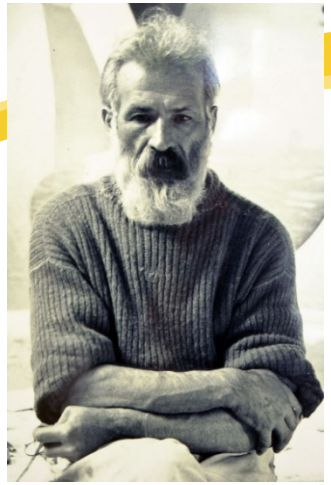


Ne aflăm într-o sferă, ne jucăm cu alte sfere, le îmbinăm, le facem să clipească.

We are in a sphere, play with other spheres, combine them, make them blink.

Constantin Brâncuşi
(1876-1957)

Biopolymer-assisted synthesis of materials with spherical structures

Oana Carp

Institute of Physical Chemistry "Ilie Murgulescu"

A 16-a ediție a Seminarului Național de Nanoștiință și Nanotehnologie
București, Biblioteca Academiei Române, 6 iunie 2017

Institute of Physical Chemistry
"Ilie Murgulescu"

Romanian Academy

Academician
Ilie G. Murgulescu
(1902-1991)

Research programs

1. Chemical thermodynamics and kinetics. Quantum chemistry
2. Catalytic materials and processes
3. Electrode processes, materials for electrochemical and corrosion systems
4. Materials science and advanced characterization methods
5. Functional and complex colloids
6. Biomedical applications and environmental protection
7. Surface science and thin films

Nanochemistry vs. NATURE

PRESERVING THE APPLICATIONS WHILE MINIMIZING OR ELIMINATING THE NEGATIVE IMPLICATIONS OF NANOMATERIALS

The design of nanoscale substances, materials, and processes through green chemistry and engineering that results in the development of new performances without adverse consequence to humans and biosphere

L. McKenzie and J. Hutchison

2004
Green Nano Chemistry

Green Chemistry
1998

There's plenty of room at the bottom, R.Feynman

Nanoscience and nanotechnology: to impart new properties and new capacities to materials on the basis of their size and geometries.

1959
NANO

The 12 Principles
P.T.Anatas and J.C.Warner

- ✓More effective and environmentally more benign chemical processes
- ✓Renewable feedstocks for chemical industry
- ✓Sustainable processing of chemical products

Green Chemistry is NOT A Solution To All Environmental Problems BUT The Most Fundamental Approach To Prevent Pollution

Toward an ideal compound: genesis and excellence

GREEN SYNTHESIS

simple

one step

safe

atom efficient

100% yield

available materials

no wasted reagents

environmentally acceptable

HARMONIOUS COMPOUND

chemical stable

thermal stable

cheap

nontoxic

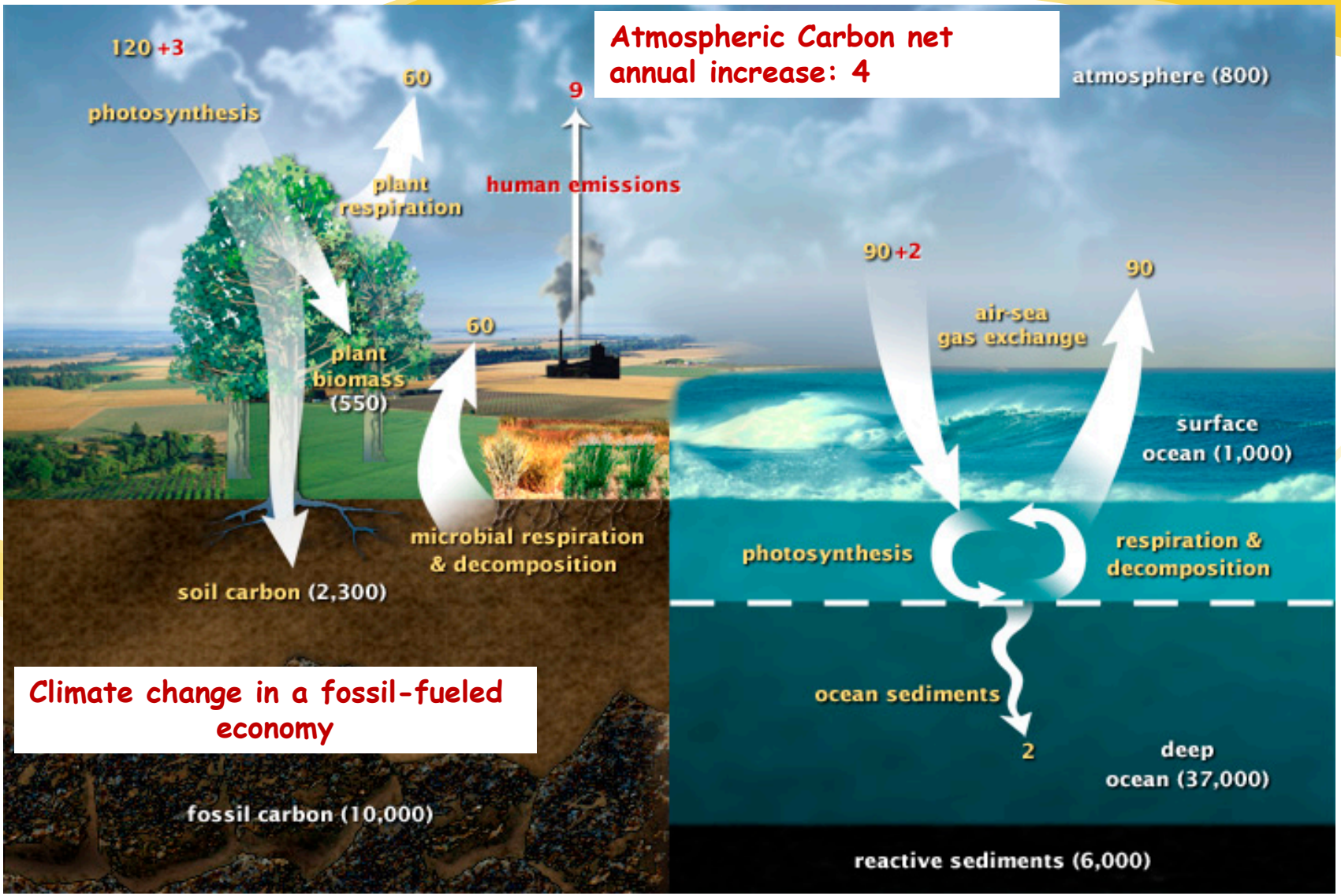
biocompatible

easy to modify

smart

multiple applications

Fast carbon cycle: the movement of carbon between land, atmosphere, and oceans.



Yellow numbers are natural fluxes, and red are human contributions in gigatons of carbon per year. White numbers indicate stored carbon. (Diagram adapted from U.S. DOE, Biological and Environmental Research Information System.)

Pushing further is possible....

To invert current development by sequestering the atmospheric CO_2

Material Science solution: incorporation by "low-tech" procedures of the biomass carbon into less degradable carbon-based advanced materials, powerful and long term CO_2 collectors.

OUTLINE

- Carbohydrates as soft templates for spherical metal oxide
- Carbohydrates as hard templates for spherical metal oxide
- Carbon based materials from carbohydrates
- Future work

- Carbohydrates as soft templates for spherical metal oxide
- Carbohydrates as hard templates for spherical metal oxide
- Carbon based materials from carbohydrates
- Future work

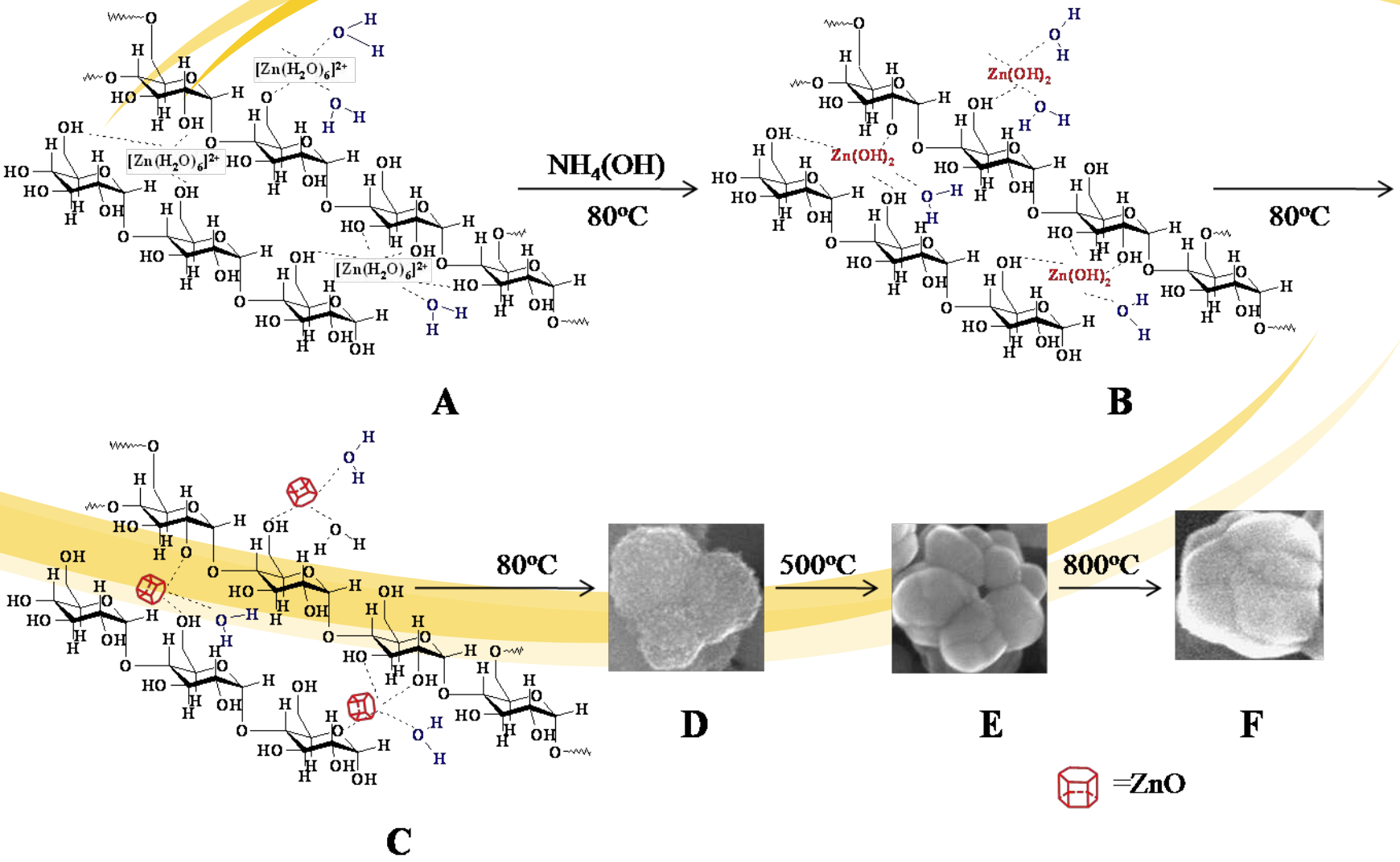
Carbohydrates: soft templates

General objective

Developing synthesis methodologies in which carbohydrates are used as growth inhibitors and crystal habit modifiers

Carbohydrates: soft templates

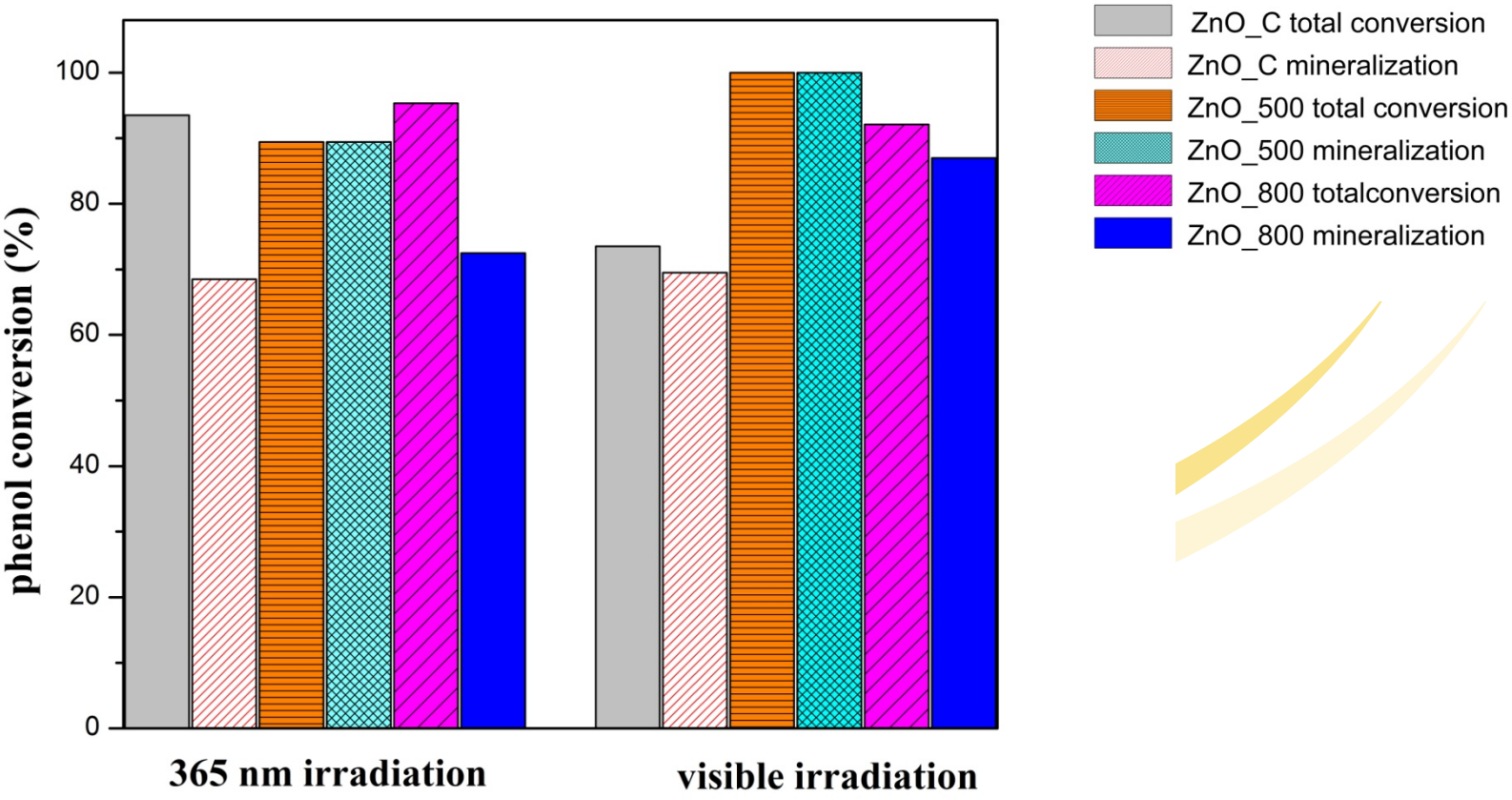
Starch: ZnO multisphere and donut-like structures



O.Carp, A.Tîrsoagă, B.Jurcă, R.Ene, S.Somăcescu, A.Ianculescu, Carbohydrate Polymers, 2015, 115, 285-293

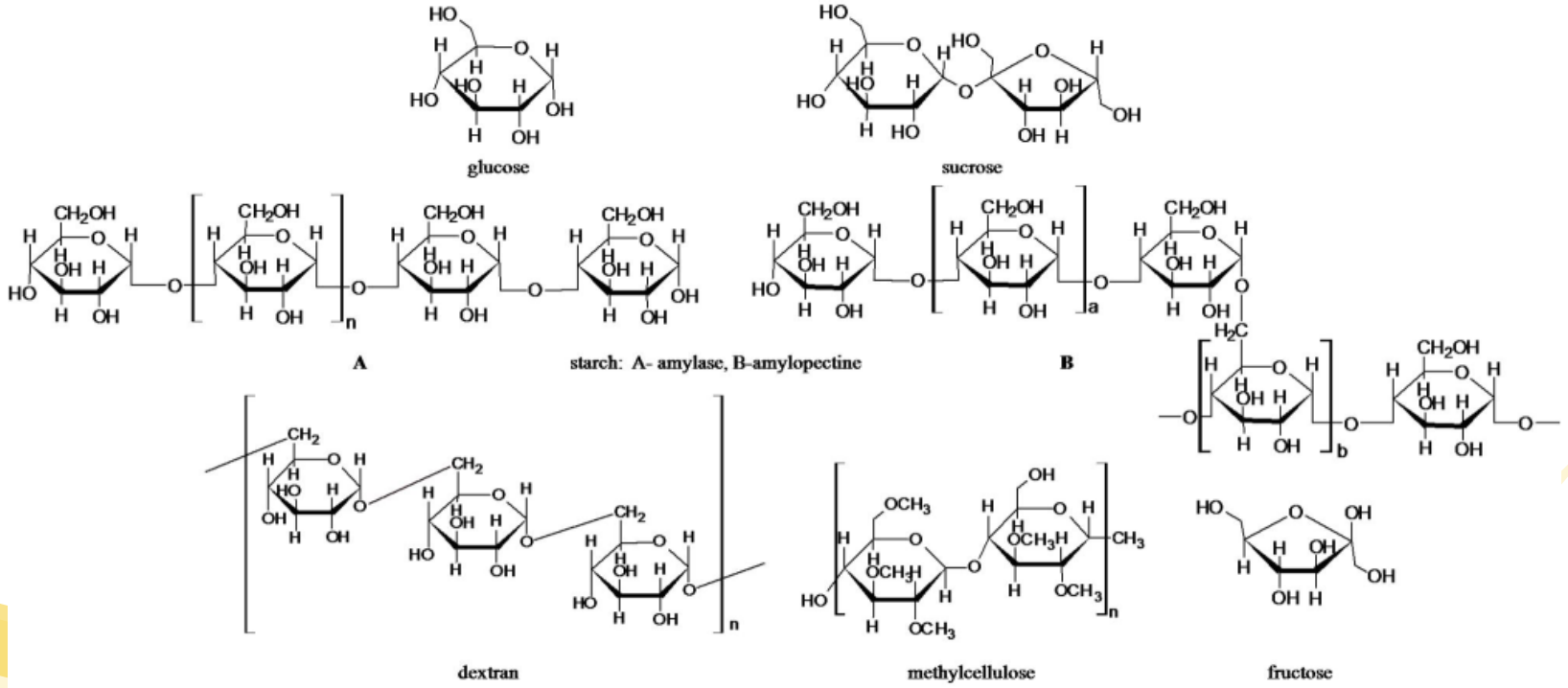
Carbohydrates: soft templates

Starch: ZnO multisphere and donut-like structures



O.Carp, A.Tîrsoagă, B.Jurcă, R.Ene, S.Somăcescu, A.Ianculescu,
Carbohydrate Polymers, 2015, 115, 285-293

Carbohydrates: soft templates

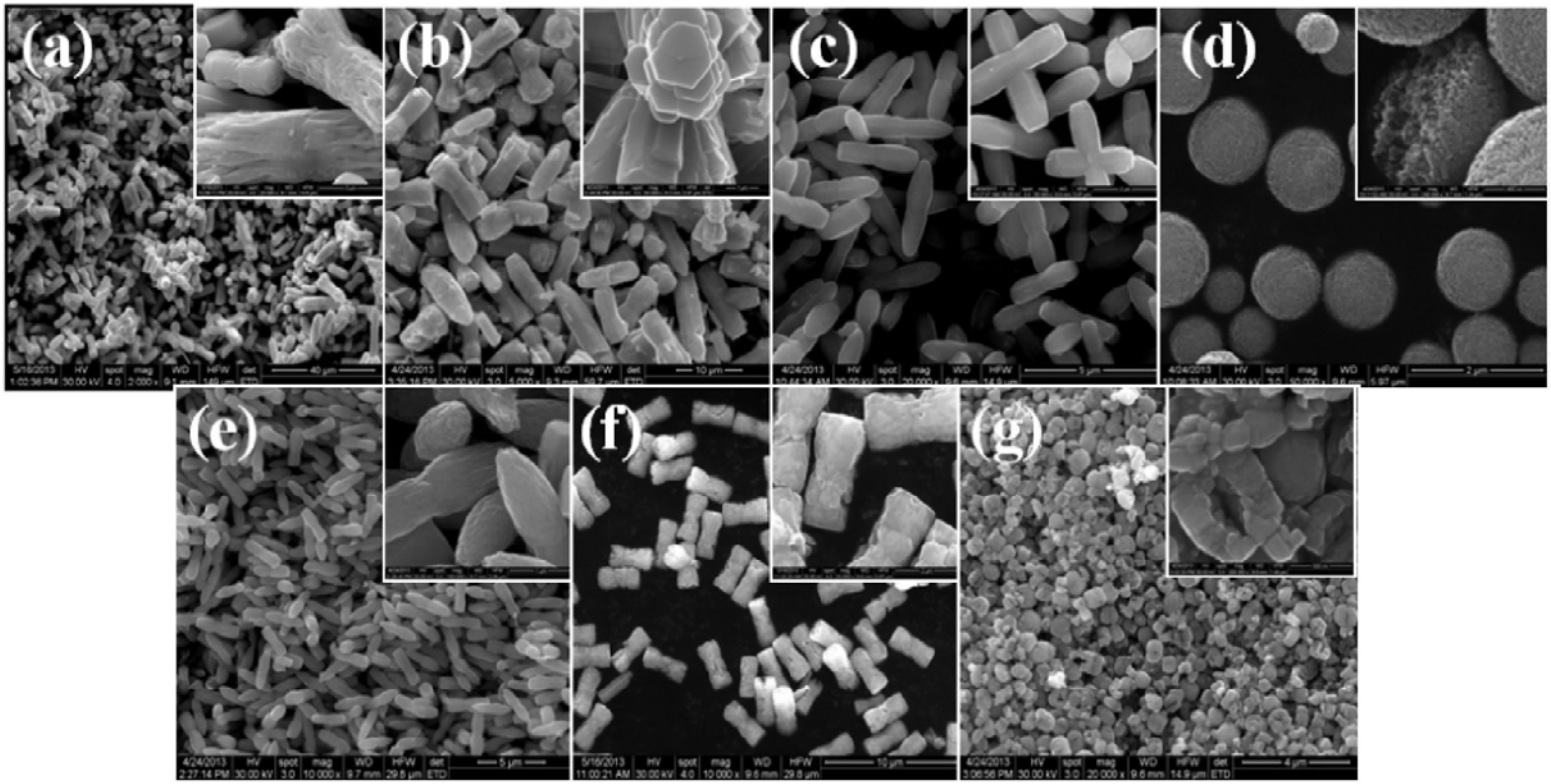


Green synthetic procedure:

120°C, 2 hours
TEA

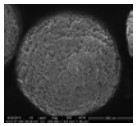
A. Stan, C. Munteanu, R. Ene, M. E. Anghel, A. M. Musuc, R. Birjega, A. Ianculescu, I. Raut, L. Jecu, M. Badea Doni, O. Carp
Dalton Trans., 2015, 44, 7844-7853

Carbohydrates: soft templates

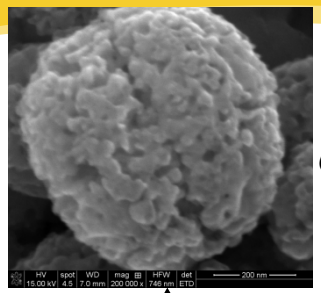


SEM images of ZnO obtained in the absence/presence of saccharides: (a) ZnO; (b) ZnO_G; (c) ZnO_S; (d) ZnO_ST; (e) ZnO_D; (f) ZnO_MC_500; (g) ZnO_F

A. Stan, C. Munteanu, R. Ene, M. E. Anghel, A. M. Musuc, R. Birjega, A. Ianculescu, I. Raut, L. Jecu, M. Badea Doni, O. Carp
Dalton Trans., 2015, 44, 7844-7853



Saccharides as soft templates : ZnO-starch spheres

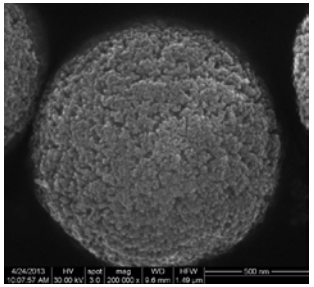


ZnO/TiO_2 core/shell composite

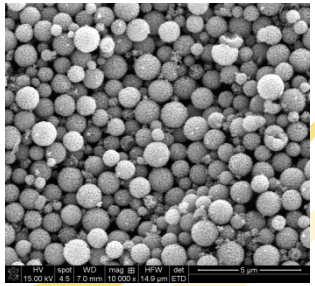
Ti source

ZnO/Ag core/shell composite

Ag source



T (°C)

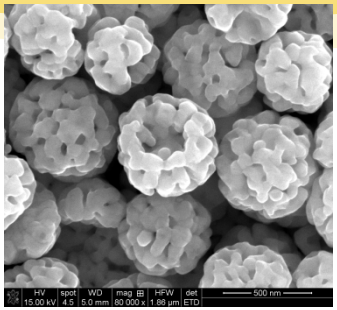


ZnO

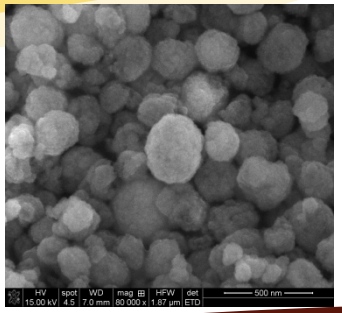
Ni source

S source

other cations also..

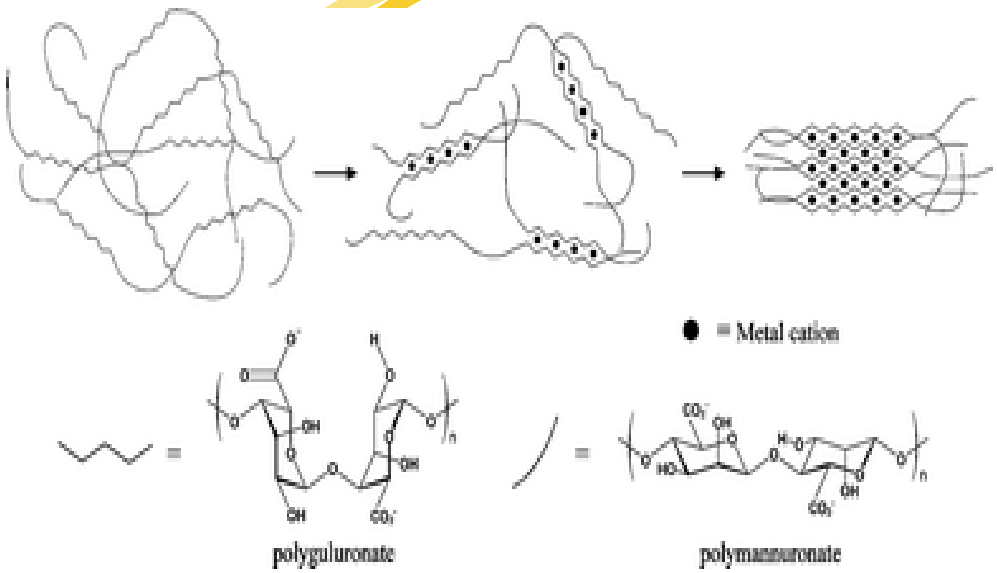


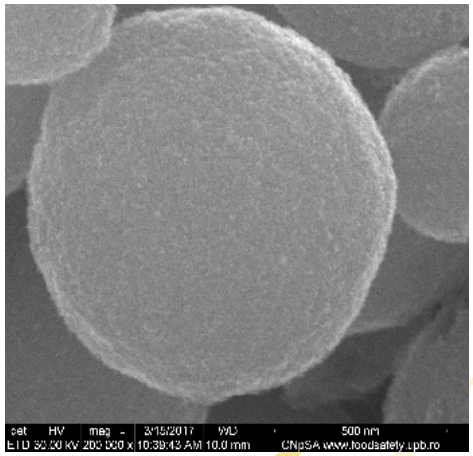
Ni^{2+}/ZnO



ZnO/ZnS core/shell composite

Saccharides as soft templates : ZnO-alginate spheres





The egg-box model of cation binding in alginate

Green synthetic procedure:

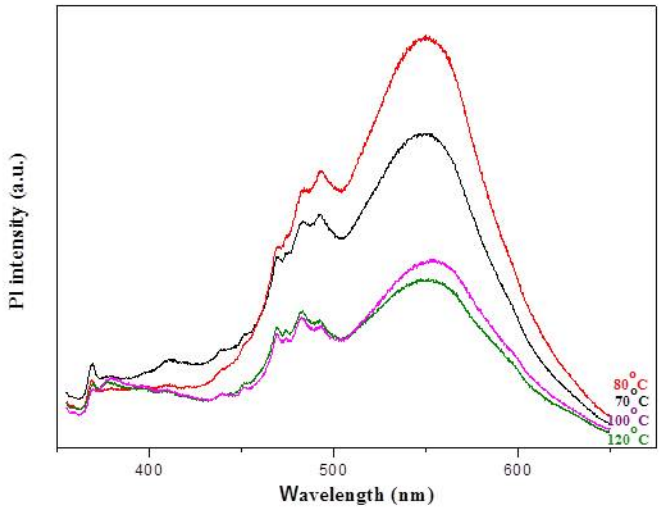
70-100°C,
30 min- 2 hours
TEA

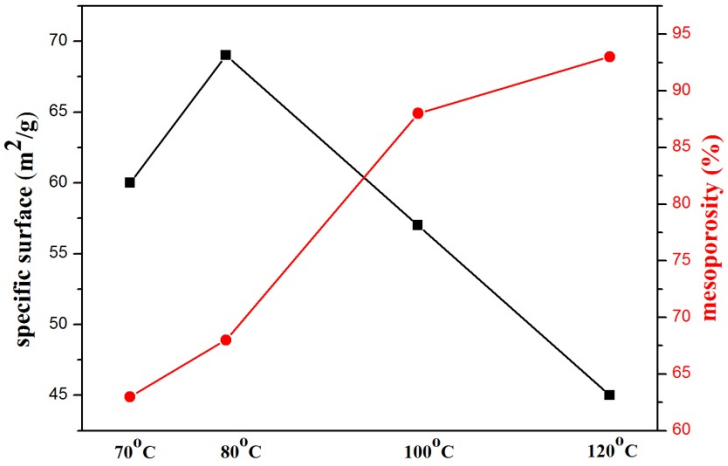
Sensitive to experimental conditions including reactants addition order !!

P.Cucos, A.Ianculescu, Daniela C. Culita, A. Cucos, I. Atkinson, M. Anghel, O.Carp, Green Chemistry (to be submitted)

Saccharides as soft templates : ZnO-alginate spheres

Reaction temperature





Order of reactants addition (100°C)

$(Zn^{2+}$+TEA)+alginate: 58 m^2/g (89% mesoporosity)
$(Zn^{2+}$+alginate)+TEA: 37 m^2/g (66% mesoporosity)

high antibacterial, antibiofilm and antifungal activity

P.Cucos, A.Ianculescu, Daniela C. Culita, A. Cucos, I. Atkinson, M. Anghel, O.Carp, Green Chemistry (to be submitted)

Carbohydrates: soft templates

✓The approach, an alternative to the conventional chemical procedures, introduces saccharides as common "chemicals" in the synthesis of high quality oxide materials.

✓The general character of the method derives from the possibility of using various bio-carbohydrates with different compositions and functionalities.

biological diversity may be easily used for attaining material functionality

A. Stan, C. Munteanu, R. Ene, M. E. Anghel, A. M. Musuc, R. Birjega, A. Ianculescu, I. Raut, L. Jecu, M. Badea Doni, O. Carp Dalton Trans., 2015, 44, 7844-7853

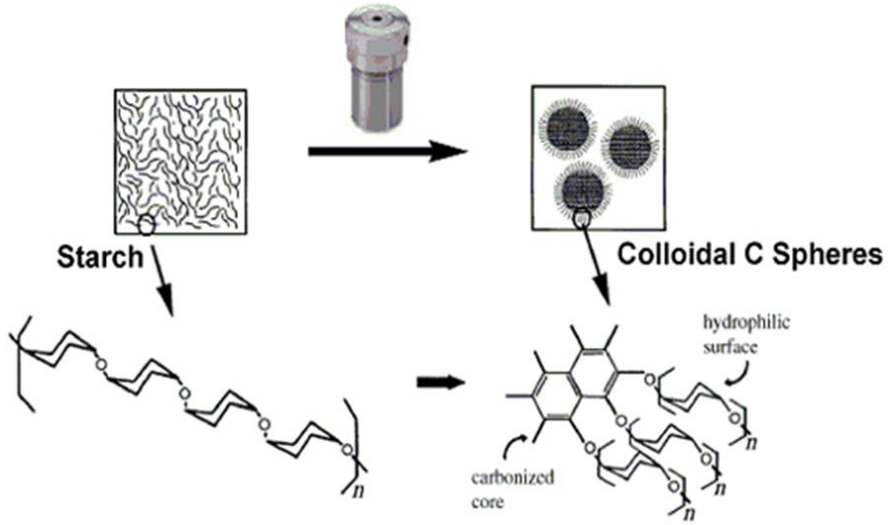
P.Cucos, A.Ianculescu, Daniela C. Culita, A. Cucos, I. Atkinson, M. Anghel, O.Carp, Green Chemistry (to be submitted)

- Carbohydrates as soft templates for spherical metal oxide
- Carbohydrates as hard templates for spherical metal oxide
- Carbon based materials from carbohydrates
- Future work

Carbohydrates: hard templates

hydrothermal carbonization (beginning of the twentieth century)

Friedrich Bergius
The Nobel Prize in Chemistry
1931



Hydrothermal carbonization on the presence of metal cations

Carbohydrates: hard templates

General objectives

Synthesis of hollow (mesoporous) structures with high surface/volum ratio

Synthesis of (mesoporous) spherical solid structures

Carbohydrates: hard templates

different carbohydrates templates and ZnO

hollow full

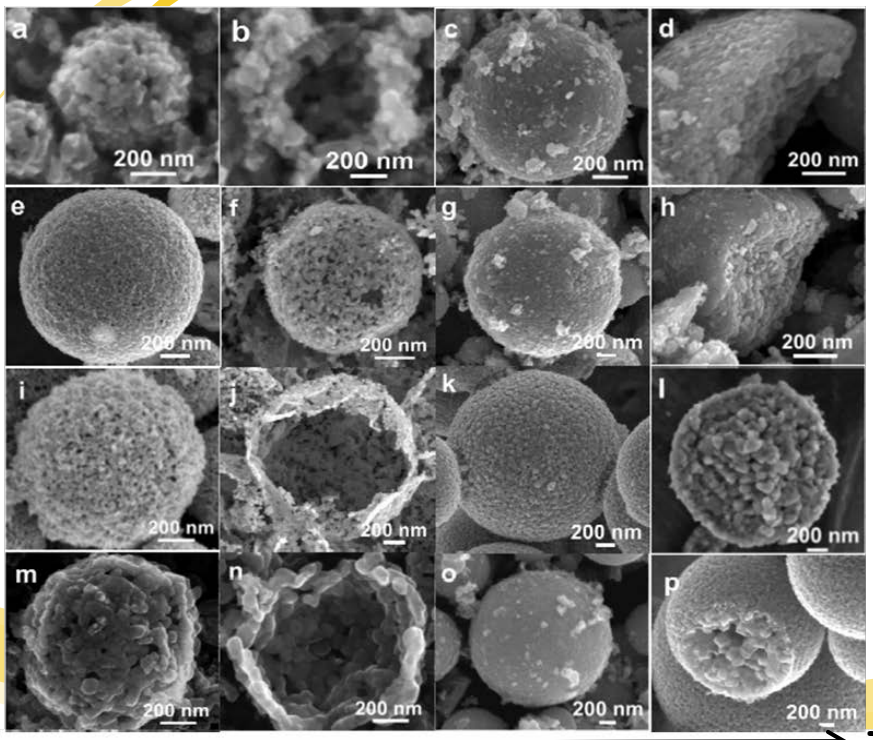
hollow/solid spheres

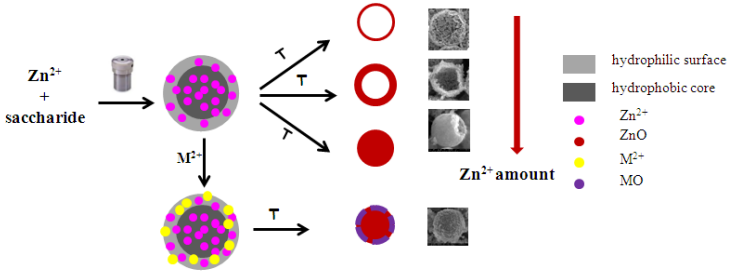
glucose

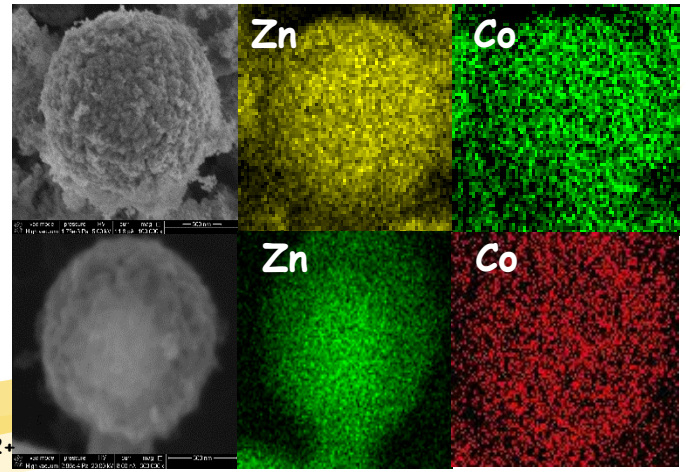
fructose

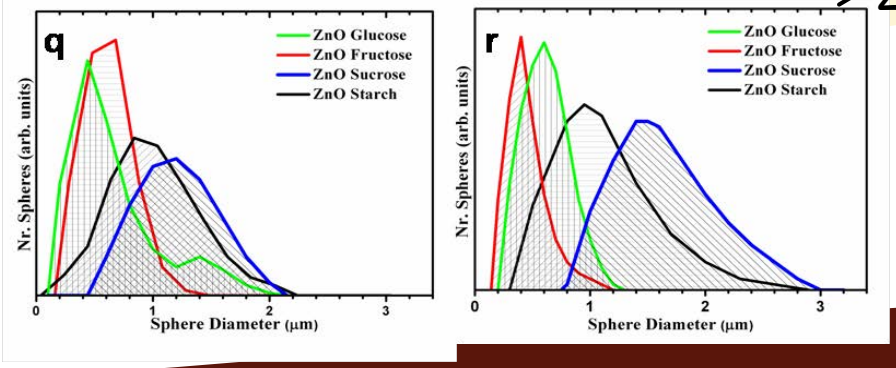
sucrose

starch









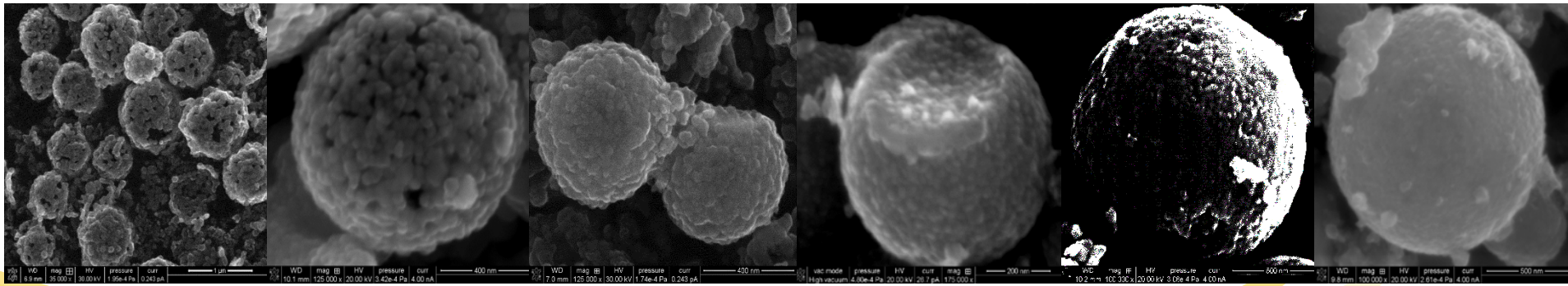
G.Pătrânoiu, J.Calderon-Moreno, R.Bîrjega, O.Carp, RSC Advances, 2015, 5, 31768-31771

Carbohydrates: hard templates

hollow/solid spheres

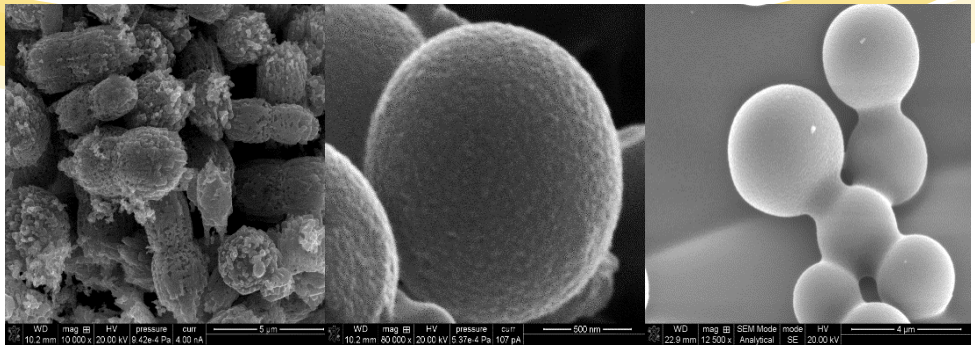
Synthesis

1. **template synthesis and cation introduction** ONE POT
2. thermal treatment (phase and composition modifications)



HOLLOW — SOLID

Zn^{2+}



Zn^{2+}/starch=constant Zn^{2+}, starch

G.Pătrânoiu, J.Calderon-Moreno, C. Chifiriuc, C. Saviuc, R.Bîrjega, O.Carp,J.Coll. Interface Sci., 2016, 462, 6474

Carbohydrates: hard templates

hollow/solid spheres

MIC and MBEC values (μg mL^{-1}) of the tested compounds on the Gram-positive and Gram-negative reference and clinical strains in planktonic and biofilm form.

Gram-positive strains	planktonic MIC		biofilm MBEC		Gram-negative strains	planktonic MIC		biofilm MBEC	
	ZnO_0.02 hollow (μg/mL)	ZnO_0.5_1 solid (μg/mL)	ZnO_0.02 hollow (μg/mL)	ZnO_0.5_1 solid (μg/mL)		ZnO_0.02 hollow (μg/mL)	ZnO_0.5_1 solid (μg/mL)	ZnO_0.02 hollow (μg/mL)	ZnO_0.5_1 solid (μg/mL)
S. aureus ATCC 6538	**31.5**	**62.5**	>500	**15.62**	*P. aeruginosa ATCC 27853*	>500	**62.5**	>500	**<0.97**
MRSA	>500	**1.95**	>500	**31.25**	*P. aeruginosa 719*	>500	**31.25**	>500	**<0.97**
B. subtilis ATCC 12488	>500	**62.5**	>500	**7.81**	*E. coli O26*	**62.5**	**<0.97**	>500	>500
B. subtilis 6683	**62.5**	**0.97**	>500	**3.9**	*K. pneumoniae 11*	>500	**15.62**	>500	>500

Carbohydrates: hard templates

- ✓ General methodology (mono-, di- and polysaccharides)
- ✓ Ease of adjustment of the structure type, size and surface features
- ✓ Accessibility for further functionalization

- Carbohydrates as soft templates for spherical metal oxide
- Carbohydrates as hard templates for spherical metal oxide
- Carbon based materials from carbohydrates
- Future work

Carbohydrates: template and carbon source

General objective

Different carbon-metal/metal oxide composites with controlled properties

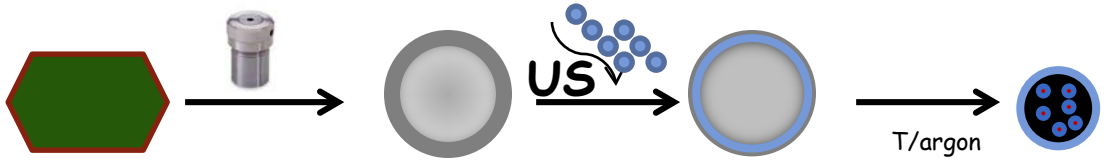
Carbohydrates: template and carbon source

ZnO-carbon

Synthesis

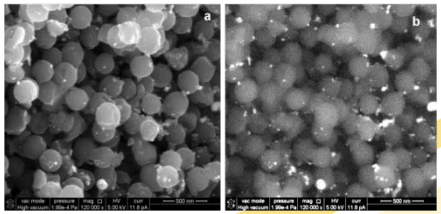
1. template synthesis
2. cations introduction
3. thermal treatment (phase and composition modifications)

INSTEAD of AIR
ARGON



XPS data:
binding energies, chemical species, atomic relative concentrations

Sample	Binding energy, eV				Atomic relative concentration, at%		
	C1s	O1s	Zn2p3/2	ZnLMM	C	O	Zn
ZnO/C as received	284,8 (C-C) 286.5(OH-C-O) 289.6 (C=O)	531.5 (O^{2-}) 533.4 (OH-C-O, C=O)	1022.5	499.2	84	8.8	7.2
ZnO/C 1 min sputtering	284,8 (C-C) 286.5(OH-C-O) 289.6 (C=O)	531.3 (O^{2-}) 533.3 (OH-C-O, C=O)	1022.5	498.9	82.3	8.3	9.4
ZnO/C 5 min sputtering	284,8 (C-C) 286.5(OH-C-O)	531.2 (O^{2-}) 533.0 (OH-C-O, C=O)	1022.5	498.7	83.0	6.8	10.2

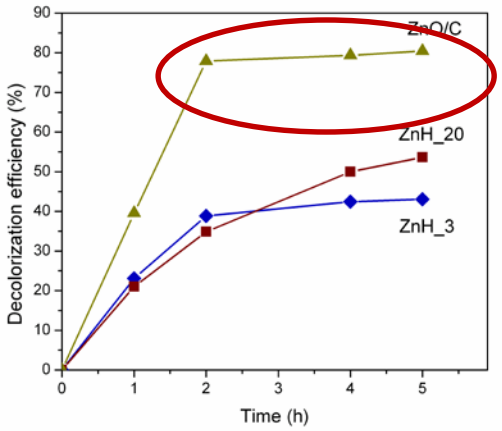


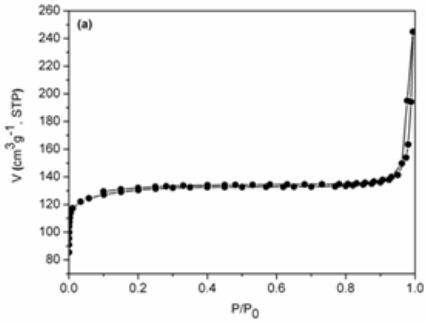
G. Păraînoiu,J. Calderon-Moreno, S. Somăcescu, N.Spătaru, A. Musuc,R.Bârjega, R.Ene, O.Carp
European Journal of Inorganic Chemistry, 2014, 6, 1010-1019

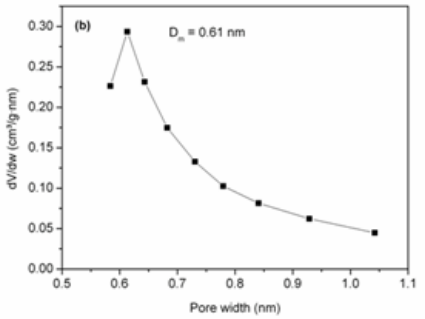
Carbohydrates: template and carbon source

ZnO-carbon

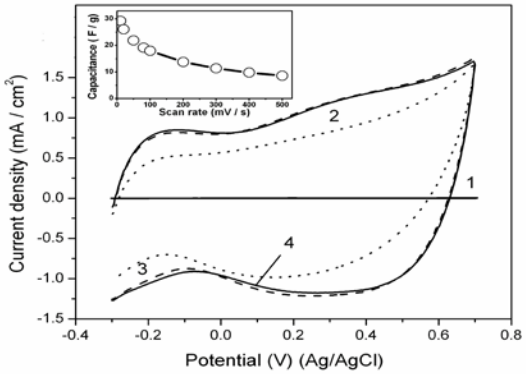
Photocatalytical activity in degradation of MB under visible irradiation







Micropore surface: 447 m^2/g (87% of total area of 512 m^2/g)

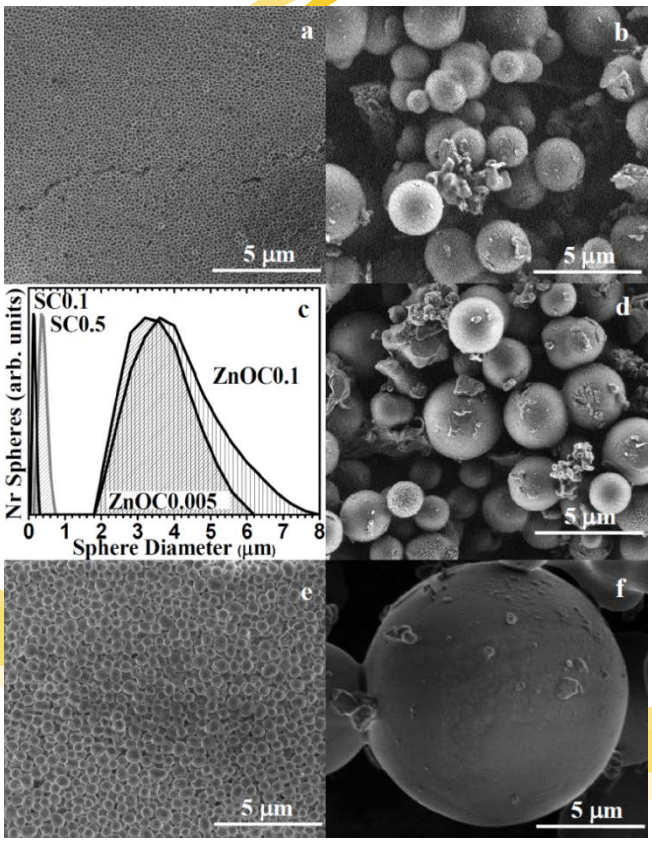


Specific capacitance of 22.13 $F \cdot g^{-1}$ (scan rate = 50 mVs^{-1})

G. Pătrânoiu,J. Calderon-Moreno, S. Somăcescu, N.Spătaru, A. Musuc,R.Bârjega, R.Ene, O.Carp
European Journal of Inorganic Chemistry, 2014, 6, 1010-1019

Carbohydrates: template and carbon source

One-pot synthesis

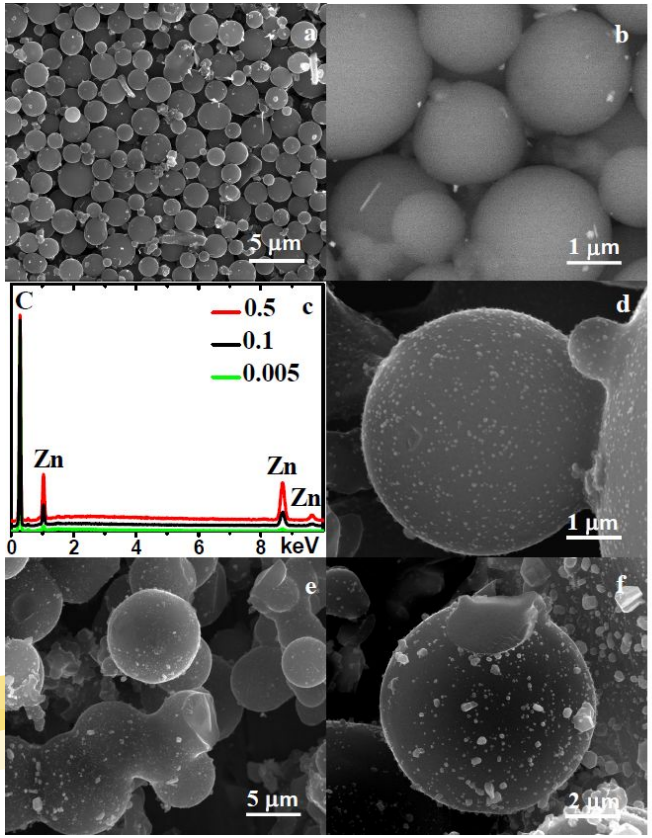


SEM images of the precursors spheres:
(a) SC0.1; (b) ZnC0.005; (c) diameter
(b) distribution of the spheres;
(c) (d) ZnC0.1; (e) SC0.5; (f) ZnC0.5.

Argon

700°C, 3h

ZnO-carbon

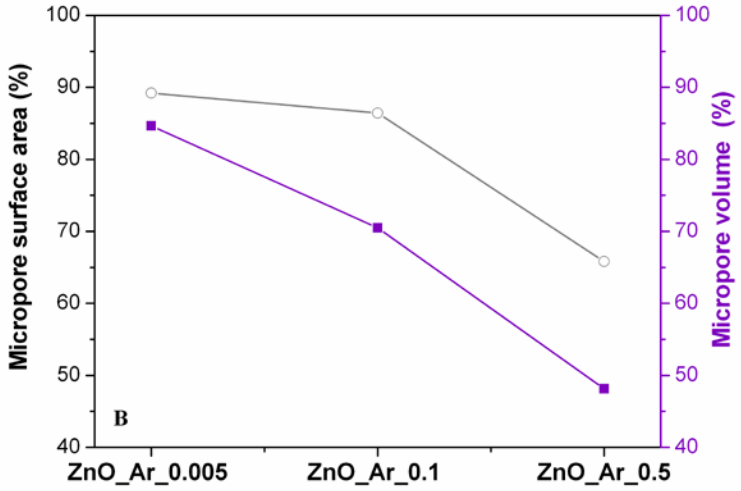


SEM images of the composite spheres ZnOCX: (a, b) ZnOC0.005; (c) their corresponding EDX spectra (d) ZnOC0.1; (e, f) ZnOC0.5.

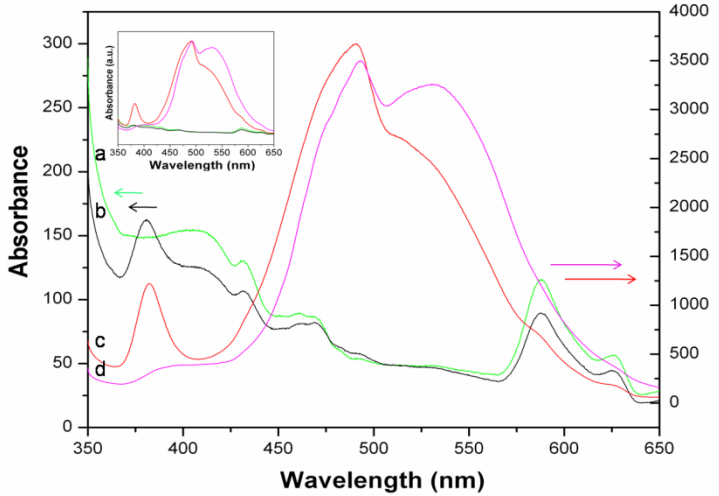
G. Patranoiu, J.Calderon-Moreno, R.Birjega, D. Culita, T.Spataru, S. Somacescu, O Carp
Physical Chemistry Chemical Physics 2016, 18, 30794-30807

Carbohydrates: template and carbon source

ZnO-carbon



Variation of micropores surface area (black line with circle symbols) and pores volume (blue line with square symbols) for the composites thermally treated in argon



Room-temperature photoluminescence of: (a) ZnOC0.005; (b) ZnOC0.1; (b) (c) ZnOC0.5 and (d) ZnO0.5.

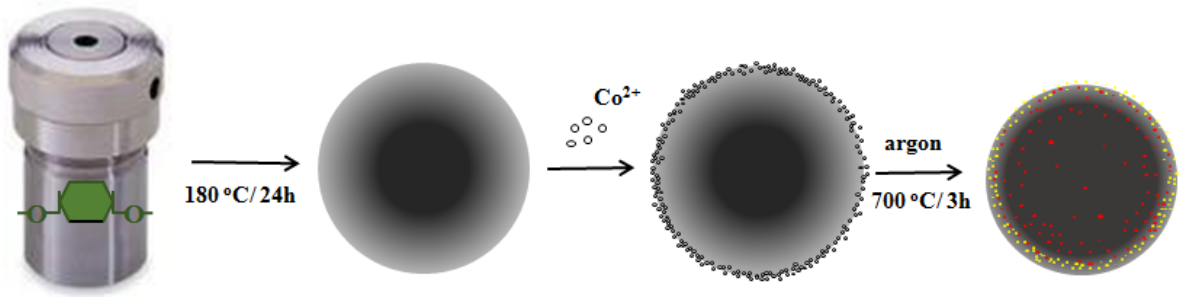
Modulation of carbon materials properties through the amount of the metal (Zn^{2+})

G. Patranoiu, J.Calderon-Moreno, R.Birjega, D. Culita, T.Spataru, S. Somacescu, O Carp
Physical Chemistry Chemical Physics, 2016, 18, 30794-30807

Carbohydrates: template and carbon source

One-pot synthesis

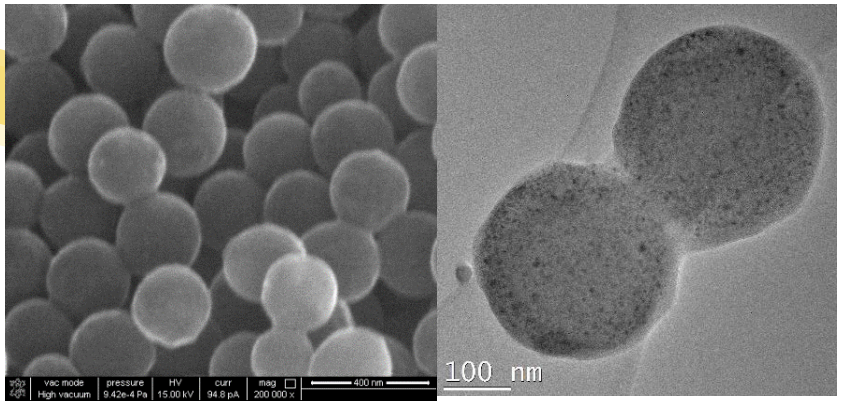
Co-CoO-carbon

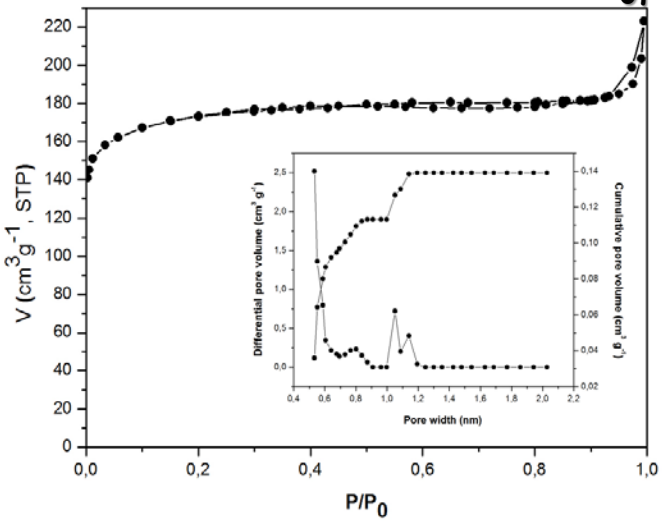


= starch = hydrophilic→ hydrophobic carbon matrix

= Co^{2+} = CoO = Co

Micropore surface: 543 m^2/g (81% of total area of 669 m^2/g)



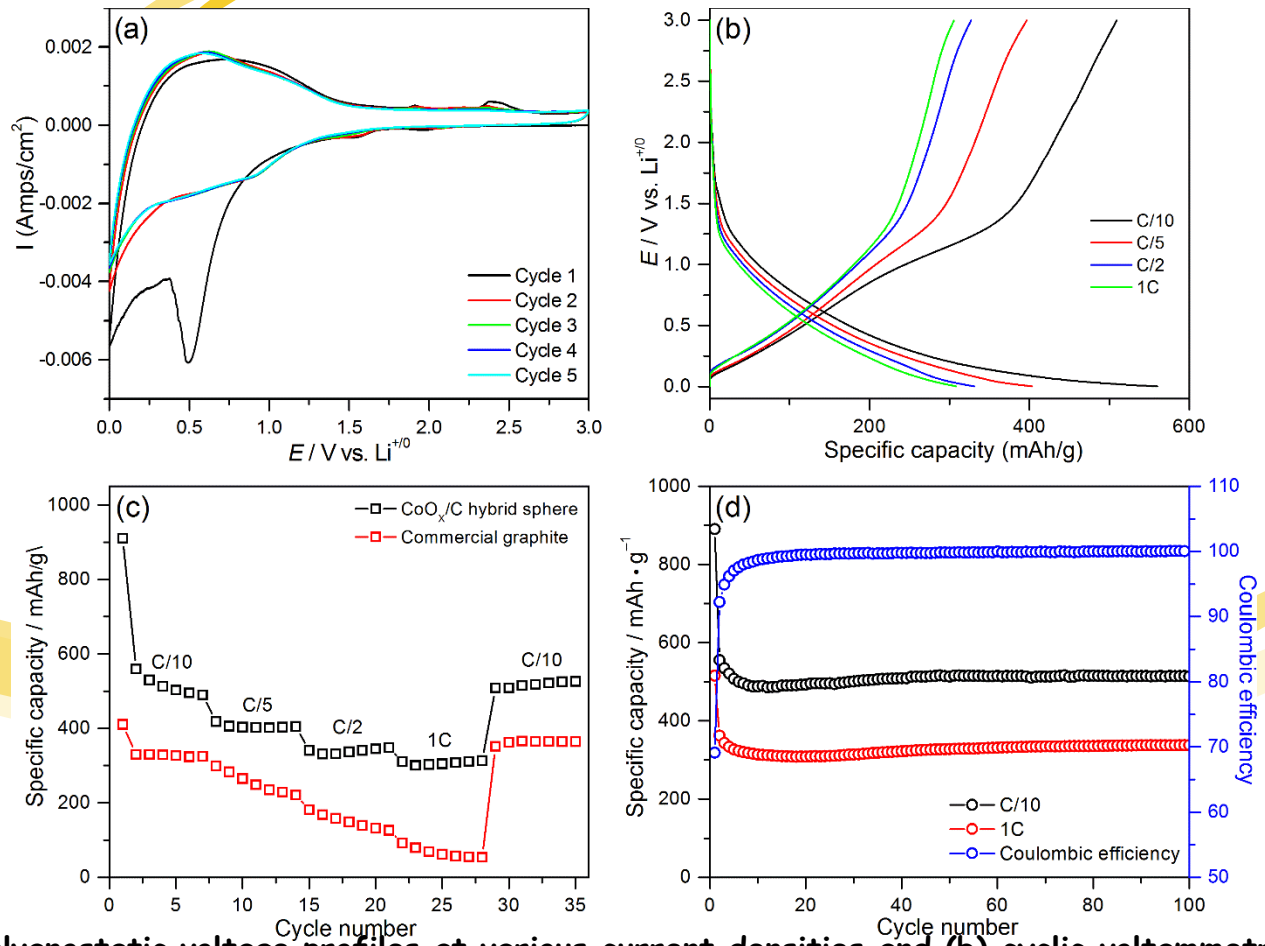


G. Patrinoiu, S. Somacescu, V.S. Teodorescu, R. Birjega, D.C. Culita, P. Vilas, J. M. Calderon-Moreno, O. Carp, Carbon (to be submited)

Carbohydrates: template and carbon source

One-pot synthesis

Co-CoO-carbon



(a) Second galvanostatic voltage profiles at various current densities and (b) cyclic voltammetry of CoPCSs hybrid sphere. (c) Electrochemical rate performance of CoPCSs hybrid sphere and commercial graphitic carbon. (d) Galvanostatic cycling performance of CoPCSs hybrid sphere at various current densities

G. Patrinoiu, S. Somacescu, V.S. Teodorescu, R. Birjega, D.C. Culita, P. Vilas, J. M. Calderon-Moreno, O. Carp, Carbon (to be submited)

Carbohydrates: template and carbon source

HTC is a resourceful procedure for design functionalized carbon materials with inorganic components. The employed doping approach dictates the localization of the new functionalities. Subsequent thermal carbonization processes enable a control over both surface and bulk chemistry.

specific interactions between a certain metal cation and a saccharide may manipulate the properties of the derived carbon material

To increase the functionality brought by the biodiversity *via* materials chemistry tools

the use of other simple representative carbohydrates and biomass

functionalization and doping approaches

Team

Dr.Greta Patranoiu (ICF)
synthesis, UV-Vis, IR,
PL spectroscopy

Dr Diana Visinescu (ICF)
synthesis, UV-Vis, IR, PL
spectroscopy

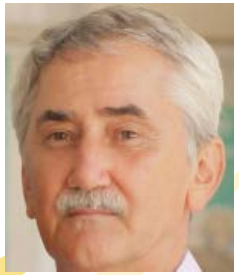
Dr Paula Cucos (ICF)
synthesis, UV-Vis, IR, PL
spectroscopy

Dr Cristian D.Ene (ICF)
synthesis, UV-Vis, IR, PL
spectroscopy, thermal analysis

Dr.Adina Musuc (ICF)
thermal analysis

Dr.Jose Calderon Moreno (ICF)
SEM, TEM

Dr.Ruxandra Barjega (INFLPR)
RX



Dr.Nicolae Spataru (ICF)
electrochemical measurements

Dr.Daniela Culita(ICF)
BET measurements

Dr.Simona Somacescu (ICF)
XPS

Prof.Carmen Chifiriuc (UB)
antimicrobial tests

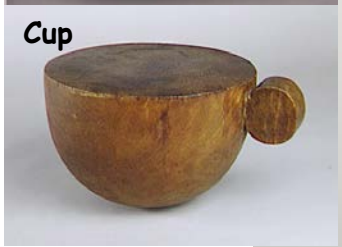
and others……

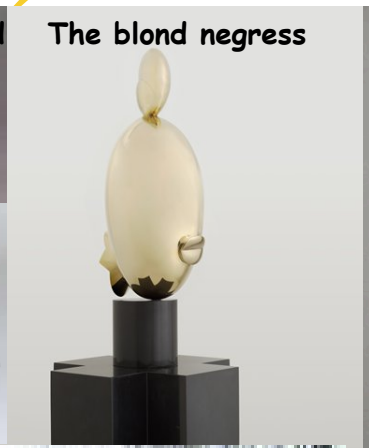
Prefer să creez aceste sculpturi şi să greşesc decât să nu greşesc şi să o recreez pe Venus din Milo, căci Venus din Milo a mai fost creată şi este, vai insurpotabil de bătrână.

I prefer to create these sculptures and be wrong than not be wrong and to recreate Venus from Milo; Venus from Milo has been already created once and oh, she's unbearably old.

Constantin Brâncuşi

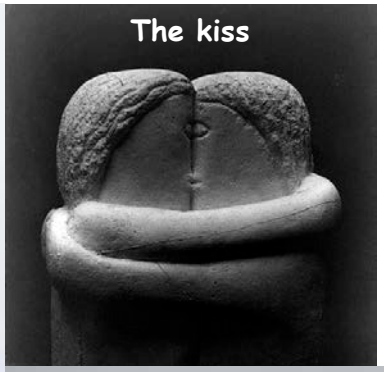

Beginning of the world


Cup


The blond negress


Portrait of miss Pogany


Danaide

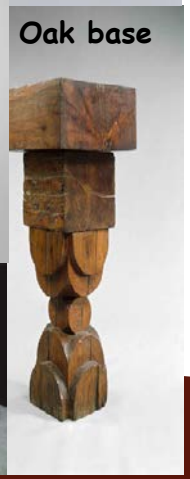

The kiss

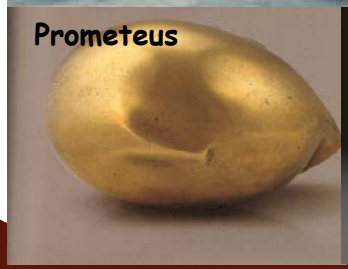

Newborn


Silent table


The gate of Kiss


The gorgeous


Oak base


Prometeus


Sleeping muse


Leda