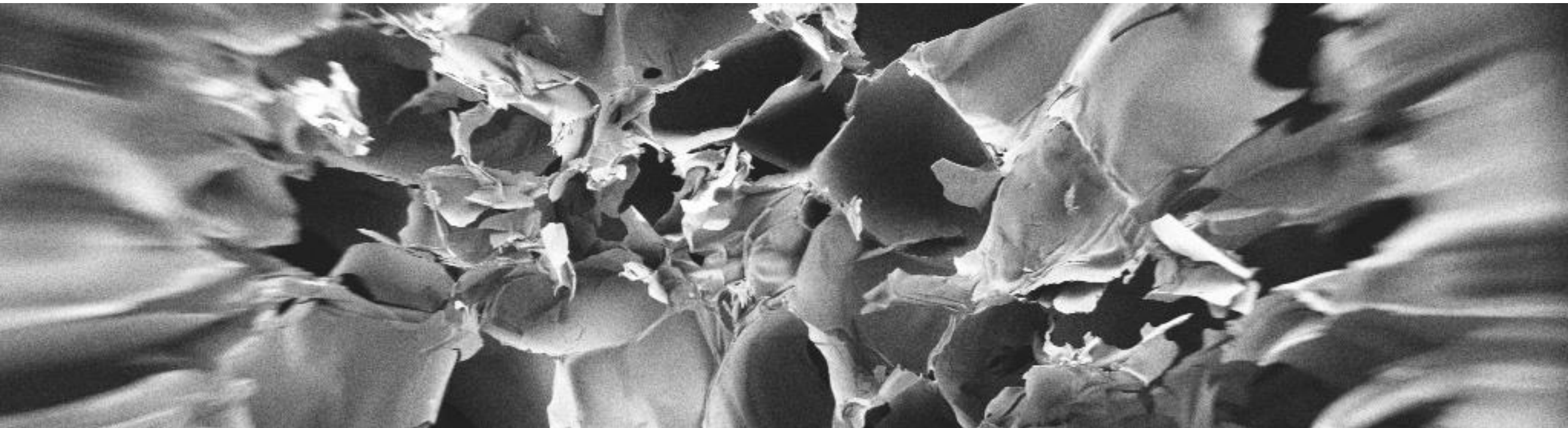




Hydrogels for chemical and energy systems

Prof. Dr. Ilja Gasan Osojnik Črnivec
Head of Laboratory for H₂ and CO₂ Technologies
National Institute of Chemistry



Funded by
the European Union

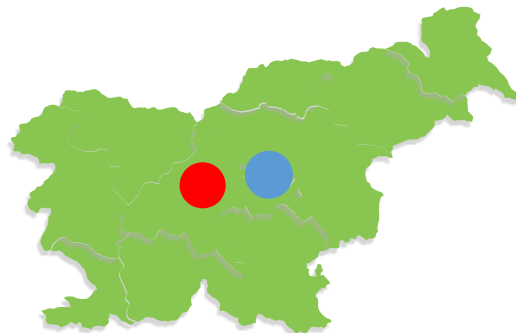


NATIONAL INSTITUTE OF CHEMISTRY



Center for Development,
Demonstration and Training
for Carbon-Free Technologies

National Institute of
Chemistry (NIC)
Ljubljana, Slovenia



Center for development,
demonstration and training
for zero carbon
technologies Kisovec,
Slovenia



Undergoing full renovation



Fully operational in 2026, 32 mio EUR investment



Co-funded by
the European Union



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REPUBLIC OF SLOVENIA
MINISTRY OF HIGHER EDUCATION,
SCIENCE AND INNOVATION





L52 Laboratory for Demonstration of H₂ and CO₂ Technologies

*Chemical engineering for **alternative energy, fine chemical production, decarbonization and energy intensive industries**, at industrially relevant operating conditions.*





R&D fields

- Development, synthesis, preparation and characterization of materials, esp. catalysts, sorbents, electrodes and membranes
- Electro-chemical/ -catalytic production of hydrogen
- Conversion of hydrogen and carbon dioxide
- Renewable resources and waste valorisation

Personnel

Asst. Prof. Dr. Ilja Gasan Osojnik Črnivec, head

Dr. Janvit Teržan, hydrogen technologies, magnetic heating

Dr. Maja Čič, environmental engineering, electrochemical processes

Dr. Elena Sutormina, reaction calorimetry, nanomaterials

Dr. Marko Soderžnik, preparation and characterization of materials, enhanced electrochemistry

Dr. Muhammad Irshad, nanomaterials, reactor engineering

Dr. Patricia Jovičević Klug, advanced microscopy and low-carbon sustainable CRM recovery

Dr. Matic Jovičević Klug, magnetic and hydrogen based autocatalytic CRM recovery

Experts

Dr. Leon Kaluža, Petra Stražar Gatalo, Nina Ojsteršek, Uroš Dežman, Tomaž Čebela

Doctoral students

Vojtěch Škopek, Vuk Martinović



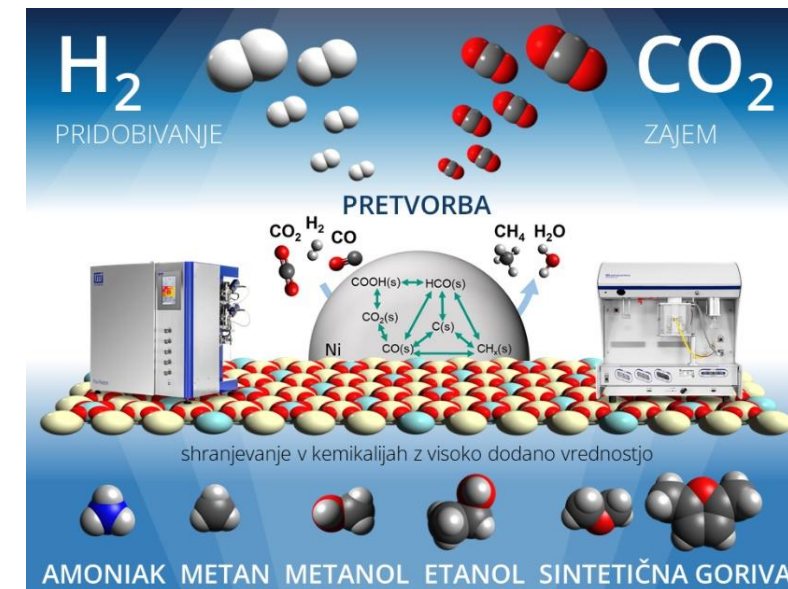
Pridobivanje in
pretvorba vodika

kataliza in elektroliza



Zajem ogljikovega
dioksida

trdni in tekoči sistemi





NATIONAL INSTITUTE OF CHEMISTRY



Center for Development,
Demonstration and Training
for Carbon-Free Technologies

Members



Expertise

Akcijski načrt za doseganje ciljev v NEPN na področju vodika do leta 2030 in s pogledom do leta 2040 (AN H2)



REPUBLIC OF SLOVENIA
MINISTRY OF THE ENVIRONMENT,
CLIMATE AND ENERGY



UNITED NATIONS
INDUSTRIAL DEVELOPMENT ORGANIZATION

Coordination



HyBReED
SI H₂ and battery RRI
TRL 3-6 programe



CarbNETs
CO₂ heat & water RRI
TRL 3-6 programe



Erasmus+



Co-funded by
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REPUBLIC OF SLOVENIA
MINISTRY OF HIGHER EDUCATION,
SCIENCE AND INNOVATION



Researcher mobility and bilateral cooperation

ENFiber

European Network for Valorizing Food
Processing Waste into Sustainable
Fibers (CA24111)



MXeneCatSus

MXene-Based Catalysts for
Sustainability Chemical Challenges
(CA25132)

Gastro-FIB

STE-CA-HYDROGEN





Green Hydrogen

for sustainable industrial processes

ENERGY CARRIER

substitution of fossil energy carriers

SI: glass ✓, ceramic, lime, metallurgic – aluminum, (steel)
long-haul transport: ships, trucks, ...

HEAT RECOVERY

utilization of high temperature industrial heat

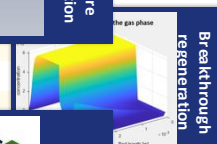
ELECTROLYSIS & BIOMETHANE

standalone production of hydrogen

SI: glass and chemical industry

FEEDSTOCK

substitution of fossil hydrogen sources
methanol, ethanol, jet fuel, ammonia etc.



Carbon Capture

supporting H₂ technologies and biomass recovery

NOVEL SORBENTS & TECH

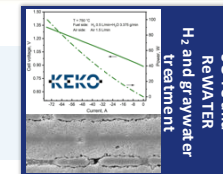
(CO₂ composition, process heat, gas purity)

FEEDSTOCK

fuels, polymers, advanced ceramics/minerals

Water Security

supporting decarbonization

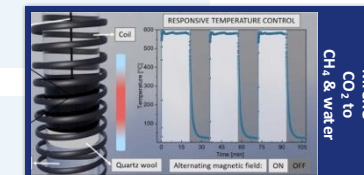


ELECTROLYSIS

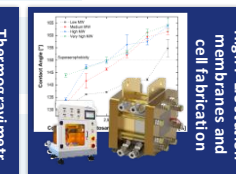
Water treatment and alternative water sources

BIOBASED MATERIALS

Biobased sorbents for emerging pollutants and hazardous gasses removal



Biobased PFAS-free advanced coating and polymer adhesive alternatives



NOVEL PROCESSES

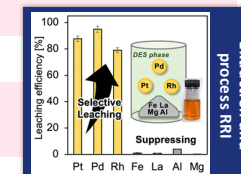
Residual water production
High pressure electrolysis

Critical Raw Materials

value chains for high added value materials

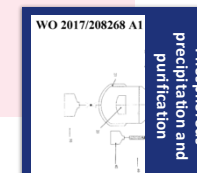
ADVANCED NANOMATERIALS

novel selective recovery and/or separation of metals



PHOSPHOROUS RECOVERY

novel solvents and electrochemical extraction systems
SI value chain: sludges to technical agents, electrolytes, electrodes and absorbent producers.



Functional bio-based hydrogels for energy applications

Advanced materials for H₂ and CO₂ technologies

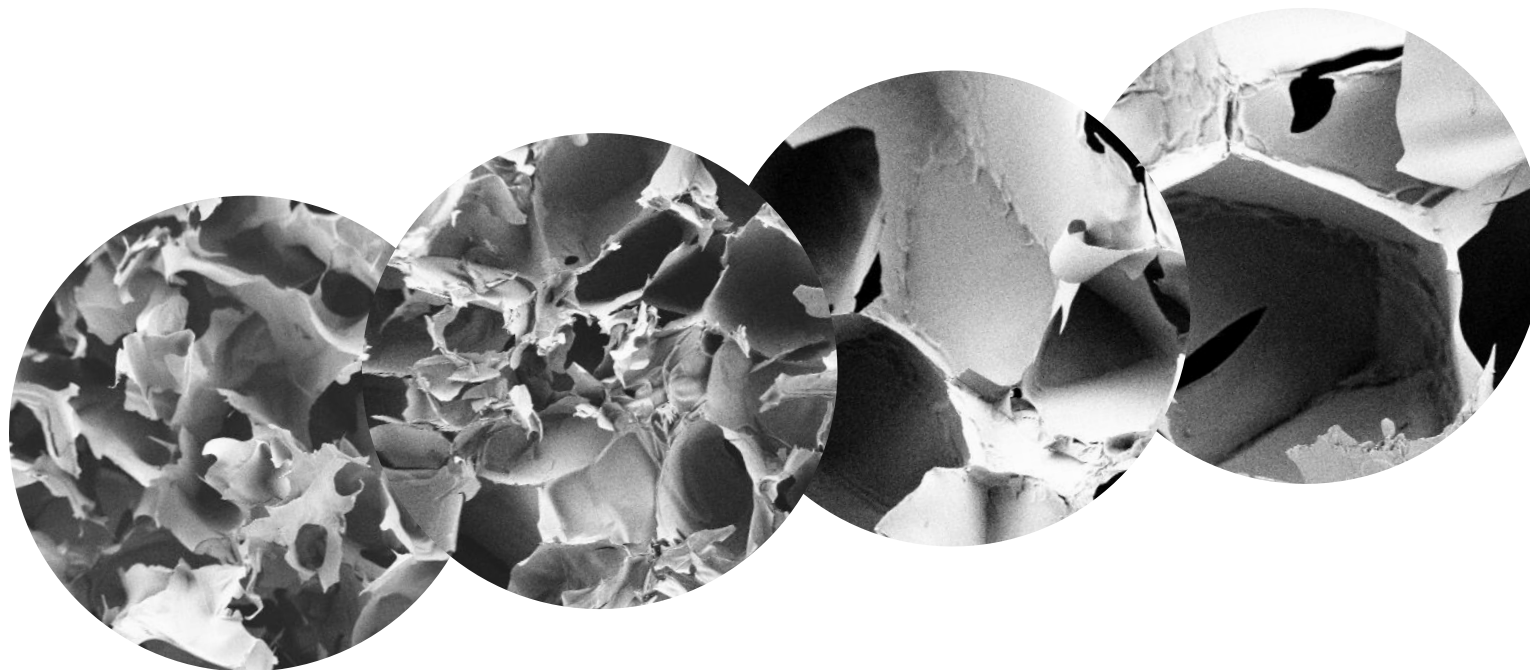
Responsive and tunable bio-based hydrogels

Hydrogel based electrode coatings

Hydrogel based electrolysis membranes

Hydrogel based sorbent development

Hydrogel based nano-catalyst templates

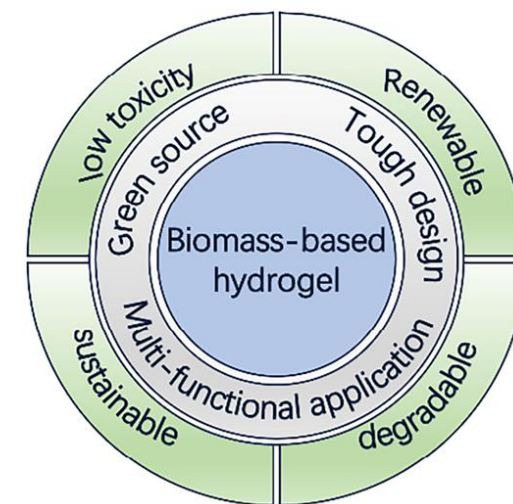
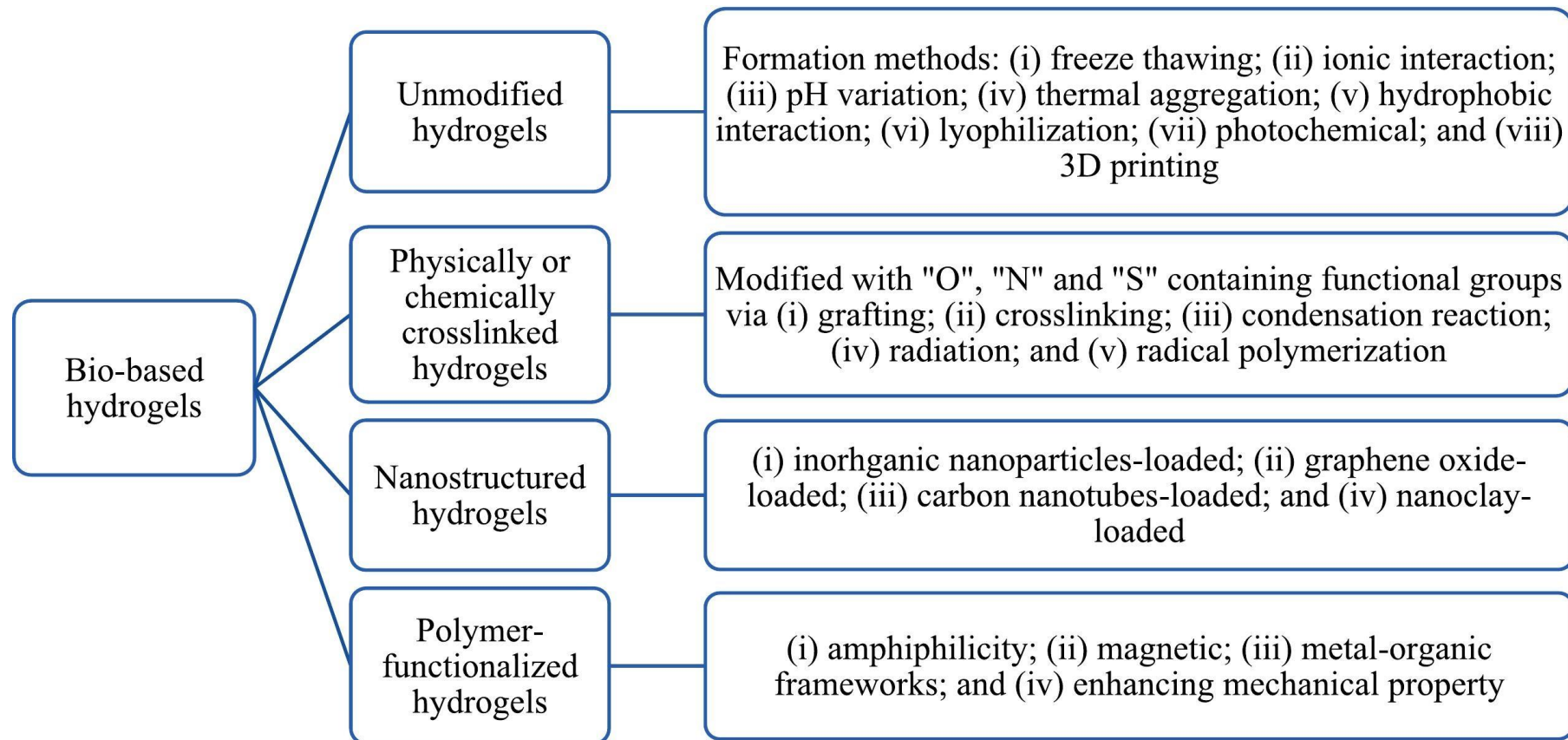




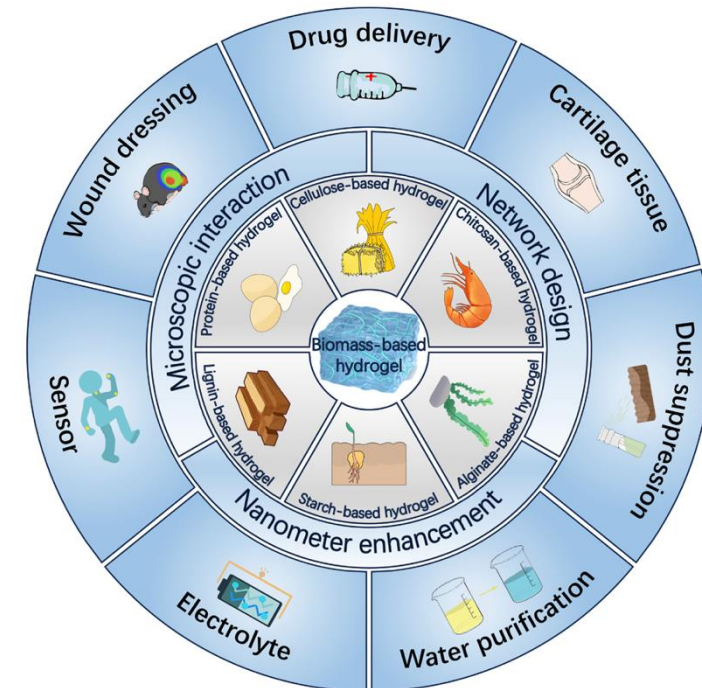
Bio-based hydrogels



Bio-based hydrogels



!! not always everything !!

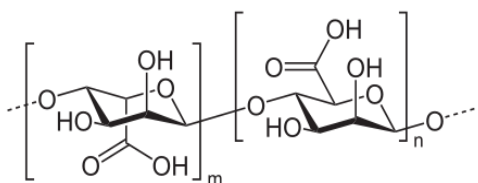


Polysaccharides

ALGINATE (E400–404)



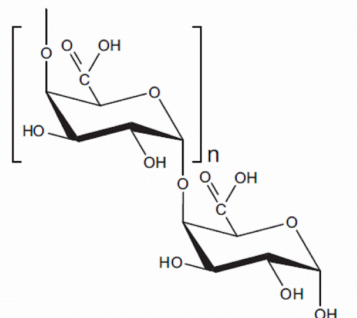
Anionic polysaccharide from brown algae. In the presence of multivalent cations (e.g. Ca^{2+}), hydrogels are formed.



PECTIN (E 440)



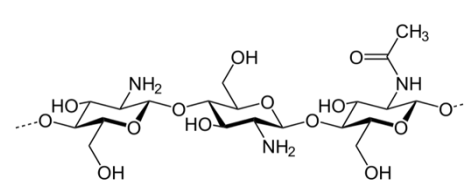
Anionic polysaccharide, from peels of citrus, apples, quinces etc. Forms hydrogels, similarly to alginate..



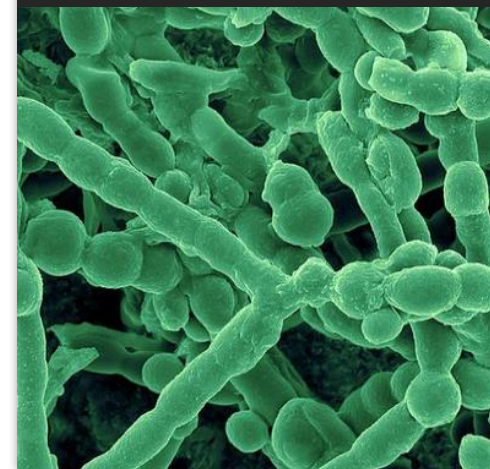
CHITOSAN (GRAS FDA)



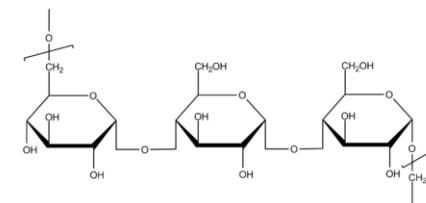
Cationic polysaccharide, obtained from the deacetylation of chitin, forming gels with multivalent anions (PO_4^{3-} , alginate, ...).



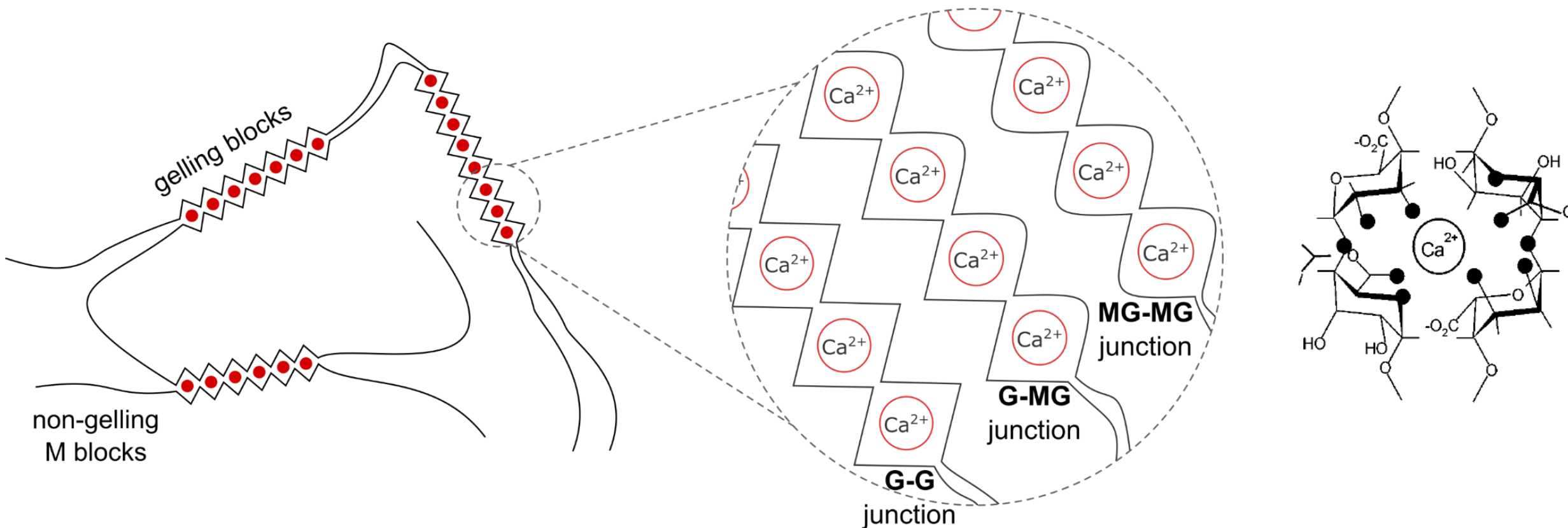
PULLULAN (E 1204)



Neutral polysaccharide, from the fermentation of starch by the fungus *Aureobasidium pullulans*.



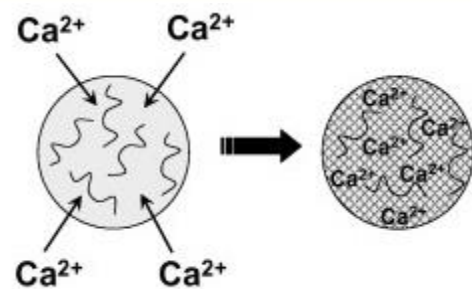
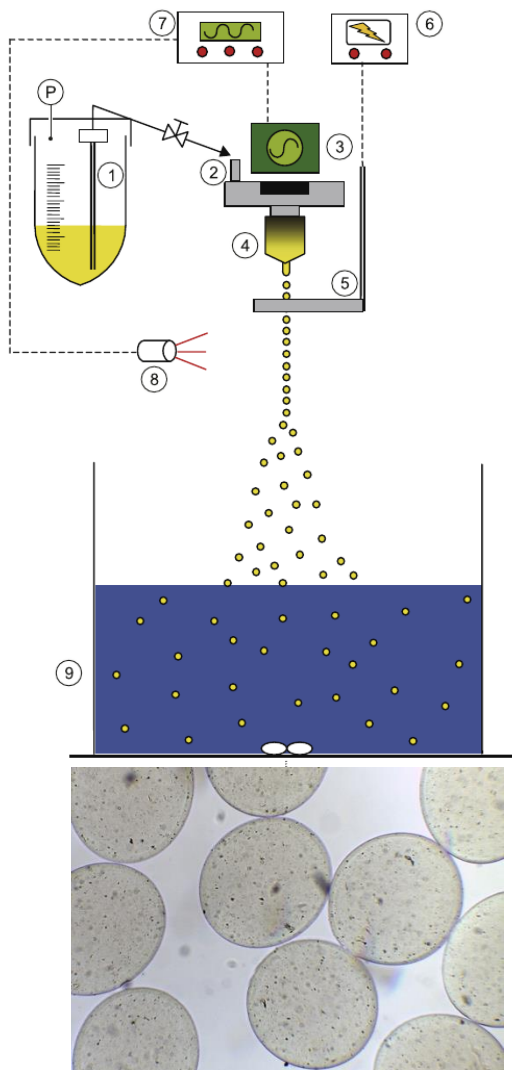
Ionic cross-linking



Schematic model of alginate gelation in the presence of multivalent cations.
Stable cross-linking occurs in the presence of G-regions with > 6–10 monosaccharide units.

Ionic cross-linking

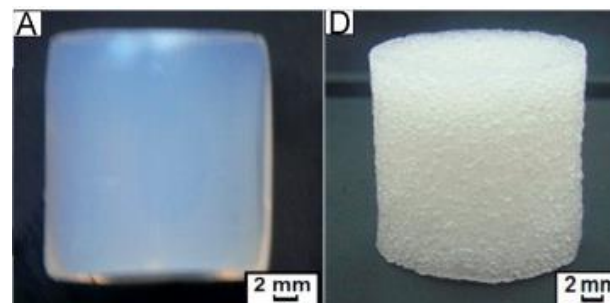
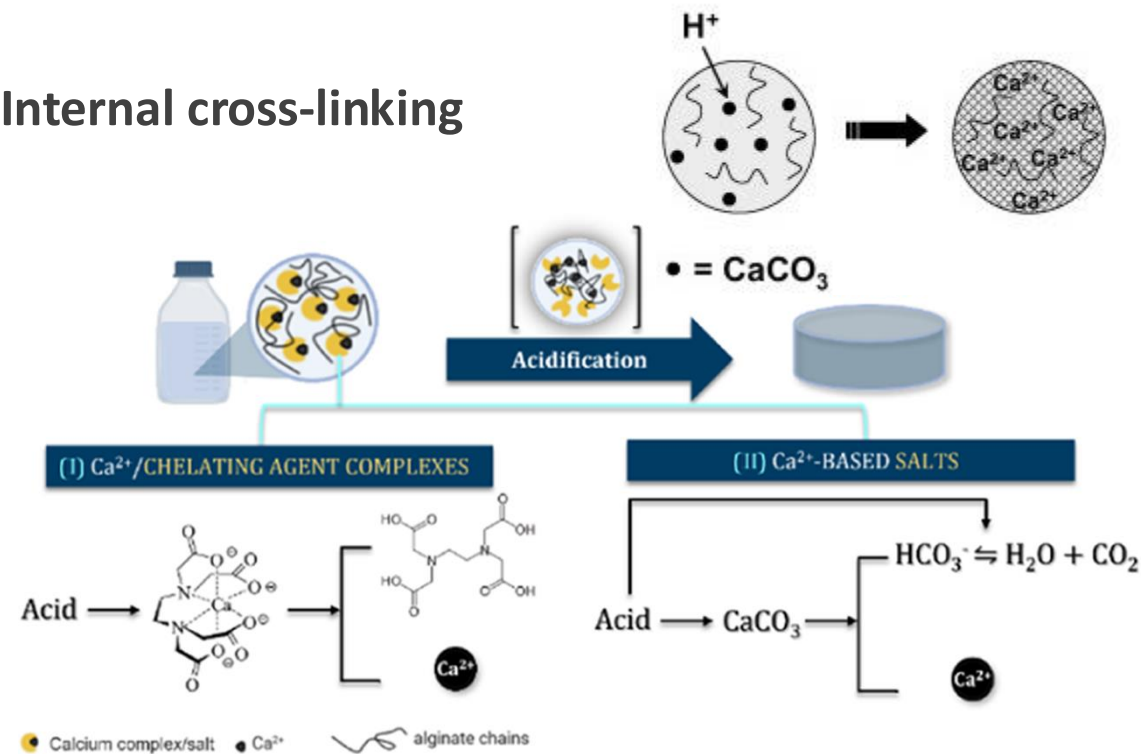
External cross-linking



Encapsulator B-395 Pro

Polysaccharide solution is introduced into a corresponding hardening solution containing crosslinking ions. A vibration nozzle and electrode enable the formation of microbeads.

Internal cross-linking



All gelation components are within the mixture, an environment change (time, pH, temperature, ..) initiates gelation.

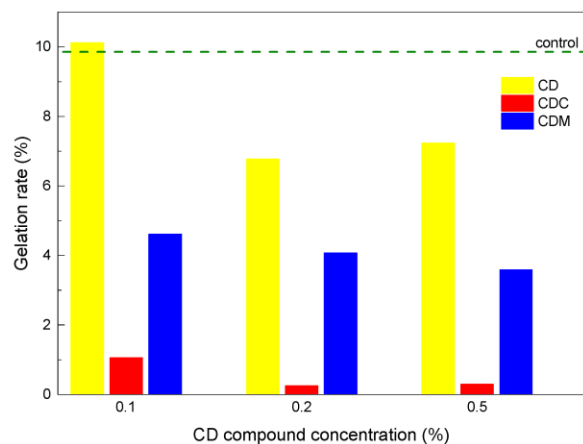
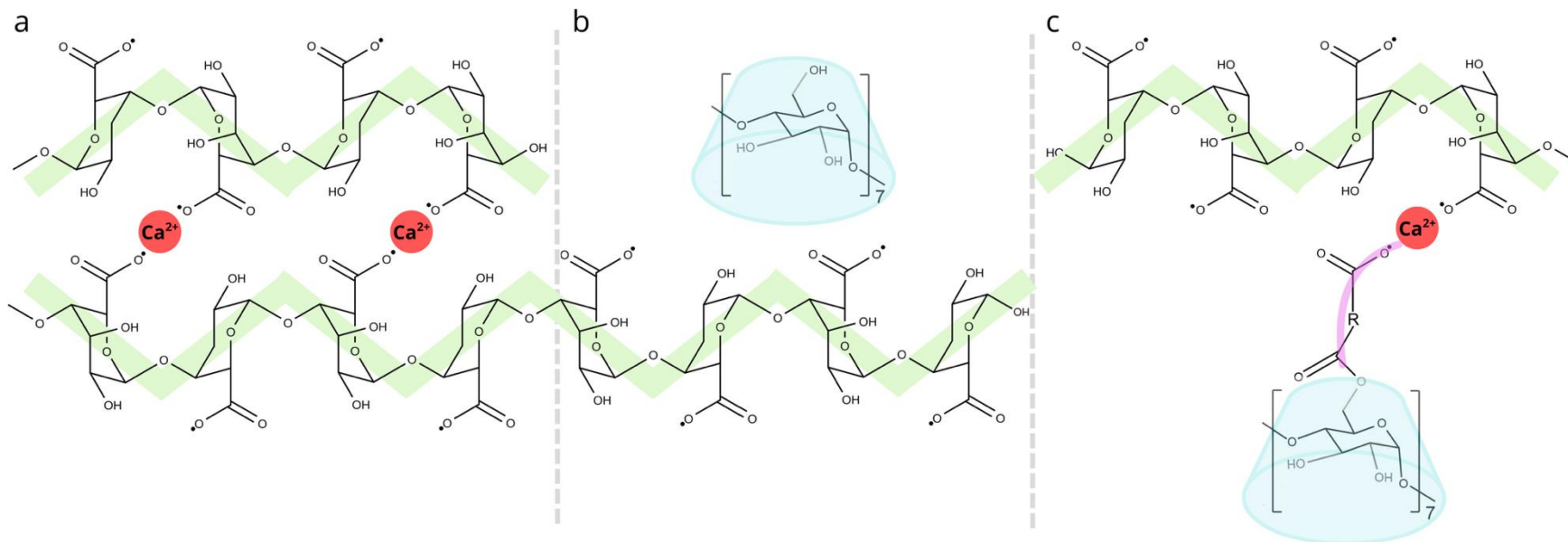


Features of bio-based hydrogels

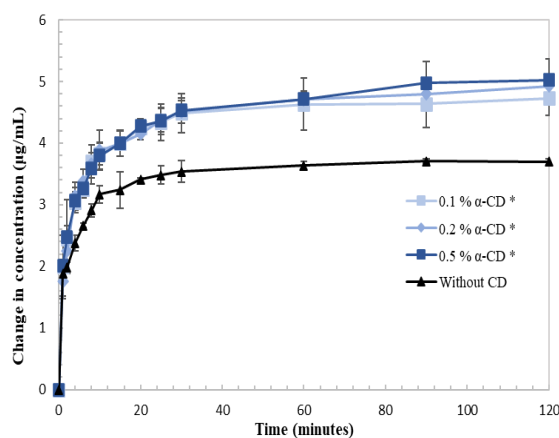


Gel porosity modulation

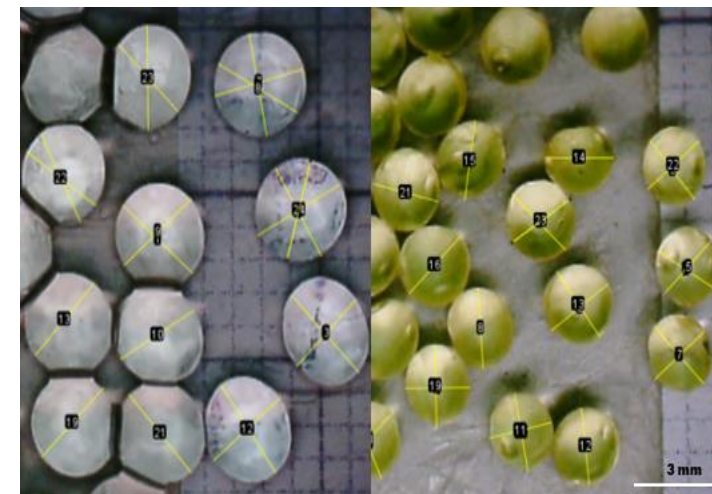
Alginate gel with β -cyclodextrin inclusion



Cyclodextrin reduces solution viscosity, gel deformation resistance (G') and increase flow (G'').

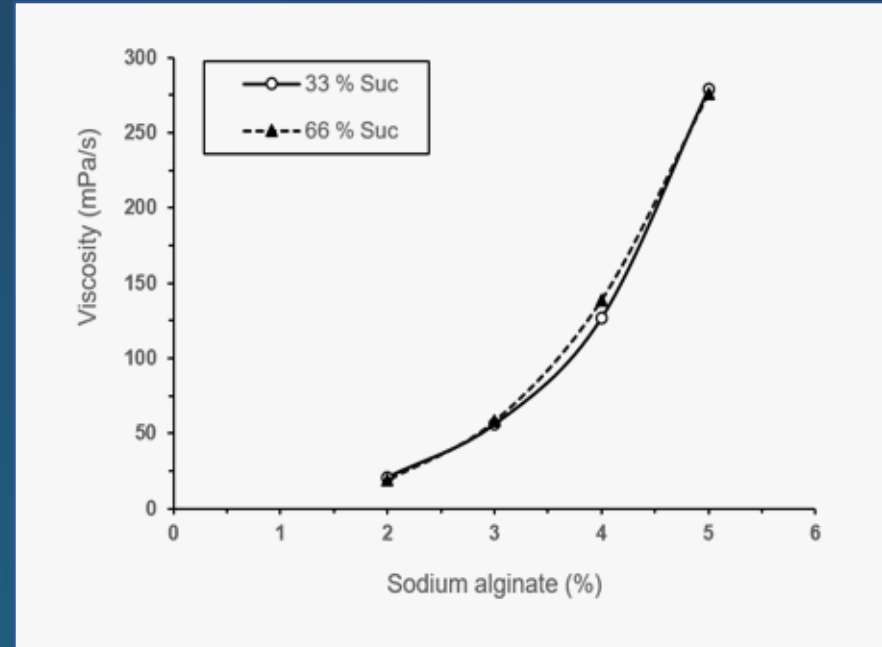


Cyclodextrin improves the rate and capacity for hydrophobic compounds integration (example for curcumin).

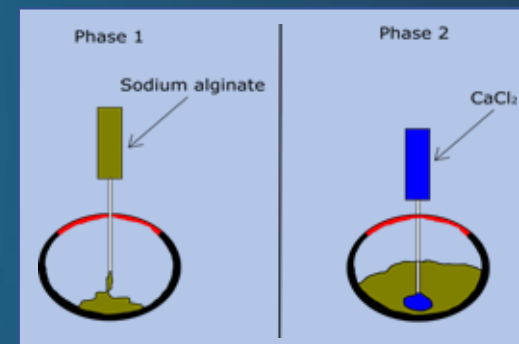


3D extrusion inks

- Fast ion induced gelation (Ca^{2+})
- Rapid solubility/hydration in cold water (minutes at no/minimal mixing instead hours at intensive agitation)
- Versatile entrappment (also hydrophobic instead of only hydrophilic)
- All materials EFSA and FDA approved



Viscosity of rapidly dissolving alginate matrix

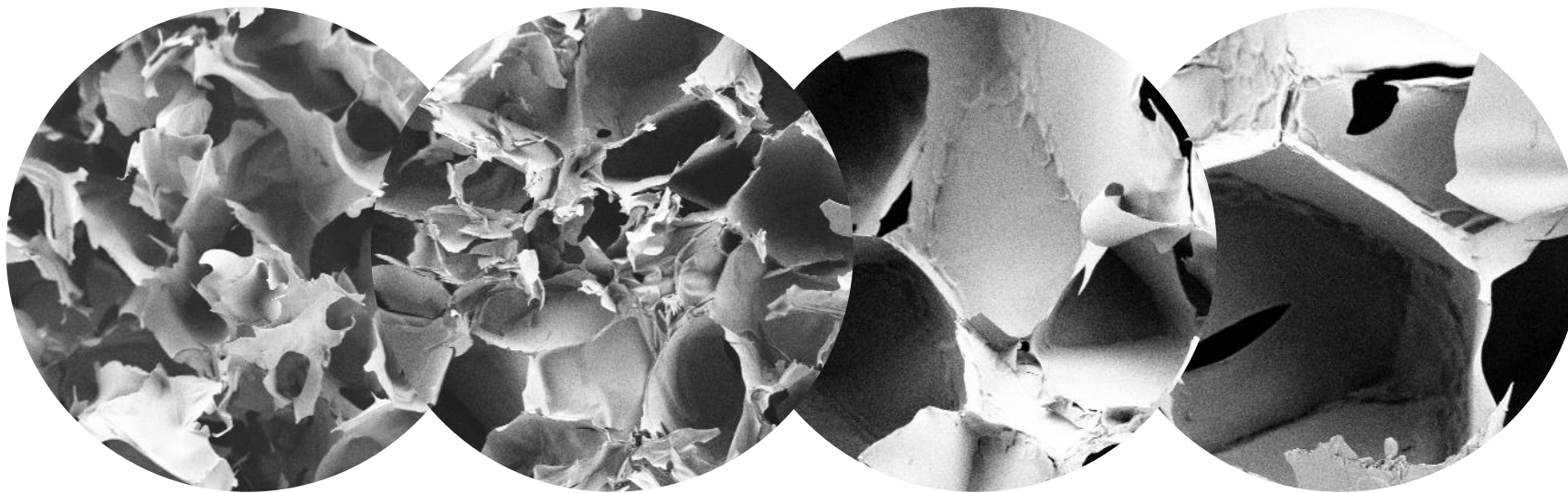


Extrusion steps for the gelation of Na-alginate



Printing nozzle inside the machine





Functional coatings



Hydrogen

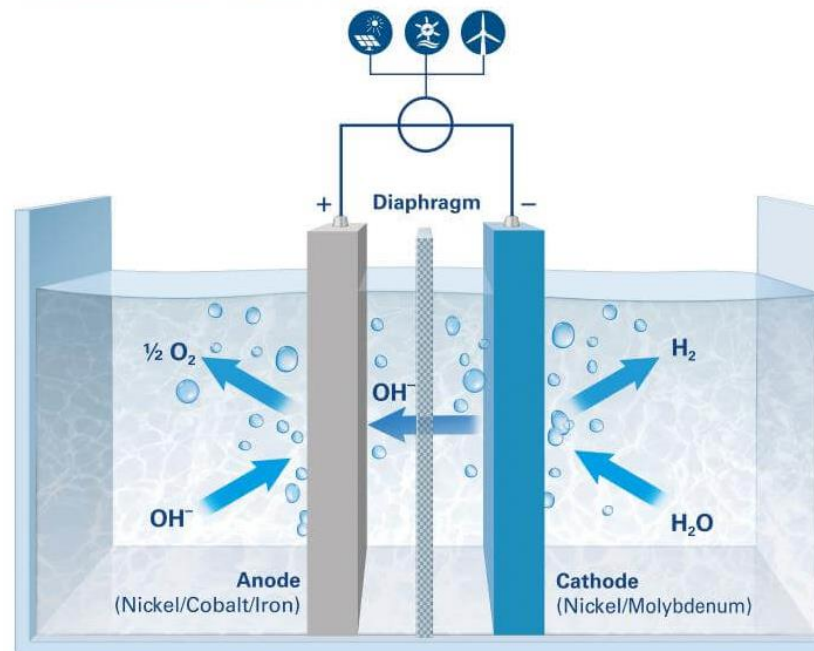
Versatile energy carrier

- the highest **energy content** per mass
- 15x lighter than air
- **Power-X** to for surplus energy

Storage and **transport** challenges, **on demand** production is beneficial.



Alkaline Water Electrolysis

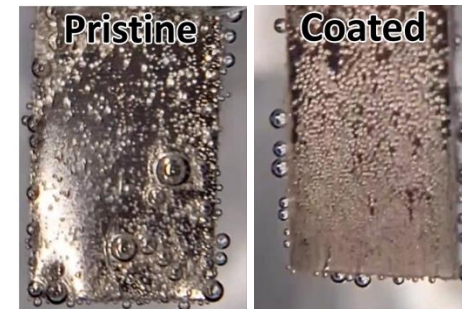
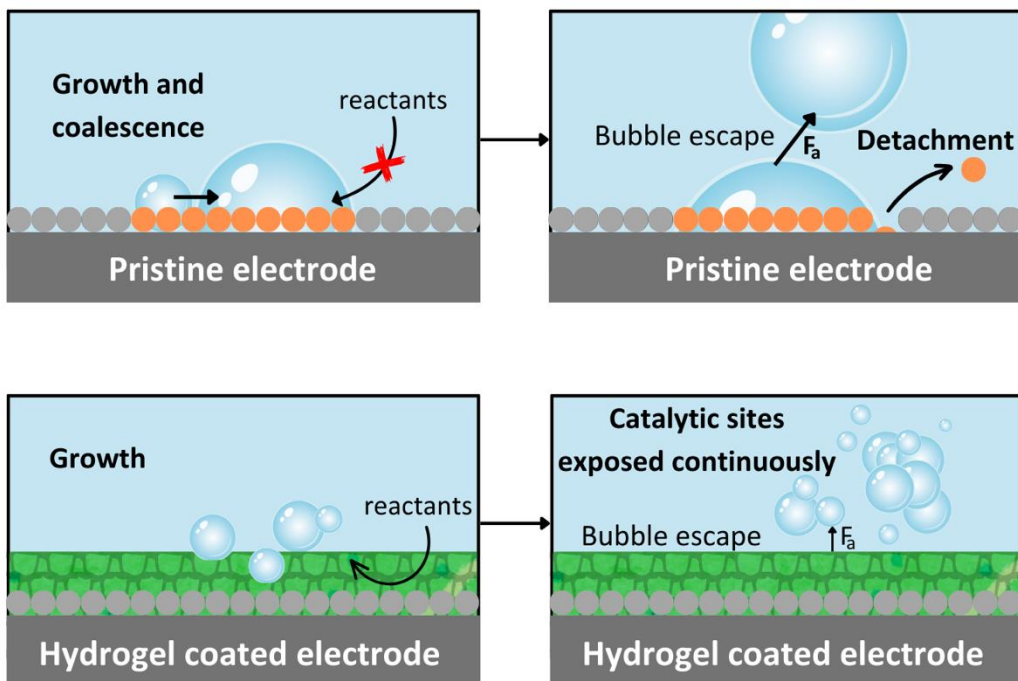


Water electrolysis

- produces 99.99% **pure hydrogen**
- **green hydrogen** with PV/wind
- room temperature and ambient pressure
- Industrial feedstock
- can feed directly into fuel cells

Challenges in hydrogen evolution reaction (HER)

- **high energy consumption**
- **noble metals** as electrodes (e.g., Pt)
- gas bubble at electrodes **reduce efficiency** by blocking active sites
- new alternatives required to boost HER performance



SUPERAEROPHOBIC COATINGS^[1]

- improved bubble detachment
- reduced overpotential
- overall boost in efficiency

However, **toxic** and **expensive**:

- **M13 virus** with specific conditions^[2]
- Fossil based and persistent (polyallylethylamine, polyethyleneimine)^[3]
- toxic crosslinker (glutaraldehyde)

[1] BAE, M. et al. Superaerophobic Polyethyleneimine Hydrogels for Improving Electrochemical Hydrogen Production by Promoting Bubble Detachment. In *Advanced Energy Materials*. 2022. Vol. 12, no. 29, s. 2201452.

[2] JEON, D. et al. Superaerophobic hydrogels for enhanced electrochemical and photoelectrochemical hydrogen production. In *Science Advances*. 2020. Vol. 6, no. 15, s. eaaz3944.

[3] KANG, Y. et al. Versatile, Stable, and Scalable Gel-Like Aerophobic Surface System (GLASS) for Hydrogen Production. In *Advanced Functional Materials*. 2024. Vol. 34, no. 2.

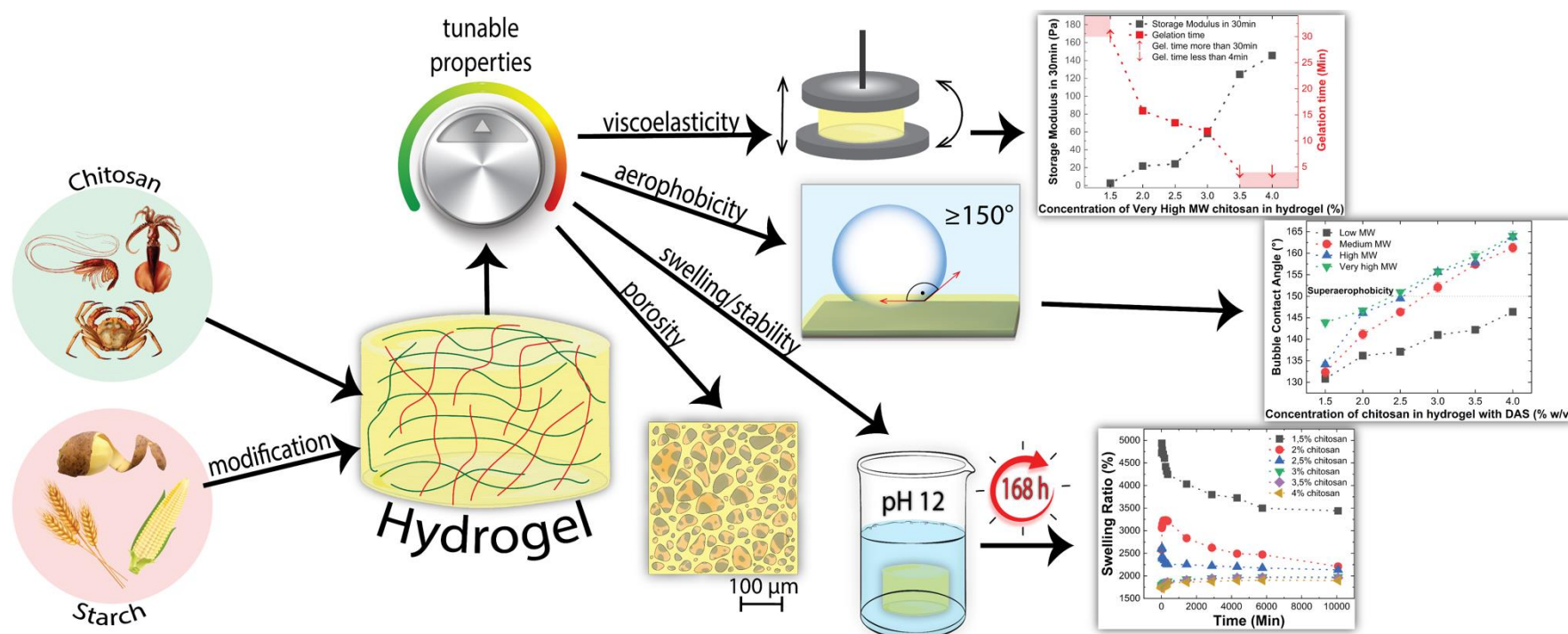
Towards alkaline resistant properties

Chitosan

- Derived from chitin
- Only natural cationic polysaccharide
- Biocompatible, adhesive, modifiable
- High number of hydroxy and amino groups to achieve high hydrophilicity

limitations

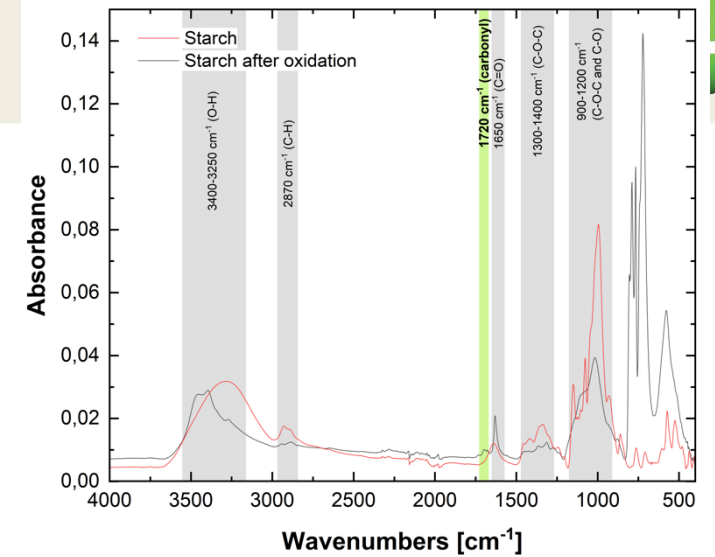
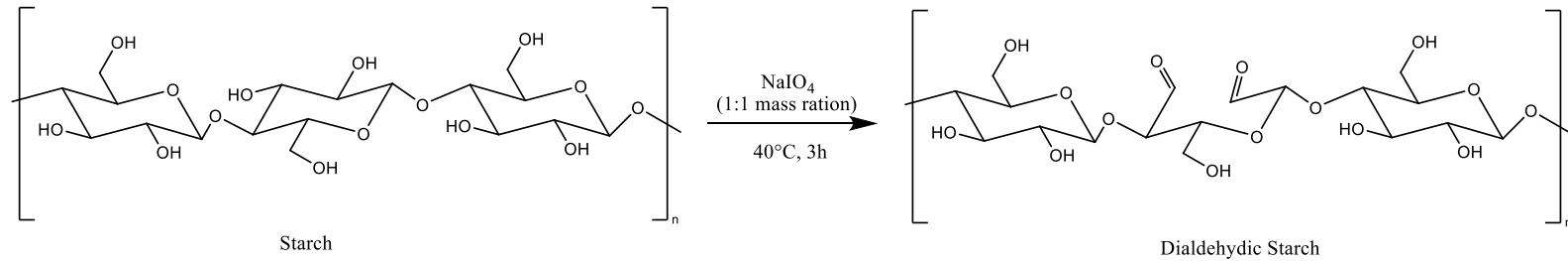
- Common crosslinkers are usually toxic (glutaraldehyde, glyoxal) or expensive (genipin)
- Searching for non-toxic and abundant alternatives



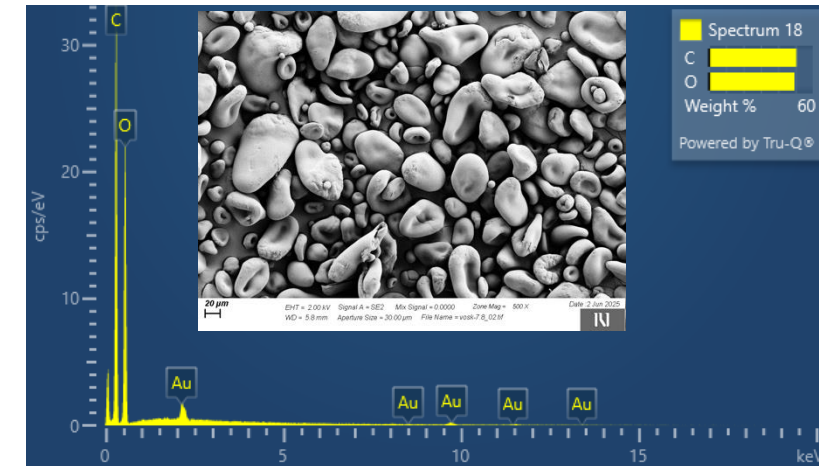
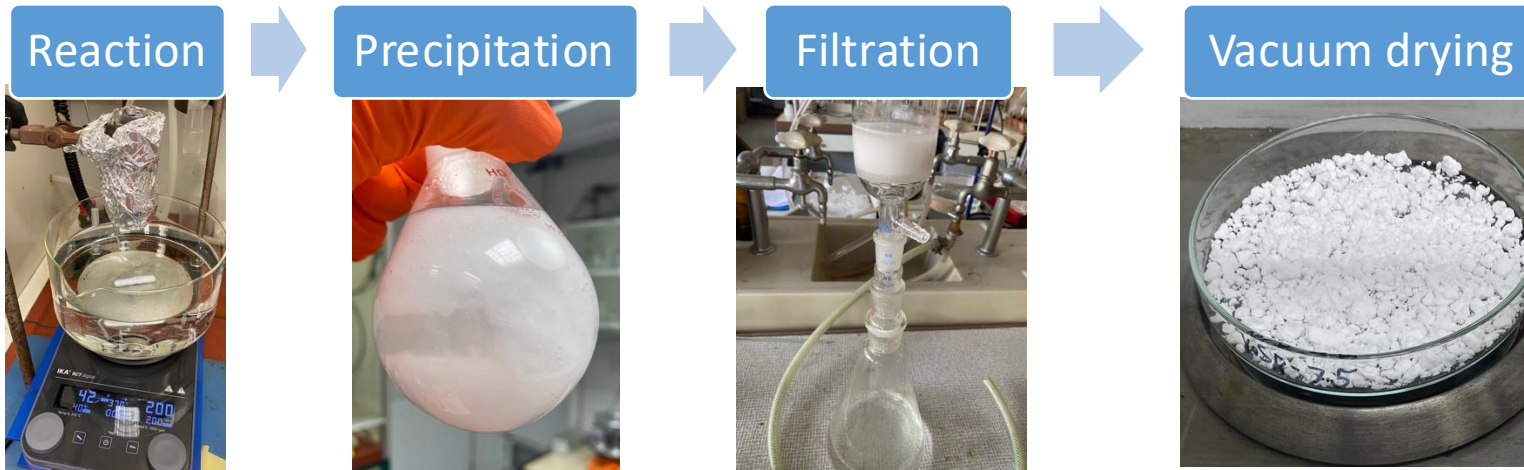


Bio-based covalent crosslinker development

Preparation of dialdehyde starch

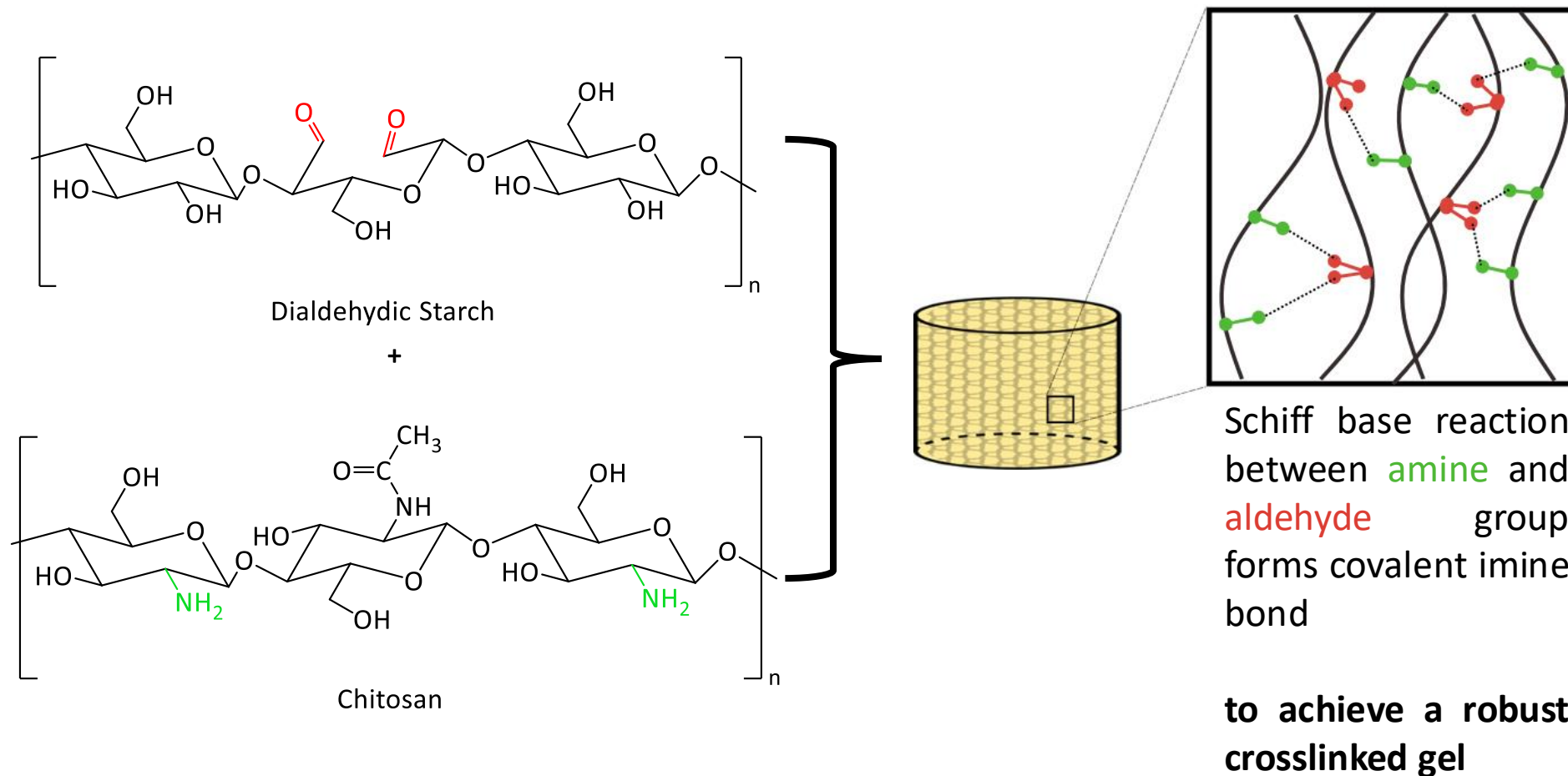


FTIR spectra to confirm new aldehydic group



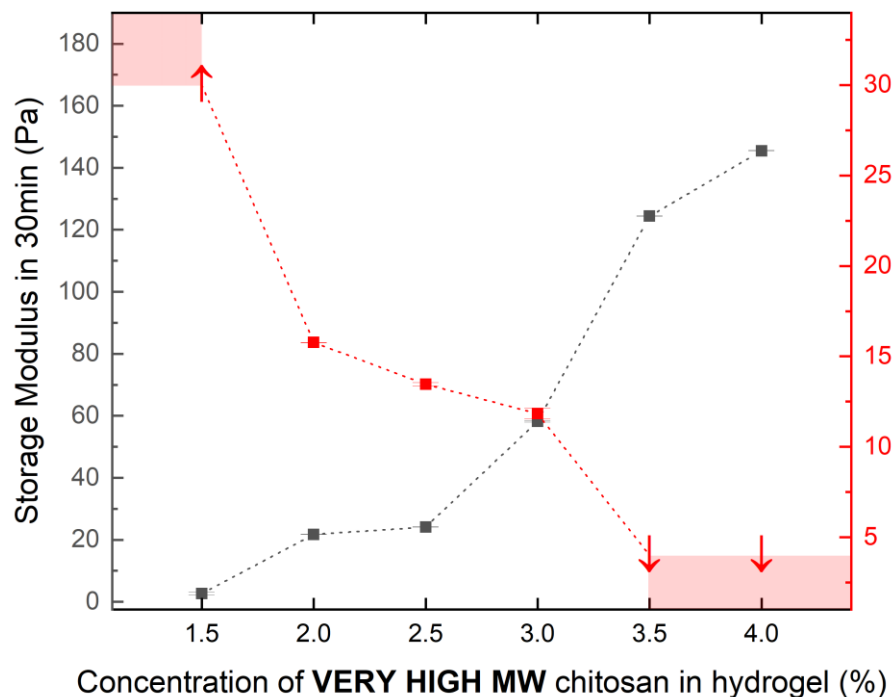
EDS elemental surface composition to confirm crosslinker purity

Hydrogel synthesis

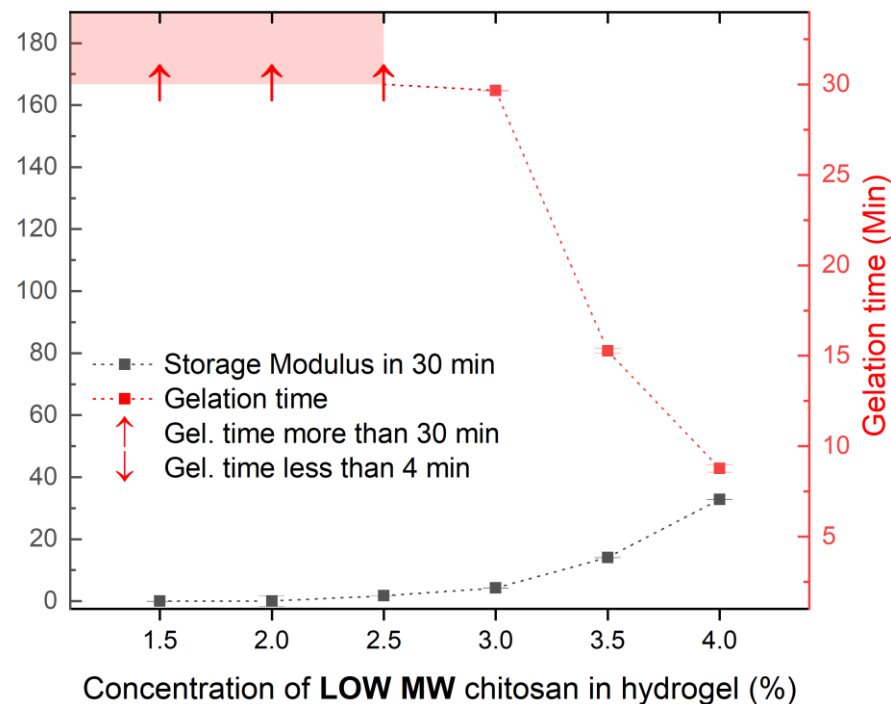


Viscoelasticity and gelation tuning

- Tunability with changing **polymer concentration** and **molecular weight**
- With the right tuning **rapid gelation** (under 4 min)



VS.

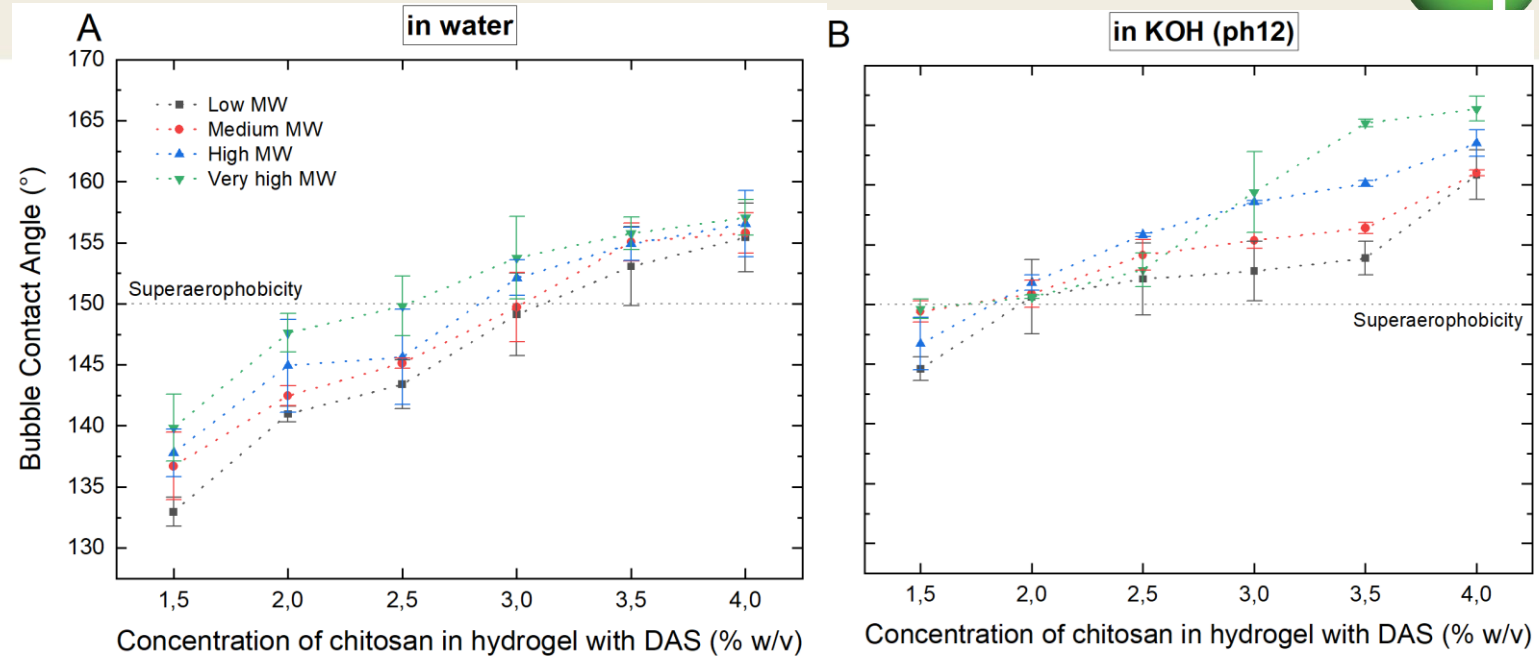




Bubble contact angle

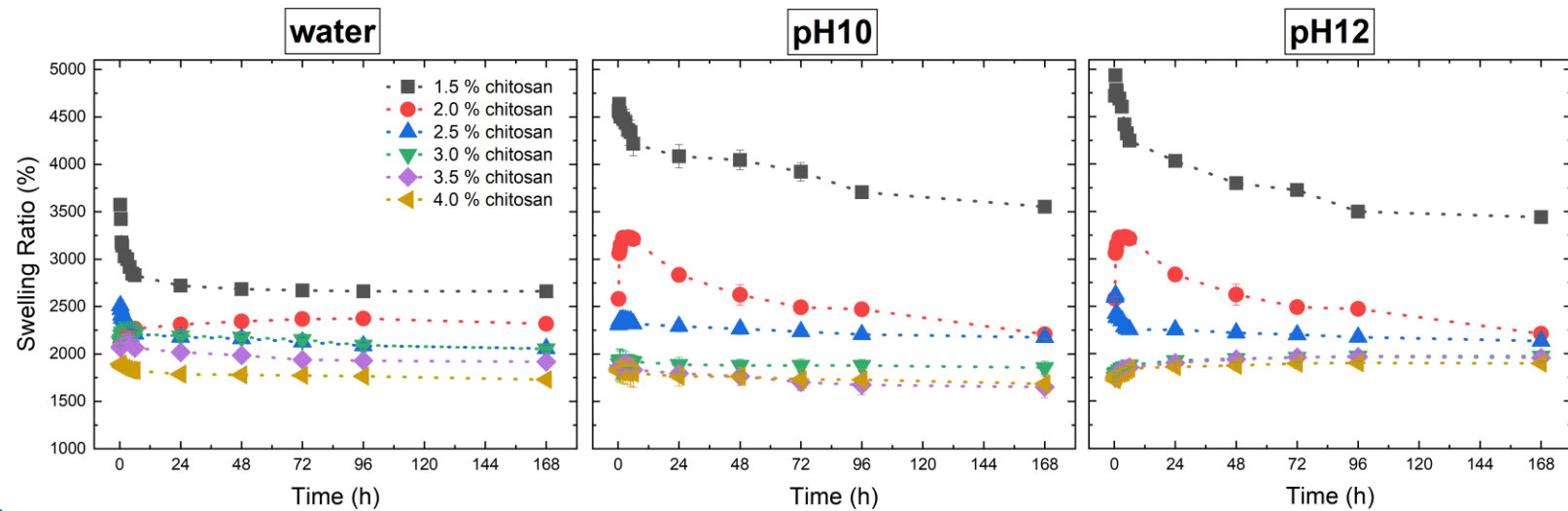
Contact angles between air bubble and hydrogel film

Superaerophobicity @150° and above



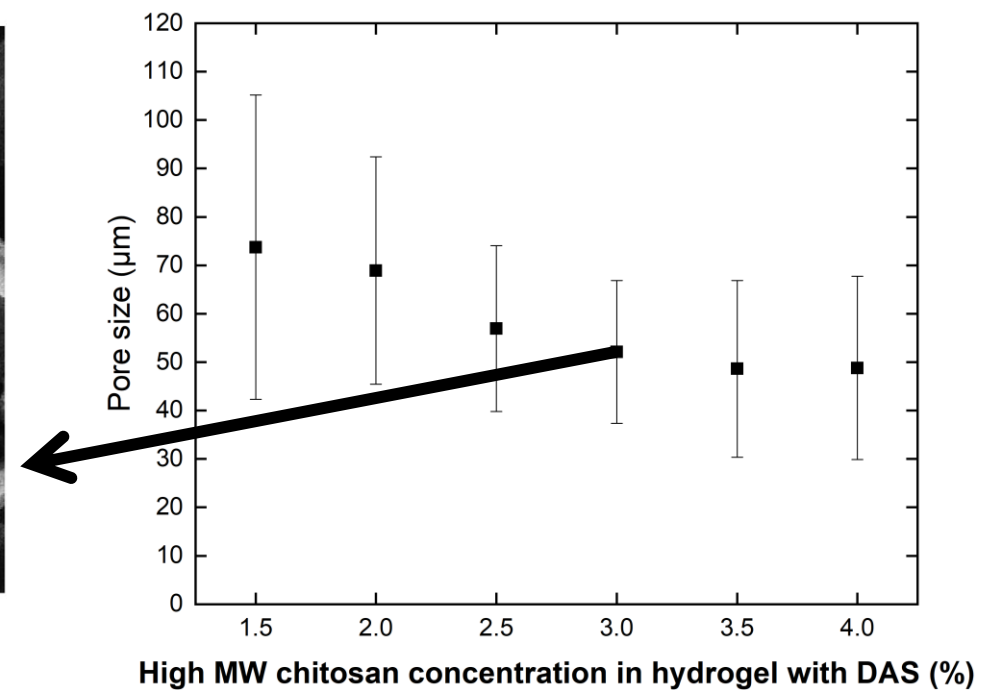
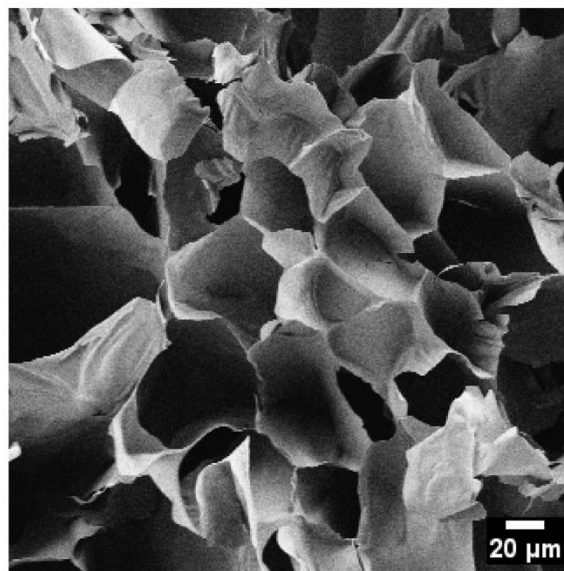
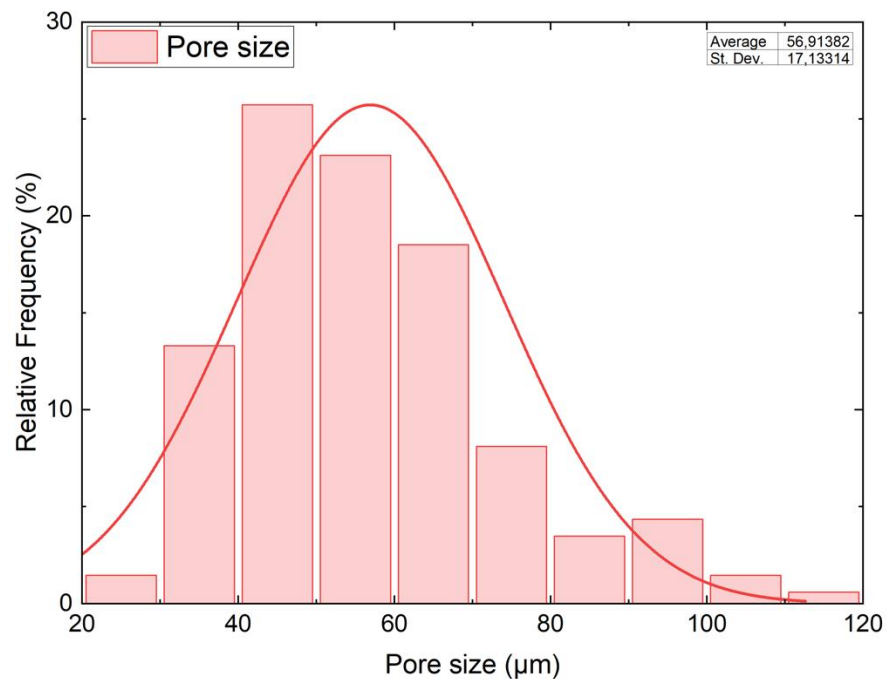
Stability in alkaline environment

Stable swelling behavior over period of **7 days**



Pore size distribution

- open **porous 3D structure**
- pore diameters ranging **10-100 μm**



Structure-feature relationship

↑ C_{chitosan} :

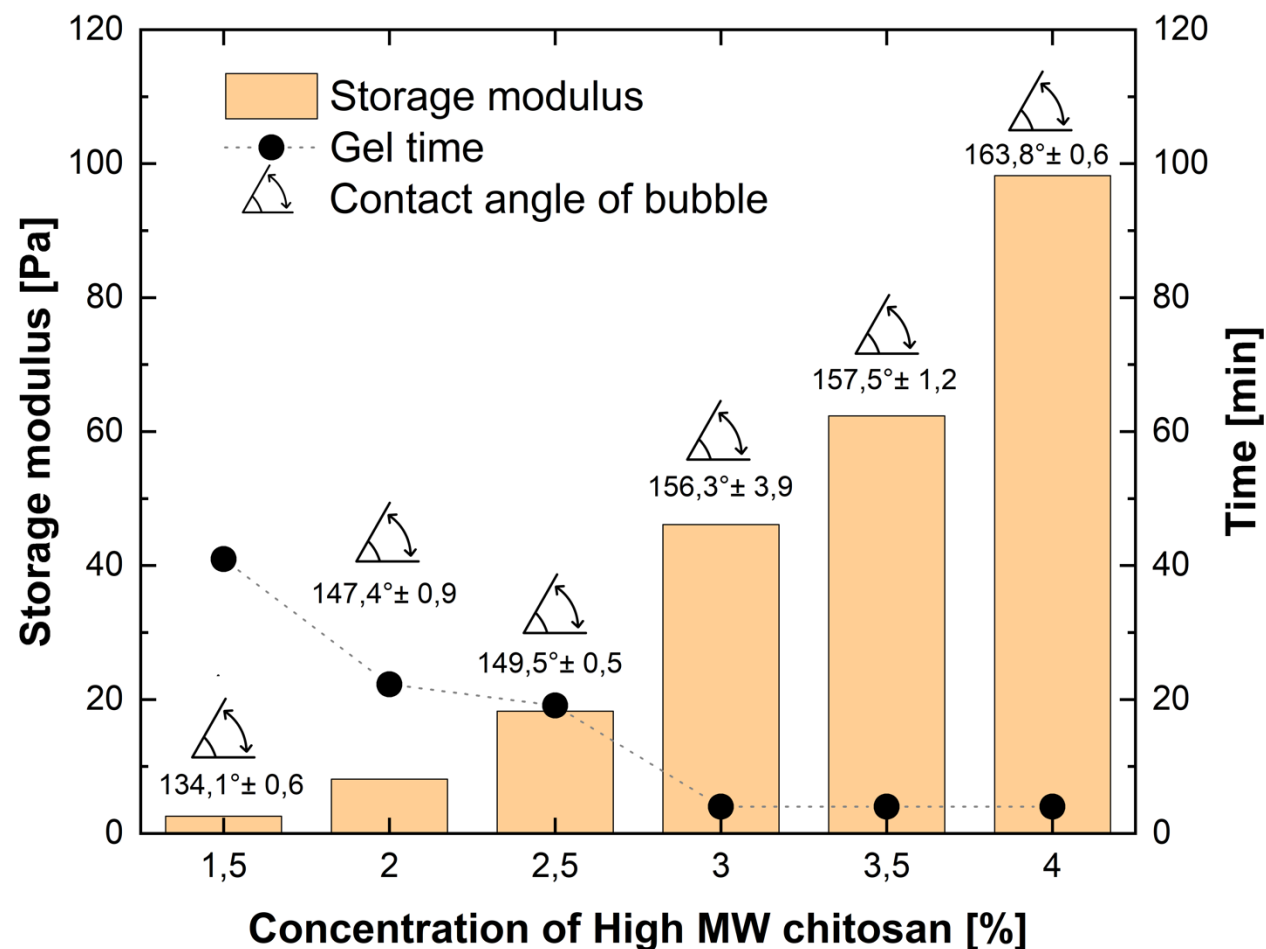
- Faster gelation
- Improved physical properties
- Higher surface aerophobicity (hydrophilicity)

Fully bio-based chitosan/dialdehyde starch hydrogels with tunable properties.

Excellent swelling stability in highly alkaline media (pH 12) over 7 days.

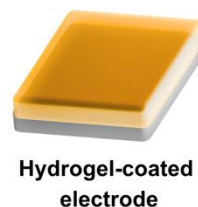
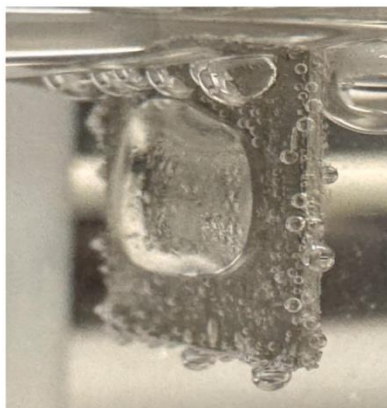
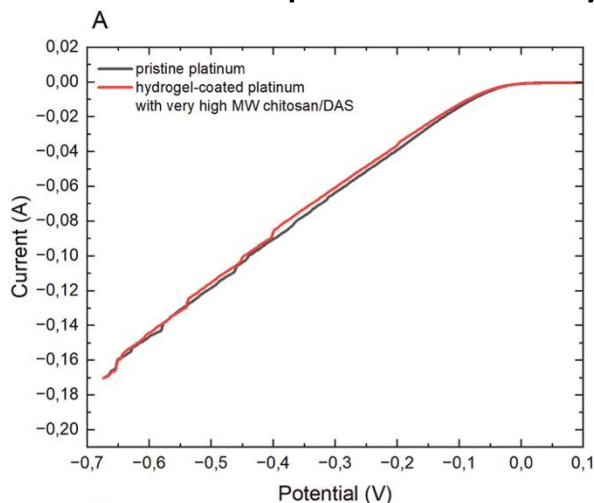
Superaerophobic hydrogels (bubble contact angle $\geq 170^\circ$).

Promising candidates for alkaline-resistant energy and environmental applications.

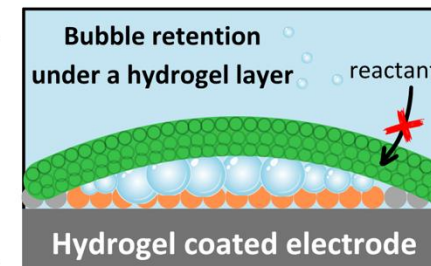
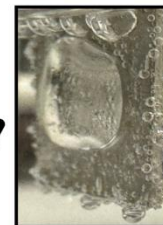


Electrochemical performance

Linear sweep voltammetry

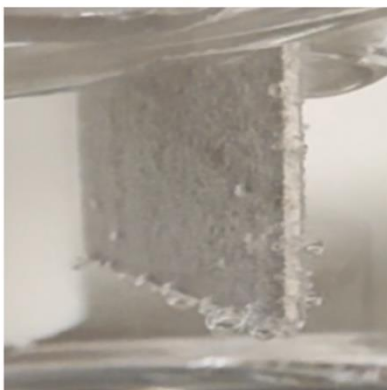
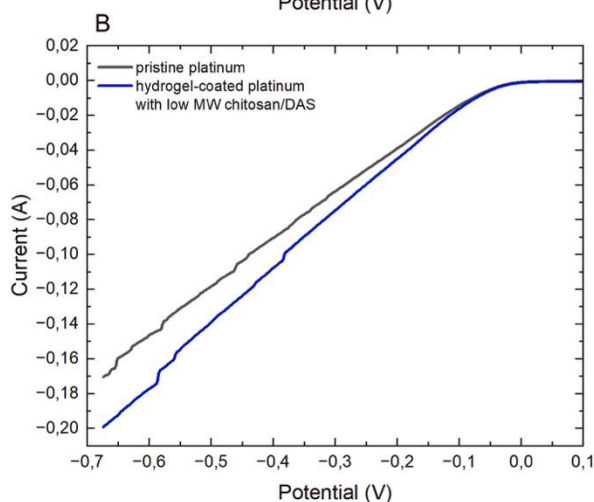


Thick layer
Slow RPM of spin-coating



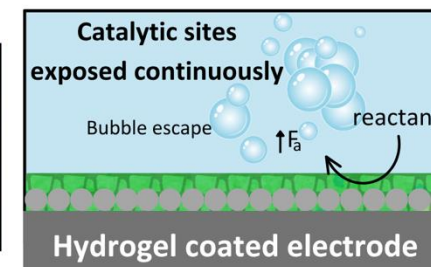
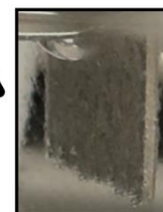
✗ Gas trapped under the layer of hydrogel

✗ Rupture of hydrogel membrane



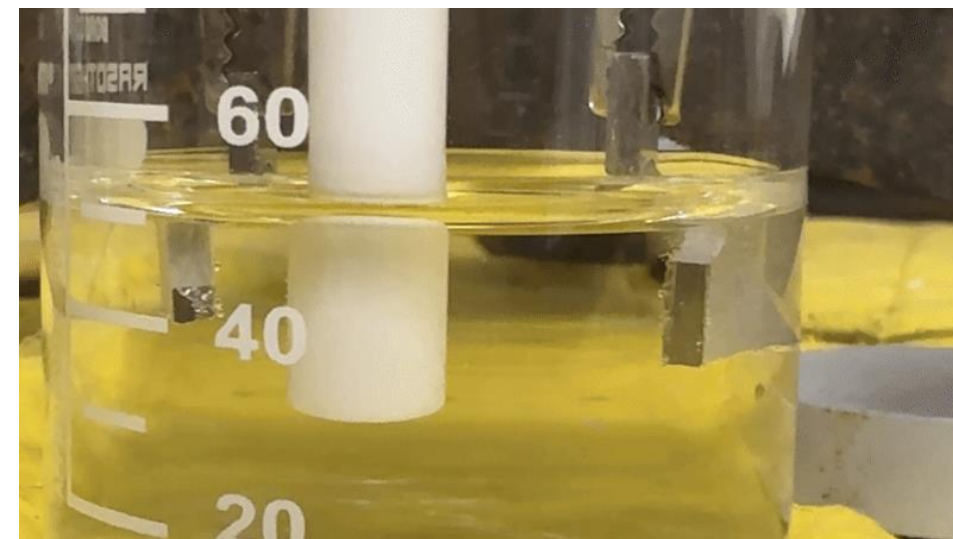
Notable performance increase in LSV, especially at higher overpotentials associated with hydrogen evolution.

Thin layer
Fast RPM of spin-coating



✓ Enhanced ion transport

✓ Lower concentration overpotential



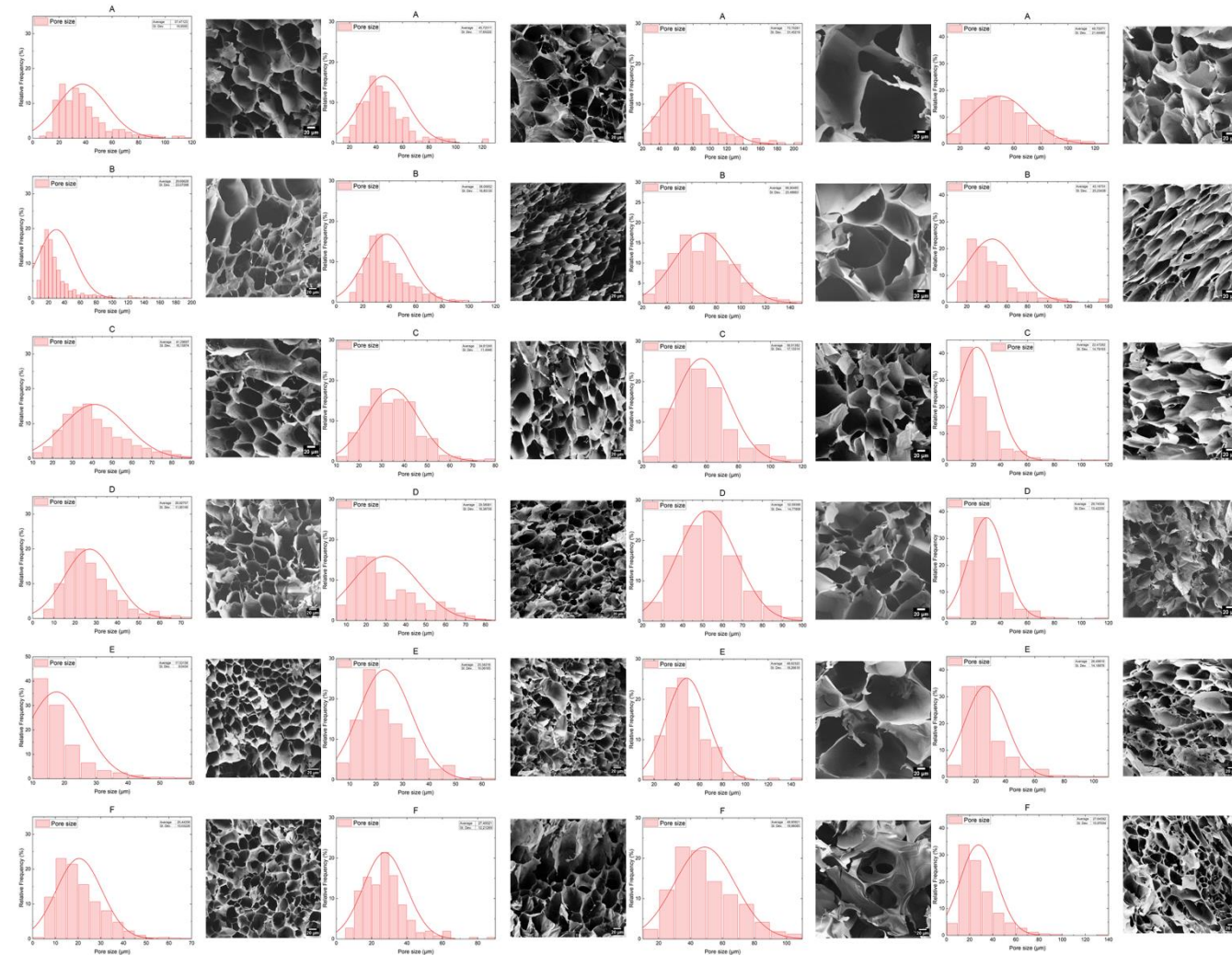
Conclusions

Hydrogels are highly customizable well defined chemical environments.

Shown for **chitosan/DE starch** – **excellent alkaline stability**, **superaerophobicity** ($\alpha \geq 165^\circ$).

Fibers to sustainable hydrogels to replace synthetic and PFAS-based ingredients, particularly for emerging applications of **solid-liquid-gas interfaces** in **harsh alkaline-resistant environments**:

- energy production and storage
- corrosion protective coatings
- environmental absorbents and sensors



Acknowledgement

This presentation is based upon work from **COST Action ENFiber, CA24111**, supported by COST (European Cooperation in Science and Technology), as well as the **Scientists4Future Slovenia** project, the MSCA Seal of Excellence HORIZON-MSCA-2021-COFUND (2023-2027, supported by Republic of Slovenia, Ministry of Higher Education, Science and Innovation); **DUBT Centre for Development, Demonstration and Training for Carbon-Free Technologies** project (2023-2026, supported by Republic of Slovenia, Ministry of Higher Education, Science and Innovation, and the European Union under the Just Transition Fund) and the **CarbNETs TRL3-6 programme** (2026-2029, supported by Republic of Slovenia, Ministry of Education, Science and Youth, and by the European Union under the Cohesion Policy Fund).

COST (European Cooperation in Science and Technology) is a funding agency for research and innovation networks. Our Actions help connect research initiatives across Europe and enable scientists to grow their ideas by sharing them with their peers. This boosts their research, career and innovation.



Center for Development,
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REPUBLIC OF SLOVENIA
MINISTRY OF HIGHER EDUCATION,
SCIENCE AND INNOVATION



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the European Union



CarbNETs



Slovenian Research and Innovation Agency

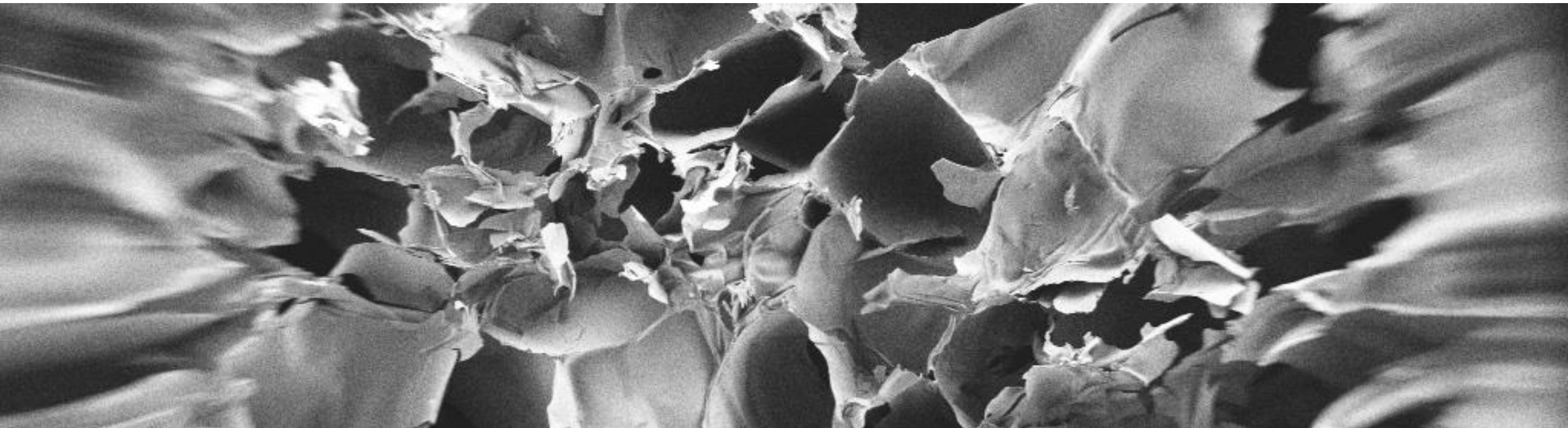


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Hydrogels for chemical and energy systems

Prof. Dr. Ilja Gasan Osojnik Črnivec
Head of Laboratory for H₂ and CO₂ Technologies
National Institute of Chemistry

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