New Applications of Crosslinked Cellulose Nanocrystal Aerogels:

Sorbents, Bone Implants and Energy Production & Storage Devices

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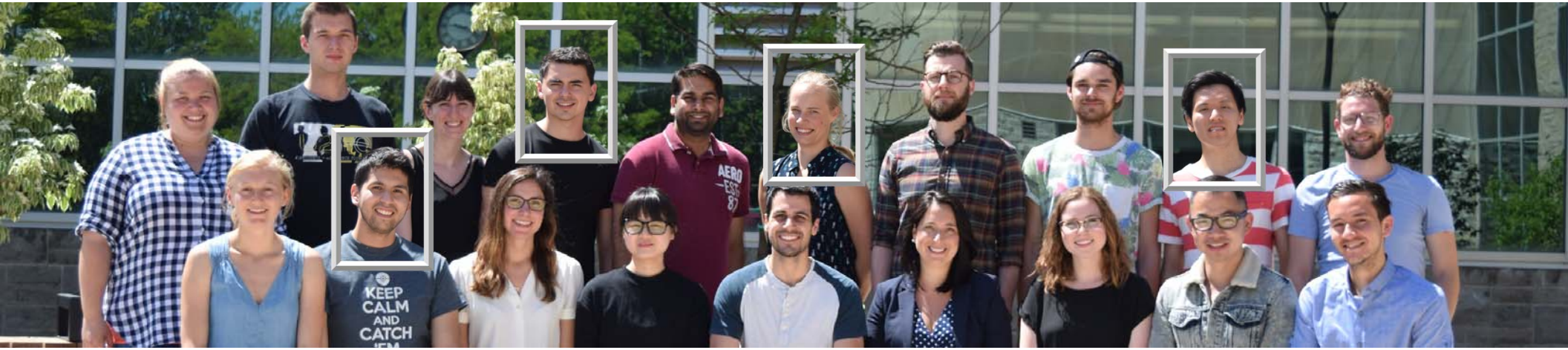
TAPPI

Outline

1. Covalently crosslinked CNC aerogels
2. New processing methods
3. Applications
   a) Bone scaffolds
   b) Dye sensitized solar cells
   c) Water splitting



Nanocellulose

Sustainable bio-based nanomaterial derived from wood pulp and other natural cellulose sources

Source: Wikipedia - Cladophora and Tunicate

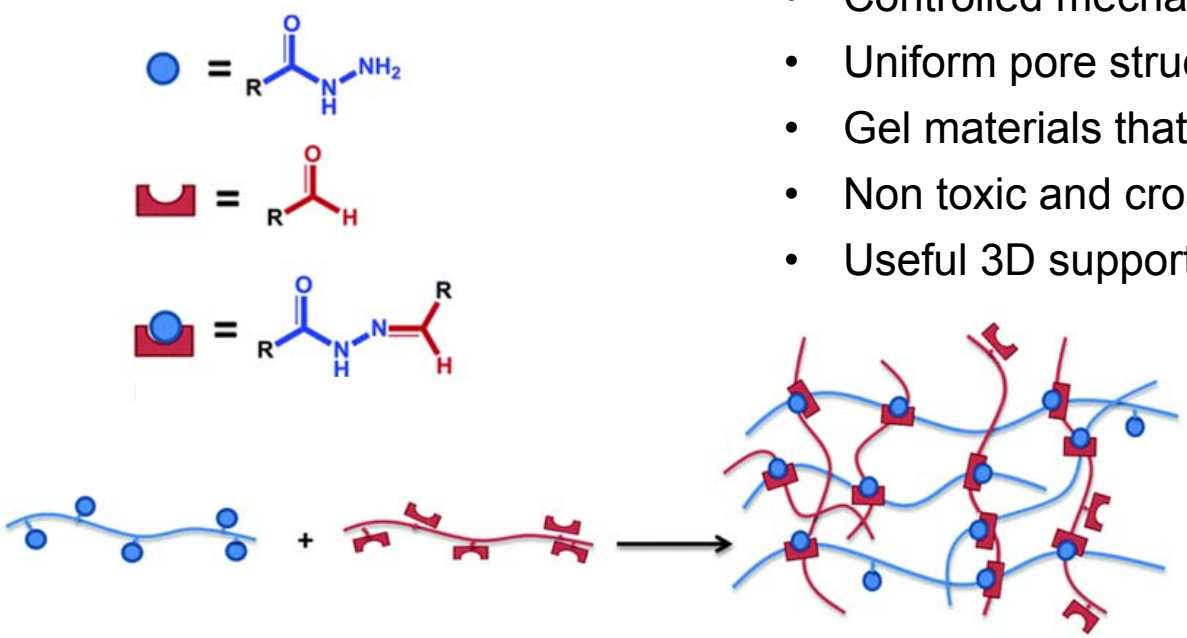
We break down cellulose into small crystals or fibres and add surface charge so that they form a stable colloidal suspension in water (extracted)

Crosslinked CNC Aerogels

Goal: Create an "entangled" and highly porous network of cellulose nanocrystals

Hypothesis: Chemical crosslinking will give

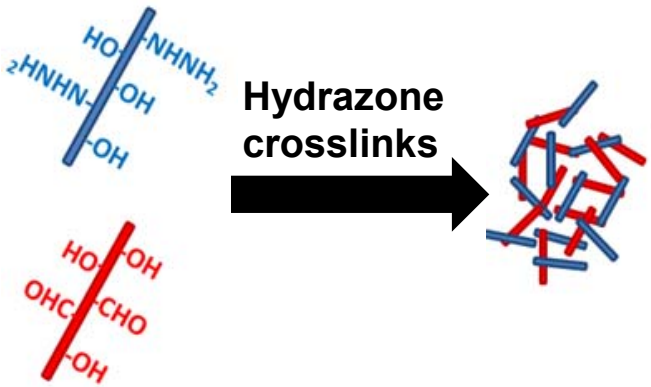
- Controlled mechanical properties
- Uniform pore structure
- Gel materials that do not re-disperse
- Non toxic and crosslinks degrade *in vivo*
- Useful 3D support materials



Hydrazone cross-linking (fast & initiator free)

Smeets, Bakaic, Hoare, *Chemical Communications* **2014**, *50*, 3306

Crosslinked CNC Aerogels



Hydrazone crosslinks

2. Freeze
3. EtOH exchange
4. Critical point dry

1. Vortex functionalized CNCs (0.5-2 wt.%)

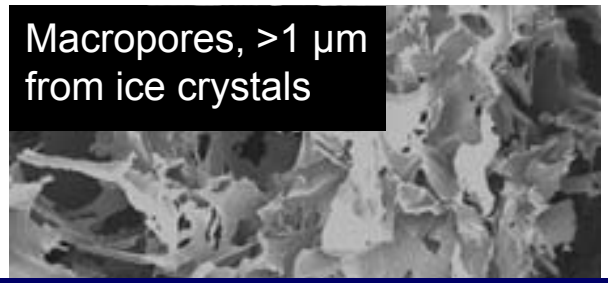
Density: 5.6 – 21.7 mg/cm^3
Porosity: 99.6 – 98.8%
Surface area: 200 m^2/g

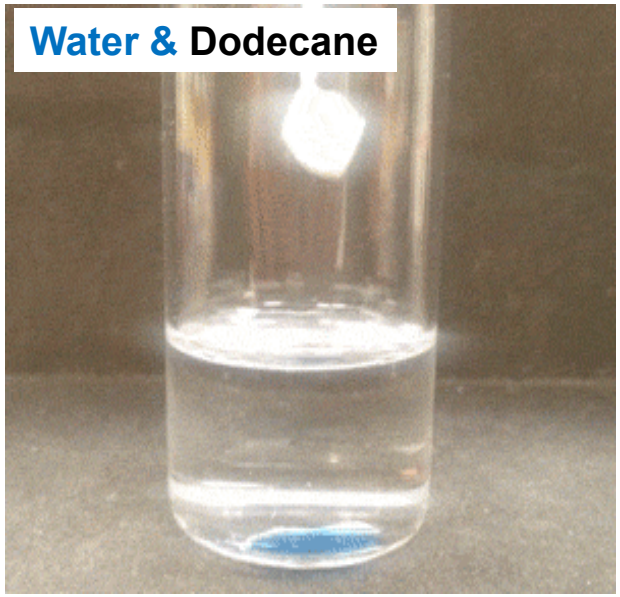
Rigidity of CNC and crosslinks is key to aerogel functionality and properties

Yang and Cranston, *Chemistry of Materials* **2014**, *26*, 6016

Bimodal Pore Size Distribution

- Shape-recovery with no disintegration in liquids
- Superabsorbent, flexible, lightweight





Applications: Energy storage devices, water purification, insulation, catalysis supports, templates, ad/absorbents, dehydrating agent, tissue engineering, drug delivery, solar energy devices…

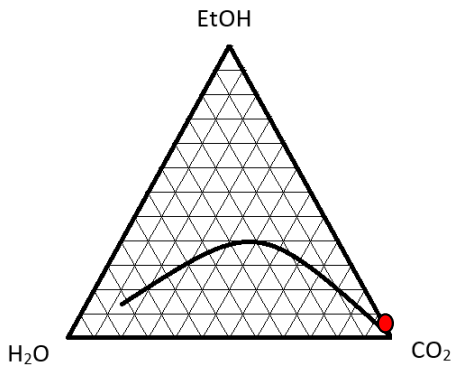
Yang, Shi, Zhitomirsky, Cranston. *Advanced Materials* **2015**, *27*, 6104
Yang, Shi, Cranston and Zhitomirsky, *Adv. Funct. Mat.* **2016**, *26*, 6437
Zhu, Yang, Zhu and Cranston, *Advanced Materials* **2016**, *28*, 7652

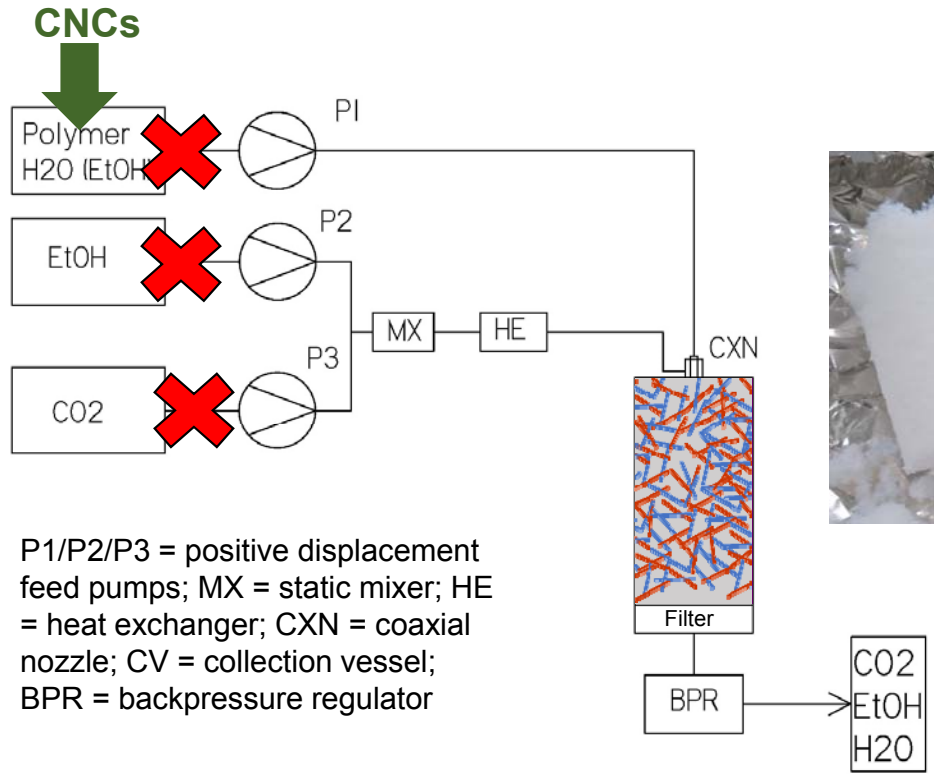
New Processing Methods

Scaled-Up Aerogel Production

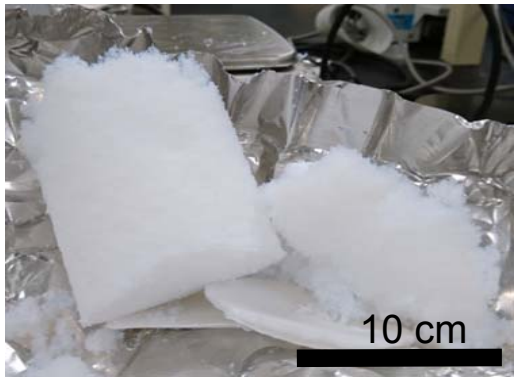
- Pressurized gas expansion drying (PGX) – supercritical CO_2

Temp = 40 ˚C
Pressure = 100 Bars





P1/P2/P3 = positive displacement feed pumps; MX = static mixer; HE = heat exchanger; CXN = coaxial nozzle; CV = collection vessel; BPR = backpressure regulator



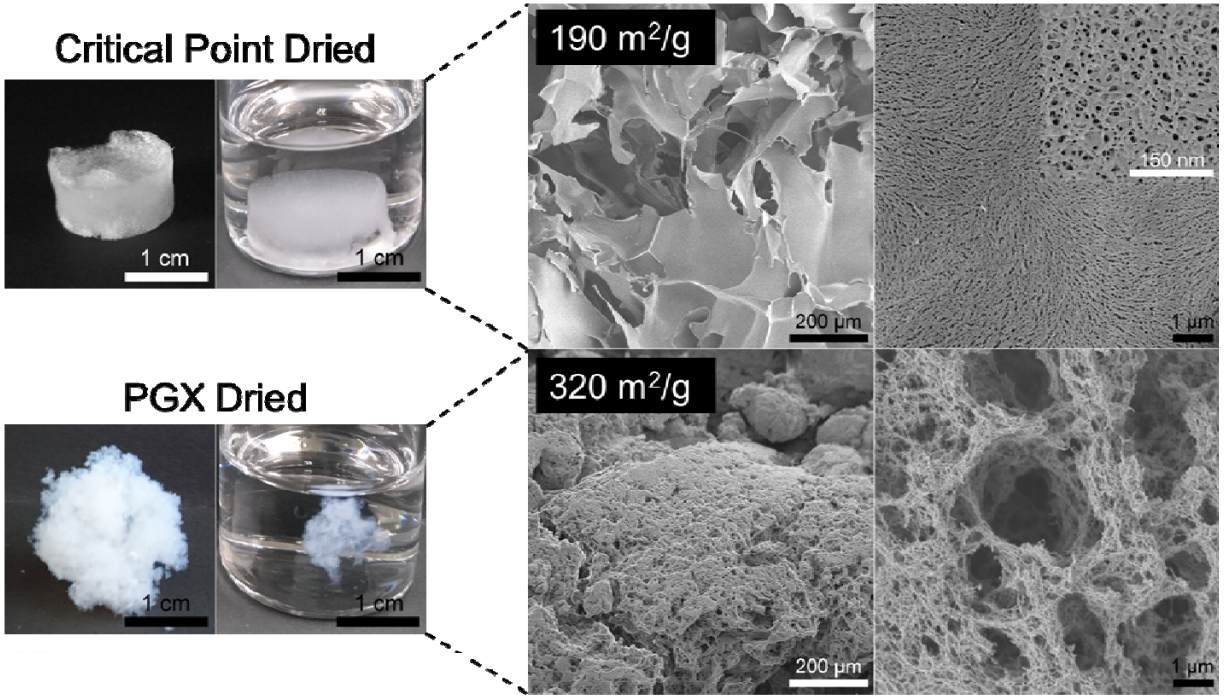
CEAPRO Nature Enhancing Life®

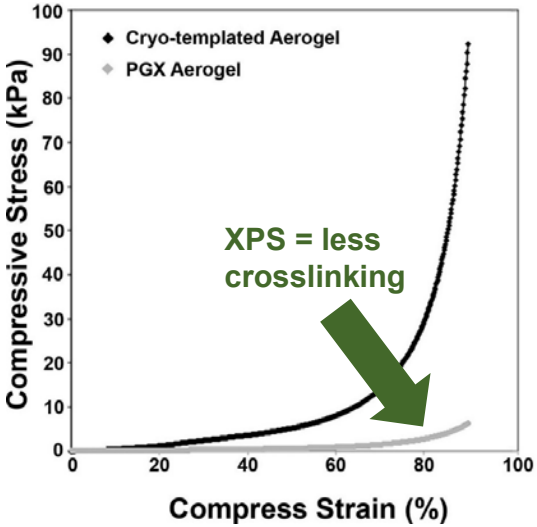
Seifried, Temelli. *U.S Patent: US9249266 B2* 2011, 1-62.

Osorio et al., *J. Mater. Sci.* **2018**, *52*, 9842

Scaled-Up Aerogel Production

- PGX dried aerogels have different morphology and mechanics



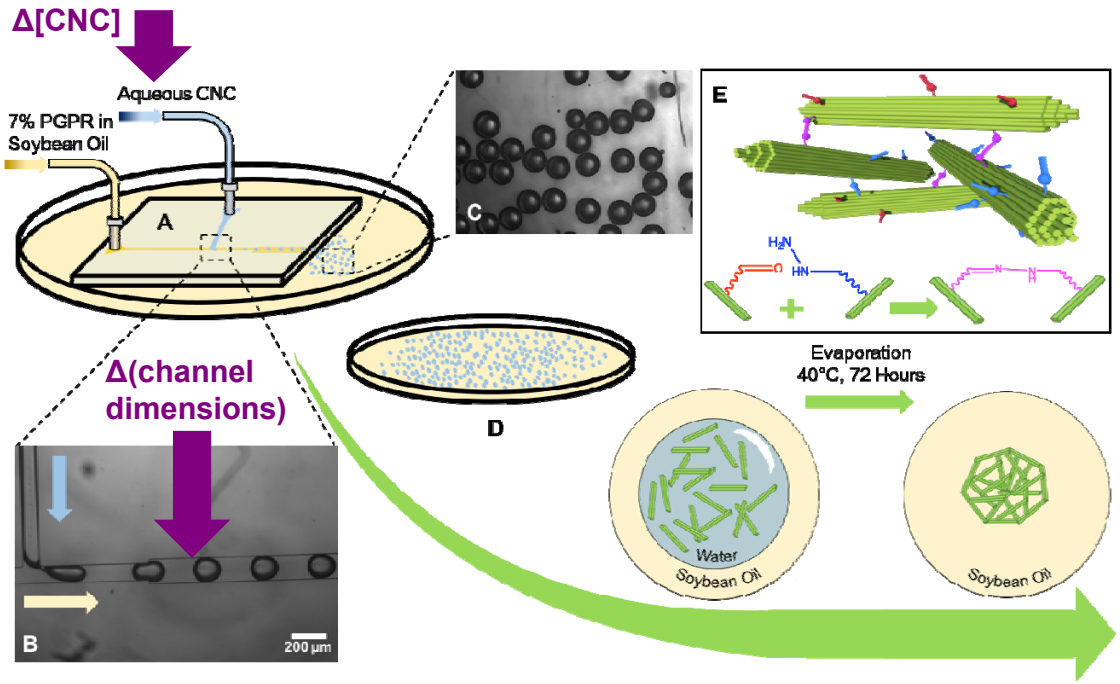


- **Process method**
- **Process parameters**
- **Crosslink density**

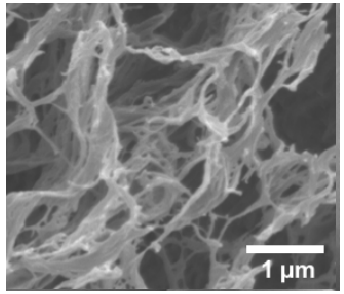
Osorio et al., *J. Mater. Sci.* **2018**, *52*, 9842

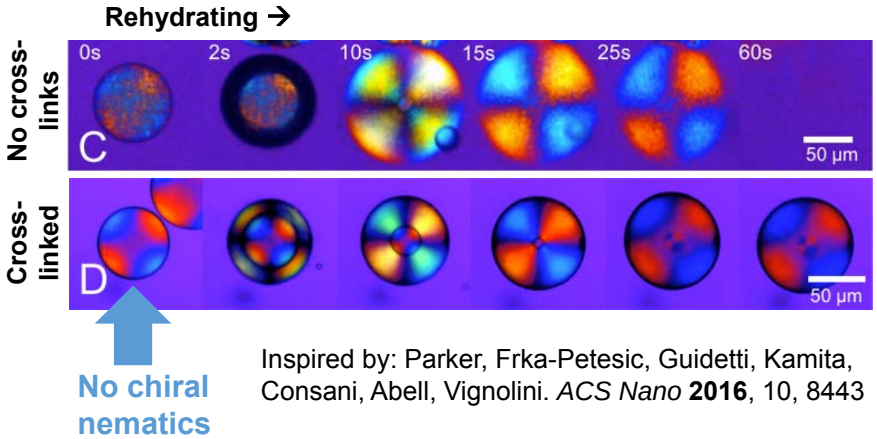
Microfluidic Aerogel Bead Processing

- Templated uniform CNC porous spherical microbeads (30-110 μm)
- Tunable absorption, binding, swelling and mechanics



Robust micromaterial with nanoparticle specific surface area



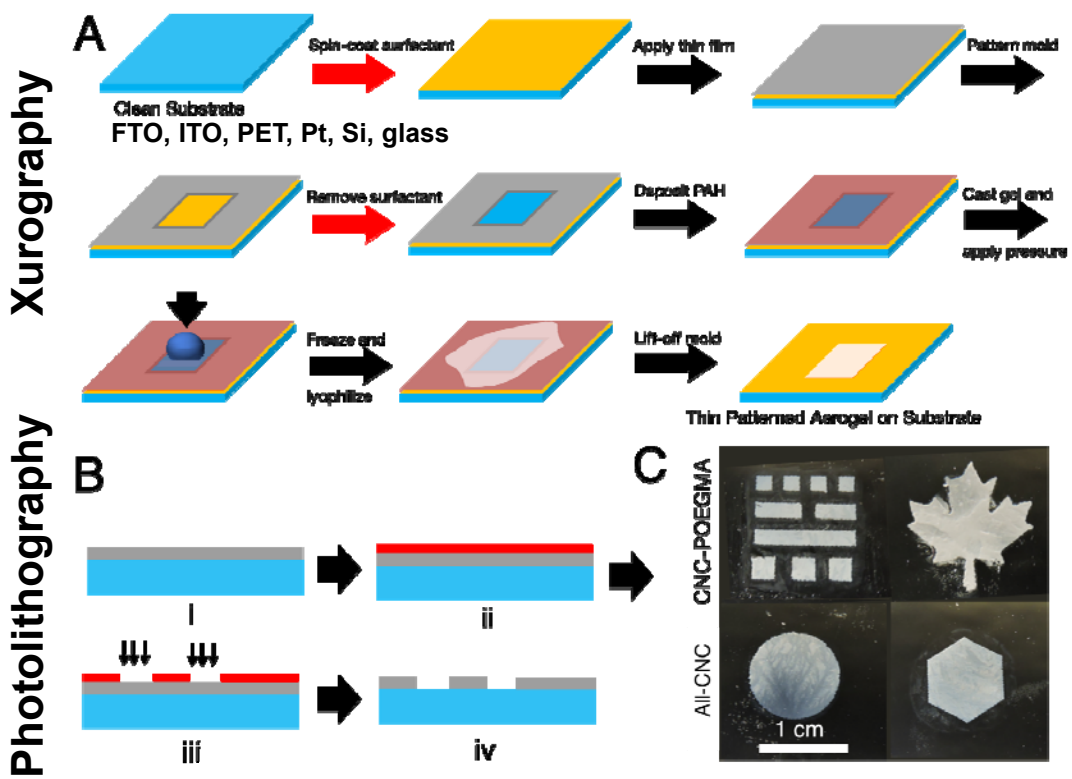


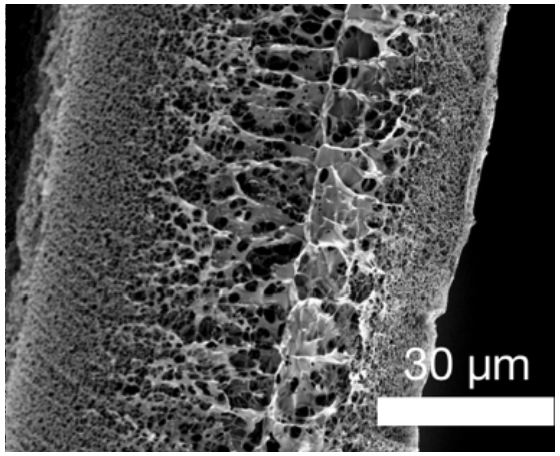
Inspired by: Parker, Frka-Petesic, Guidetti, Kamita, Consani, Abell, Vignolini. *ACS Nano* **2016**, 10, 8443

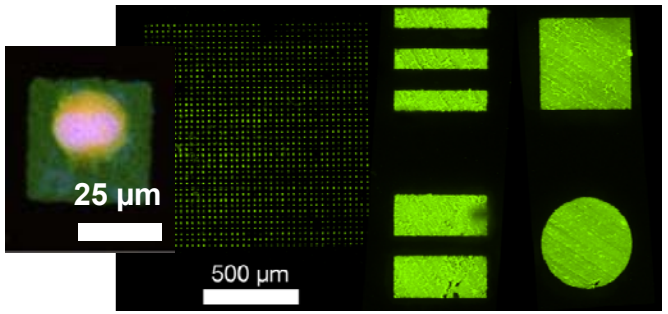
Levin, Saem, Osorio, Cerf, Cranston, Moran-Mirabal. *Chemistry of Materials* **2018**, 30, 8040

Aerogel Patterning

- Pressure-aided freeze casting procedure (Parylene molds: 3-85 µm)







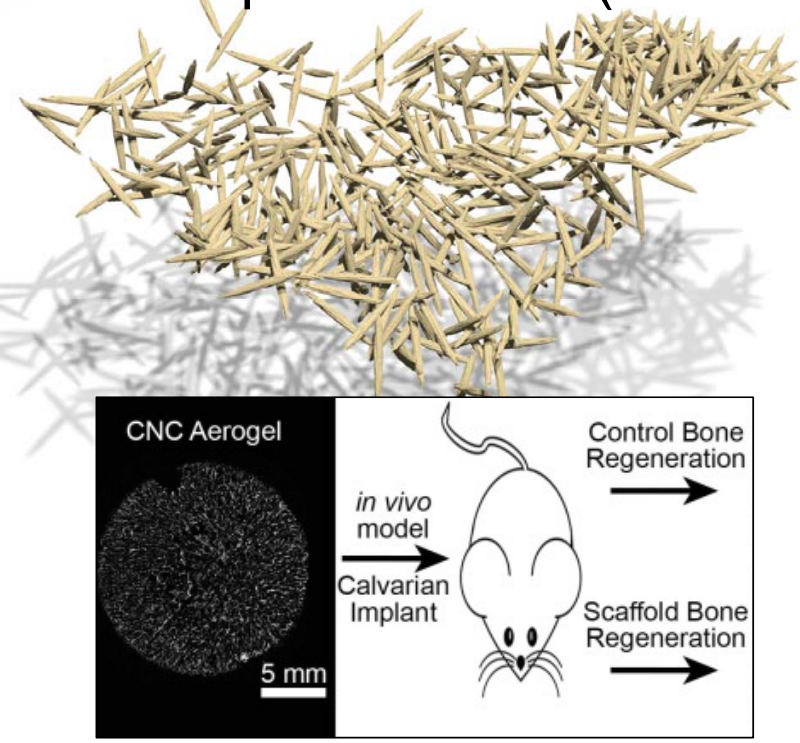
Control porosity, thickness, mechanics for cells

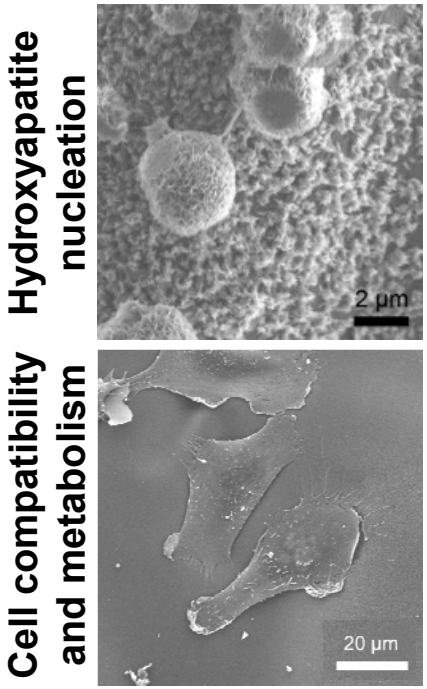
Or, Saem, Esteve, Osorio, De France, Vapaavuori, Hoare, Cerf, Cranston, Moran-Mirabal, *in revision*

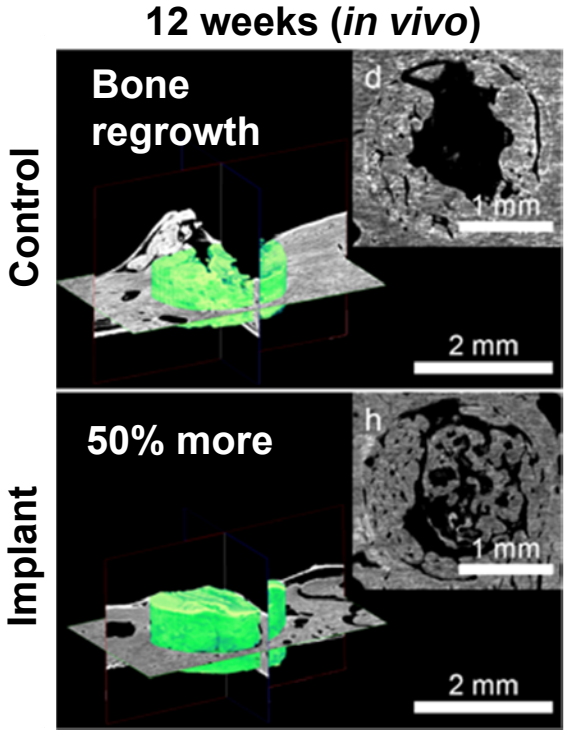
Proof-of-Principle Applications

Bone Scaffolds

- CNC aerogel flexibility and porosity promotes bone healing in complex cavities (non load-bearing) → bioresorbable



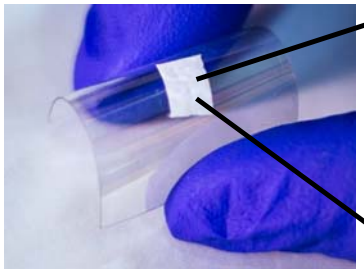




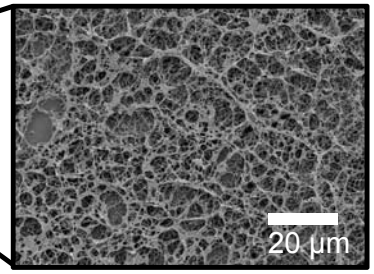
Osorio…Cranston, Grandfield. *Acta Biomaterialia* **2019**, *87*, 152

Quasi-Solid Gel Electrolytes - DSSC

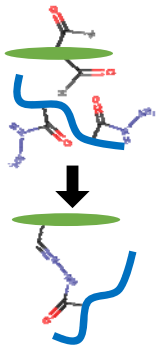
- Crosslinked CNCs and POEGMA polymer = **electrolyte absorbers** in dye-sensitized solar cells (no leakage, evaporation, corrosion)



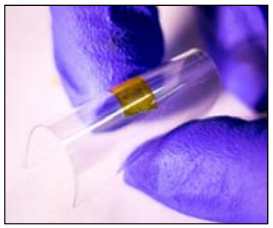
Flexible DSSC Electrode

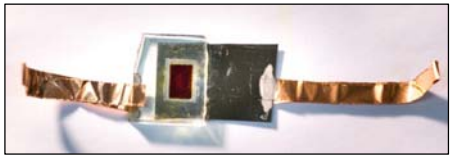


Crosslinked CNC Aerogel

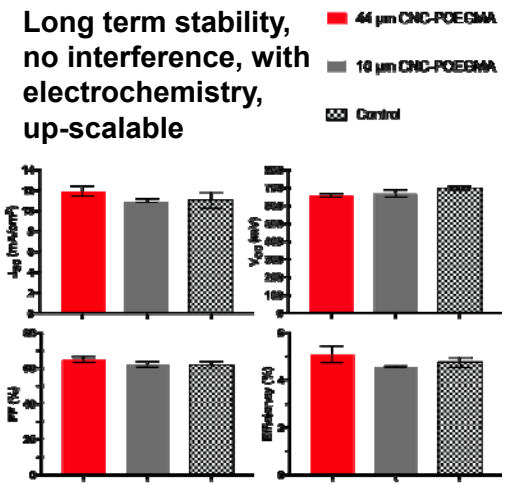


Add Electrolyte
I^-/I_3^- electrolyte in ACN or 3-methoxy propionitrile



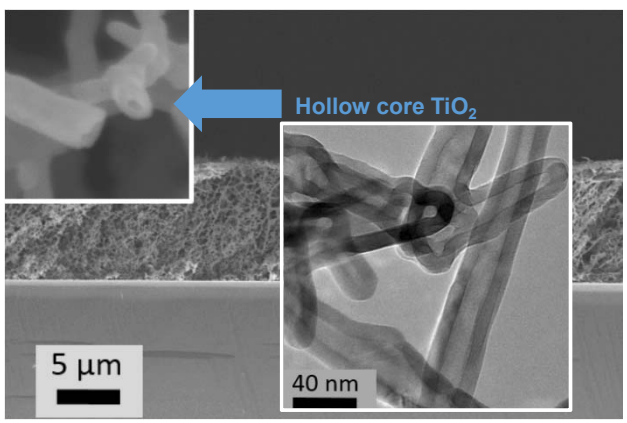


Long term stability, no interference, with electrochemistry, up-scalable



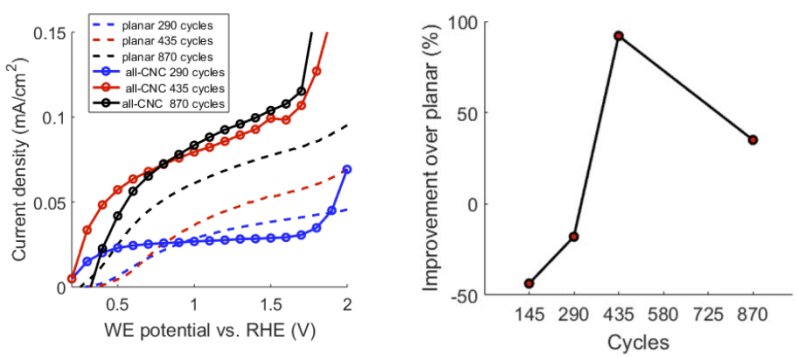
Template for TiO_2 Solar Water Splitting

- Mesoporous 3D nanostructure + atomic layer deposition TiO_2 (200°C)
- Sunlight decomposes H_2O@TiO_2 interface → energy as H_2(g)



ALD precursors penetrate the CNC network uniformly (145 cycles = 7 nm), calcined at 500°C

TiO_2 aerogel = photoanode for PEC cell



<7 nm ALD-TiO_2 coating collapsed
15 nm thick = 100% improved efficiency

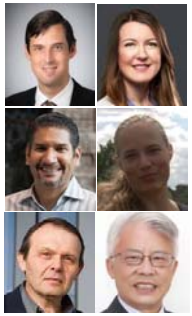
Hiltunen, Or, Lahtonen, Ali-Löytty, Tkachenko, Valden, Sarlin, Cranston, Moran-Mirabal, Vapaavuori, *submitted*

Conclusions

1. The hydrazone **crosslinking technology** presents a new way to design scalable CNC networked structures (aerogels)
2. **Universal substrate**
3. For tissue engineering - versatile & compatible
4. For energy applications - electrolyte absorption/function and high specific surface area templates

"Greener" next generation nano-devices, templates and scaffolds!

Collaborators:



- *Crosslinking:* Prof. Todd Hoare (McMaster)
- *Bone implants:* Prof. Kathryn Grandfield (McMaster)
- *Microfluidics, DSSC, water-splitting*: Prof. Jose Moran-Mirabal (McMaster) and Prof. Jaana Vapaavuori (Aalto)
- *Supercapacitors*: Prof. Zhitomirsky (McMaster)
- *Water purification*: Prof. Shiping Zhu (McMaster)

NSERC CRSNG

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Thank you

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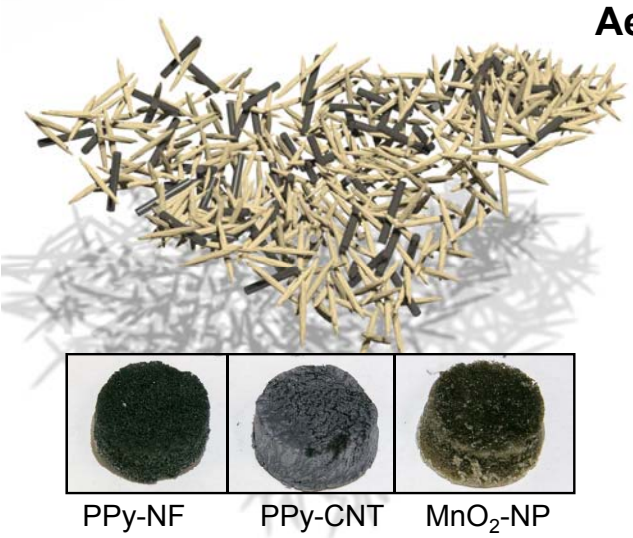
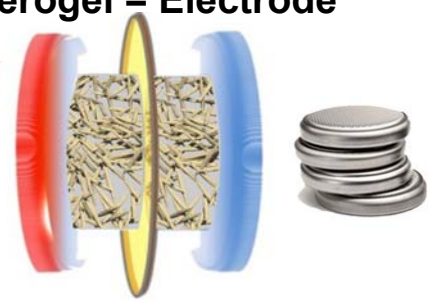
Supercapacitor Devices

- Capacitive nanoparticles trapped in CNC aerogels

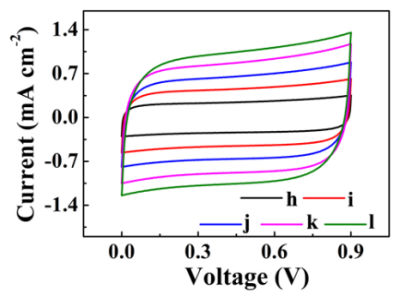


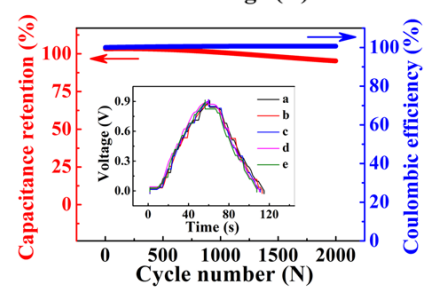
Aerogel = Electrode



- **Good capacitance**
- **Fast charge/discharge**
- **Good rate capability**
- **Cycle stability**
- **High efficiency**

4 mF/cm² → 2 F/cm²

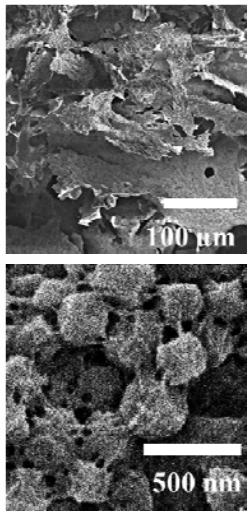




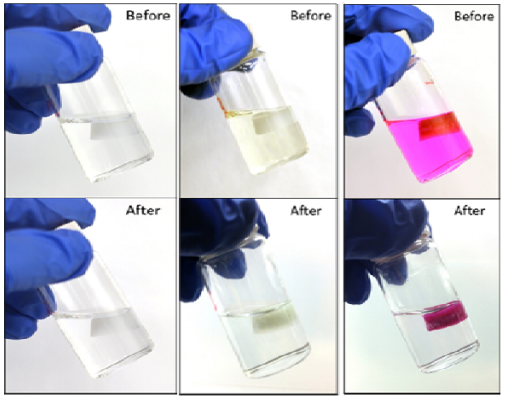
Yang, Shi, Zhitomirsky, Cranston. *Advanced Materials* **2015**, *27*, 6104
Yang, Shi, Cranston and Zhitomirsky, *Adv. Funct. Mat.* **2016**, *26*, 6437

Water Purification Devices

- Metal organic frameworks trapped in CNC aerogels



Re-usable water purification sponges

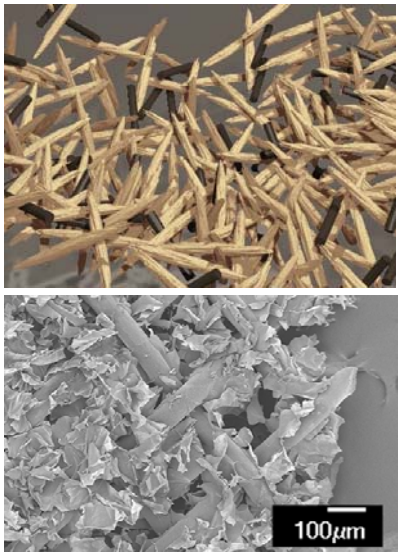
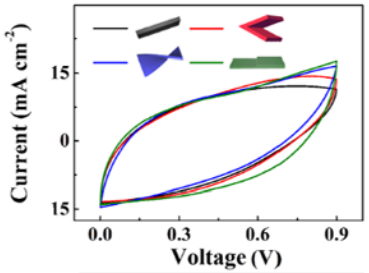
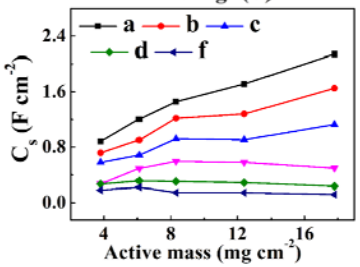


ZIF-8 *Benzotriazole* | **UiO-66** *Cr(IV)* | **MIL-100(Fe)** *Rhodamine B*

Zhu, Yang, Zhu and Cranston, *Advanced Materials* **2016**, *28*, 7652

Better Supercapacitor Devices!

- Backfilled CNC-CNT aerogels with polypyrrole → 2 F/cm^2



Aerogel = Electrode + Current Collector