SUSTAINABLE CARBON MATERIALS

Design, Properties and Applications

by Maria-Magdalena Titirici

Max-Planck Institute of Colloids and Interfaces

Potsdam, Germany

within the course "Modern Methods in Heterogenous Catalysis Research"
Fritz Haber Institute of the Max Planck Society
Berlin, 19.11.2010

OUTLINE

- **Introducing the green chemistry concept**

- **Sustainable Carbon**

1. Biomass derived nanotructured carbon materials with valuable applications

1.1 Bottom up approach: Porous Carbohydrates

1.2 Top down approach: Hydrothermal Carbonization

2. Biochar production for CO_2 sequestration and soil regeneration

- **Conclusions**

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- Conclusions

GREEN CHEMISTRY

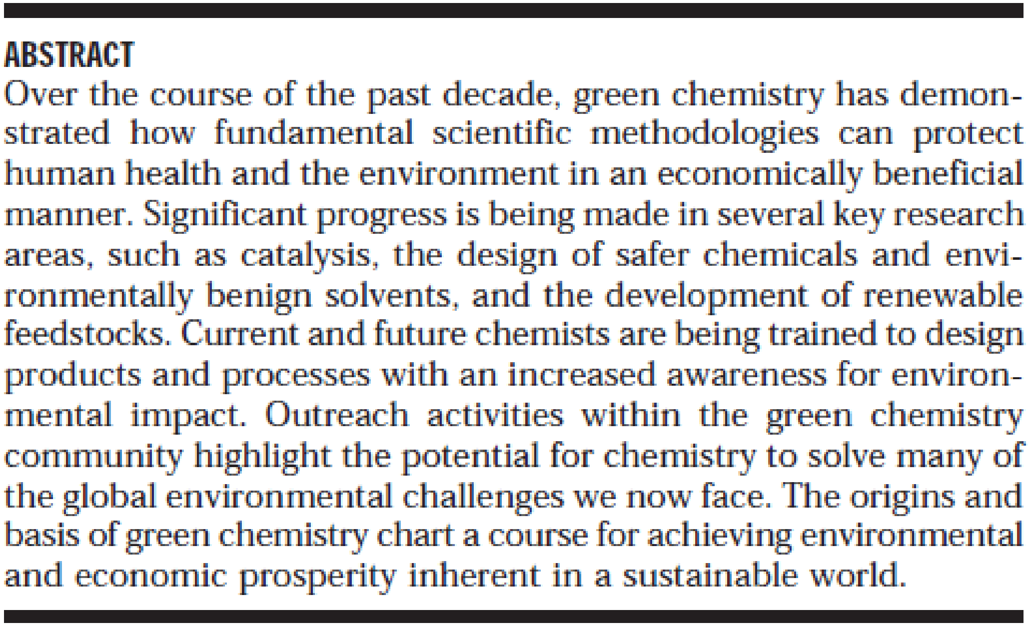
Definition

Green chemistry, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.

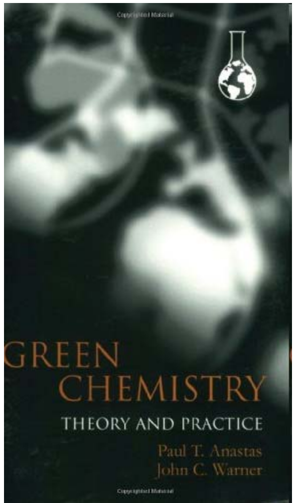
Acc. Chem. Res. **2002,** *35,* 686−694

Origins, Current Status, and Future Challenges of Green Chemistry†

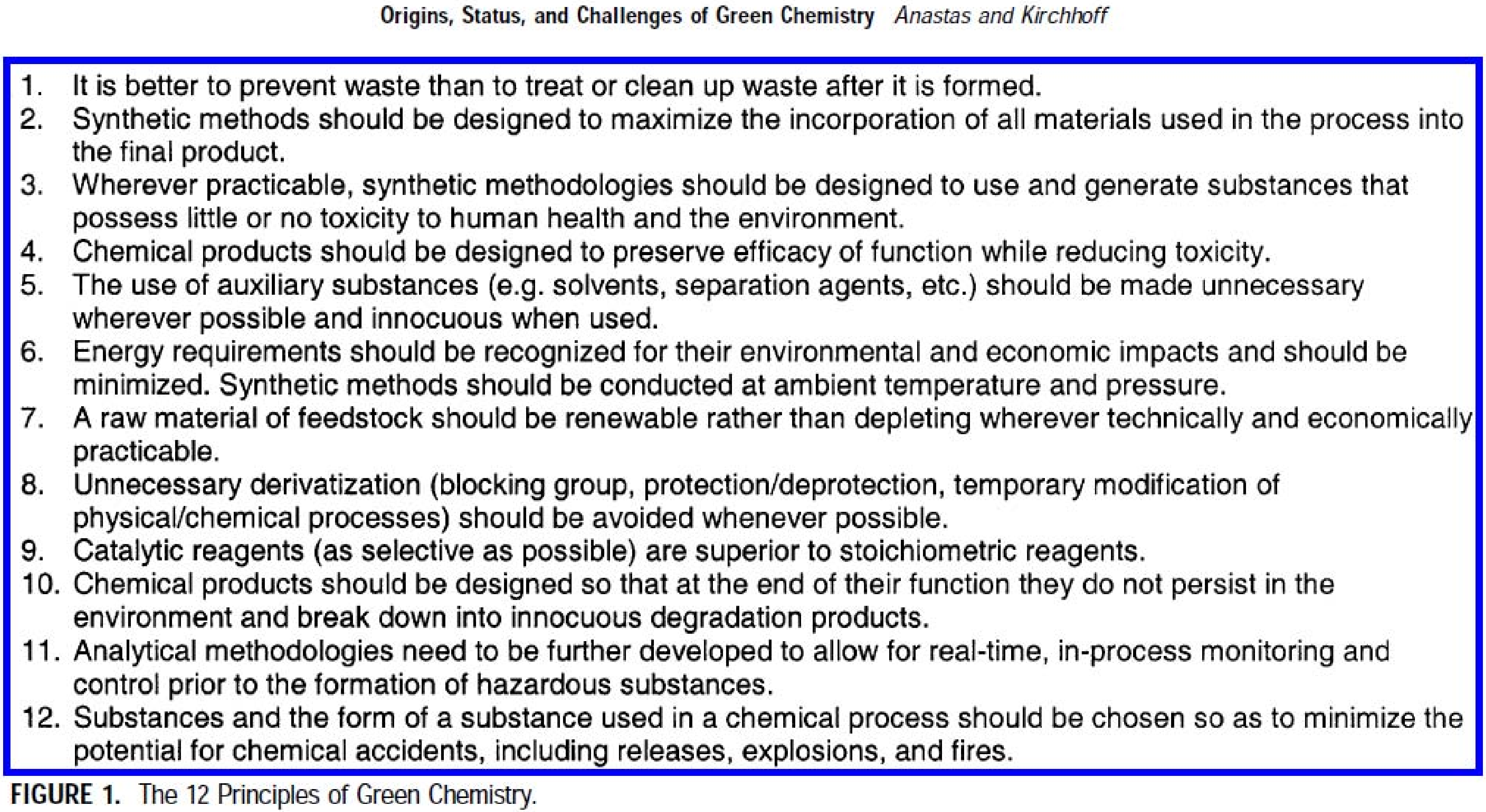
PAUL T. ANASTAS*,‡ AND
MARY M. KIRCHHOFF§



ABSTRACT
Over the course of the past decade, green chemistry has demonstrated how fundamental scientific methodologies can protect human health and the environment in an economically beneficial manner. Significant progress is being made in several key research areas, such as catalysis, the design of safer chemicals and environmentally benign solvents, and the development of renewable feedstocks. Current and future chemists are being trained to design products and processes with an increased awareness for environmental impact. Outreach activities within the green chemistry community highlight the potential for chemistry to solve many of the global environmental challenges we now face. The origins and basis of green chemistry chart a course for achieving environmental and economic prosperity inherent in a sustainable world.



GREEN CHEMISTRY



Origins, Status, and Challenges of Green Chemistry *Anastas and Kirchhoff*

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

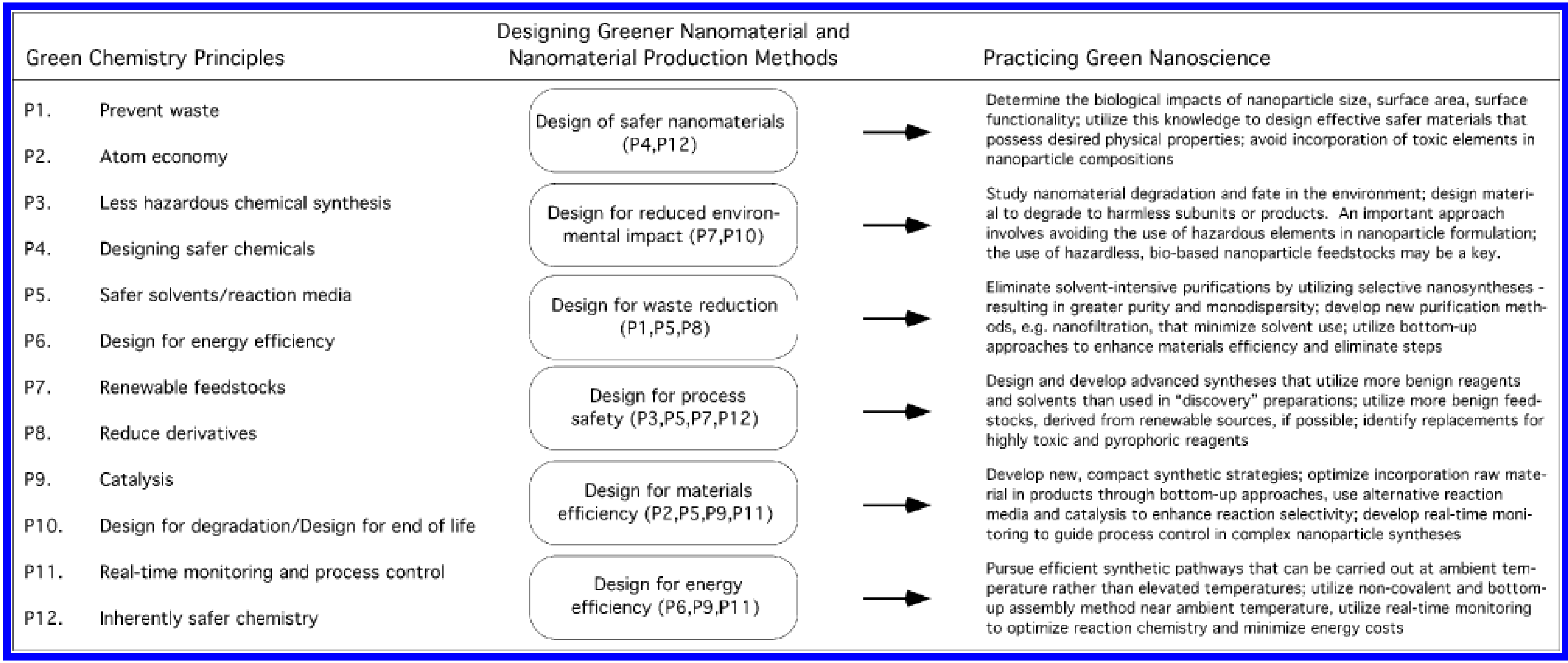
FIGURE 1. The 12 Principles of Green Chemistry.

GREEN CHEMISTRY AND NANOMATERIALS

Chem. Rev. **2007,** *107,* 2228–2269

Toward Greener Nanosynthesis

Jennifer A. Dahl, Bettye L. S. Maddux, and James E. Hutchison*



Green Chemistry Principles

- P1. Prevent waste
- P2. Atom economy
- P3. Less hazardous chemical synthesis
- P4. Designing safer chemicals
- P5. Safer solvents/reaction media
- P6. Design for energy efficiency
- P7. Renewable feedstocks
- P8. Reduce derivatives
- P9. Catalysis
- P10. Design for degradation/Design for end of life
- P11. Real-time monitoring and process control
- P12. Inherently safer chemistry

Designing Greener Nanomaterial and Nanomaterial Production Methods	Practicing Green Nanoscience
Design of safer nanomaterials (P4,P12)	Determine the biological impacts of nanoparticle size, surface area, surface functionality; utilize this knowledge to design effective safer materials that possess desired physical properties; avoid incorporation of toxic elements in nanoparticle compositions
Design for reduced environmental impact (P7,P10)	Study nanomaterial degradation and fate in the environment; design material to degrade to harmless subunits or products. An important approach involves avoiding the use of hazardous elements in nanoparticle formulation; the use of hazardless, bio-based nanoparticle feedstocks may be a key.
Design for waste reduction (P1,P5,P8)	Eliminate solvent-intensive purifications by utilizing selective nanosyntheses - resulting in greater purity and monodispersity; develop new purification methods, e.g. nanofiltration, that minimize solvent use; utilize bottom-up approaches to enhance materials efficiency and eliminate steps
Design for process safety (P3,P5,P7,P12)	Design and develop advanced syntheses that utilize more benign reagents and solvents than used in "discovery" preparations; utilize more benign feedstocks, derived from renewable sources, if possible; identify replacements for highly toxic and pyrophoric reagents
Design for materials efficiency (P2,P5,P9,P11)	Develop new, compact synthetic strategies; optimize incorporation raw material in products through bottom-up approaches, use alternative reaction media and catalysis to enhance reaction selectivity; develop real-time monitoring to guide process control in complex nanoparticle syntheses
Design for energy efficiency (P6,P9,P11)	Pursue efficient synthetic pathways that can be carried out at ambient temperature rather than elevated temperatures; utilize non-covalent and bottom-up assembly method near ambient temperature, utilize real-time monitoring to optimize reaction chemistry and minimize energy costs

Figure 1. Translating the 12 green chemistry principles for application in the practice of green nanoscience. The principles are listed, in abbreviated form, along with the general approaches to designing greener nanomaterials and nanomaterial production methods and specific examples of how these approaches are being implemented in green nanoscience. Within the figure, P*X*, where $X = 1-12$, indicates the applicable green chemistry principle.

GREEN CHEMISTRY AND NANOMATERIALS

Green nanochemistry

DOI: 10.1002/smll.200700048

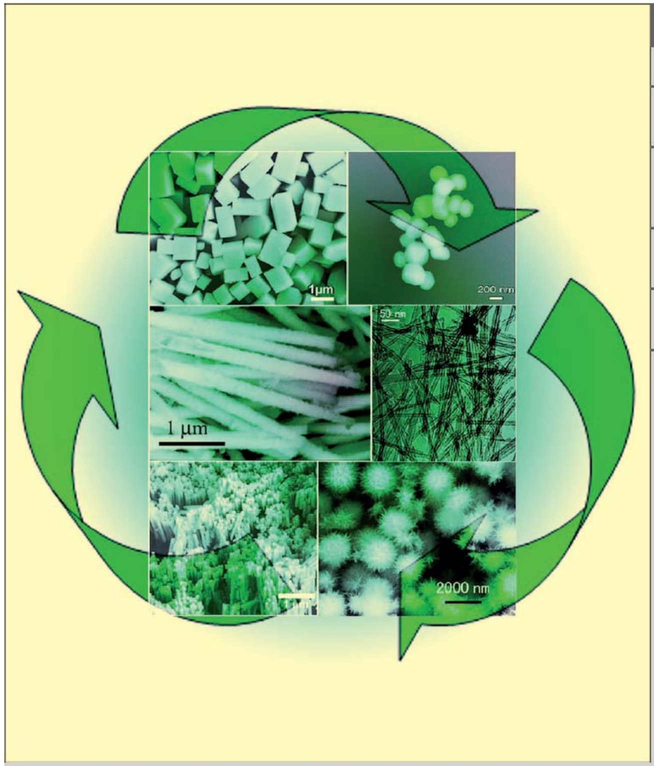
Environmentally Friendly Methodologies of Nanostructure Synthesis

small 2007, 3, No. 7, 1122 – 1139

*Yuanbing Mao, Tae-Jin Park, Fen Zhang, Hongjun Zhou, and Stanislaus S. Wong**

Green Routes to Nanomaterials

Environmentally friendly synthetic methodologies have gradually been implemented as viable techniques in the synthesis of a range of nanostructures. In this work, we focus on the application of green-chemistry principles to the synthesis of complex metal oxide and fluoride nanostructures. In particular, we describe advances in the use of the molten-salt synthetic methods, hydrothermal protocols, and template-directed techniques as environmentally sound, socially responsible, and cost-effective methodologies that allow us to generate nanomaterials without the need to sacrifice sample quality, purity, and crystallinity, while allowing control over size, shape, and morphology.

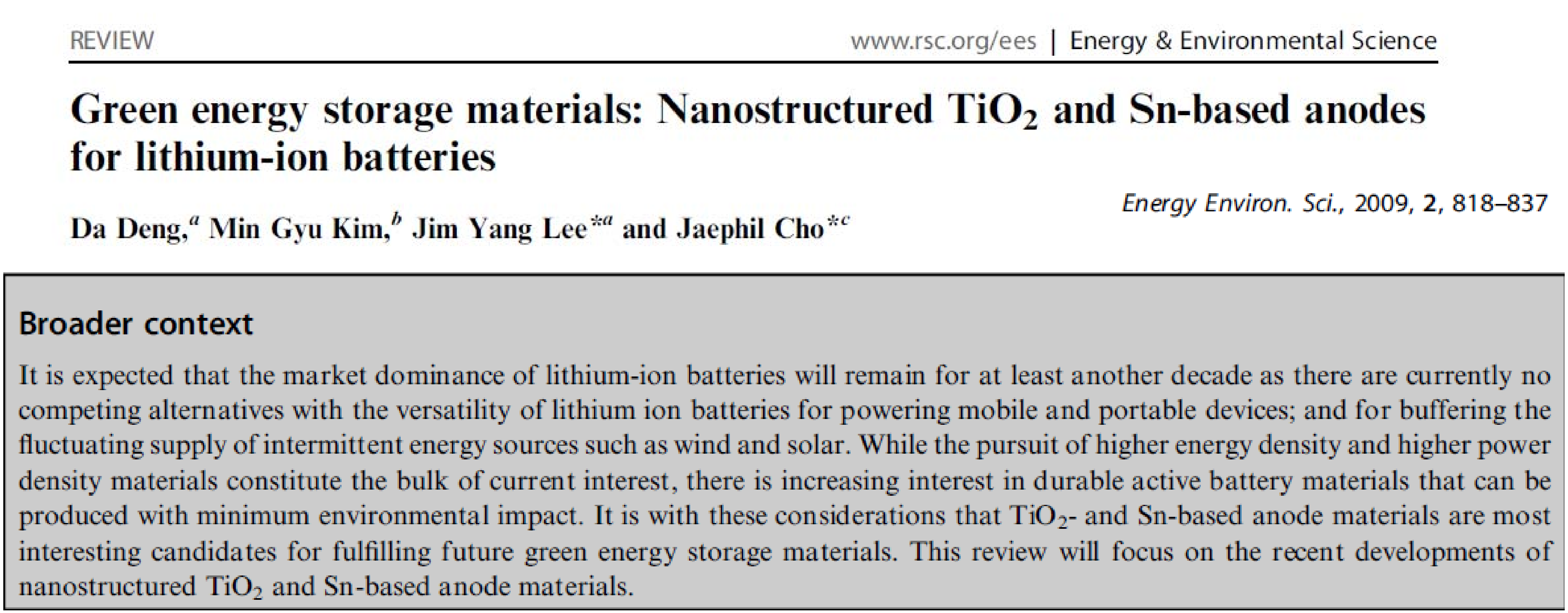


Various shapes of oxide and fluoride nanomaterials prepared by environmentally friendly techniques.

From the Contents

Keywords:
- green chemistry
- hydrothermal synthesis
- molten-salt synthesis
- nanostructures
- template synthesis

GREEN CHEMISTRY AND NANOMATERIALS



REVIEW

www.rsc.org/ees | Energy & Environmental Science

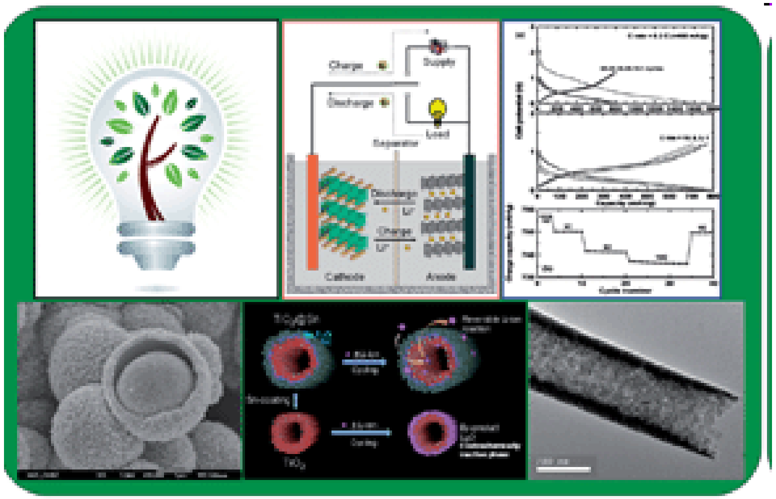
Green energy storage materials: Nanostructured TiO_2 and Sn-based anodes for lithium-ion batteries

Energy Environ. Sci., 2009, **2**, 818–837

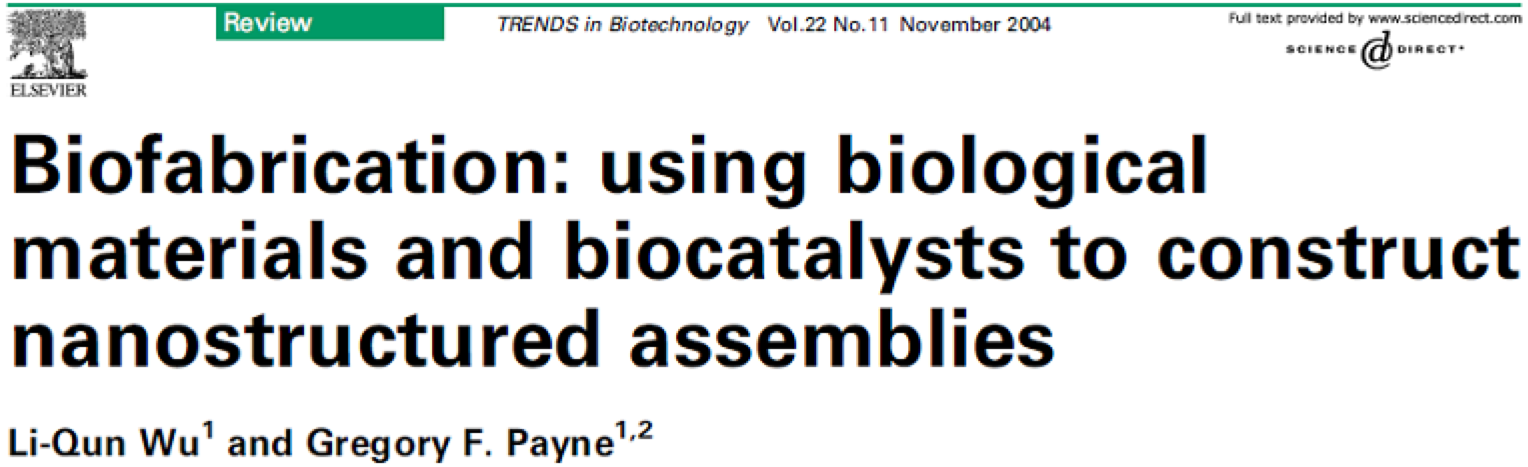
Da Deng,[a] Min Gyu Kim,[b] Jim Yang Lee*[a] and Jaephil Cho*[c]

Broader context

It is expected that the market dominance of lithium-ion batteries will remain for at least another decade as there are currently no competing alternatives with the versatility of lithium ion batteries for powering mobile and portable devices; and for buffering the fluctuating supply of intermittent energy sources such as wind and solar. While the pursuit of higher energy density and higher power density materials constitute the bulk of current interest, there is increasing interest in durable active battery materials that can be produced with minimum environmental impact. It is with these considerations that TiO_2- and Sn-based anode materials are most interesting candidates for fulfilling future green energy storage materials. This review will focus on the recent developments of nanostructured TiO_2 and Sn-based anode materials.



NANOMATERIALS FROM NATURAL RESOURCES



ELSEVIER

Review

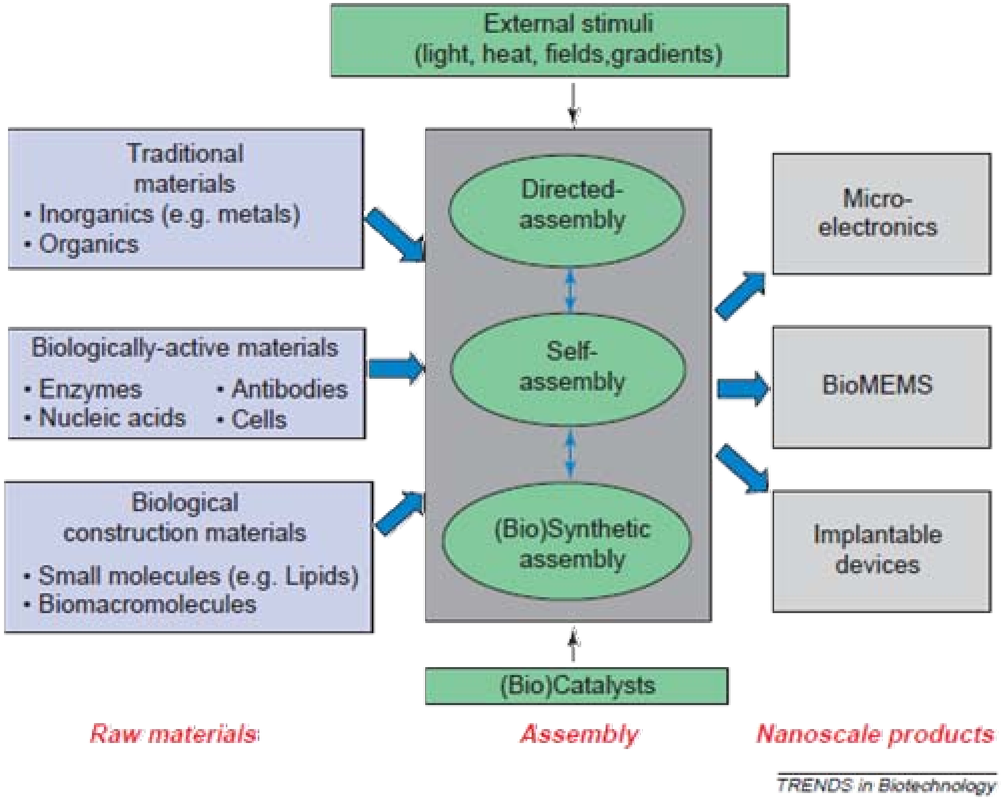
TRENDS in Biotechnology Vol.22 No.11 November 2004

Full text provided by www.sciencedirect.com

SCIENCE DIRECT

Biofabrication: using biological materials and biocatalysts to construct nanostructured assemblies

Li-Qun Wu[1] and Gregory F. Payne[1,2]

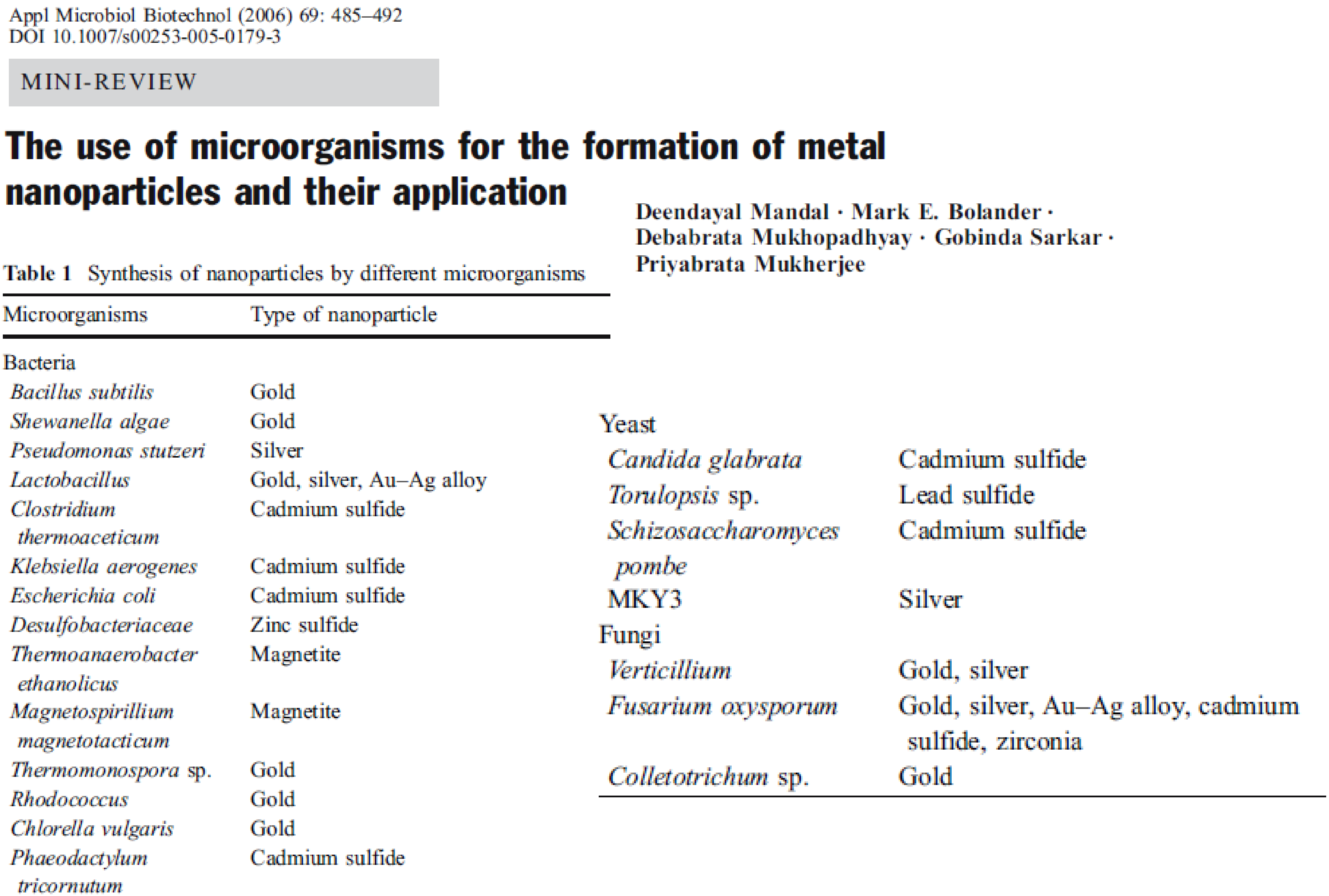


TRENDS in Biotechnology

- Biological construction materials facilitate assembly through a broad range of options.

- Such biological materials can be used as processing aids to construct products that ultimately contain no biological components (e.g. next-generation micro-electronics) or can form the structural network for products that contain exclusively biological materials (e.g. artificial organs).

NANOMATERIALS FROM NATURAL RESOURCES



Appl Microbiol Biotechnol (2006) 69: 485–492
DOI 10.1007/s00253-005-0179-3

MINI-REVIEW

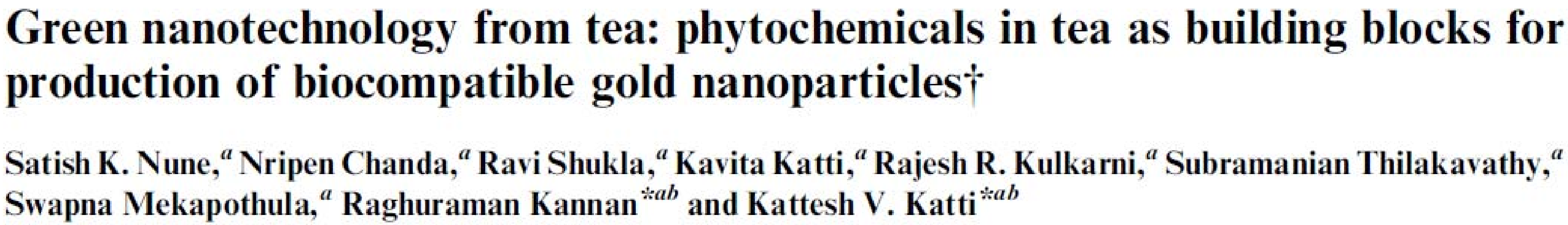
The use of microorganisms for the formation of metal nanoparticles and their application

Deendayal Mandal · Mark E. Bolander · Debabrata Mukhopadhyay · Gobinda Sarkar · Priyabrata Mukherjee

Table 1 Synthesis of nanoparticles by different microorganisms

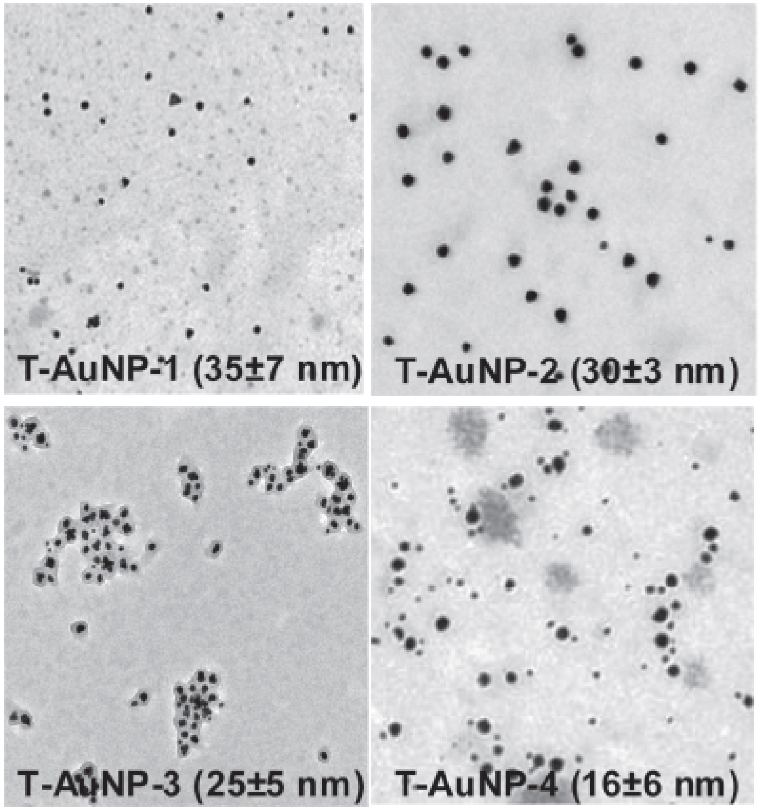
Microorganisms	Type of nanoparticle
Bacteria	
Bacillus subtilis	Gold
Shewanella algae	Gold
Pseudomonas stutzeri	Silver
Lactobacillus	Gold, silver, Au–Ag alloy
Clostridium thermoaceticum	Cadmium sulfide
Klebsiella aerogenes	Cadmium sulfide
Escherichia coli	Cadmium sulfide
Desulfobacteriaceae	Zinc sulfide
Thermoanaerobacter ethanolicus	Magnetite
Magnetospirillium magnetotacticum	Magnetite
Thermomonospora sp.	Gold
Rhodococcus	Gold
Chlorella vulgaris	Gold
Phaeodactylum tricornutum	Cadmium sulfide
Yeast	
Candida glabrata	Cadmium sulfide
Torulopsis sp.	Lead sulfide
Schizosaccharomyces pombe	Cadmium sulfide
MKY3	Silver
Fungi	
Verticillium	Gold, silver
Fusarium oxysporum	Gold, silver, Au–Ag alloy, cadmium sulfide, zirconia
Colletotrichum sp.	Gold

NANOMATERIALS FROM NATURAL RESOURCES



Green nanotechnology from tea: phytochemicals in tea as building blocks for production of biocompatible gold nanoparticles†

Satish K. Nune,[a] Nripen Chanda,[a] Ravi Shukla,[a] Kavita Katti,[a] Rajesh R. Kulkarni,[a] Subramanian Thilakavathy,[a] Swapna Mekapothula,[a] Raghuraman Kannan*[ab] and Kattesh V. Katti*[ab]



J. Mater. Chem., 2009, *19*, 2912–2920

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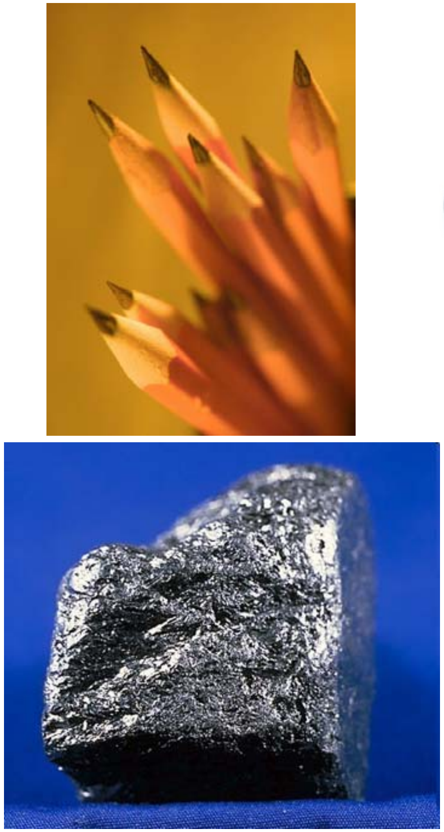
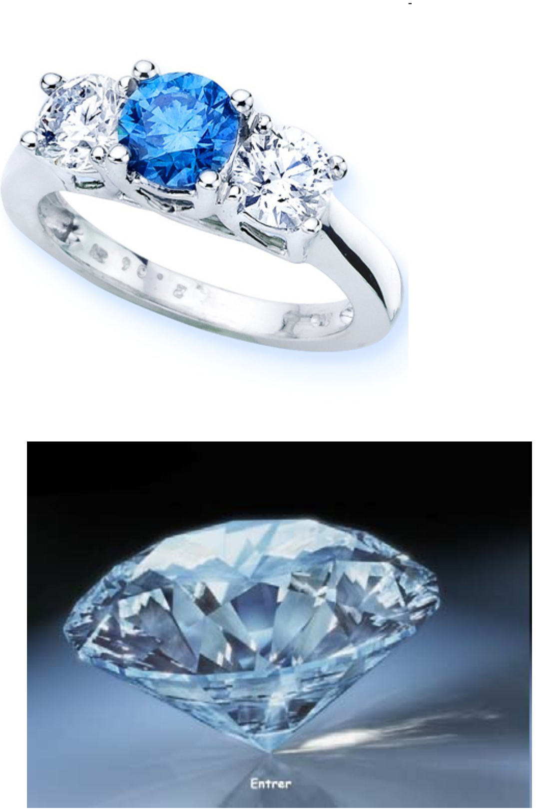
CRYSTALLINE CARBON

Bulk Carbon

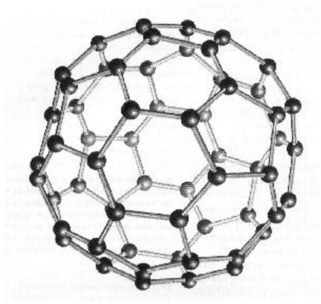


Graphite

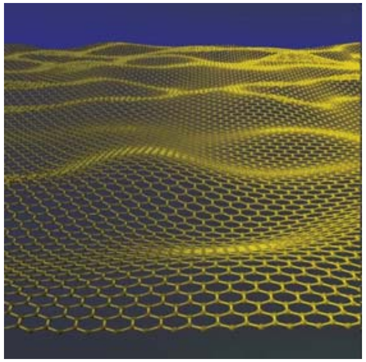


Diamond

Nanoscale Carbon

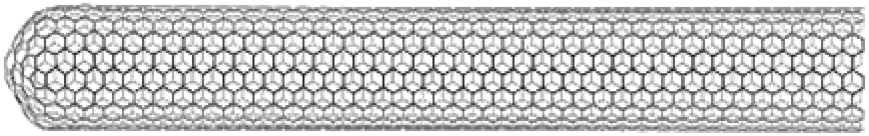


C_{60} (Buckeyball)
Smalley, Curl, Kroto
1996 Nobel Prize



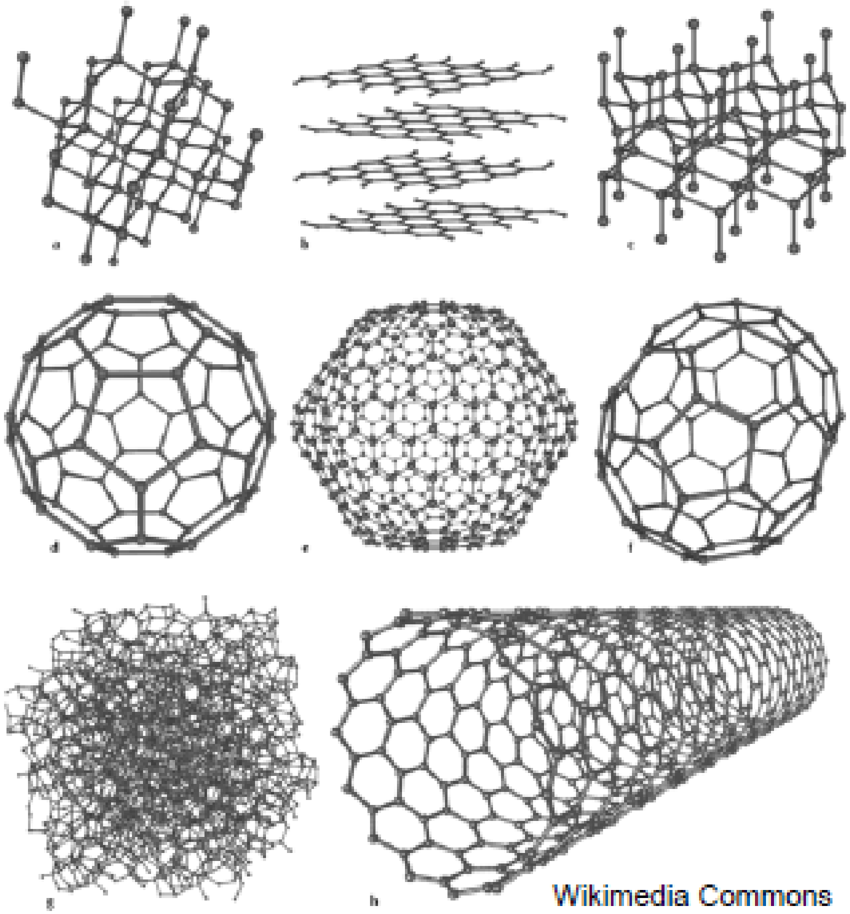
Graphene

Andre Geim
Konstantin Novoselov
2010 Nobel Prize



Carbon Nanotubes
Sumio Iijima - 1991

CARBON NANOSTRUCTURES



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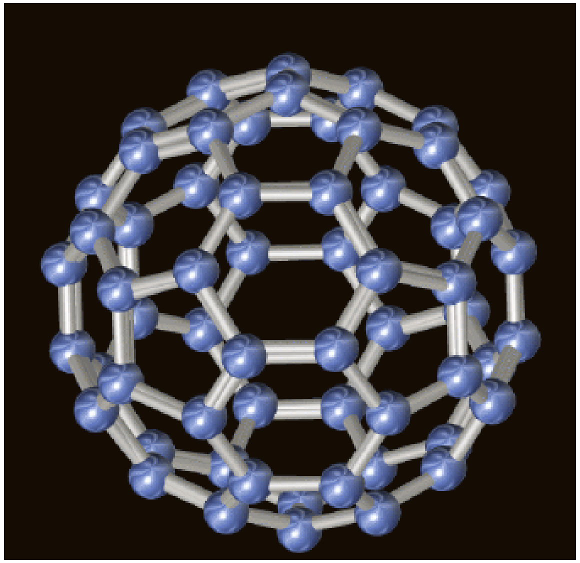
- Fullerenes
- Carbon nanotubes
- Graphene

FULLERENES



The Montreal Biosphère by Buckminster Fuller, 1967

- C60 Molecule (1985) by R.E. Smalley, R.F. Curl and H.W. Kroto at the University of Sussex and Rice University,**– Nobel Prize 1996**

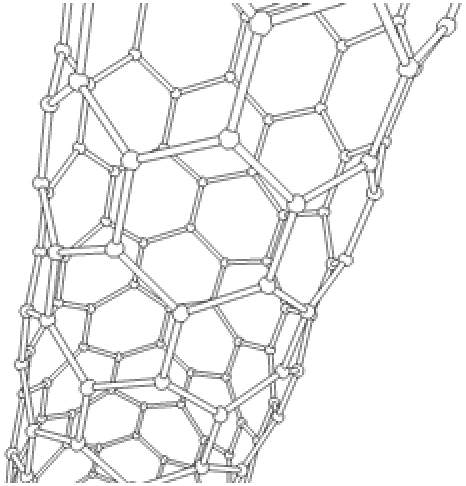
- Named after Richard Buckminster Fuller (Geodesic domes)

- Made entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube

- Used for microelectrics, sensors and composite materials

- It was a new form of Carbon, besides graphite, diamond and amorphous

CARBON NANOTUBES



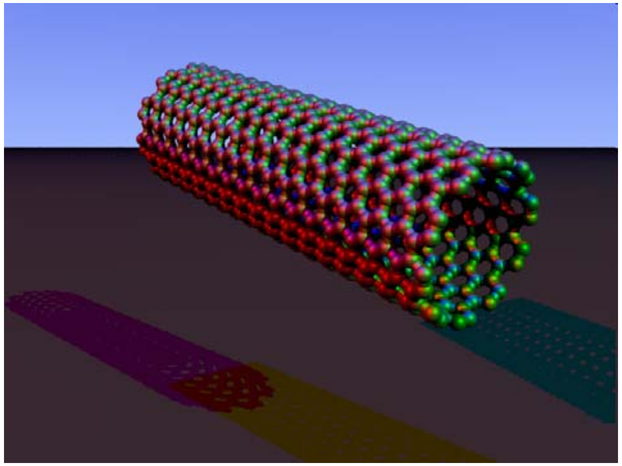
- single sheet of graphite rolled up
- discovered by Sumio Iijima in 1991

(though origin of discovery is debated)

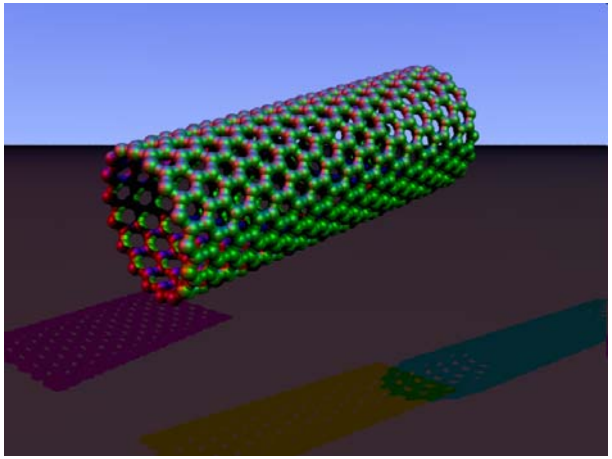
RELEVANCE:

Another new form of Carbon, has excellent mechanical, thermal and chemical properties.

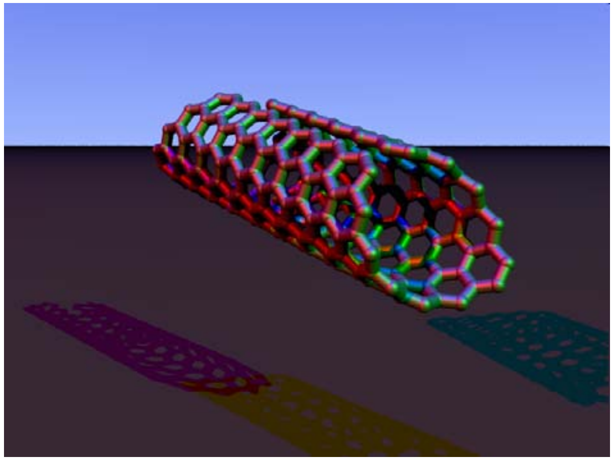
Armchair



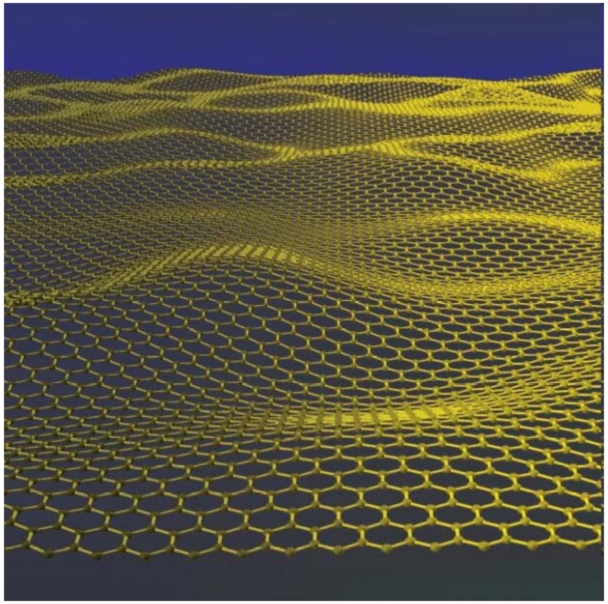
Zig-Zag



Chiral



CARBON NANOTUBES



Is a single planar sheet of sp^2-bonded carbon atoms. Graphenes are the 2-D counterparts of 3-D graphite

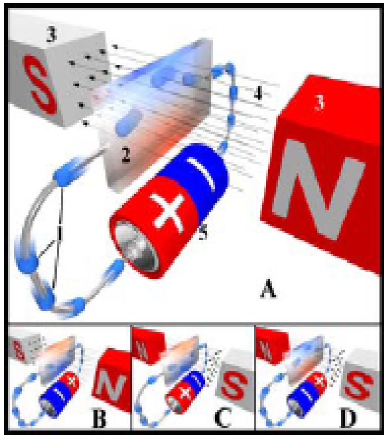
***Nobel Prize, 2010* (Andre Geim Konstantin Novoselov)**

RELEVANCE:
Electrons behave as if they had no mass (2D electron gasses)

Room T quantum Hall effect

$$\sigma = \nu \frac{e^2}{h},$$

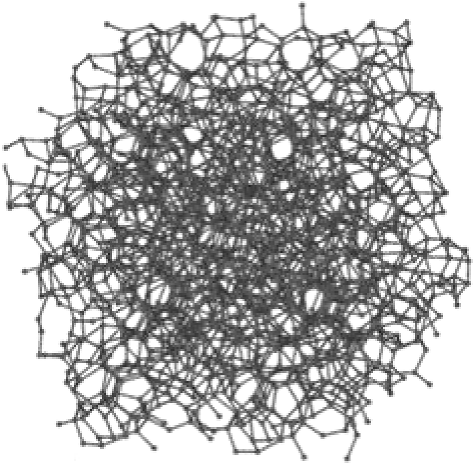
e=elementary electric charge



The quantum Hall effect is relevant for accurate measuring standards of electrical quantities

It concerns the dependence of a transverse conductivity on a magnetic field, which is perpendicular to a current-carrying stripe

AMORPHOUS CARBON

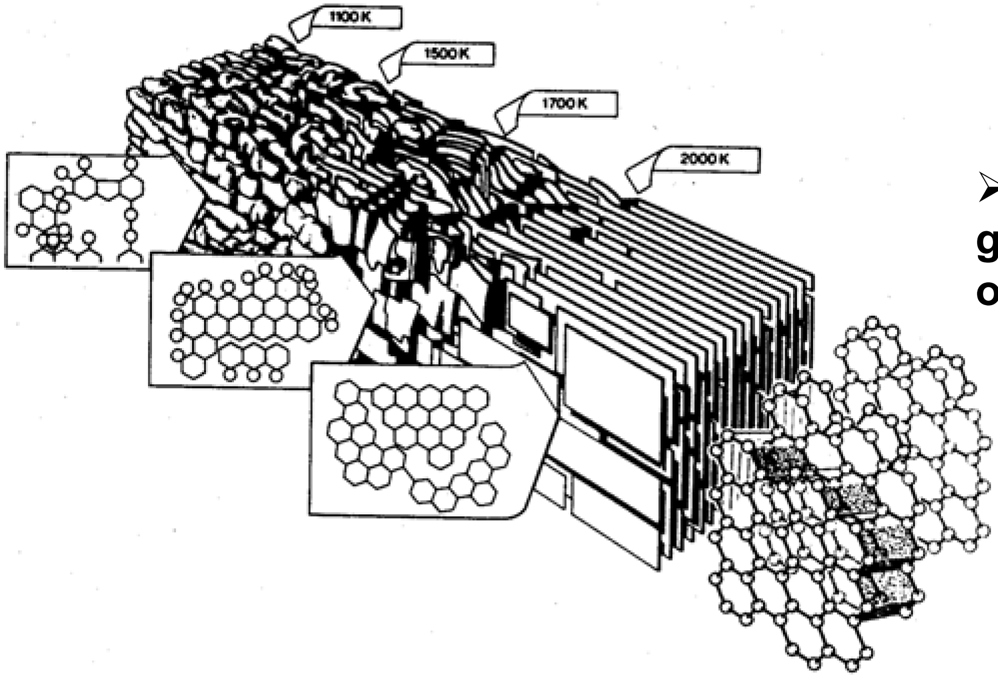


- is an allotrope of carbon that is neither graphite or diamond

- some short-range order can be observed.

- in a crystallographic sense, these materials are not truly amorphous, but are polycrystalline or nano-crystalline materials of graphite or diamond within an amorphous carbon matrix.

Examples: activated carbons, carbon backs, glassy carbons, soot, chars etc



➢**Some of the amorphous carbons can be graphitized@ high temperatures depending on the ratio of C/O**

SUSTAINABLE CARBON

Carbon Materials (can be crystalline or amorphous, nanoscaled or bulk) prepared following the principle of green chemistry:

- *The precursors used need to be low cost with as low toxicity as possible*
- *The synthesis needs to be done under mild conditions (not very high temperatures) with minimum energy consumption*
- *The use of toxic reagents and formation/elimination of toxic gases must be avoided*
- *The catalysts used need to be low cost and benign*
- *The synthesis should have as little steps as possible*
- *Waste should be avoided*
- *The resulting materials should posses equal if not superior properties compared with the standard counterparts*

NANOCARBON FROM NATURAL RESOURCES

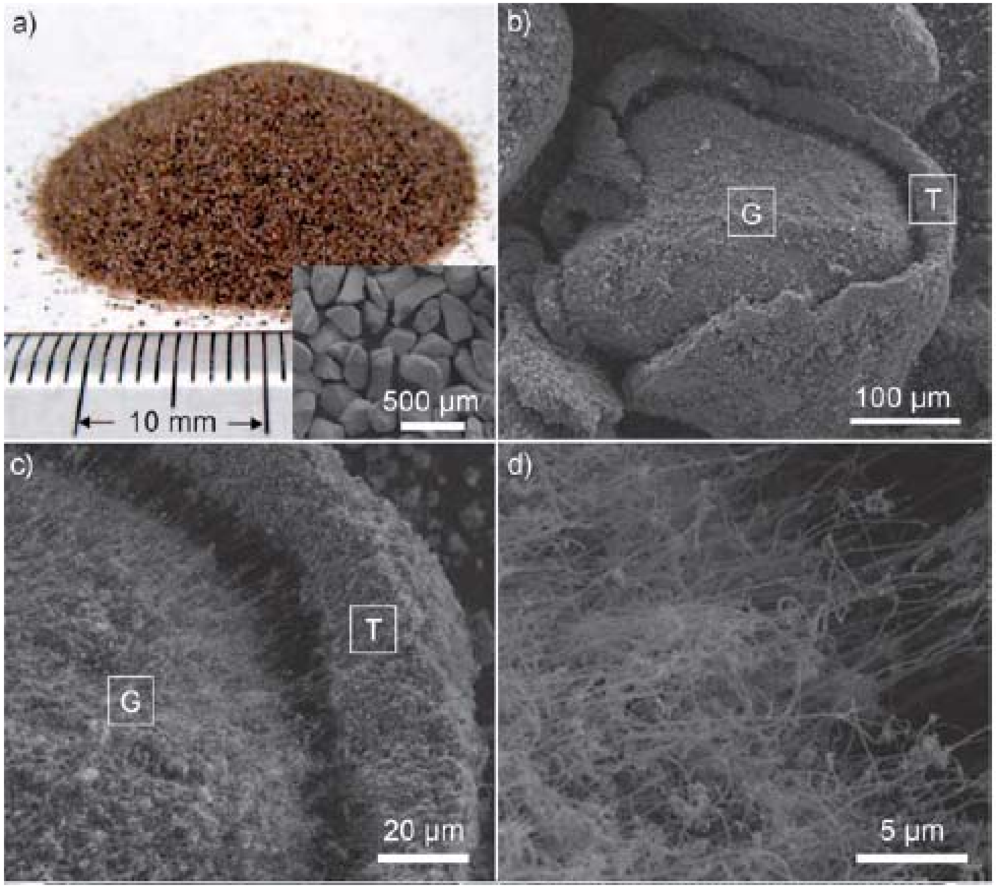
DOI: 10.1002/cssc.200900046

The Use of Natural Materials in Nanocarbon Synthesis

Dang Sheng Su*[a]

Nanomaterials are shifting from laboratory-scale preparation to industrial production. The energy costs and starting materials (feedstock, catalyst, and support) consumed or used in the mass production of nanomaterials are issues that limit their broad application. Natural materials, such as sand, rock, and lava, contain small or trace amounts of metals or metal oxides of nanometer-scale sizes and have been recently used as catalysts for the production of carbon nanotubes (CNTs), providing an interesting way to lower the production cost of CNTs. However, the sustainability of the whole production process still needs to be explored. Layered minerals (e.g., clays) are used to produce CNT–clay hybrids, which can be further used to synthesize polymer–CNT–clay nanocomposites. Natural materials and some byproducts of industrial production processes have been explored as carbon sources for nanocarbon synthesis. This Minireview highlights some recent promising work and prospects for the use of natural materials in the synthesis of CNTs, carbon nanofibers (CNFs), and nanocomposites, and their applications in catalysis and in materials science.

ChemSusChem **2009**, *2*, 1009 – 1020



Green carbon as a bridge to renewable energy

NATURE MATERIALS | VOL 9 | NOVEMBER 2010

James M. Tour, Carter Kittrell and Vicki L. Colvin

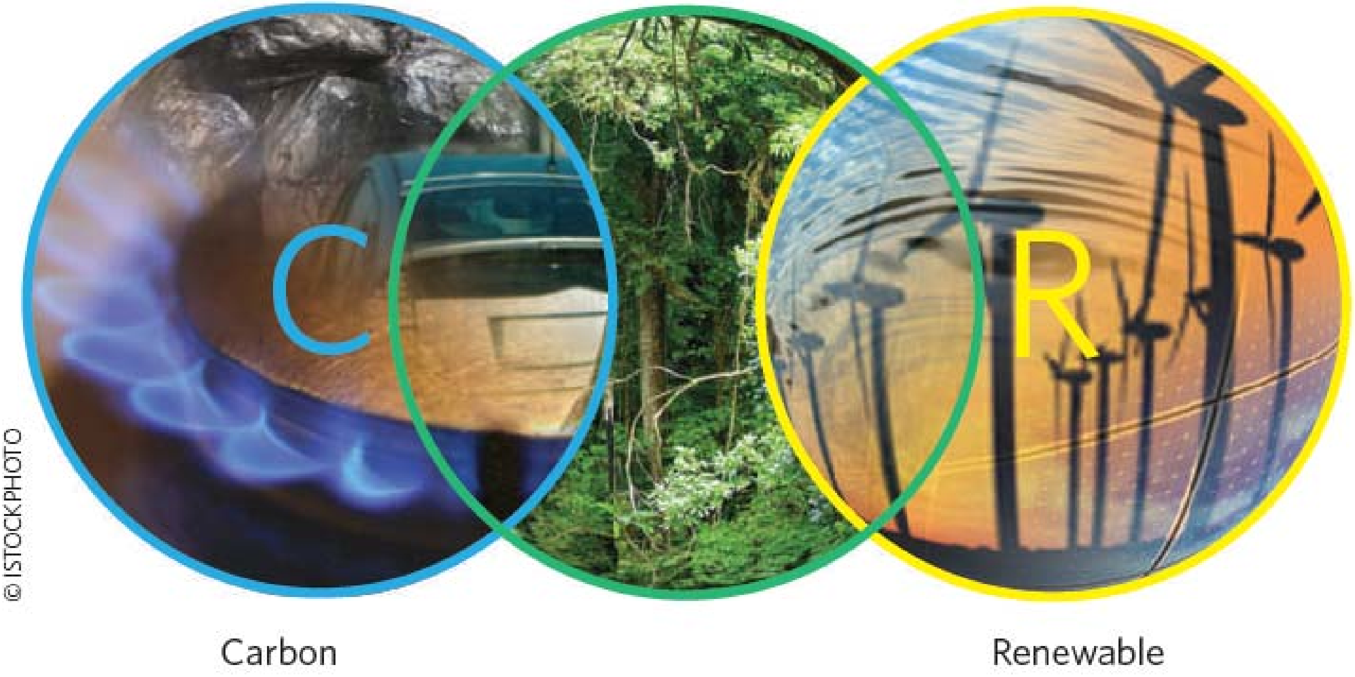


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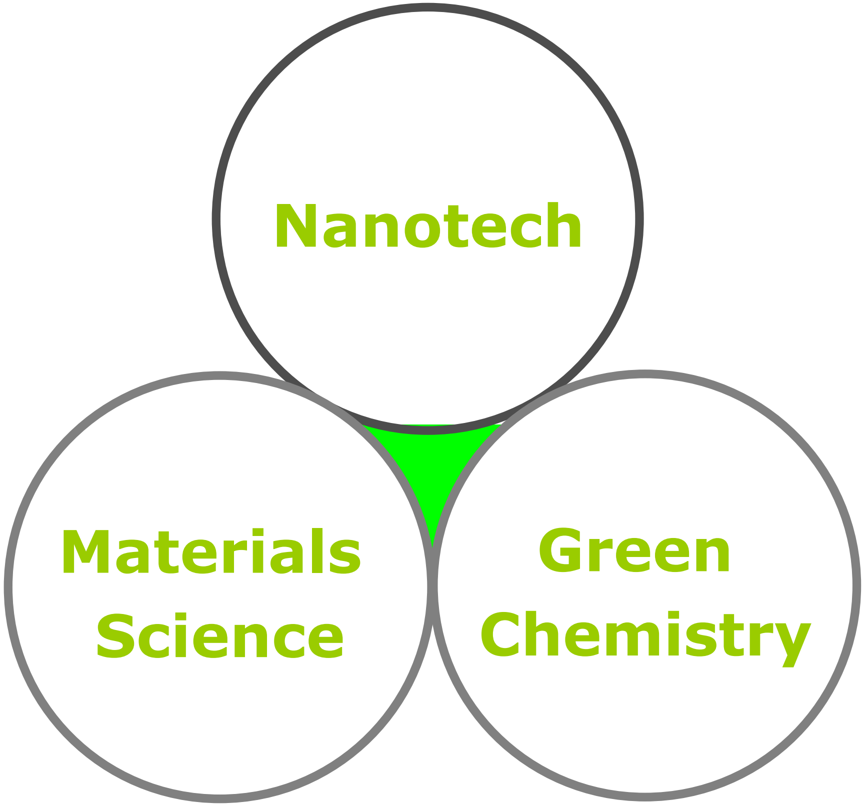
Figure 1 | The green carbon bridge envisages a gradual transition from carbon-derived energy resources to a more diverse renewable-energy economy.

NANOCARBON FROM NATURAL RESOURCES



Nanotech

Materials Science

Green Chemistry

Integration of different technologies to produce chemicals, biofuels, biomaterials and power from biomass raw materials.

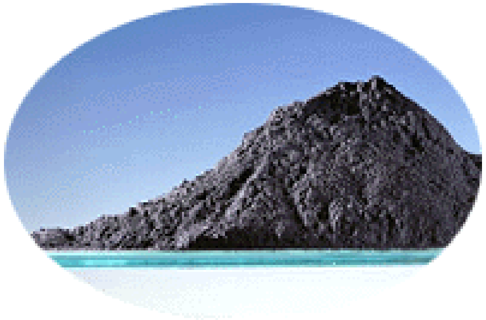
“The challenge of sustainability will be met with new technologies that provide society with products we depend on in an environmentally responsible manner”

NANOCARBON FROM NATURAL RESOURCES

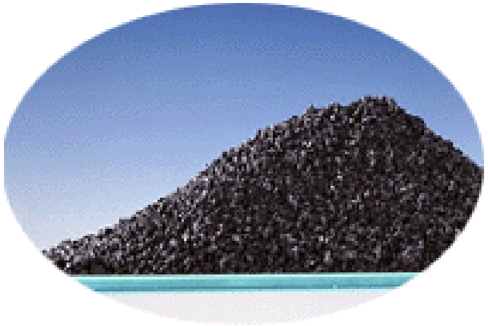
Activated Carbons

- Activated Carbon is a generic term used to describe a family of carbonaceous adsorbents possessing a highly crystalline form and extensively developed internal pore structure.

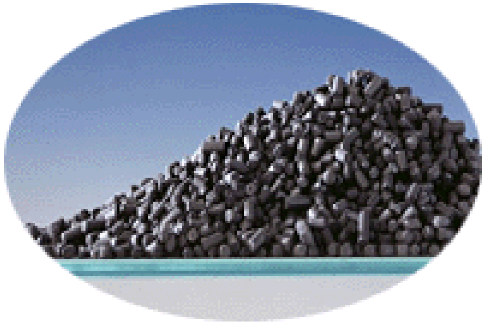
- This unique structure of Activated Carbon produces a very large surface area>1000 m^2/g)



Powdered



Granular



Pelleted / Extruded

ACTIVATED CARBON

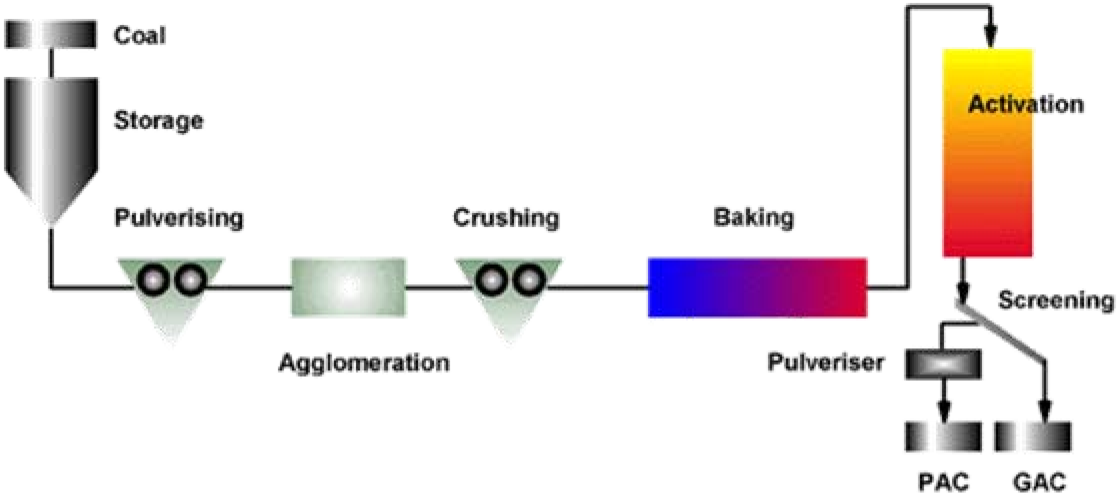
The choice of raw material has a large influence on the characteristics and performance of the AC, each producing an AC with differing surface areas, total pore volume, pore radius and pore volume distribution.

Carbon Type	Total Pore Volume (ml/g)	Mean Pore Radius (Angstroms)	Surface Area (m^2/g)
Coconut Shell	0.5 – 0.6	10 – 11	1000-1100
Peat	0.6 – 0.7	11 – 12	1000-1275
Bituminous Coal	0.6 – 0.7	12 – 14	1000-1150
Bituminous Coal	0.7 – 0.8	14 – 16	900-1050
Lignite Coal	0.9 – 1.0	29 – 32	900-1050
Peat	1.1 – 1.2	23 – 26	600-675
Wood	1.4 – 1.8	22 - 26	1200-1600

The Activation Process

The raw materials are first *carbonized* via a controlled heating process at “low” temperatures (200 - 300°C) in an oxygen-clean environment which keeps the material from burning. This process converts the raw material into a disordered carbon structure full of tiny pores.

The carbonized materials are then *activated* by steam (or chemical treatment). Steam activation is carried out at high temperatures (982°C) and the carbonized materials react with the steam to form carbon monoxide and hydrogen which exit as gases leaving behind a highly porous activated carbon material

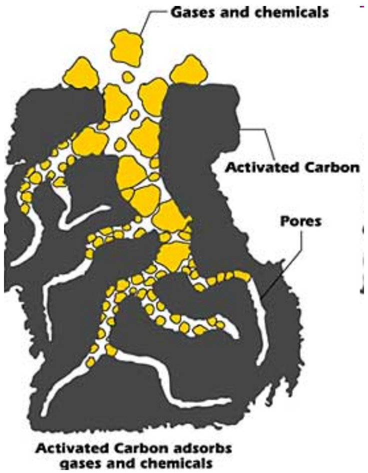


ACTIVATED CARBON

The main application is ADSORPTION FOR PURIFICATION PURPOSES

- **Different purification goals require different activated carbon properties.**

- **There are >150 types of carbon available**



- **The AC surface is non-polar which makes non-polar organic molecules most readily adsorbed.**

- **Will not adsorb salts**
- **Will not adsorb alcohols**

Adsorbs: Heavy Metals (Cd, Pb, Co, Cu), Oxidantes (Chlorine, Chloramine), Polyaromatics…etc

OUTLINE

- Introducing the green chemistry concept
- Sustainable Carbon

1. Biomass derived nanotructured carbon materials with valuable applications

    1.1 Bottom up approach: Porous Carbohydrates

    1.2 Top down approach: Hydrothermal Carbonization

2. Biochar production for CO_2 sequestration and soil regeneration

- Conclusions

Porous Polysaccharide-Derived Materials

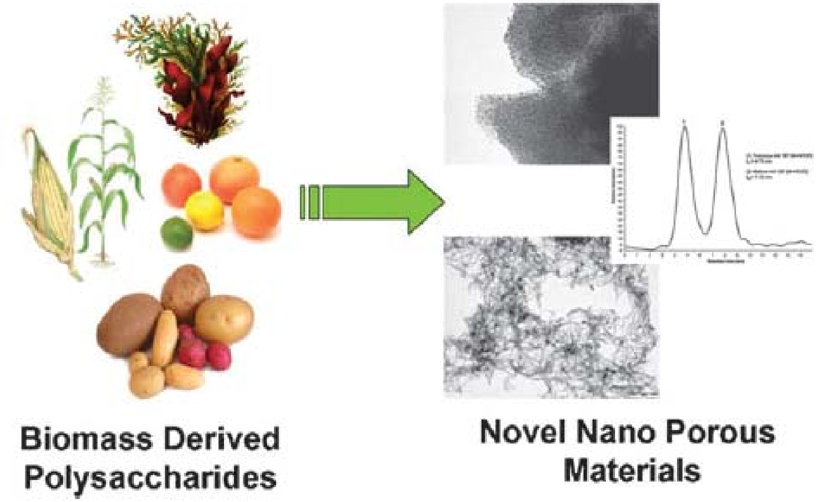
TUTORIAL REVIEW www.rsc.org/csr | Chemical Society Reviews

Tuneable porous carbonaceous materials from renewable resources

Robin J. White,[ab] Vitaly Budarin,[a] Rafael Luque,*[ac] James H. Clark*[a] and
Duncan J. Macquarrie[a]

Robin J. White

Robin White obtained his PhD at the Green Chemistry Centre of Excellence (York, UK), under the supervision of Prof. James Clark. He is currently a post-doctoral researcher at the Max Planck Institute for Colloids and Interfaces (Berlin, Germany), working with Dr Maria-Magdalena Titirici and Prof. Markus Antonietti. His research interest focuses on the development of novel sugar biomass derived porous carbons via soft templating, for applications in chromatography, electrochemistry and heterogeneous catalysis.



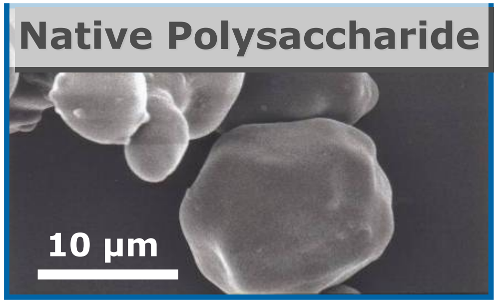
Scheme 1 Overview of research objective; transformation of non-porous native polysaccharide into useful porous carbonaceous materials.

Chem. Soc. Rev., 2009, **38**, 3401–3418

Porous polysacharides derived materials

Native Polysaccharide

- Highly functional
- Low surface area / non-porous
- Limits application potential



Gelation

Aquagel

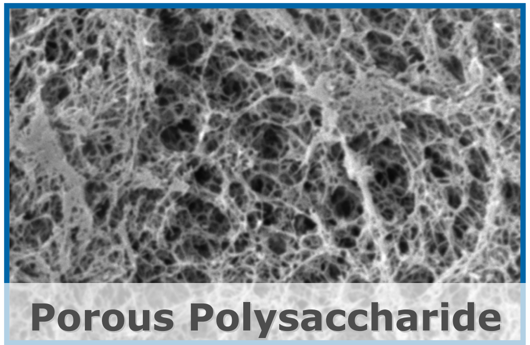
- Sol-gel process
- Entropy driven
- H-bond network formation

Polysaccharide Gel

H_2O removal

Nanoporous Material

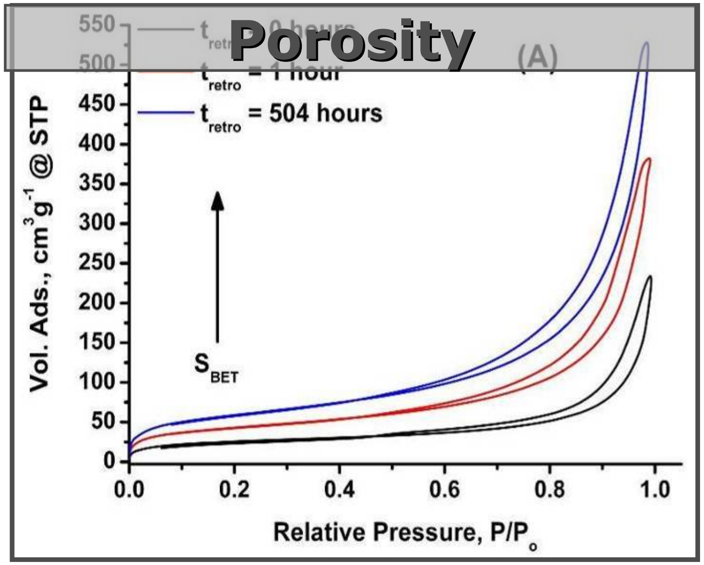
- Exchange / Drying
- $S_{BET} > 150\ m^2g^{-1}$
- $V_{pore} > 0.5\ cm^3g^{-1}$



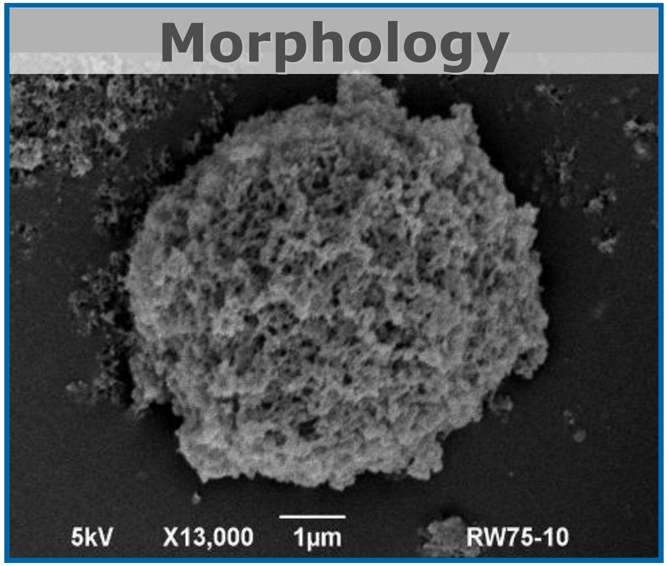
Porous polysacharides derived materials

Idea Extension

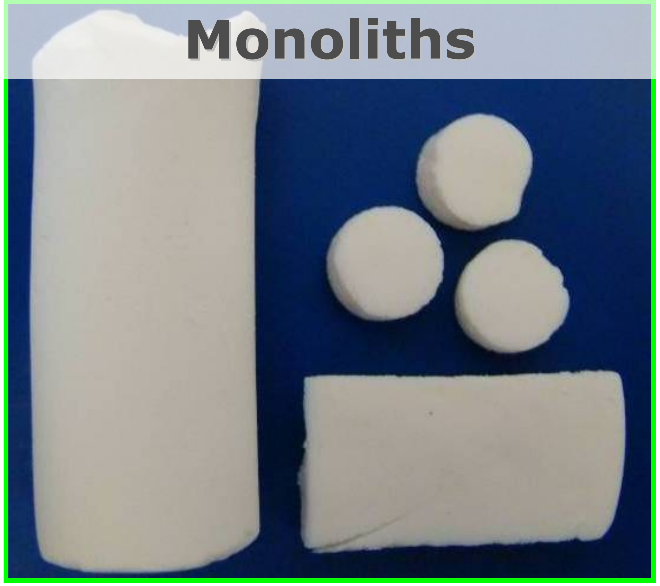
Control



Porosity



Morphology



Monoliths

- Gelation route
- Concentration
- Recrystallisation
- Additive
- Polysaccharide

Porous polysacharides derived materials

Idea

Extension

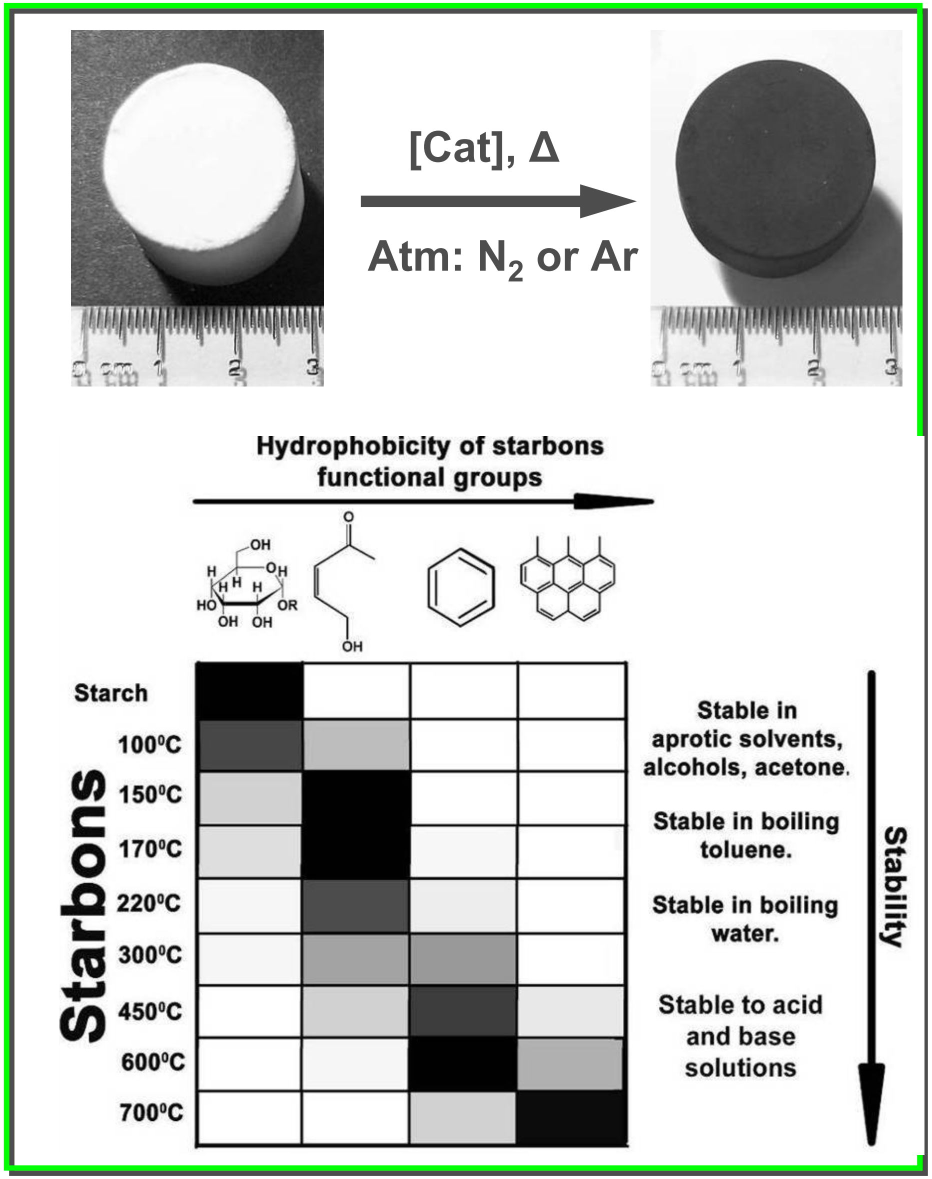
Limitations

1 **Metastable**

2 **Hygroscopic**

Solution → **Stabilisation**

Starch to Carbon: Starbons



- 1^{st} Generation starch-derived
- $[H^+]$ catalysed decomposition
- $S_{BET} \sim 300 – 550\ m^2g^{-1}$
- $V_{meso} \sim 0.4 – 0.6\ cm^3g^{-1}$
- Pore diameter; 8 – 16 nm

- *Commercially available*
- **Surface chemistry**

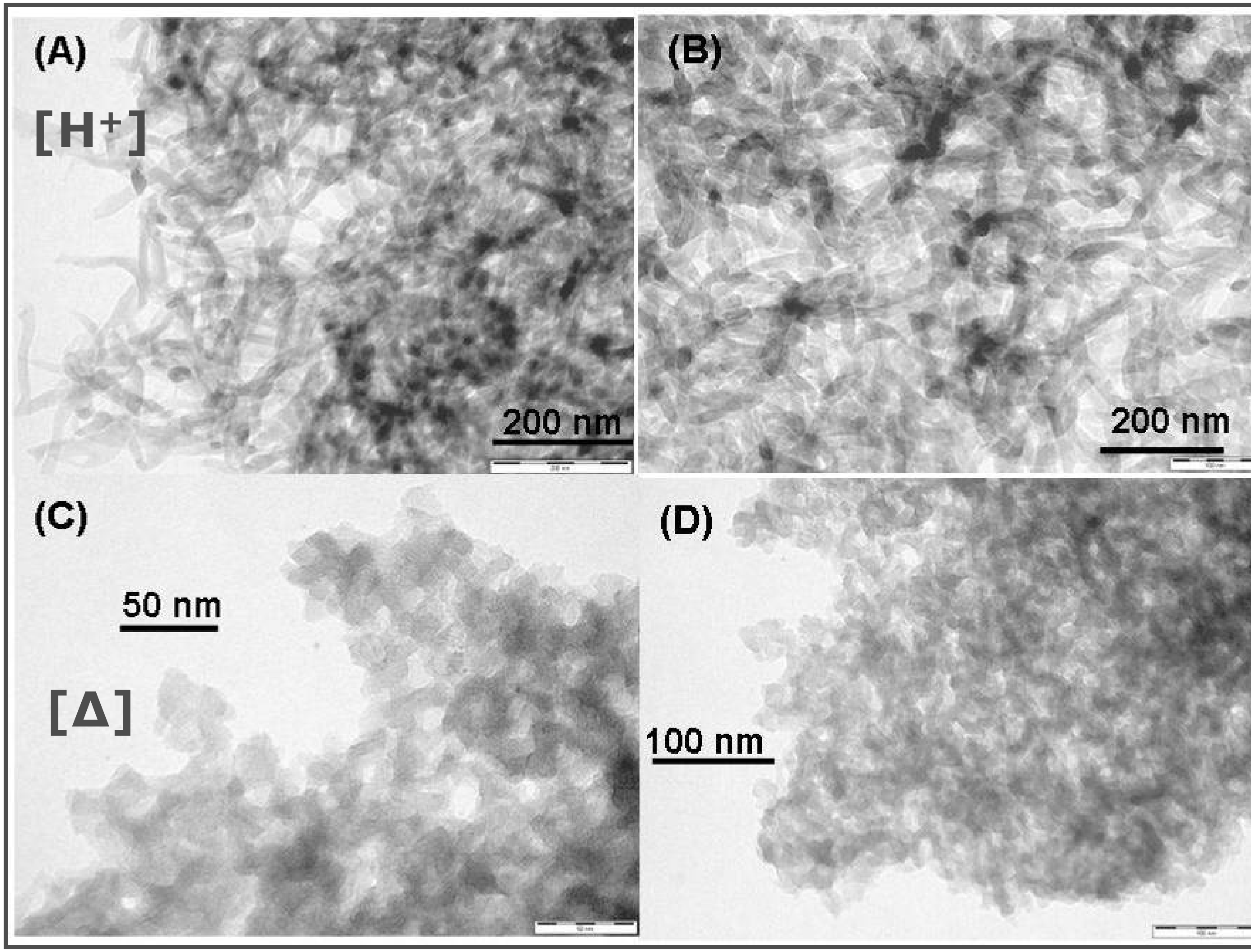
Clark at al, Angew. Chem. Int. Ed. 45, 3782-3786

2-nd Generation Starbons

Idea Extension

Development

Pectin

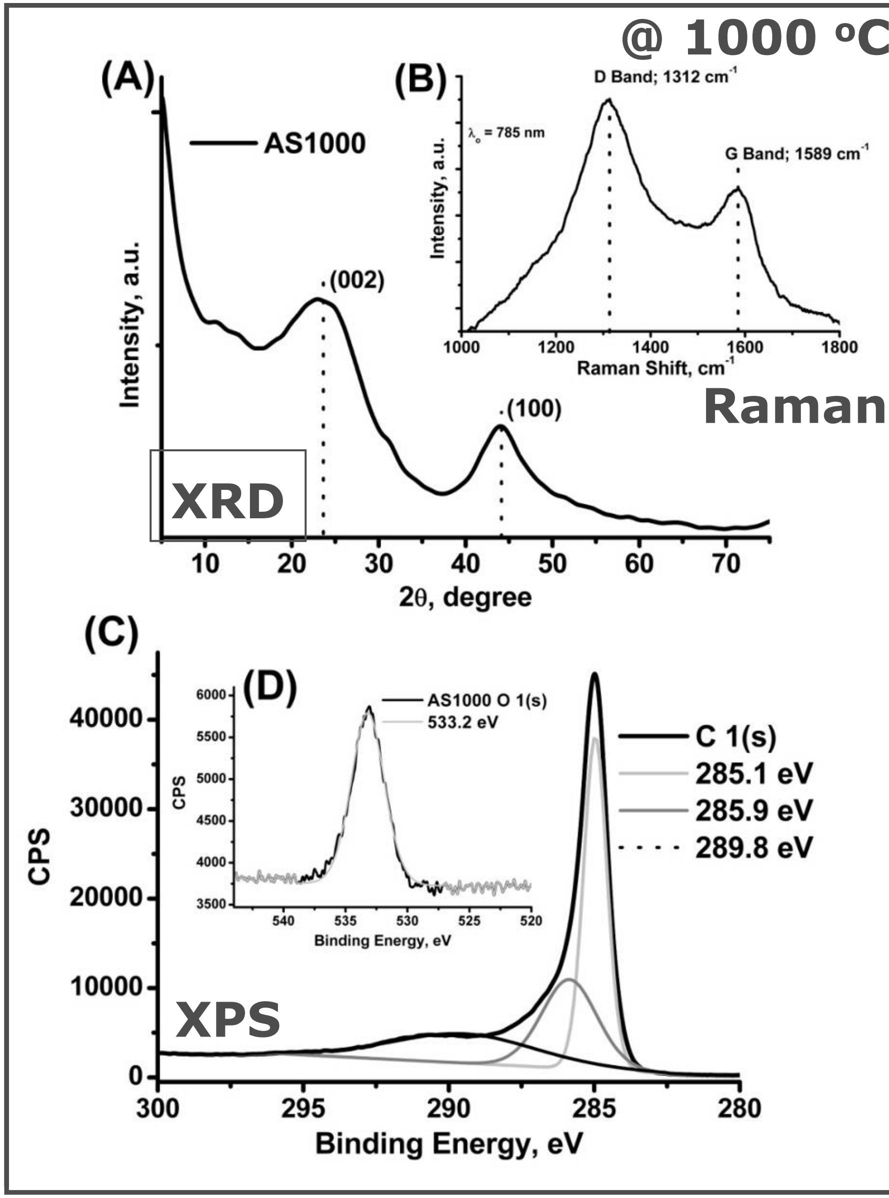


White at al, Chem. Eur. J., 2010, *16*, 4, 1326.

2-nd Generation Starbons

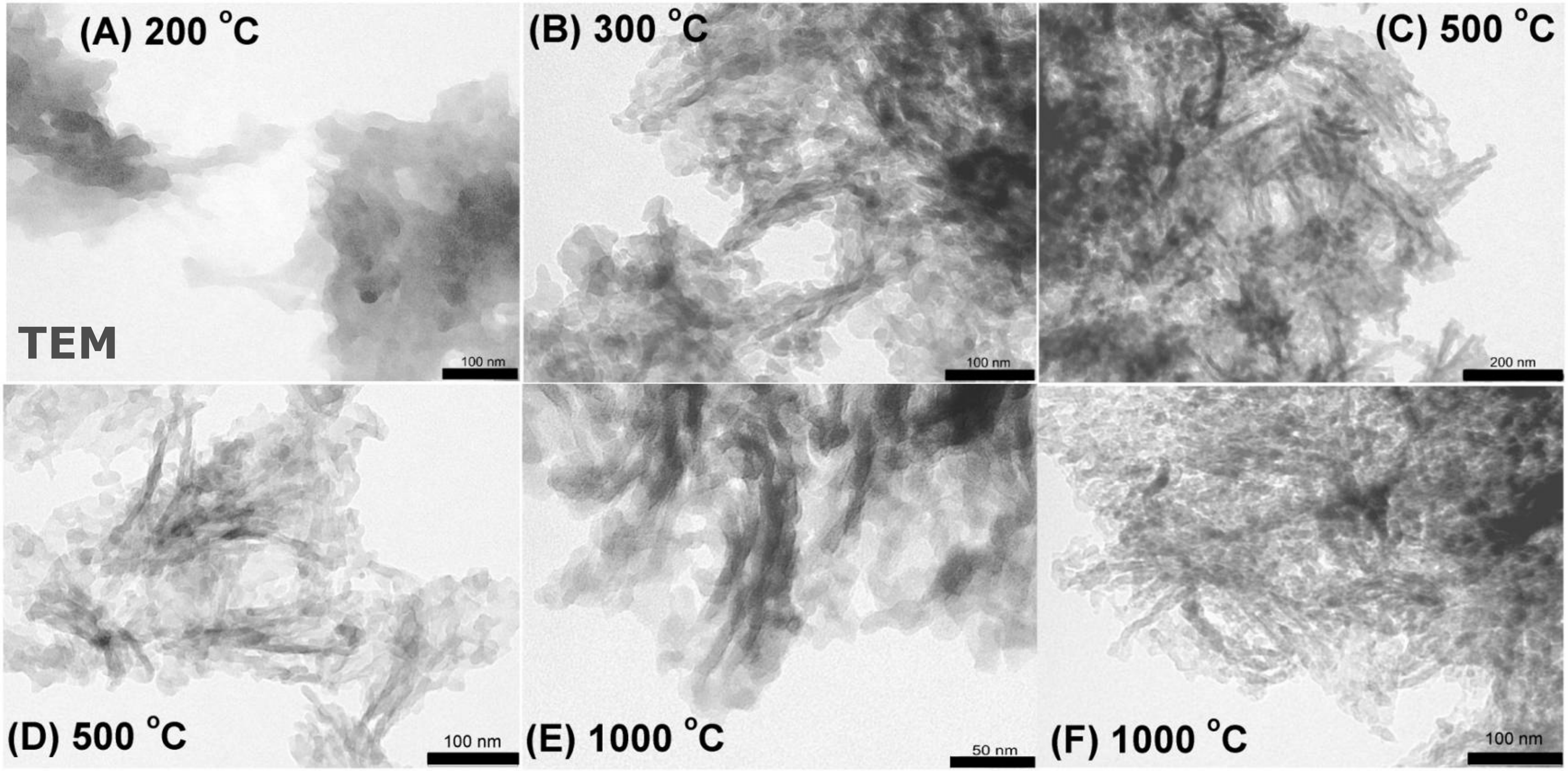
Alginic Acid

- Seaweed-derived
- *M + G block copolymer*
- pK_a ~ 3.0 - 3.8
- Direct conversion
- S_{BET} > 200 m^2g^{-1} / V_{meso} > 1 cm^3g^{-1}
- Pore diameter > 14 nm
- Highly functional high mesopore volume materials
- Stable at high temperatures (e.g. 1000 °C)



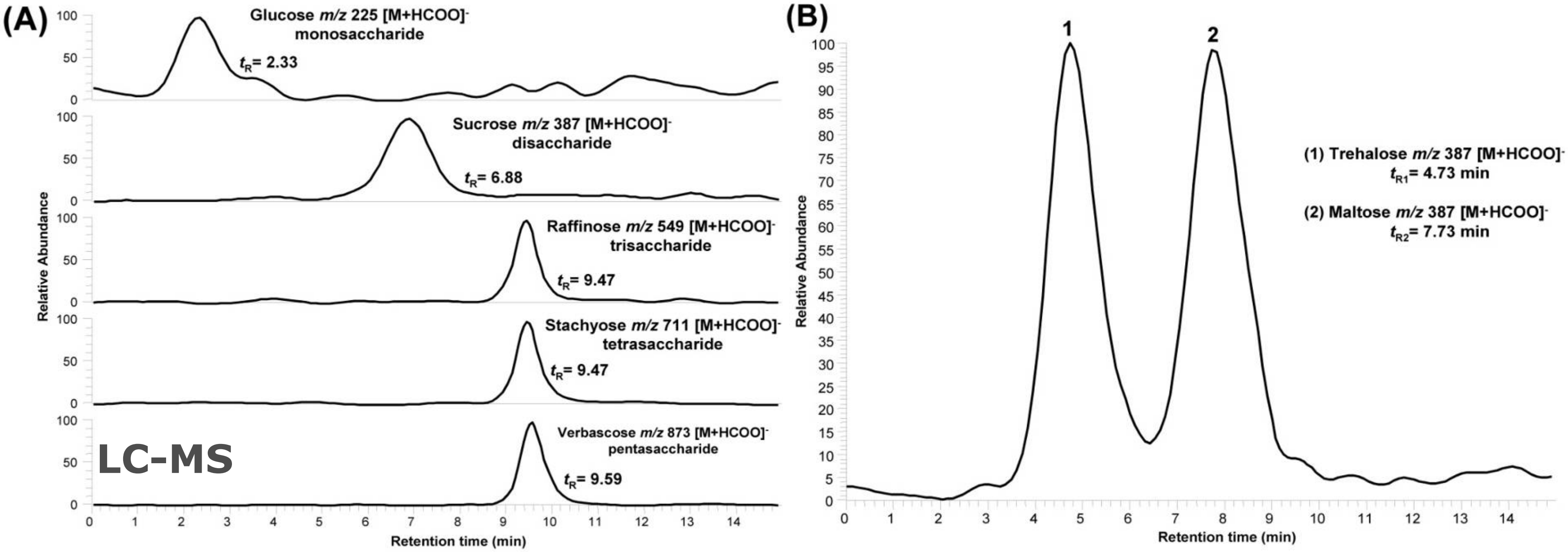
White at al, Adv. Funct. Mater., 2010, *20*, 11, 1834.

2-nd Generation Starbons



- Layered hierarchical tectonic slit structure
- Bulk decomposition event ($< 200\ ^{o}C$)
- Limited micropore content ($V_{micro} < 0.06\ cm^3g^{-1}$)

Applications of Starbons- HPLC Stationary Phases



Separation of Polar Sugars

- A challenge on conventional phases (e.g. $[SiO_2]_x$- C18)
- Porous graphitised carbon ((PGC) Hypercarb®) (Knox *et al*.)
- Multistep, high T synthesis ➔ No scope for π character control
- Successful separation of polar sugars and disaccharide isomers!

Applications of Starbons-aqueous phase esterifications

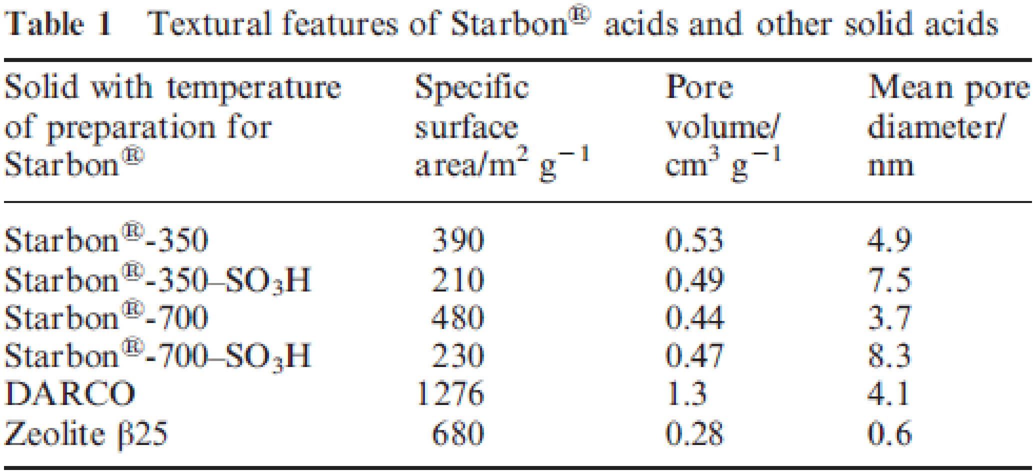
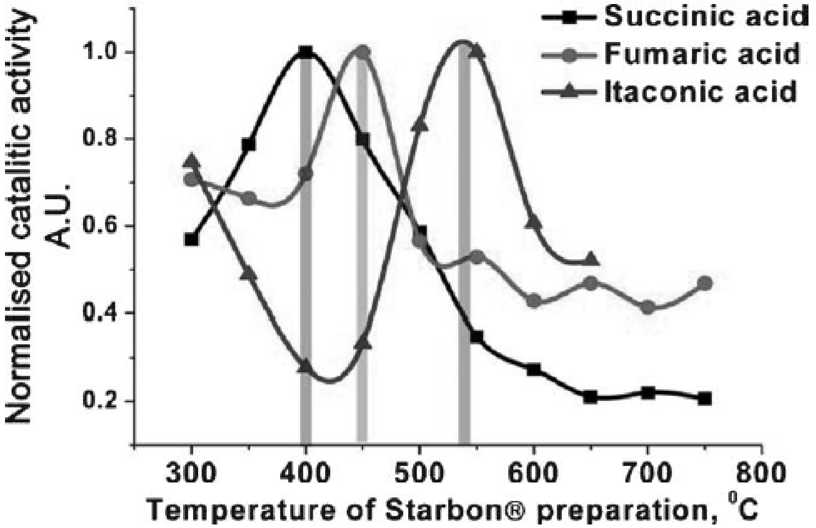


Table 1 Textural features of Starbon® acids and other solid acids

Solid with temperature of preparation for Starbon®	Specific surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}	Mean pore diameter/ nm
Starbon®-350	390	0.53	4.9
Starbon®-350–SO$_3$H	210	0.49	7.5
Starbon®-700	480	0.44	3.7
Starbon®-700–SO$_3$H	230	0.47	8.3
DARCO	1276	1.3	4.1
Zeolite β25	680	0.28	0.6



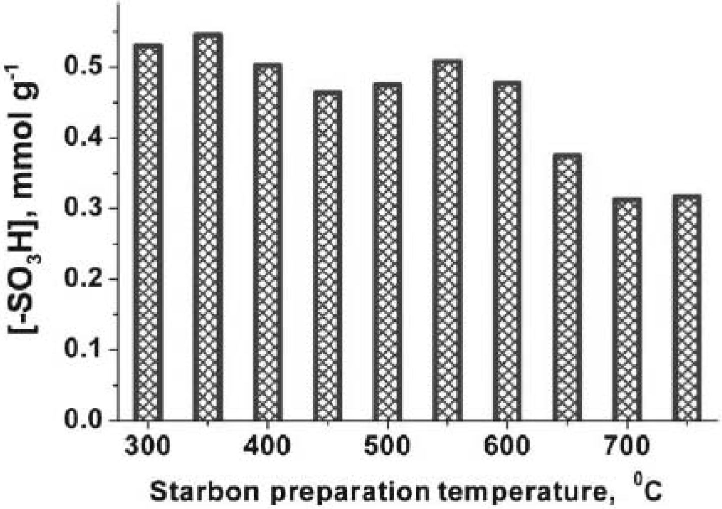


Fig. 2 Influence of Starbon® temperature preparation on the active acid sites (–SO$_3$H, mmol g^{-1}) loading measured by TG-IR.

- **Normalised catalytic activity of Starbon acids in the esterification of succinic, fumaric and itaconic acids depending of the parent Starbon preparation temperature**
- **Maximum catalytic activities were: succinic acid (400°C, k = 32 x10^{-5} s^{-1}); fumaric acid (450 °C, k = 5x 10^{-5} s^{-1}); itaconic acid (550°C, k = 15.4x10^{-5} s^{-1})**

Clark at al, Green Chem., 2007, 9, 992–995

OUTLINE

- Introducing the green chemistry concept

- Sustainable Carbon

1. Biomass derived nanotructured carbon materials with valuable applications

    1.1 Bottom up approach: Porous Carbohydrates

    1.2 Top down approach: Hydrothermal Carbonization

2. Biochar production for CO_2 sequestration and soil regeneration

- Conclusions

Hydrothermal Carbonization of Biomass (HTC)

TUTORIAL REVIEW www.rsc.org/csr | Chemical Society Reviews

Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization

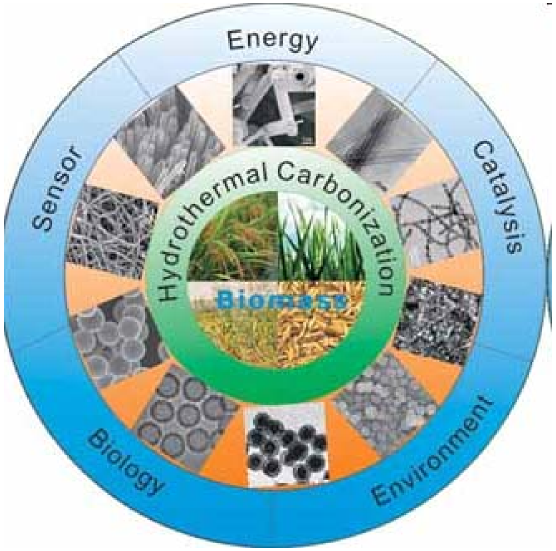
Maria-Magdalena Titirici* and Markus Antonietti

Chem. Soc. Rev., 2010, **39**, 103–116

Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass

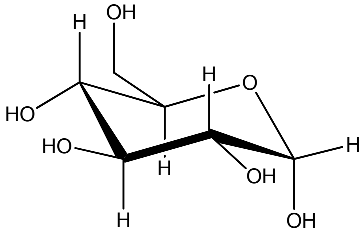
By *Bo Hu, Kan Wang, Liheng Wu, Shu-Hong Yu,* Markus Antonietti*, and *Maria-Magdalena Titirici**

Adv. Mater. **2010**, *22*, 1–16



HYDROTHERMAL CARBONIZATION

INPUT



“Sugars”

(e.g. D-Glu)

Biomass

- Mild conditions:
  - T ~ 130 - 200 °C,
  - P < 10 bar.
  - H_2O solvent

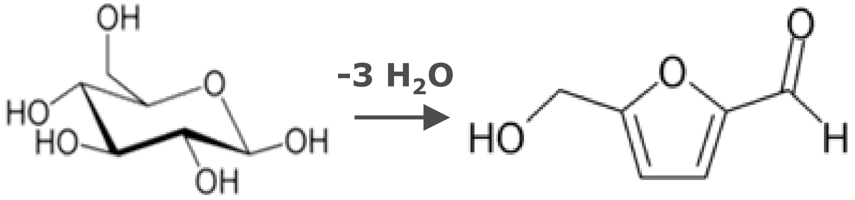
OUTPUT

- Uniform spherical particles
- Functional surfaces (e.g. -OH, -C=O, -C(O)OH)
- Hydrophilic *vs*. Hydrophobic
- Carbon sequestration

F. Bergius, *Knapp, Halle/Saale, 1913*
Antonietti et al., *New J. Chem.*, 2007, 6, 787

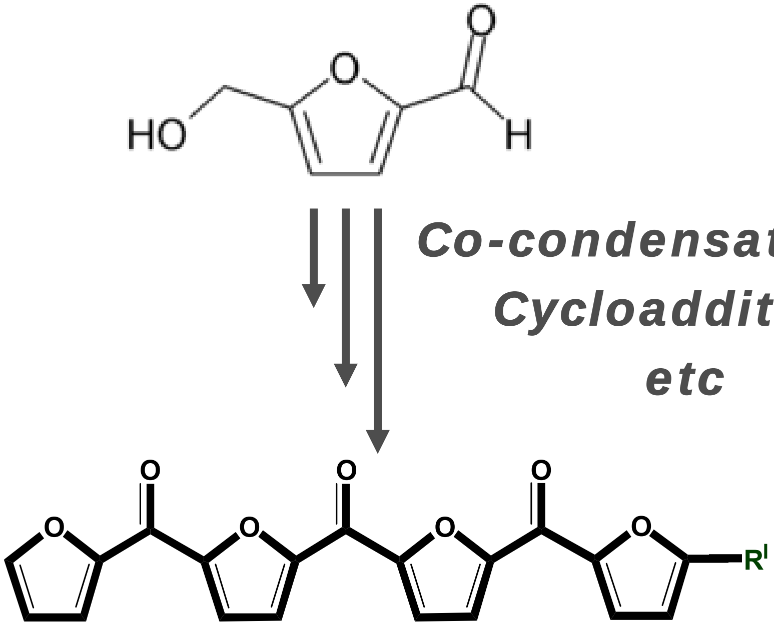
HYDROTHERMAL CARBONIZATION

1) Dehydration



D-Glu **HMF**

2) Polymerisation

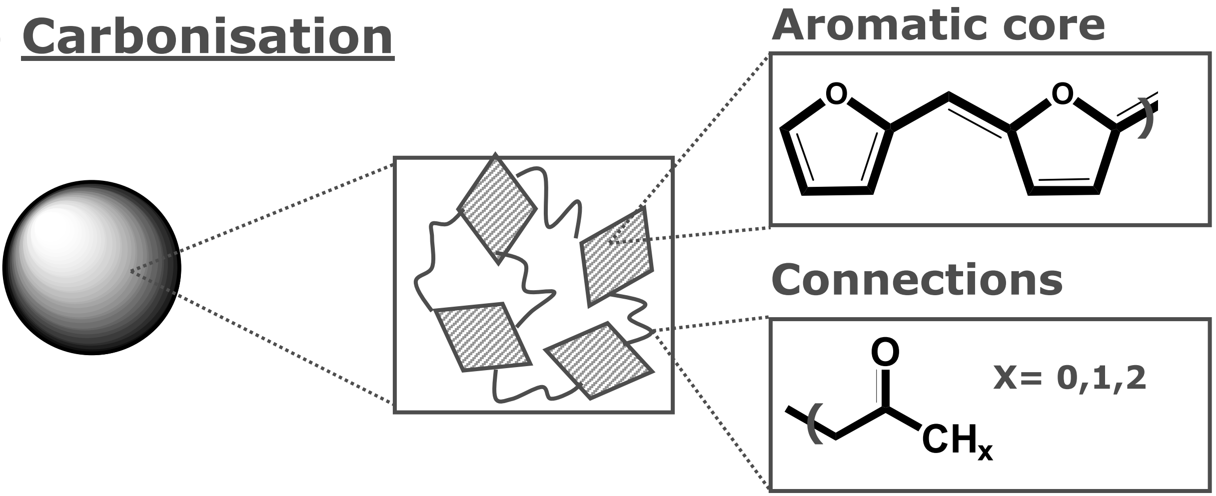


Co-condensation / Cycloaddition etc

"Idealised Structure"

HYDROTHERMAL CARBONIZATION

3) Carbonisation



Aromatic core

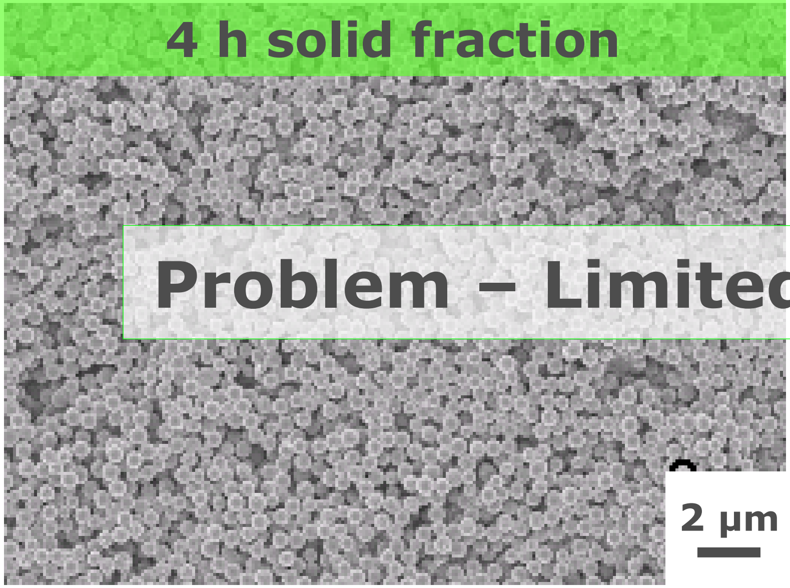
Connections

X= 0,1,2

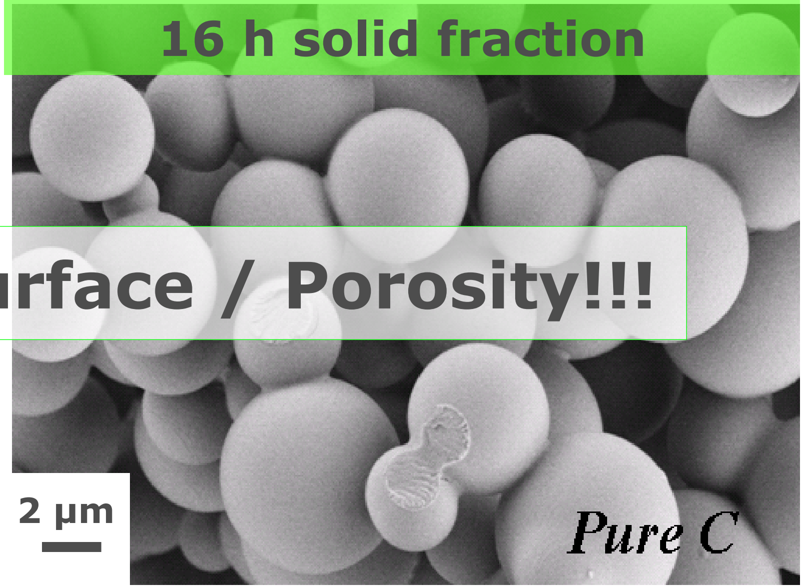
≥ 16 h

%C = 70

%O = 25



4 h solid fraction

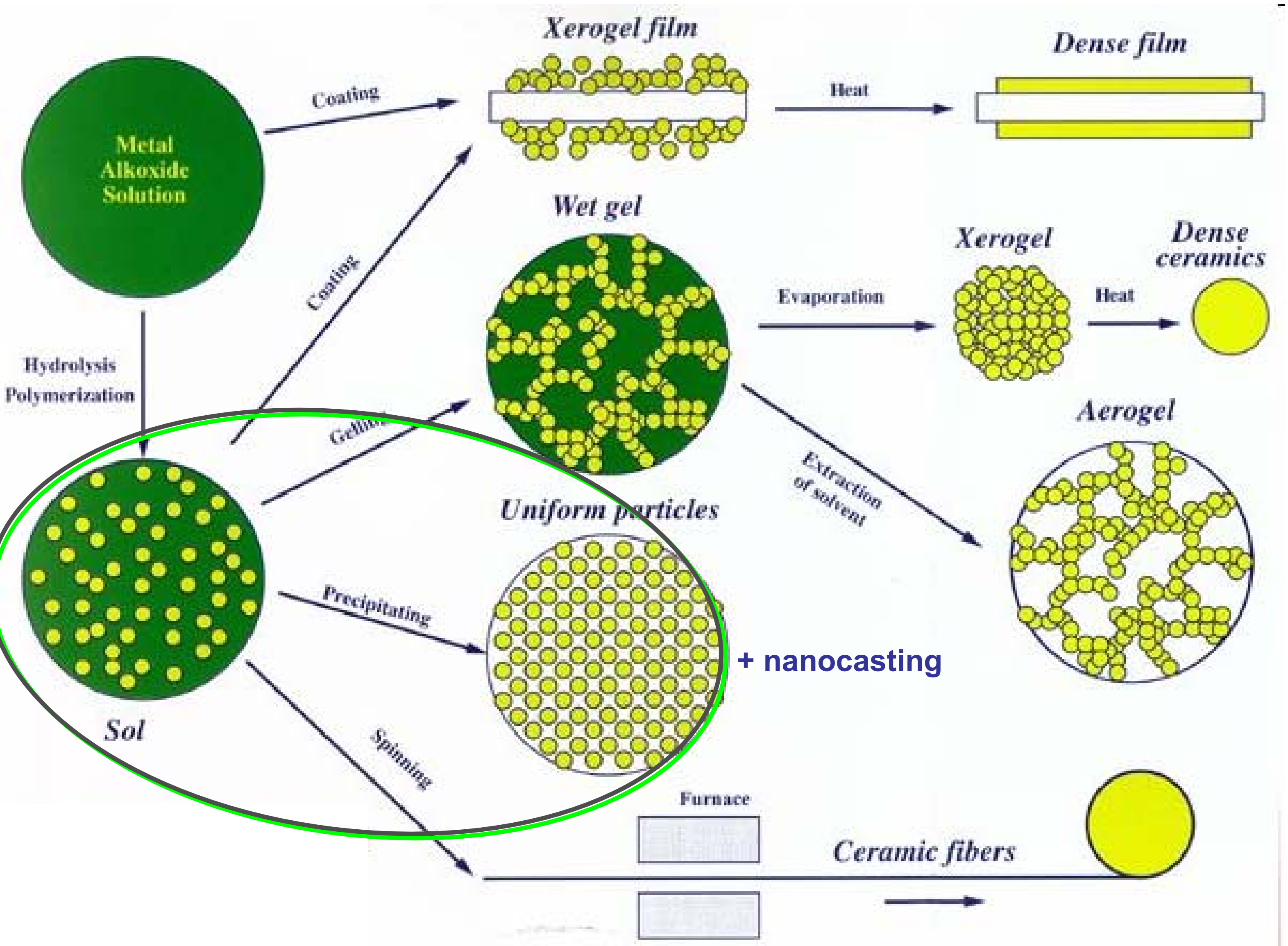


16 h solid fraction

Problem – Limited Surface / Porosity!!!

Titirici *et al.*, *J. Phys. Chem. C*, 2009, 113, 22, 9644

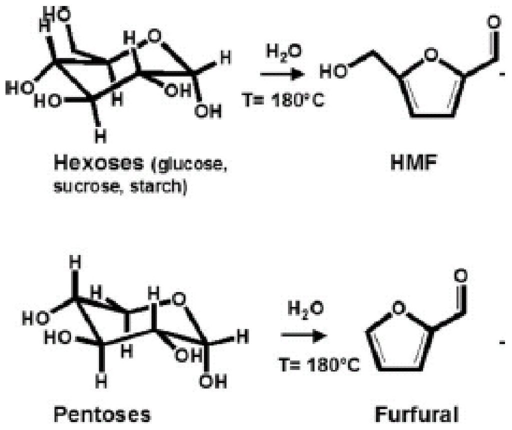
HTC~ Sol Gel: Chemie Douce de Carbon

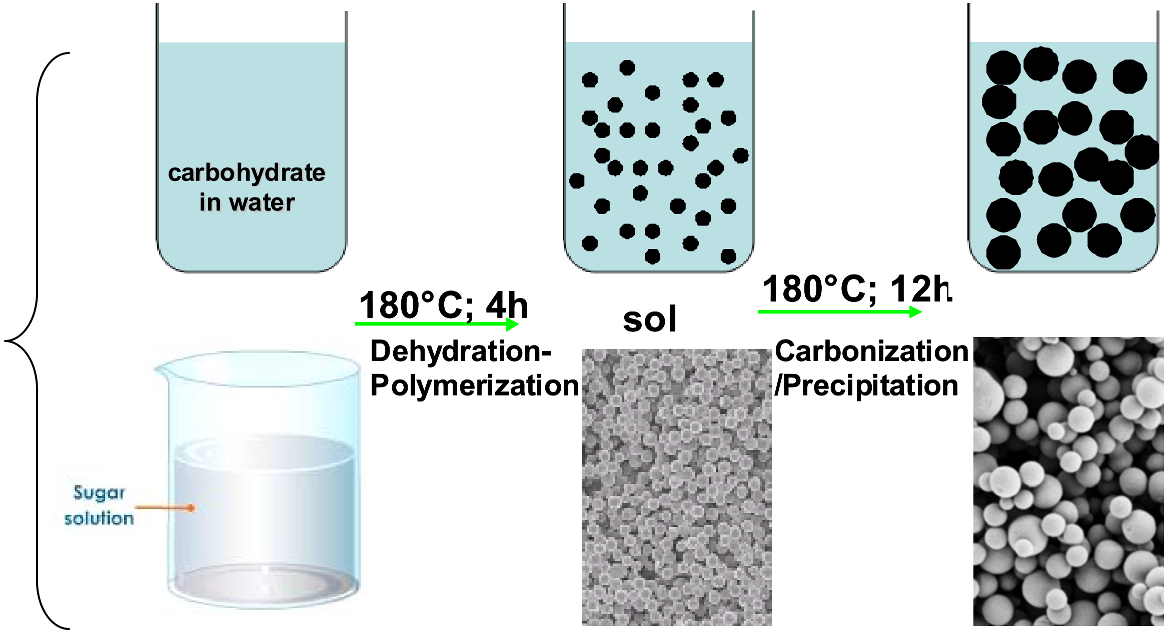


+ nanocasting

Titirici at al C. R. Chimie 13 (2010) 167–173

Uniform Particles via HTC





carbohydrate in water

180°C; 4h

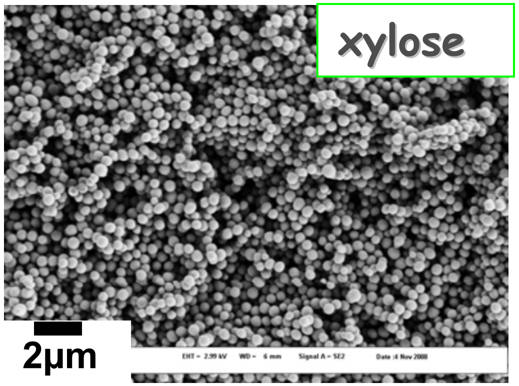
Dehydration-Polymerization

sol

180°C; 12h

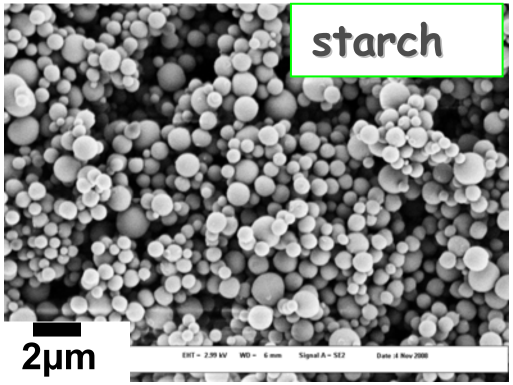
Carbonization /Precipitation

Sugar solution



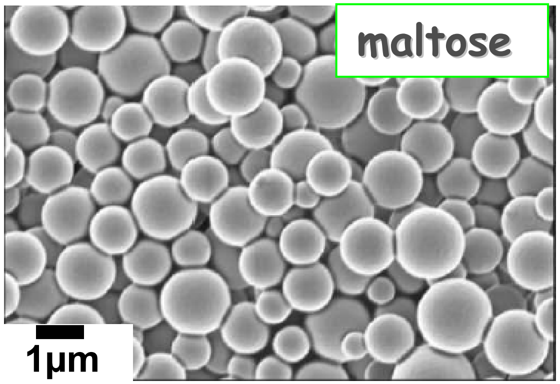
xylose

2μm



starch

2μm



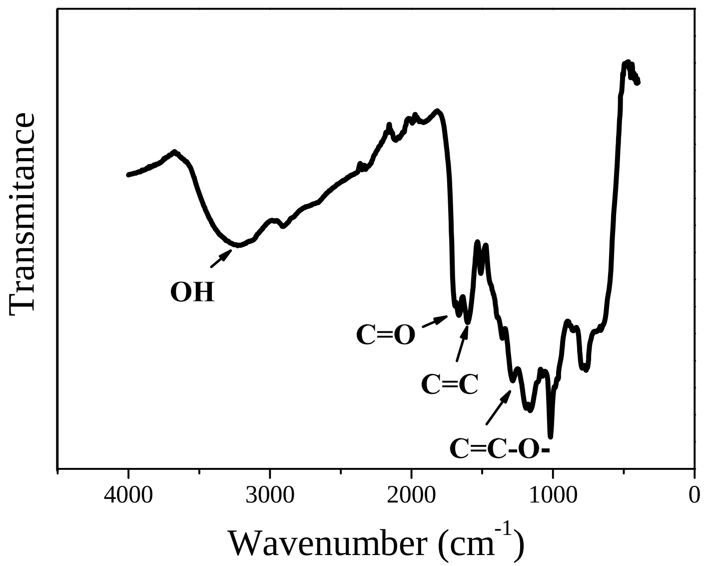
maltose

1μm

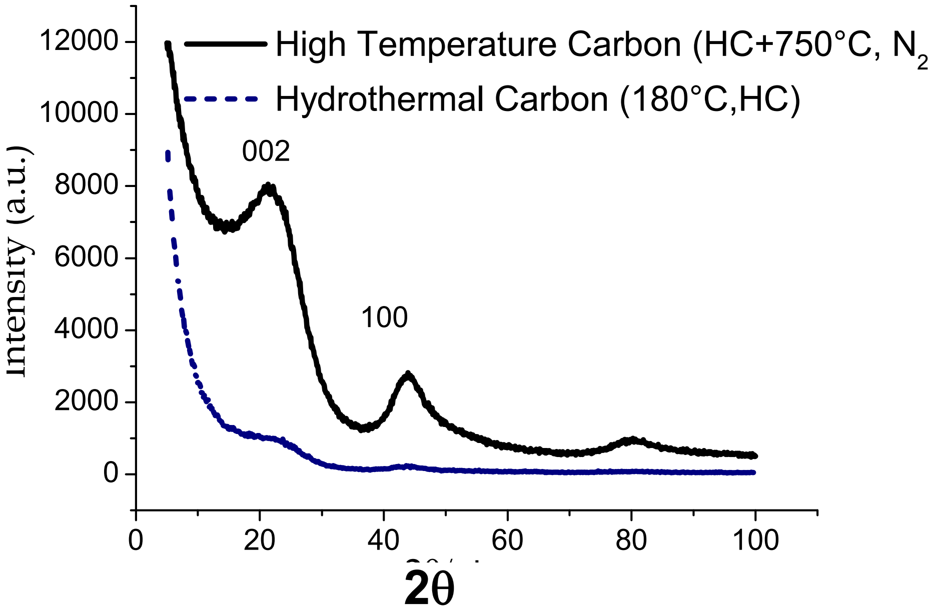
Titirici, *Green. Chem.*, **2008**, *10*, 1204

Characterization of HTC Particles

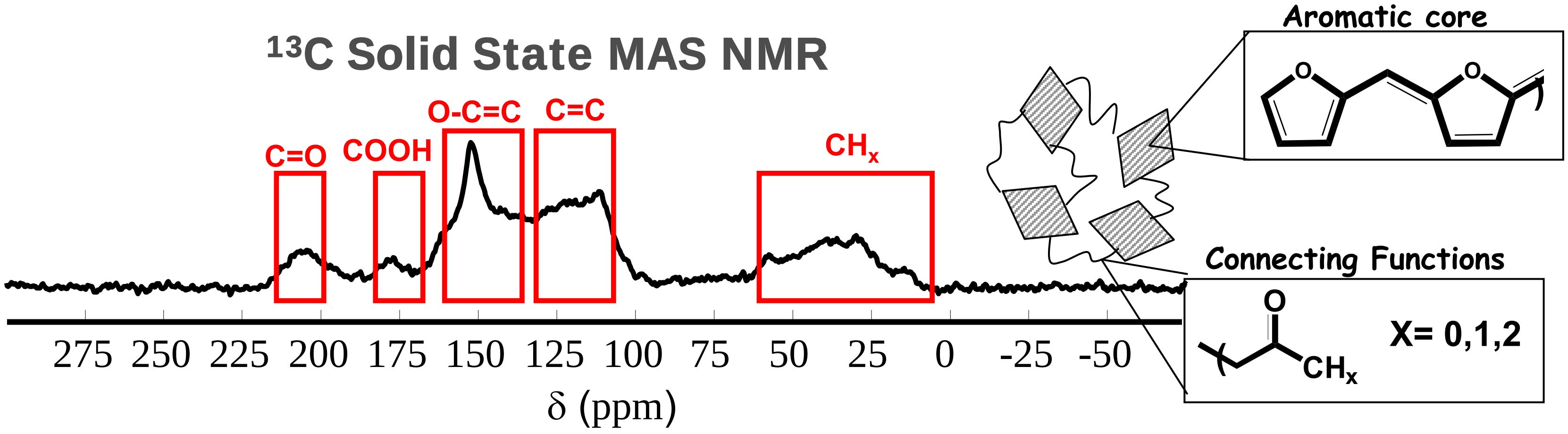
FT-IR



XRD



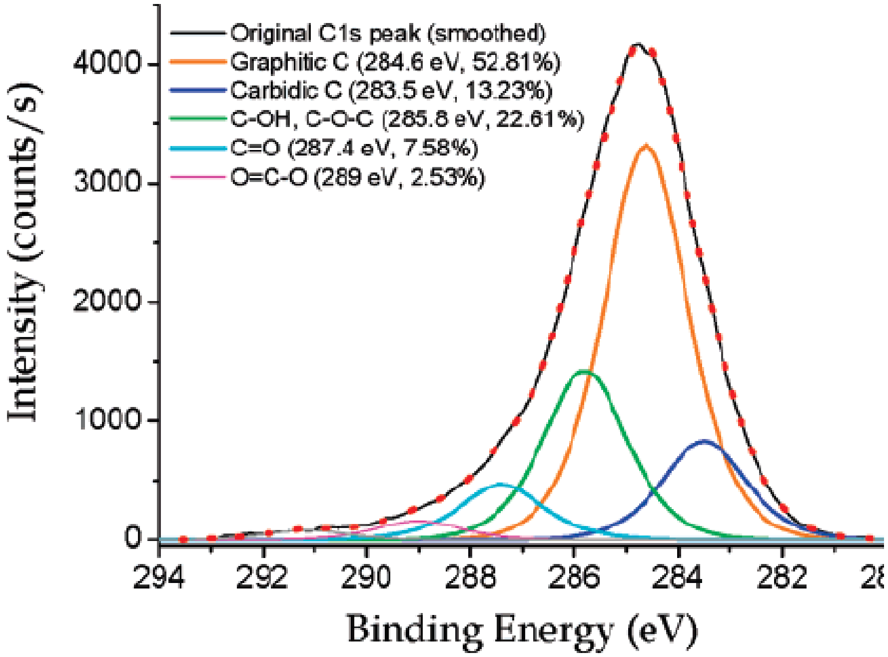
^{13}C Solid State MAS NMR

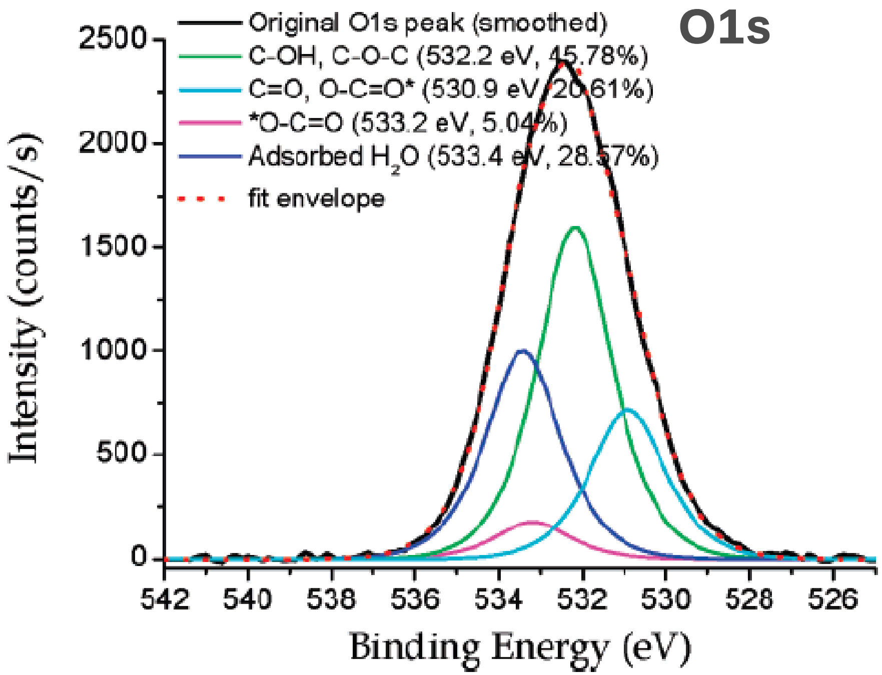


N. Baccile, *J. Phys. Chem. C*, **2009,** *113,* 9644

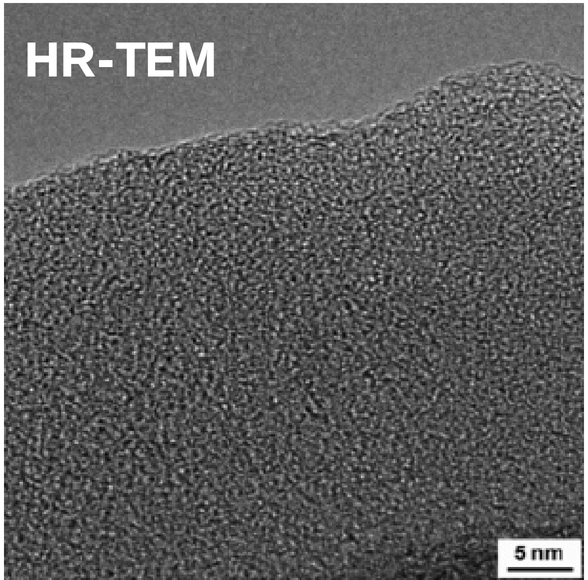
Characterization of HTC Particles

C1s **XPS**





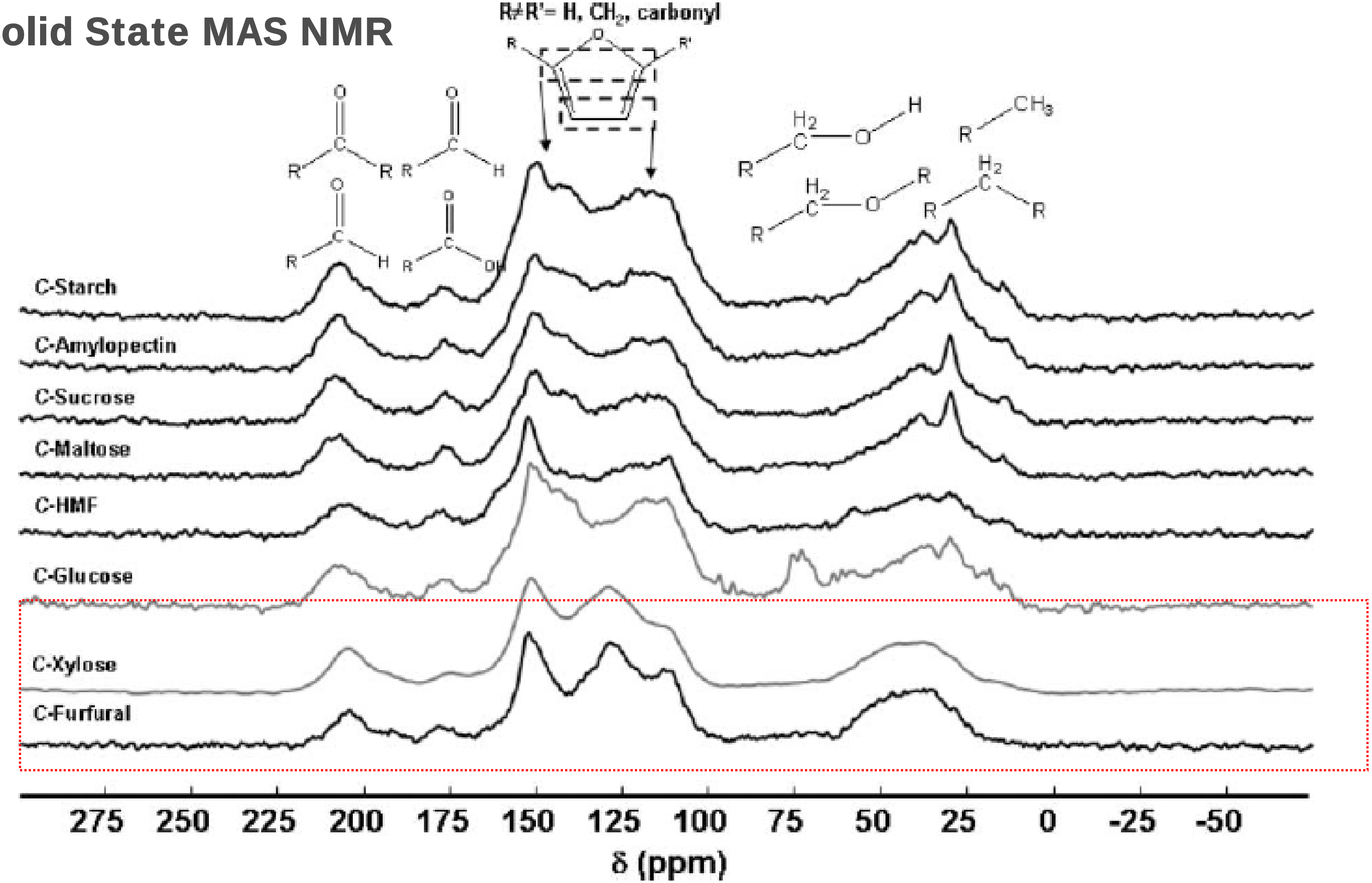
EELS



Characterization of HTC Particles

Comparison of different carbon precursors

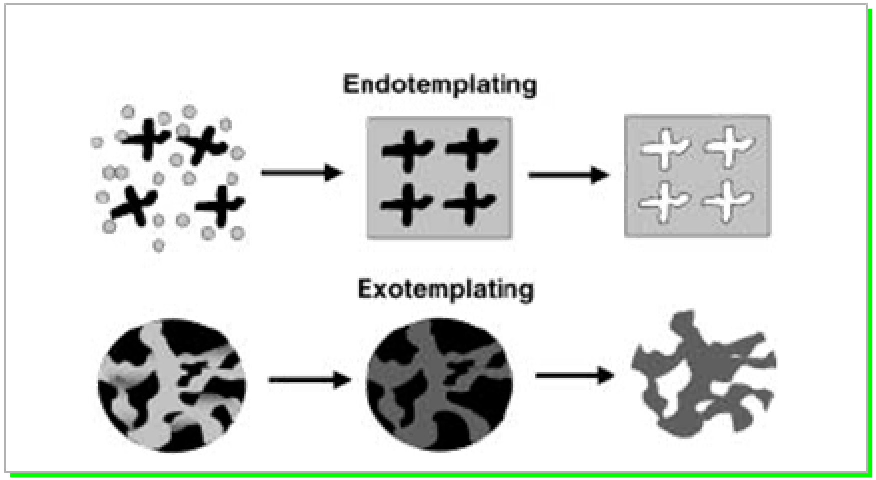
^{13}C Solid State MAS NMR



Titirici, *Green. Chem.*, **2008**, *10*, 1204

Introducing Porosity in HTC Materials

In sol-gel materials:



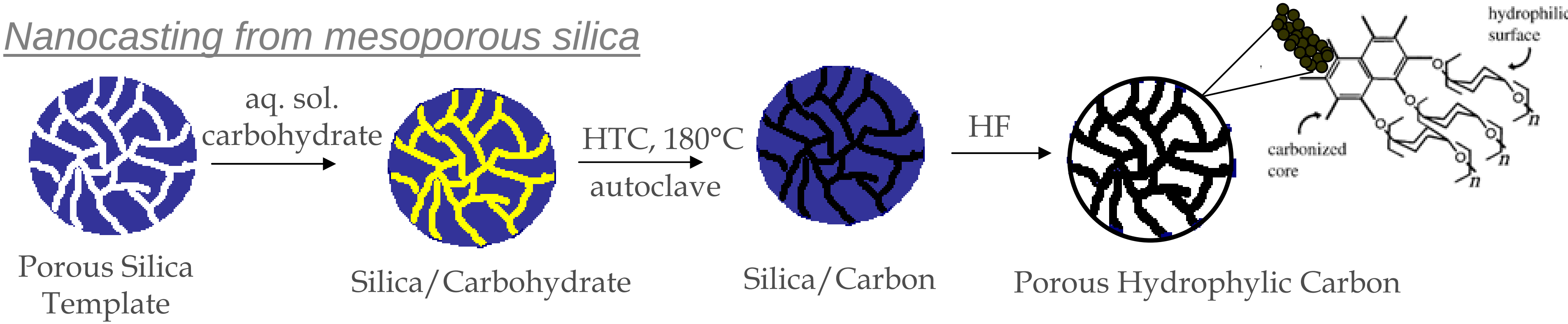
Template occluded in the forming solid → SOFT TEMPLATING

Porous solid is infiltrated with precursor for another solid → HARD TEMPLATING

same in HTC…..

Hard Templating in HTC

Nanocasting from mesoporous silica



aq. sol. carbohydrate →

HTC, 180°C → autoclave

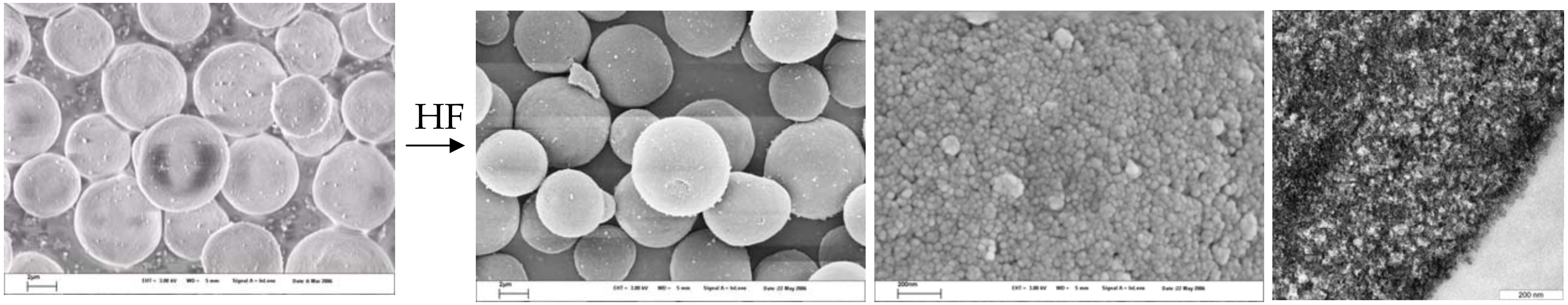
HF →

Porous Silica Template

Silica/Carbohydrate

Silica/Carbon

Porous Hydrophylic Carbon

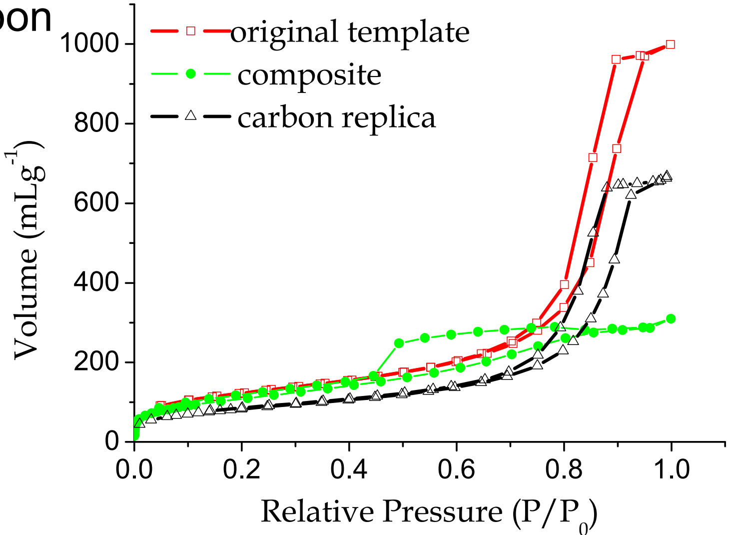


HF →

Silica

Carbon

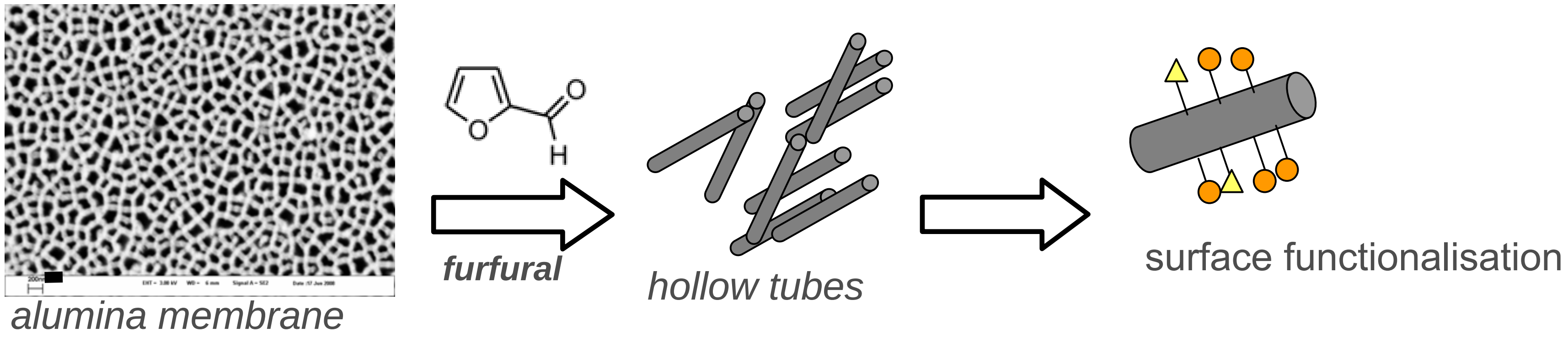
- **functional groups on the surface (OH, COOH)**
- **possibility of further functionalization**
- **tuneable functionality with temperature**
- **potential stationary phase in chromatography**



Titirici et al, Adv. Funct. Mater. **2007**, *17*, 1010–1018

Hard Templating in HTC

Nanocasting from macroporous alumina membrane

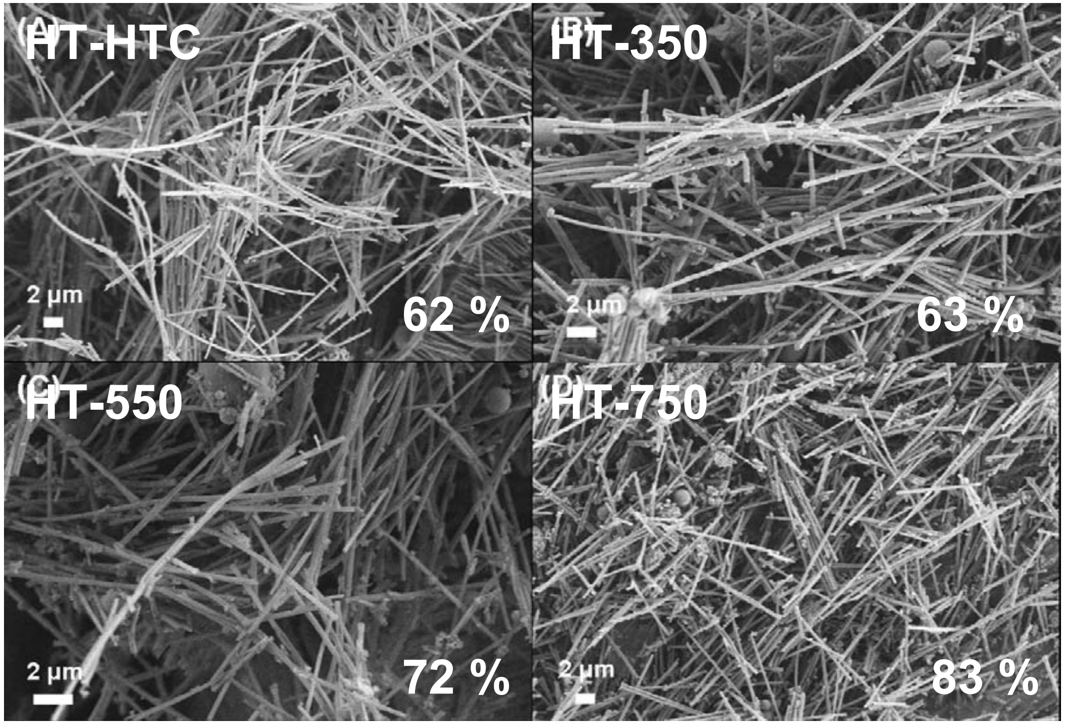


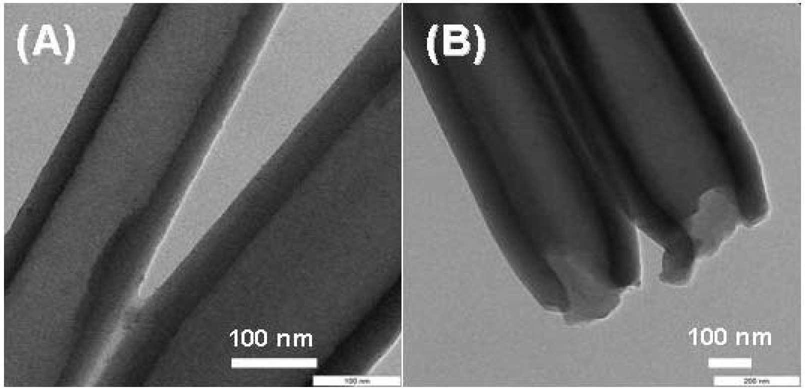
alumina membrane

furfural

hollow tubes

surface functionalisation





Titirici et al, Chem. Mater, 2010-accepted

Soft Templating in HTC

EO_{106}-PO_{70}-EO_{106} (BASF F127®) dissolved in water

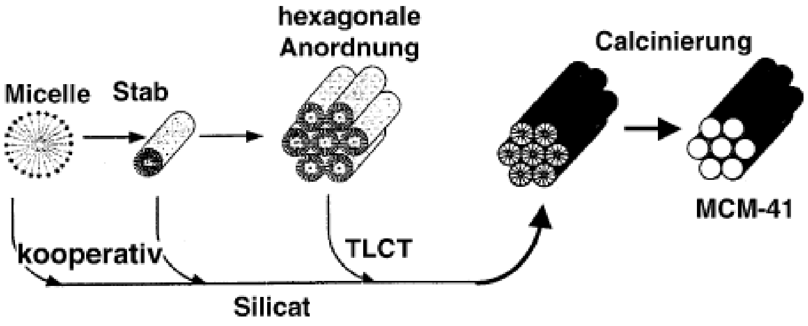
Fructose added

Autoclave HTC at 130 ^{0}C

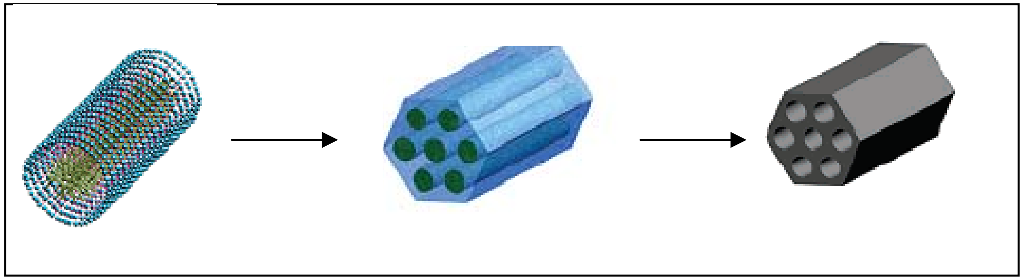
Precipitate recovered and dried

Calcined at 550 ^{0}C under N_2 for template removal

In sol-gel materials:



Same in HTC



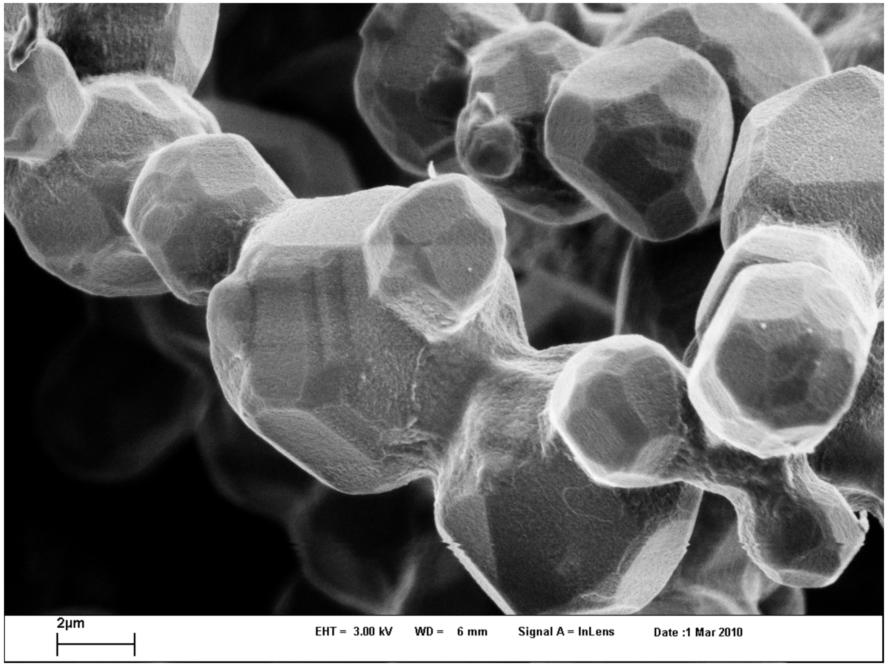
Ordered micelle

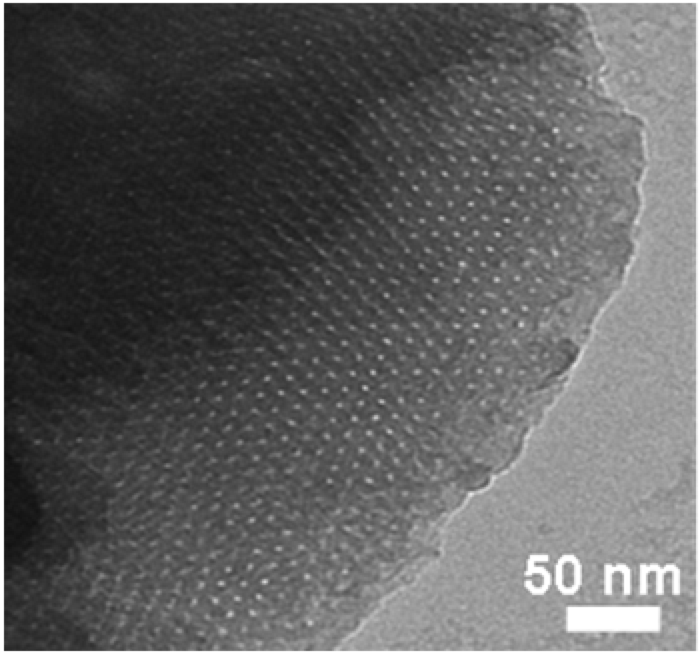
Micelle-carbon composite

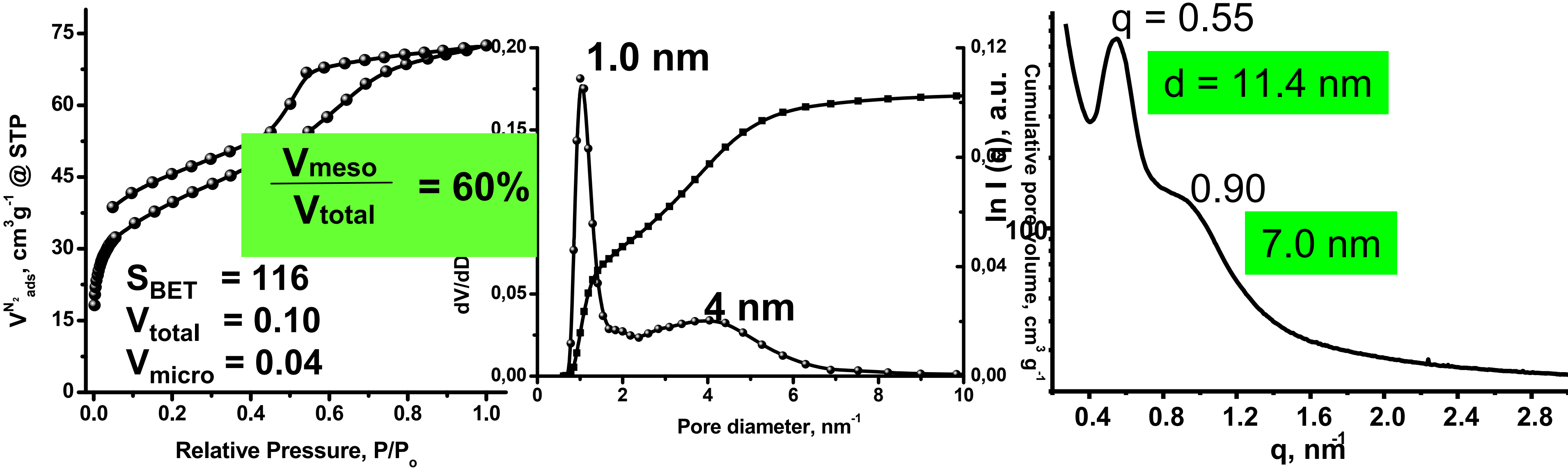
Carbon with Ordered pores

Titirici et al, Chem. Com, 2010-submitted

Soft Templating in HTC







$\frac{V_{meso}}{V_{total}}$ = 60%

S_{BET} = 116

V_{total} = 0.10

V_{micro} = 0.04

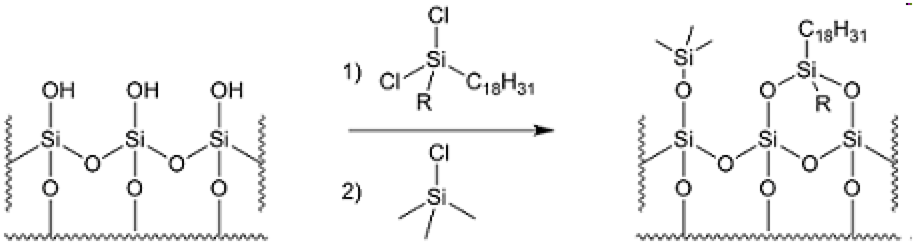
d = 11.4 nm

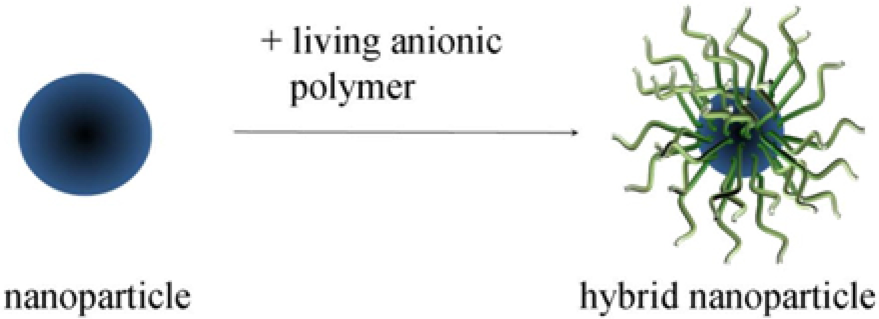
7.0 nm

Functionalization of HTC particles

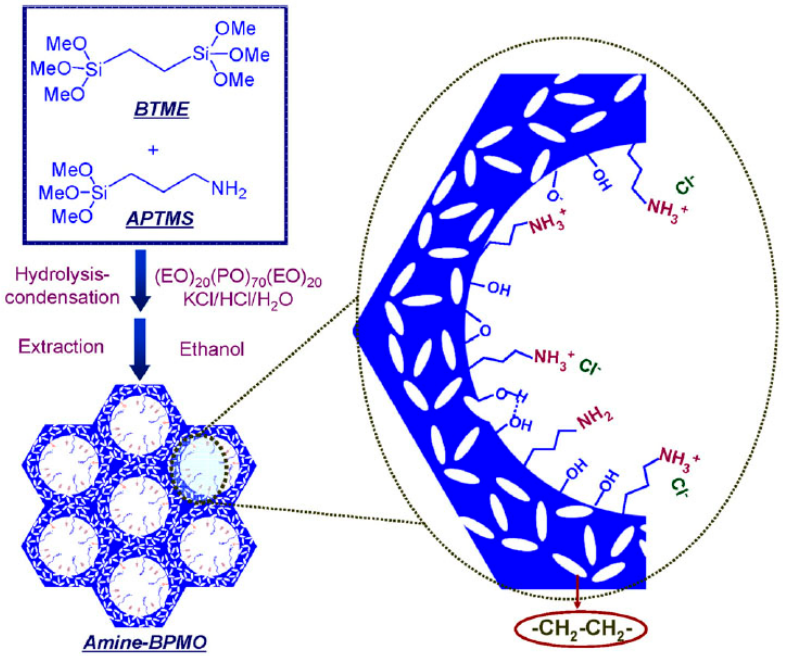
In sol-gel process:

a) Post functionalization





b) In situ functionalization

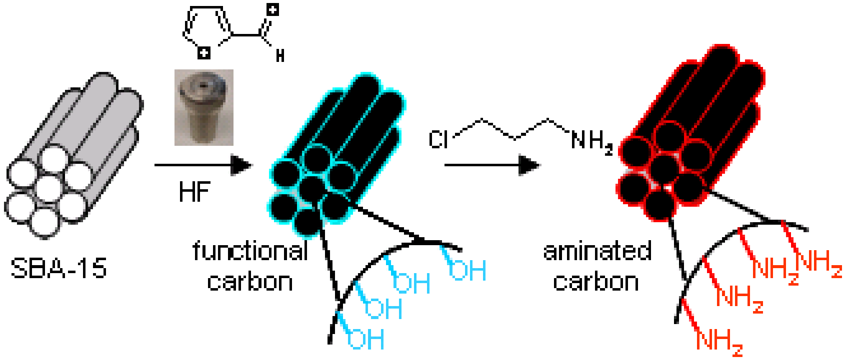


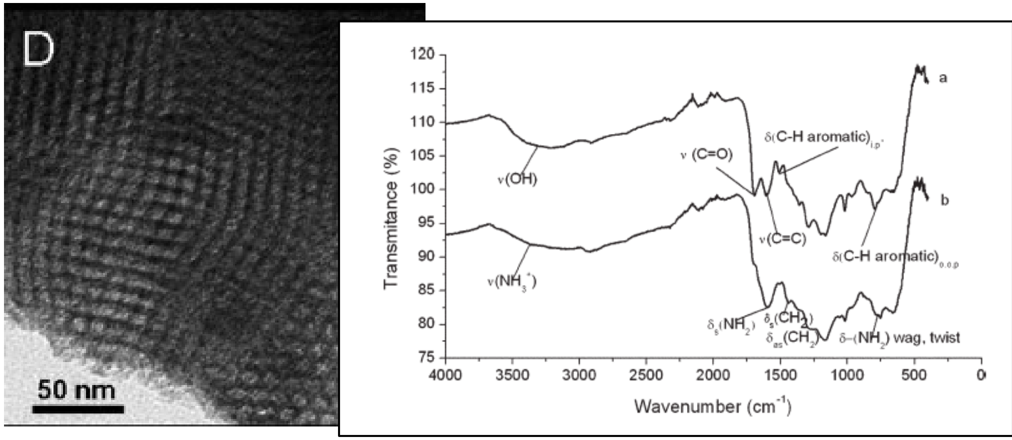
the same in HTC process

Functionalization of HTC particles

Post functionalization approach

a) Post functionalization with amono groups

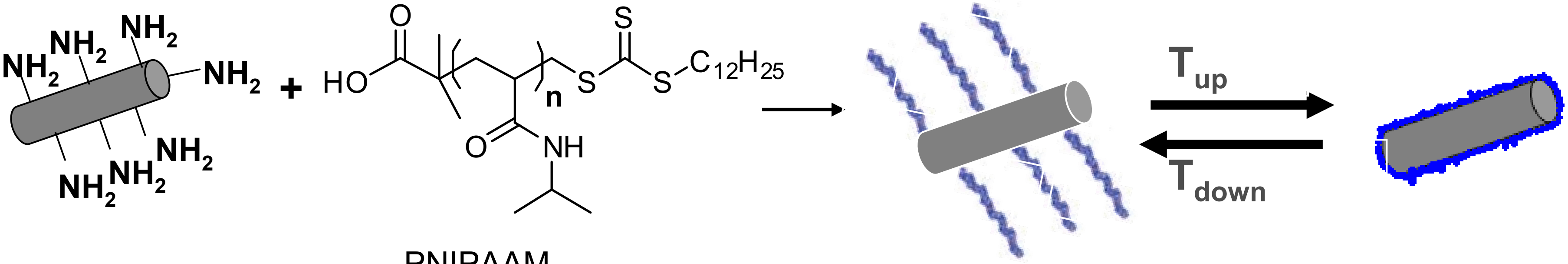




Titirici et al, J. Mater. Chem., 2007, 17, 3412–3418

b) Post functionalization with polymer chains

Stimuli responsive carbon

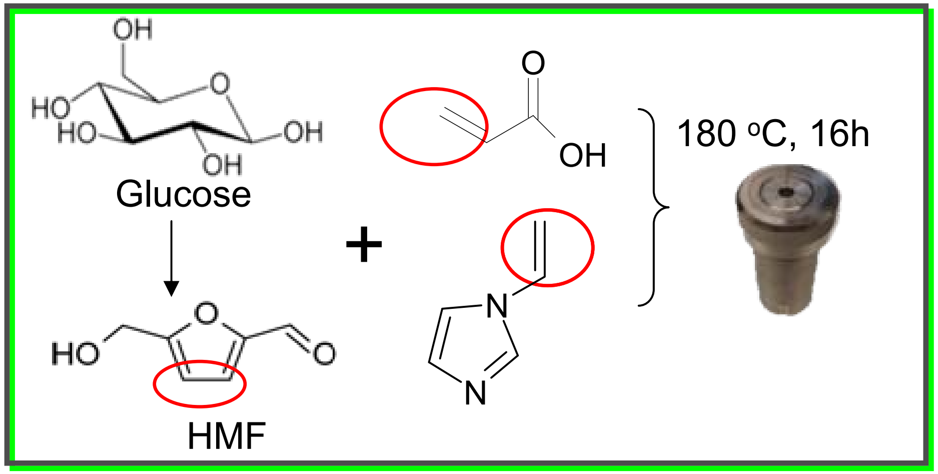


PNIPAAM

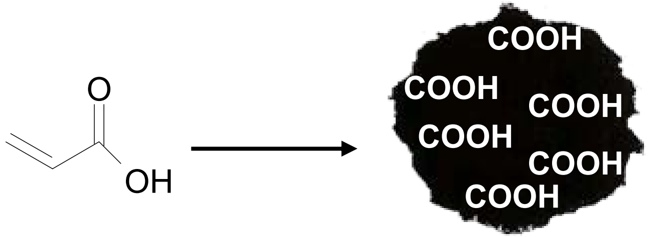
Titirici et al, Chem. Mater, 2010, accepted

Functionalization of HTC particles

In situ functionalization with organic monomers

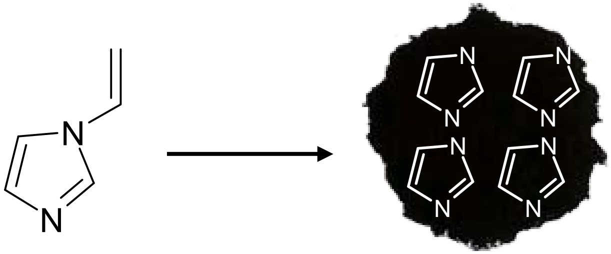


Acrylic Acid (AcA)



Carboxylate Functionalized Hydrothermal Carbon

Vinyl Imidazole (Im)



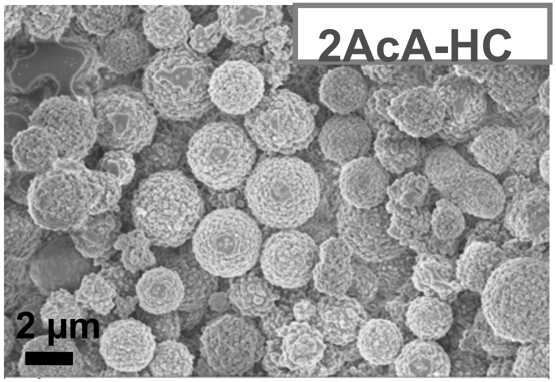
Imidazole Functionalized Hydrothermal Carbon

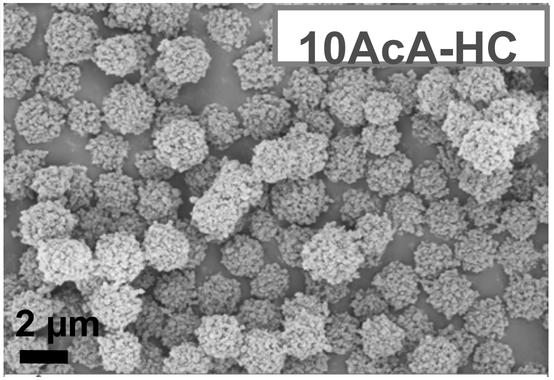
Titirici et al.,Chem. Materials, **2009**, *21*, 484

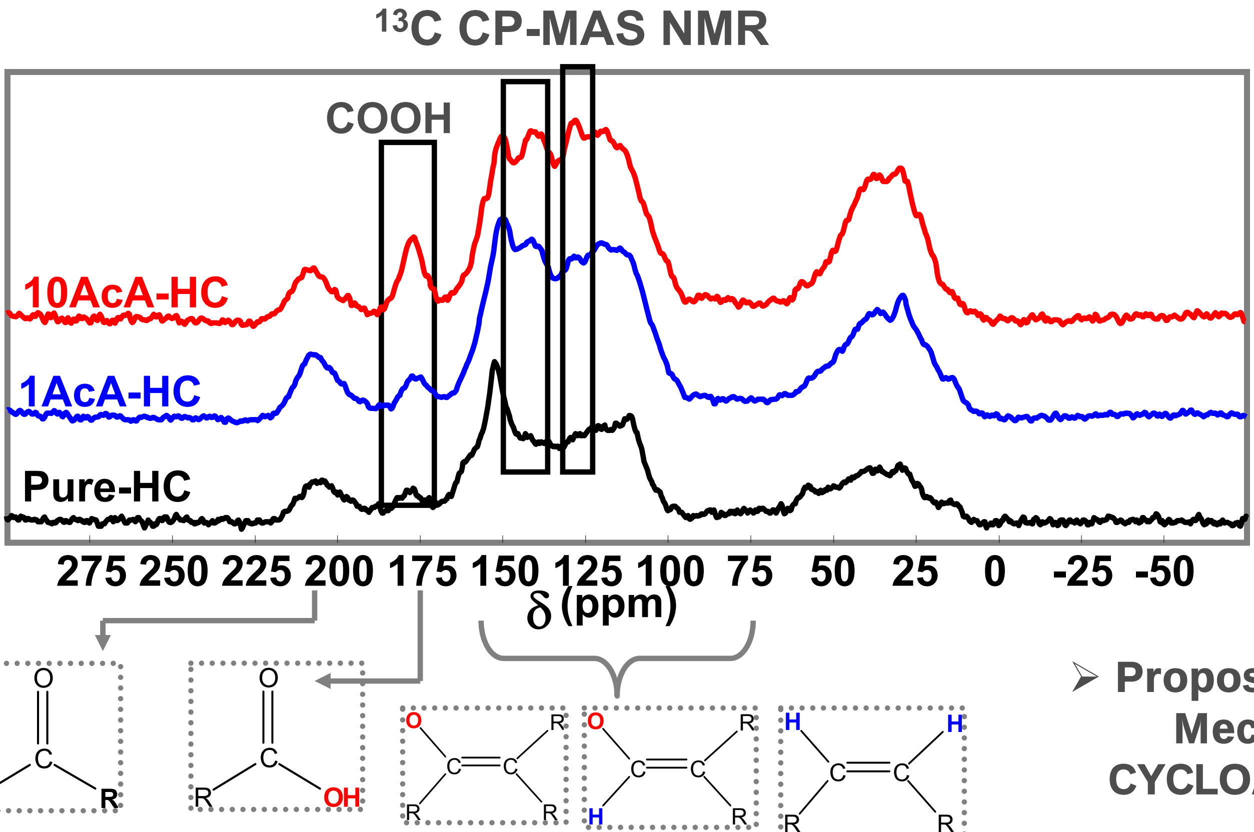
Titirici et al., Cat. Today, **2010**, *150*, 115

Functionalization of HTC particles

In situ functionalization with organic monomers






^{13}C CP-MAS NMR

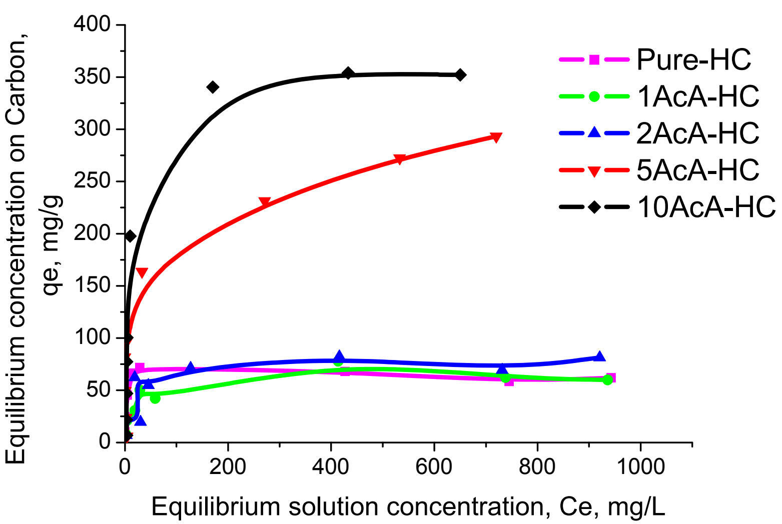
- **Proposed Reaction Mechanism**
  CYCLOADDITION

Functionalization of HTC particles

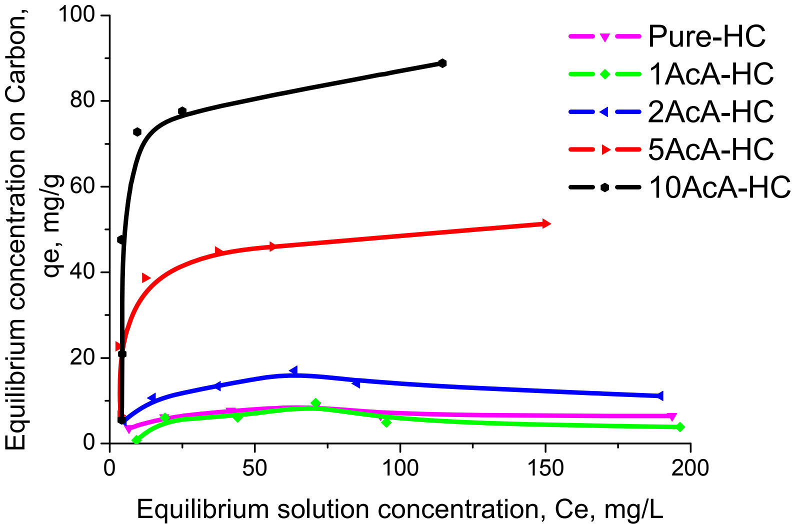
In situ functionalization with organic monomers

Application: Adsorption of Heavy Metals

Pb (II) Removal @ pH 6, RT



Cd (II) Removal @ pH 6, RT



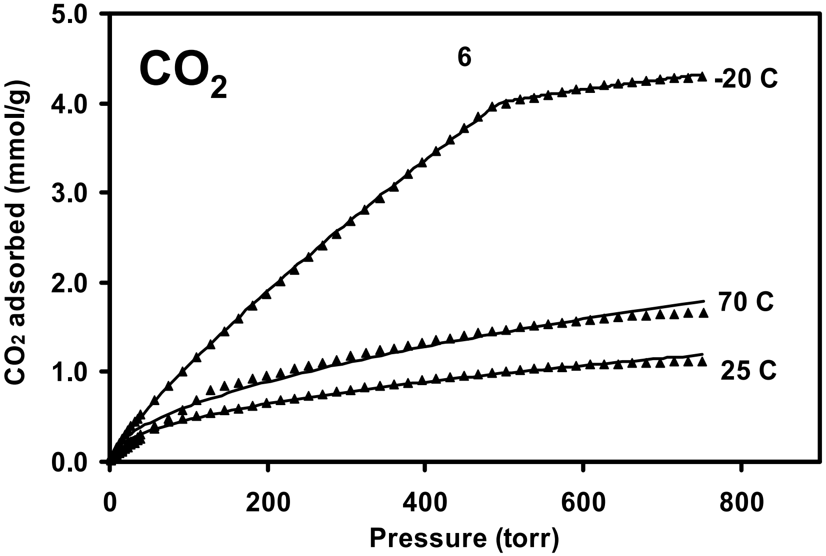
➢ 10AcA-HC : Highest metal uptake capacity

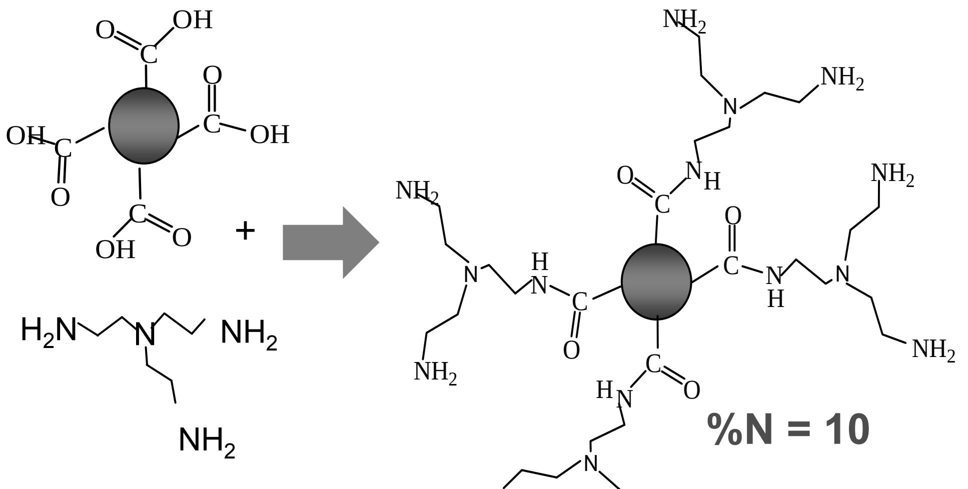
Pb (II) = 350 mg/g

Cd (II) = 90 mg/g

Titirici et al., Chemistry of Materials, ***2009***, 21, 484

Functionalization of HTC particles

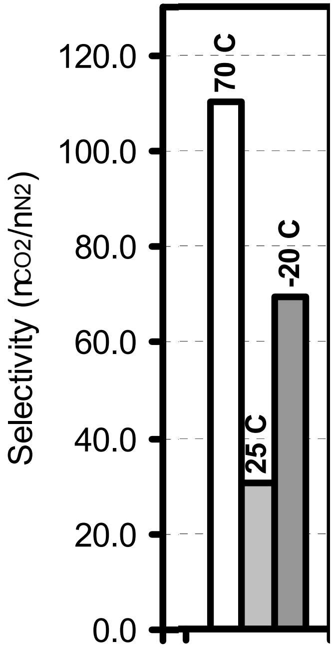




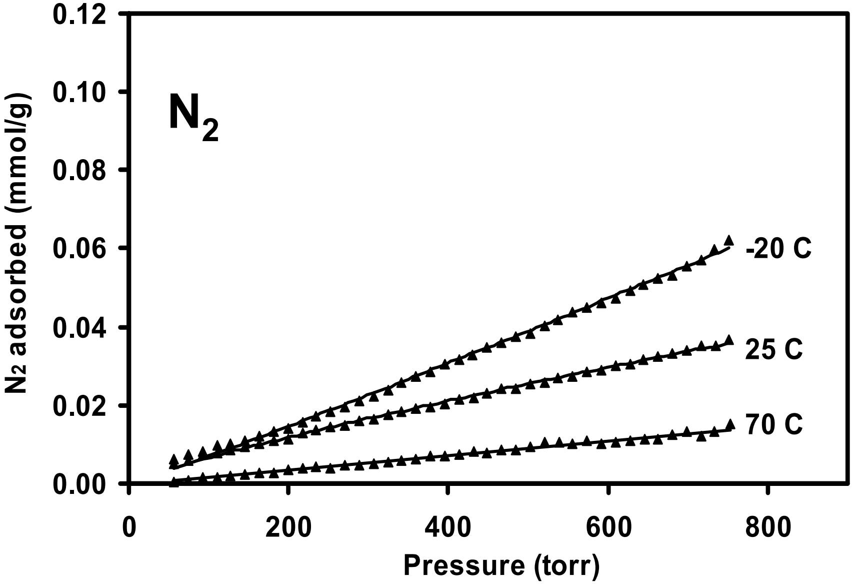
%N = 10

~ 7.8 mmol/g NH$_2$

High Selectivity
nCO_2/nN_2



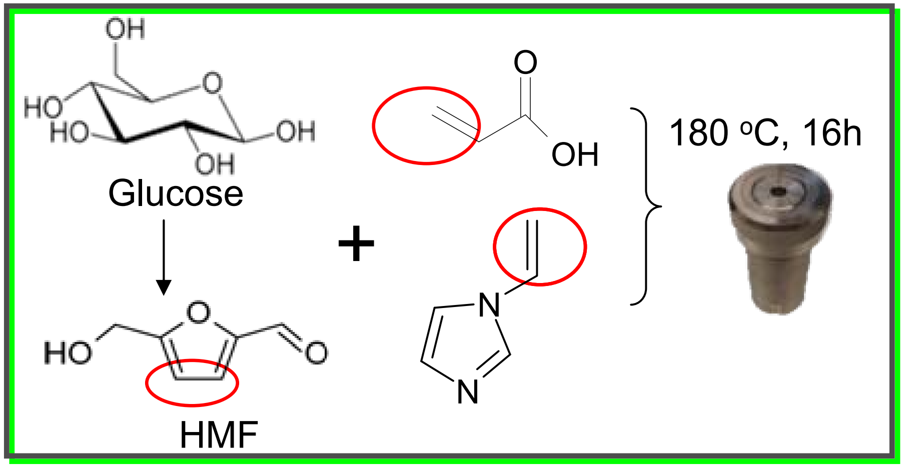
- high and specific CO$_2$ uptake
- potential use as selective adsorbent for CO$_2$ in specific applications (flue gas)



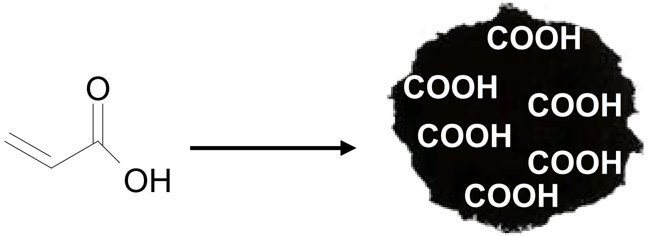
Titirici et al. ChemSusChem, ***2010***, 3, 840

Functionalization of HTC particles

In situ functionalization with organic monomers-tuning

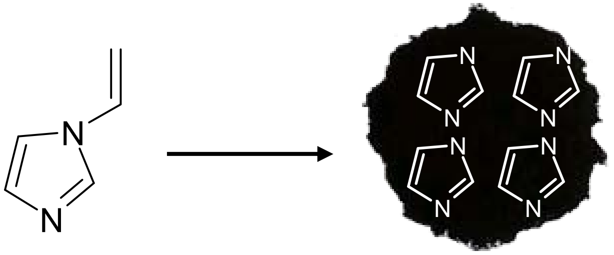


Acrylic Acid (AcA)



Carboxylate Functionalized Hydrothermal Carbon

Vinyl Imidazole (Im)



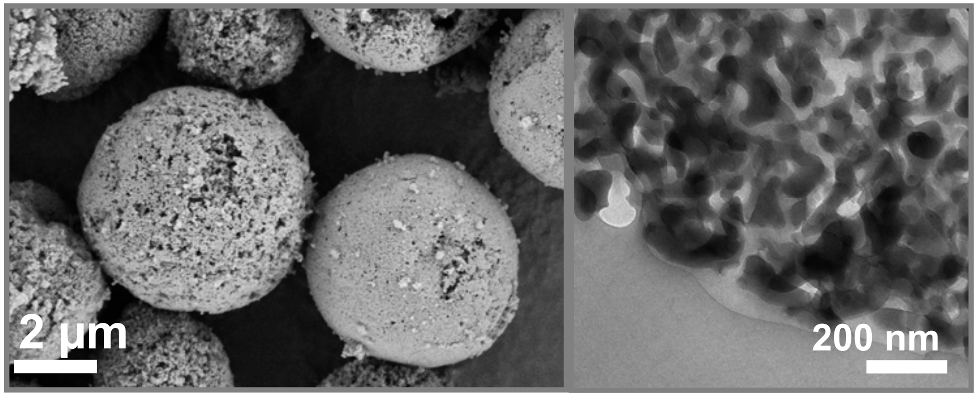
Imidazole Functionalized Hydrothermal Carbon

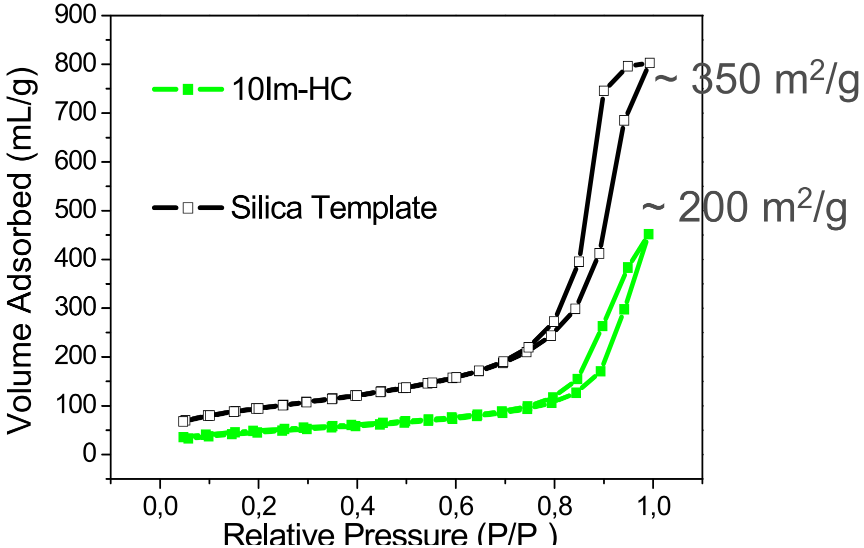
Titirici et al., Cat.Today, **2010**,150,115

Functionalization of HTC particles

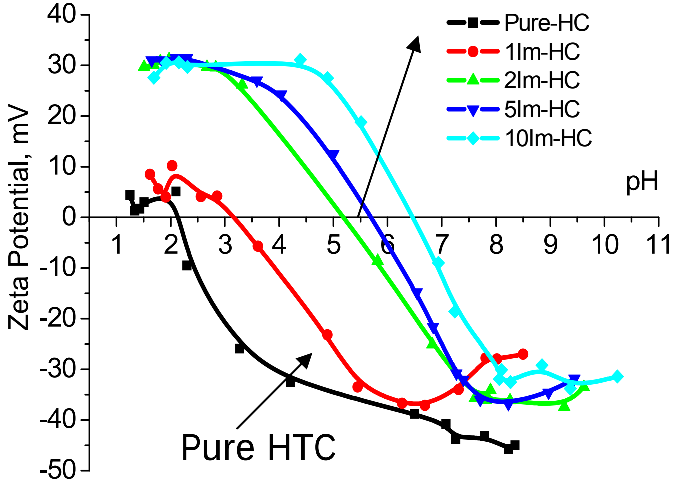
In situ functionalization with organic monomers+nanocasting

Glucose+Vinylimidazole+Mesoporous Silica-HTC+Nanocasting





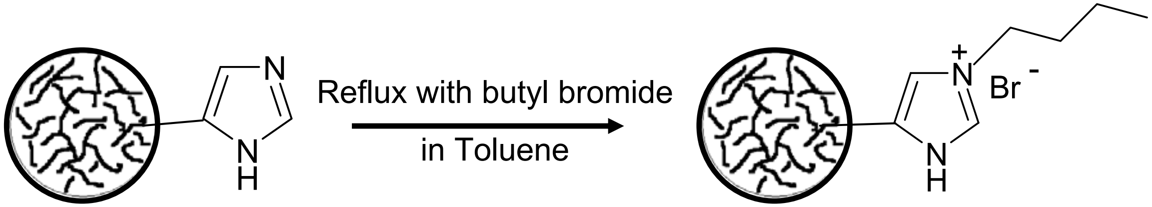
HTC + imidazole



Zeta potential experiment proves the presence of imidazole groups

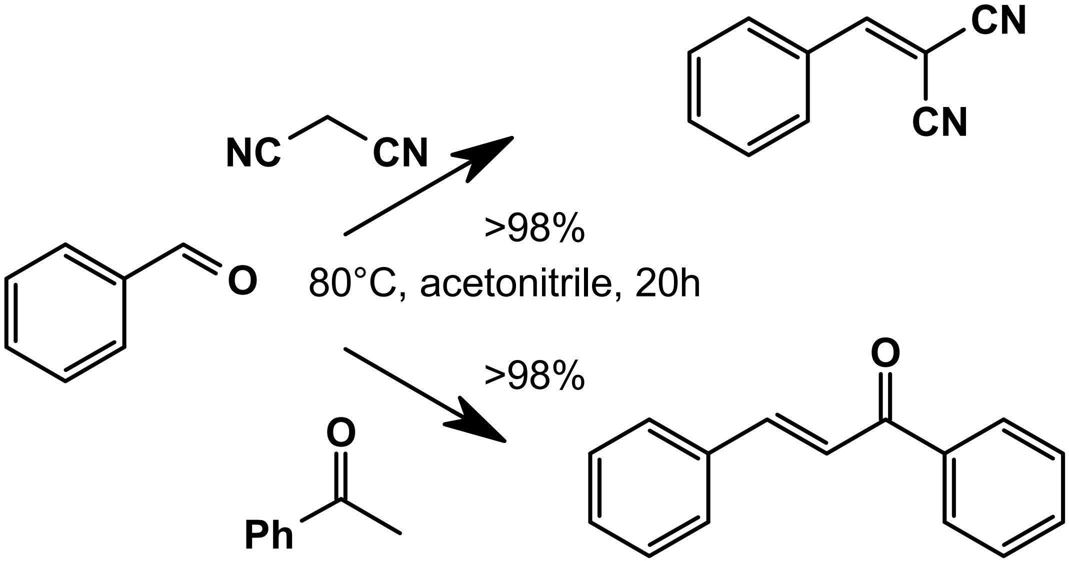
Functionalization of HTC particles

Application: metal free heterogenous catalysis



Imidazolium Functionalized Hydrothermal Carbon

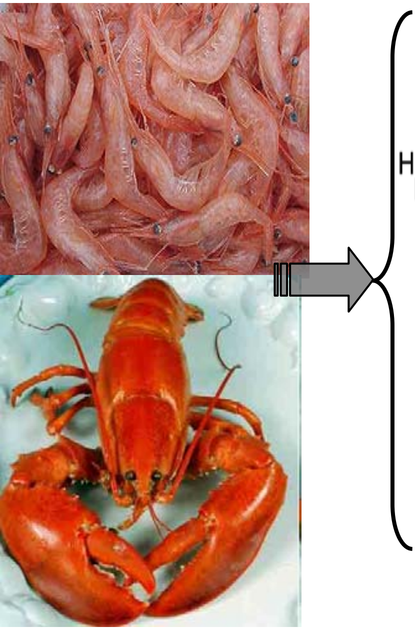
Knoevenagel and Aldol Reaction:

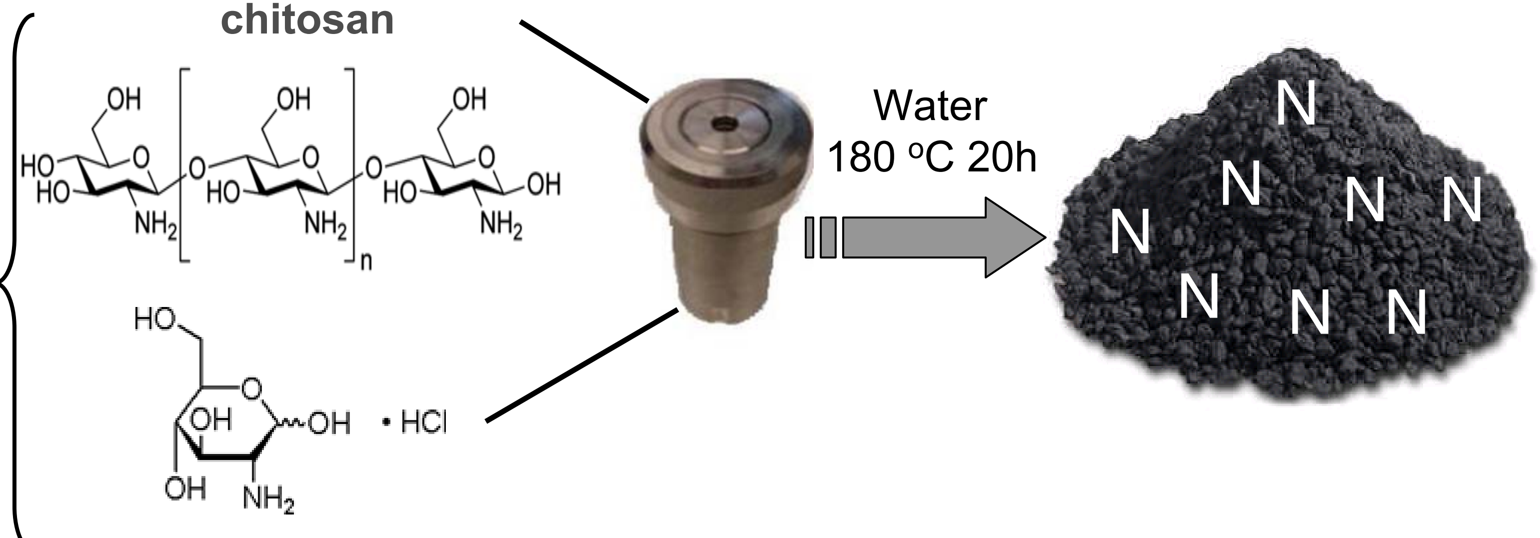


No solvent, 120°, 20h

Functionalization of HTC particles

In situ functionalization using amino containing carbohydrates

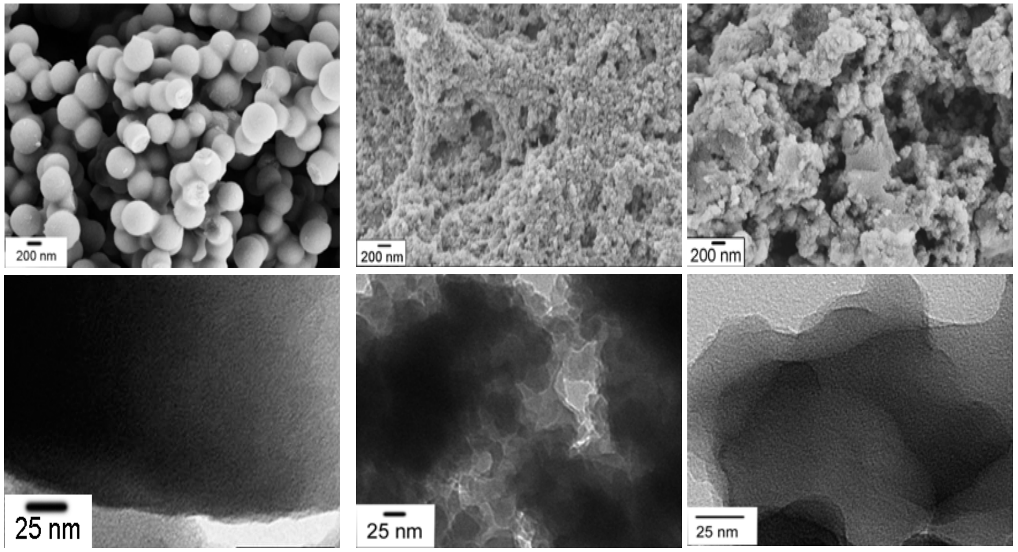




chitosan

Water
180 ^{o}C 20h

glucosamine· HCl



HC-G (glucose) **HC-CH** **HC-GA**

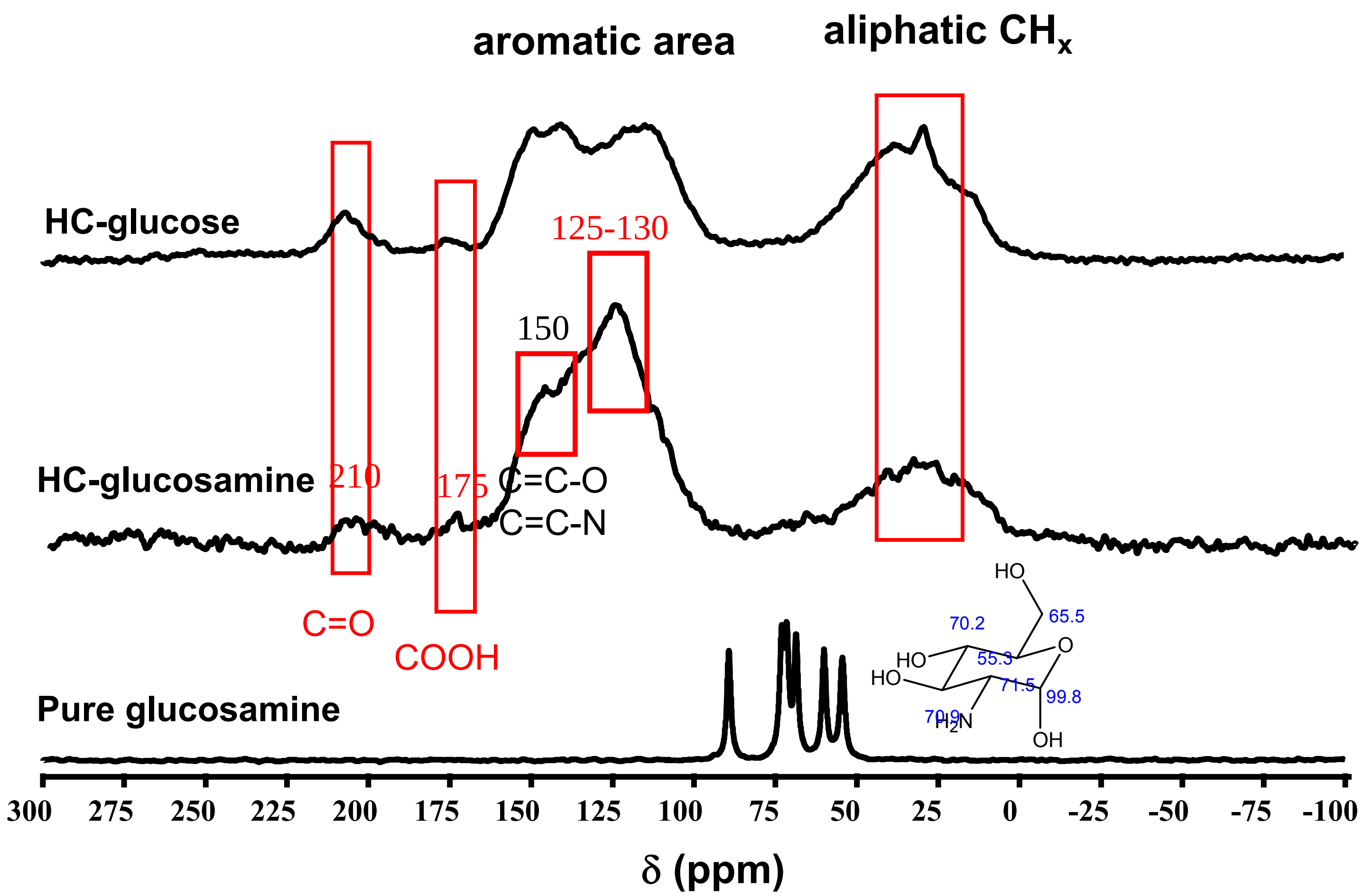
- ❖ Biowaste-based precursors
- ❖ One step
- ❖ No templates or surfactants
- ❖ All in water

Titirici et, al. ***Carbon****, 2010, 48(13), 3778*

Functionalization of HTC particles

In situ functionalization using amino containing carbohydrates

^{13}C CP-MAS NMR



aromaticity at low temperature

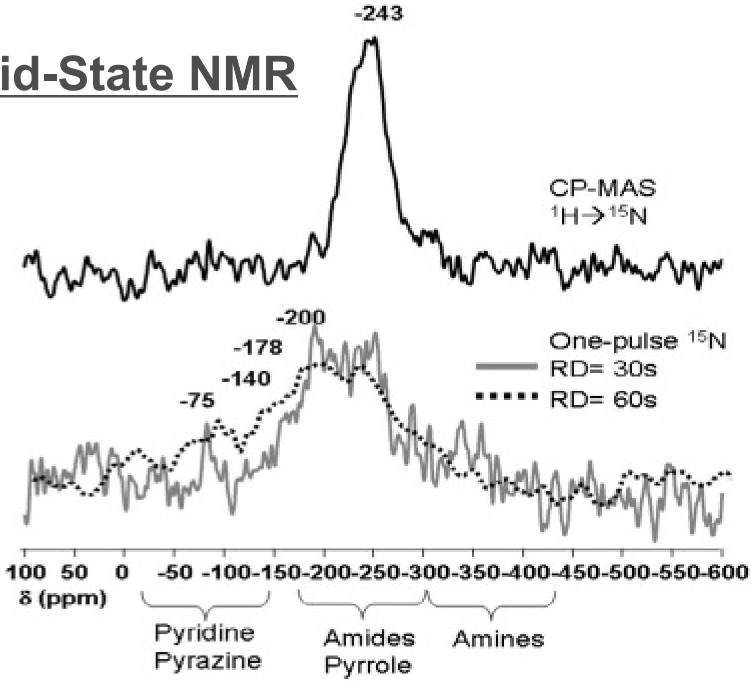
Functionalization of HTC particles

In situ functionalizationusing amino containing carbohydrates

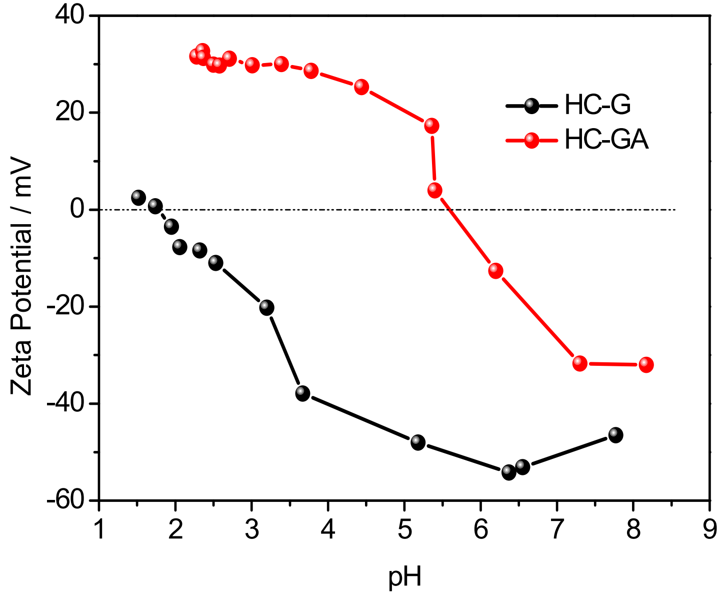
Elemental Analysis & XPS

Material	Elemental Analysis		XPS		N1s XPS	
	C%	**N%**	C%	**N%**	Binding energy (eV)	Assignment
Pure GA	33.4	**6.5**	43.1	**8.5**	398.5	N-H
					400.5	Protonated amine
HC-GA	66.6	**6.7**	79.9	**5.6**	399.3	**Pyridine N**
					401.3	**Quaternary N**

^{15}N Solid-State NMR



Zeta-Potential

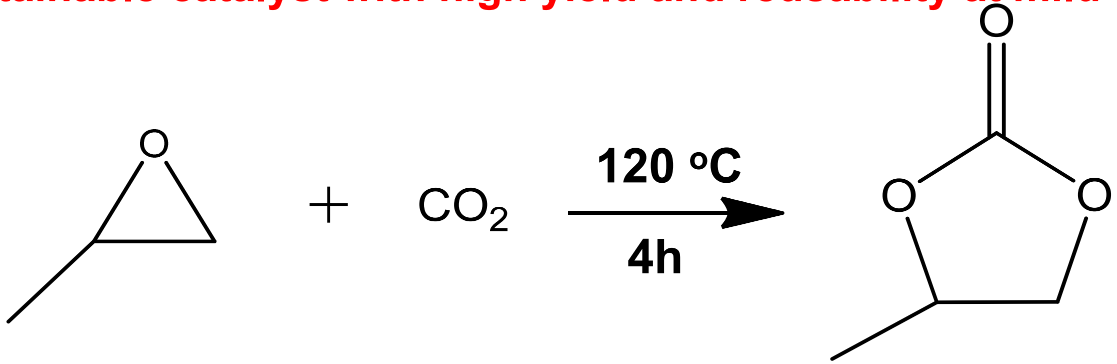


Functionalization of HTC particles

Application 1: Base Catalyst in Cycloaddition Reaction

- Industrially important reaction: propylene carbonate is a highly polar solvent, used as electrolyte for Li-batteries and intermediate in polymer synthesis.
- CO_2 is inexpensive and abundant; utilization of CO_2 is very important.
- Reported catalysts usually have low activity, need for co-solvents, poor reusability

Sustainable catalyst with high yield and reusability at mild conditions

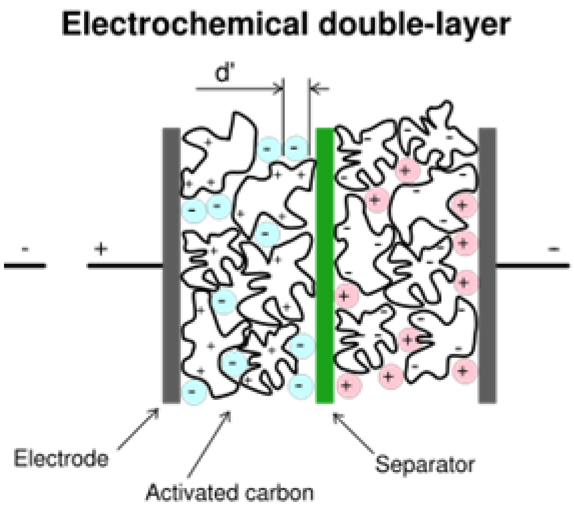


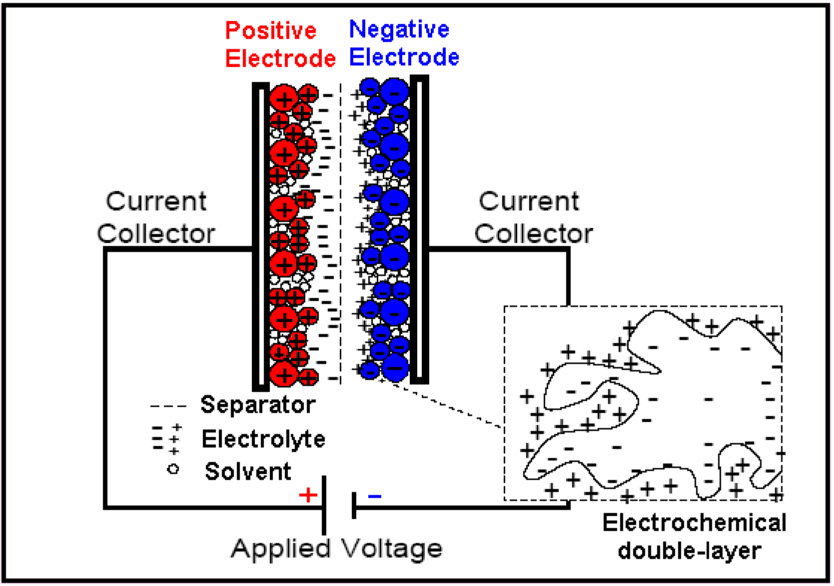
Catalyst	Temperature/ ℃	Pressure/ MPa	Yield/%
$C_2H_5Br/(C_2H_5)_3N$	180 - 200	7.0~8.0	<60
MX_n+PPh_3	150 - 170	7.0~8.0	<60
$ZnCl_2$-Bu_4NI	>150	5.0~6.0	<80
KBr/PEG	150	5.0	<50

Reaction condition: 0.5g catalyst, 70 mmol propylene oxide, 2.0 MPa CO2, 120 °C , 4h.

Functionalization of HTC particles

Application 2: Energy Storage in Supercapacitors





- Electrochemical capacitors fill in the gap between batteries and conventional capacitors

- Supercapacitors store energy in the electrochemical double layer formed at the solide-ectrolyte interface

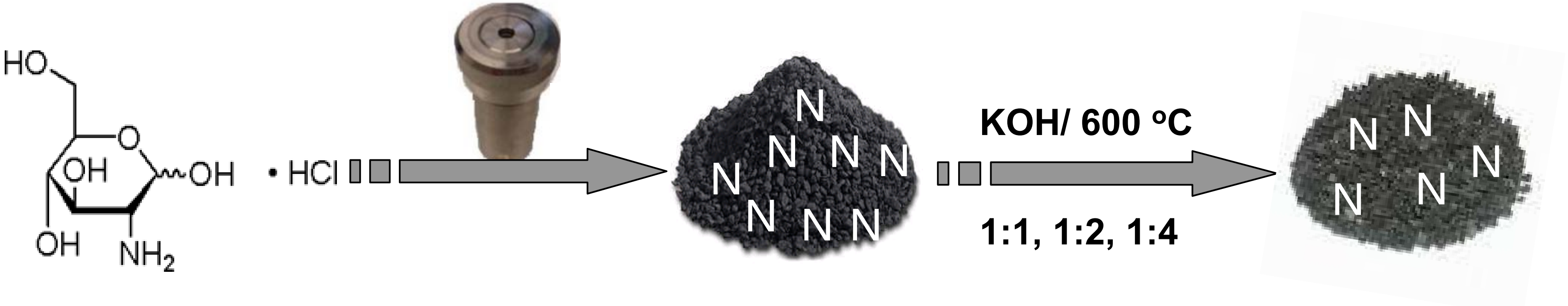
- Pseudocapacitance arises from Faradaic processes at electrode surface and yields to high capacitance

- Nitrogen doped activated carbon materials combine both the high surface and microporosoty with the pseudo capacitance effect leading to an increase in capacity

Functionalization of HTC particles

Application 2: Energy Storage in Supercapacitors

Chemical activation is a well-known method to obtain microporous carbons from biomass



KOH/ 600 °C

1:1, 1:2, 1:4

Glucosamine· HCl

HC-GA

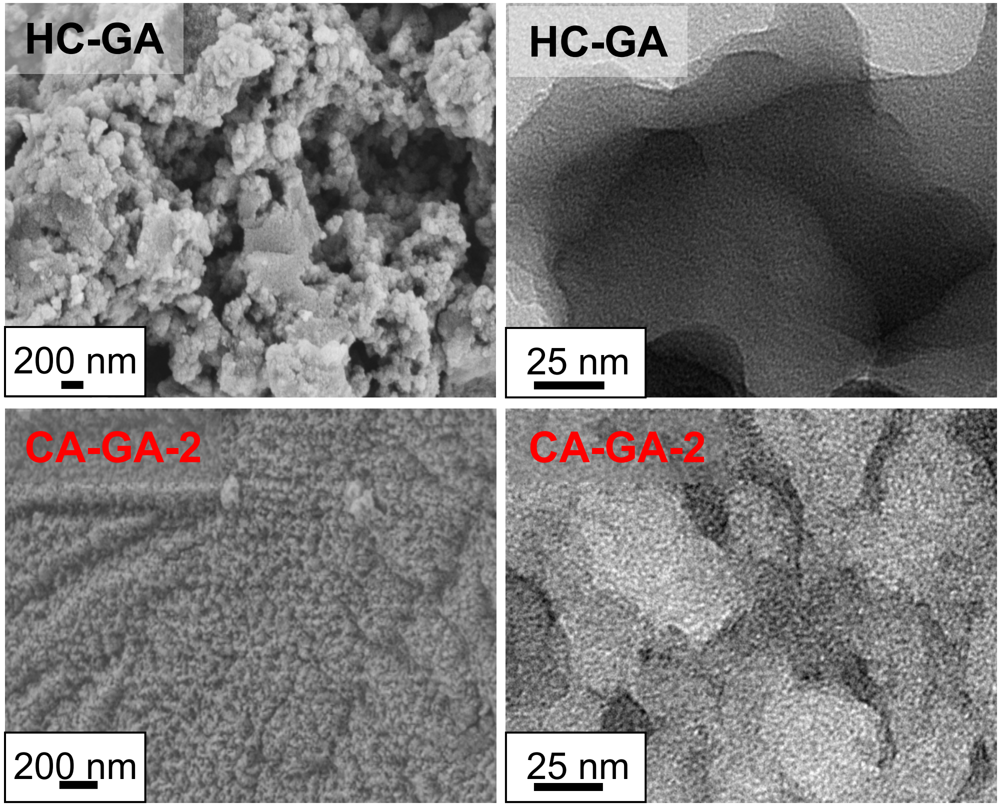
CA-GA-x (x=1, 2 or 4)

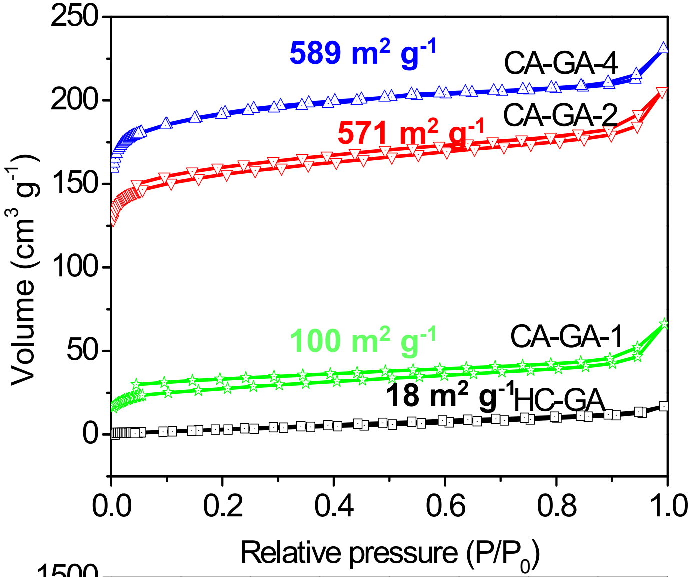
- Nitrogen incorporated into the microporous carbon structure
- The nitrogen functionalities can enhance the supercapacitance performance

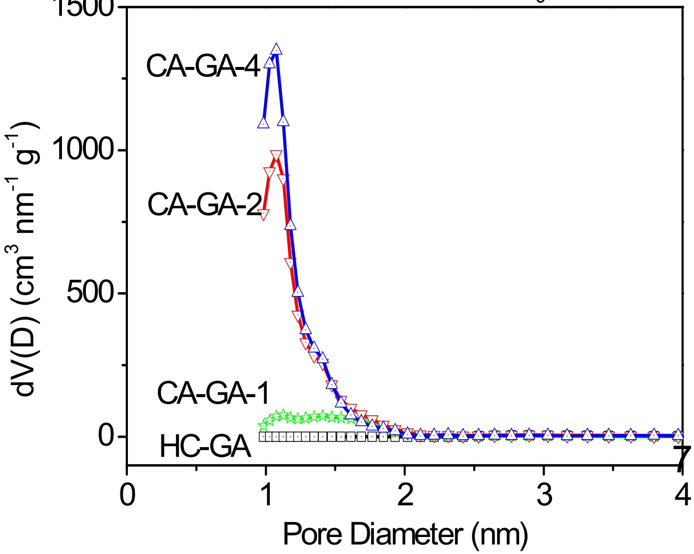
Functionalization of HTC particles

Application 2: Energy Storage in Supercapacitors

SEM & TEM







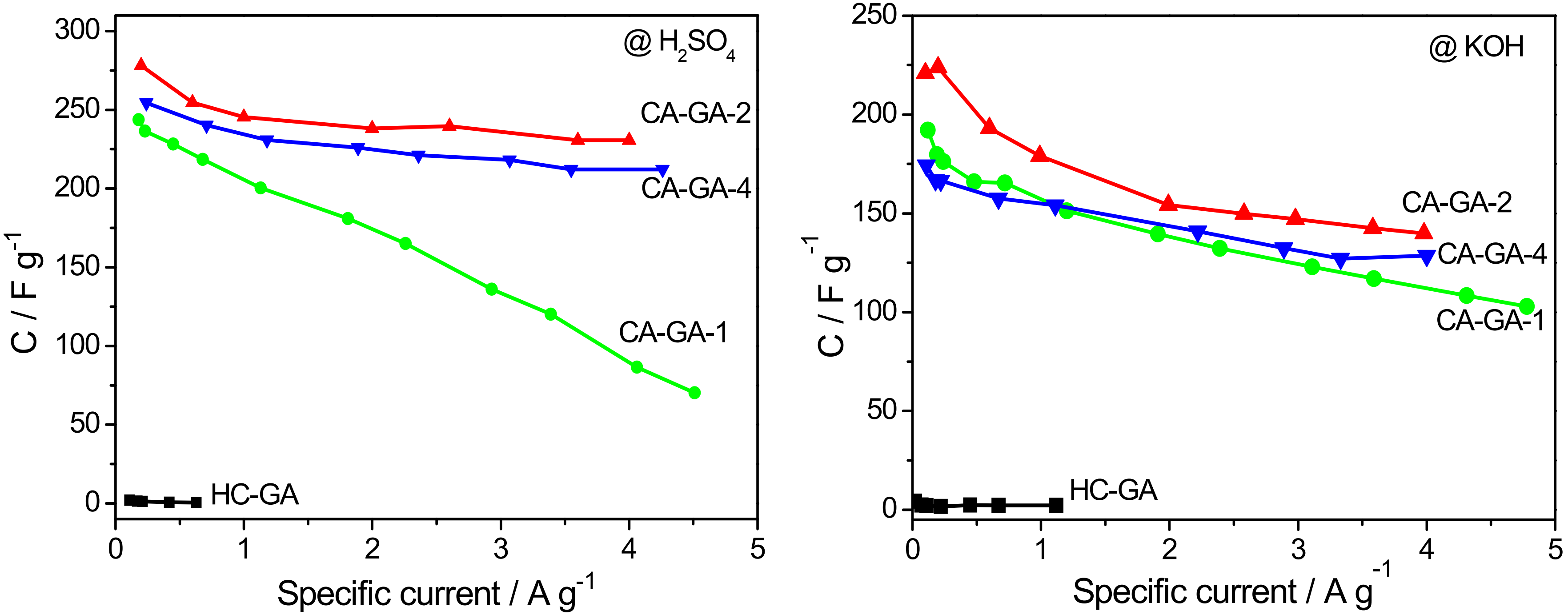
Titirici et al, Adv. Mater, DOI: 10.1002/adma. 201002647

Functionalization of HTC particles

Supercapacitance Performance:

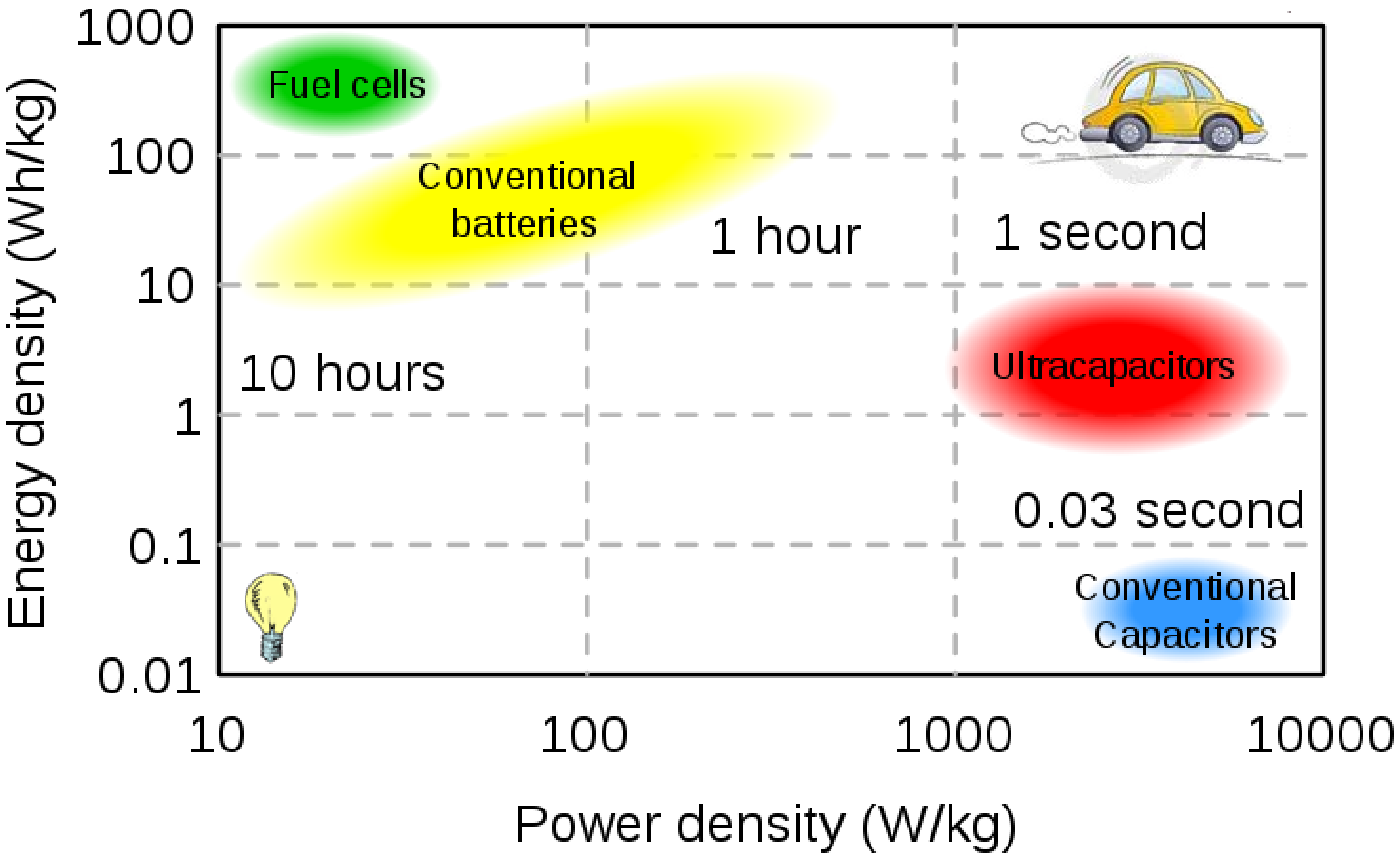
Previously Reported:

S ($m^2\ g^{-1}$)	C ($F\ g^{-1}$)
500	< 100
571	**~300**
3000	200-300



Ragone Charts

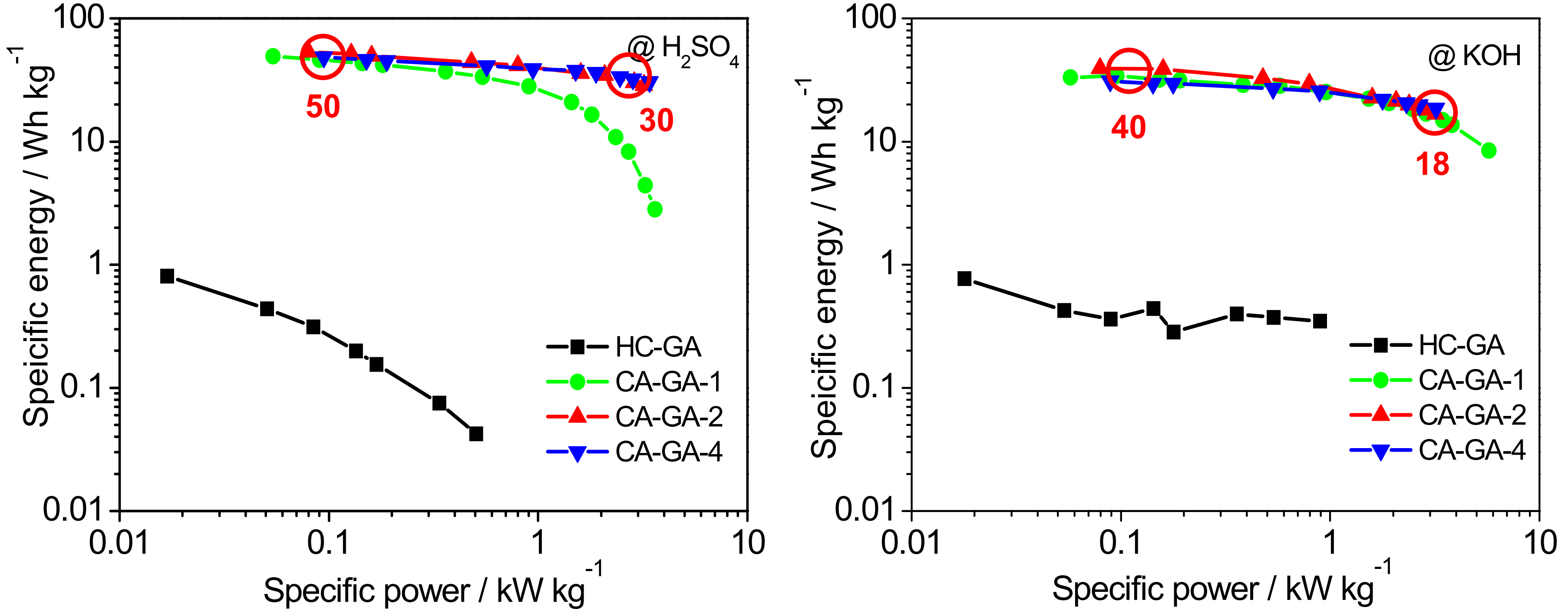
Performance comparison of various energy storing devices



Functionalization of HTC particles

High Specific Energy and Cyclic Stability

Ragone plots in basic and acidic electrolytes

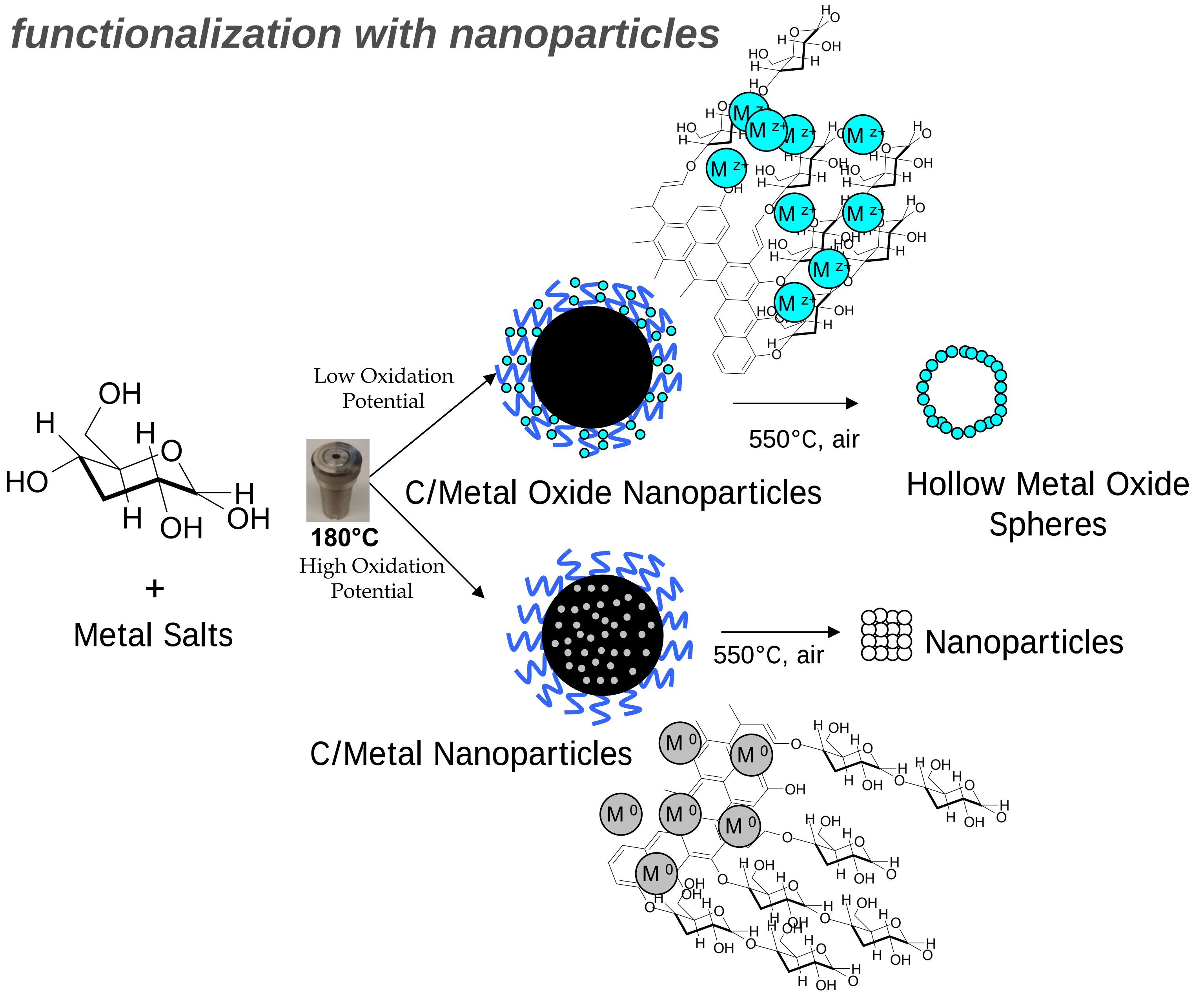


- **After 2000 cycles, 7% loss @H_2SO_4 and 5% loss @KOH**

Titirici et al, Adv. Mater, DOI: 10.1002/adma. 201002647

Functionalization of HTC particles

In situ functionalization with nanoparticles



\+

Metal Salts

180°C

Low Oxidation Potential

High Oxidation Potential

C/Metal Oxide Nanoparticles

550°C, air

Hollow Metal Oxide Spheres

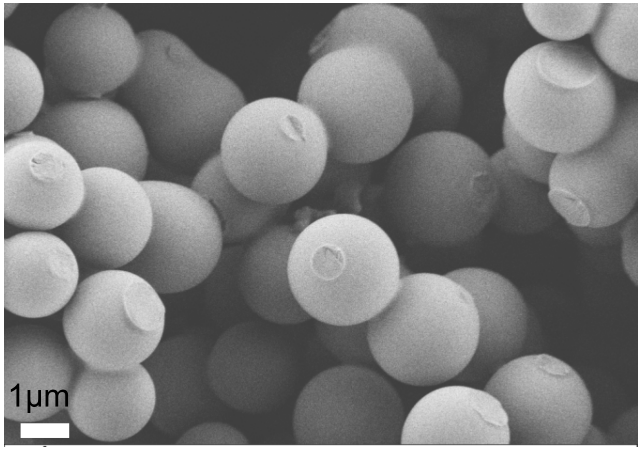
C/Metal Nanoparticles

550°C, air

Nanoparticles

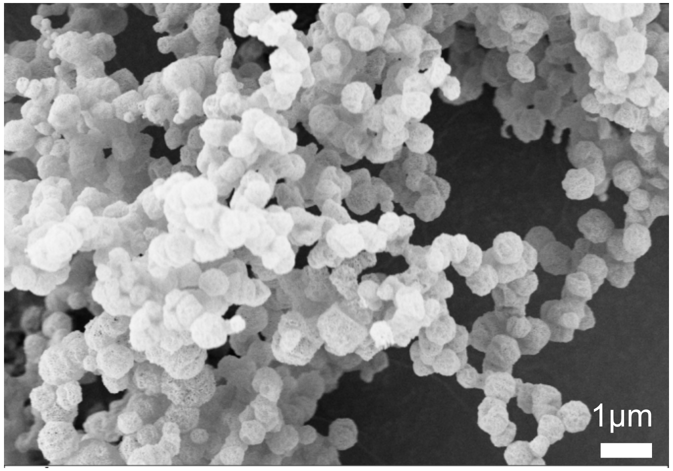
Functionalization of HTC particles

Application: production of nanostructured hollow spheres

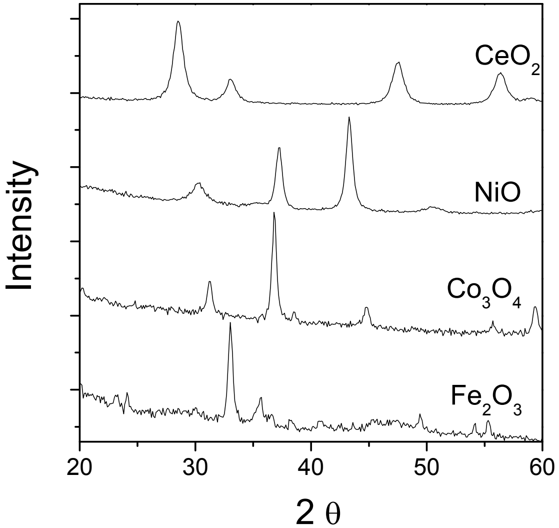


Carbon / Fe $^{3+}$

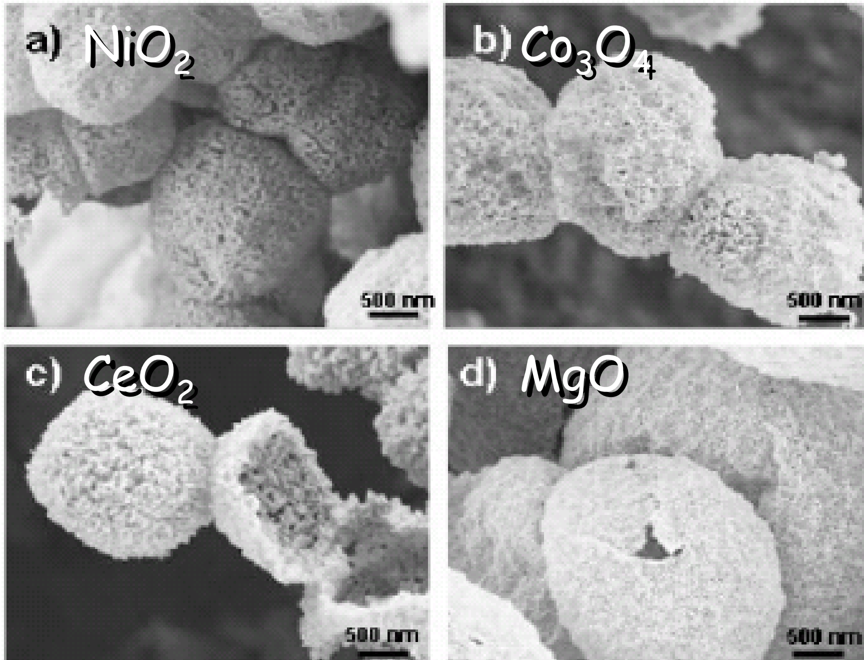
$\xrightarrow[\text{air}]{550°C}$



Fe_2O_3 hollow spheres

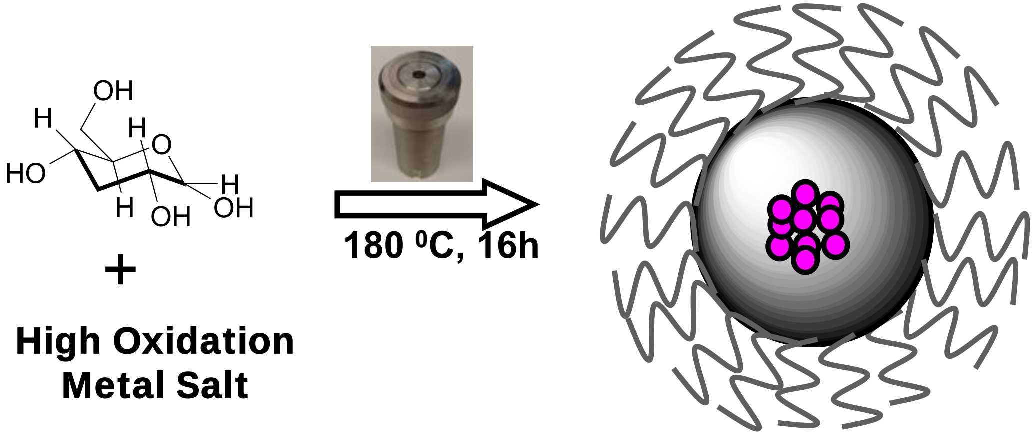


Titirici et al, *Chem. Mater*, **2006**, *18* (87), 1773



Functionalization of HTC particles

In situ functionalization with nanoparticles

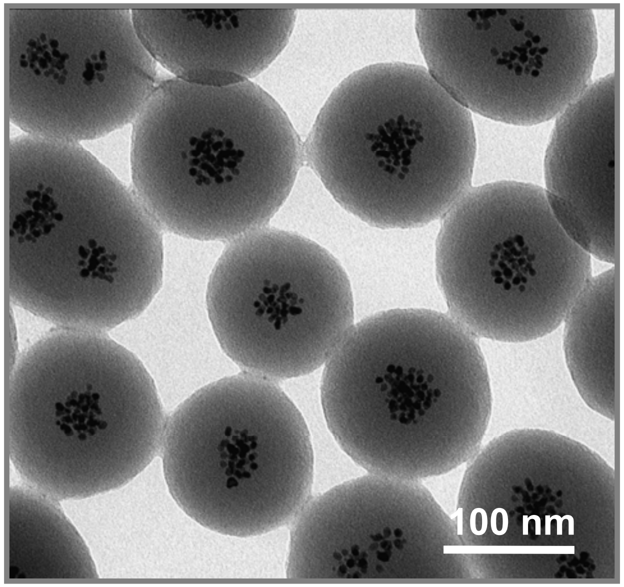


+

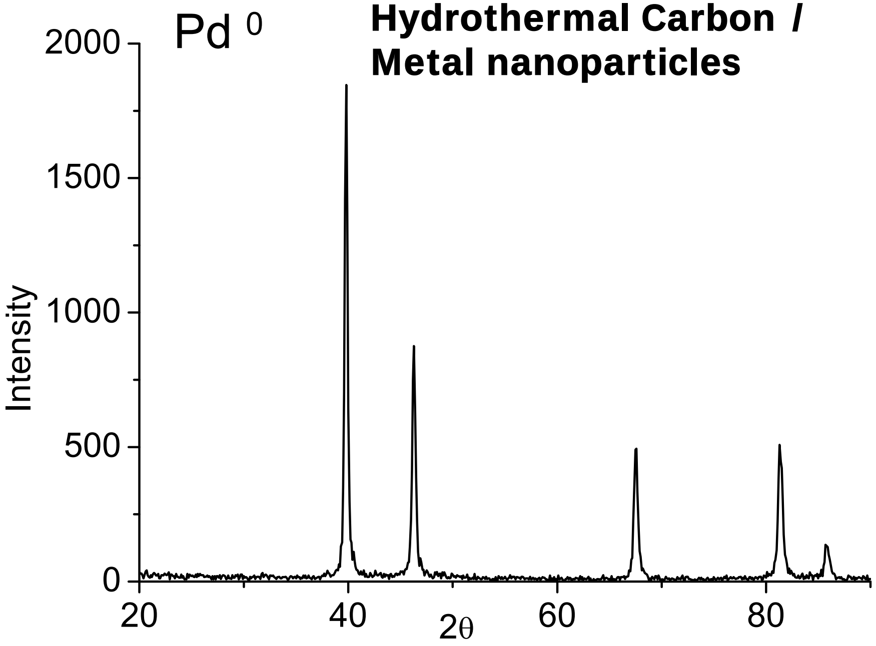
High Oxidation Metal Salt

180 ^{0}C, 16h

Hydrothermal Carbon / Metal nanoparticles



Pd / Hydrothermal Carbon



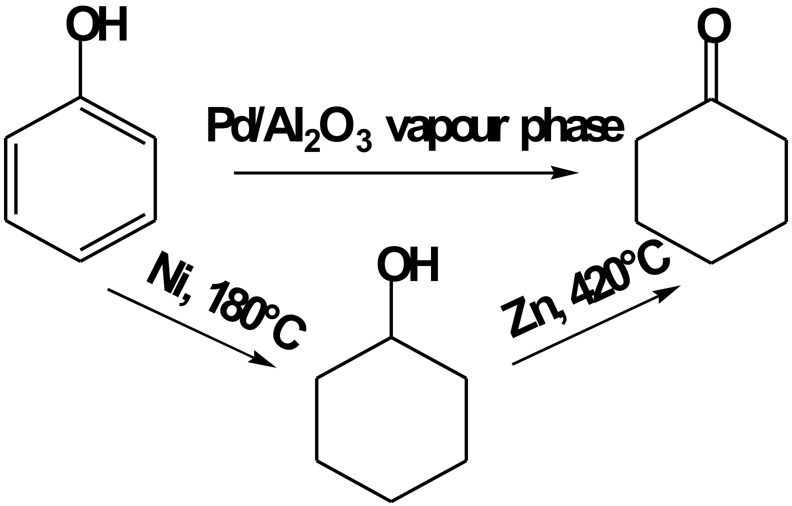
Functionalization of HTC particles

Application: Hydrogenation Catalysis

Hydrogenation of phenol to cyclohexanone in liquid phase

- Cyclohexanone is a very important intermediate in the production of carprolactam, which is used in the manufacturing of nylon based products

- In general, cyclohexanone can be obtained from phenol by either a one-step or a two-step process.



Titirici *et al.*, Chemical Communications, ***2008***, 999

Functionalization of HTC particles

Application: Hydrogenation Catalysis

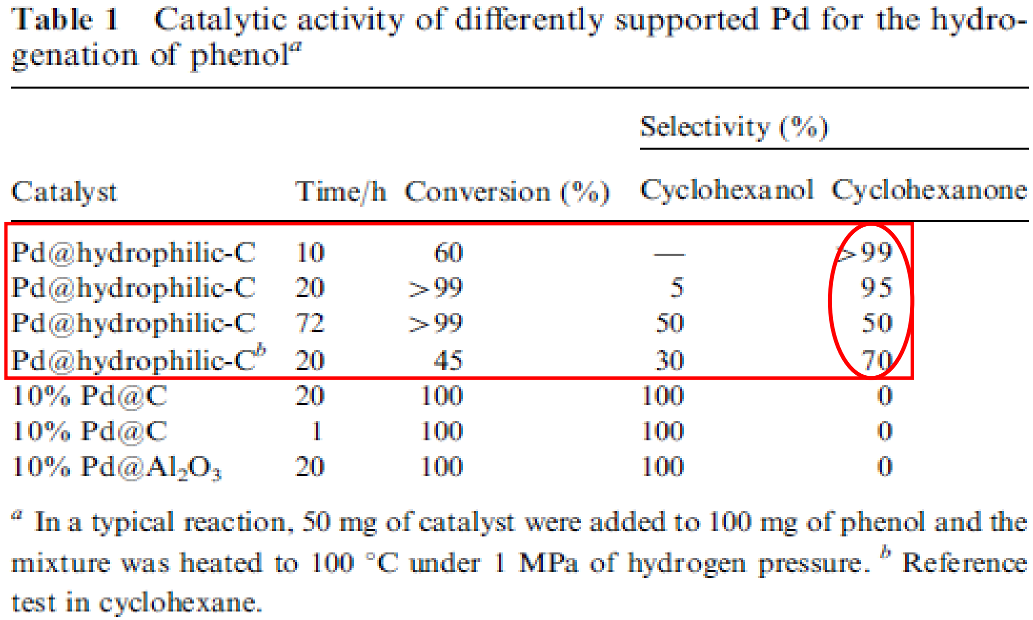
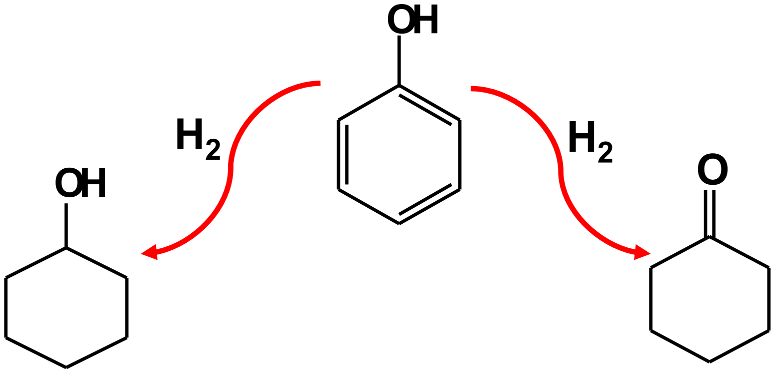


Table 1 Catalytic activity of differently supported Pd for the hydrogenation of phenol[a]

Catalyst	Time/h	Conversion (%)	Selectivity (%) Cyclohexanol	Selectivity (%) Cyclohexanone
Pd@hydrophilic-C	10	60	—	>99
Pd@hydrophilic-C	20	>99	5	95
Pd@hydrophilic-C	72	>99	50	50
Pd@hydrophilic-C[b]	20	45	30	70
10% Pd@C	20	100	100	0
10% Pd@C	1	100	100	0
10% Pd@Al_2O_3	20	100	100	0

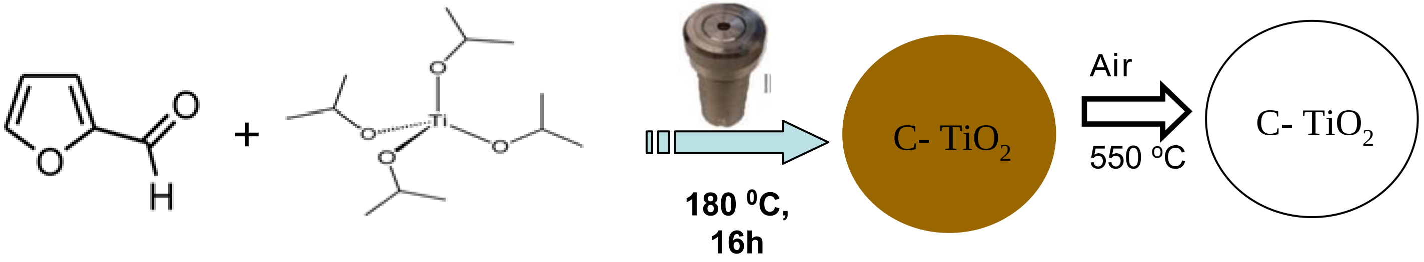
[a] In a typical reaction, 50 mg of catalyst were added to 100 mg of phenol and the mixture was heated to 100 °C under 1 MPa of hydrogen pressure. [b] Reference test in cyclohexane.

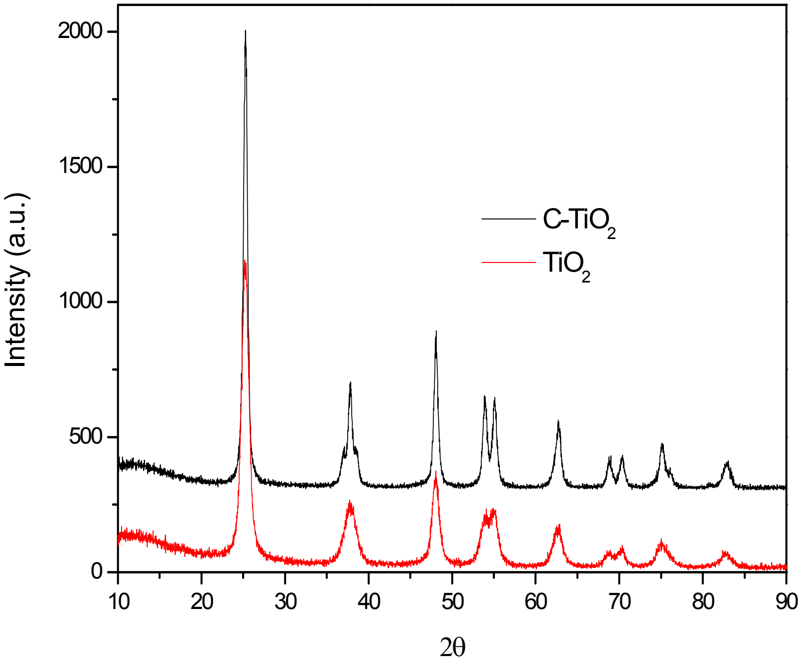
SELECTIVITY

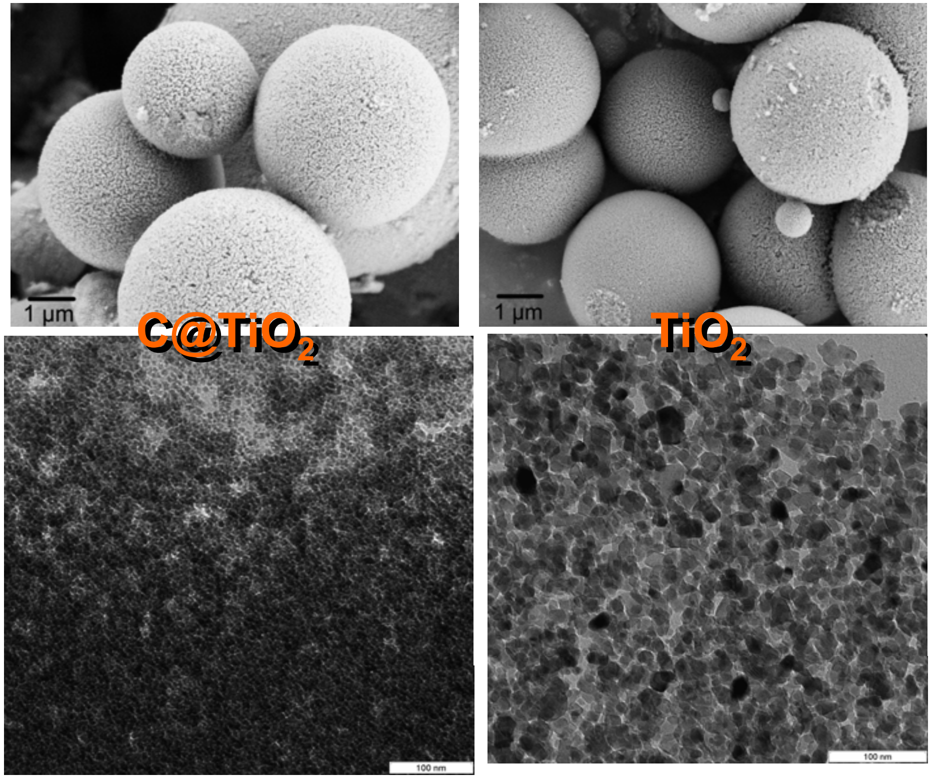


Functionalization of HTC particles

In situ functionalization with nanoparticles





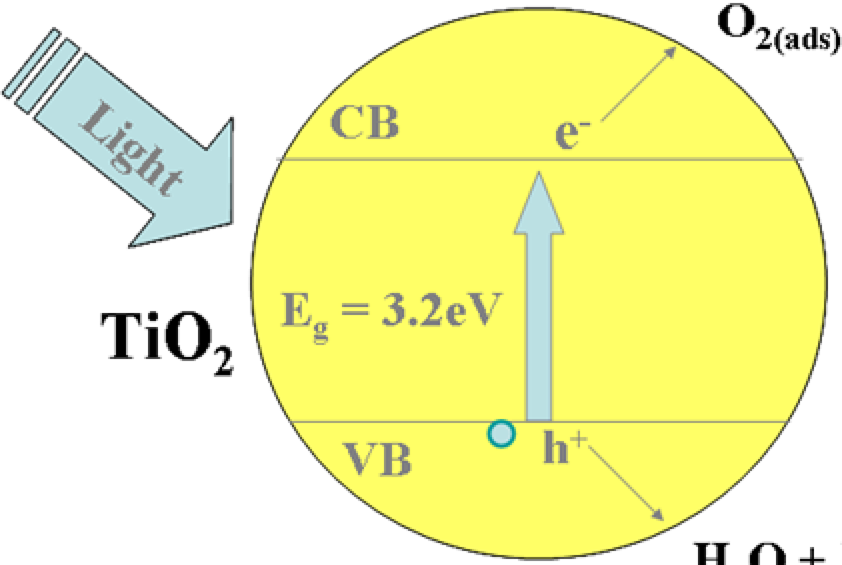


Titirici et al-Adv. Mater. **2010**, *22*, 3317–3321

Photocatalysis

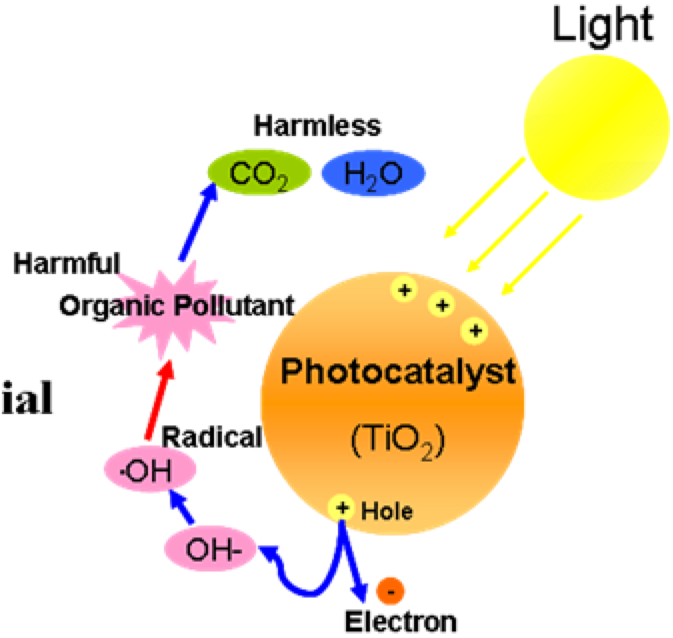
Soft Oxidation Potential

$O_{2(ads)} + e^{-} \rightarrow O_2{}^{\circ -}{}_{(ads)}$



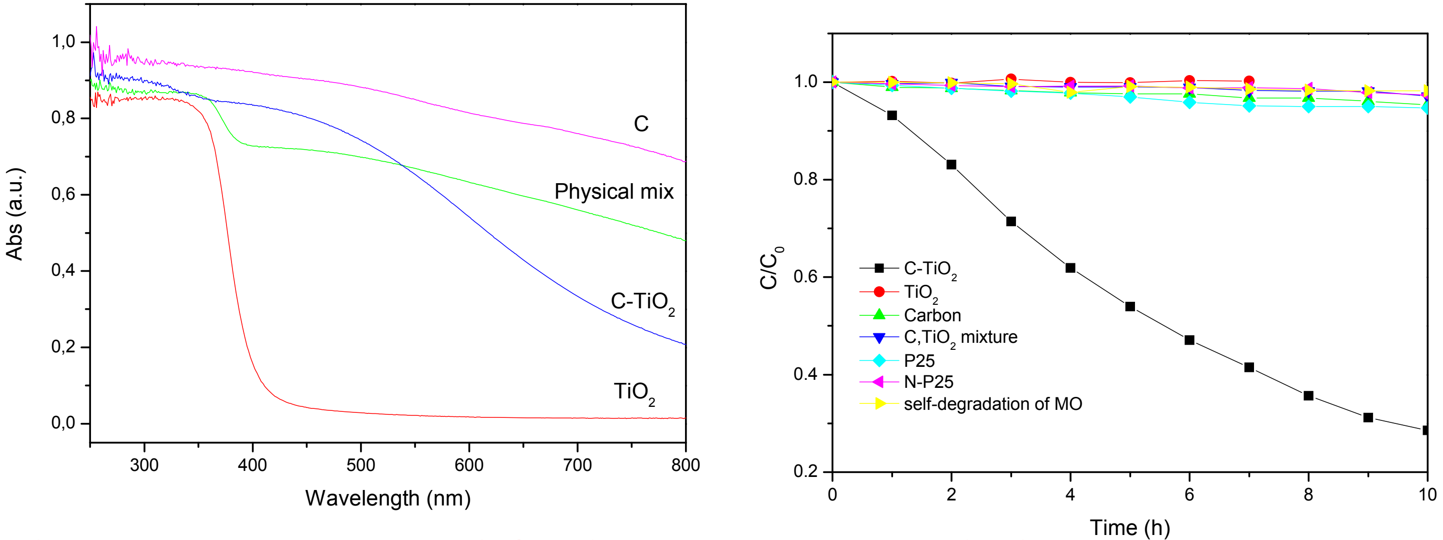
$H_2O + h^{+} \rightarrow OH^{\circ} + H^{+}$

Strong Oxidation Potential

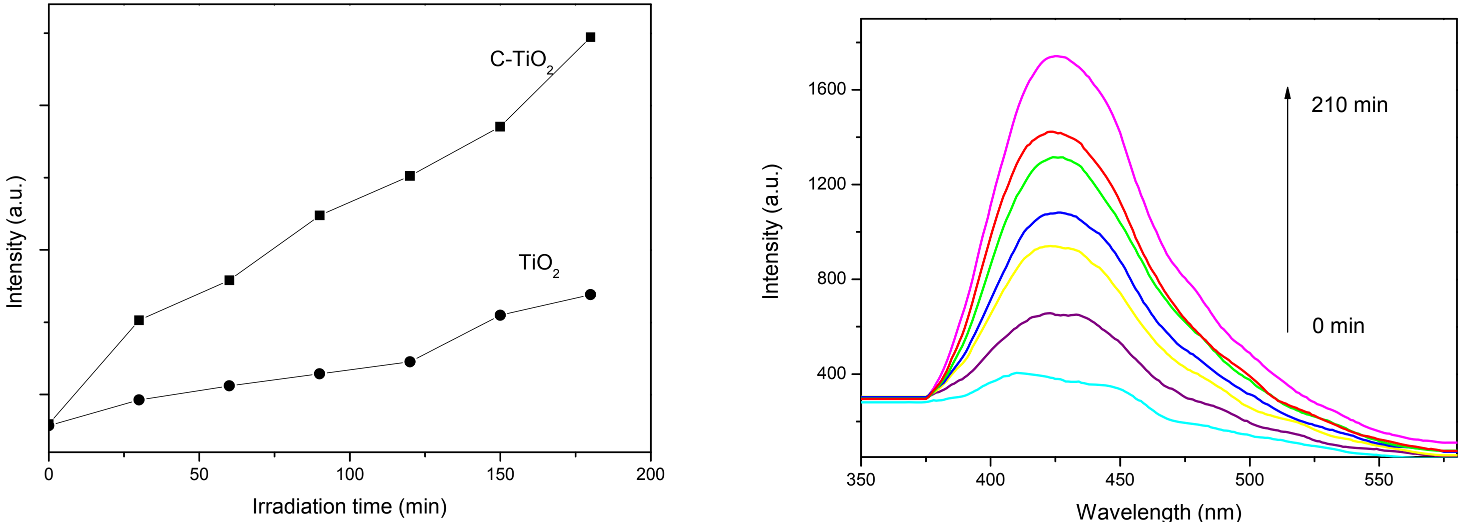


Photocatalysis

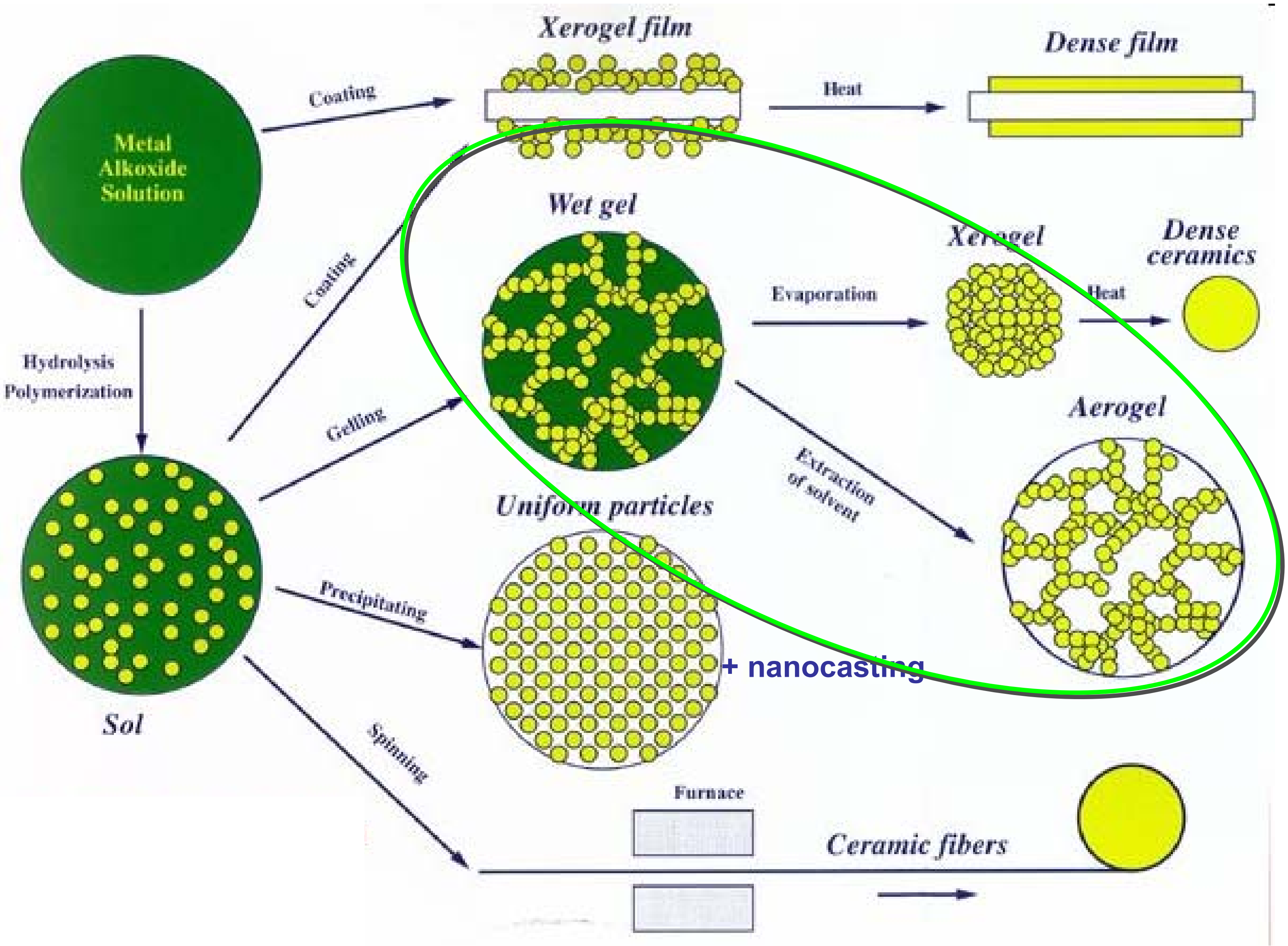
Photocatalytic degradation of MO in the presence of C@TiO_2 and other samples under visible light irradiation (λ > 420 nm)



Comparison between C@TiO2 and the pure TiO_2 fluorescence spectra of the supernatant solutions irradiated with visible light (λ > 420 nm).



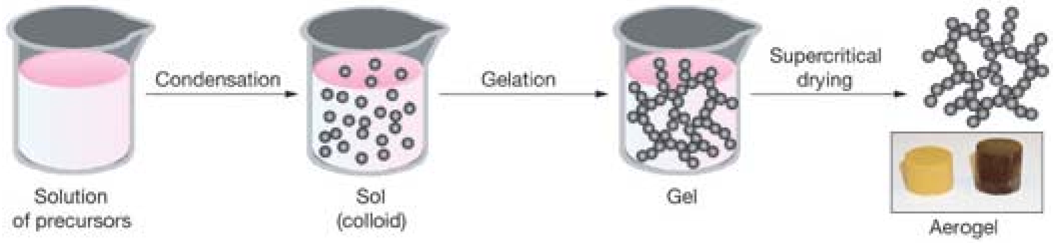
HTC~ Sol Gel: Chemie Douce de Carbon



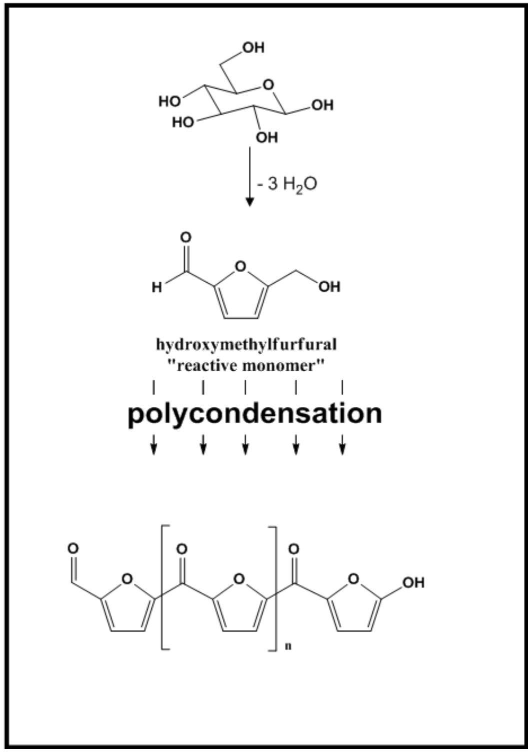
Titirici at al C. R. Chimie 13 (2010) 167–173

HTC aerogels

In sol-gel chemistry:



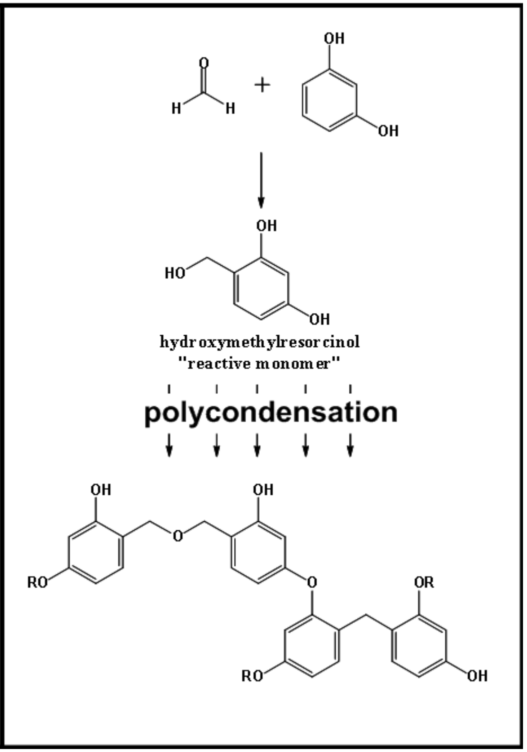
HTC



hydroxymethylfurfural
"reactive monomer"

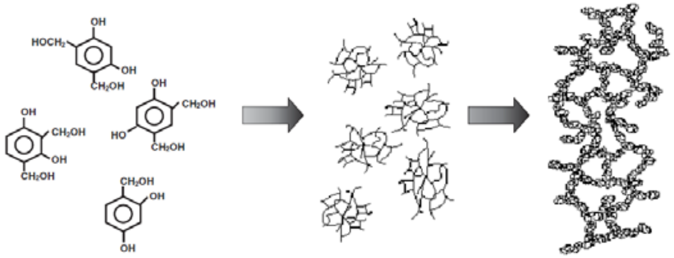
polycondensation

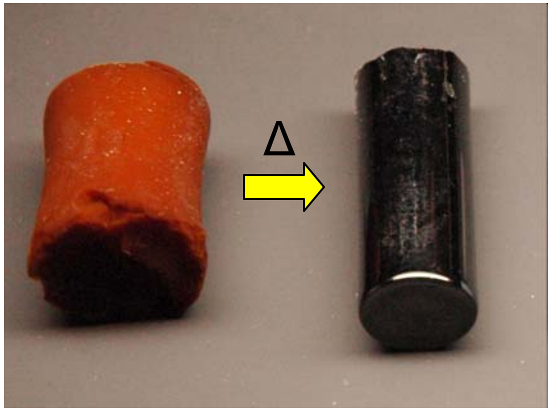
Resorcinol-formaldehyde



hydroxymethylresorcinol
"reactive monomer"

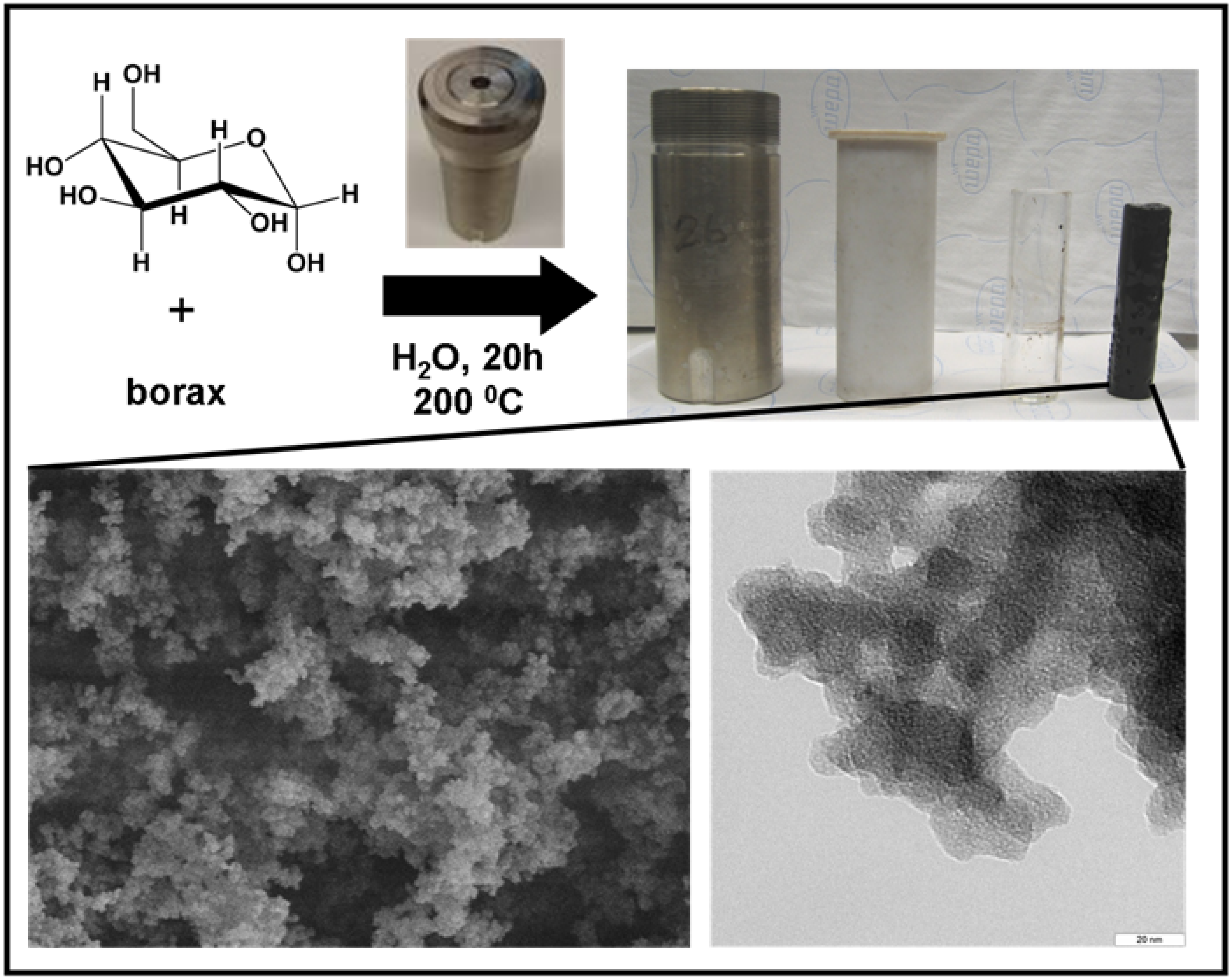
polycondensation





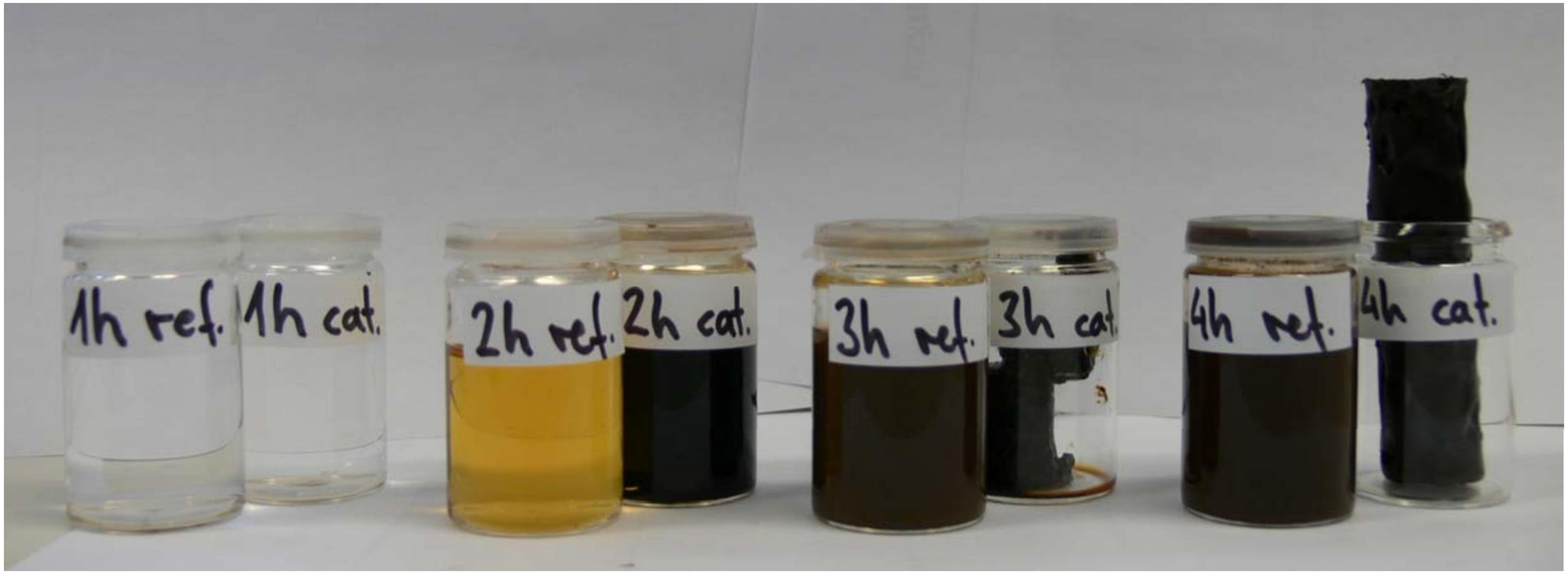
HTC aerogels

Borax catalyses the formation of carbogels



HTC aerogels

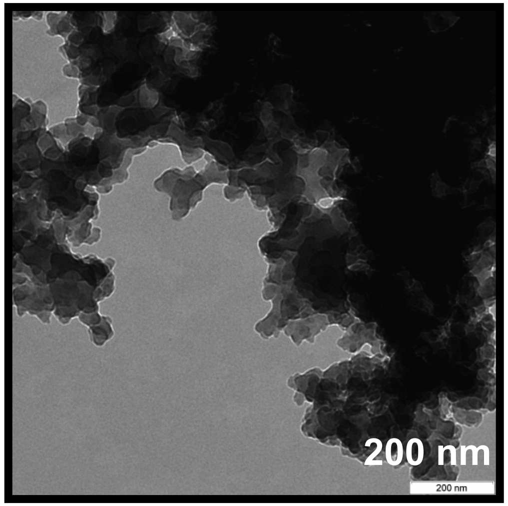
Borax catalyses the formation of carbogels

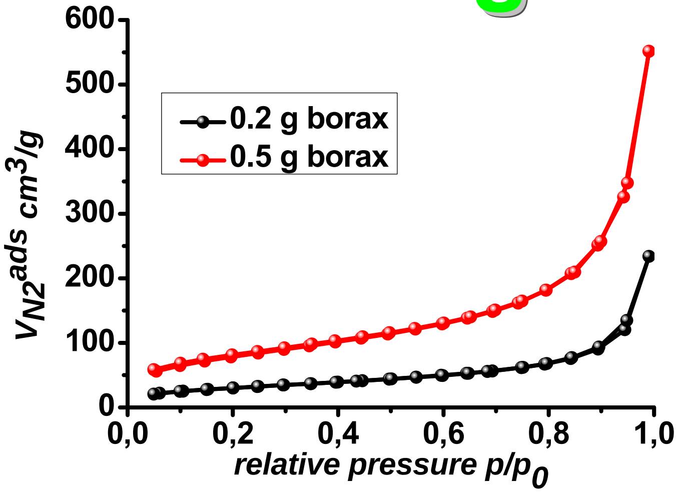


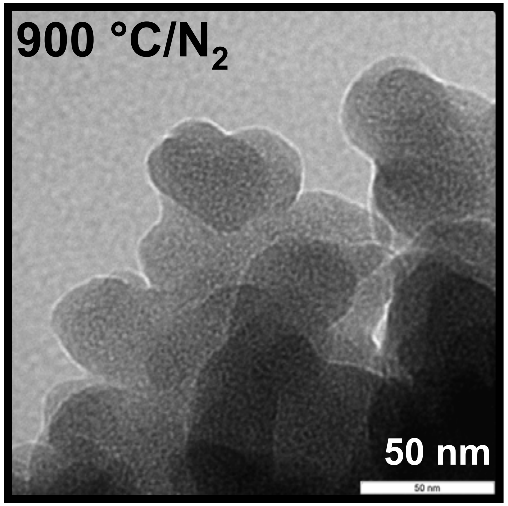
time

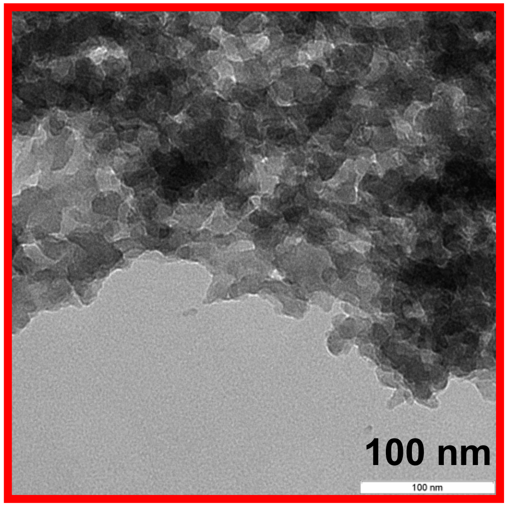
Carbon Yield @ 200 °C	
Glucose (ref)	**Glucose + Borax (cat)**
~ 55 %	**~ 80 %**

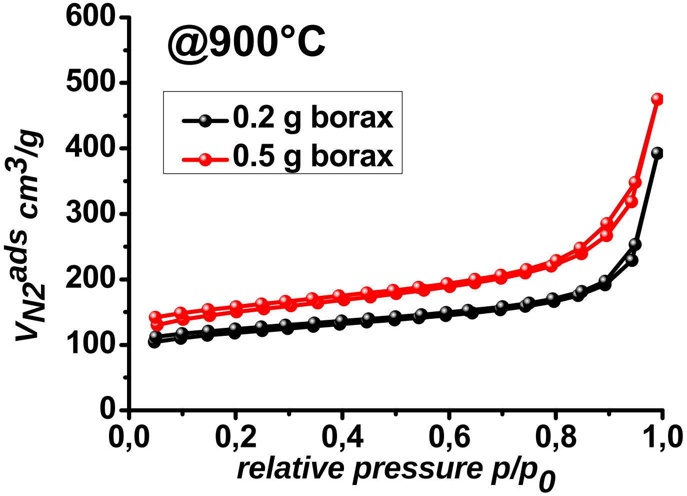
HTC aerogels

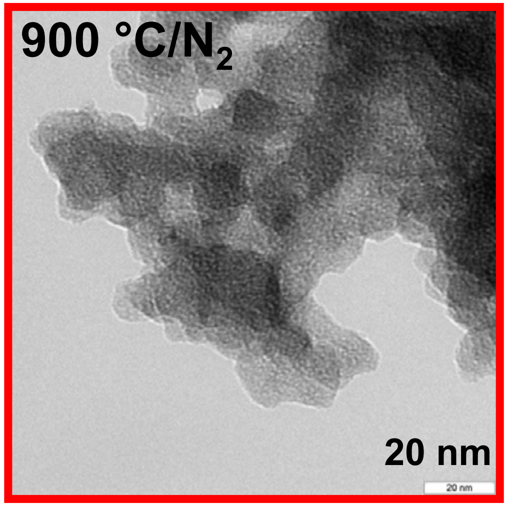










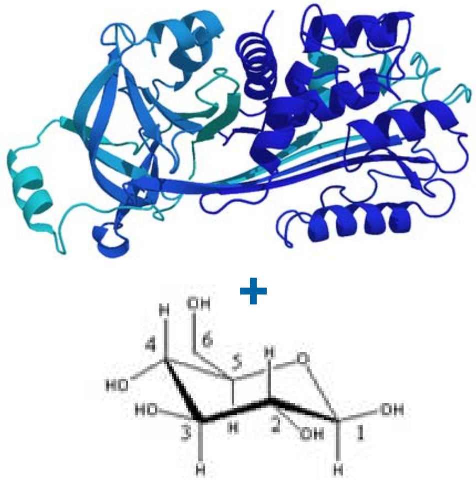


glucose g / borax g / Tp, °C	$^{a}S_{BET}$, m^{2}g^{-1}
6.5 / 0.2 / 200	180
6.5 / 0.5 / 200	280
6.5 / 0.2 / 900	379
6.5 / 0.5 / 900	462

HTC aerogels

Albumine promotes the formation of nitrogen doped carbogels

Ovalbumin (Alb)



D-Glucose

H_2O

180 °C

→

1.5 g D-Glu /
0.3 g Alb
/ 13.5 mL H_2O

t = 5.5 h

↓ $ScCO_2$

$S_{BET} > 250\ m^2g^{-1}$

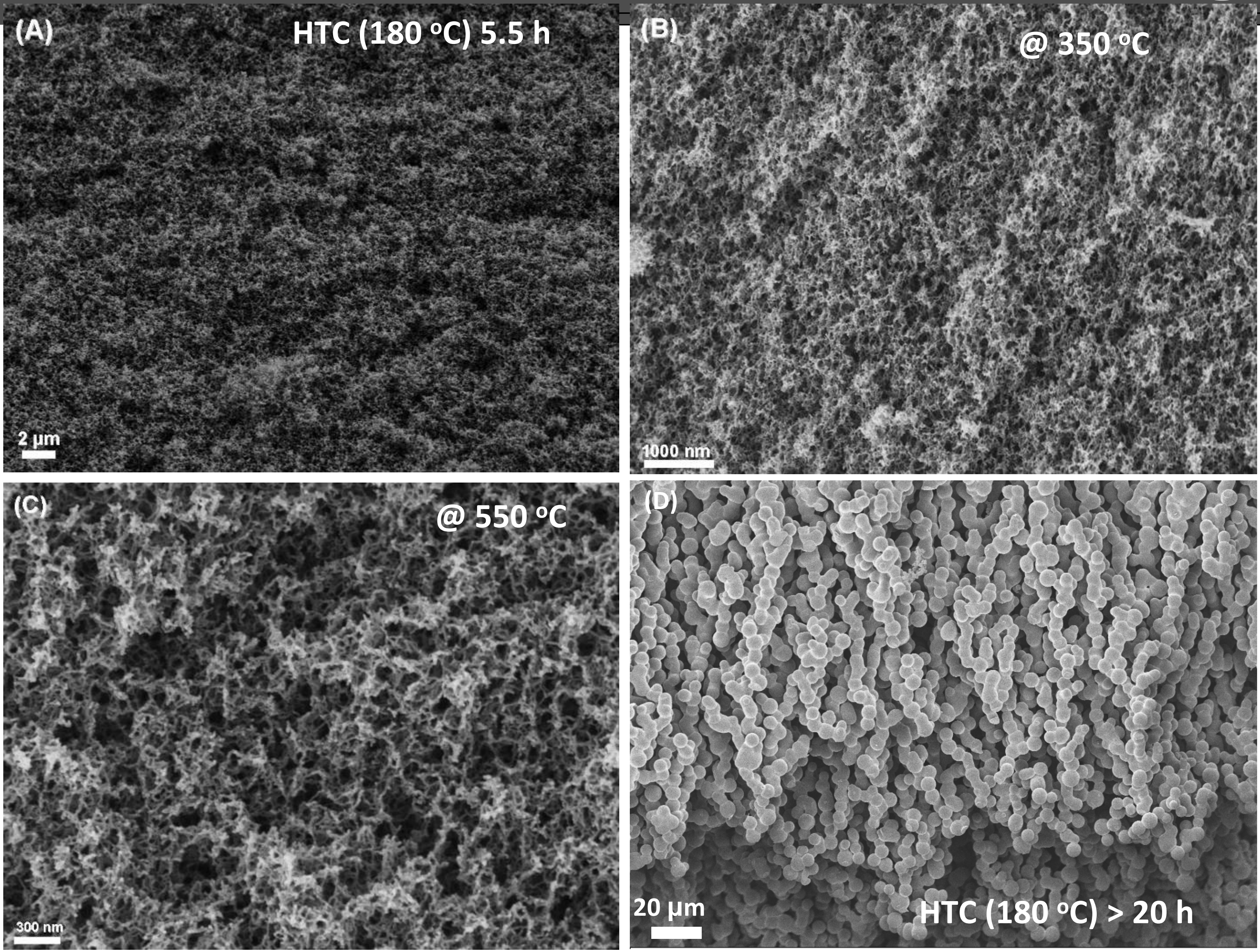
3D Pore System

$V_{pore} > 0.4\ cm^3g^{-1}$

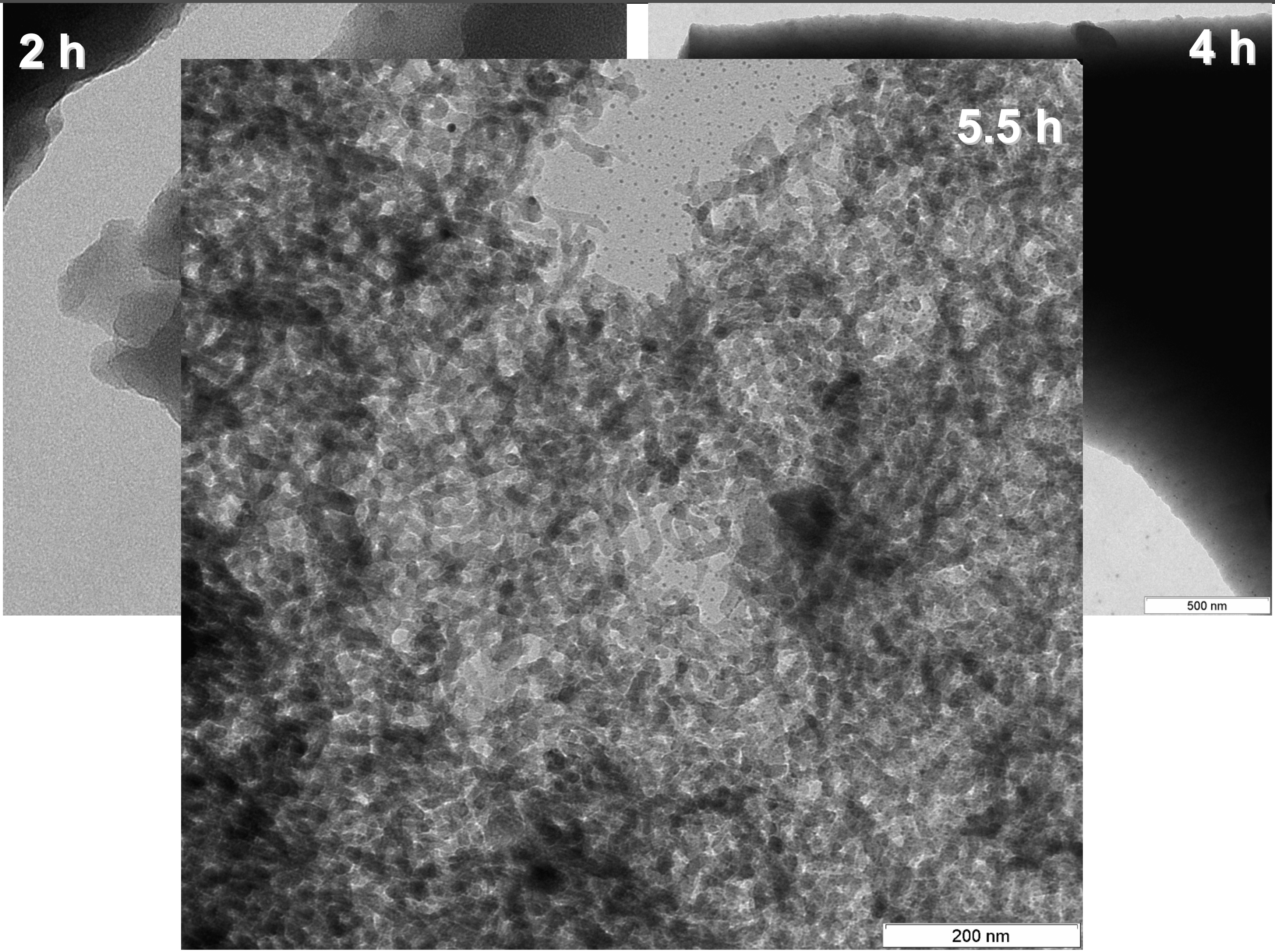
- 2° Biomass (i.e. Glycoprotein)
- Maillard chemistry
- Surface stabilising agent(s)

Titirici et al-Adv. Mater. **2010**-submitted/Pattent

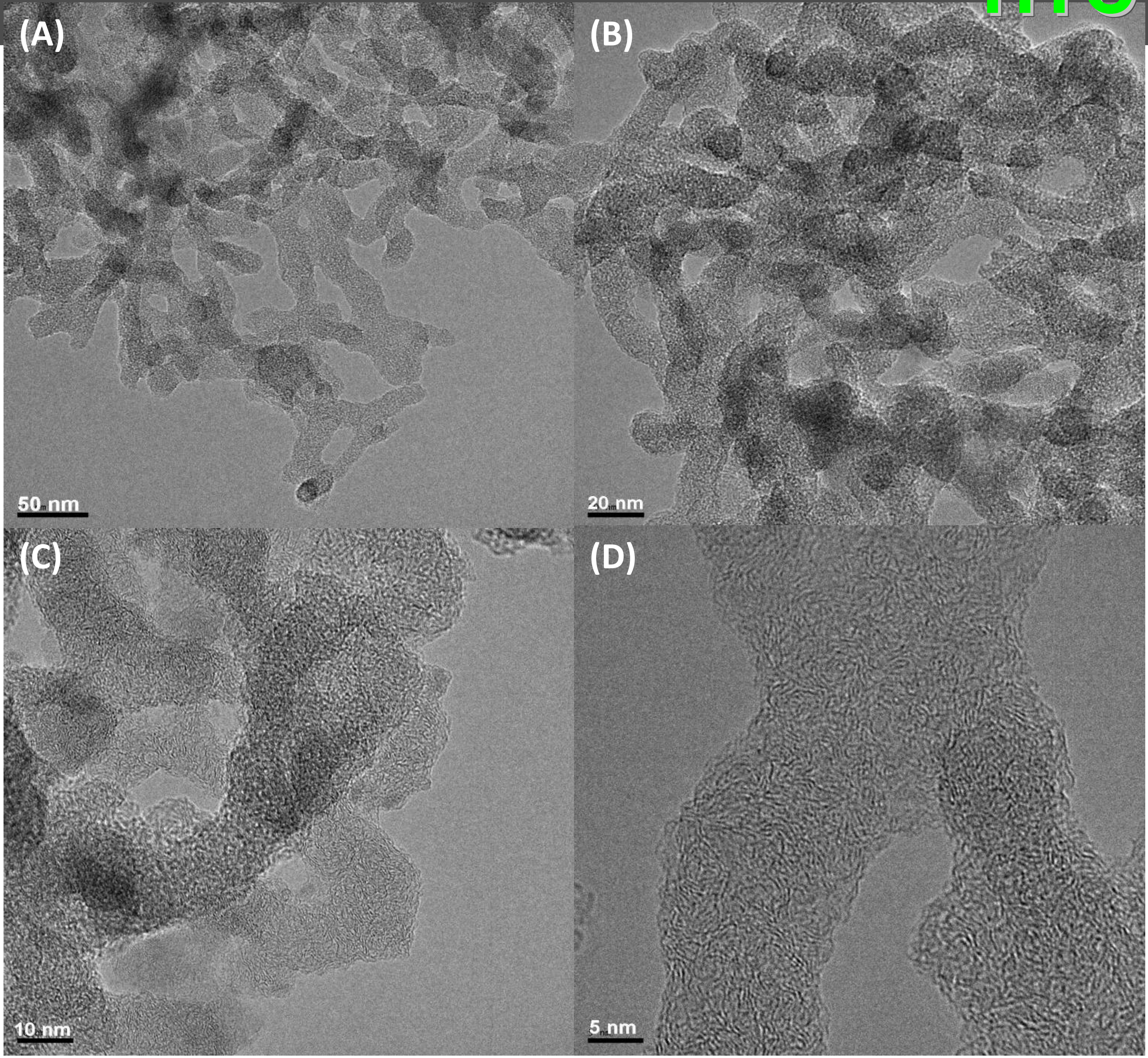
HTC aerogels



HTC aerogels

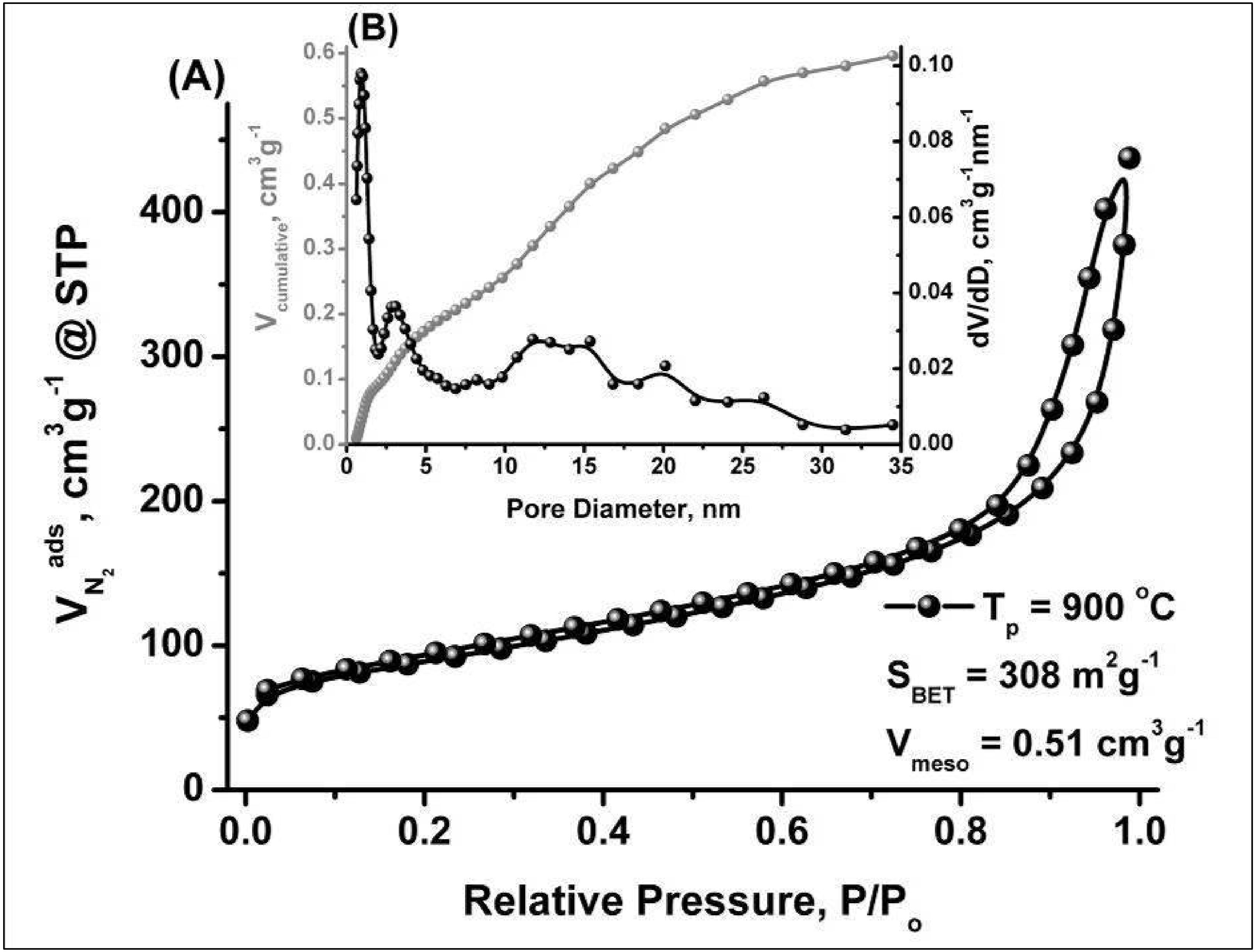


HTC aerogels



R. White & M. Titirici, Adv. Mater, 2010submitted

HTC aerogels



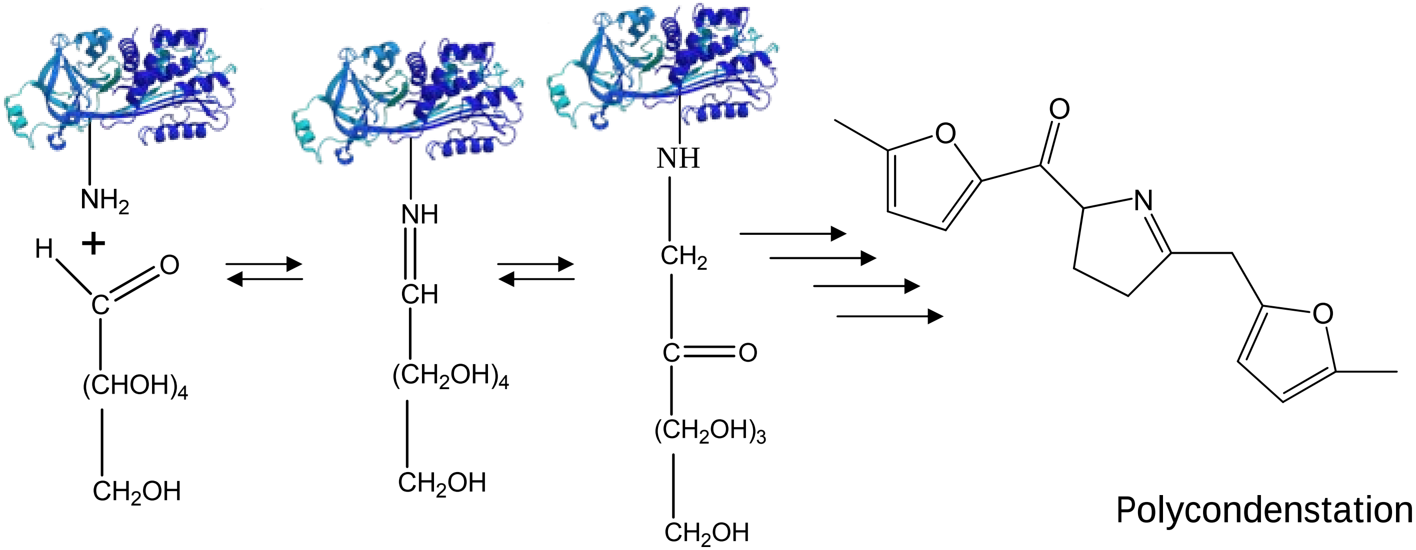
HTC aerogels

T_p, °C	S_{BET}, m^2g^{-1}	V_{total}, cm^3g^{-1}	V_{meso}, cm^3g^{-1}	PD, nm	%C (EA/XPS)	%N (EA/XPS)
180	276	0.49	0.41	3.2	57.6 / 72.3	**7.5 / 6.8**
350	247	0.42	0.40	3.1	65.0 / 78.4	**8.0 / 7.3**
550	476	0.57	0.40	3.4	79.6 / 90.4	**7.3 / 5.4**
750	300	0.73	0.62	3.3	83.8 / 92.4	**6.0 / 5.3**
900	308	0.68	0.65	3.2	84.8 / 93.2	**5.9 / 3.6**

- Large V_{meso} !!!
- Broad PSD – nature of continuous network
- Variation – system condensation??
- Scope for increasing N content.

HTC aerogels

❑ **Maillard reaction (e.g. –NH_2 + reducing sugar (D-Glu))**



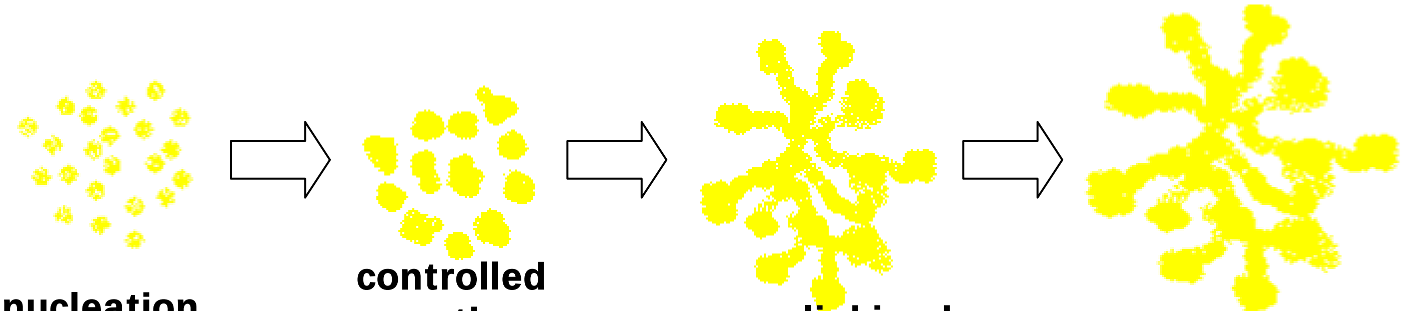
Alb / D-Glu

Schiff Base

Amadori / Cleavage

Polycondenstation

❑ **Globular protein ➔ gel forming**



nucleation

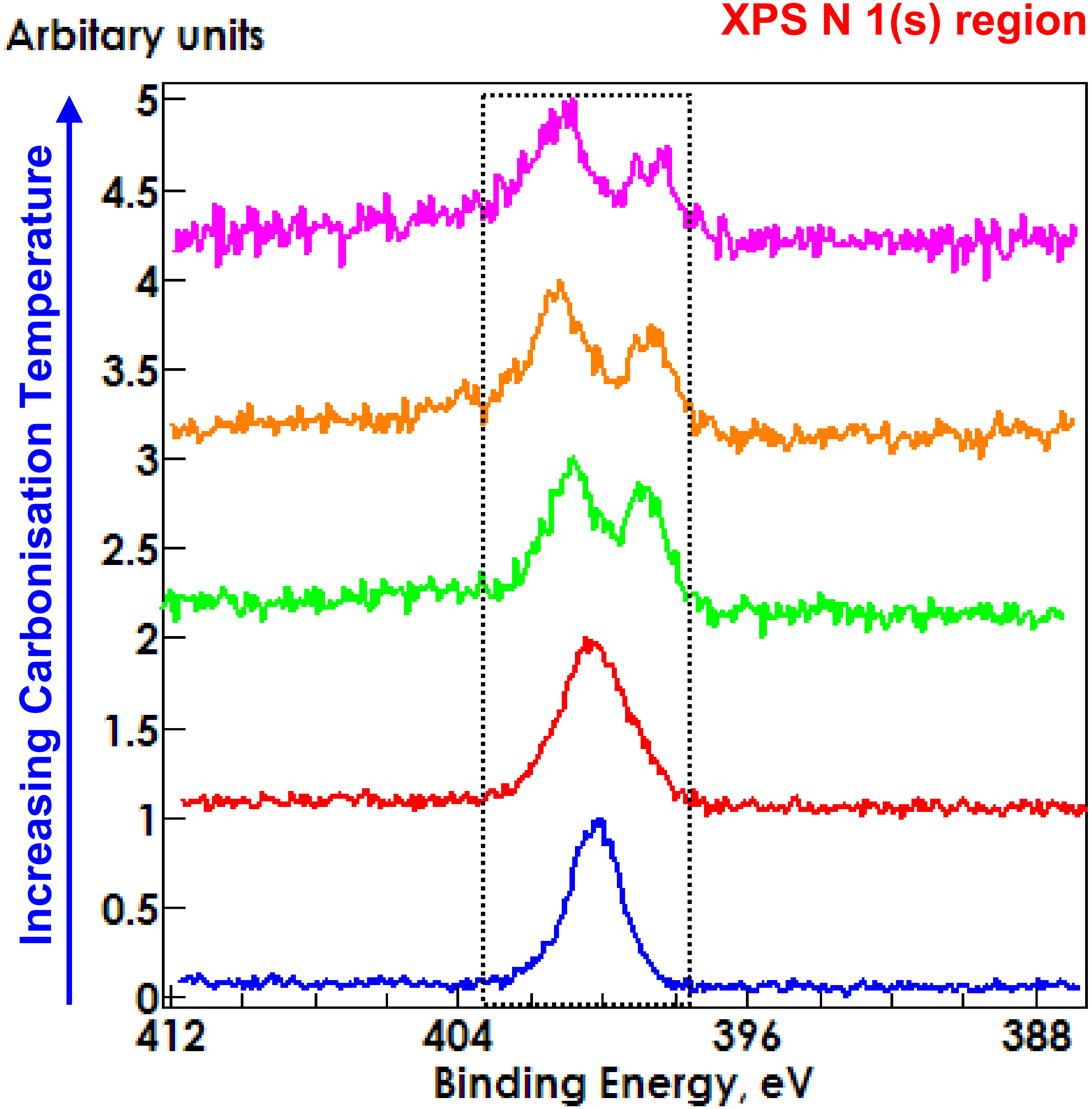
controlled growth stabilized by the protein

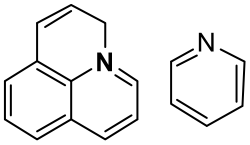
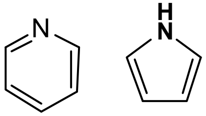
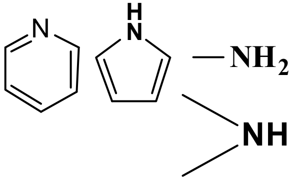
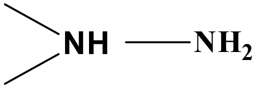
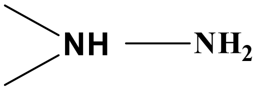
cross-linking by denaturation of the protein

ripening

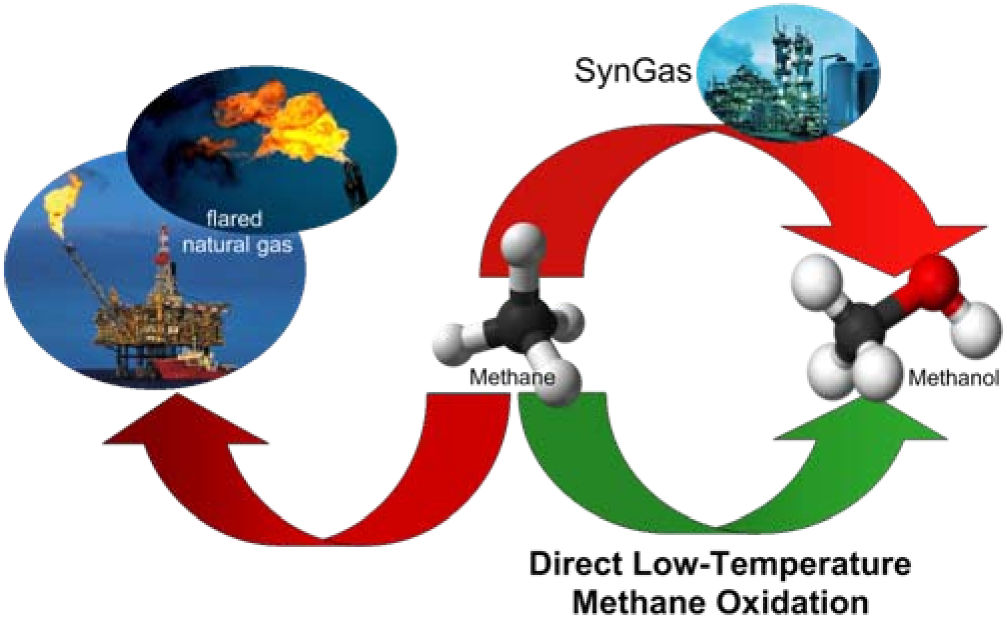
HTC aerogels

XPS N 1(s) region

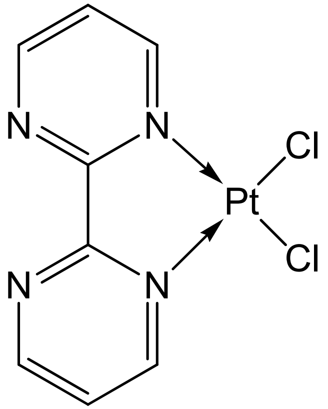


T_p	%N	
900	Bulk 5.9 XPS 3.6	
750	Bulk 6.0 XPS 5.3	
550	Bulk 6.5 XPS 5.4	
350	Bulk 8.0 XPS 7.3	
180	Bulk 7.5 XPS 6.8	

Applications of HTC aerogels



Periana/Catalytica System



dichloro(2,2´-bipyrimidyl)platinum(II)

(bpym)$PtCl_2$

~90 % methane conversion

81 % selectivity to methanol

reaction conditions:

220°C

2.5 hours

Oleum (20 wt.% SO_3)

Collaboration with MPI Mulheim

Applications of HTC aerogels

Periana/Catalytica System

$$CH_4 + {}^{1}/_{2}\,O_2 \longrightarrow CH_3OH \cancel{\longrightarrow} CO_2 + H_2O$$

chemically protected against overoxidation

I $CH_4 + H_2SO_4 + SO_3 \xrightarrow{\text{cat.}} CH_3OSO_3H + H_2O + SO_2$

II $CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4$

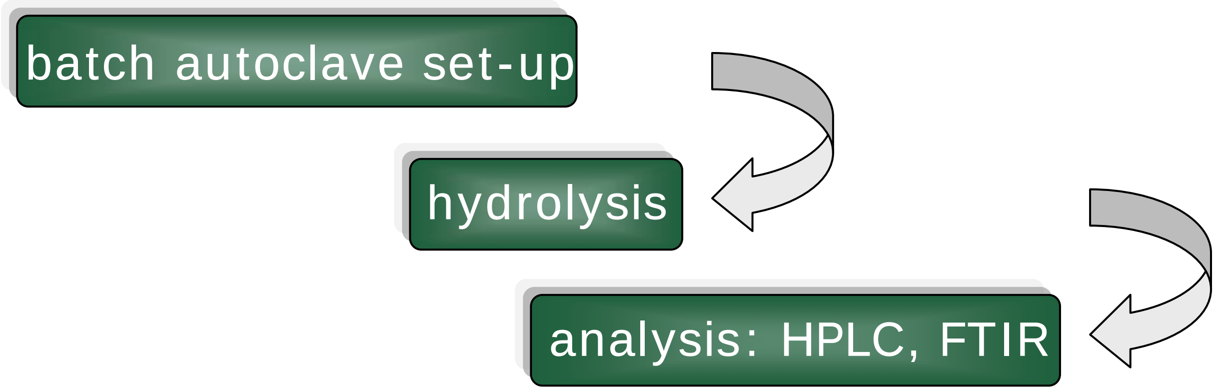
III $SO_2 + {}^{1}/_{2}\,O_2 \longrightarrow SO_3$

possible continuous three-step process

Periana, R.A. *et al*., *Science* **1998**, 280, 560-564.

Applications of HTC aerogels

Catalytic Activity in Direct Methane Oxidation



batch autoclave set-up

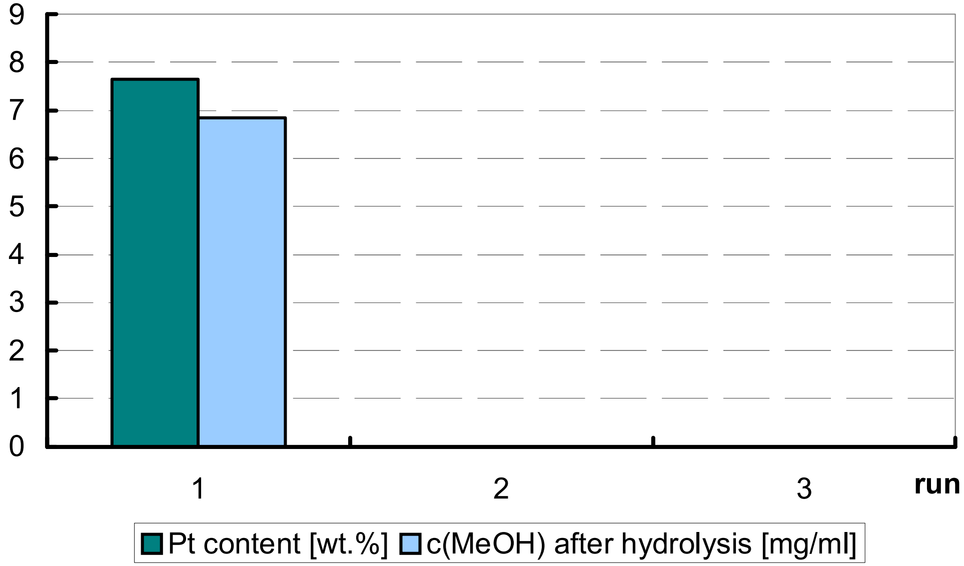
hydrolysis

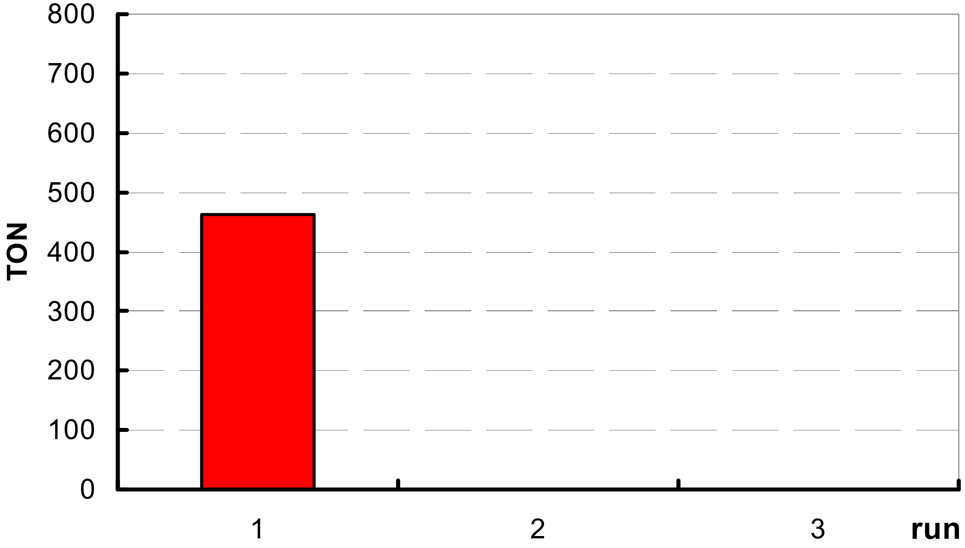
analysis: HPLC, FTIR

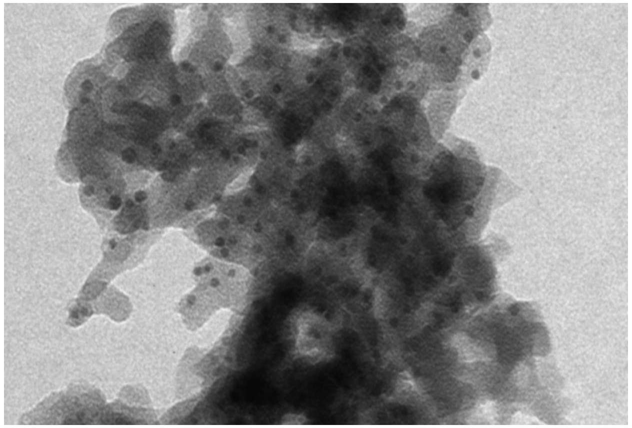
reaction conditions:

- 45 bar CH_4
- 215°C
- 15 mL fuming sulfuric acid (20 wt.% SO_3)
- 40 mg catalyst
- 1-2.5 h reaction time

Catalytic Activity of Glucose/Albumin-derived Carbon Aerogel in Direct Methane Oxidation

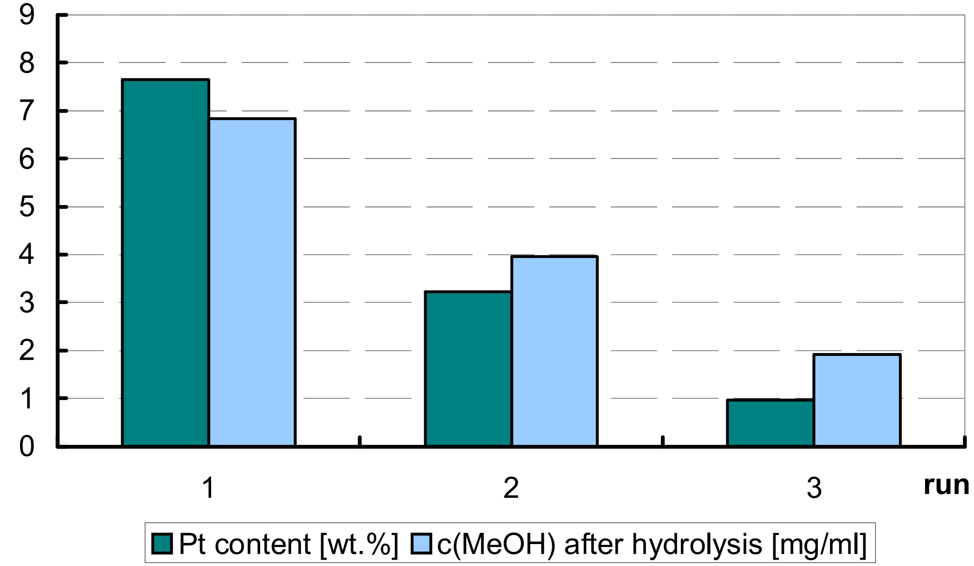






Carbogel 900/Pt

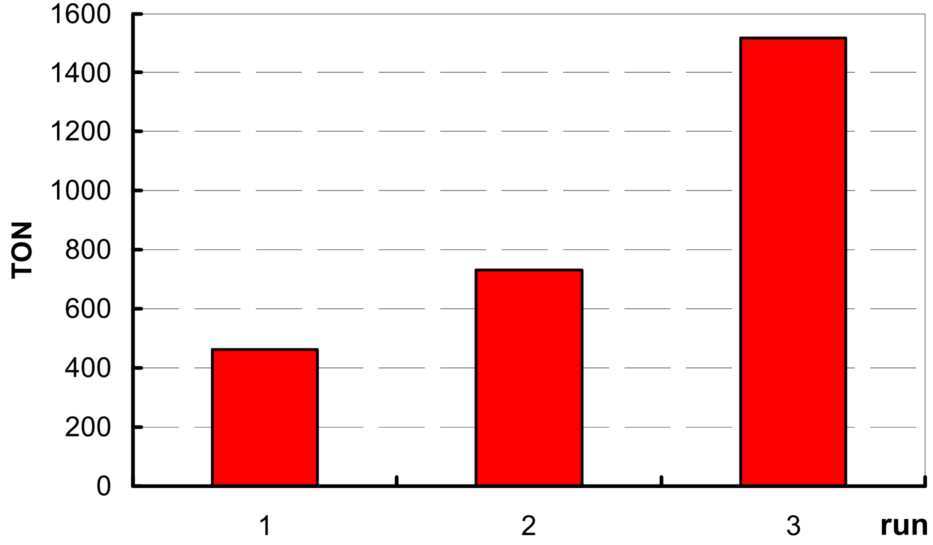
Catalytic Activity of Glucose/Albumin-derived Carbon Aerogel in Direct Methane Oxidation



- leaching of Pt species

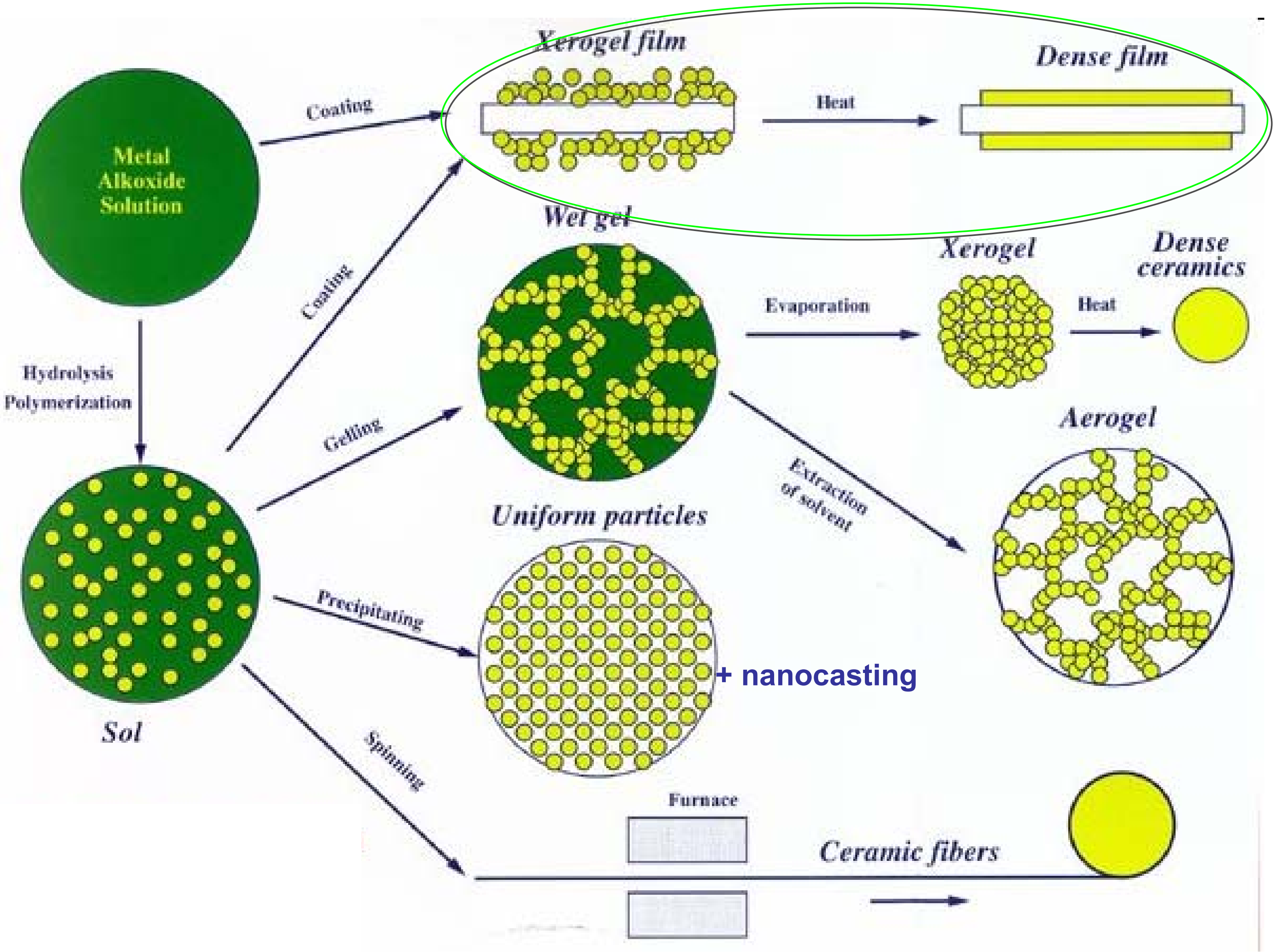
or

- decomposition of polymeric material



→ increasing turnover number over the first 3 runs

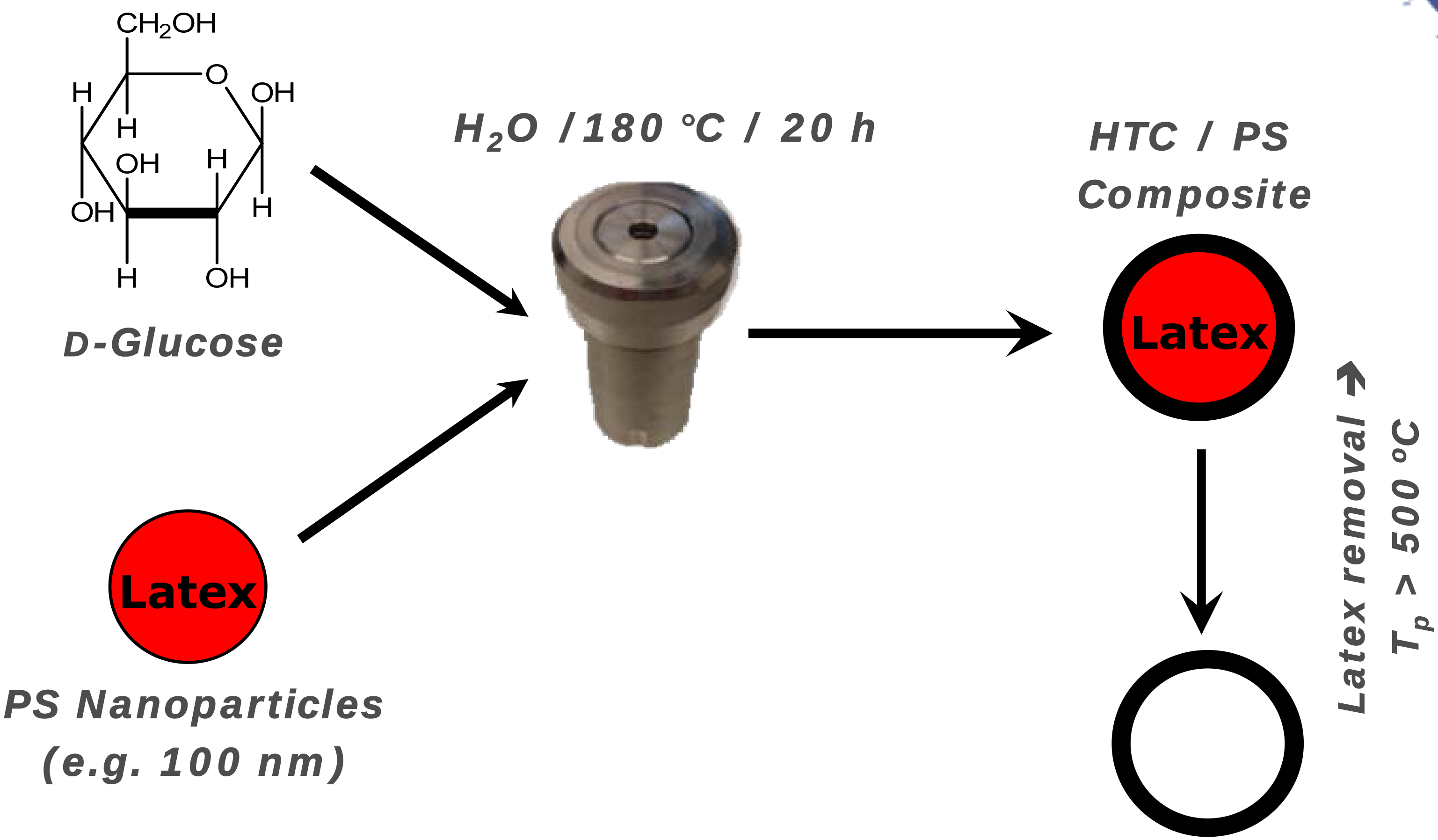
HTC~ Sol Gel: Chemie Douce de Carbon



+ nanocasting

Titirici at al C. R. Chimie 13 (2010) 167–173

HTC coatings on nanolatex



D-Glucose

H_2O / 180 °C / 20 h

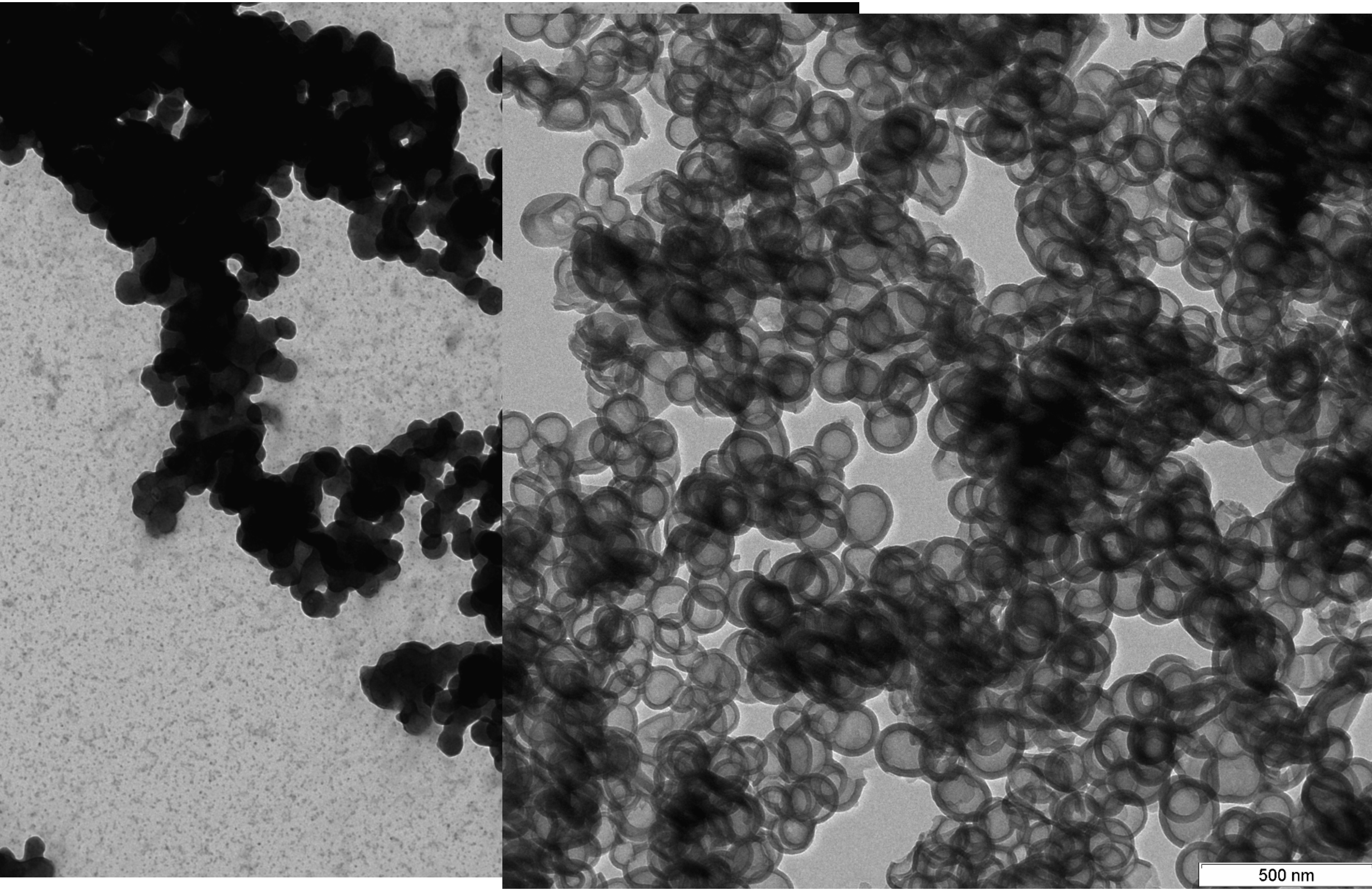
HTC / PS Composite

PS Nanoparticles (e.g. 100 nm)

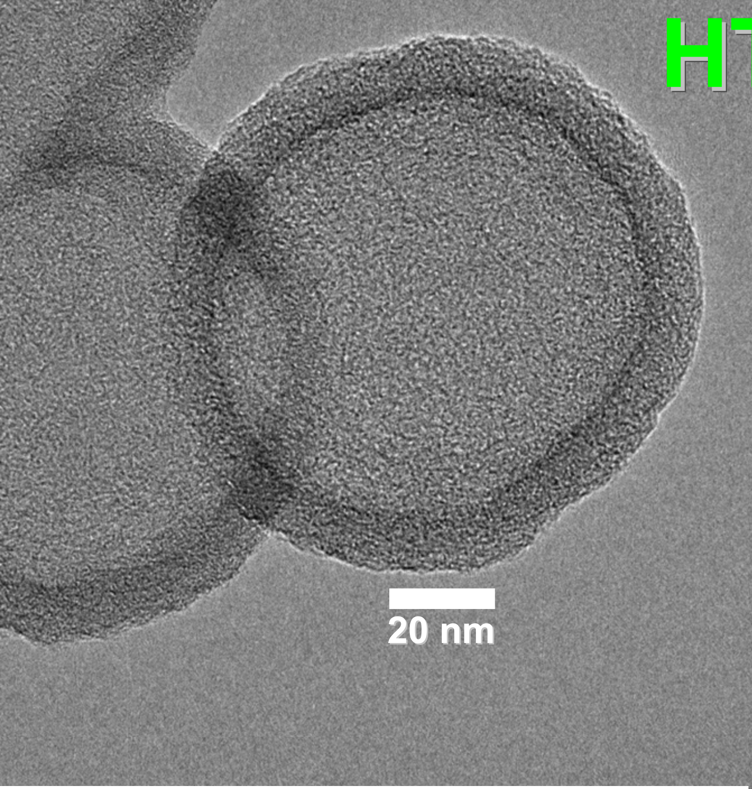
Latex removal → T_p > 500 °C

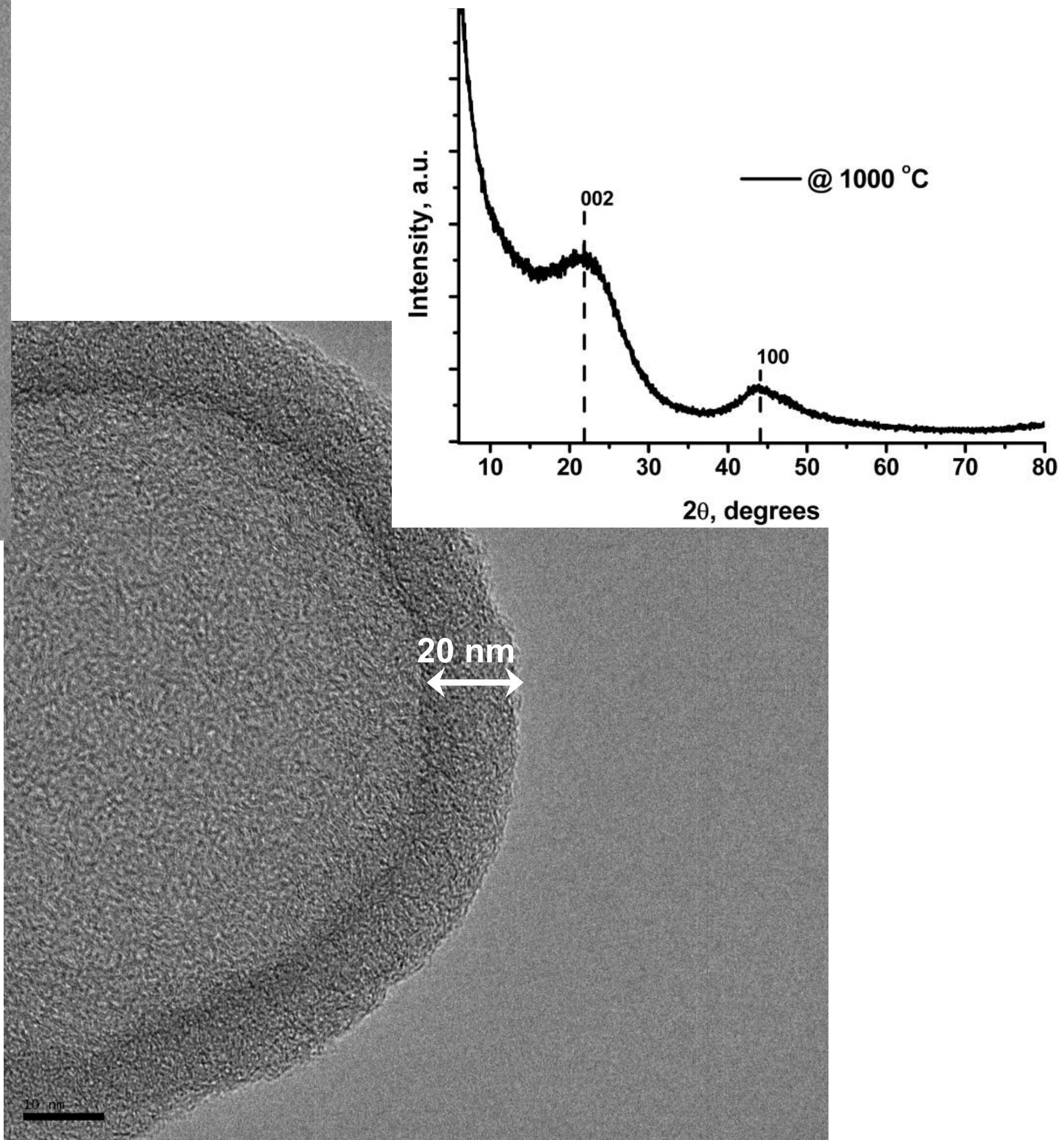
Titirici et al, J. Am. Chem. Soc., 2010, accepted

HTC coatings on nanolatex



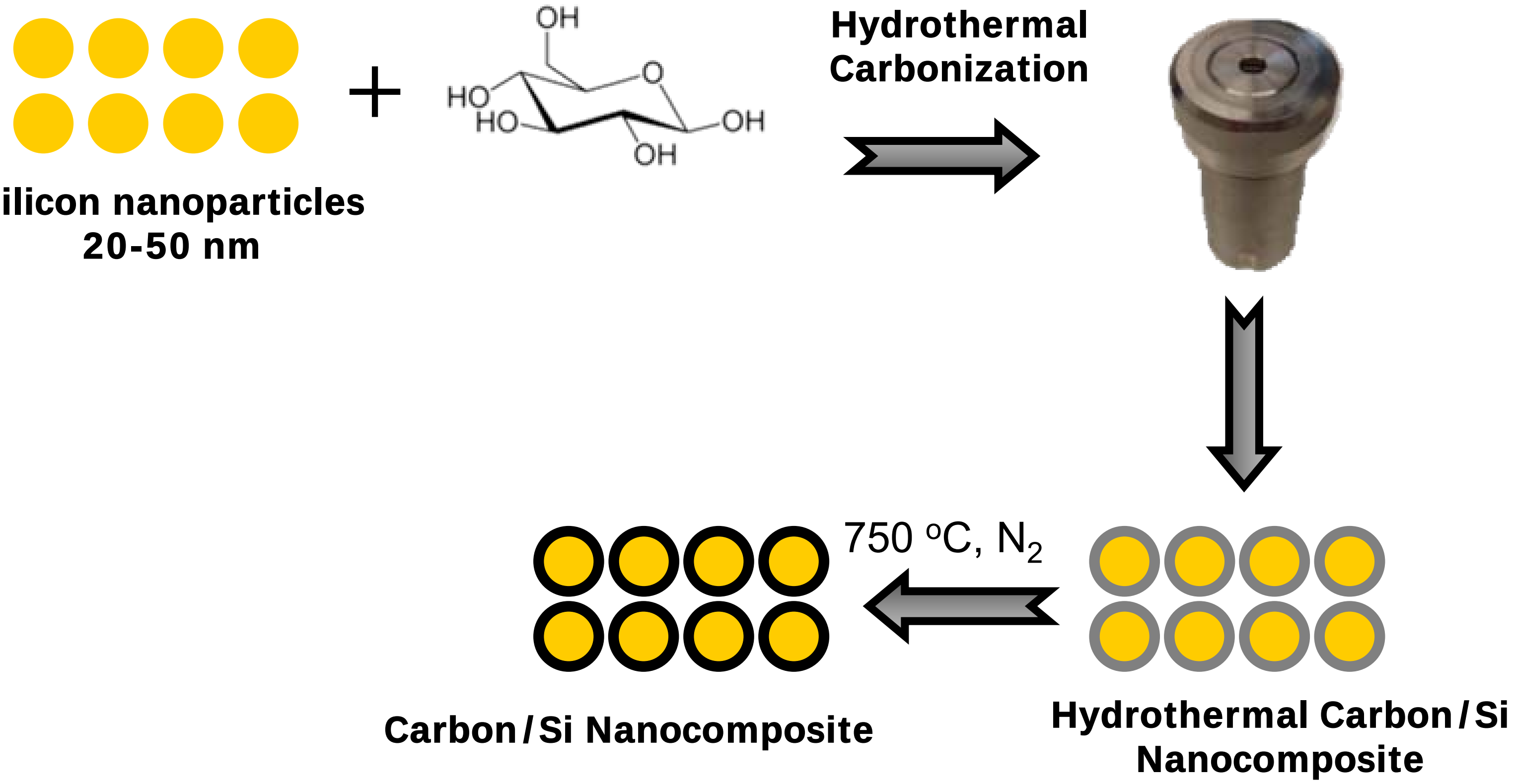
HTC coatings on nanolatex





- Stable at 1000 ^{o}C
- Uniform wall *(ca. 20 nm)*
- Turbostratic-type carbon

HTC coatings on nanosilicon



Silicon nanoparticles
20-50 nm

Hydrothermal
Carbonization

750 ^{o}C, N_2

Carbon/Si Nanocomposite

Hydrothermal Carbon/Si
Nanocomposite

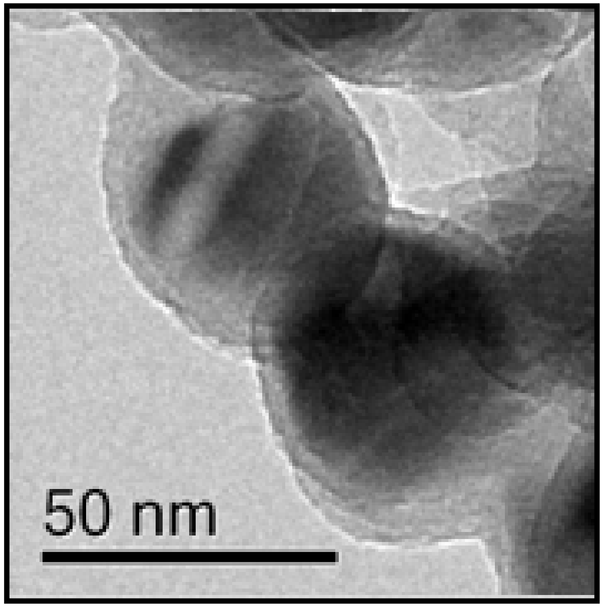
Si/C

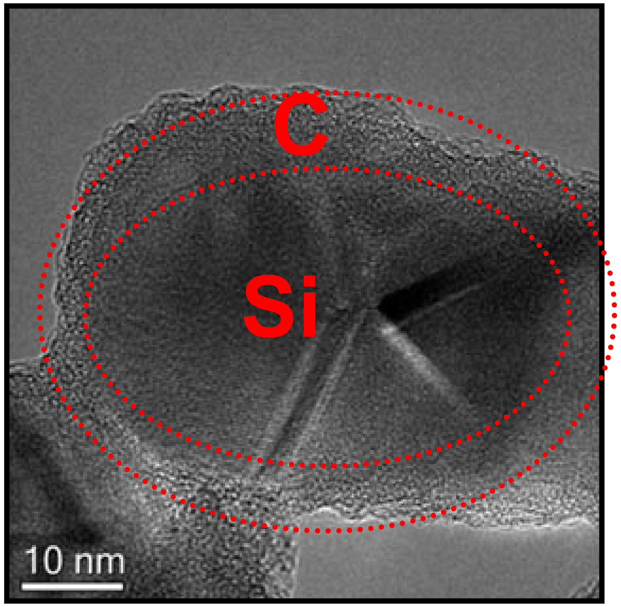
Si coated by carbon

Titirici, *Angew. Chem. Int. Ed,* **2008**, *47*, 1645

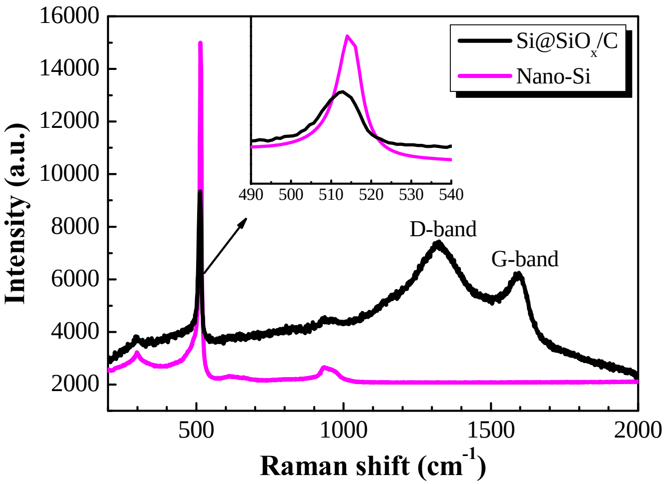
In collaboration with MPI-FKF, Stuttgart)

HTC coatings on nanosilicon

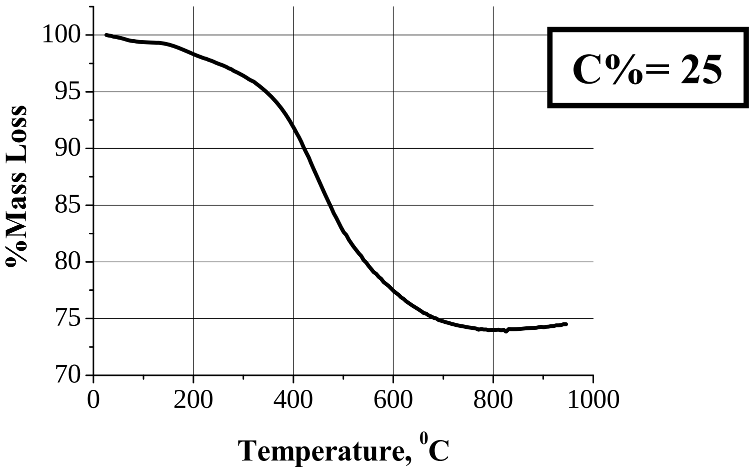




RAMAN



TGA

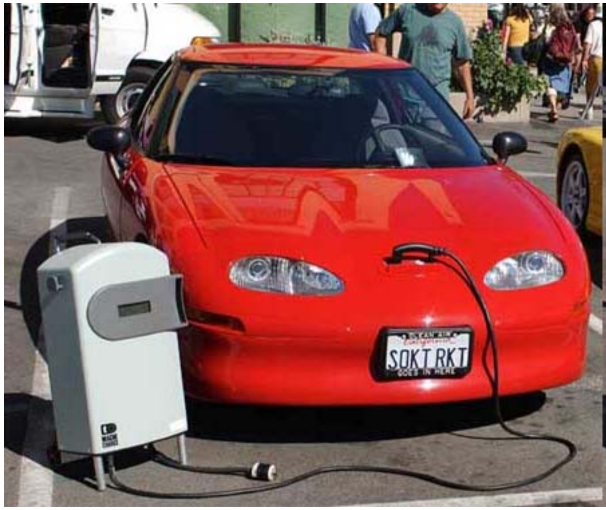


Li Ion Batteries

Permanent issue:

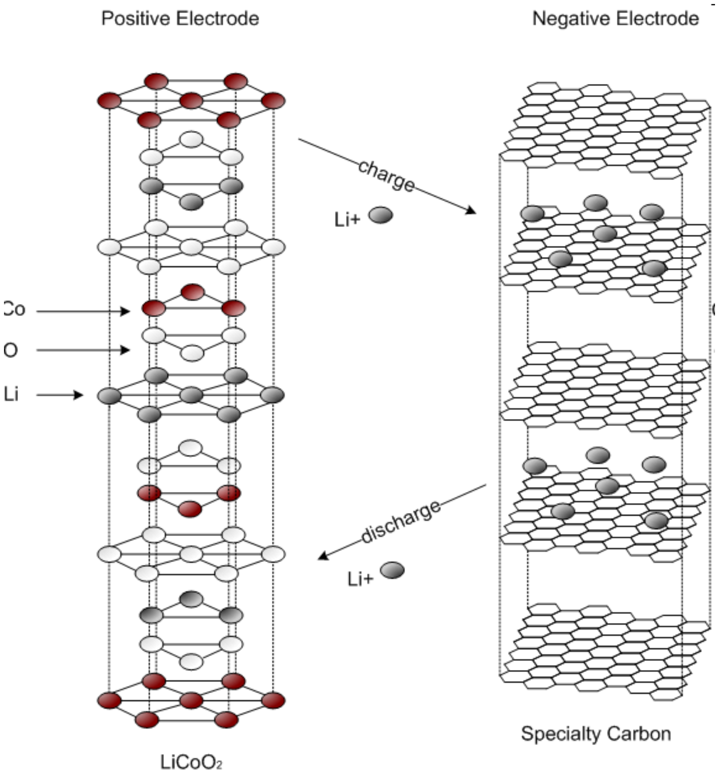
The first cars were electric cars (1885) !

Jenatzy´s world speed record vehicle „La Jamais Contente“ (1899) with 106 km/h.



Li Ion Batteries

Most common battery



$$\text{Cathode:}\quad \mathrm{LiCoO_2} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_{1-x}\mathrm{CoO_2} + x\mathrm{Li}^+ + xe^-, \qquad (1)$$

$$\text{Anode:}\quad 6\mathrm{C} + x\mathrm{Li}^+ + xe^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_x\mathrm{C}_6, \qquad (2)$$

$$\text{Total reaction:}\quad 6\mathrm{C} + \mathrm{LiCoO_2} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \mathrm{Li}_{1-x}\mathrm{CoO_2} + \mathrm{Li}_x\mathrm{C}_6. \qquad (3)$$

The lithium ions are transported to and from the cathode or anode,

Oxidization Co^3+ to Co^{4+} during charging

Reduction Co^{4+} to Co^{3+} during discharge.

<u>Anode</u>: C

Cathode: Metal Oxide ($LiCoO_2$)

Electrolyte: Li salt in an organic solvent

HTC coatings on nanosilicon

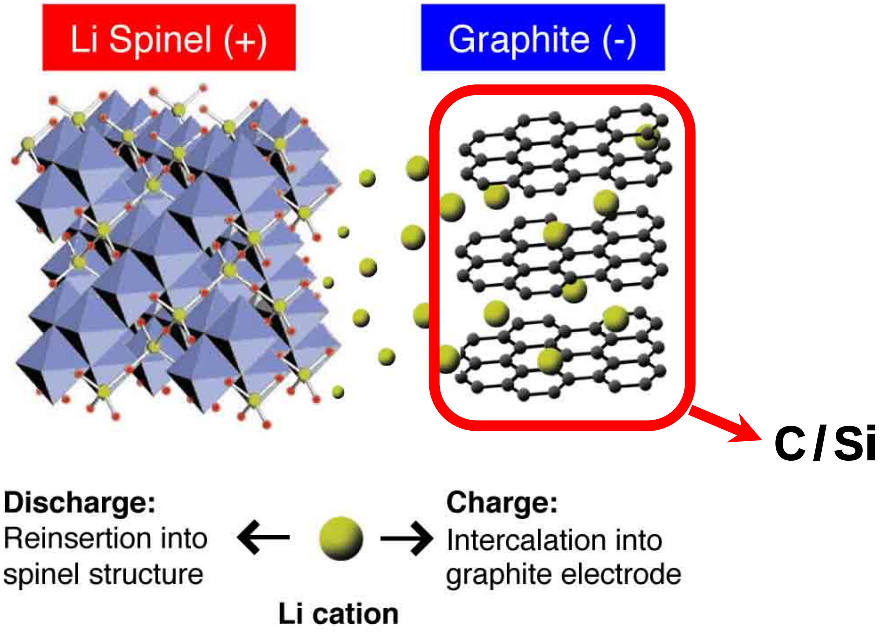
CARBON

- 👍 High coulombic efficiency
- 👍 Long cycle life
- 👍 Preventing the production of lithium dendrites

- 👎 Rather low capacity (372 mAh/g)

SILICON

- 👍 Highest theoretical capacity ~ ($Li_{4.4}Si$ 4200 mAh/g)
- 👍 Low cost
- 👍 Abundant source
- 👎 Low electric conductivity
- 👎 Severe volume change
- 👎 Poor cycling performance



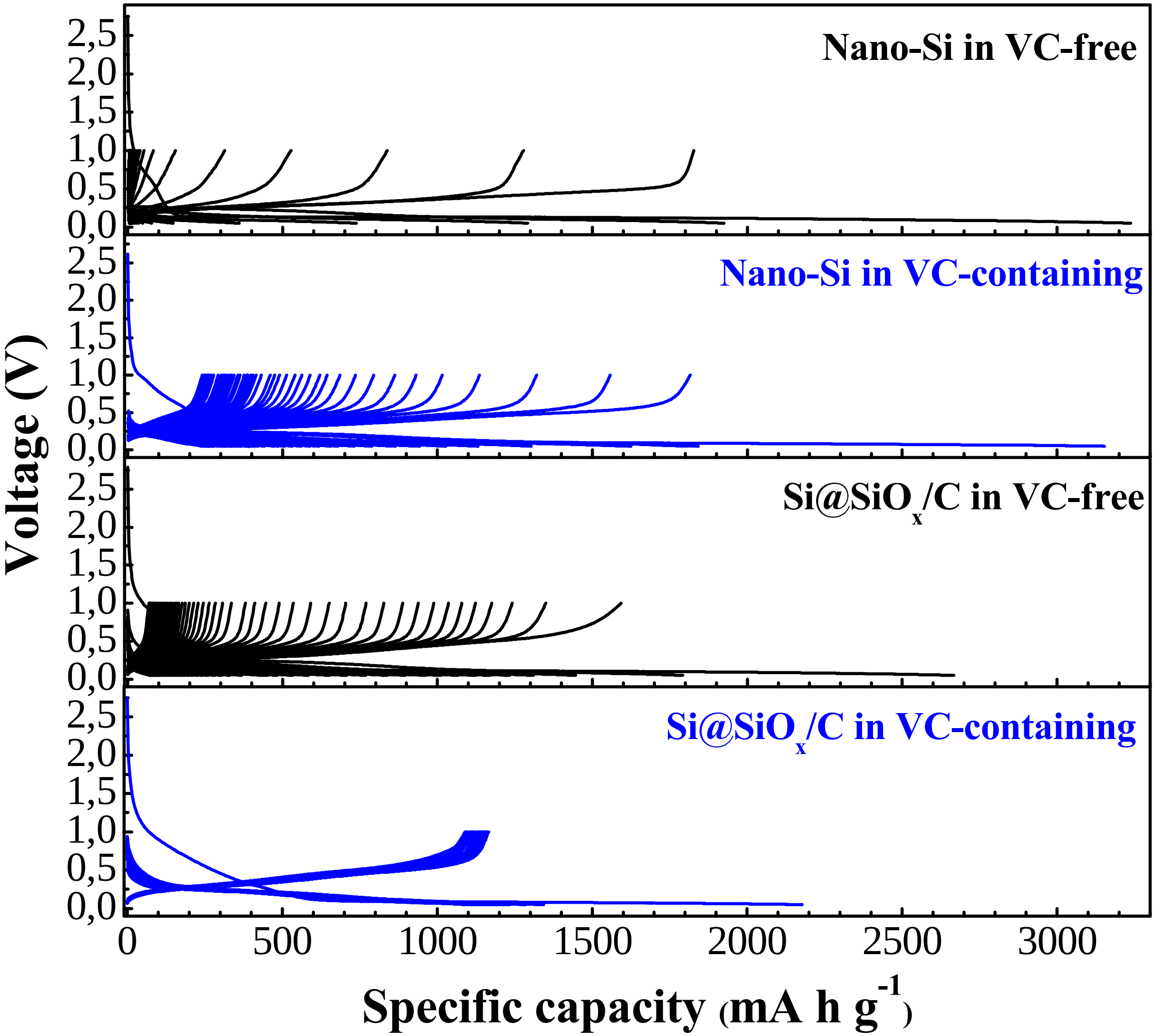
Discharge: Reinsertion into spinel structure ←

→ **Charge:** Intercalation into graphite electrode

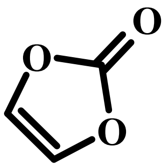
HTC coatings on nanosilicon

Galvanostatic Charge/Discharge Profiles

(150 mA/g, 0.05-1 V, 1M LiPF6 in EC/DMC)



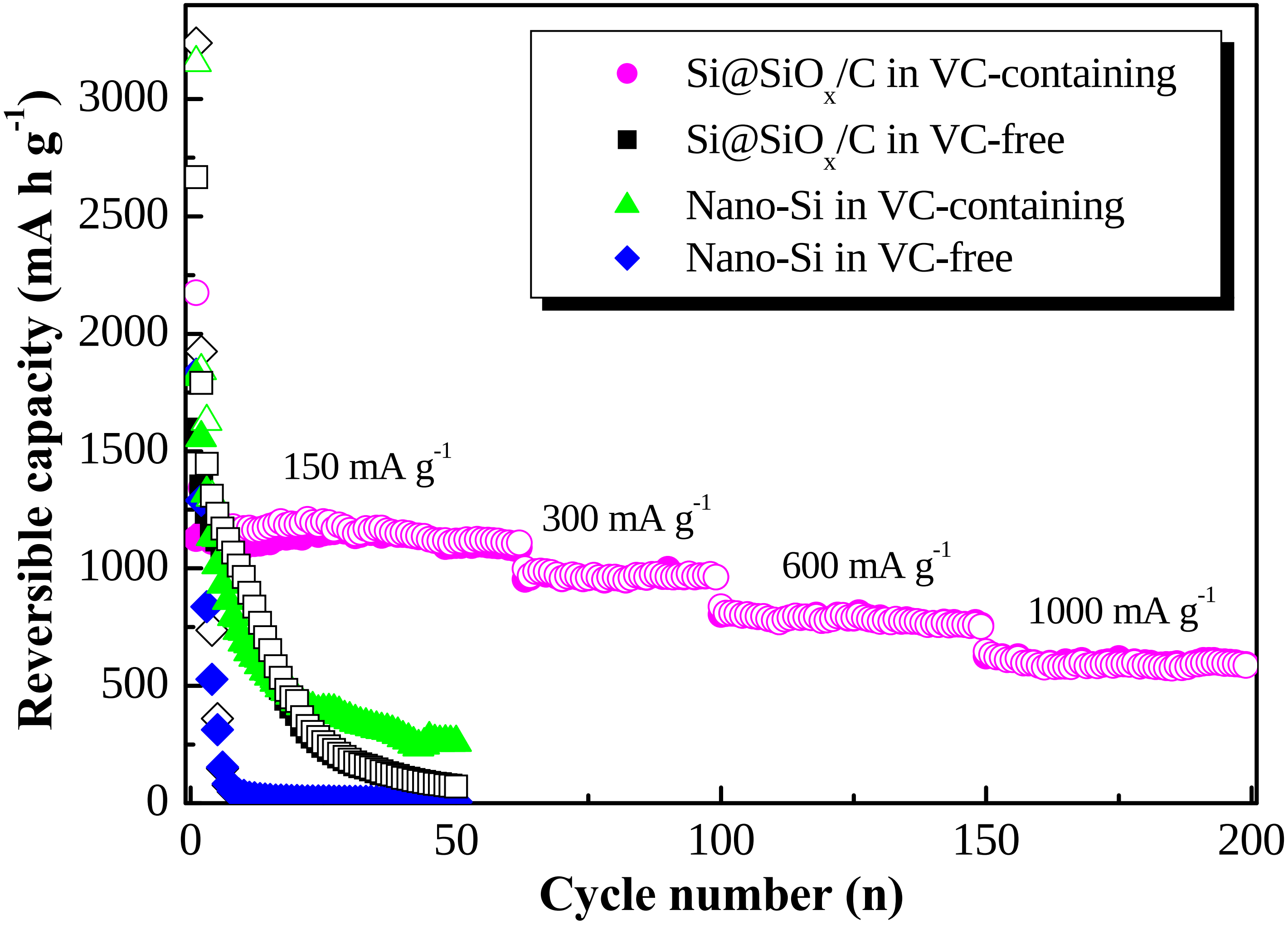
VC =



Coulombic efficiency > 99%

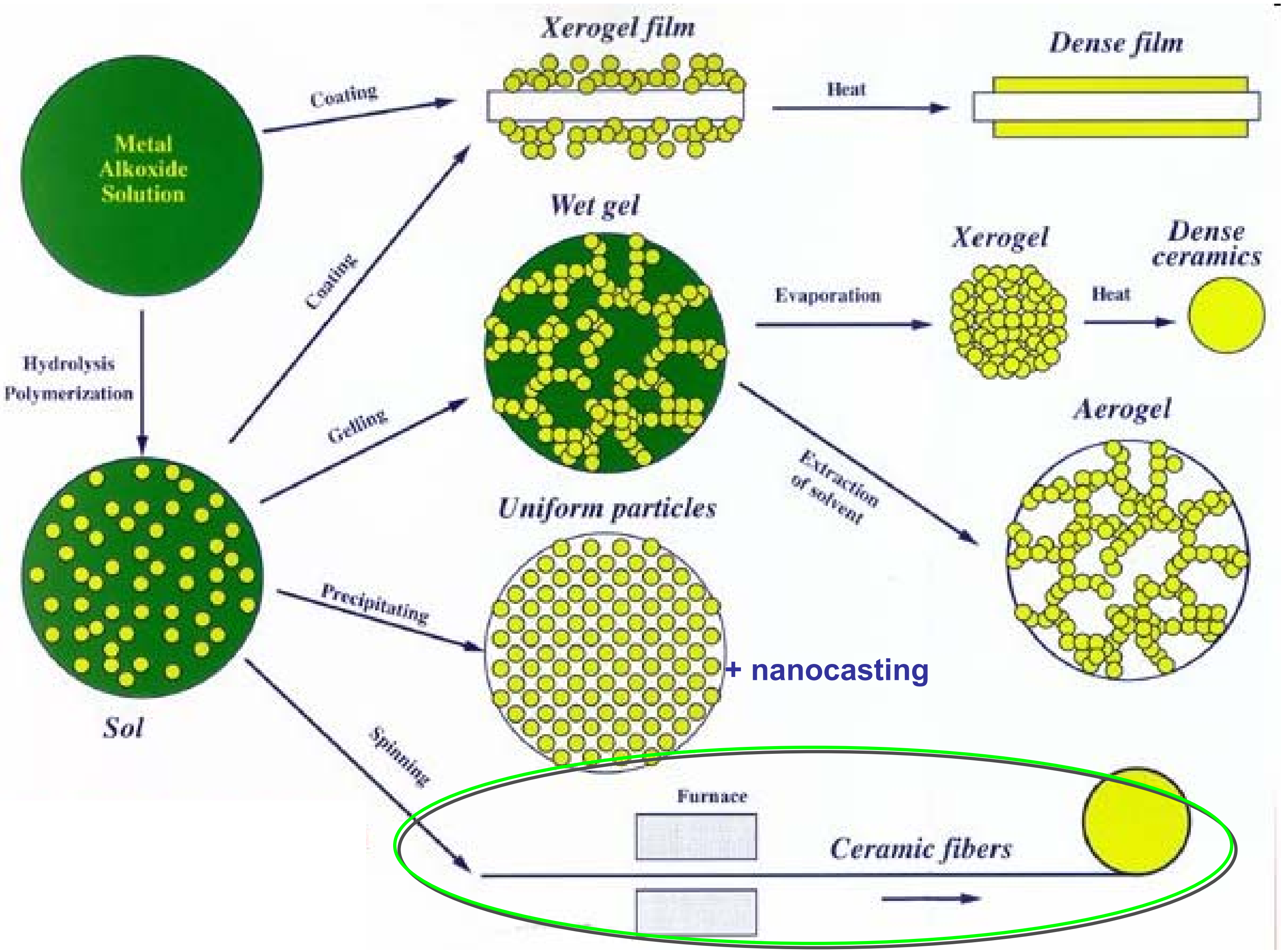
HTC coatings on nanosilicon

Cycling and Rate Performance



Titirici et al, *Angew. Chem. Int. Ed*, 2008, *47*, 1645

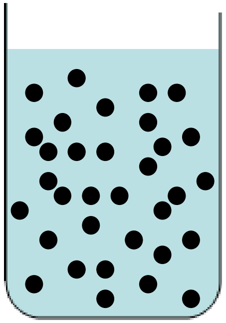
HTC~ Sol Gel: Chemie Douce de Carbon



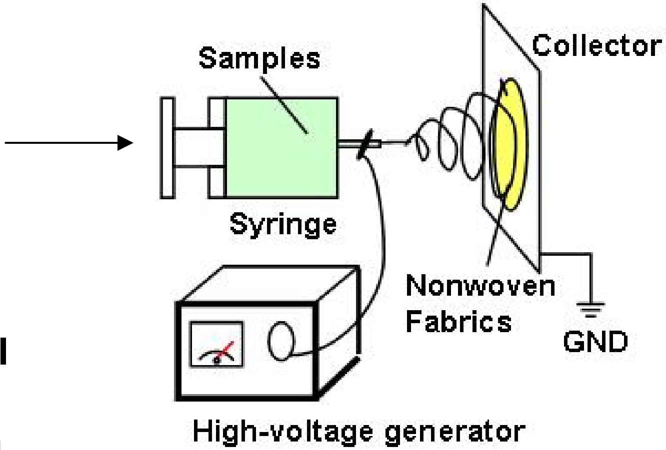
+ nanocasting

Titirici at al C. R. Chimie 13 (2010) 167–173

HTC Electrospinning

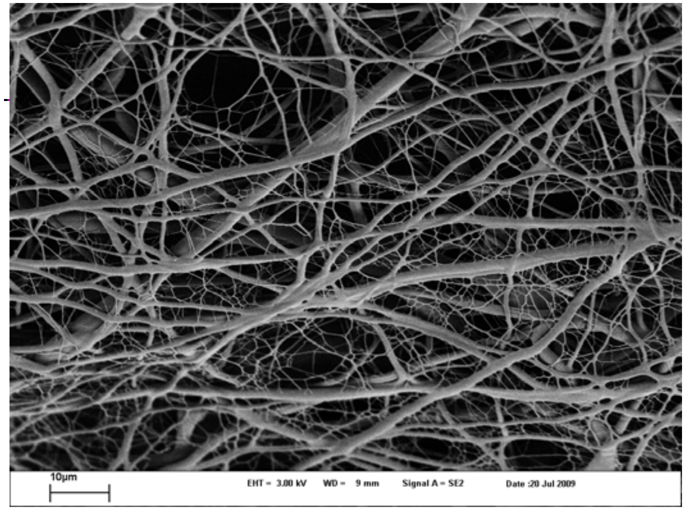


Chitosan sol after HTC at 200°C for 4h

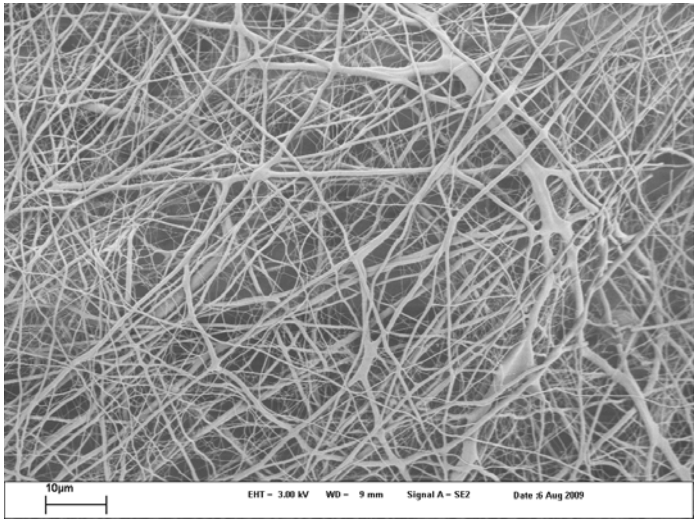


occurs when the electrical forces at the surface of the sol overcome the surface tension and cause an electrically charged jet to be ejected

- Spinning conditions: feed rate 0.2 mL/h, distance tip-collector 8 cm, voltage 13 kV, 15% rel. humidity
- TFA solution 6.6 w/v%



900°C



Nitrogen doped carbon fibers %N= 8

OUTLINE

- Introducing the green chemistry concept

- Sustainable Carbon

1. Biomass derived nanotructured carbon materials with valuable applications

    1.1 Bottom up approach: Porous Carbohydrates

    1.2 Top down approach: Hydrothermal Carbonization

2. Biochar production for CO_2 sequestration and soil regeneration

- Conclusions

HTC ~ Coal Formation

The Overall Process

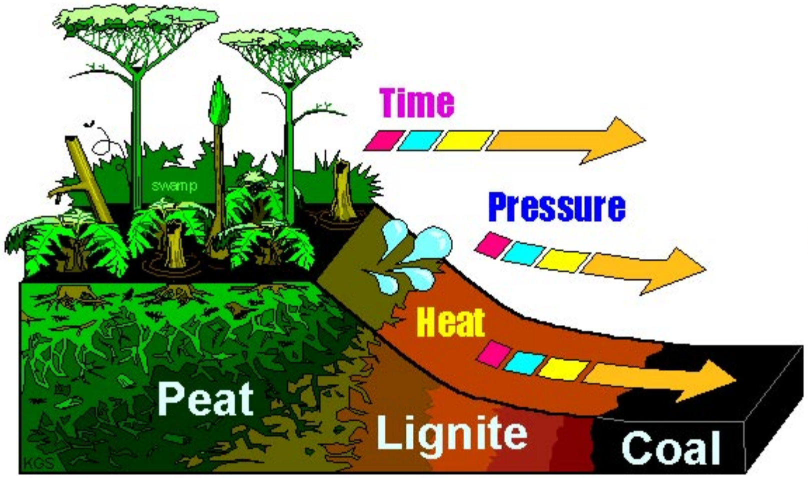
+

Δ

180 - 220 °C

18 – 24 h

Mimicking Natural Coal Formation



- Terrestrial biomass growth amounts 118×10^9 tons/year as dry matter
- A “zero emission” carbon source
- Potential to generate a new chemical CO_2 disposal” industry
- To become an “effective” carbon sink the carbon has to stay fix by “low-tech” operations

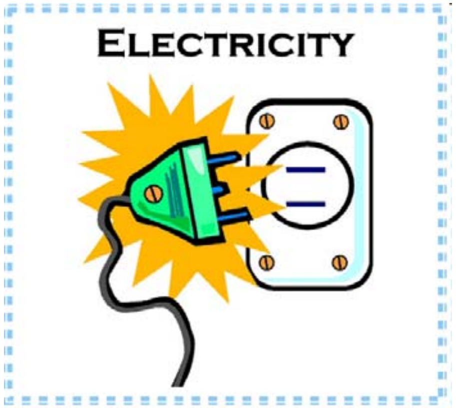
Biomass Treatement

Hydrothermal Treatment

Temperature

Gasification

Syngas



Liquefaction

Liquid fuel

Valuable chemicals

Carbonization

CO_2 sequestration

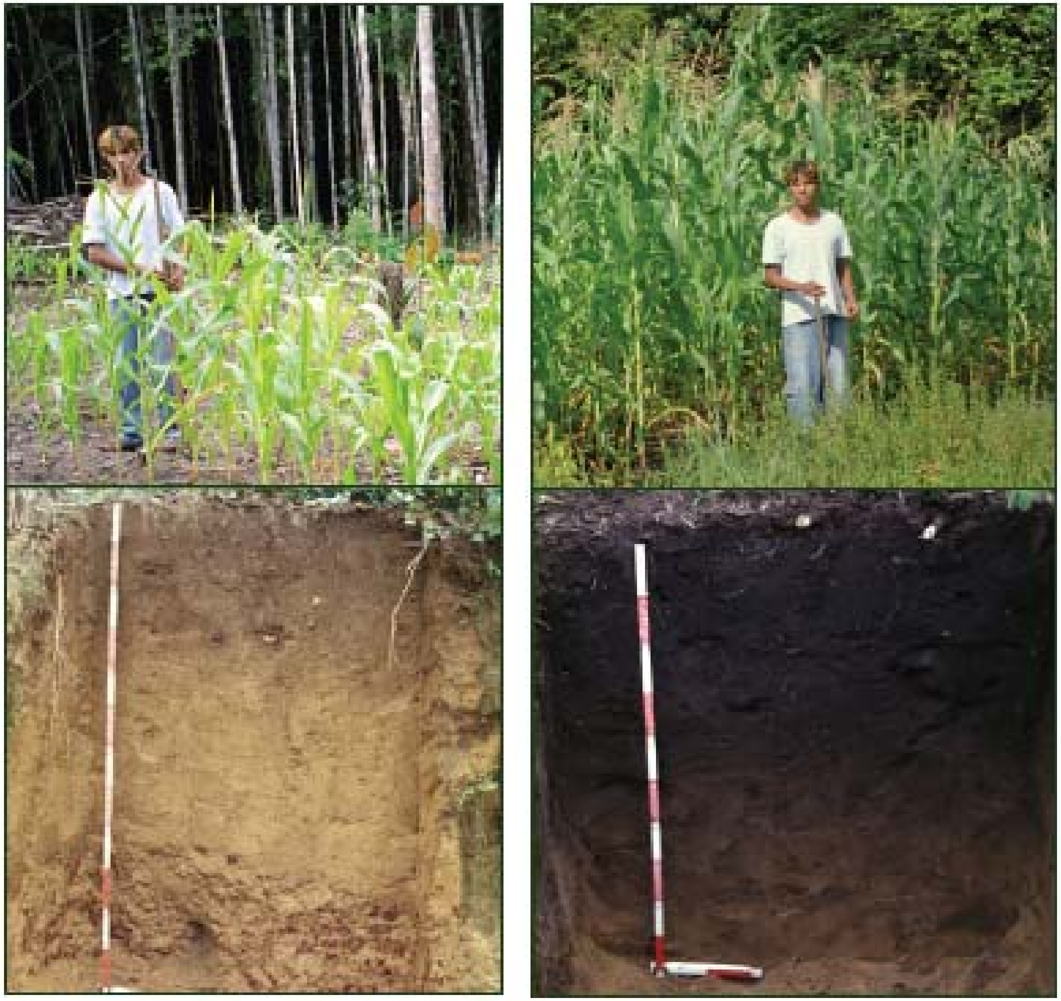
Novel materials synthesis

CE =1

Antonietti et al., *New J. Chem.*, 2007, 6, 787

Biochar in soil

Terra preta do indio or the "black earth of the Amazons"



Biochar and Terra Preta Soils

Terra preta

- Fine dark loamy soil
- up to 9% carbon, (adjacent soil 0.5% C)
- high nutrient content and high fertility
-3 times the phosphorous and nitrogen

- Developed over thousands of years by human habitation correspond to ancient settlements

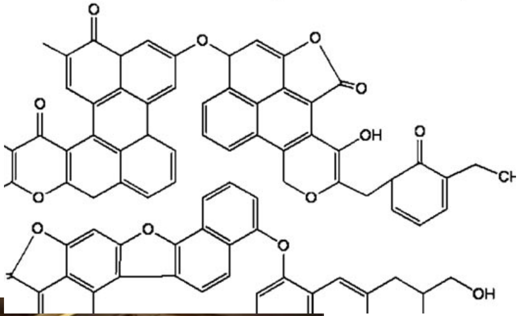
- Results from long-term mulching of charcoal production from hearths and bone fragments with soil application

- Persistent in soil, recalcitrant, resistant to decomposition.

HTC ~ Biocahr

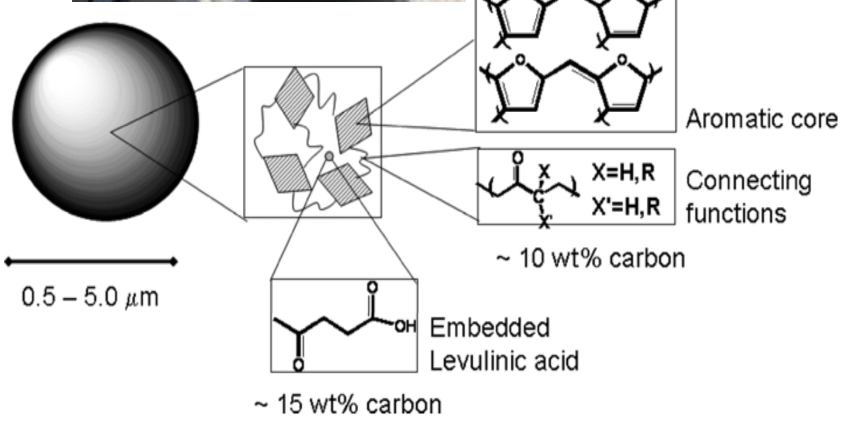
CLASSICAL BIOCHAR

- Produced from dry biomass above 500 ºC
- Contains ~ 90% C as Carbon black
- Not very hydroscopic
- Highly aromatic, porous
- Gas emission (CO_2, NO_2) during production



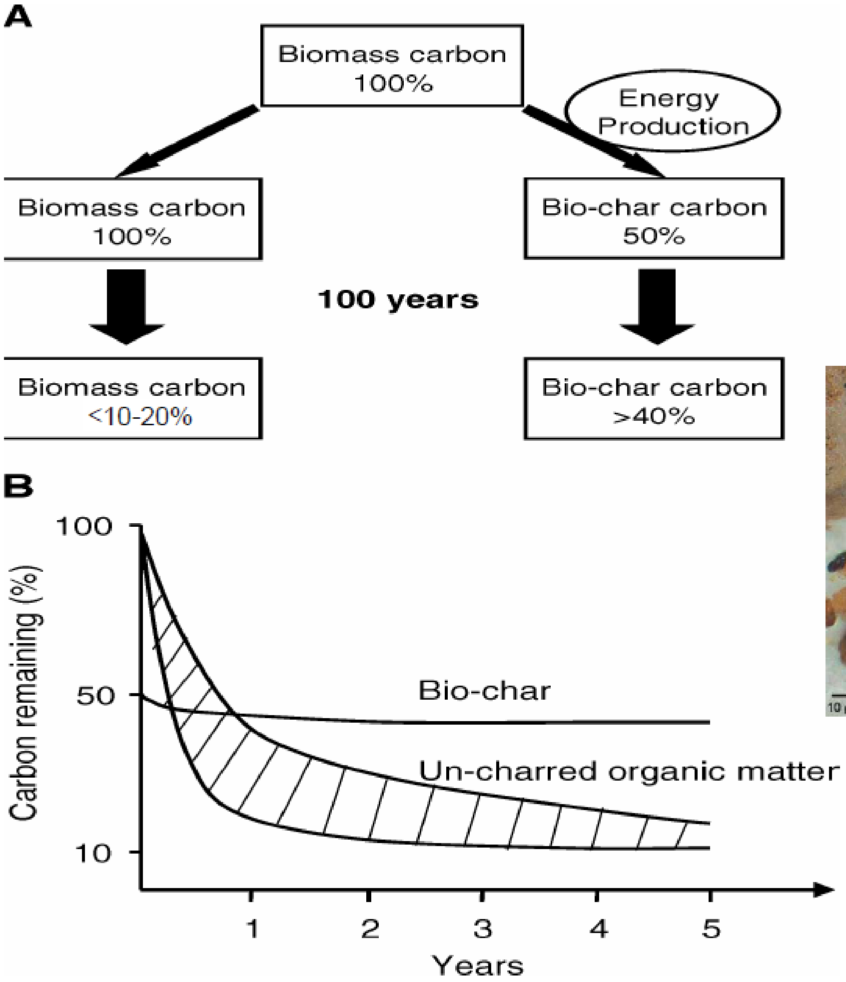
HTC Carbon

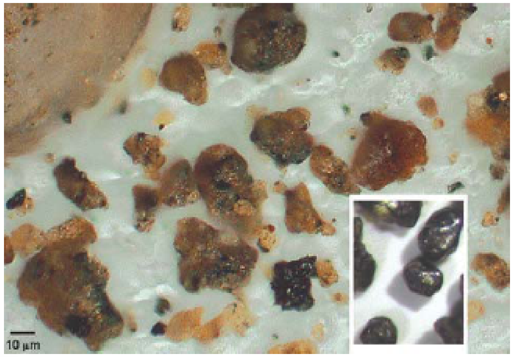
- Produced from wet biomass at 180°C
- Contains ~60%C
- Very Hydroscopic
- Polymer –like, non-porous



CO_2 Sequestration Potential of Biocahr

Schematics for biomass or bio-char remaining after charring and decomposition in soil



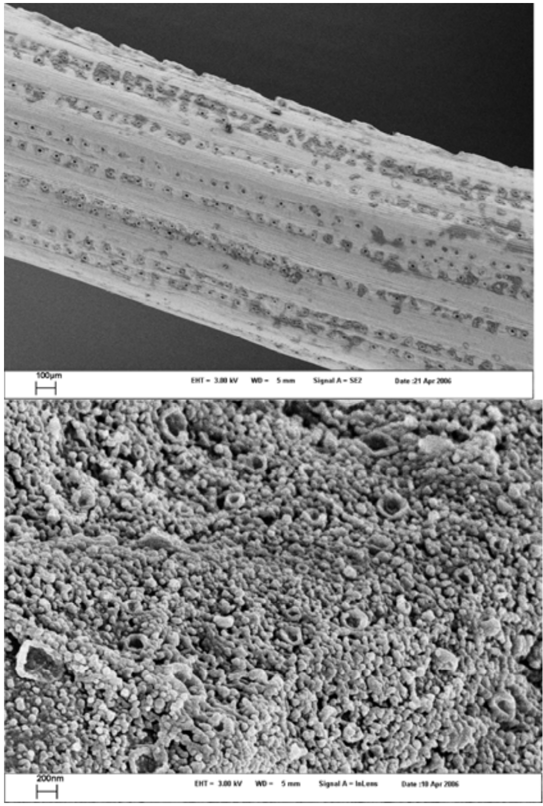


Lehmann et al., 2006. Mitigation Adap.Strat. Glob. Change 11: 403

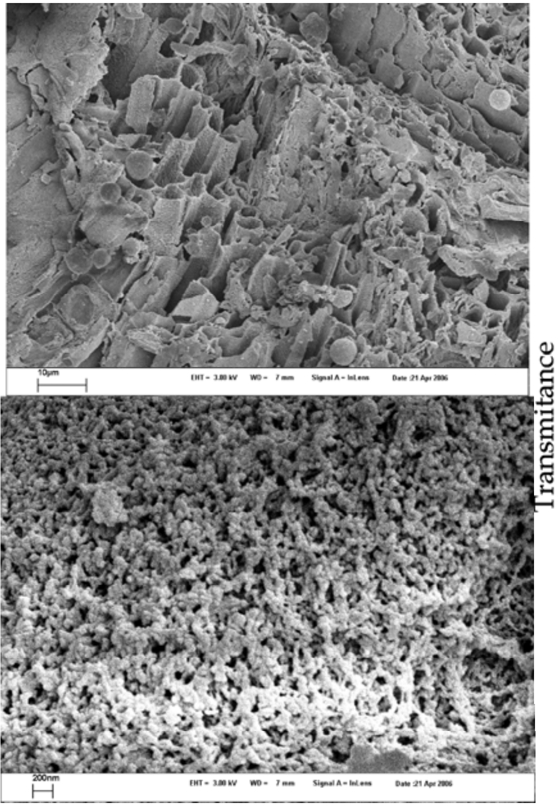
HTC of real biomass

More complex kinds of biomass

i.e. Pine needles and Oak leaves

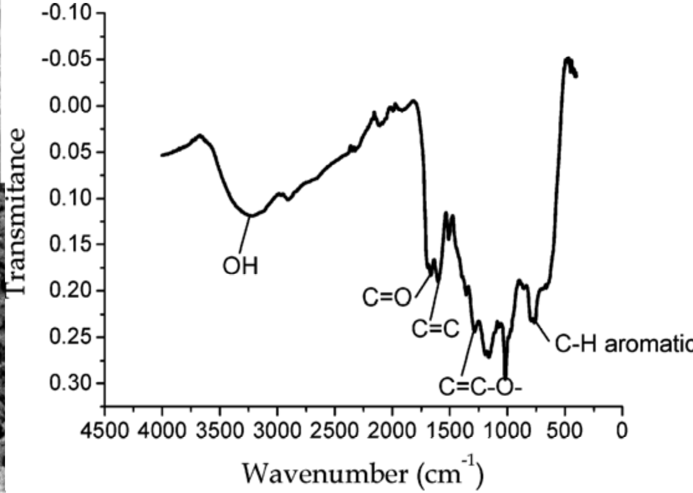


HRSEM of pine needles (a) before and (b) after being hydrothermally carbonized at 200 C for 12 h. Upper scale bar, 100 m; lower scale bar, 200 nm.



(a) Low-magnification SEM overview of a HTC treated oak leaf; scale bar 10 m; (b) high-magnification picture (scale bar, 200 nm

FTIR

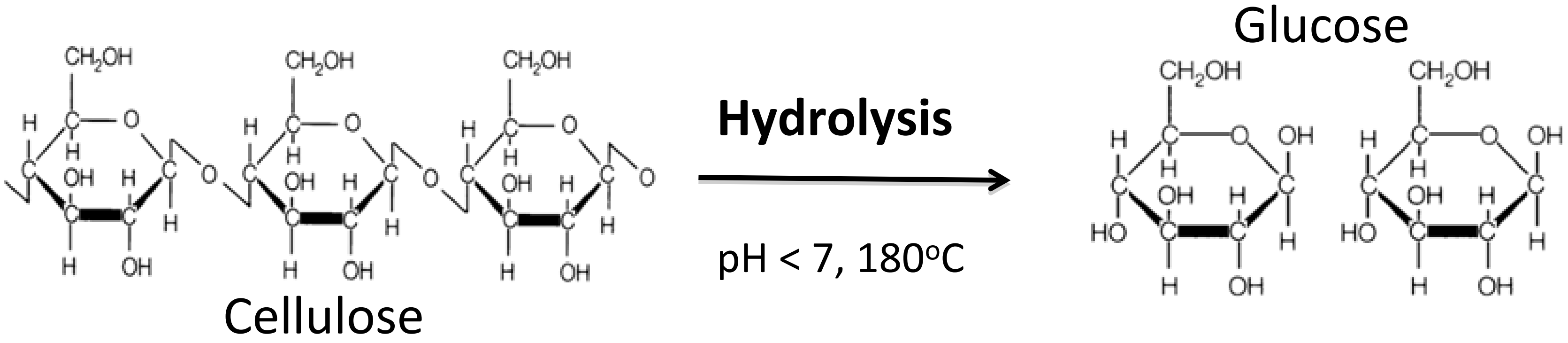


Titirici et al, *Chem. Mater.* ***2007, 19, 4205-4212***

Rye Straw Study

HTC of real biomass

Postulated Mechanism



Cellulose

Hydrolysis

pH < 7, 180^{o}C

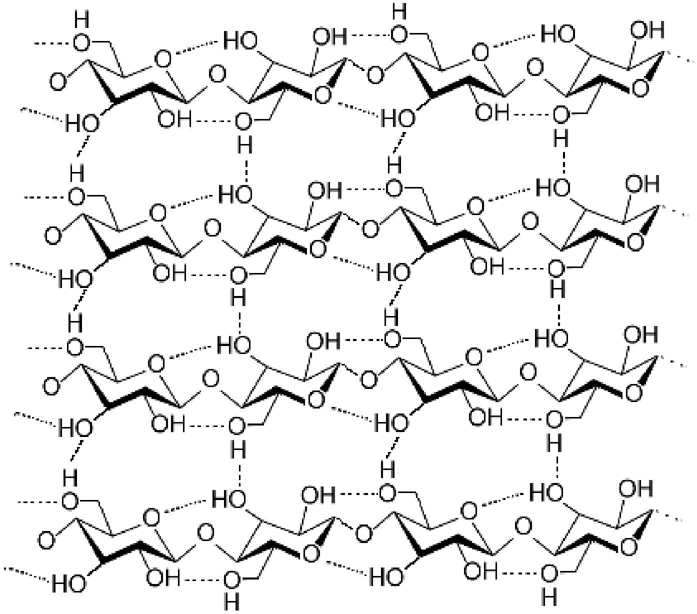
Glucose

There are some problems:

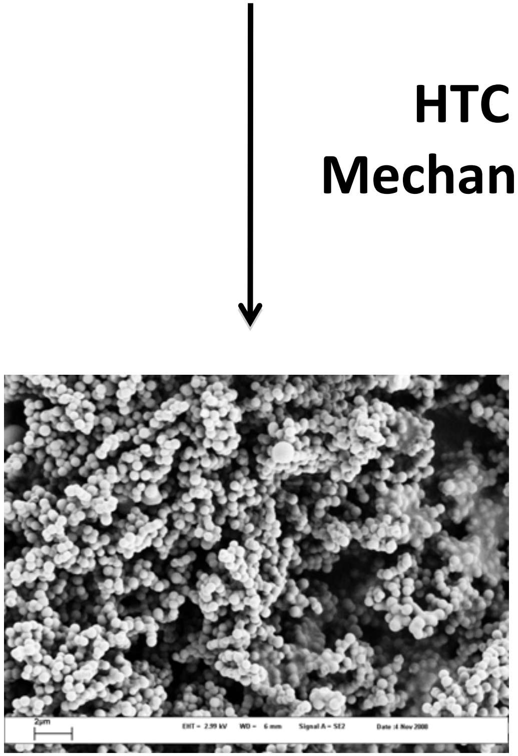
- Strong H-bonded interconnected network

- Makes cellulose insoluble in water

- Hydrolysis cannot take place.



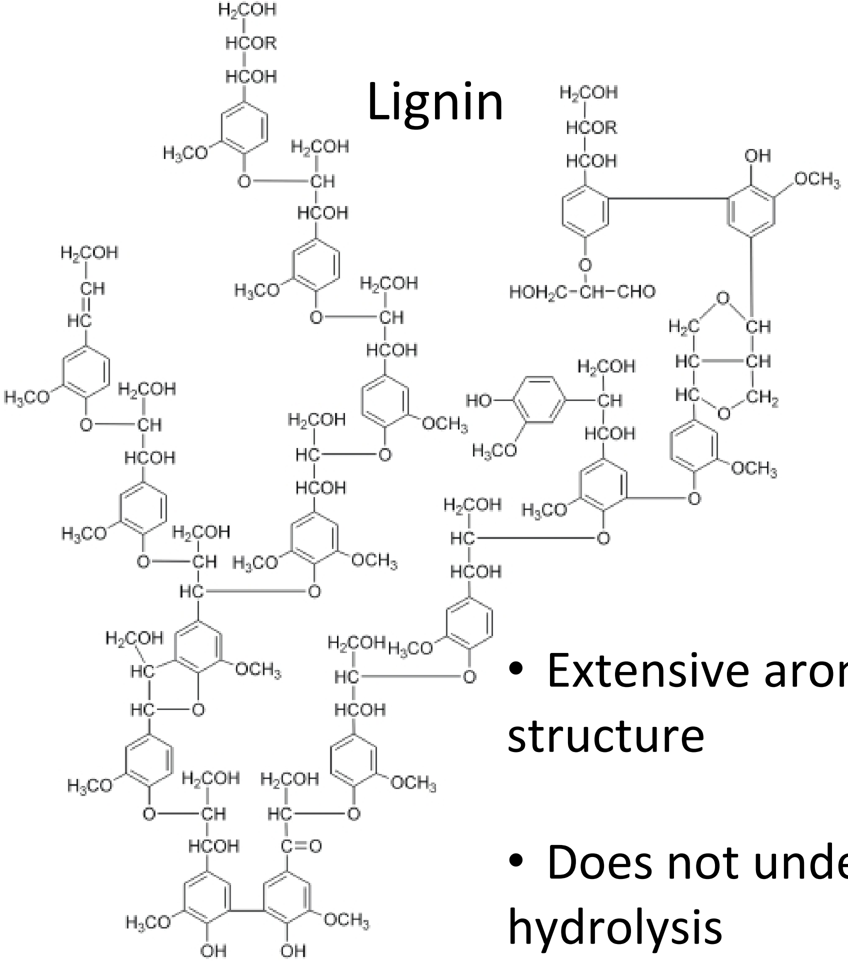
HTC Mechanism



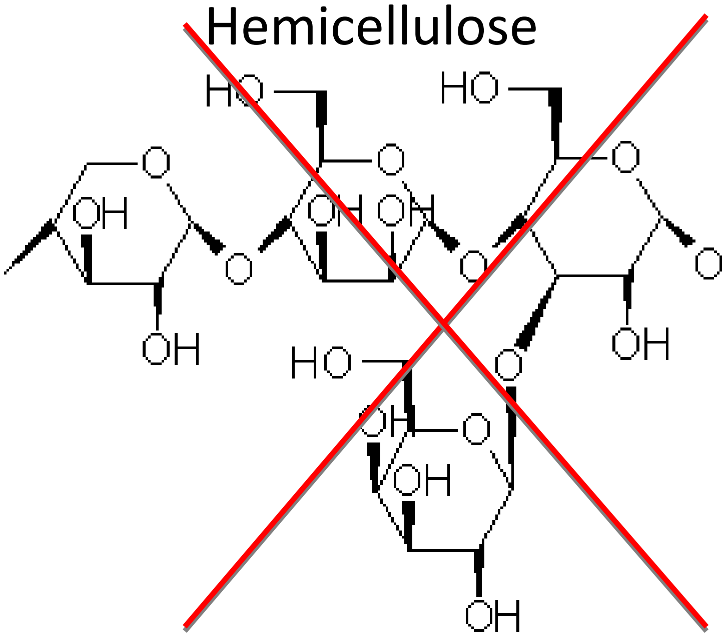
HTC of real biomass

- There are some other components:

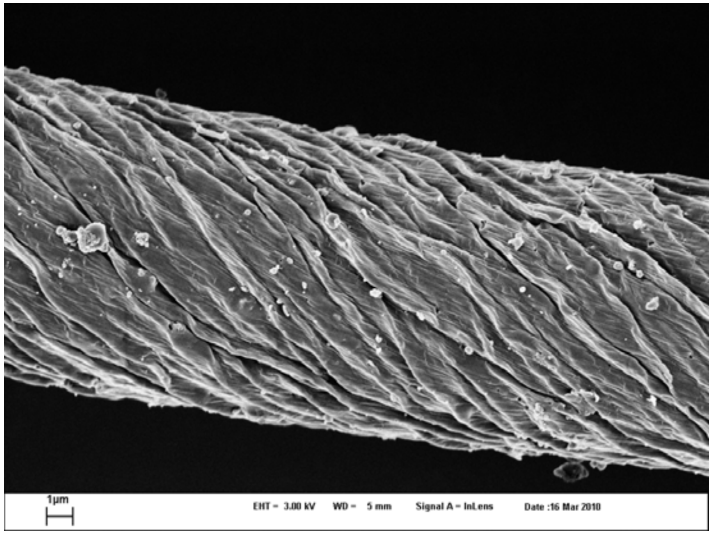
Lignin



Hemicellulose



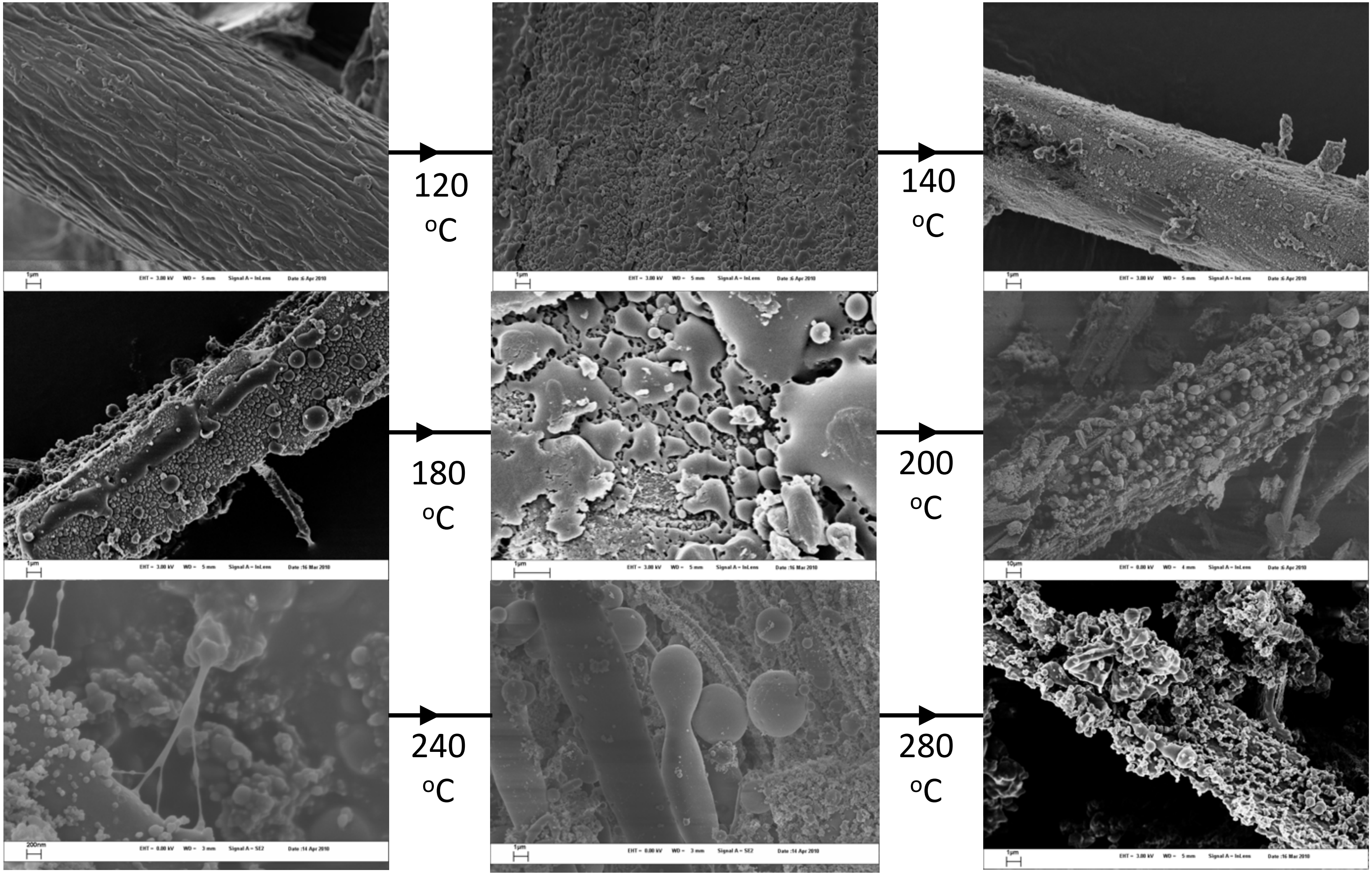
- Extensive aromatic structure
- Does not undergo hydrolysis
- Provides a further stable scaffold for cellulose to anchor to



Rye Straw Study

HTC of real biomass

Temperature experiments



120 °C

140 °C

180 °C

200 °C

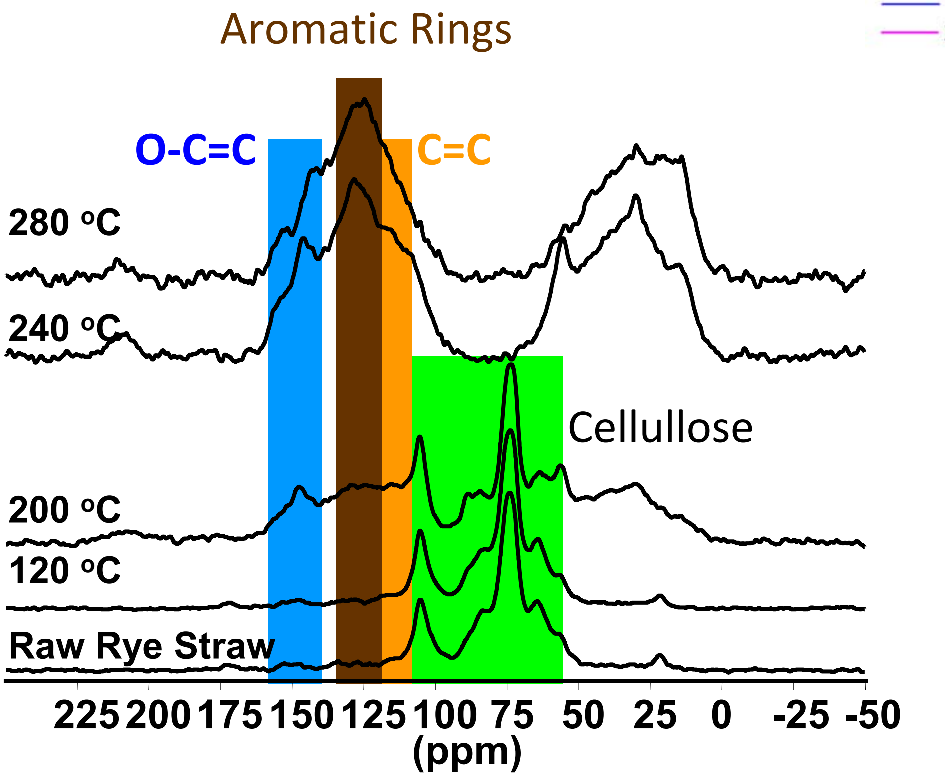
240 °C

280 °C

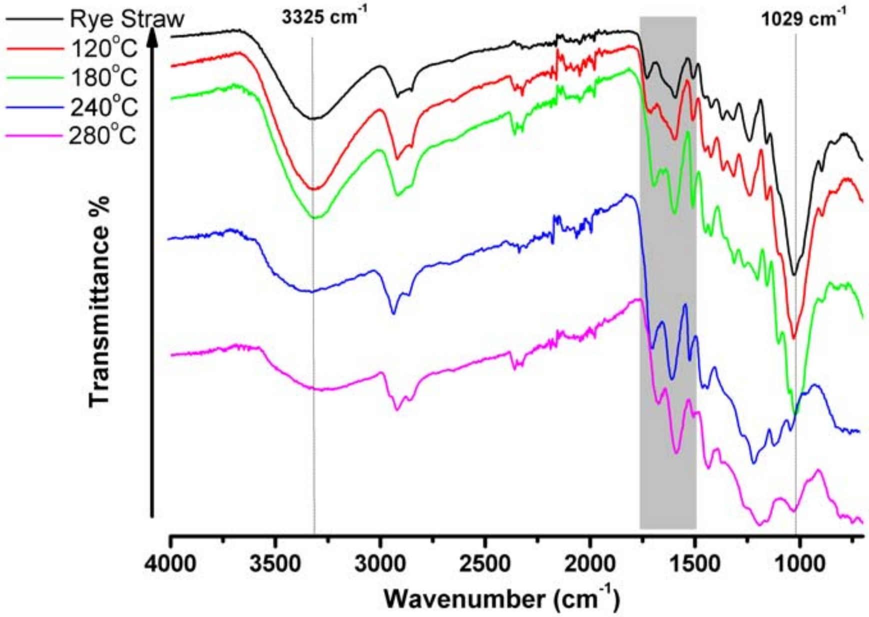
Rye Straw Study

HTC of real biomass

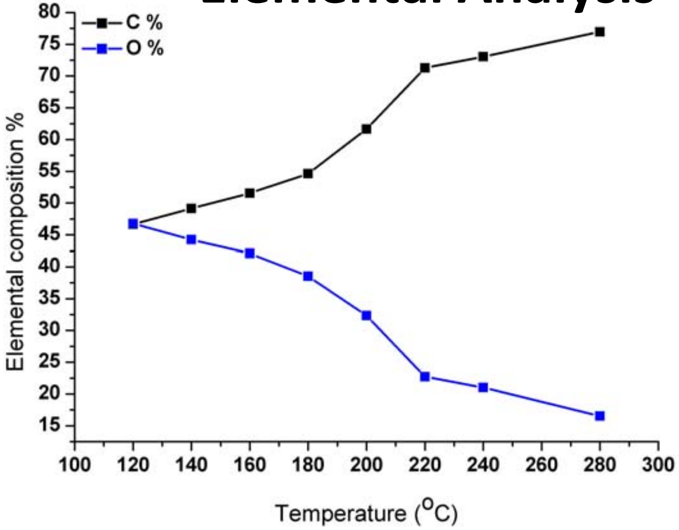
^{13}C Solid State MAS NMR



FTIR



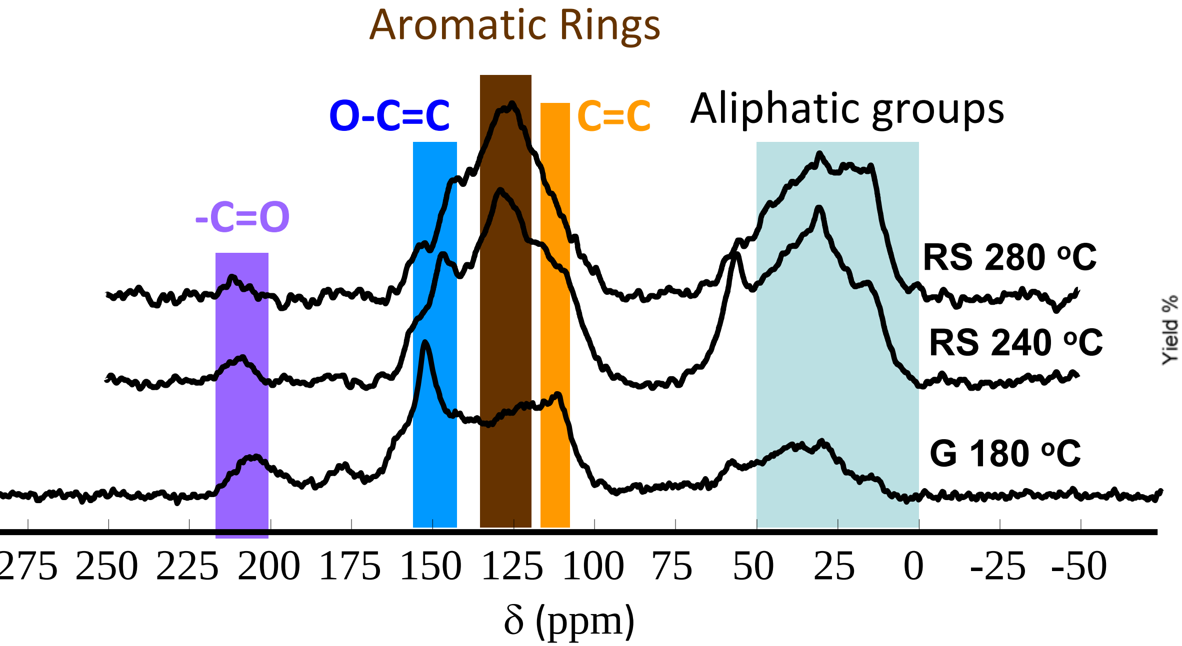
Elemental Analysis



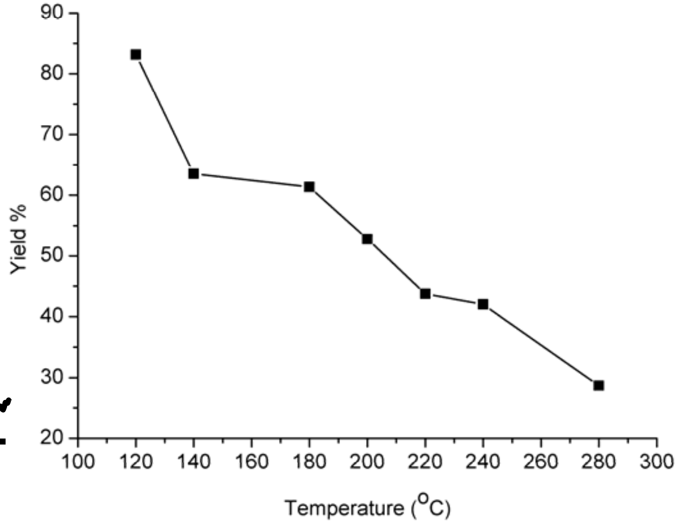
Rye Straw Study

HTC of real biomass

Glucose vs Rye Straw

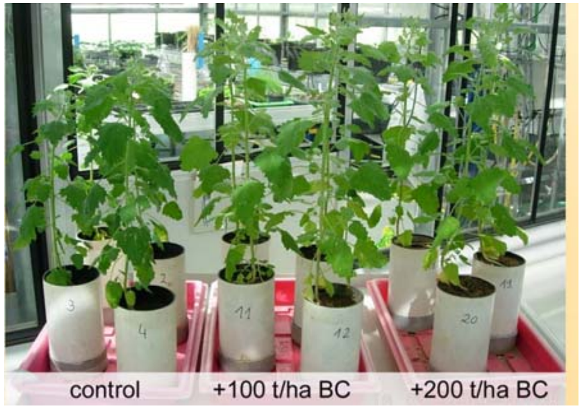


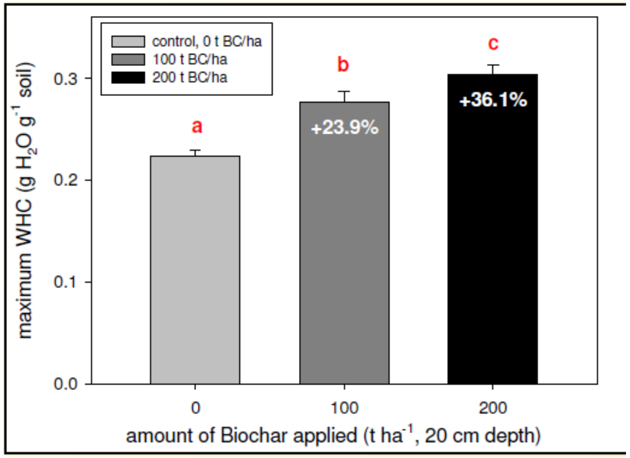
Yield Analysis



- HTC of Rye Straw (complex biomasses) follows a different mechanism than Glucose
- Increasing the HTC temperature leads to:
  - Aromatization of the HTC carbon
  - More sphere-like morphology
  - Loss of Functionality & Lower Reaction Yield
- Chemically the Rye Straw HTC carbon is still very alike to the glucose one
  - ➢ It can still be employed for soil enrichment
- For other applications, there is the need for an HTC carbon with a more ordered morphology

Biocahr in soil ??





- May be a substance mostly suited to severely weathered and deprived soils (low pH, absent potassium, low or no humus)

- Clearly, there is the real potential for carbon sequestration, not accessible to normal microbial decay. Soils require active carbon to maintain micro and macro populations, not the inactive form found in biochar .

- Biochar can prevent the leaching of nutrients out of the soil, partly because it absorbs and immobilizes certain amounts of nutrients, however, too much immobilization can be harmful It

- Although it is far from a perfect solution in all economies, biochar can be utilized in many applications as a replacement for or co-terminous strategy with other bioenergy production strategies

HTC in soil ??

Questions:

How stable is HTC in soil over time?

Oxigenated surface groups may lead to a fast CO_2 release which makes the technology not appropriate for CO_2 sequestration (pyrolysis might be better!!)

How harmful is HTC and what is released upon decomposition in soil?

Levulinic acid and very low pH might not be the best answer for large scale agrciculral productions

Answers require long term experiments !!!

There are already (in Germany) several HTC power plants:

- Carbon Solutions *(Berlin Teltow)*
- Terra Nova Energy *(Birkenfeld)*
- Hydrocarb *(Giessen)*

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CONCLUSIONS

- The use of renewable resources to produce carbon materials is already a very well established field

- Two different approaches were presented :

➢ *A bottom up approach based on introducing porosity into carbohydrates followed by carbonization*

➢ *A top down approach using the carbohydrates similarly to a sol-gel process resulting in particles, porous carbon materials, aerogel, coatings or fibers*

- In this respect the HTC technology provides a quite useful range of applications including adsorption, energy storage, catalysis and many others

- The HTC technology is now investigated at a feasible method to produce large amounts of char for CO_2 sequestration and soil application

ACKNOWDELEMENTS

MY GROUP:

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Niki Baccile Rezan Demir-Cakan, Farnoosh Roohi, Fernado Perez, Jérôme Roeser

2010

2008