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# Valorization of lignocellulosic biomass: nanomaterials for advanced applications

Juan Carlos Colmenares

CELISE Med Term Meeting  
24<sup>th</sup>-25<sup>th</sup> of July-2023, Warsaw, POLAND



Engineering Research Institute  
Universidad Cooperativa de Colombia



# Outlines



IChF  
Institute of Physical Chemistry PAS

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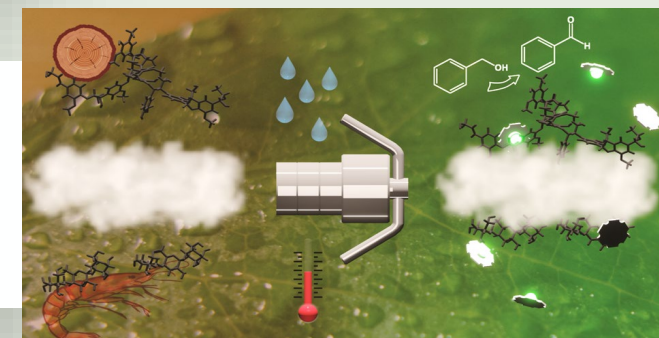
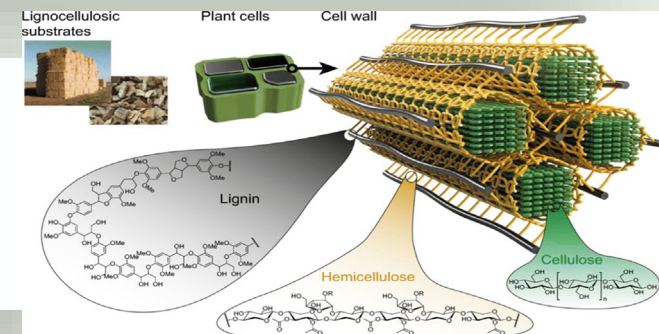
**Colombia-Poland, Process intensification, Photocatalysis, Sustainability, TiO<sub>2</sub>/carbon-based materials, Lignin valorization, Nanomaterials, SDGs, Water purification,....**



**1.** Generalities of Colombia-Poland Cooperation and the possibilities of using lignin for photocatalysts' fabrication



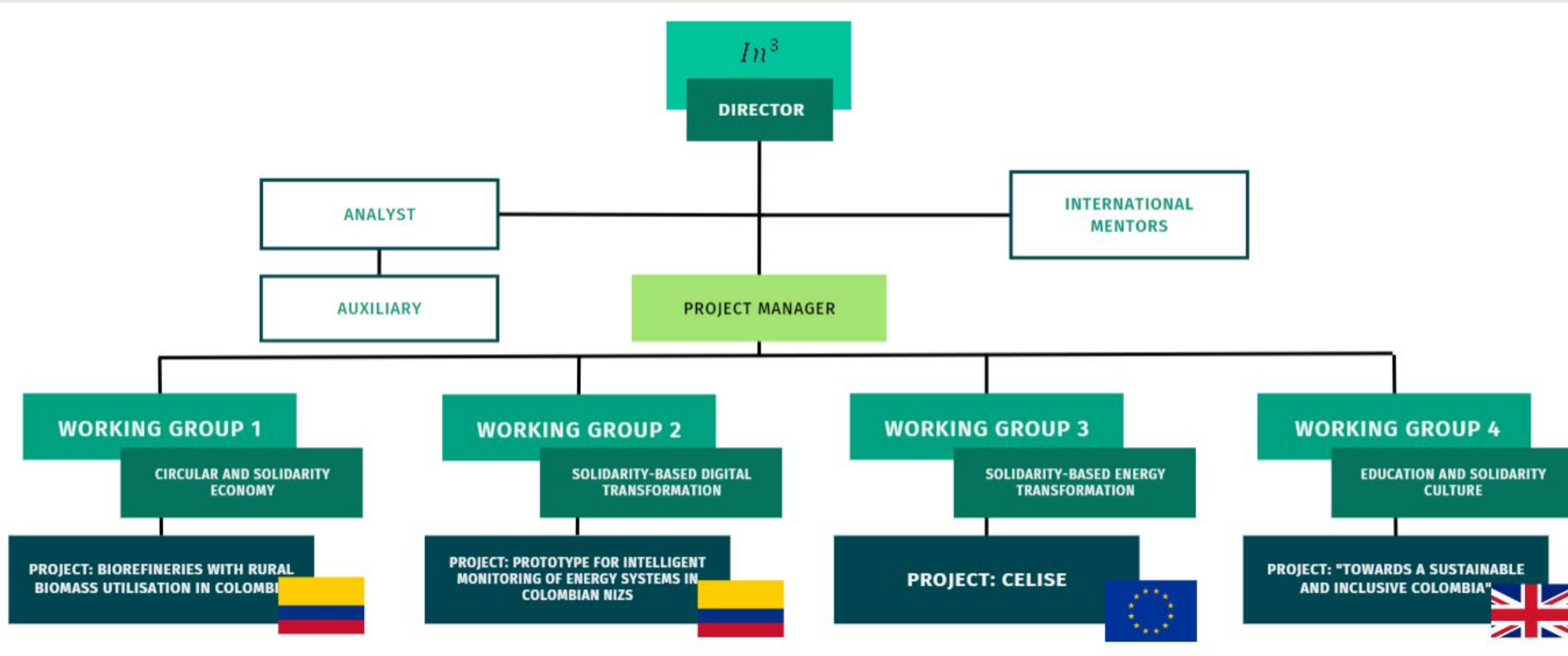
**2.** Titania/Chitosan-Lignin nanocomposite as an efficient photocatalyst for the selective oxidation of benzyl alcohol under UV and visible light.





# Engineering Research Institute Universidad Cooperativa de Colombia

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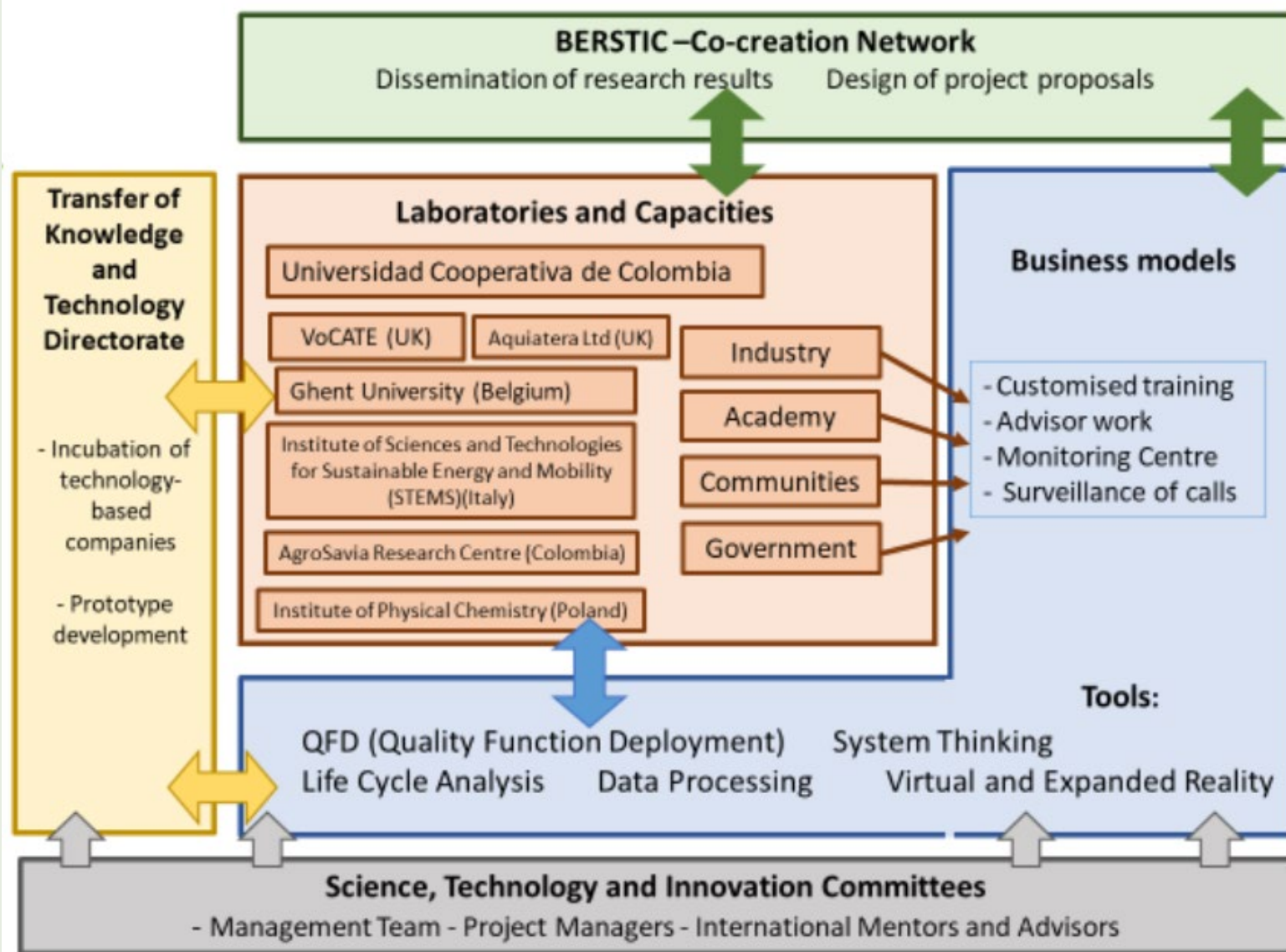
# Projects in execution through the Network: BERSTIC



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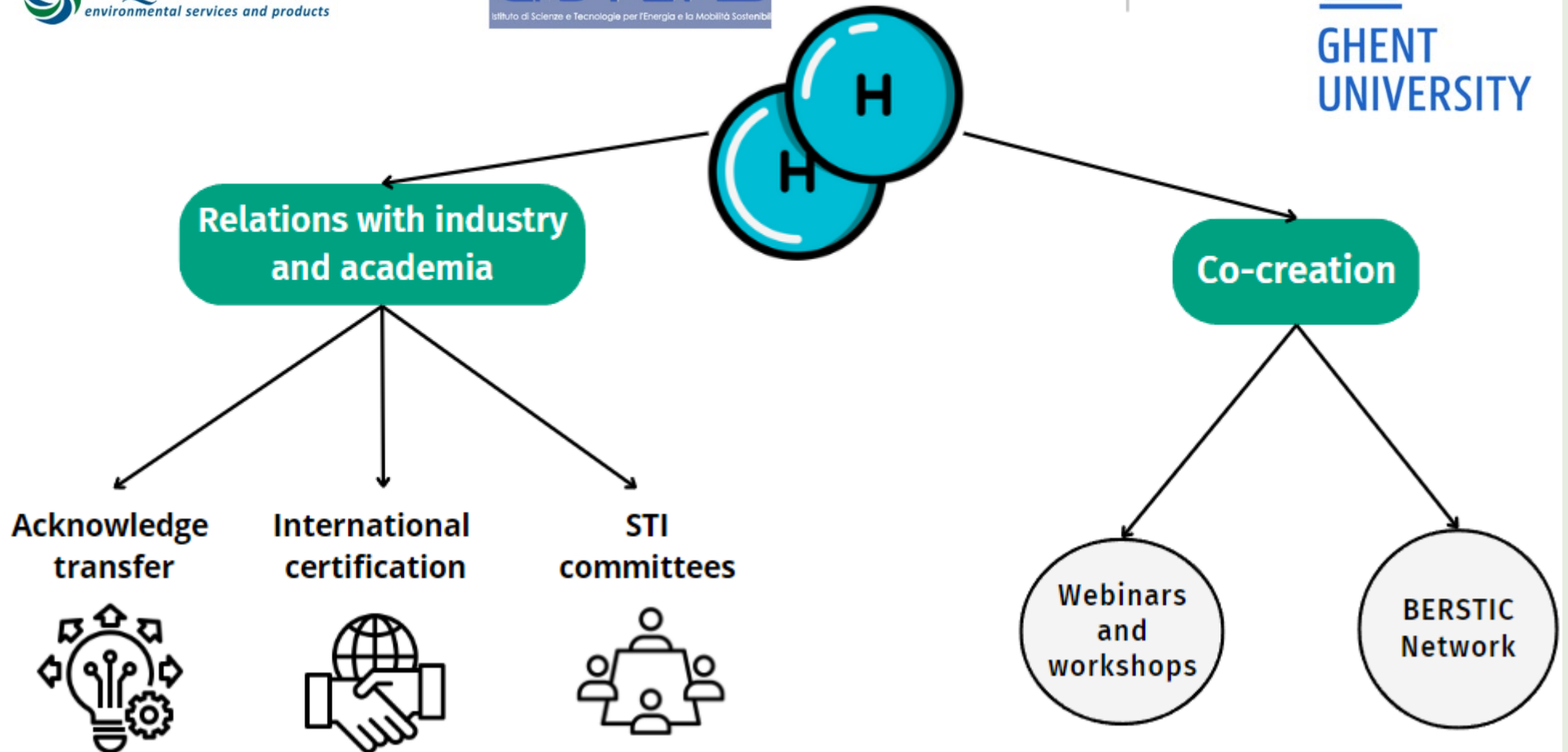
<https://berstic.edu.co/>



# Network of International Collaborators



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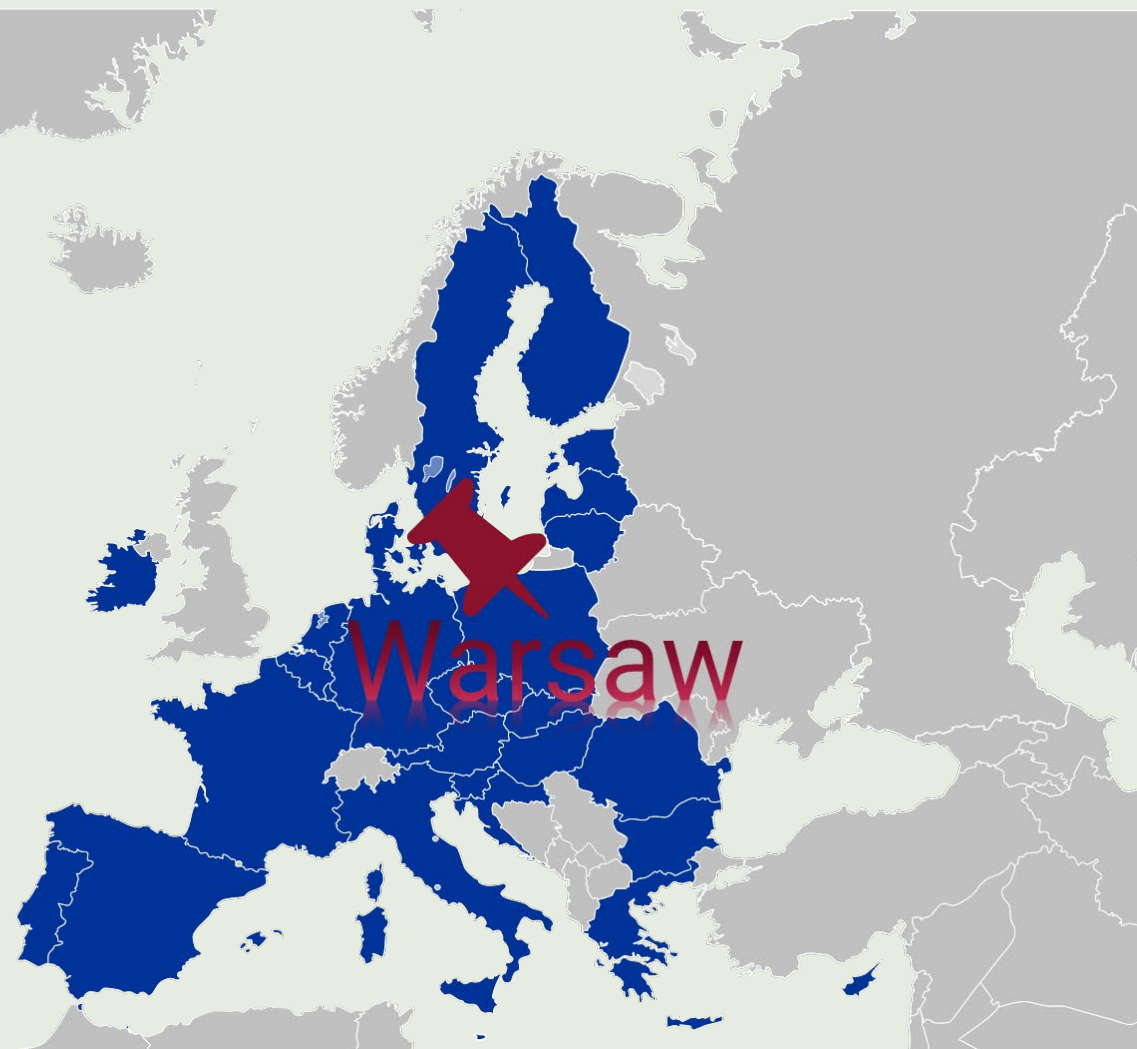






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Where to find us?







**IChF**

Institute of Physical Chemistry PAS

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# Our mission

## Research

- ~250 research papers / year
- 70 running projects funded externally

## Innovations

- ~15 patents / year
- Spin-offs

## Education

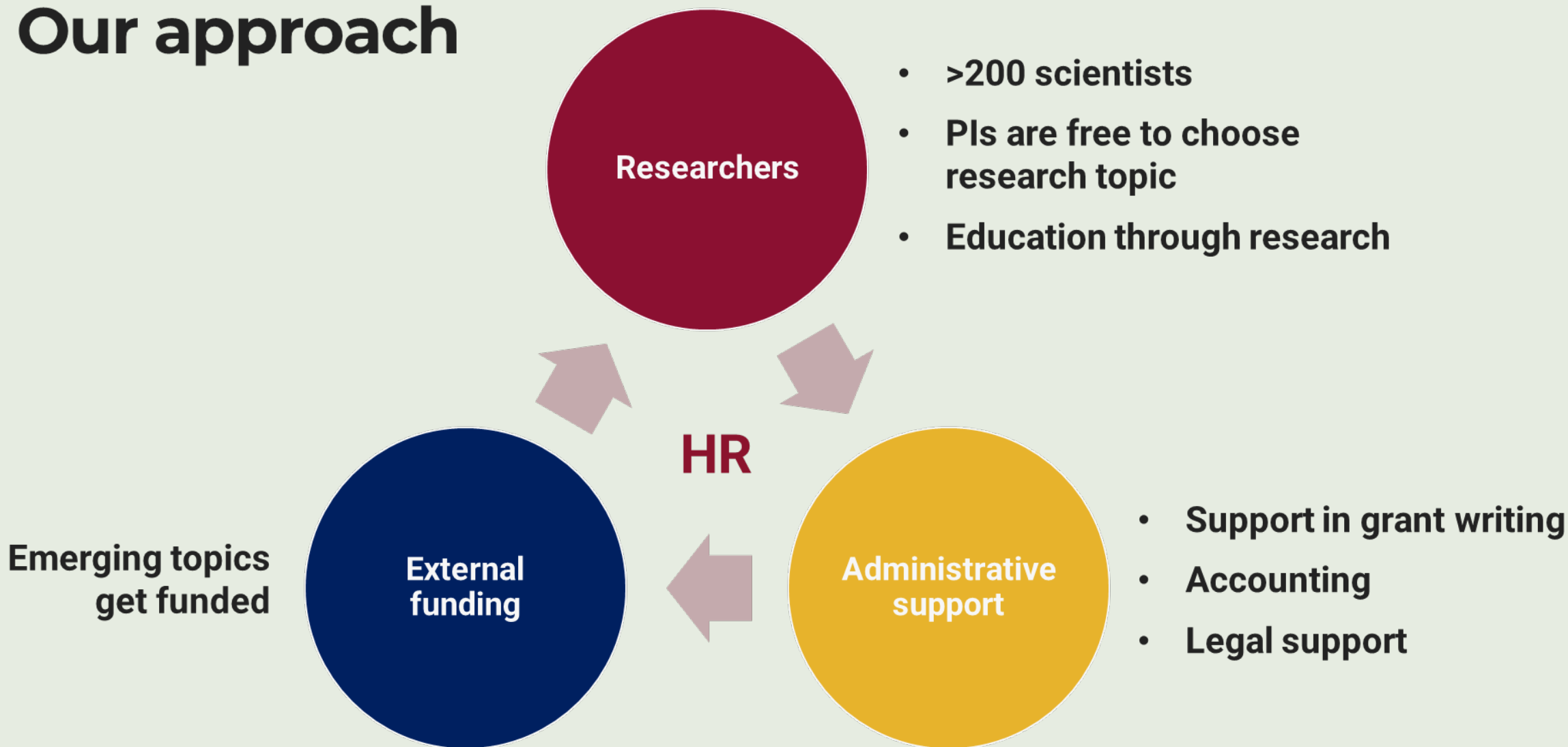
- Doctoral School
- Science promotion





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# Our approach







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# Our **spin-offs/outs**





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- ❑ Rational design of functionalized nanosized catalysts using unconventional methodologies (e.g., sonication, photo-assisted methodologies).

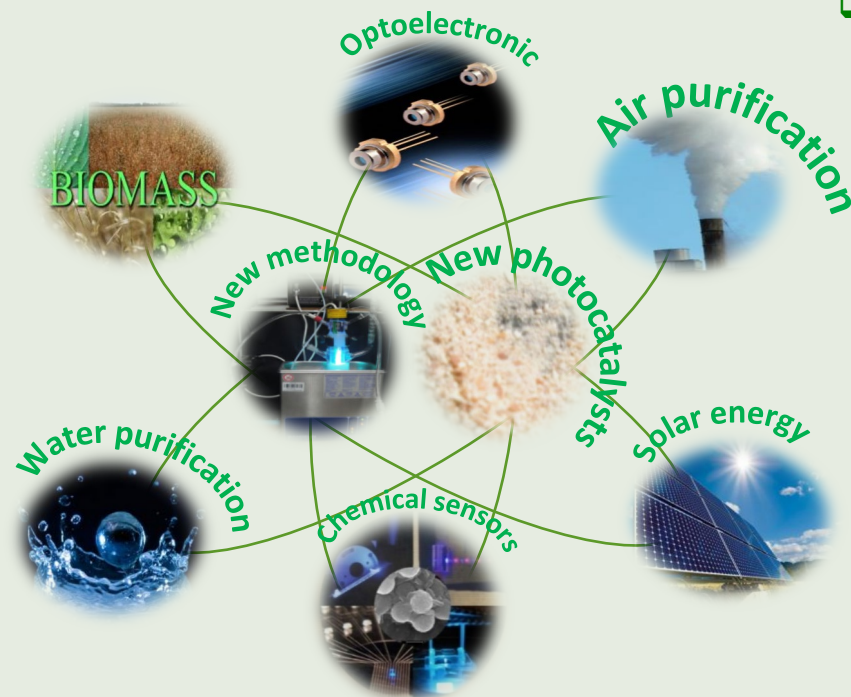
- ❑ Sonocatalytic and photocatalytic green pathways in organic synthesis.

- ❑ Catalytically harvesting of solar energy in the shape of chemical energy.

- ❑ Development of novel proof of concepts of catalytic processes for the treatment and purification of water and air.

- ❑ Catalyst preparation and optimization, surface chemistry, nanoengineering, catalyst poisoning/degradation, catalytic process design, chemical/reactor engineering and reaction kinetics.

- ❑ Thermo-catalytically, Sono-catalytically and Photo-catalytically valorization of any kind of organic wastes (CO<sub>2</sub> included) in aqueous and gaseous systems.







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## Research group nr 28:

*“Catalysis for sustainable energy production and environmental protection, CatSEE”*

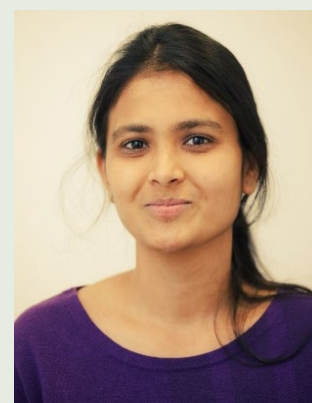
Visit our web site: <http://photo-catalysis.org/>



Hanggara



Juan Carlos



Swaraj



Nilesh



Dariusz



Behdokht



Abdul



Maya





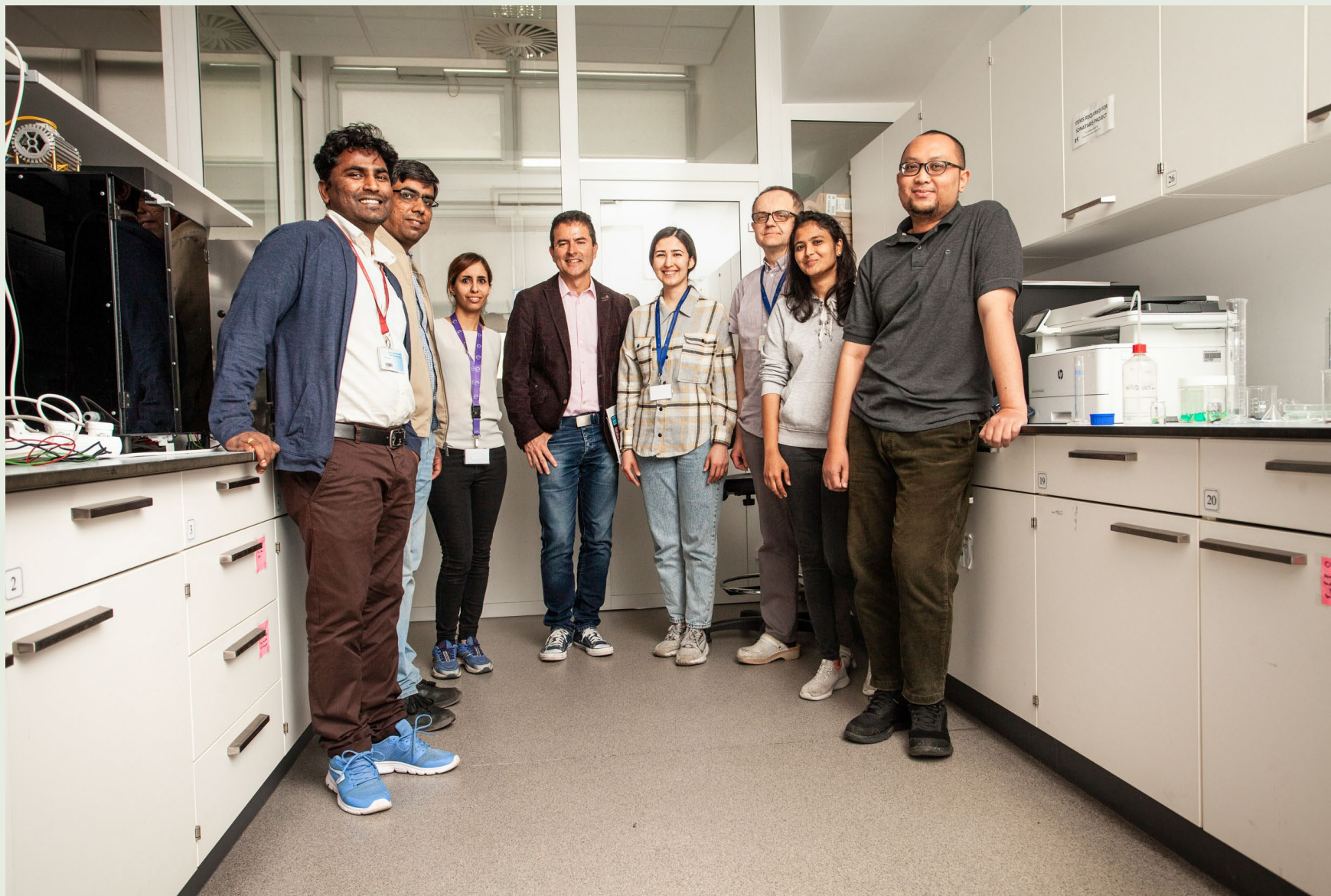
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**Research group 28:**

*“Catalysis for sustainable energy production and environmental protection, CatSEE”*



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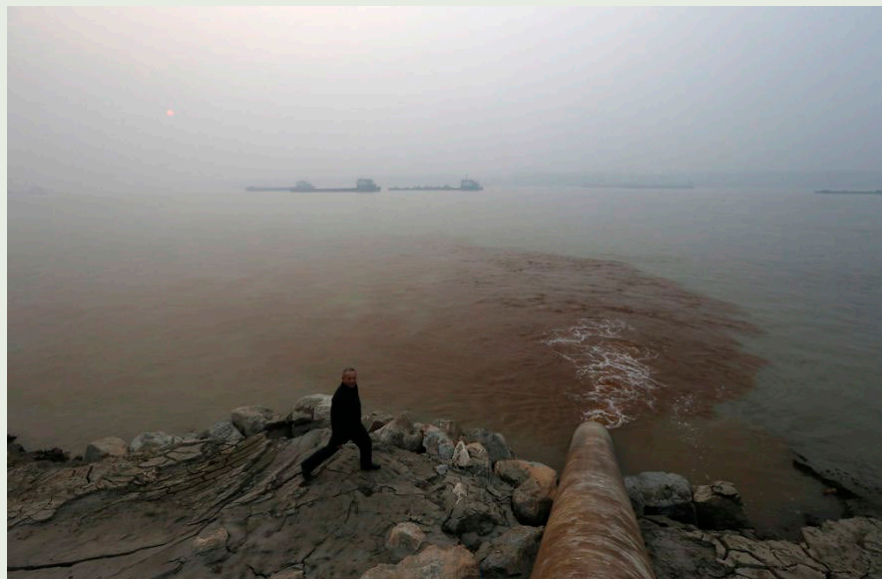




# What do these images tell you?



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# ITS ALWAYS THE SAME THING.....

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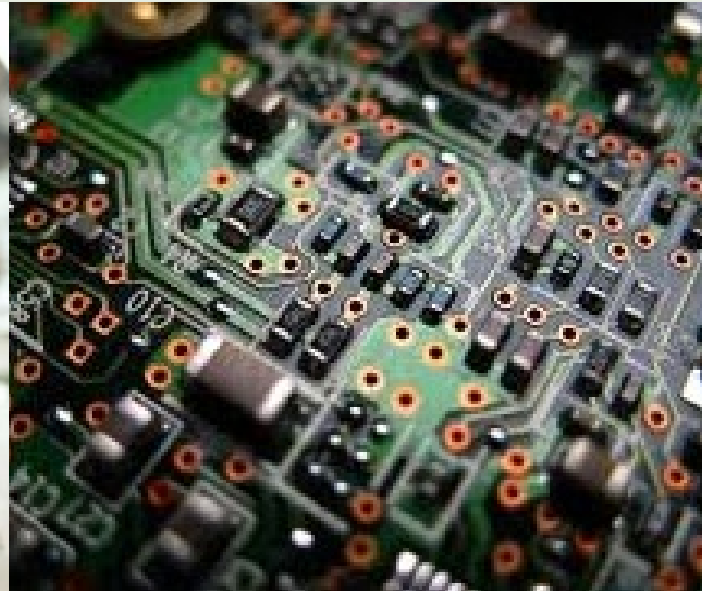
Produce



Use



Dispose



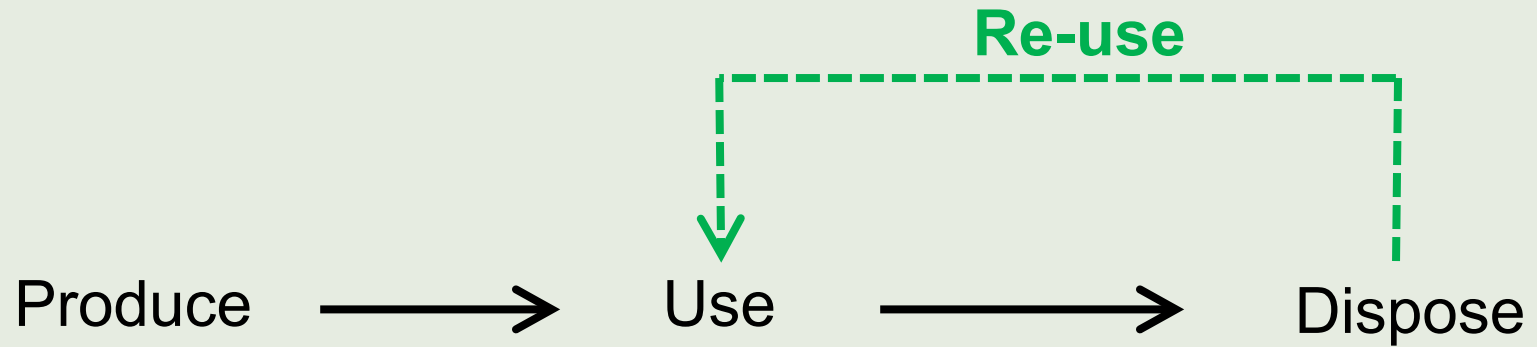
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# We have to change our mindset!!!



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- Reduce  
To use things with care to reduce the amount of waste generated
- Reuse  
To repeat use of items or parts of items
- Recycle  
To use waste as resources

Recycle

**ERGONOMIC SCIENCE!**



# Green Technologies & Sustainability

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## SUSTAINABLE DEVELOPMENT GOALS

<p><b>1</b> NO POVERTY</p>	<p><b>2</b> ZERO HUNGER</p>	<p><b>3</b> GOOD HEALTH AND WELL-BEING</p>	<p><b>4</b> QUALITY EDUCATION</p>	<p><b>5</b> GENDER EQUALITY</p>	<p><b>6</b> CLEAN WATER AND SANITATION</p>
<p><b>7</b> AFFORDABLE AND CLEAN ENERGY</p>	<p><b>8</b> DECENT WORK AND ECONOMIC GROWTH</p>	<p><b>9</b> INDUSTRY, INNOVATION AND INFRASTRUCTURE</p>	<p><b>10</b> REDUCED INEQUALITIES</p>	<p><b>11</b> SUSTAINABLE CITIES AND COMMUNITIES</p>	<p><b>12</b> RESPONSIBLE CONSUMPTION AND PRODUCTION</p>
<p><b>13</b> CLIMATE ACTION</p>	<p><b>14</b> LIFE BELOW WATER</p>	<p><b>15</b> LIFE ON LAND</p>	<p><b>16</b> PEACE, JUSTICE AND STRONG INSTITUTIONS</p>	<p><b>17</b> PARTNERSHIPS FOR THE GOALS</p>	

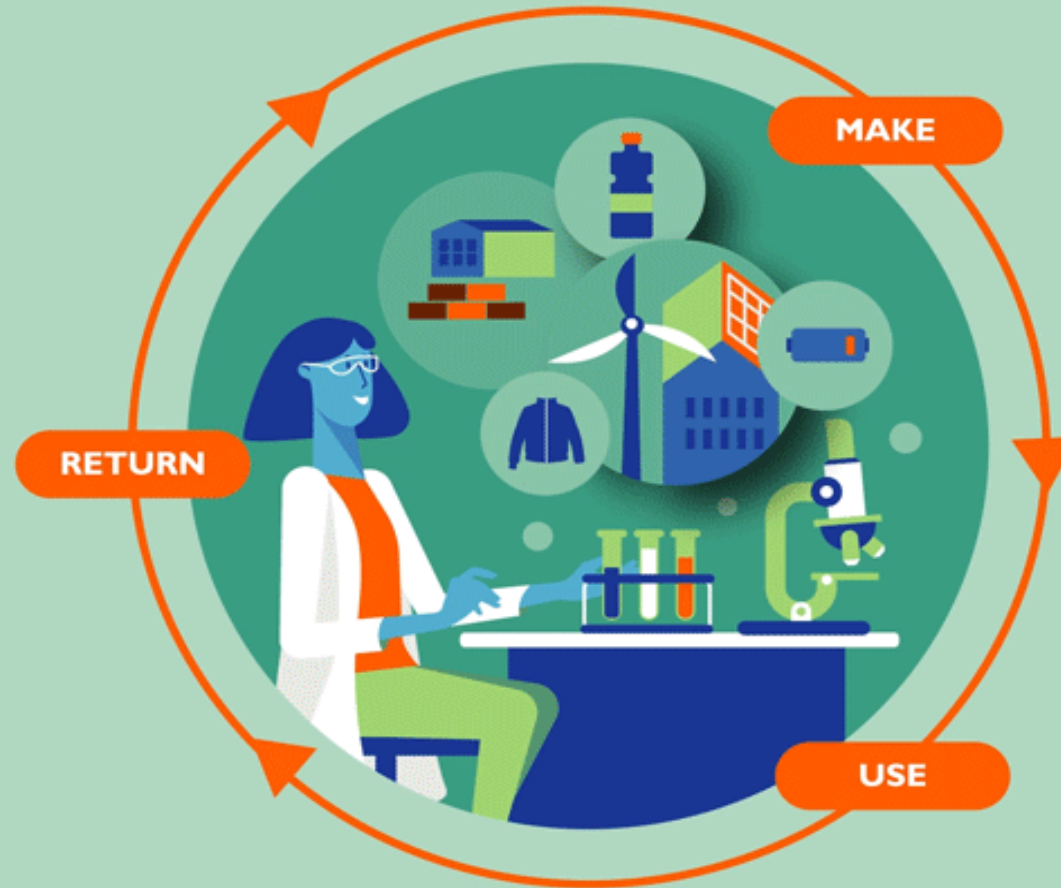




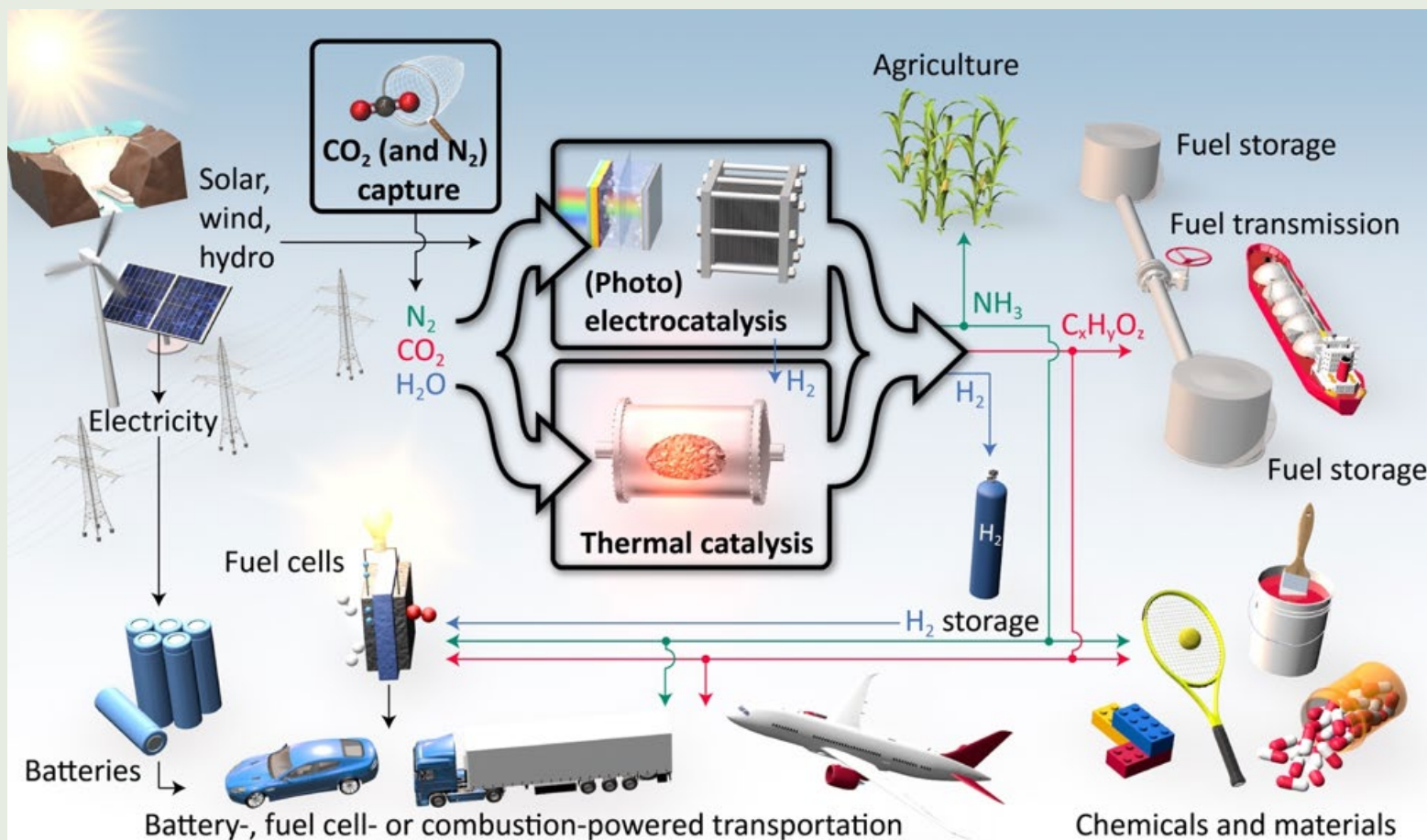
# CIRCULAR ECONOMY

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**Value of materials, products, and resources is sustained in the economy as much as possible with minimal generation of waste**



# The resource transition: Towards a Sustainable, Circular Economy



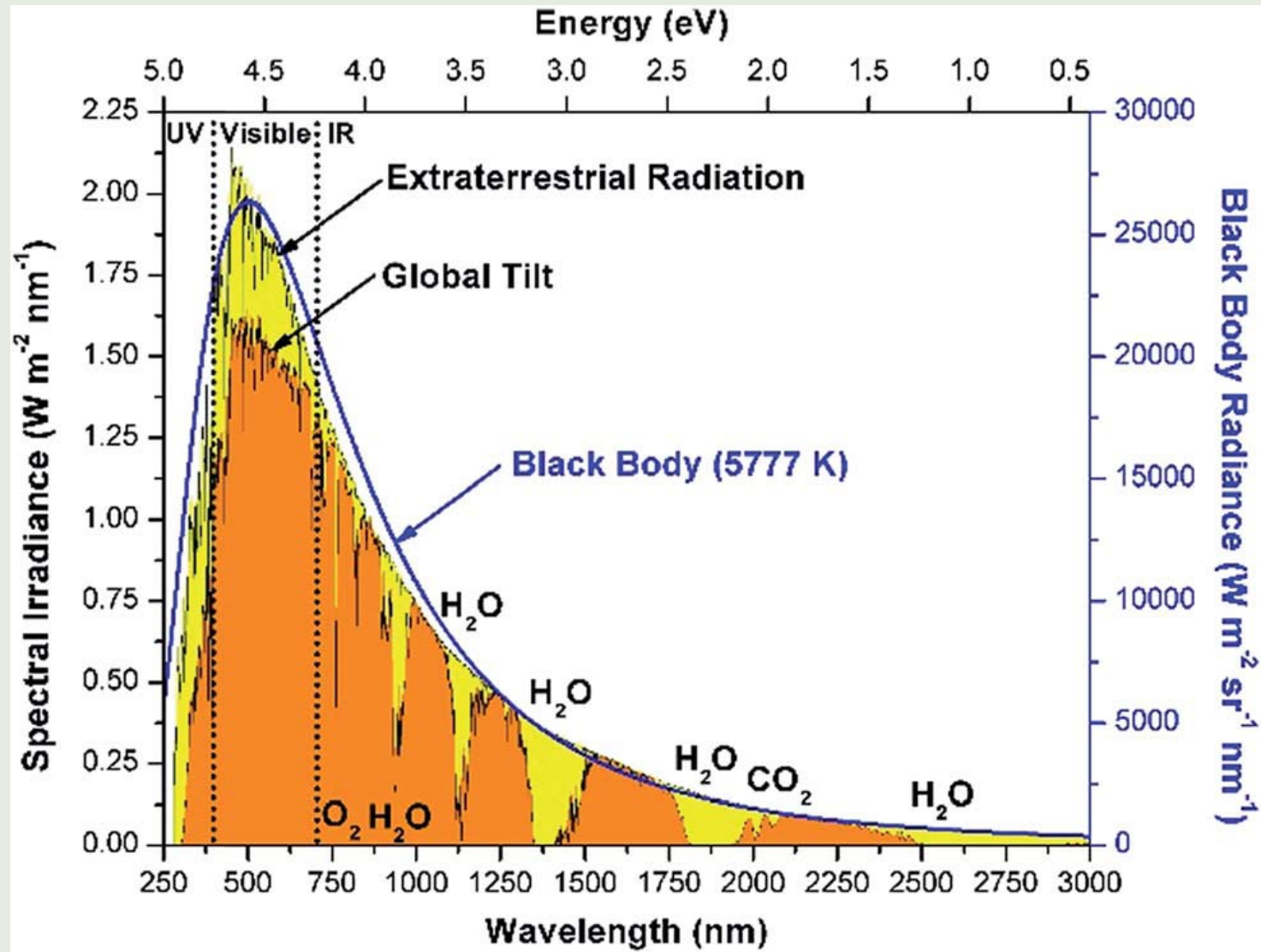
**Illustration of a sustainable energy system:** Key processes are: electrochemical water splitting and thermal and electrochemical CO<sub>2</sub> and N<sub>2</sub> reduction. (Graphics courtesy of Jakob Kibsgaard, DTU)





# Solar Spectral Irradiance: Air Mass 1.5

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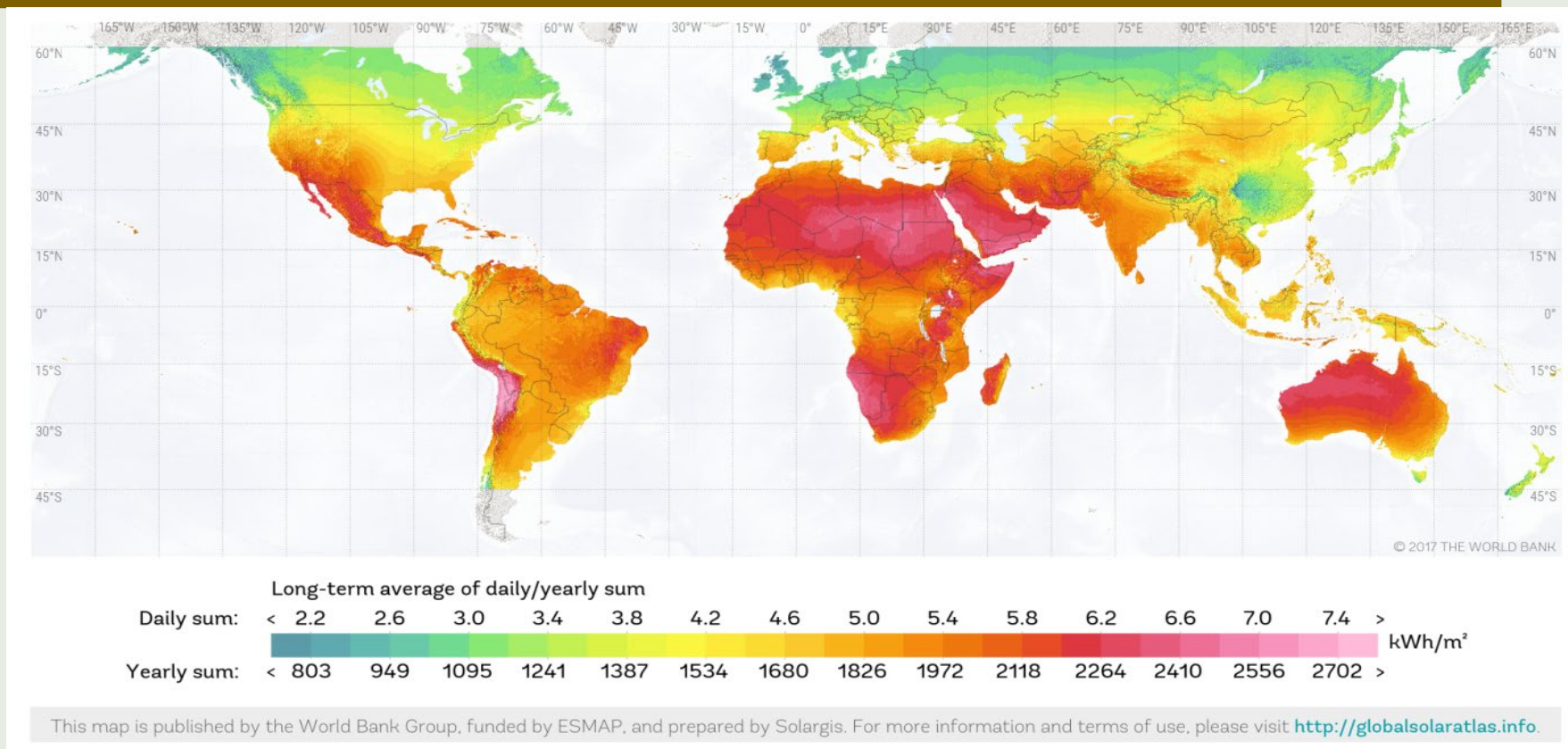
<http://rredc.nrel.gov/solar/spectra/am1.5/>, accessed June 2014.

01/08/2023



# Global Horizontal Irradiation

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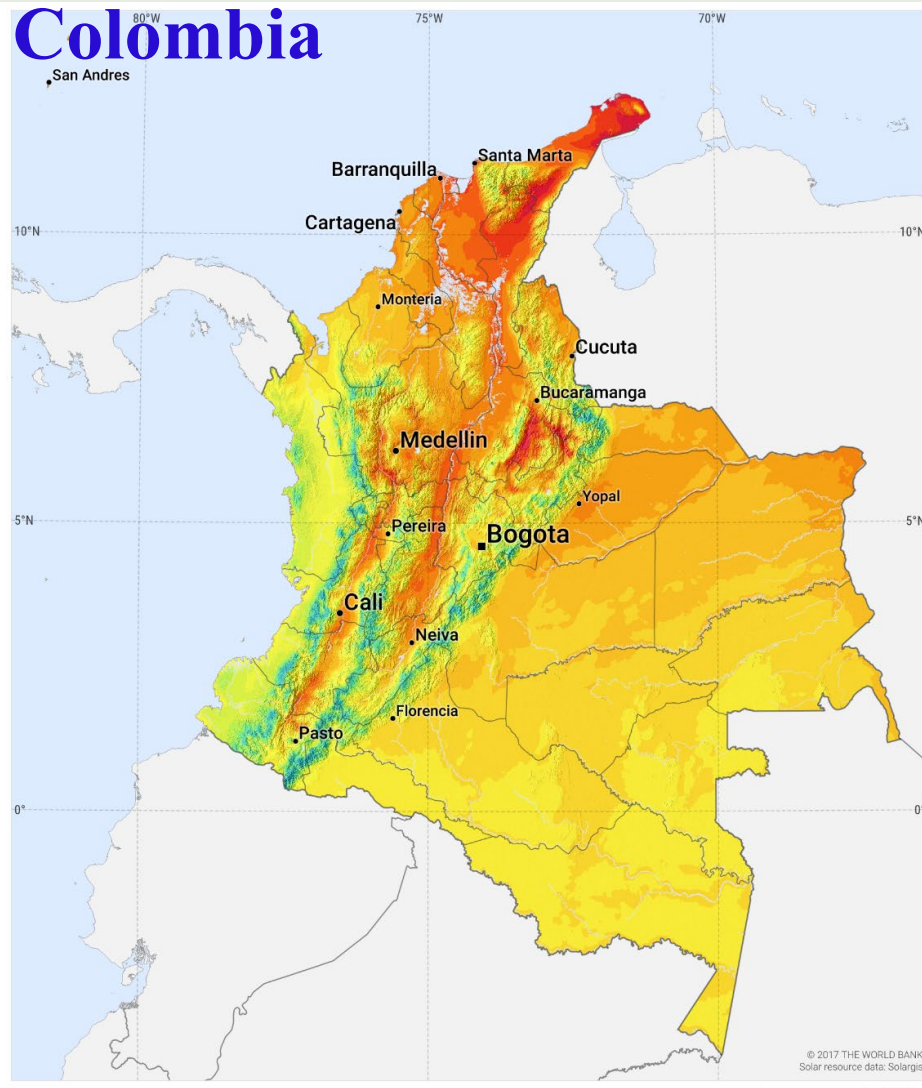
The quantity of radiation incident on our planet's surface depends on a good number of factors: **(1) location, (2) time of the day, (3) declination and inclination of the Earth's surface, (4) weather, among others.** The intermittent nature of solar radiation is one of the major and important challenges in designing solar fuels technologies. Thus, storing solar energy is very important for continuous processing at the time of these fluctuations



# Colombia and Poland Horizontal Irradiation



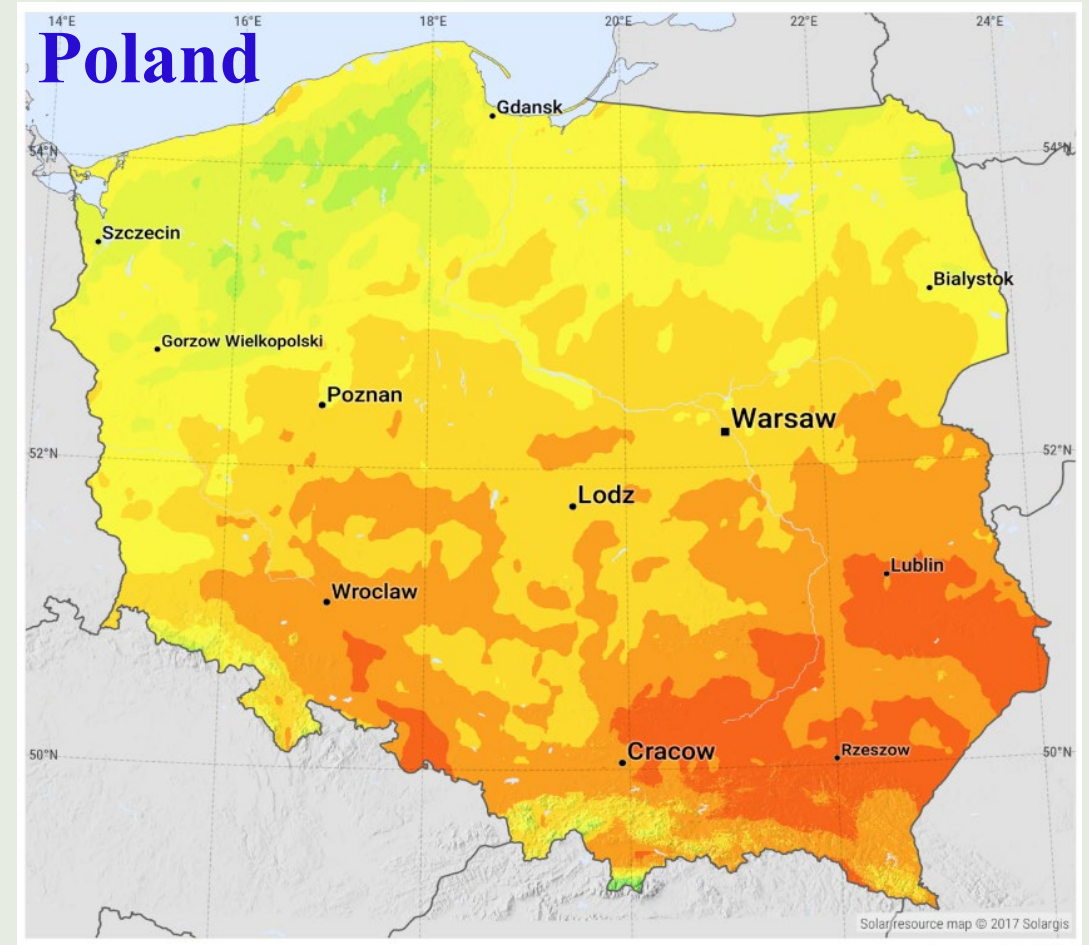
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Long term average of GHI, period 1999-2015

Daily totals:	3.2	3.6	4.0	4.4	4.8	5.2	5.6	6.0	kWh/m <sup>2</sup>
Yearly totals:	1168	1314	1461	1607	1753	1899	2045	2191	

This map is published by the World Bank Group, funded by ESMAP, and prepared by Solargis. For more information and terms of use, please visit: <http://globalsolaratlas.info>



Average annual sum of GHI, period 1994-2016

1000	1050	1100	1150 kWh/m <sup>2</sup>
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# Knowing chemical composition is the key to success!!!

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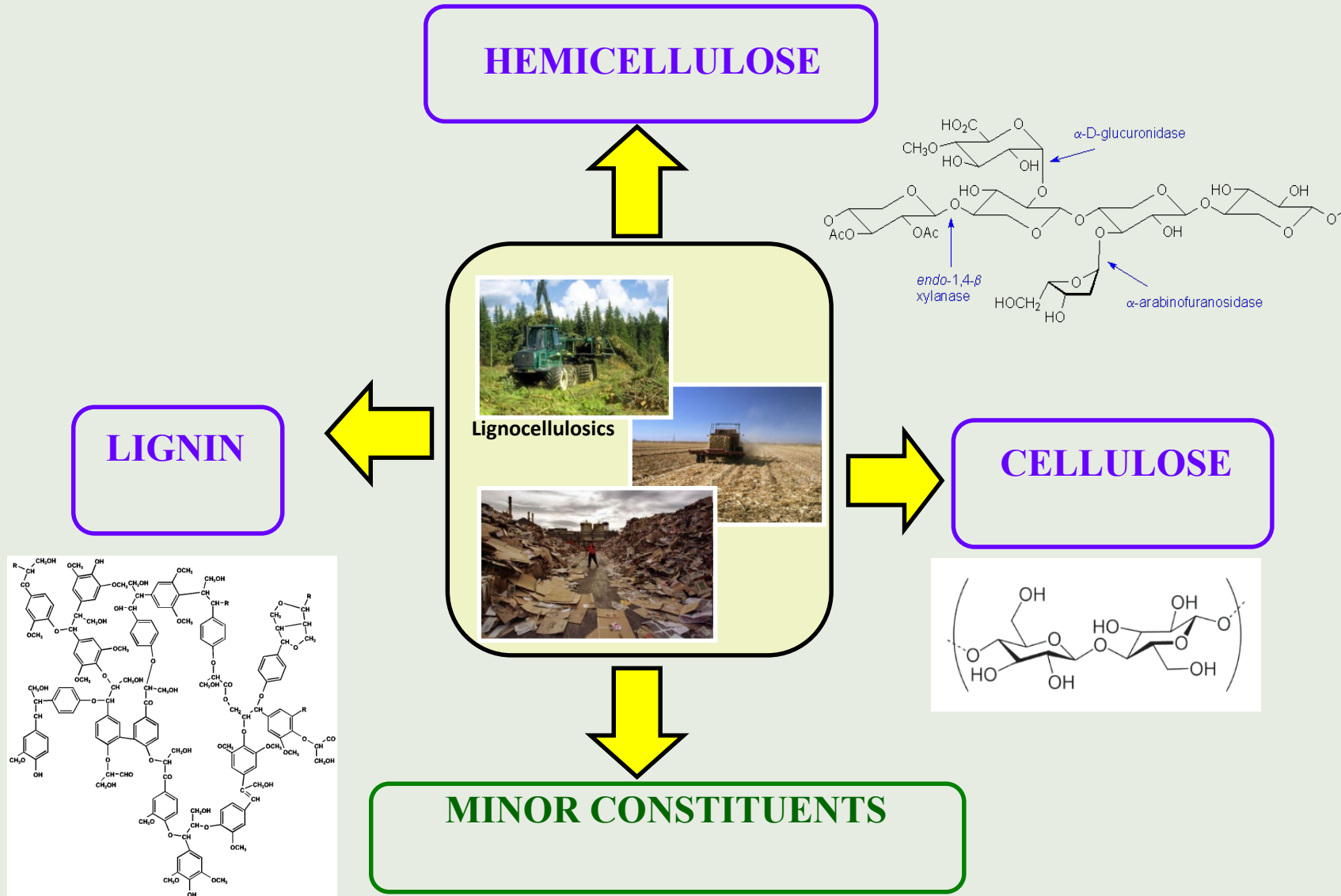


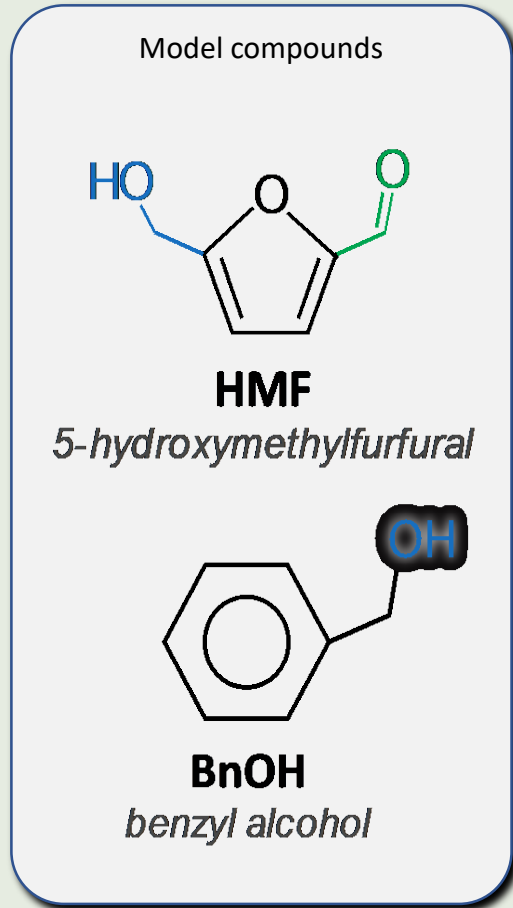
Image: Courtesy of Prof. Rafael Luque





# Lignocellulose valorization

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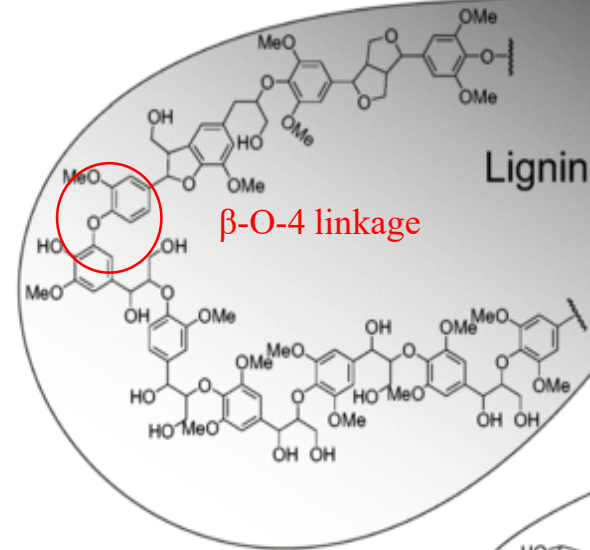
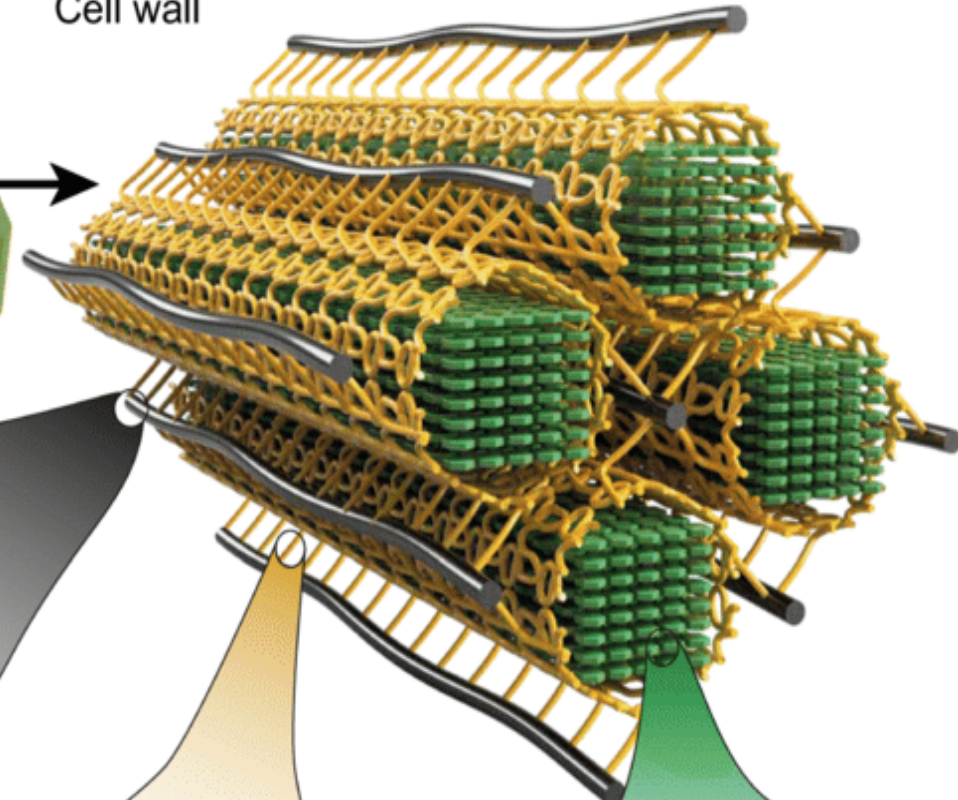
Lignocellulosic substrates



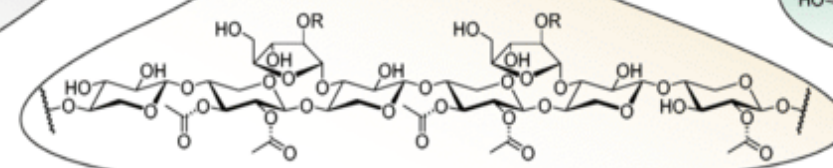
Plant cells



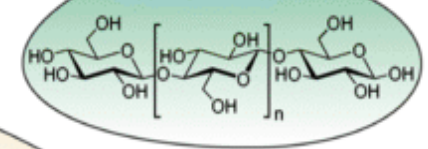
Cell wall



Hemicellulose



Cellulose

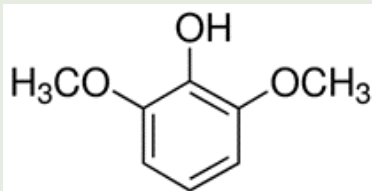




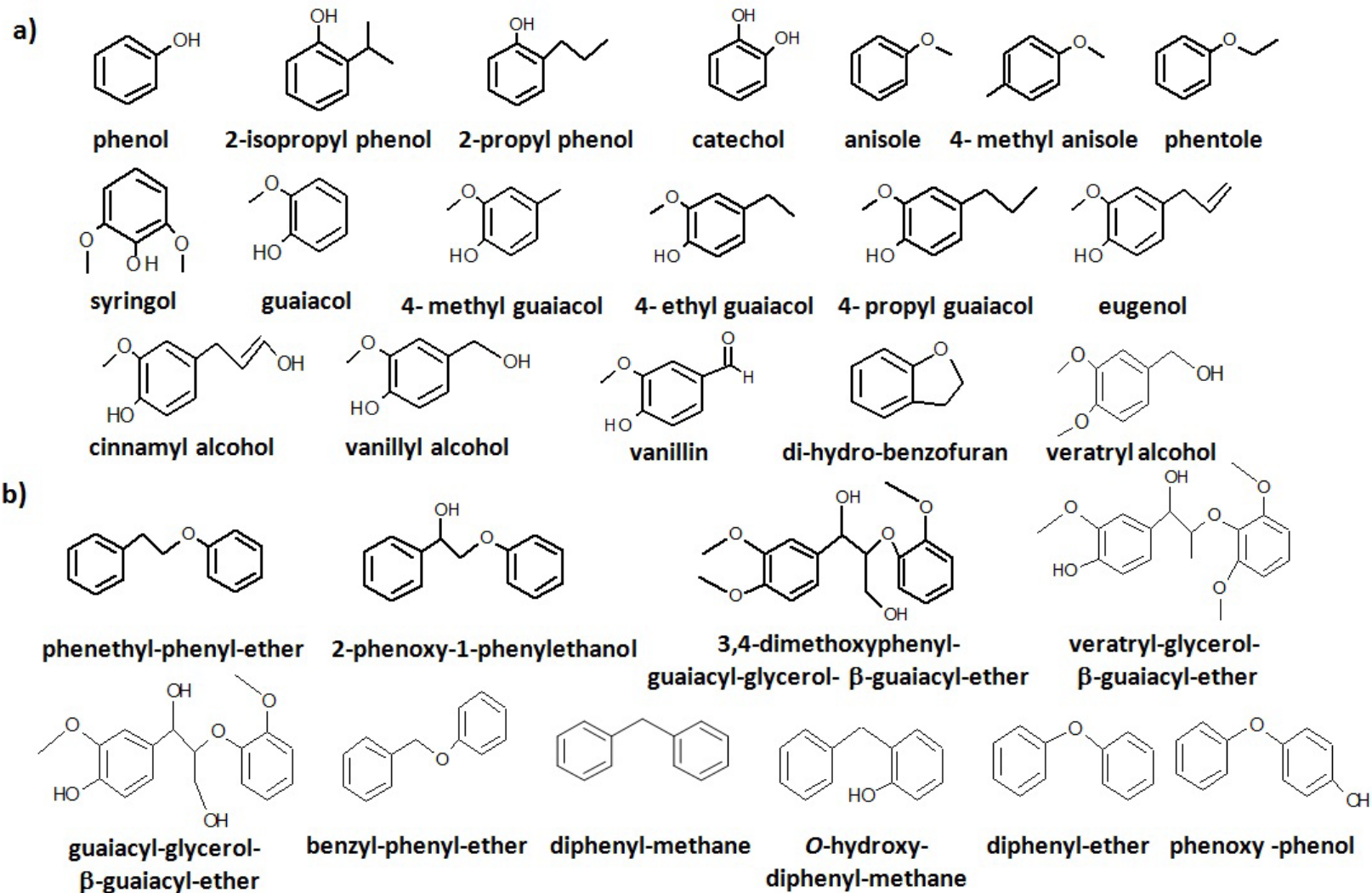
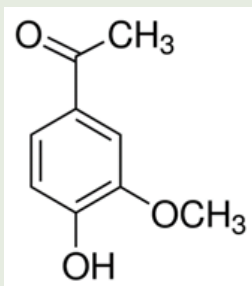
# Lignin model compounds of (a) monomers (b) dimers

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2,6-dimethoxyphenol

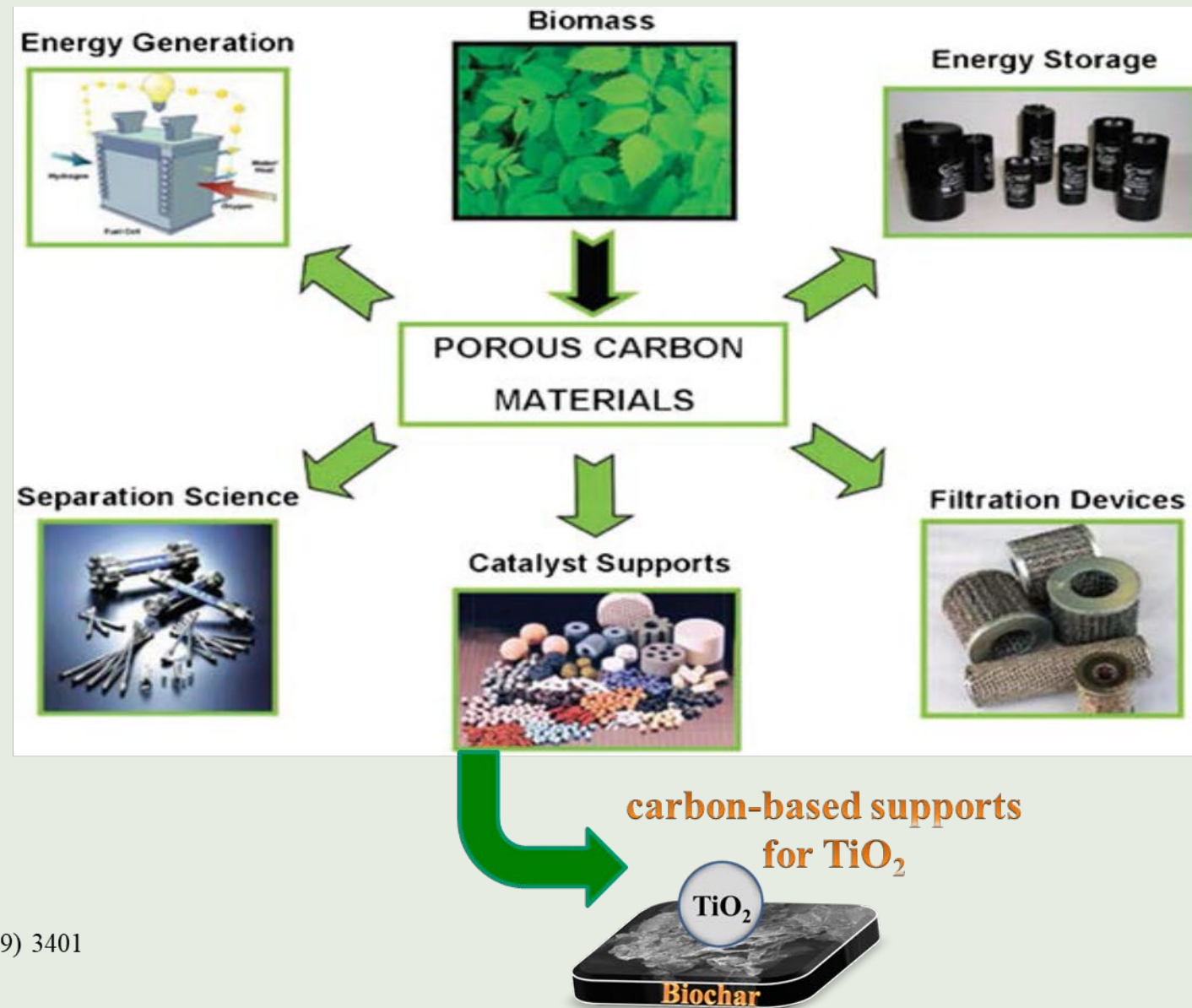


Acetovanillone





# Lignocellulose-based carbonaceous materials: countless possibilities for application



Adapted from *Chem. Soc. Rev.*, 38 (2009) 3401

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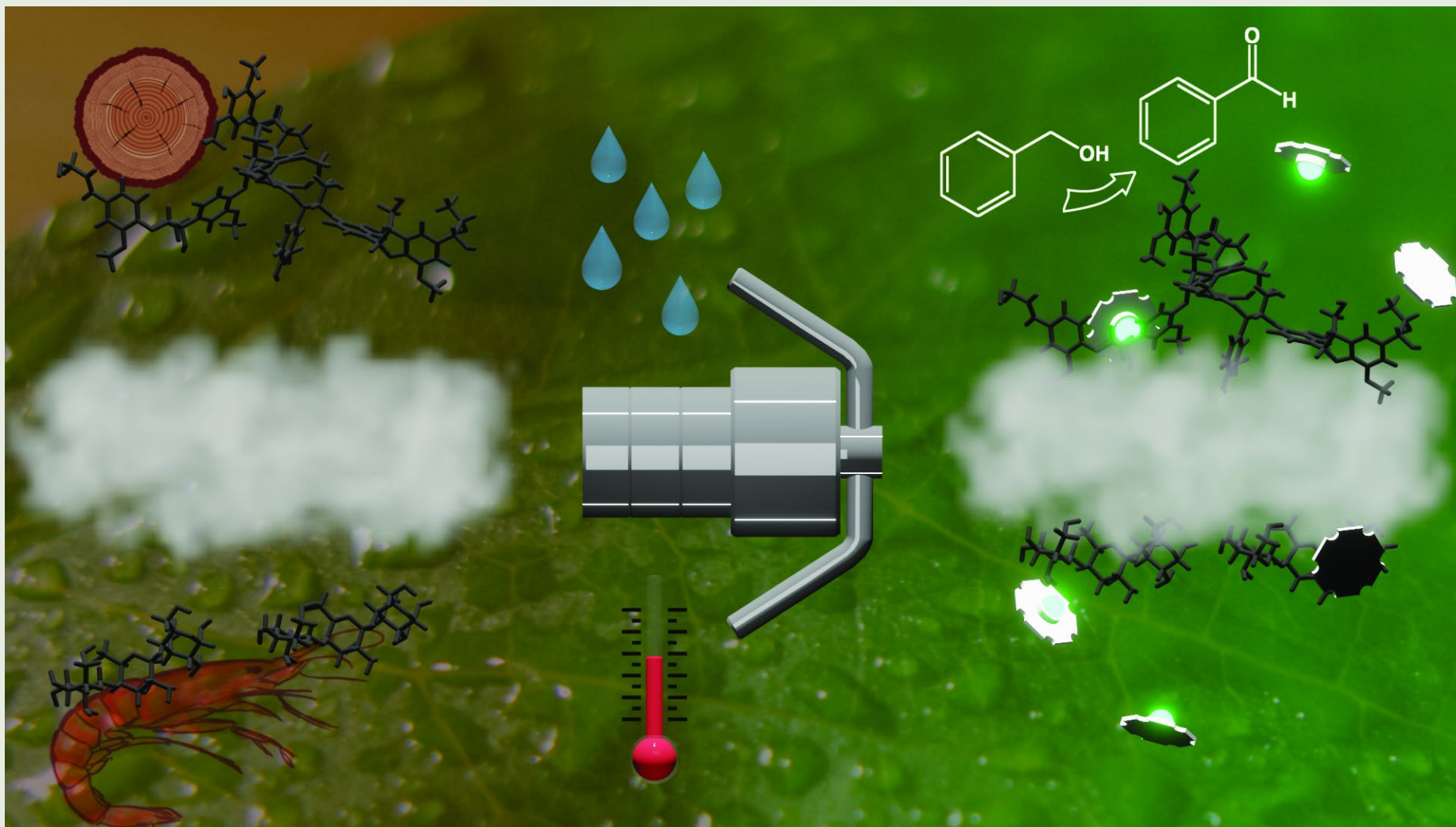
Let's go...research!!!



# Titania/Chitosan-Lignin nanocomposite as an efficient photocatalyst for the selective oxidation of benzyl alcohol under UV and visible light



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*Colmenares, et al. RSC Adv., 11 (2021) 34996-35010*

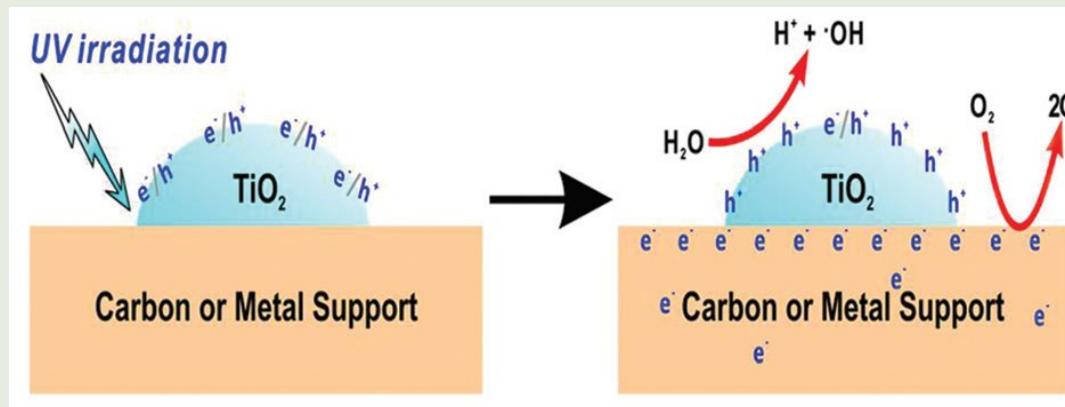
01/08/2023



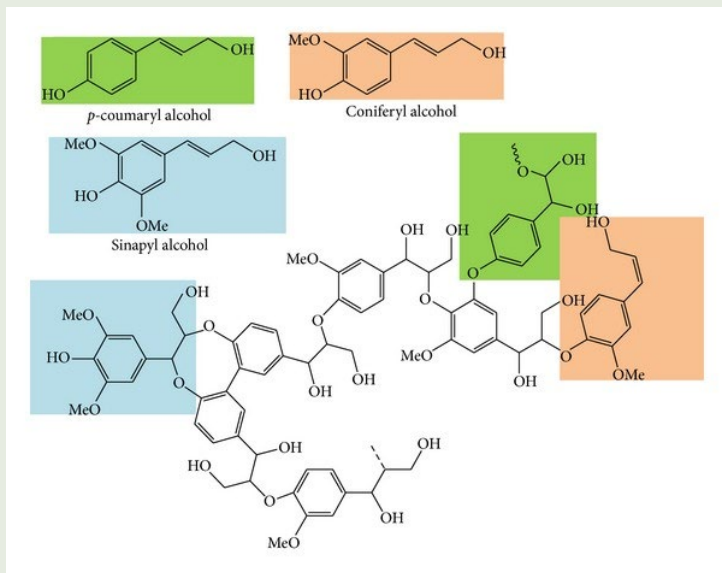
# Titania-Carbon composite

## Synergetic photocatalytic effect of TiO<sub>2</sub>/carbon support

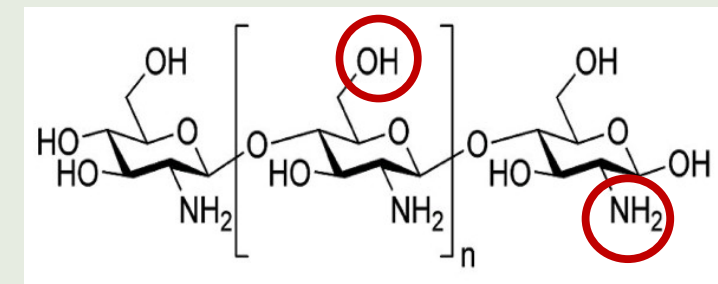
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J. Shi, Chem. Rev., 2013, 113, 2139–2181.



### Lignin



### Chitosan



# Nanocomposites of titania and carbon materials:

## Objectives

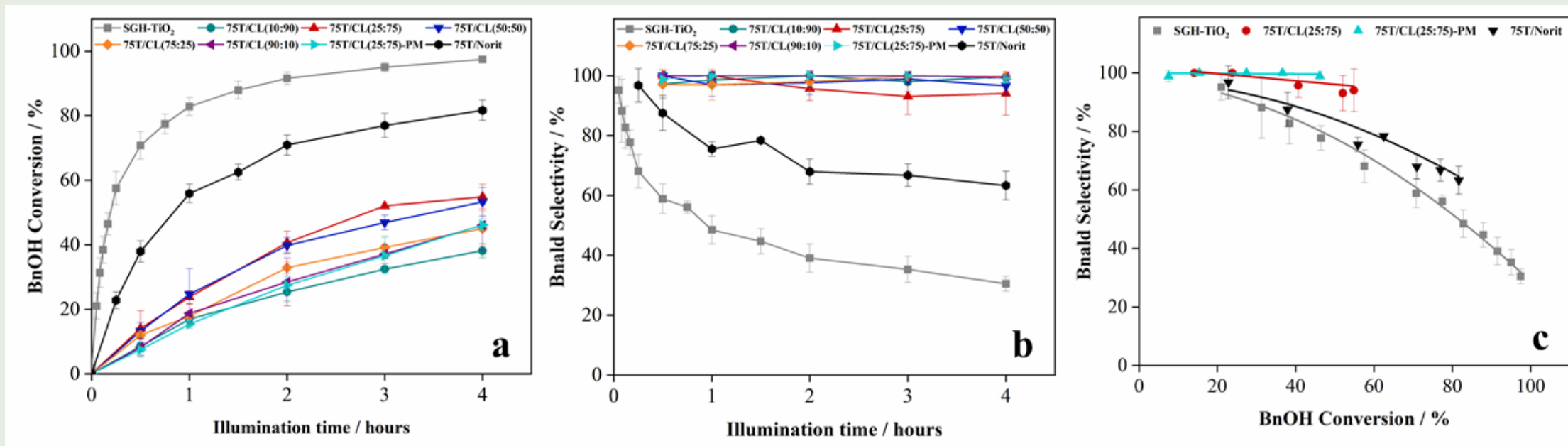
- ✓ *Design a hydrothermal synthesis route for* the preparation of chitosan-lignin (CL) composite.
- ✓ *Develop a sol-gel and hydrothermal method* to prepare titania/chitosan-lignin (T/CL) nanocomposite for the selective oxidation of benzyl alcohol (BnOH) to benzaldehyde (Bnald) under visible light (515 nm). *Free of additives/oxidizing agents!!!*
- ✓ *Compare the activity of T/CL nanocomposite* with Norit (activated carbon)-based nanocomposite (T/Norit).
- ✓ *Understand the synergy of titania and chitosan-lignin composite in T/CL nanocomposite by characterizing them through wide range of techniques*, e.g. X-ray diffraction (XRD), N<sub>2</sub> physisorption, FTIR spectroscopy, DRS UV-Visible spectroscopy, and X-ray photoelectron spectroscopy (XPS).

01/08/2023



# The PhotoCatalytic Results: under UV light (375 nm)

(a) BnOH conversion profile of SGH-TiO<sub>2</sub>, 75T/CL nanocomposites and 75T/Norit nanocomposite as a function of time under UV light (375 nm) (b) Bnald selectivity profile of SGH-TiO<sub>2</sub>, 75T/CL nanocomposites and 75T/Norit nanocomposite as a function of time under UV light (375 nm) (c) BnOH conversion versus Bnald selectivity plot for SGH-TiO<sub>2</sub>, 75T/CL(25 : 75) nanocomposite and 75T/Norit nanocomposite under UV light (375 nm).





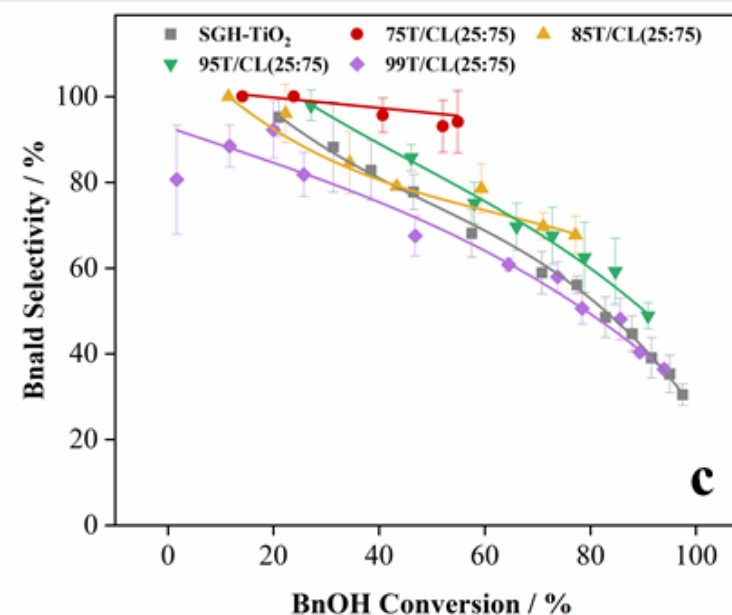
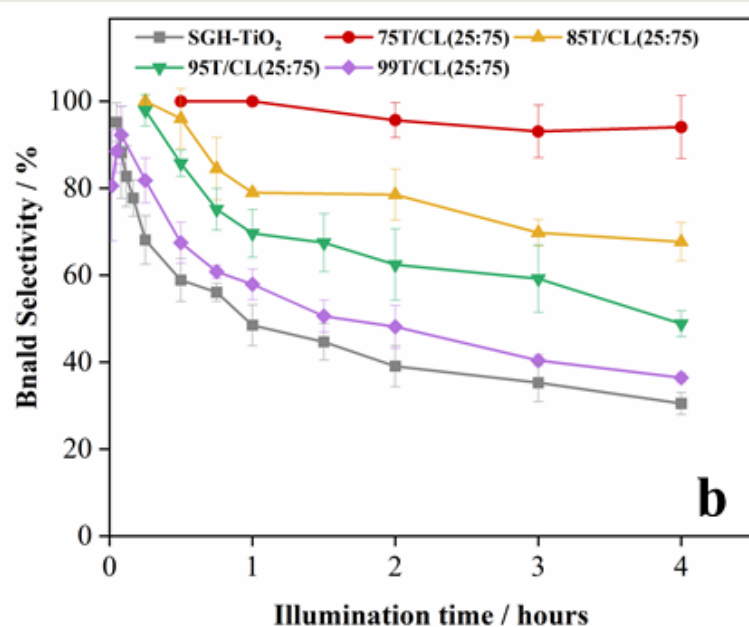
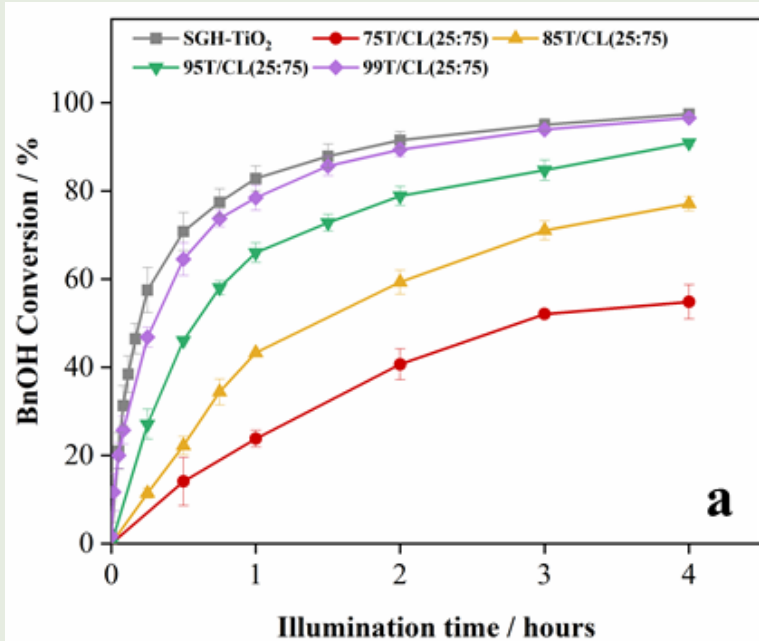


# The PhotoCatalytic Results: under UV light (375 nm)

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(a) Effect of titania content in nanocomposites on the BnOH conversion profile as a function of time under UV light (375 nm) (b) effect of titania content in nanocomposites on the Bnald selectivity profile as a function of time under UV light (375 nm) (c) effect of titania content in nanocomposites on BnOH conversion versus Bnald selectivity plot under UV light (375 nm).



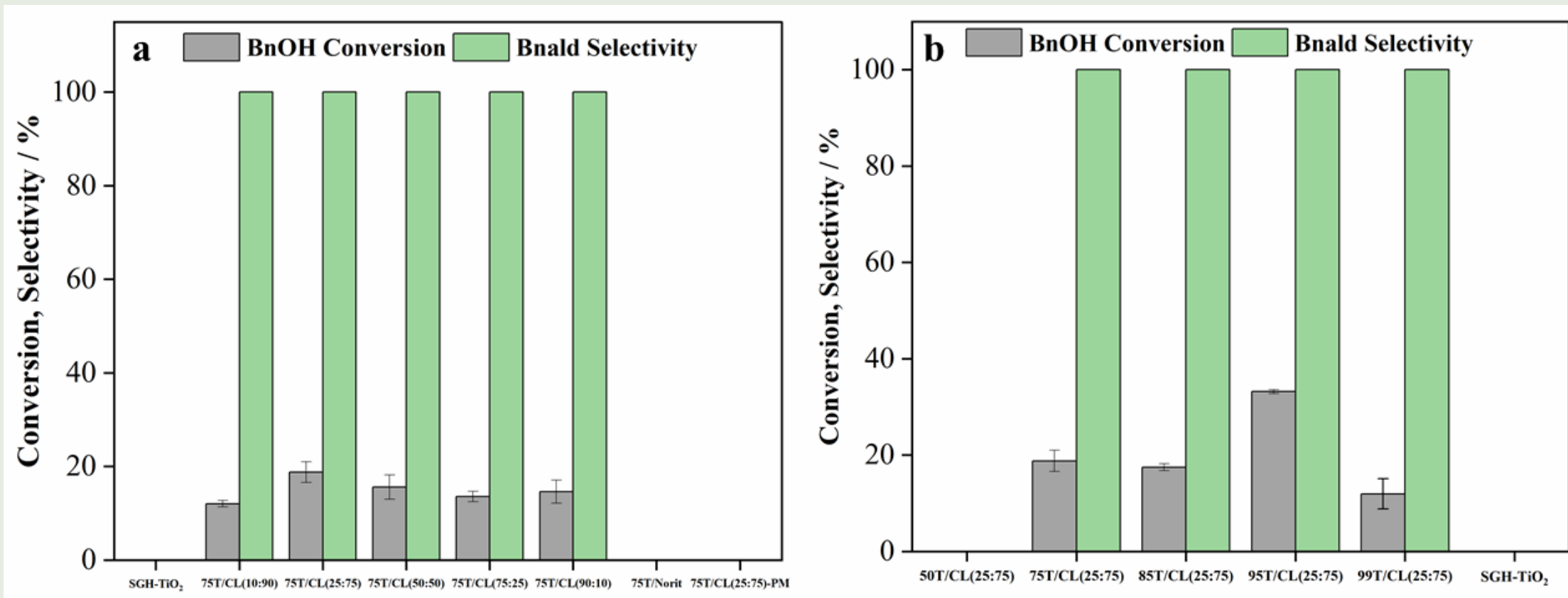


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# The PhotoCatalytic Results: under visible light (515 nm)

(a) Photocatalytic performance of SGH-TiO<sub>2</sub>, 75T/CL nanocomposites, and 75T/Norit nanocomposite for the selective oxidation of BnOH under visible light (515 nm) (b) effect of titania content on the photocatalytic performance of nanocomposites for the selective oxidation of BnOH under visible light (515 nm).



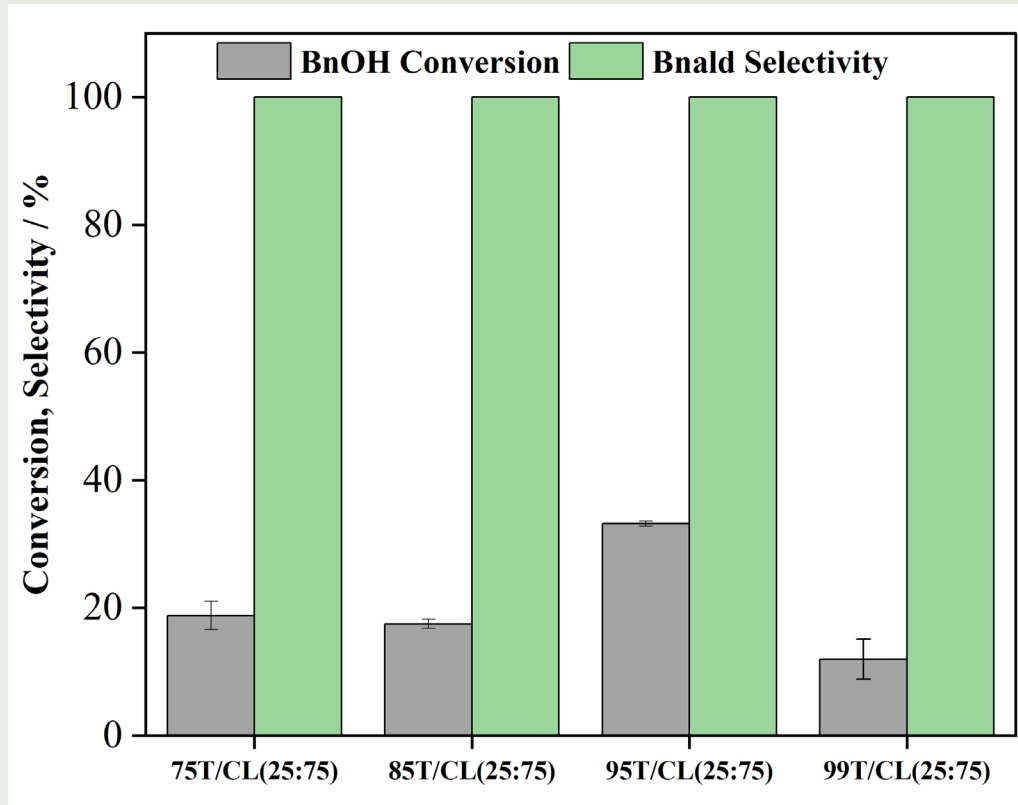




# The PhotoCatalytic Results: under visible light (515 nm)

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## Effect of titania content on the photocatalytic activity of nanocomposites for the selective oxidation of BnOH under visible light (515 nm)



Other photocatalysts	BnOH Conv. / %	Bnald Sel. / %
25T/CL(25:75)	x	x
50T/CL(25:75)	x	x

Colmenares et al., RSC Adv., 11 (2021) 34996-35010

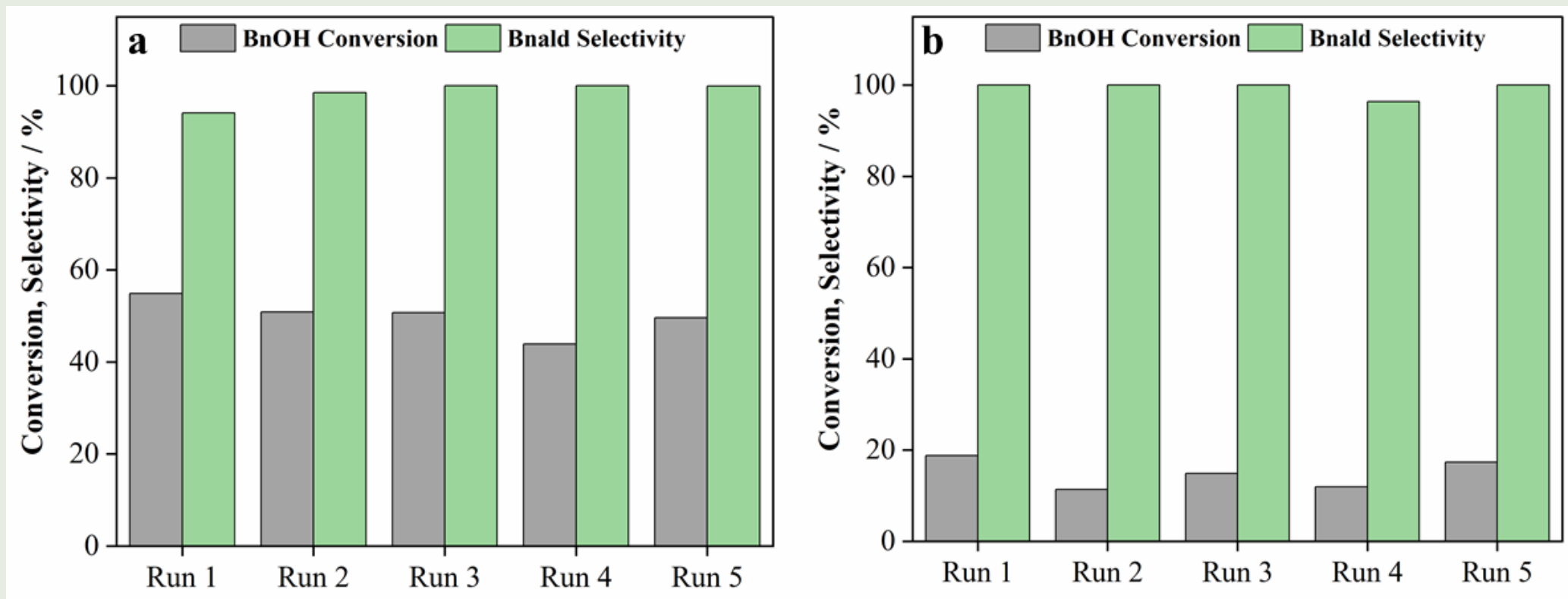
- Increasing the titania content in the nanocomposite (95T/CL(25:75)), increases the conversion of BnOH



# The PhotoCatalytic Results: 75T/CL(25:75) stability

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The recycling of 75T/CL(25:75) nanocomposite for the selective oxidation of BnOH under **(a)** UV light (375 nm) irradiation **(b)** visible light (515 nm) irradiation



Colmenares et al., RSC Adv., 11 (2021) 34996-35010

01/08/2023

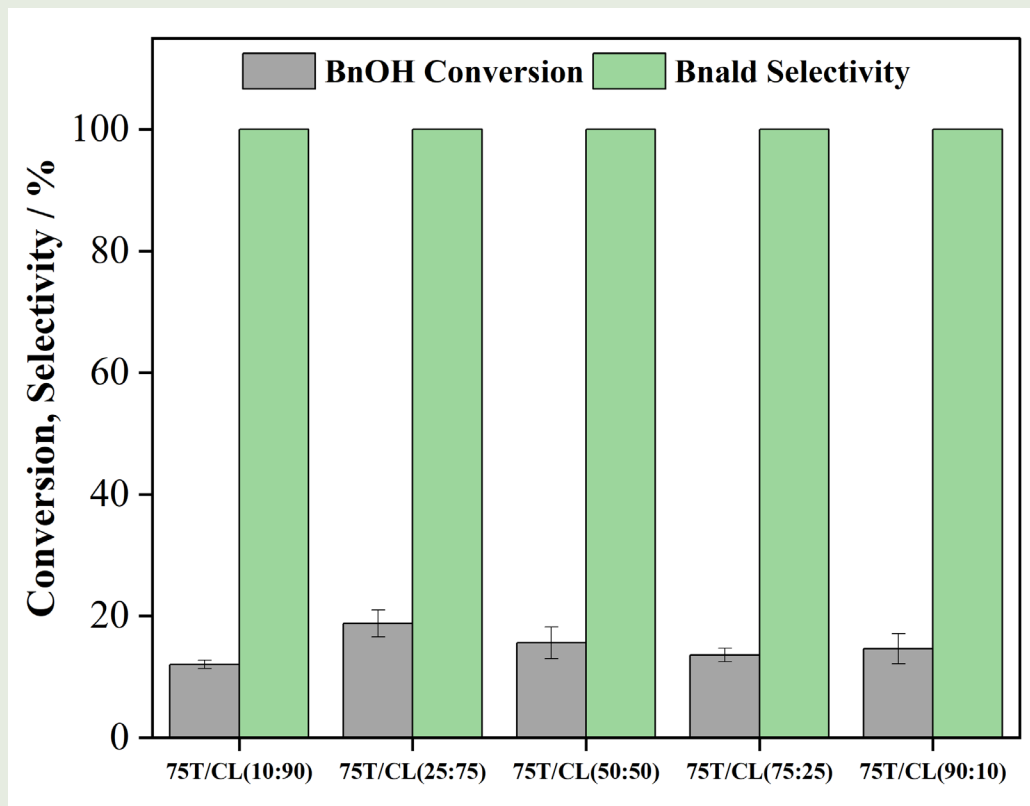




# The PhotoCatalytic Results: Short summary for 75T/CL(25:75)

Photocatalytic activity of 75T/CL nanocomposites, SGH-TiO<sub>2</sub> and 75T/Norit nanocomposite for the selective oxidation of BnOH to Bnald under visible light (515 nm)

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Other photocatalysts	BnOH Conv. / %	Bnald Sel. / %
SGH-TiO <sub>2</sub>	×	×
75T/Norit	×	×
75T/CL(25:75)-PM	×	×
75T/L	×	×
75T/C	14	100

Colmenares et al., RSC Adv., 11 (2021) 34996-35010

➤ The photocatalytic activity of 75T/CL nanocomposites under visible light may attribute to the nitrogen doping of titania by chitosan

# Textural and crystallographic features of nanocomposites



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Entries	Samples	SSA/ (m <sup>2</sup> g <sup>-1</sup> )	Ratio of crystalline phases	Crystal size	
			Anatase:Brookite / %	Anatase / nm	Brookite / nm
1	*Norit	558	NA	NA	NA
2	SGH-TiO <sub>2</sub>	177	74:26	5	6
3	75T/CL(10:90)	162	83:17	5	6
4	75T/CL(25:75)	174	79:21	5	6
5	75T/CL(50:50)	170	78:22	5	6
6	75T/CL(75:25)	169	81:19	5	6
7	75T/CL(90:10)	164	74:26	5	5
8	*75T/Norit	239	66:30	6	8

Colmenares et al., RSC Adv., 11 (2021) 34996-35010

*\*Sample contain traces of silica,*

*CL composites showed specific surface area (SSA) in the range of 10-16 m<sup>2</sup>g<sup>-1</sup>*

*75T/CL nanocomposites and SGH-TiO<sub>2</sub> showed comparable specific surface area and crystallographic features*

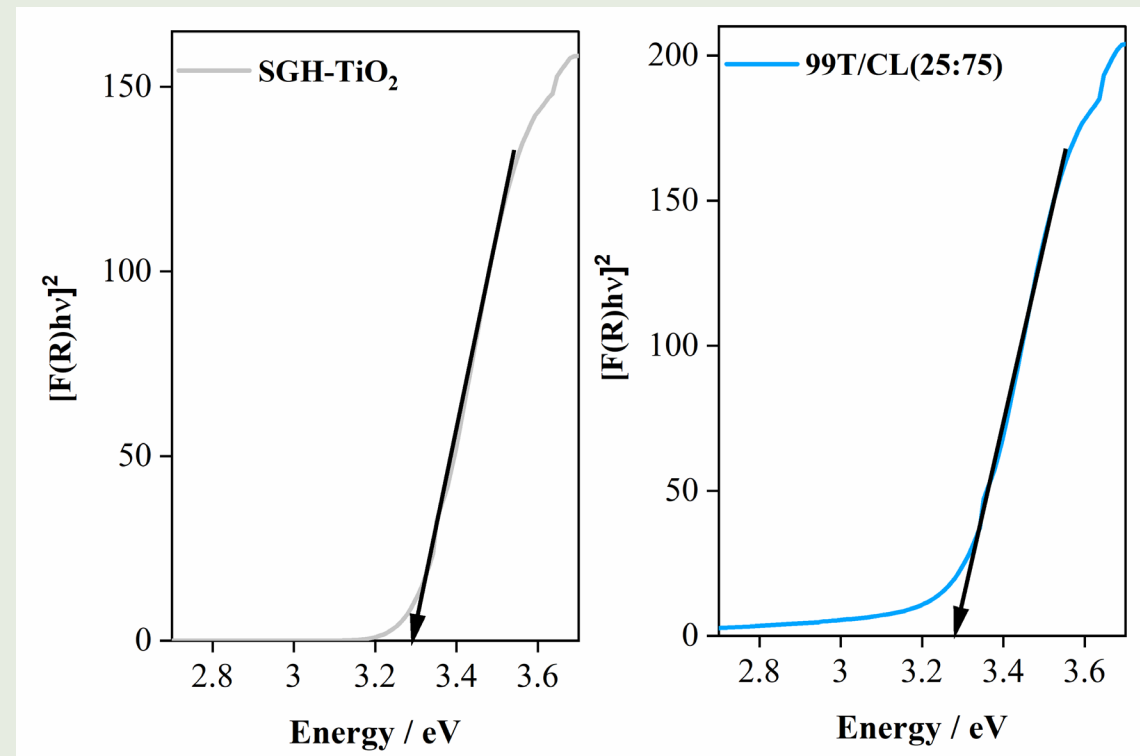
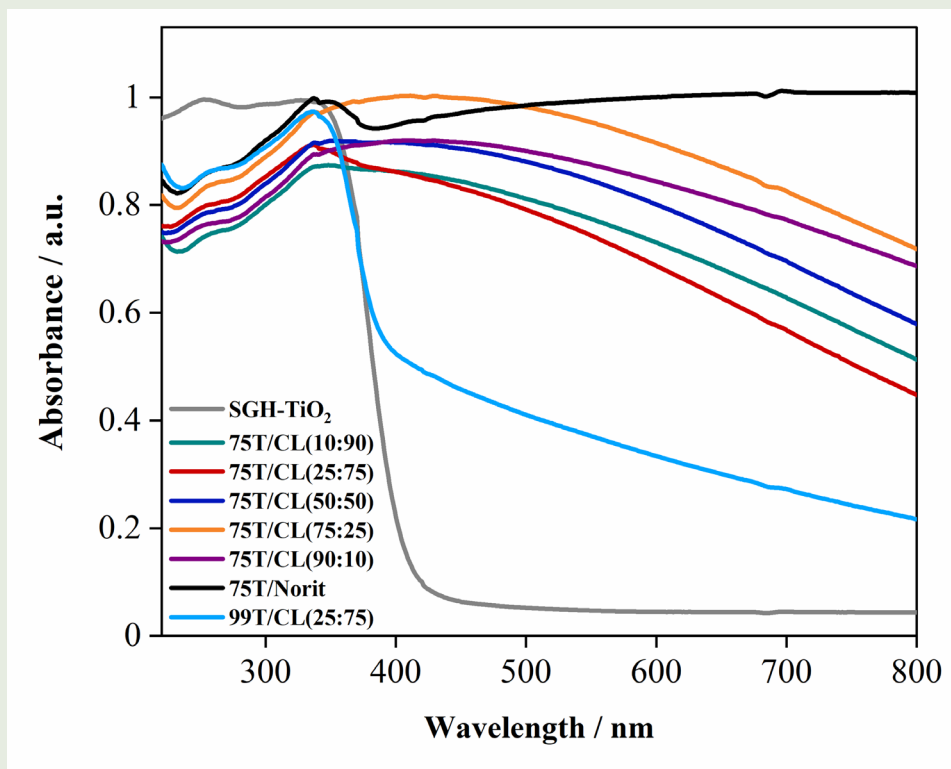




# UV-Visible DRS analysis

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**75T/CL nanocomposites showed absorption in the entire UV-Visible region (220-800 nm), which could be advantageous for visible light photocatalysis**



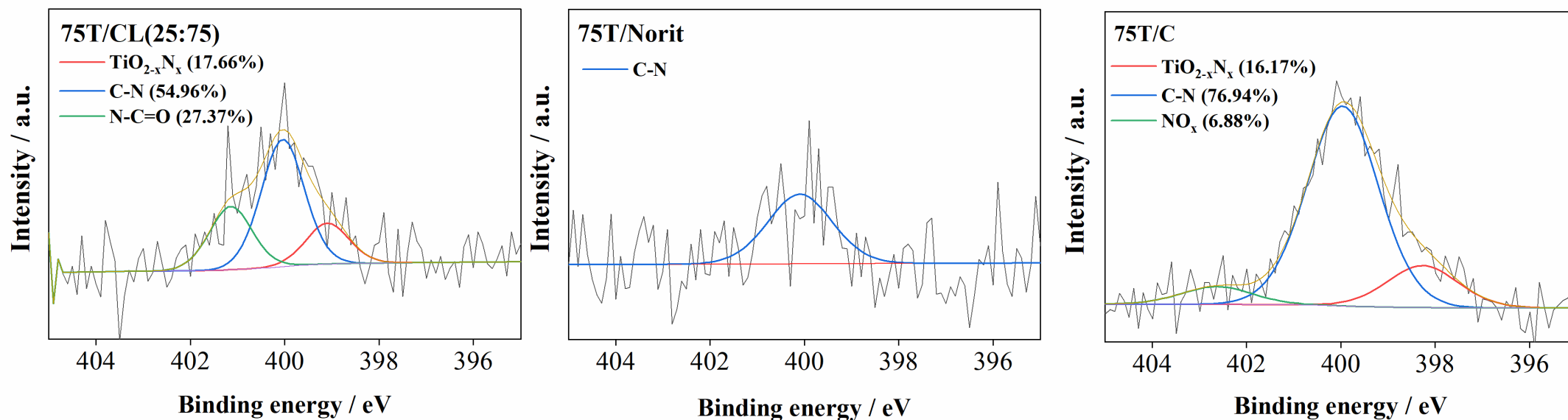
Colmenares et al., RSC Adv., 11 (2021) 34996-35010



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# XPS analysis

**Doping of nitrogen into titania framework is related to the presence of chitosan.  
This could be advantageous from the viewpoint of photocatalytic activity of  
75T/CL(25:75) nanocomposite under visible light**



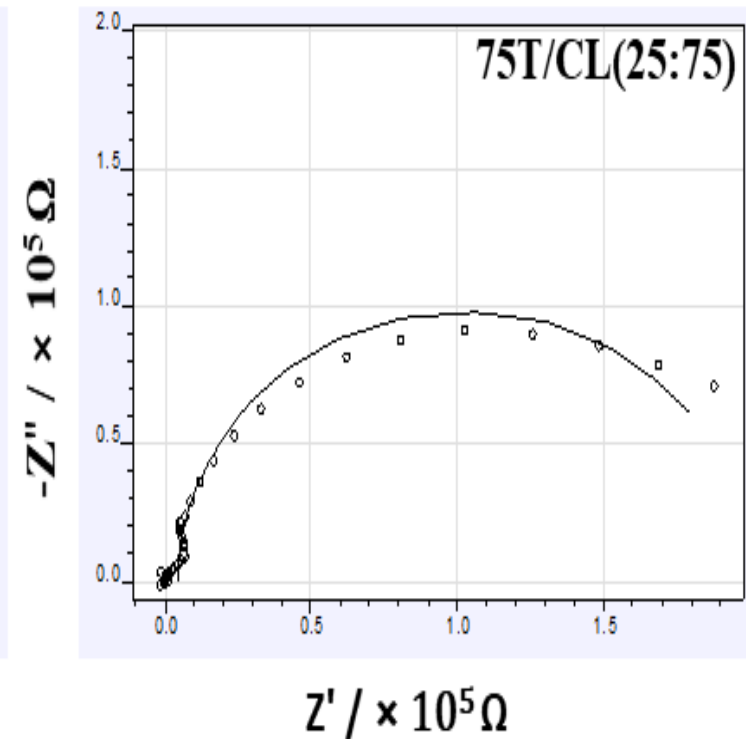
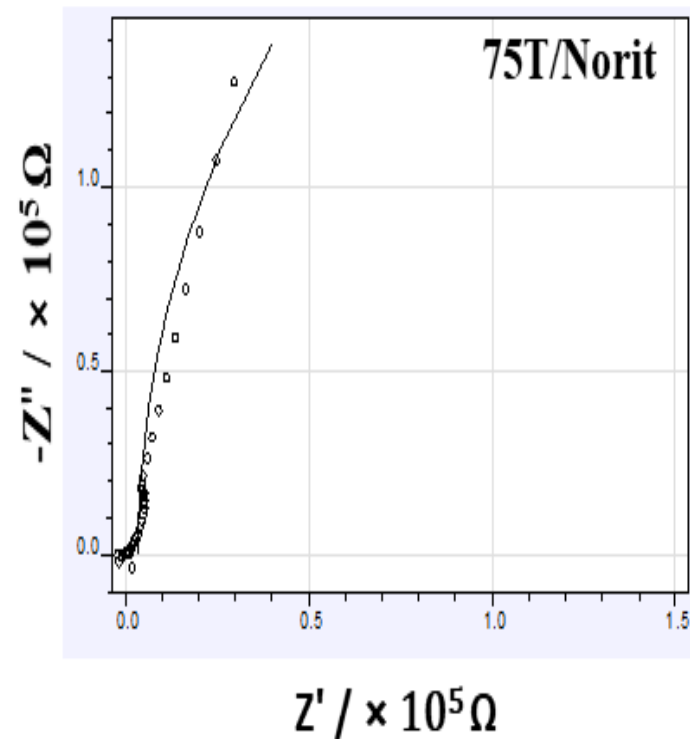
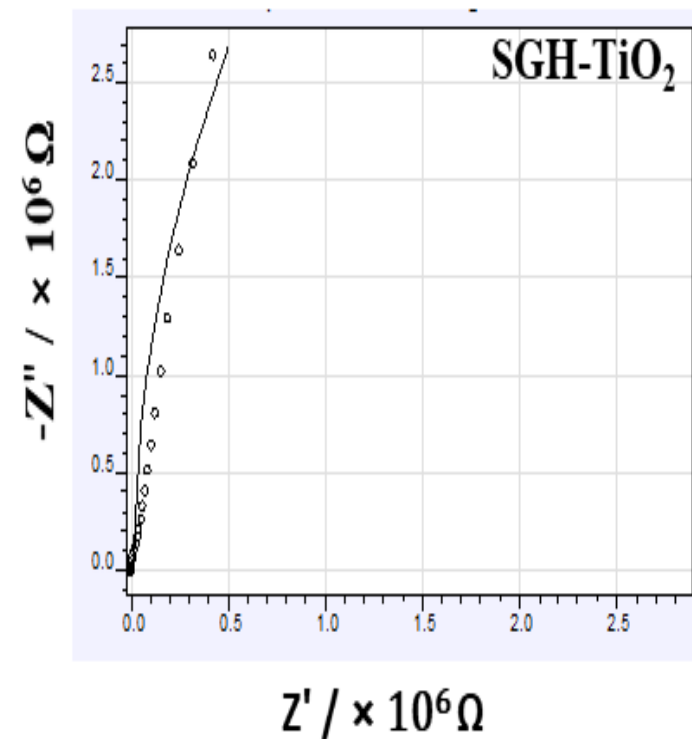
Colmenares et al., RSC Adv., 11 (2021) 34996-35010





# Impedance spectroscopy studies

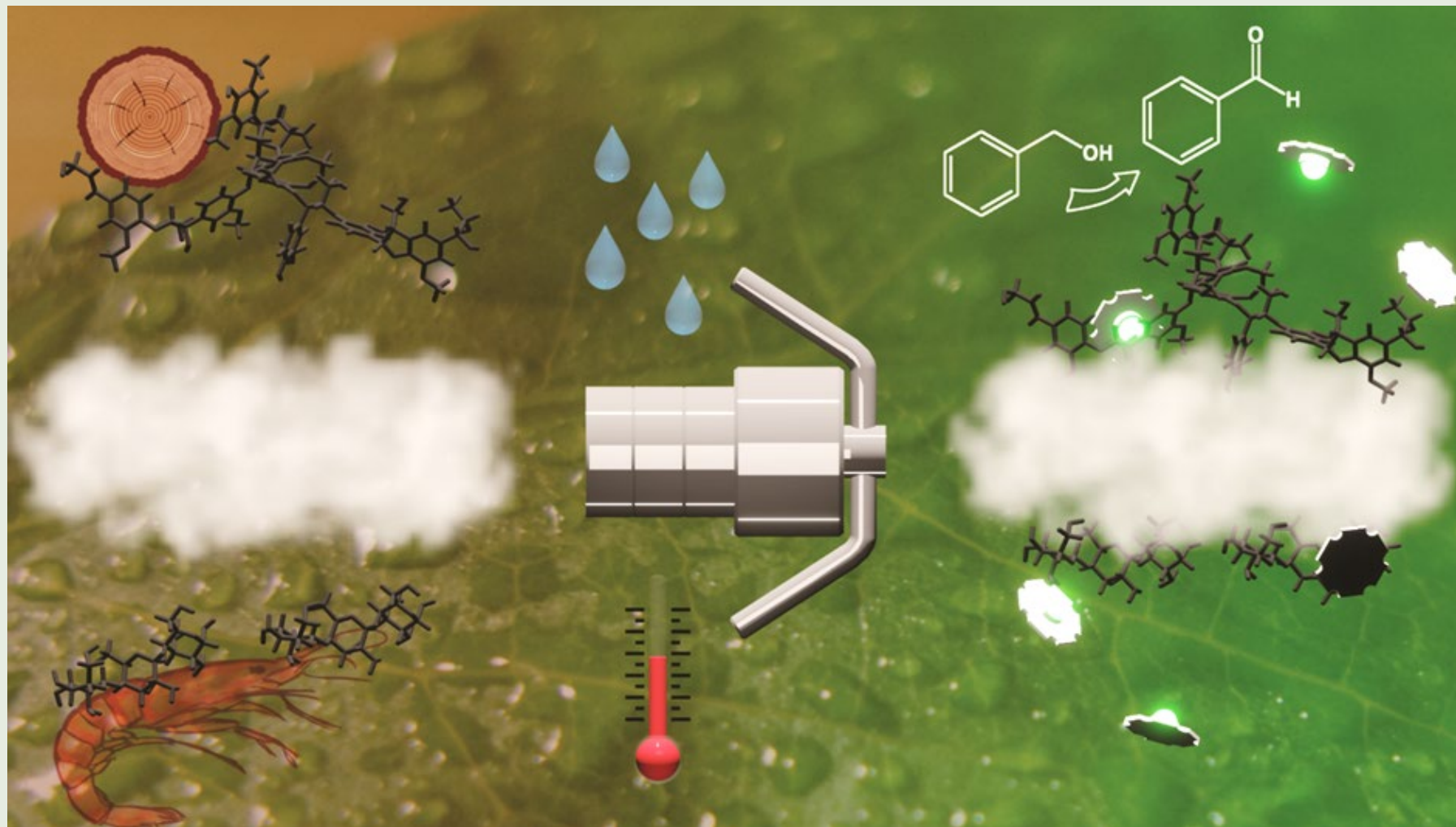
The Nyquist curves of SGH-TiO<sub>2</sub>, 75T/Norit and 75T/CL(25:75) were fitted with the Randles equivalent circuit





# Take-Home Message

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# What next?: Colombian coffee wastes for lignin extraction... and something else...



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ARISTOTLE  
UNIVERSITY  
OF THESSALONIKI

*Prof. K. Triantafyllidis*  
<https://ktrianta.webpages.auth.gr>  
*Group...*



Laboratory of Chemical & Environmental Technology



IChF

Institute of Physical Chemistry PAS

Thank  
you



# Acknowledgments

**OPUS-20** project nr 2020/39/B/ST5/00076



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**CELISE Med Term Meeting**  
**24<sup>th</sup>-25<sup>th</sup> of July-2023, Warsaw, POLAND**



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