Biopolymer-assisted synthesis of materials with spherical structures

Oana Carp

Institute of Physical Chemistry “Ilie Murgulescu”
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
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 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

P.T. Anatas and J.C. Warner

The 12 Principles

- 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

Green Nano Chemistry

2004

PRESERVING THE APPLICATIONS WHILE MINIMIZING OR ELIMINATING THE NEGATIVE IMPLICATIONS OF NANOMATERIALS
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.)
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
General objective

Developing synthesis methodologies in which carbohydrates are used as growth inhibitors and crystal habit modifiers
Carbohydrates: soft templates

Starch: ZnO multispheres 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

![Graph showing phenol conversion under 365 nm and visible light irradiation.

O.Carp, A.Tîrsoagă, B.Jurcă, R.Ene, S.Somăcescu, A.Ianculescu,
Carbohydrate Polymers, 2015, 115, 285-293]
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
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: \( \text{ZnO-starch spheres} \)

- \( \text{ZnO/Ag core/shell composite} \)
- \( \text{Ag source} \)
- \( \text{Ni source} \)
- \( \text{S source} \)
- \( \text{Ni}^{2+}/\text{ZnO} \)
- \( \text{ZnO/ZnS core/shell composite} \)
- \( \text{ZnO/TiO}_2 \) core/shell composite

Other cations also..
Saccharides as soft templates: \( \text{ZnO-} \text{alginate spheres} \)

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)
(Zn²⁺+TEA)+alginate: 58 m²/g (89% mesoporosity)
(Zn²⁺+alginate)+TEA: 37 m²/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)
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
Hydrothermal carbonization on the presence of metal cations

Friedrich Bergius
The Nobel Prize in Chemistry
1931
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

Synthesis

1. template synthesis and cation introduction

2. thermal treatment (phase and composition modifications)

Zn\textsuperscript{2+}/starch=constant

**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.**

<table>
<thead>
<tr>
<th>Gram-positive strains</th>
<th>Planktonic MIC</th>
<th>Biofilm MBEC</th>
<th>Gram-negative strains</th>
<th>Planktonic MIC</th>
<th>Biofilm MBEC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ZnO_0.02</strong></td>
<td></td>
<td></td>
<td><strong>ZnO_0.5_1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hollow (µg/mL)</td>
<td></td>
<td></td>
<td>solid (µg/mL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S. aureus ATCC 6538</td>
<td>31.5</td>
<td>&gt;500</td>
<td>15.62</td>
<td>&gt;500</td>
<td>&lt;0.97</td>
</tr>
<tr>
<td>MRSA</td>
<td>&gt;500</td>
<td>1.95</td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>&lt;0.97</td>
</tr>
<tr>
<td>B. subtilis ATCC 12488</td>
<td>&gt;500</td>
<td>62.5</td>
<td>&gt;500</td>
<td>62.5</td>
<td>&gt;500</td>
</tr>
<tr>
<td>B. subtilis 6683</td>
<td>62.5</td>
<td>0.97</td>
<td>&gt;500</td>
<td>3.9</td>
<td>&gt;500</td>
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<tr>
<td>P. aeruginosa ATCC 27853</td>
<td>&gt;500</td>
<td>31.25</td>
<td>&gt;500</td>
<td>31.25</td>
<td>&gt;500</td>
</tr>
<tr>
<td>P. aeruginosa 719</td>
<td>&gt;500</td>
<td>31.25</td>
<td>&gt;500</td>
<td>31.25</td>
<td>&gt;500</td>
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<tr>
<td>E. coli O26</td>
<td>&gt;500</td>
<td>62.5</td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>&gt;500</td>
</tr>
<tr>
<td>K. pneumoniae 11</td>
<td>&gt;500</td>
<td>15.62</td>
<td>&gt;500</td>
<td>&gt;500</td>
<td>&gt;500</td>
</tr>
</tbody>
</table>

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
General objective

Different carbon-metal/metal oxide composites with controlled properties
Carbohydrates: template and carbon source

Synthesis

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

**ZnO-carbon**

**INSTEAD of AIR ARGON**

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding energy, eV</th>
<th>Atomic relative concentration, at%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1s</td>
<td>O1s</td>
</tr>
<tr>
<td>ZnO/C as received</td>
<td>284.8 (C-C)</td>
<td>531.5 (O²⁻)</td>
</tr>
<tr>
<td></td>
<td>286.5 (OH-C-O)</td>
<td>533.4 (OH-C-O)</td>
</tr>
<tr>
<td>ZnO/C 1 min sputtering</td>
<td>284.8 (C-C)</td>
<td>531.3 (O²⁻)</td>
</tr>
<tr>
<td></td>
<td>286.5 (OH-C-O)</td>
<td>533.3 (OH-C-O)</td>
</tr>
<tr>
<td>ZnO/C 5 min sputtering</td>
<td>284.8 (C-C)</td>
<td>531.2 (O²⁻)</td>
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<tr>
<td></td>
<td>286.5 (OH-C-O)</td>
<td>533.0 (OH-C-O)</td>
</tr>
</tbody>
</table>

G. Pătrănoiu, 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 m²/g
(87% of total area of 512 m²/g)

Specific capacitance of 22.13 F·g⁻¹
(scan rate = 50 mVs⁻¹)
One-pot synthesis

Argon

700°C, 3h

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.

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

Physical Chemistry Chemical Physics 2016, 18, 30794-30807
Modulation of carbon materials properties through the amount of the metal (Zn$^{2+}$)

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.
Carbohydrates: template and carbon source

One-pot synthesis

Co-CoO-carbon

Micropore surface: 543 m²/g (81% of total area of 669 m²/g)

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

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
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 și să greșesc decât să nu greșesc și să o recreeze pe Venus din Milo, căci Venus din Milo a mai fost creată și 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 Brâncuși