75, 2017; J. Mat. Chem. A, 5, 9591, 2017; J. Colloid Interface Sci. , 467, 239, 2016;* Carbon , 61, 543, 2013

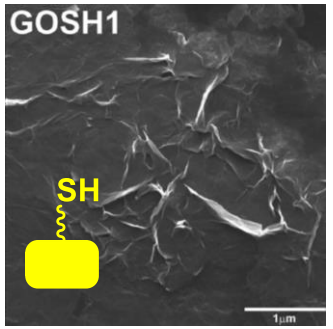
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Characterization

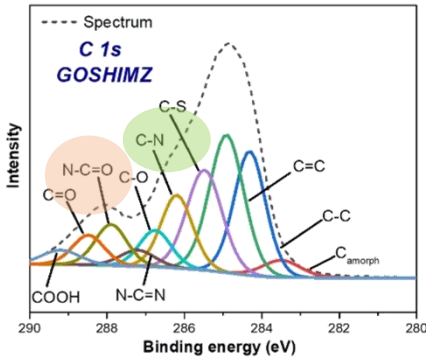
TGA



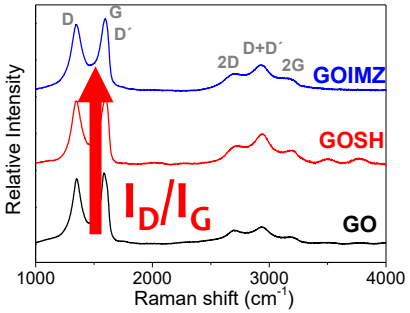
SEM



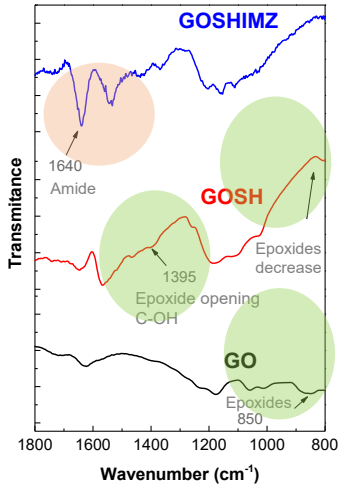
XPS



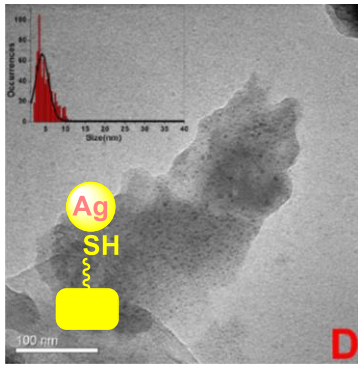
Raman



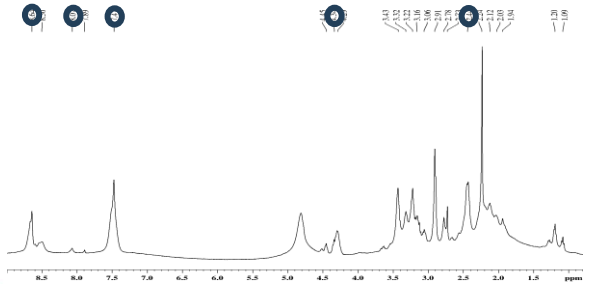
FTIR



TEM

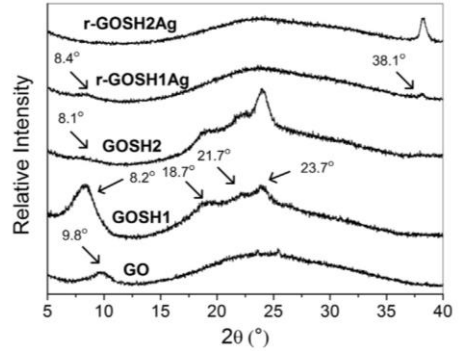


^{1}H NMR HR-MAS



- Nanoparticles
- Differ mono-bi
- Indicates functionalization
- Challenging

XRD



CHNS, TITRATION...

J. Mat. Chem. A 2024; ChemCatChem, 2024. JBCS, 2024, Frontiers Carbon, 2024. Green Chem, 2022. ACS Appl. Nano Mater. 2022; Appl Catal B-Environ, 264, 118496,2020; J. Cat. 356, 75, 2017; J. Mat. Chem. A, 5, 9591, 2017; J. Colloid Interface Sci. , 467, 239, 2016; Carbon , 61, 543, 2013

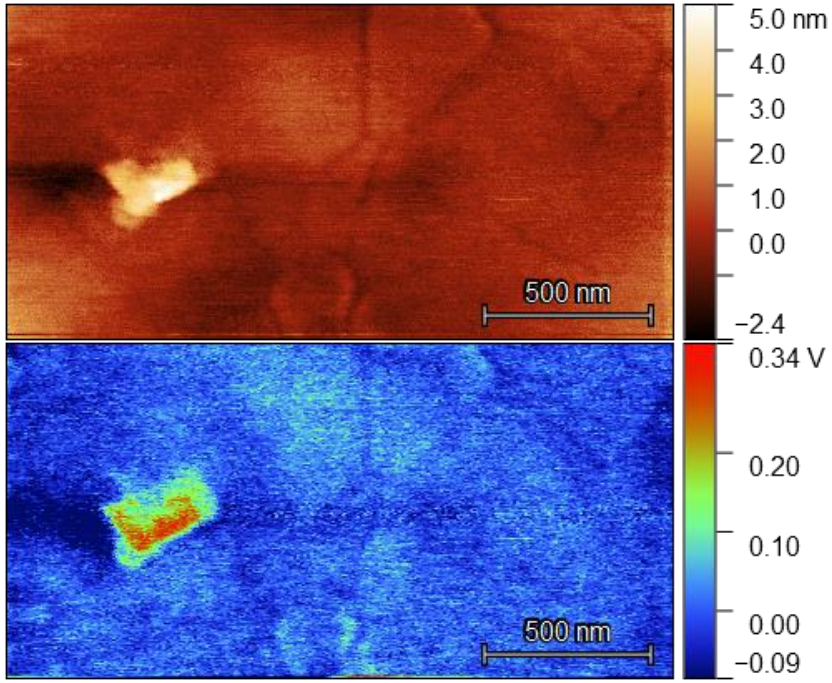
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Characterization

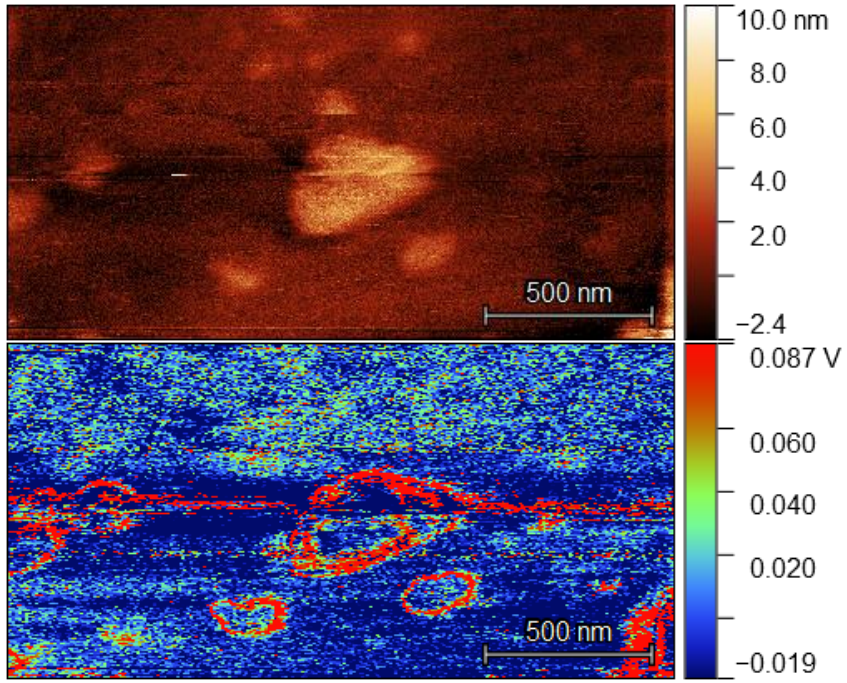
AFM-FTIR

N-H bond mapping

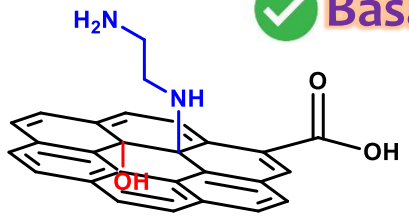
GOEDA1 (epoxide) – 1512 cm-1



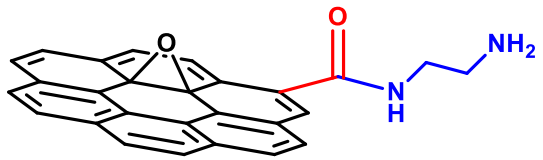
GOEDA2 (Acid) – 1556 cm-1



Basal plane

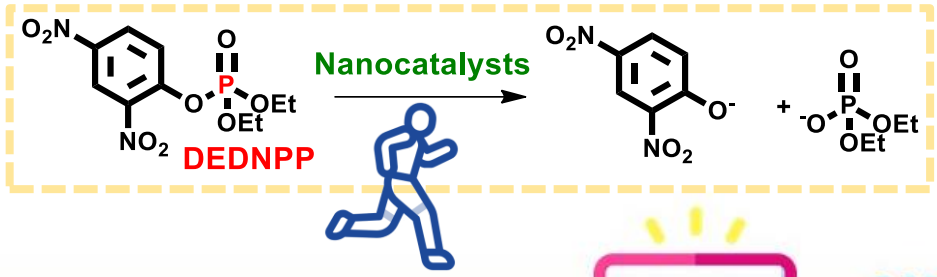


Border



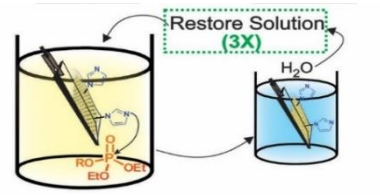
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Nanocatalytic performance: reaction lifetime?



Recycling

Activity > 5 cycles



J. Mat. Chem. A 2024; ChemCatChem, 2024. JBCS, 2024, Frontiers Carbon, 2024. Green Chem, 2022. ACS Appl. Nano Mater. 2022; Appl Catal B-Environ, 264, 118496,2020; *J. Cat. 356, 75, 2017; J. Mat. Chem. A*, 5, 9591, 2017; *J. Colloid Interface Sci. , 467, 239, 2016;* Carbon , 61, 543, 2013

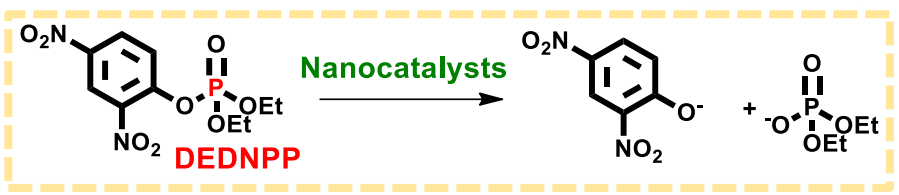
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Nanocatalytic performance: functional group anchored?

Faster

More catalytic

Years→Min



rate constants

Catalytic rate constant

10

1

Monofunctionalized

Via epoxides

Via carboxylic acids

Bifunctionalized

Via epoxides +NPs

Via carboxylic acid+epoxide

Via carboxylic acids

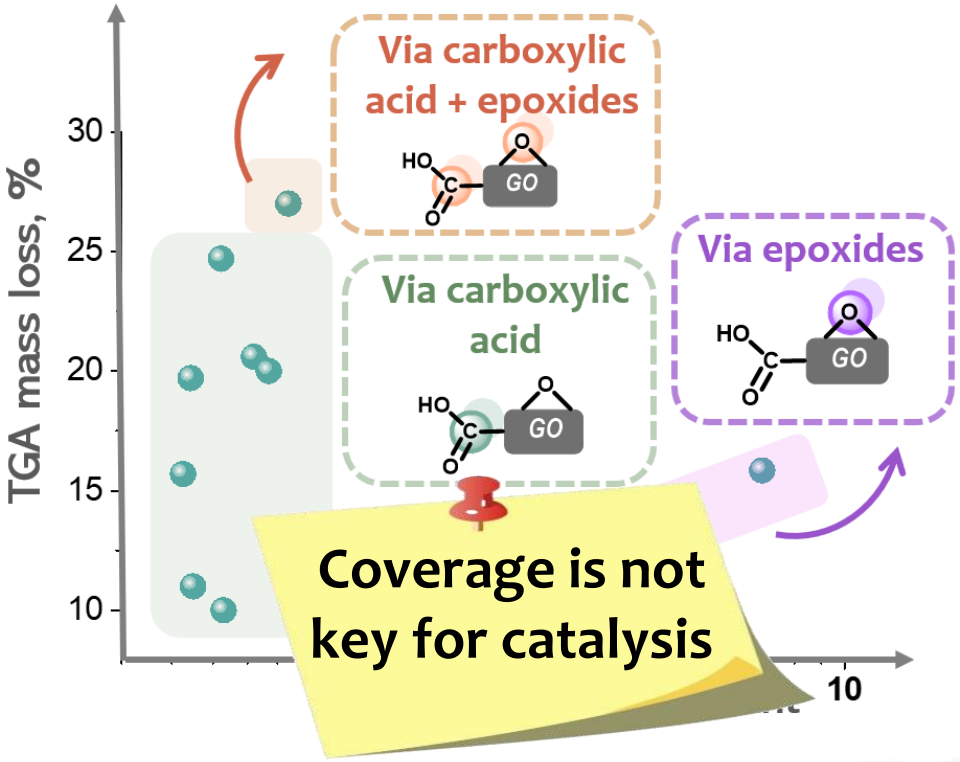
IMZ SH NH_2 HD CYS IMZ+SH IMZ+HD SH+Ag SH+CuO

Via epoxide more catalytic

Rare support/ molecules

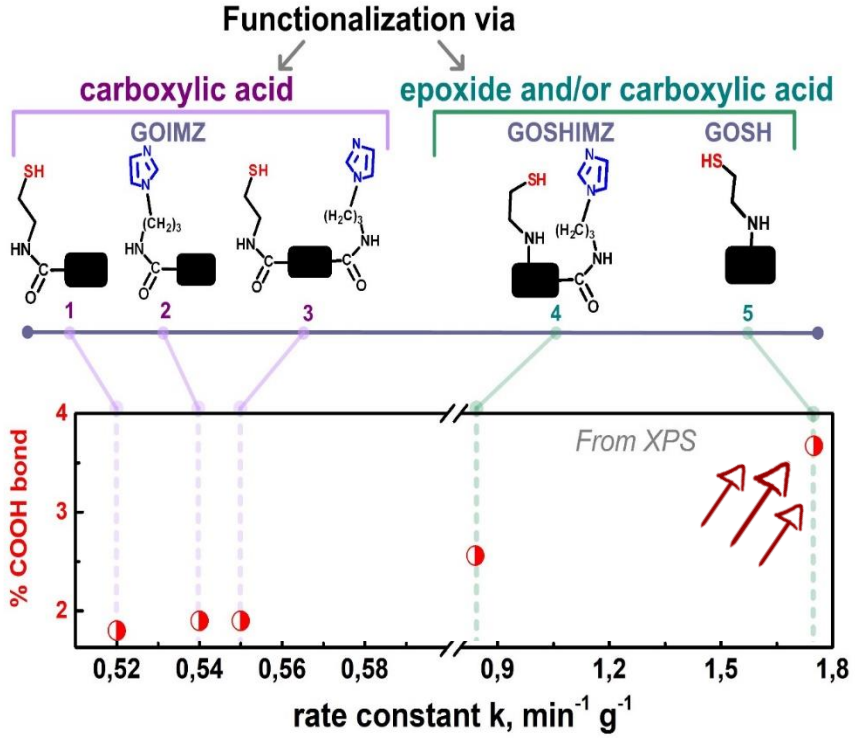
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Nanocatalytic performance: coverage vs neighboring?

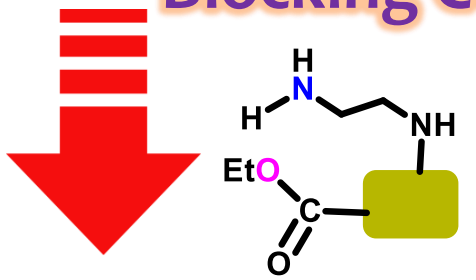


↑TGA mass loss
↑coverage

↑ Via epoxide
↑ Carboxylic acids

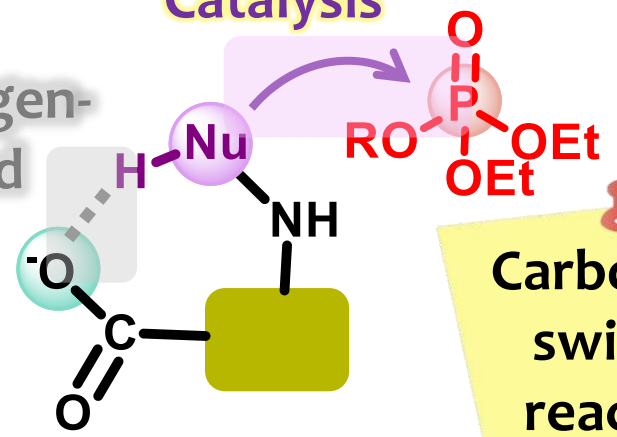


Blocking COO⁻



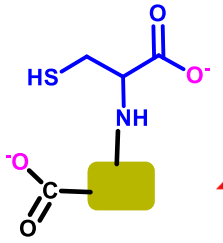
Catalysis

Hydrogen-bond



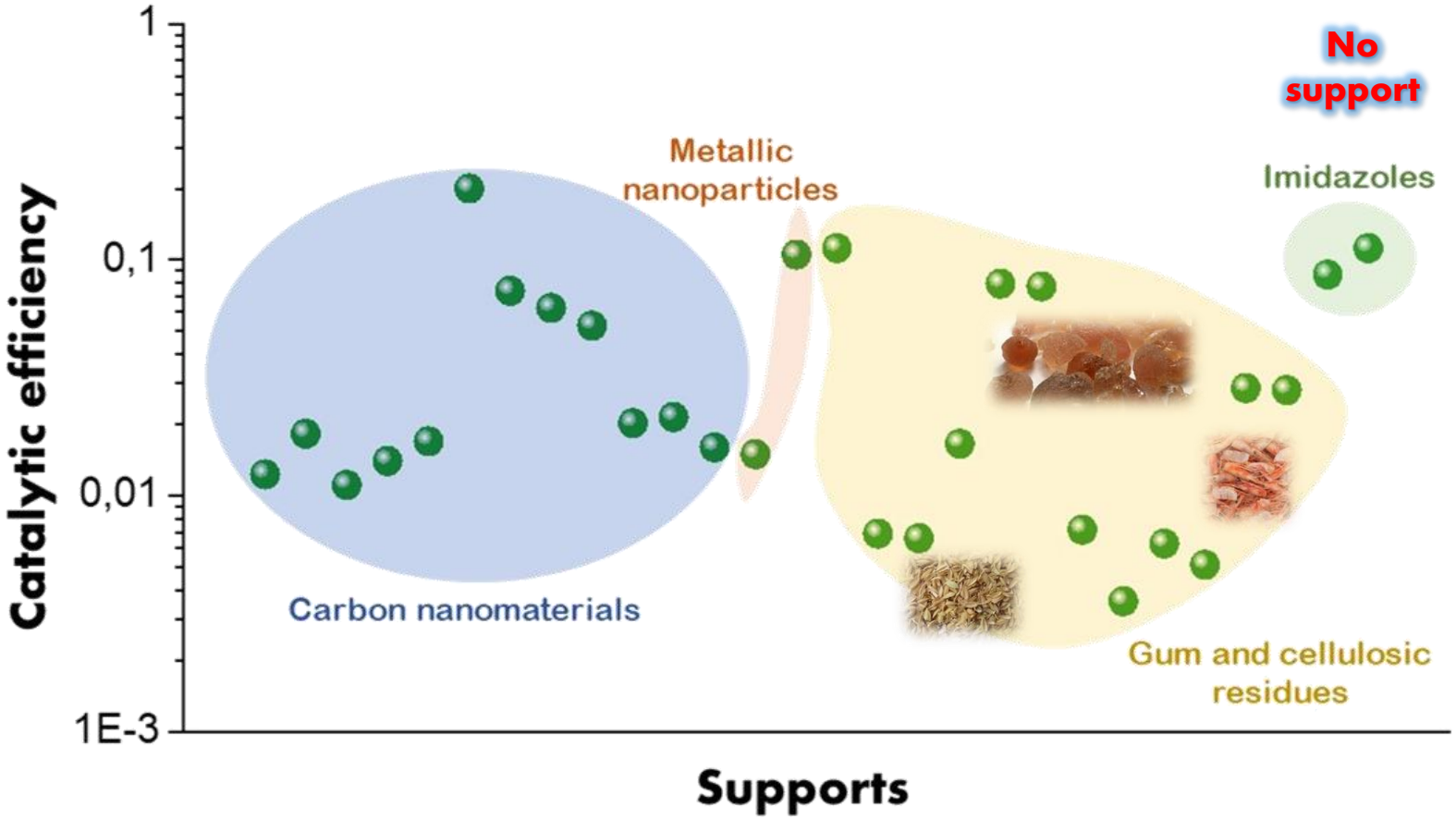
Carboxylate switches reactivity

More COO⁻



www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gec.ufpr

Are we safe? Neutralization and Detection of Agrochemicals



TODAY

1. Nanocatalysts
2. **Sustainable catalysts**
3. Detection

Sustainable biocatalysts

Precursors

Cheap

Carboxymethyl cellulose

Agricultural waste

Rice husk

Nanocellulose

Renewable

Alginate

Commercial Industrial waste

Gum arabic

Cashew tree gum

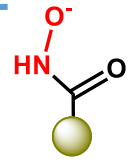
Fishery waste

Shrimp shell

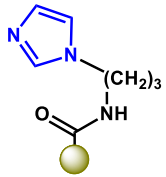
Buxixão tree gum

Homogeneous and heterogeneous

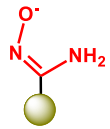
> 25 catalysts



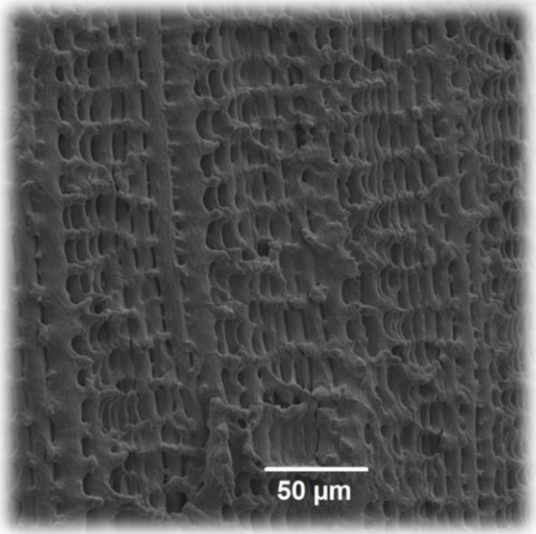
Hydroxamate



Imidazole



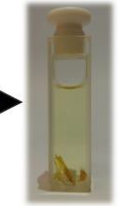
Amidoxime

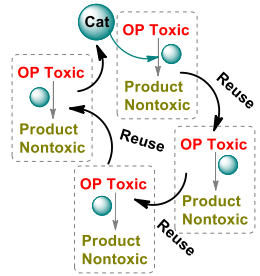


Recycling

Beginning

End



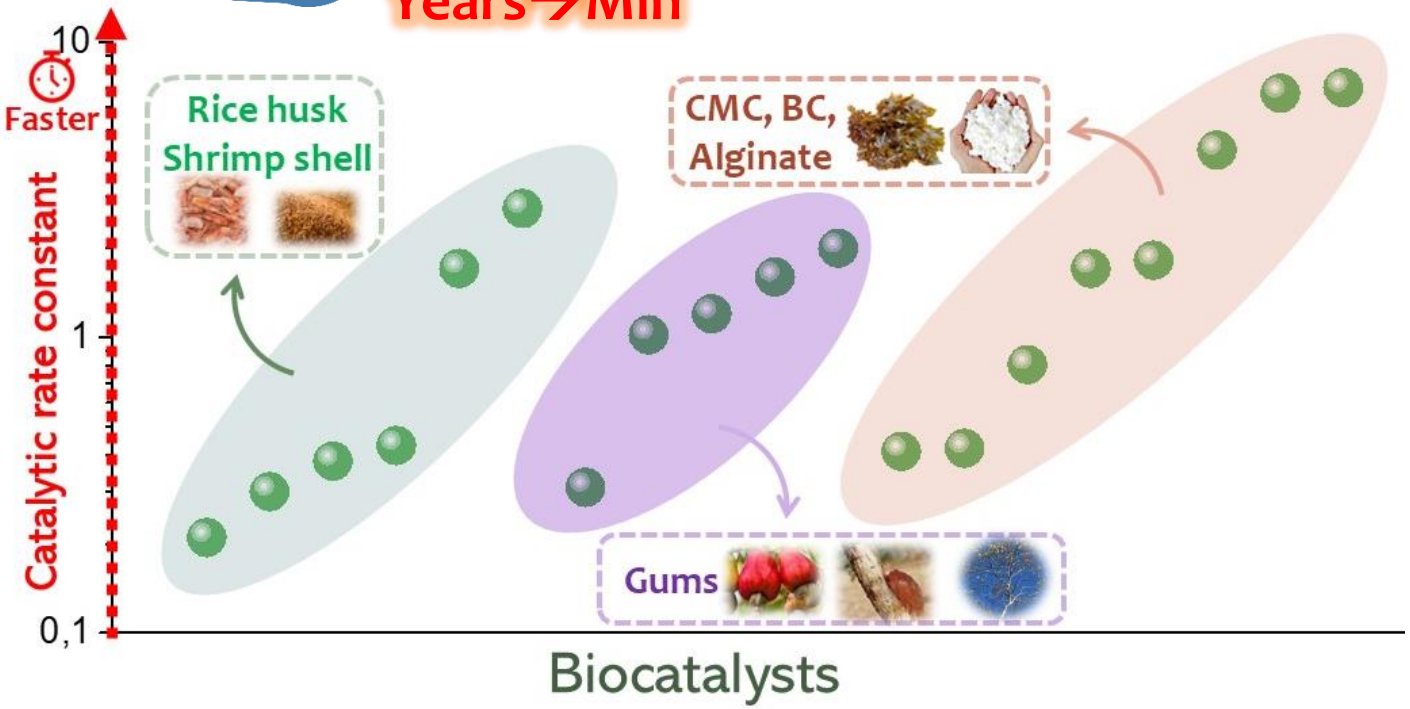


Activity > 5 cycles
FTIR, etc

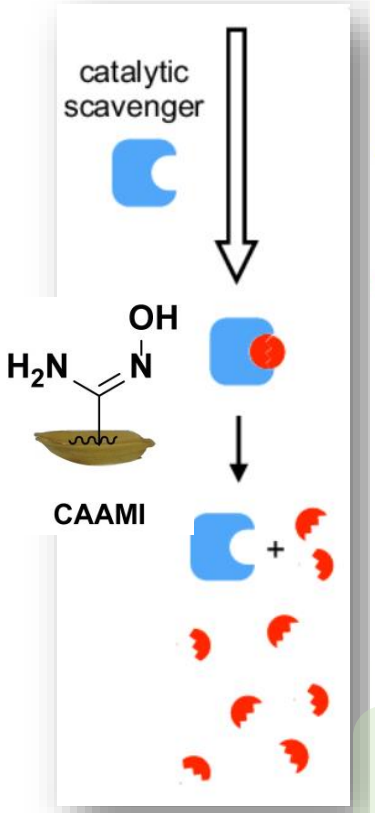
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Sustainable biocatalysts

Years→Min

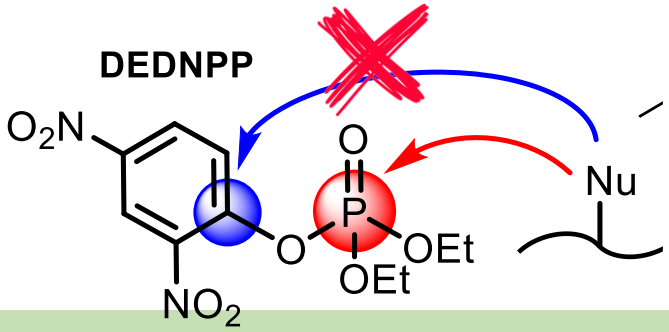


Scavenger?



Modulated by solvents

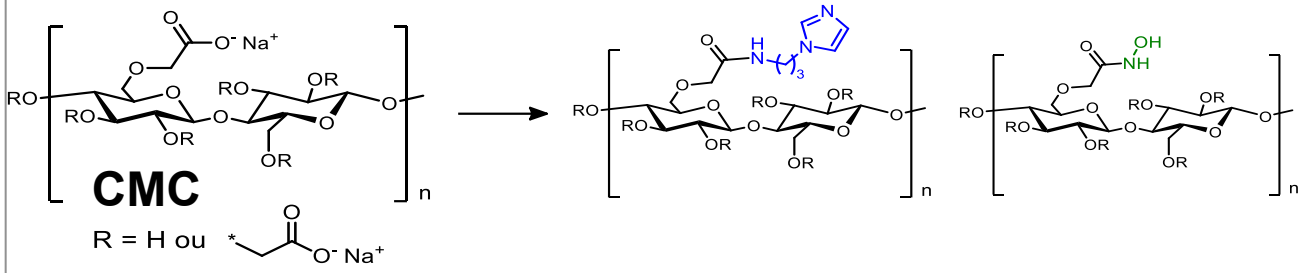
Selectivity?

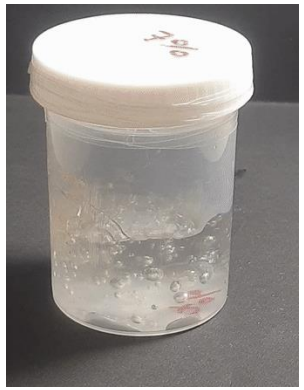


Polymer shifts towards selectivity

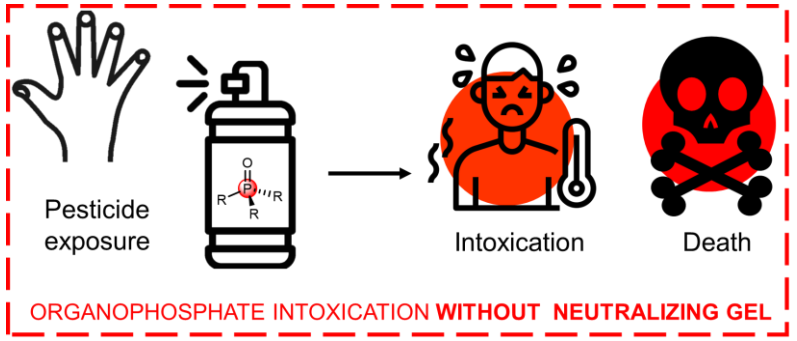
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

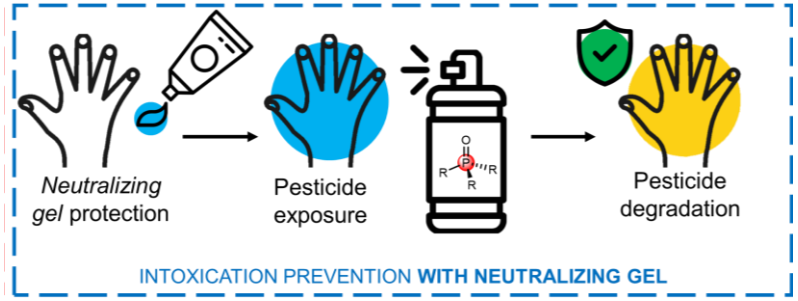
BIOCATALYSTS AND NEUTRALIZING GEL





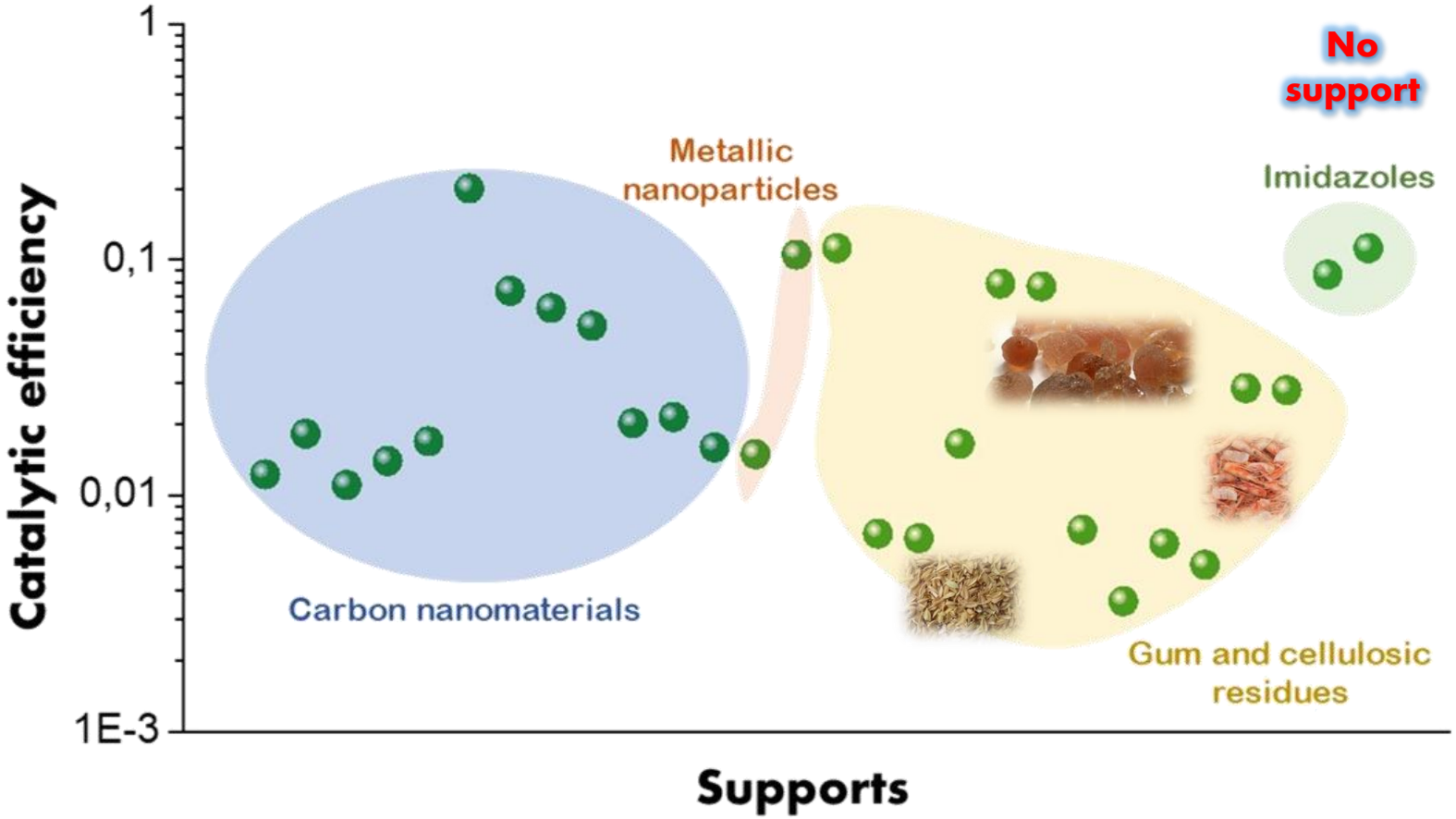
Carboxymethylcellulose





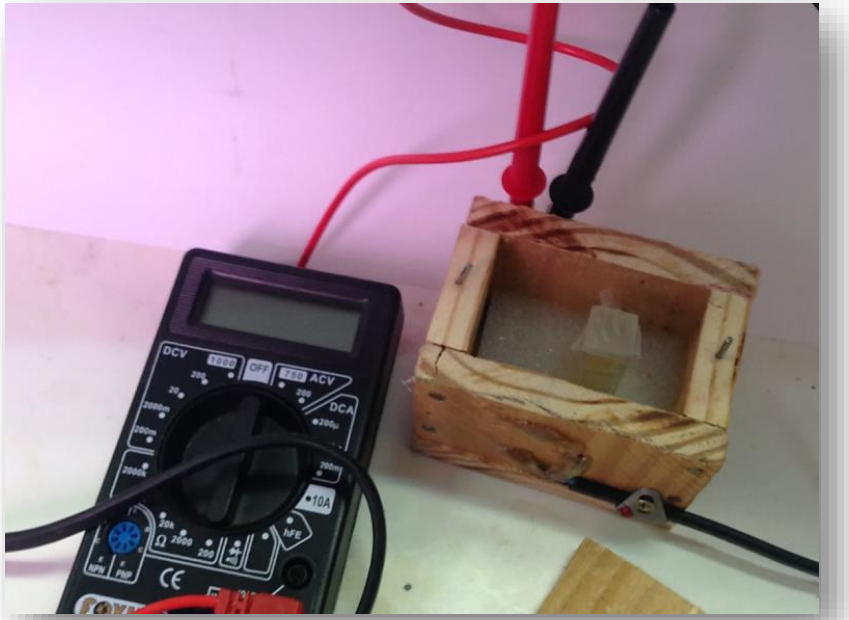
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Are we safe? Neutralization and Detection of Agrochemicals



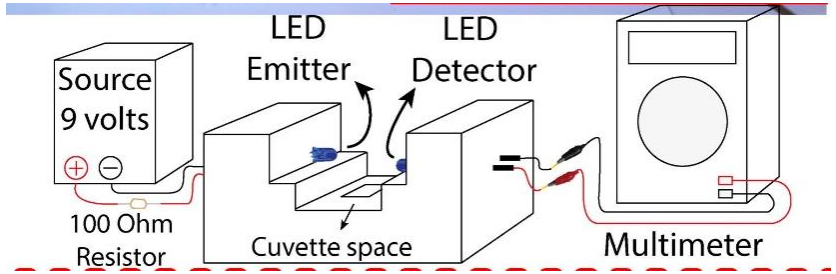
TODAY

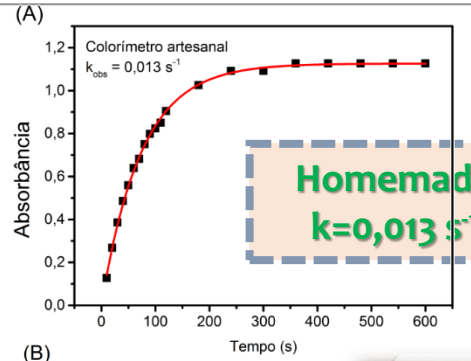
1. Nanocatalysts
2. Sustainable catalysts
3. **Detection**



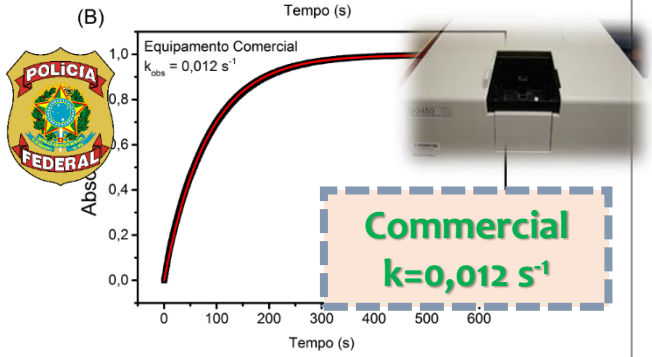
LOW TOXICITY — HIGH TOXICITY

Portable homemade detector

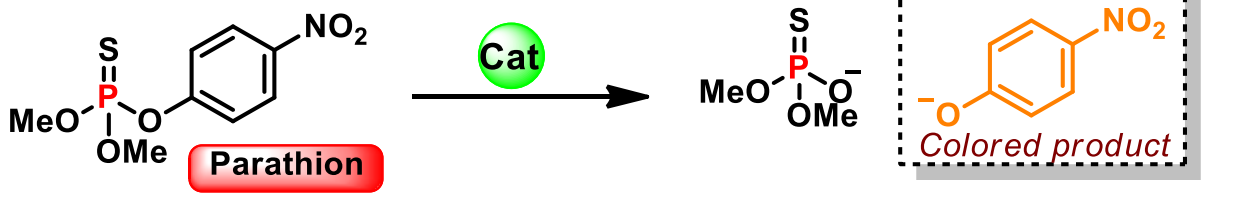




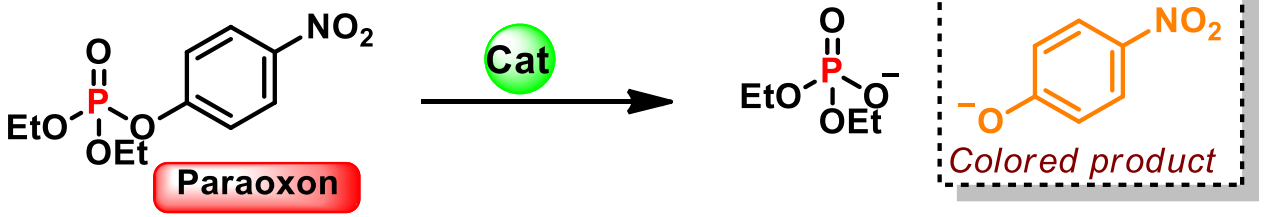
Homemade
k=0,013 s^{-1}



Commercial
k=0,012 s^{-1}



Detects in 5 min
10 rep. < 3% error
10^{-6} mol L^{-1}



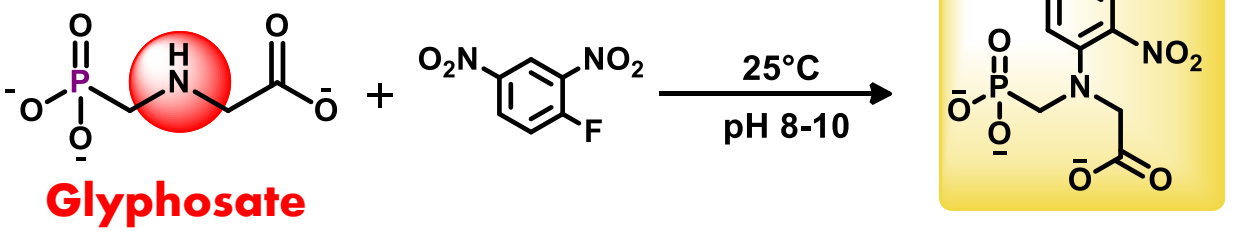
Detects in 10 min
10 rep. < 4% error
2 x 10^{-6} mol L^{-1}

Pure and Applied Chem. 2020, 92, 601;
Patent deposited, INPE, Brazil, 2018 e 2021.

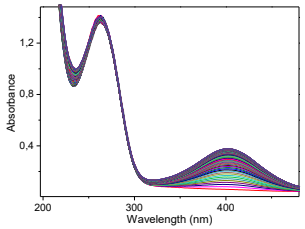
www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

Colorimetric detection

DNFB – Colouring agent

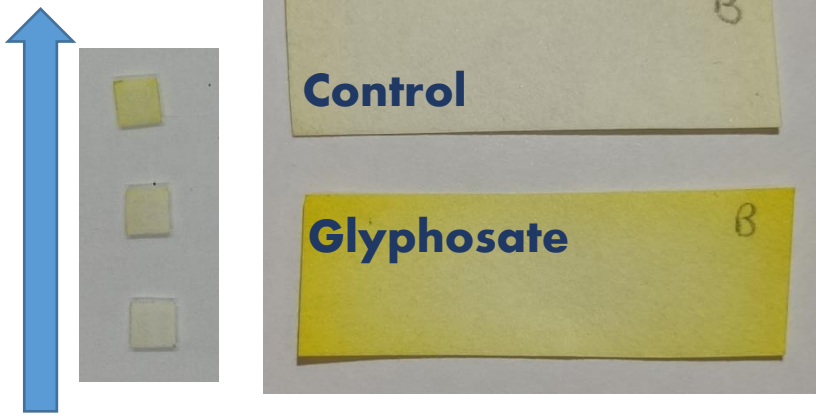


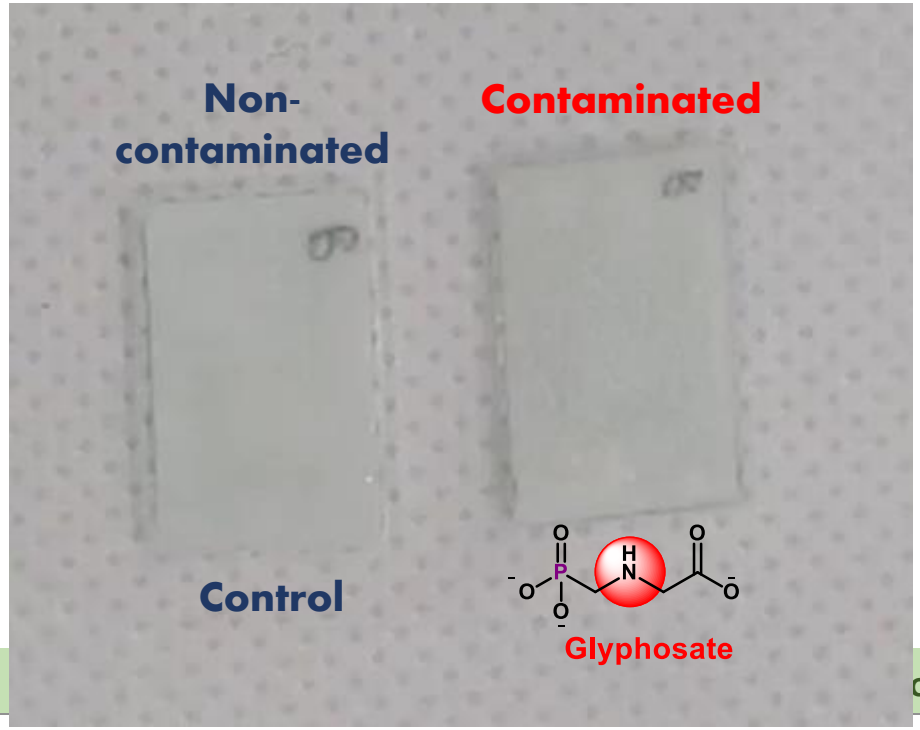
Detects in 10 min
10 rep. < 10% error



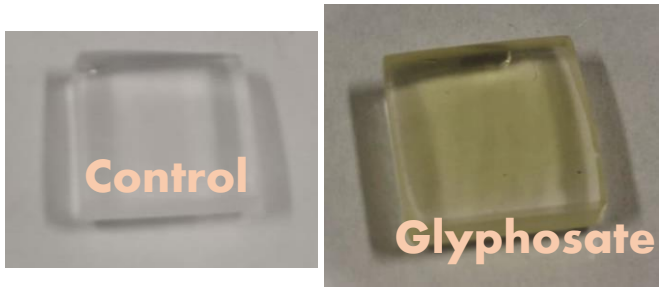
Paper sensor

Higher amount





Glass sensor- PVG



Pure and Applied Chem. 2020, 92, 601;
Patent deposited, INPE, Brazil, 2018 e 2021.

orth / elisaorth@ufpr.br / @gcc.ufpr

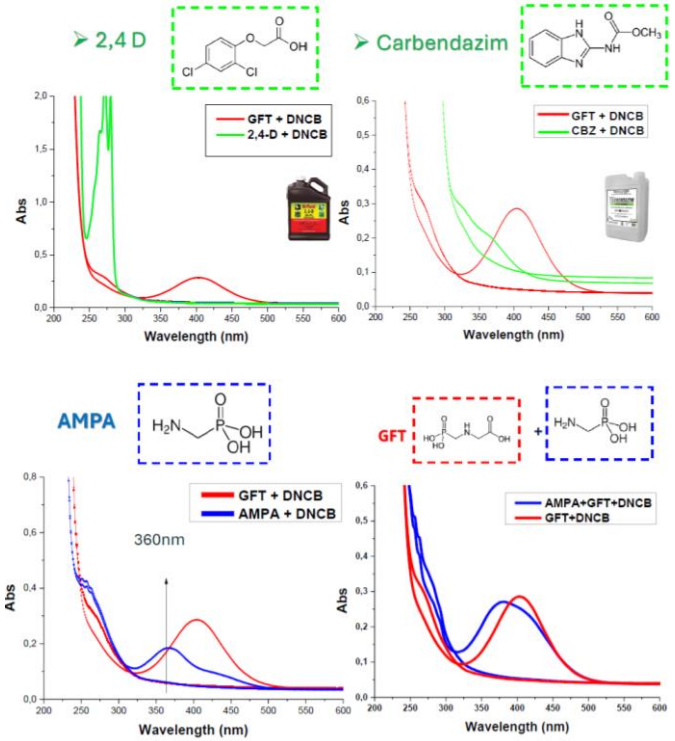
Interference and Traceability

20-50% glyphosate

50-80% incipient

Comercial	Incipient interference?	Distinguish ? (RMN)	Origen
Roundup	NÃO	☑	Brasil/Argentina/USA/Bélgica
Nufosate	NÃO	☑	Índia/China
Zavit	NÃO	☑	China
Zafera	NÃO	☑	China
Stinger	NÃO	☑	Brasil/Argentina/USA/Bélgica

Selectivity with other agrochemicals



Selective:

- 2,4D/Carbendazim
- AMPA: distinguishable

www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr

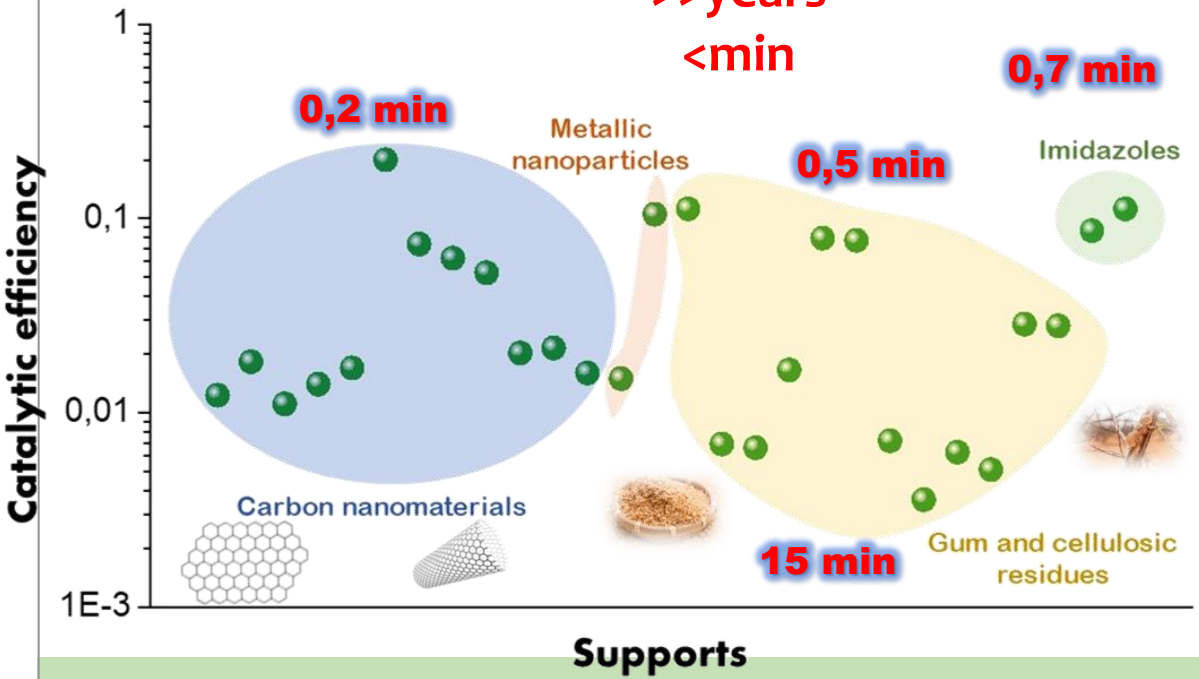
SUMMARY

Greening up?

1. Faster/Catalysis
2. Recycling
3. Avoid byproducts
4. Neutralize/Detect toxic agents
5. Renewable precursors

Tackling?

>>years
<min

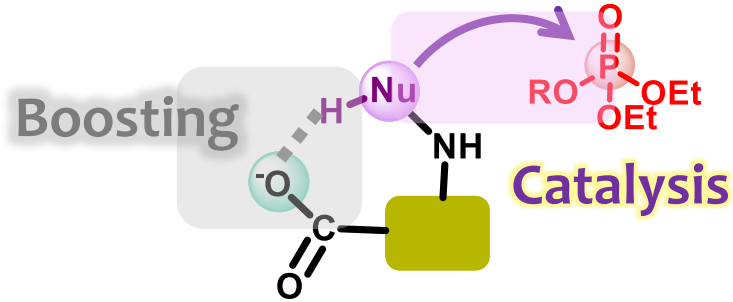


Strategy

boosts

switches

Catalysis



- Sinergism: precursors matter!
- Multiple catalyses

www.quimica.ufpr.br/elisaorth / elisaorth@ufpr.br / @gcc.ufpr


Curitiba
Curitiba
Ceará
Iguassu Falls
Ouro Preto
Maranhão
Prof. Elisa. S. Orth
Universidade Federal do Parana
elisaorth@ufpr.br
www.quimica.ufpr.br/elisaorth
@gcc.ufpr
PRO AGRO
LECTORIUM
Pantanal
Rio de Janeiro
Porto de Galinhas
Carneiros
Amazônia
Bonito
Thanks for your attention!

PRO AGRO
LECTORIUM

Thank you!