

Nanocellulose templated polymer brushes for the guided formation of metallic hybrids



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**THE UNIVERSITY
OF QUEENSLAND**
AUSTRALIA





- 1 Prevent**
REDUCE,
BORROW/HIRE/SHARE,
USE E-PRODUCTS
LONGER, SHOP
SMART
- 2 Reuse**
REUSE, REHOME,
TRADE, BUY, SELL,
DONATE, REPAIR
- 3 Recycle**
RECYCLE AT A
RECYCLING DROP-
OFF POINT OR
COLLECTION
SERVICE

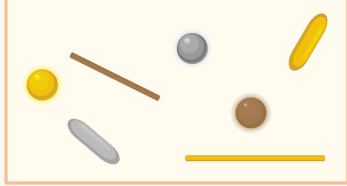
- The waste production increased by **60 %** a year within the last decade.
- The estimated generation of e-waste a year is expected to reach **75 million metric tons** by 2030
- Only 17% is getting recycled

Mettalic nanoparticle (MNP)-based hydrogels

Conductive material

Metallic nanoparticles

Gold, Silver and Copper



Binder

Surfactants

- Glycerol
- CTAB
- Acids
 - Oxalic acid
 - Adipic acid

Polymers

- PS
- PEG
- PVA
- Epoxy
- Nanocellulose

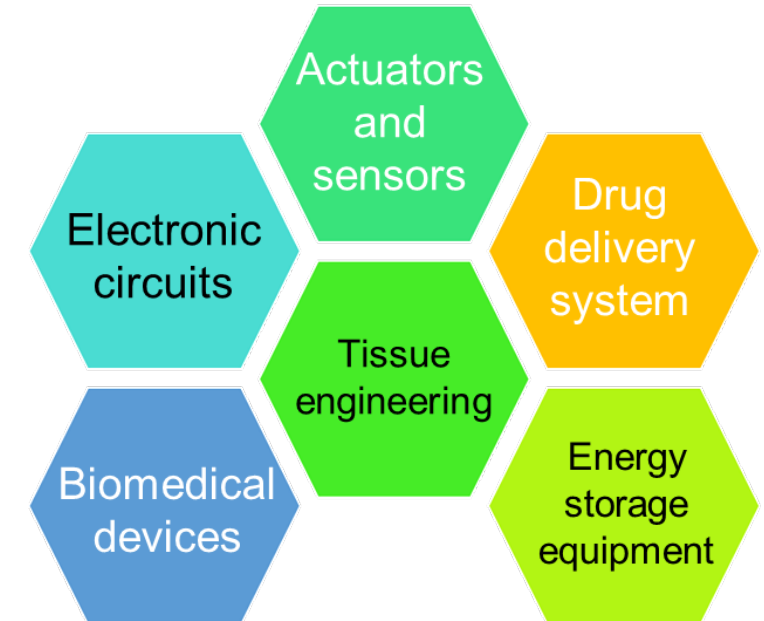
Formulation criteria

- Conductivity
 - Type of metal
 - Particle size
 - Concentration
- Hydrogel
 - Crosslinking
 - Concentration
 - Viscosity
 - Viscoelasticity
 - Surface tension
- Fabrication method

Hydrogel systems

PVA
PAA
PNIPAM
PVP
PEG / PEO

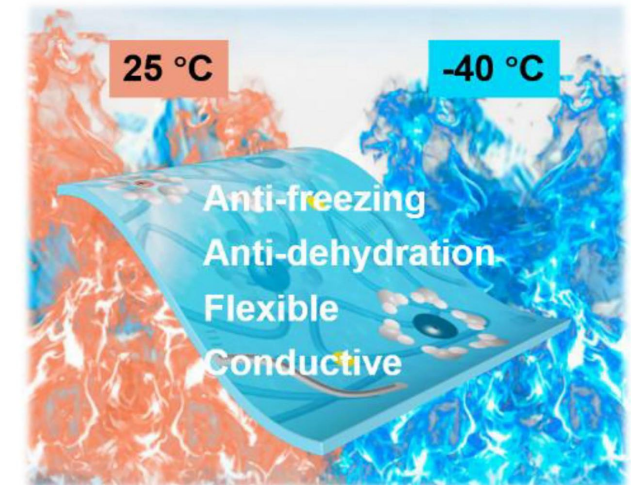
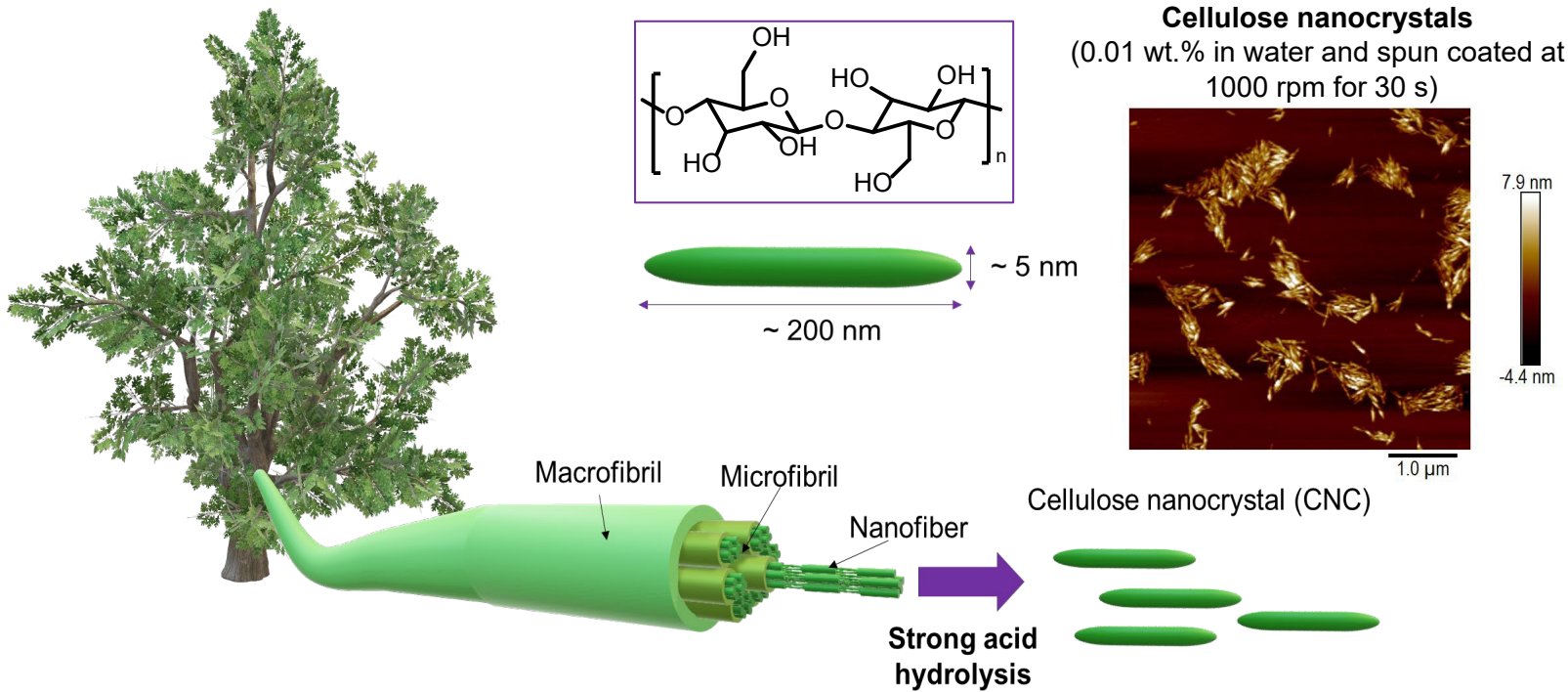
Chitosan
Gelatin
HA



Current limitations:

- Lack of a reliable method for the production of well-oriented MNPs in hydrogels
- High mechanical properties and low electrical resistance are often mutually exclusive

Nanocellulose (NC)



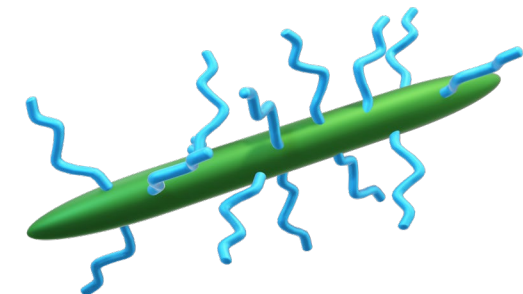
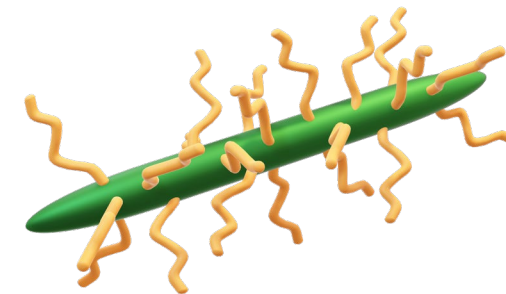
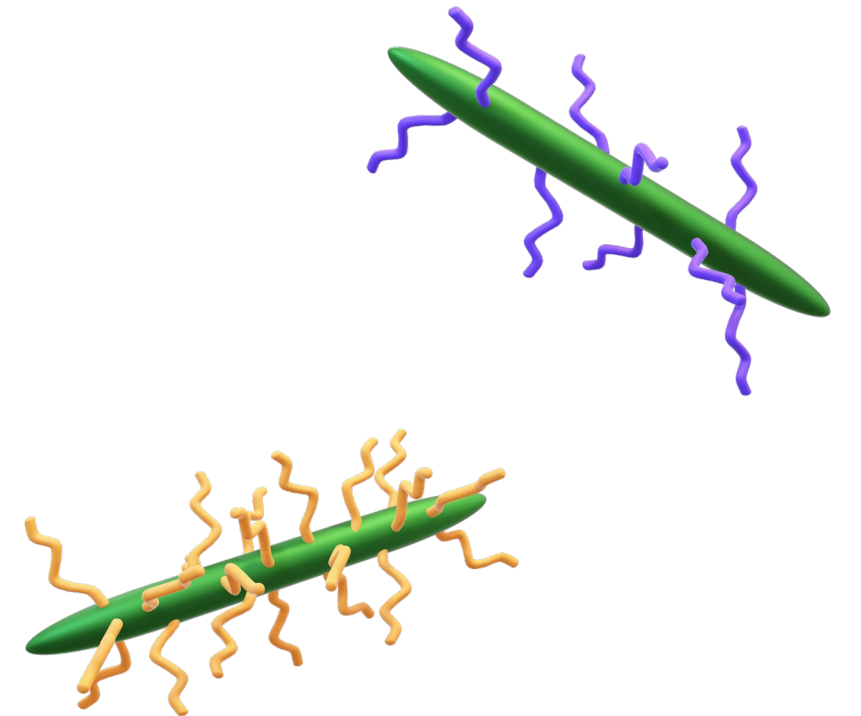
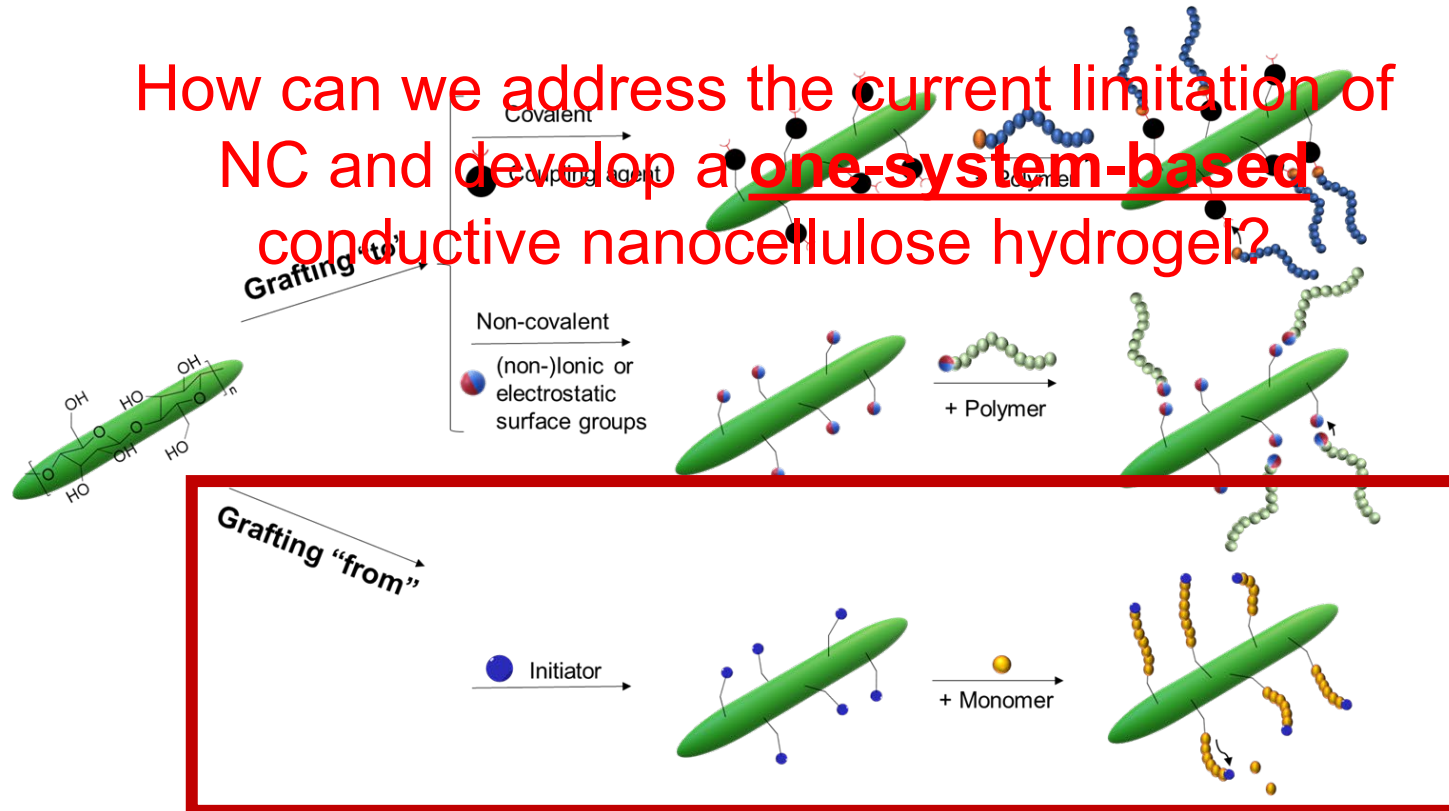
Ge et. al, *Chemical Engineering Journal* 2021



Zheng et. al, *Carbohydrate Polymer* 2020

- Are used as a stabilizing agent or template for in situ synthesis of metals
- Due to the abundant hydroxyl groups on the surface of NC, the NPs have a significant tendency for agglomeration

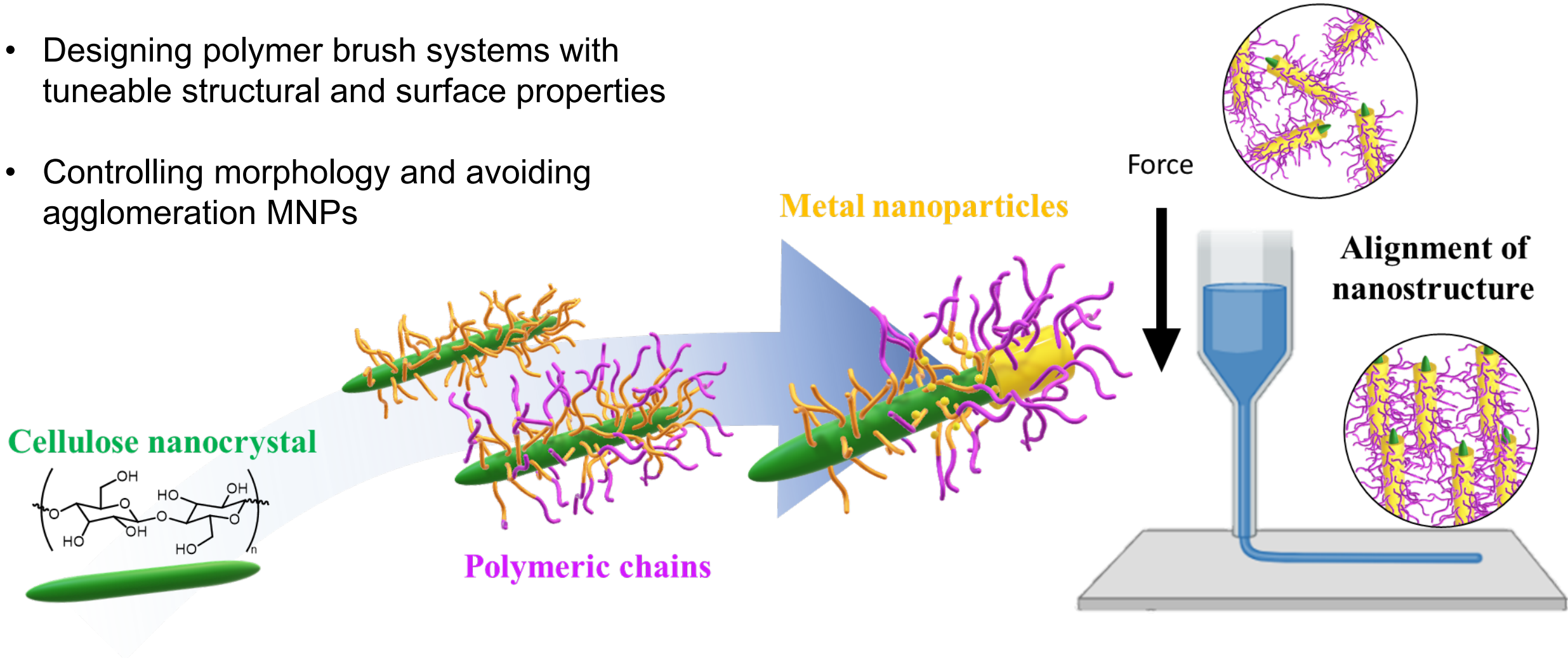
How can we address the current limitation of NC and develop a one-system-based conductive nanocellulose hydrogel?



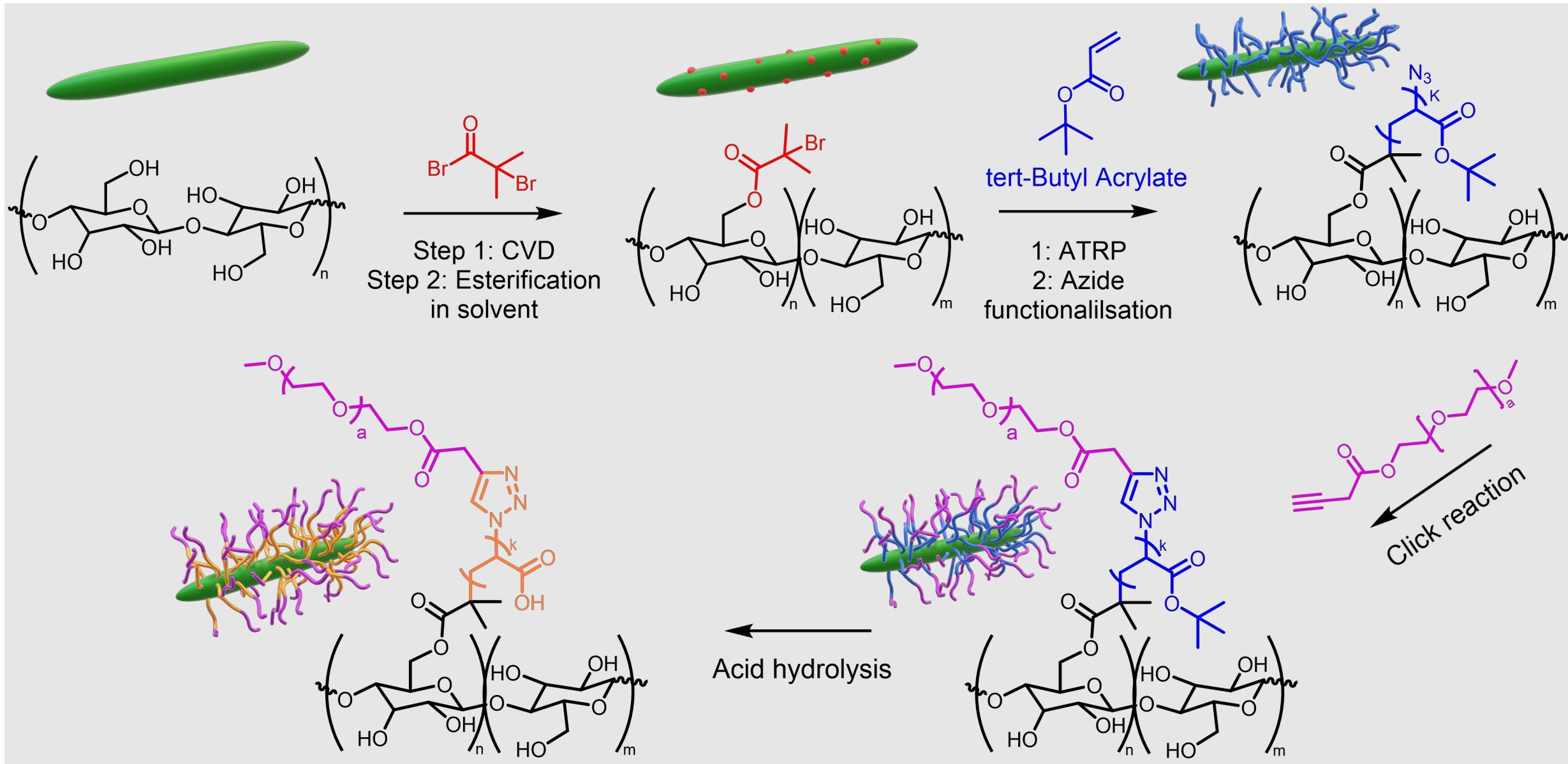
- Improving the dispersity of NC in non-polar solvents and hydrophobic polymer matrices
- Providing stimuli-responsiveness, template or carrier ability.

Nanocellulose-based polymer brush system as a **template** for the synthesis of metal NP.

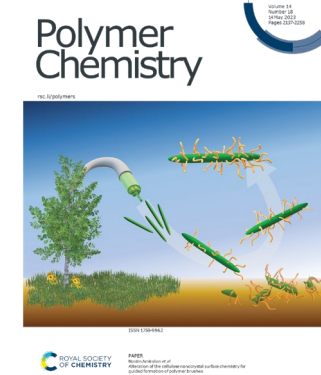
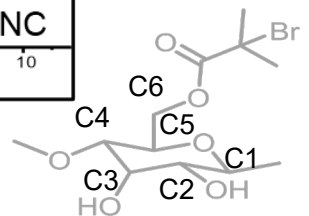
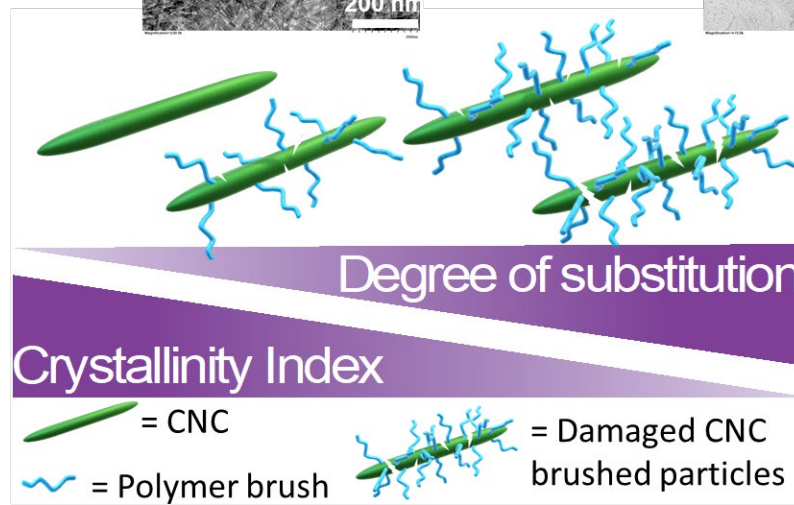
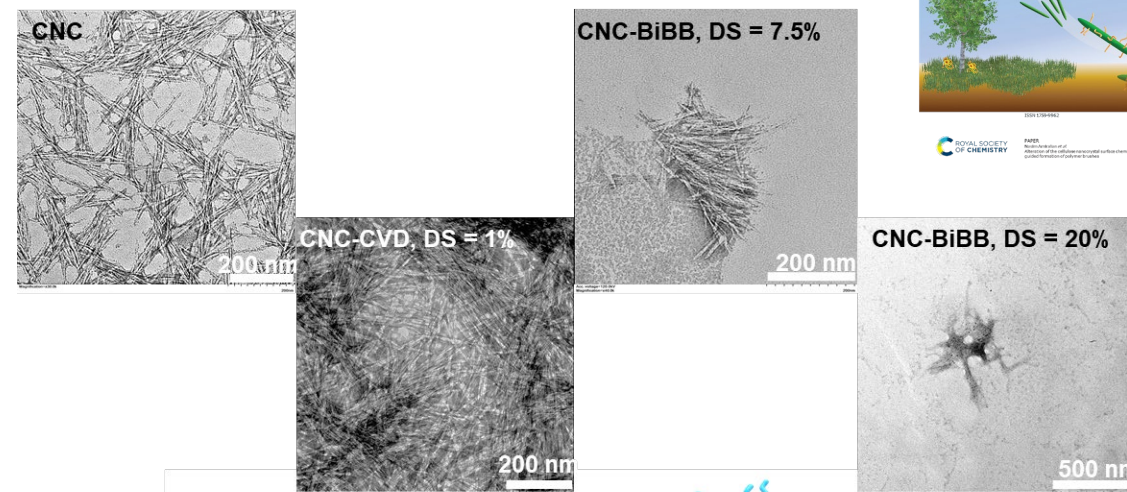
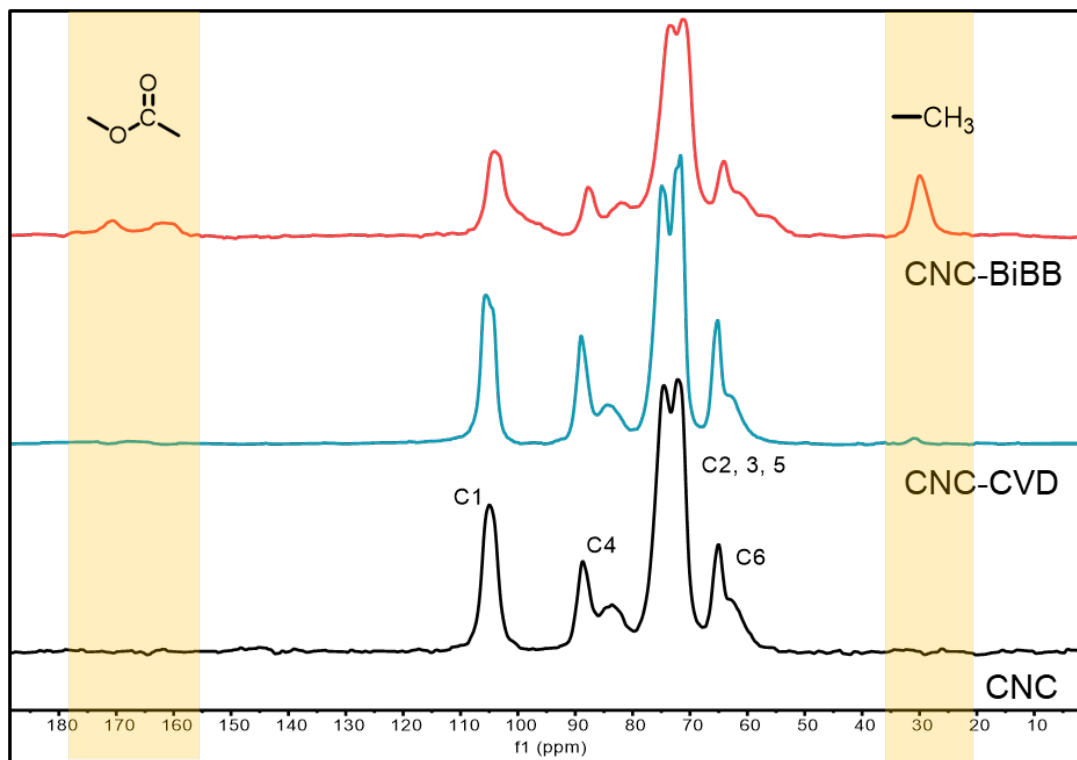
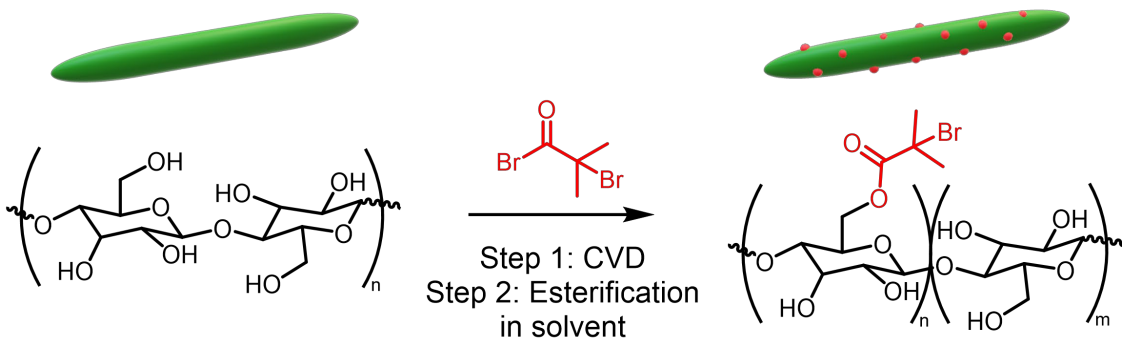
- Designing polymer brush systems with tuneable structural and surface properties
- Controlling morphology and avoiding agglomeration MNPs



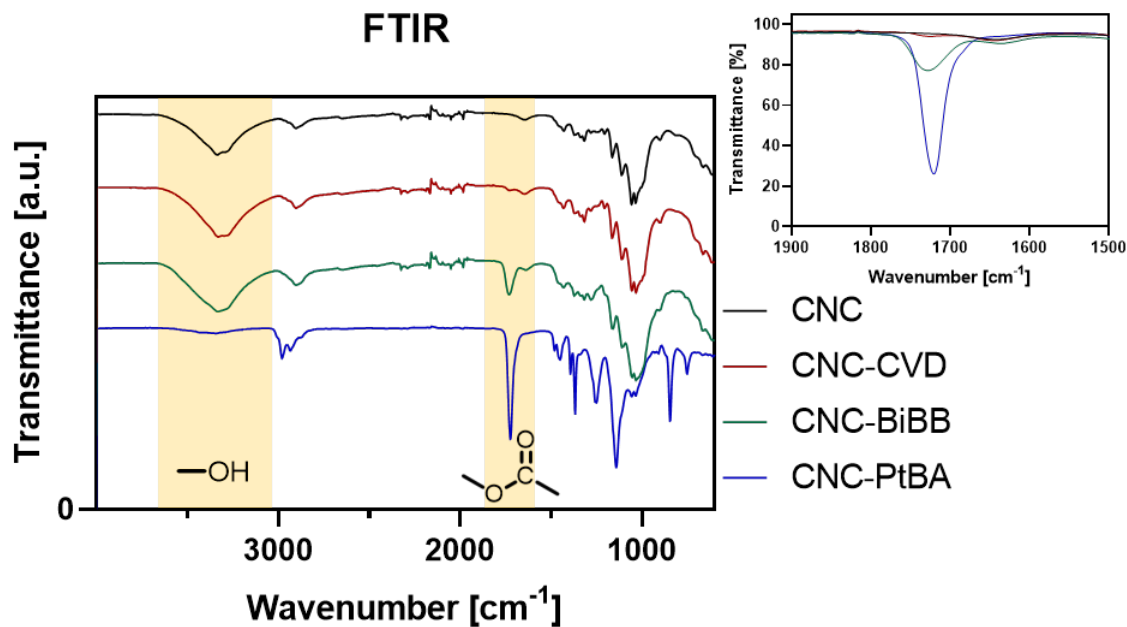
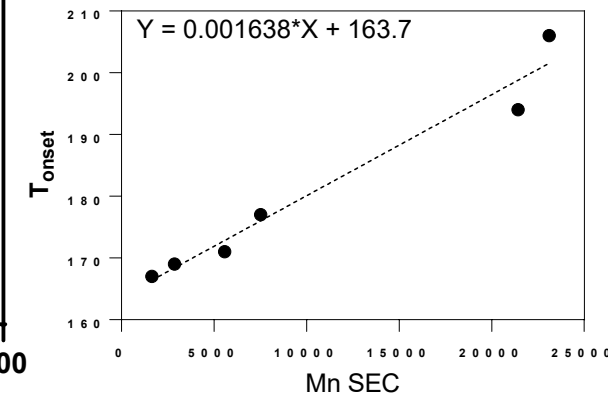
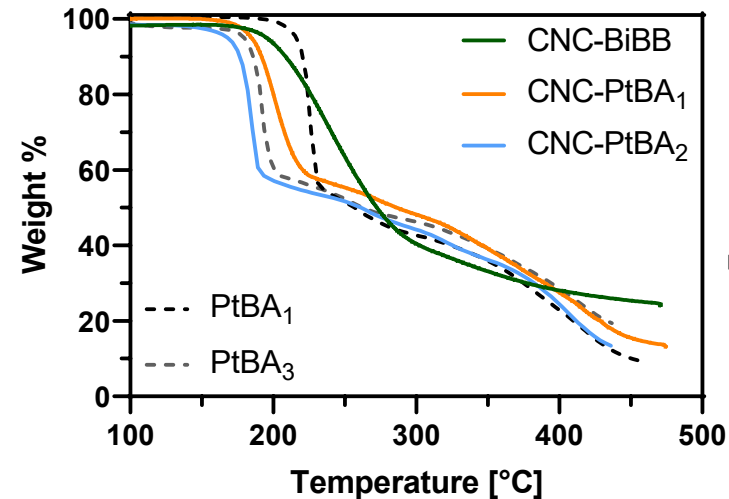
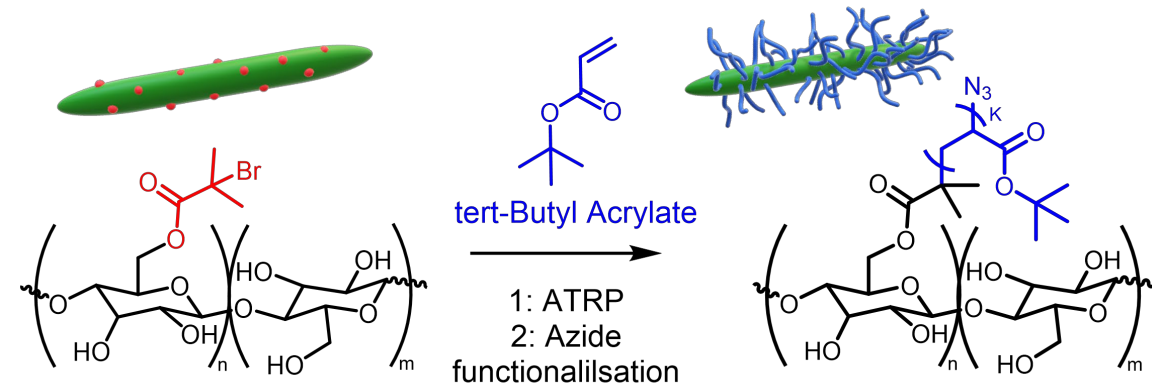
Synthesis of CNC-polymer brush systems



Esterification of CNC with BiBB, an ATRP initiator



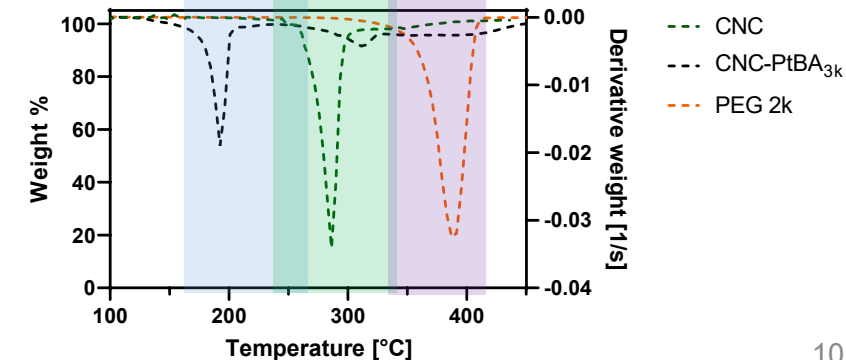
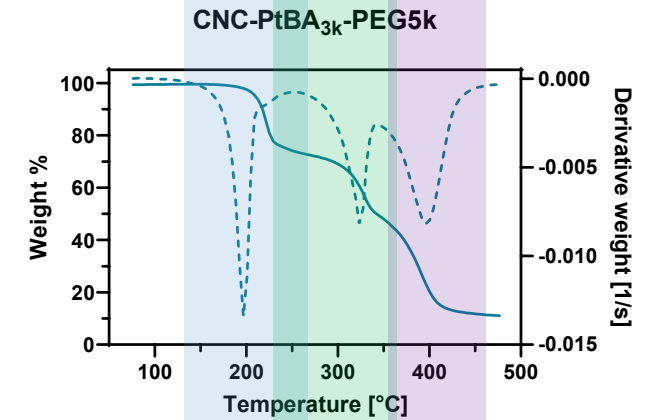
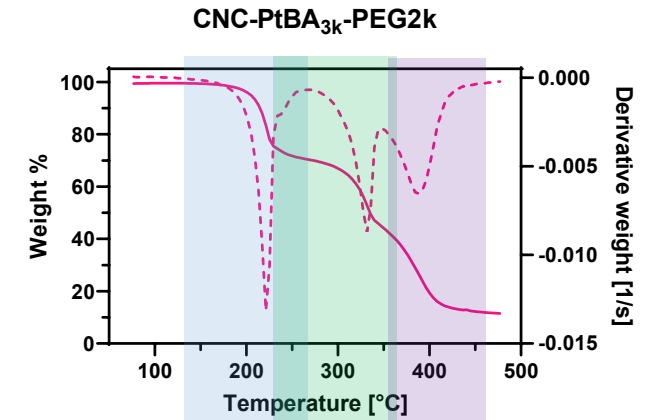
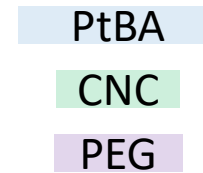
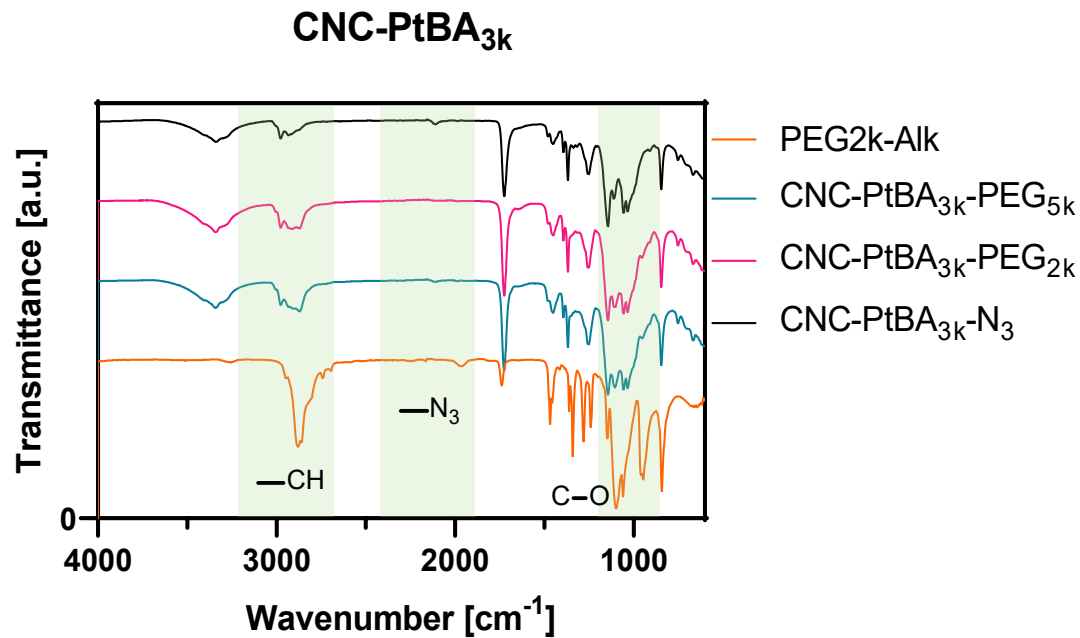
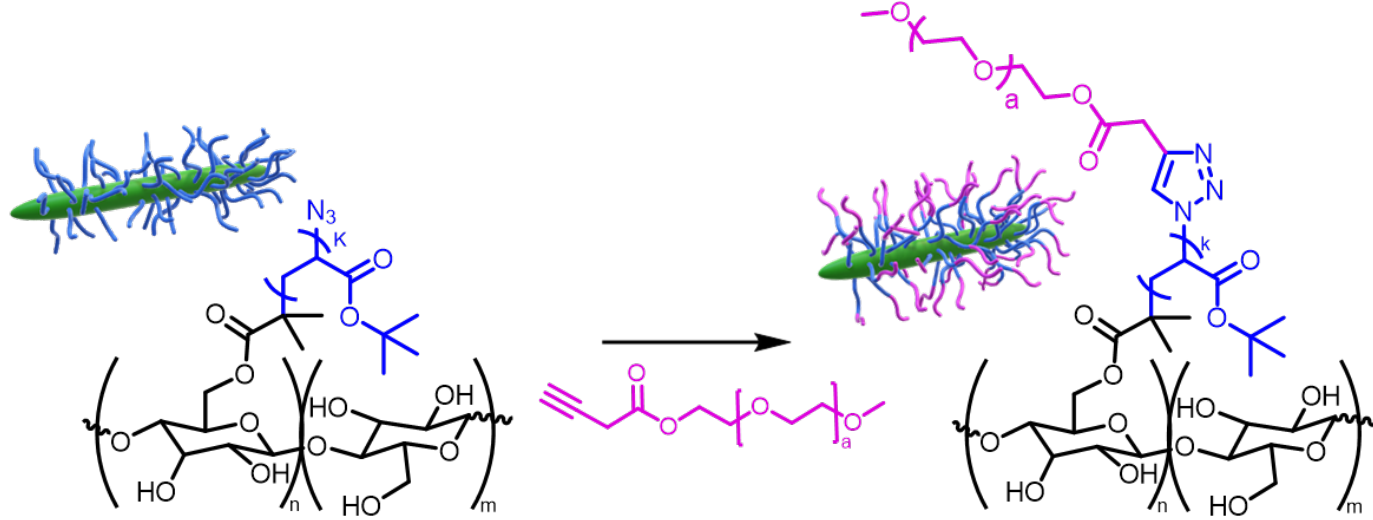
SI-ATRP, grafting polymers from CNC surface



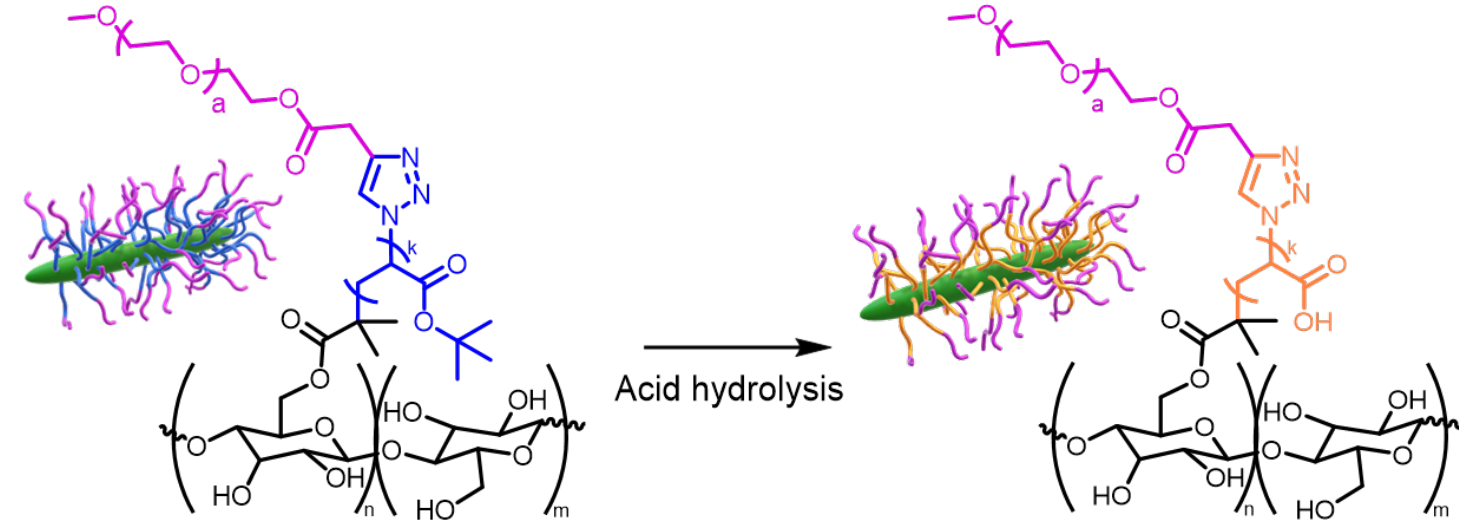
Sample	New ID	DS	T _{onset} [°C]	Mn _{gpc} *
CNC-PtBA ₁	CNC-PtBA _{11k}	7.5%	182	11200
CNC-PtBA ₂	CNC-PtBA _{8k}	10%	176	7500
CNC-PtBA ₃	CNC-PtBA _{15k}	10%	189	15400
CNC-PtBA ₄	CNC-PtBA _{3k}	10%	169	3200

*Determined by the linear relationship between Mn of PtBA and the decomposition point (T_{onset})

CNC-Block-copolymer systems



CNC-Block-copolymer systems



CNC 2 wt.% in H₂O

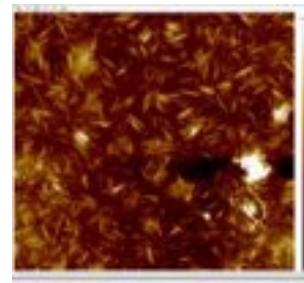
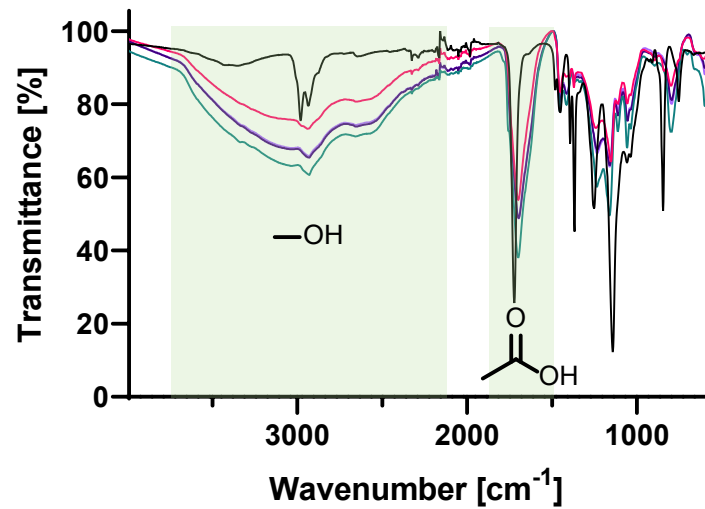
CNC-PAA 2 wt.% in buffer



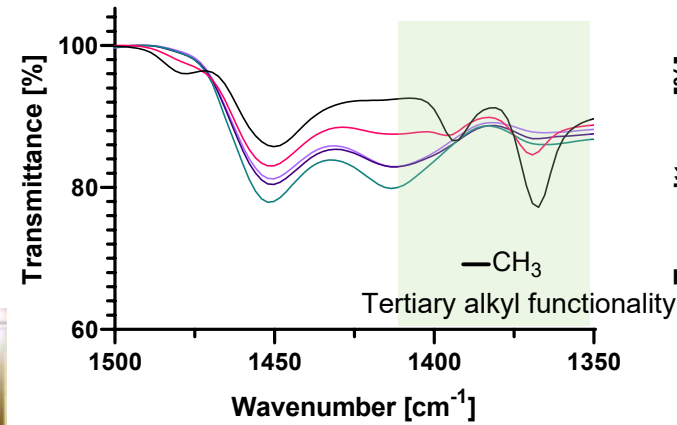
CNC-PAA 2 wt.% in H₂O



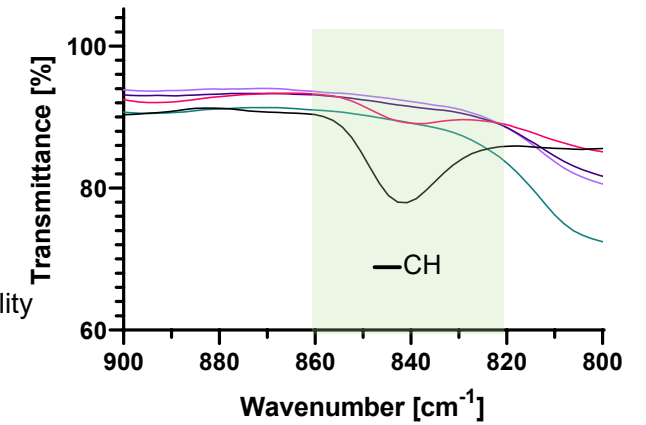
CNC-PAA



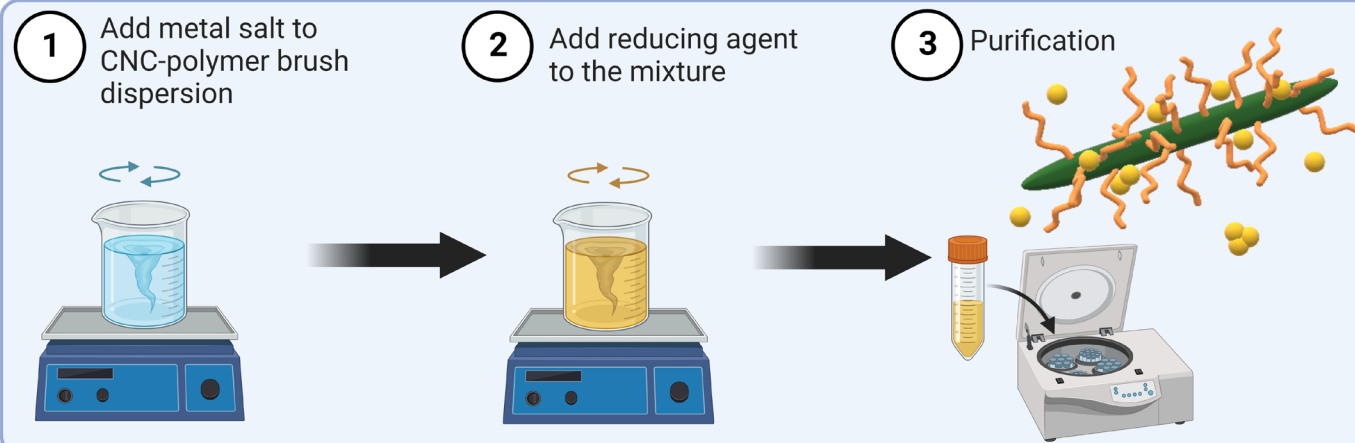
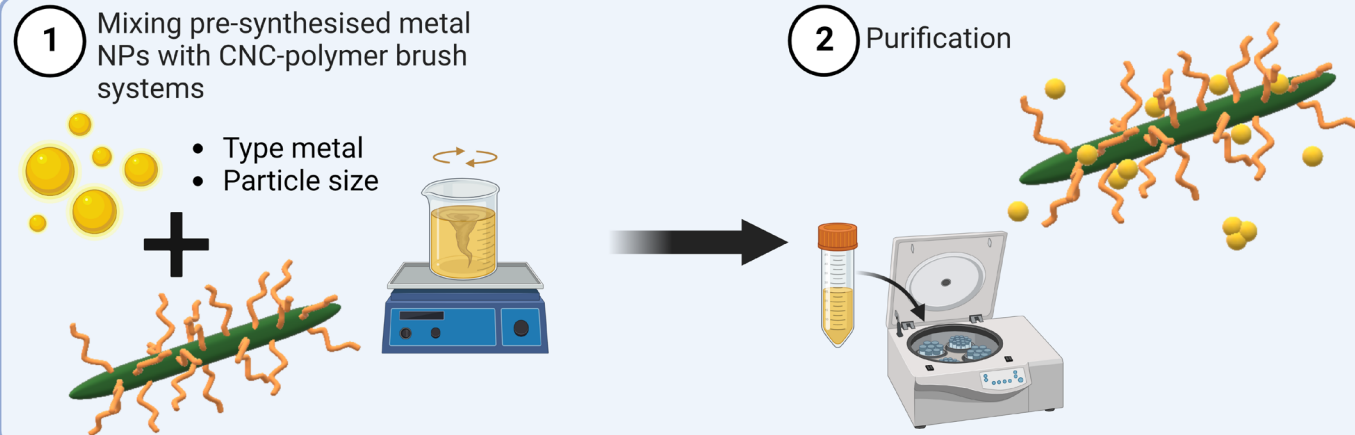
CNC-PAA



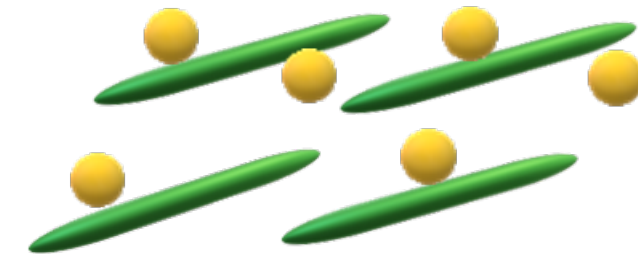
CNC-PAA



Templating approaches for CNC-polymer brush systems

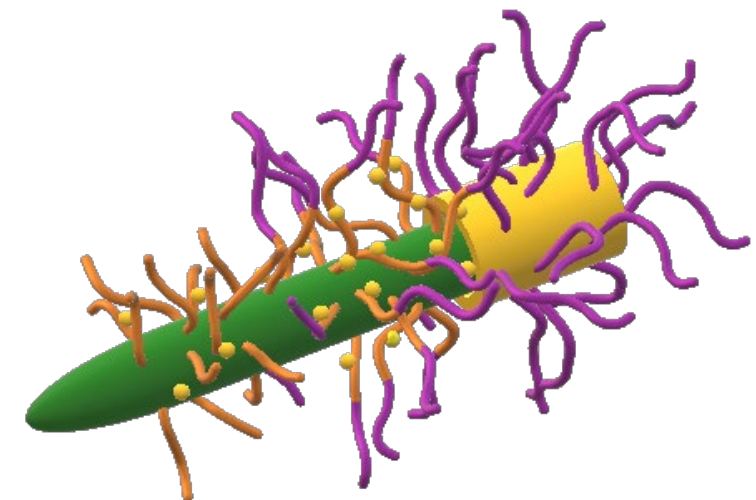


CNC + metal



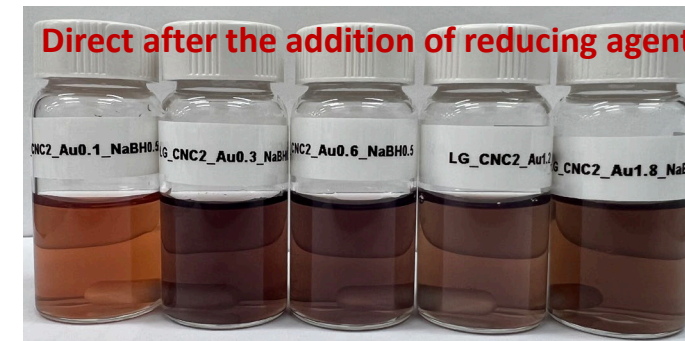
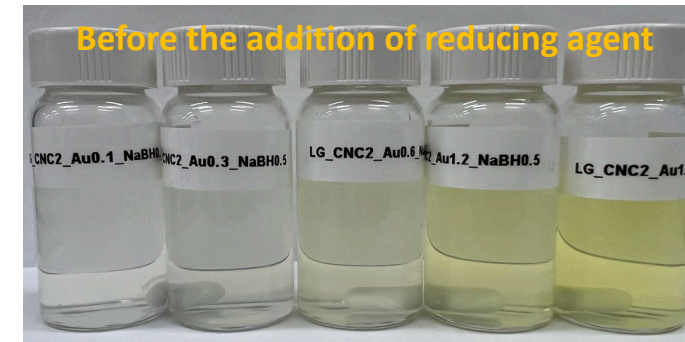
CNC-PAA + metal

CNC-PAA-PEG + metal

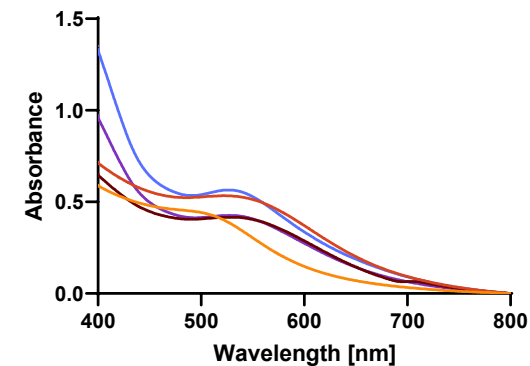


Synthesis of gold nanoparticles with CNC

- How does the presence of CNC impact the synthesis of Au NPs?
- How does the presence of Au NPs impact CNC?
- Stability, particle size, viscosity, conductivity, etc..

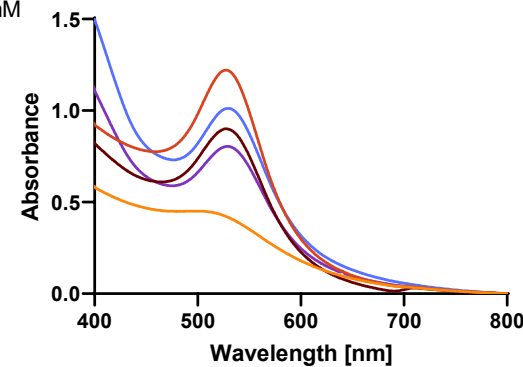


1h, CNC 2 wt.% 0.5 mM NaBH₄



— Au0.1mM
— Au0.3mM
— Au0.6mM
— Au1.2mM
— Au1.8mM

24h, CNC 2 wt.% 0.5 mM NaBH₄



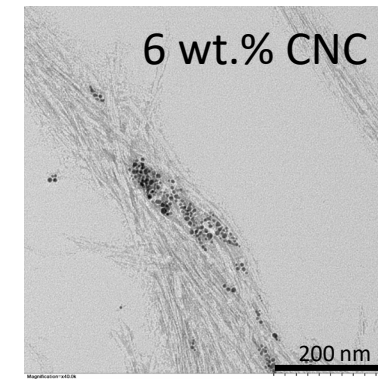
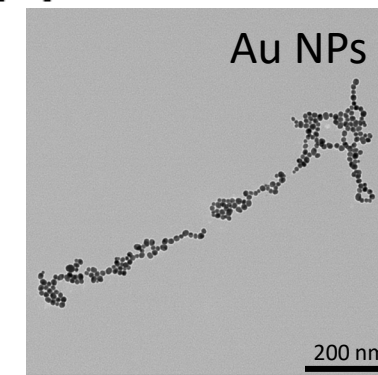
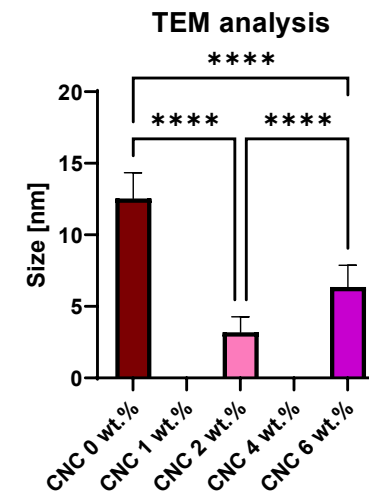
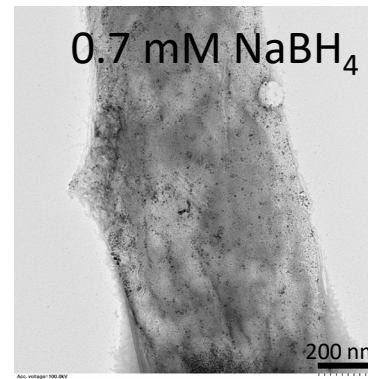
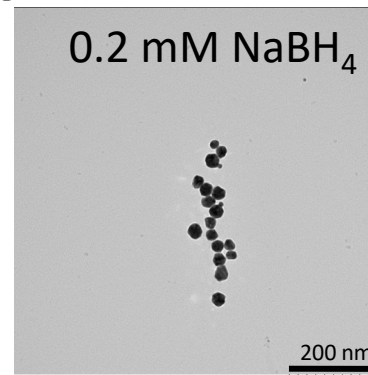
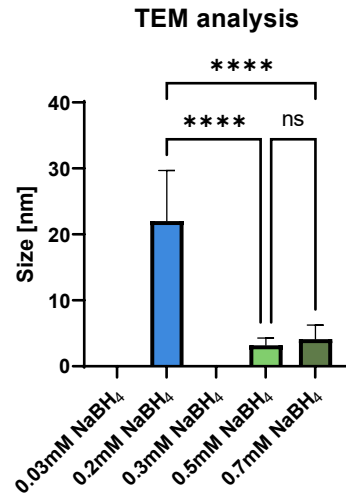
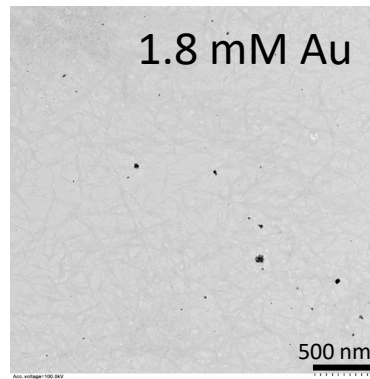
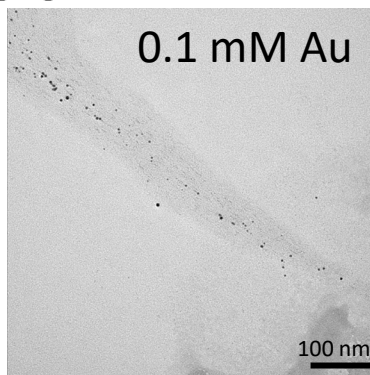
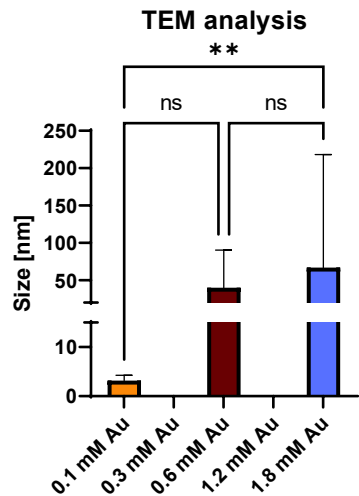
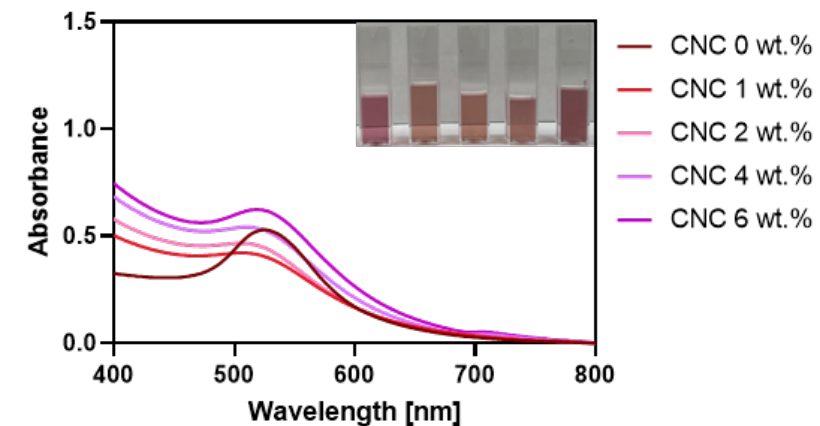
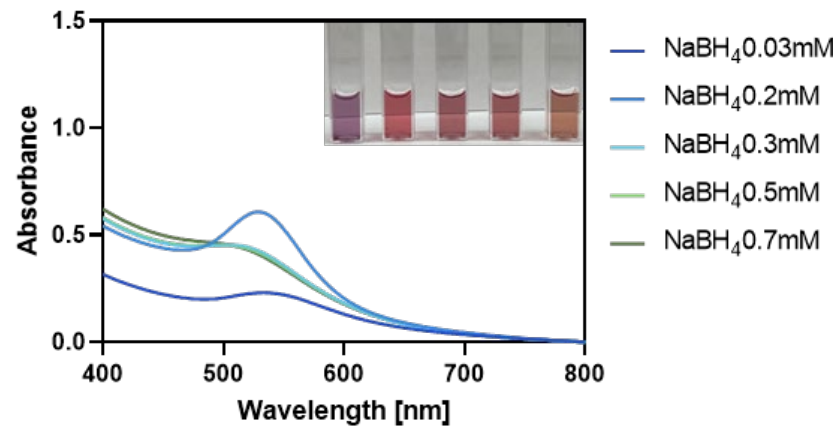
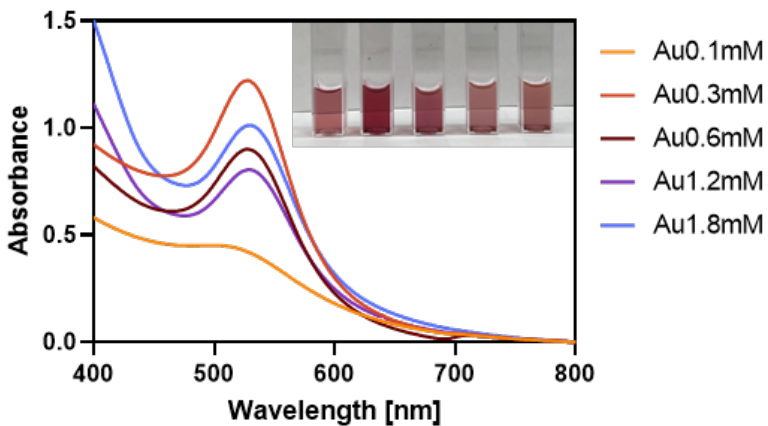
— Au0.1mM
— Au0.3mM
— Au0.6mM
— Au1.2mM
— Au1.8mM

Synthesis of gold nanoparticles with CNC

24h, CNC 2 wt.% 0.5 mM NaBH₄

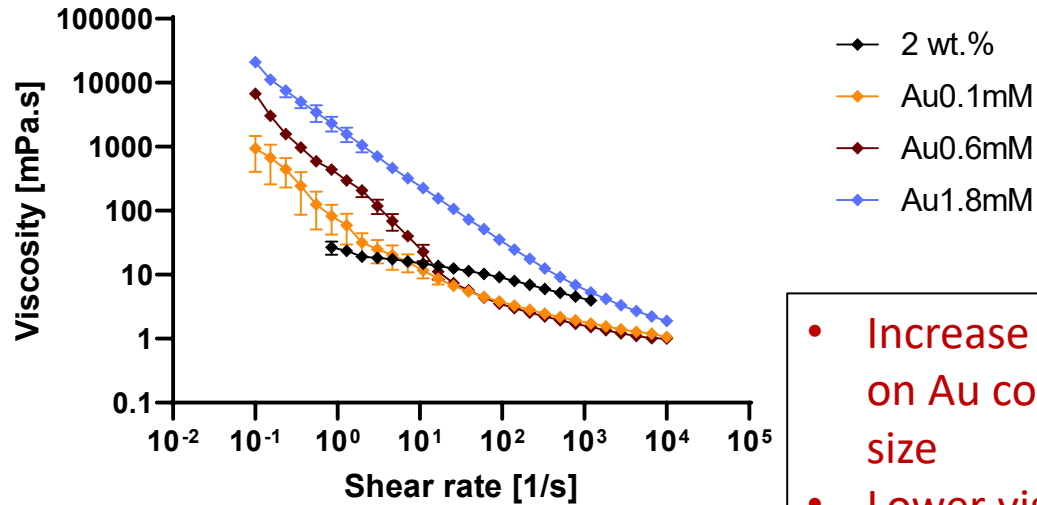
24h, CNC 2 wt.% 0.1 mM HAuCl₄

24h, 0.1 mM HAuCl₄ and 0.5 mM NaBH₄

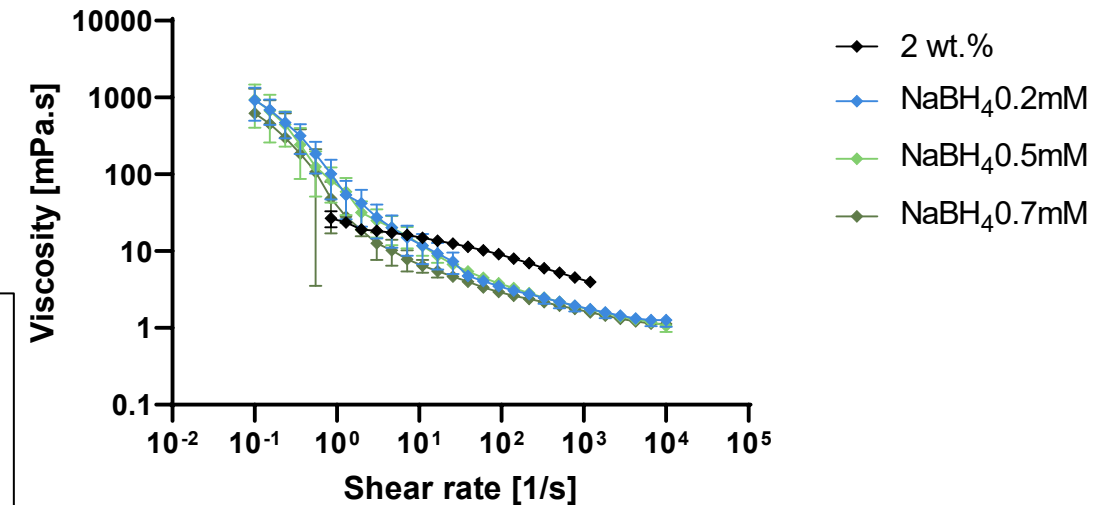


Synthesis of gold nanoparticles with CNC

CNC 2 wt.% 0.5 mM NaBH₄



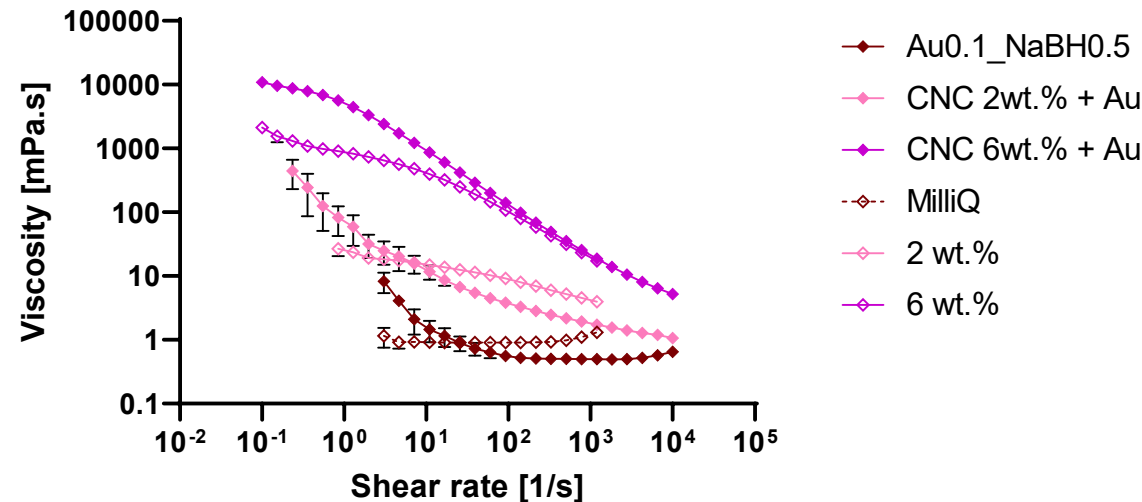
CNC 2 wt.% 0.1 mM HAuCl₄



- Increase in viscosity based on Au content and particle size
- Lower viscosity at higher share rates

- No impact with particle size
- Lower viscosity at higher share rates

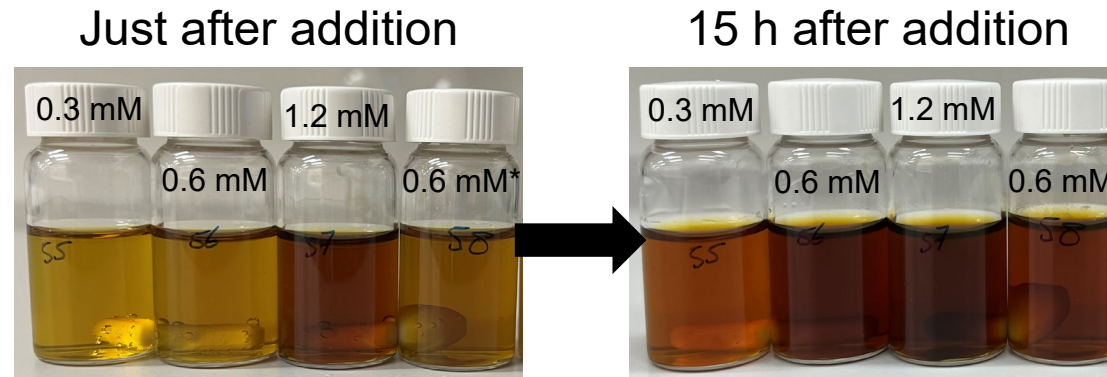
Concentration CNC



Synthesis of silver NPs with CNC

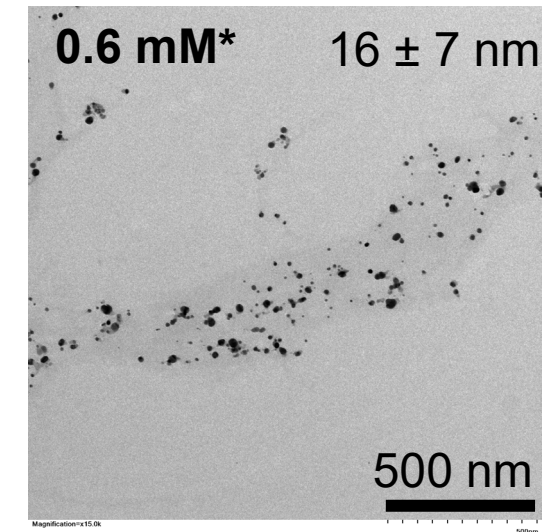
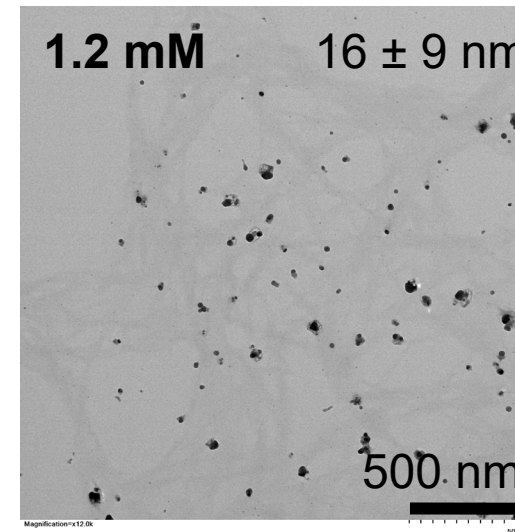
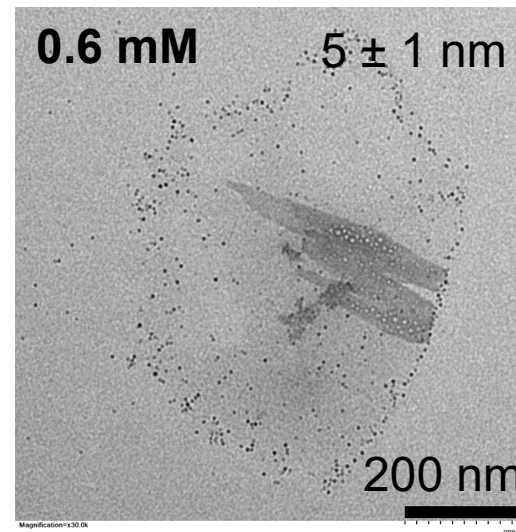
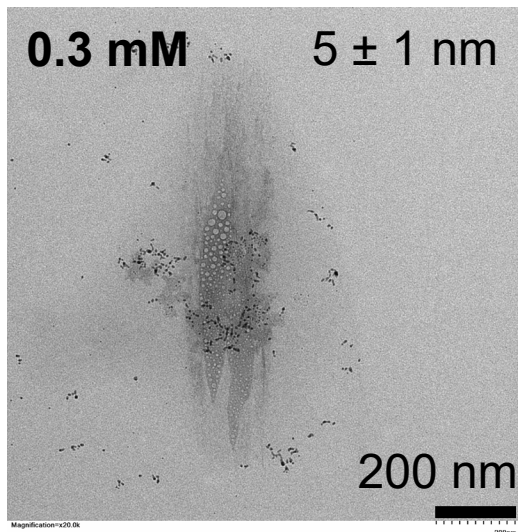
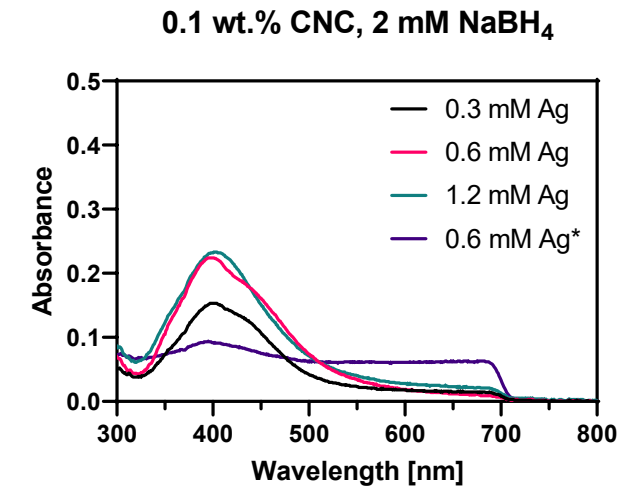
Silver (Ag) NPs

- Optical
- Electrical conductivity
- Thermal
- Antimicrobial activity



* 0.6 mM = Change in addition

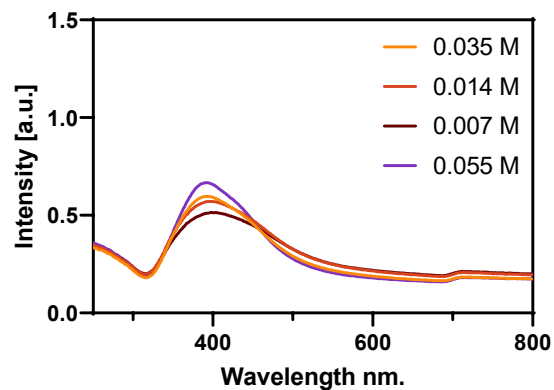
Sample	0.3 mM	0.6 mM	1.2 mM	0.6 mM*
pH	9.50	9.37	8.69	9.39



Synthesis of silver NPS with CNC-PAA

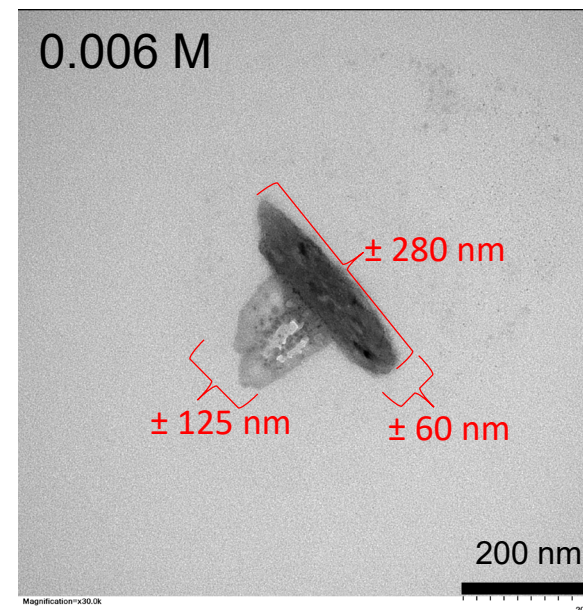
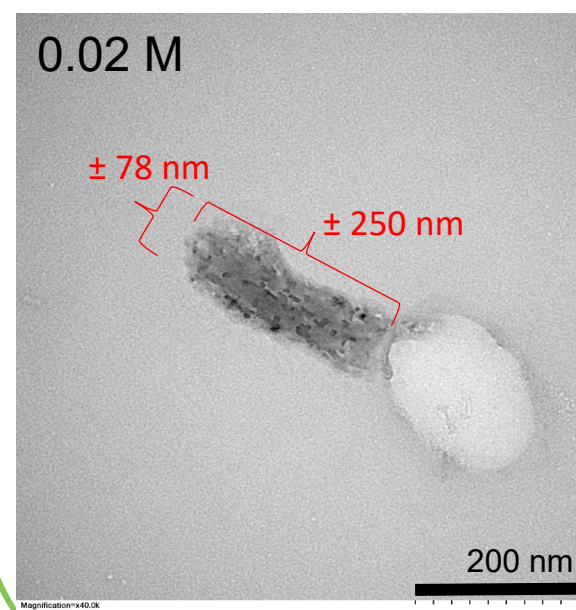
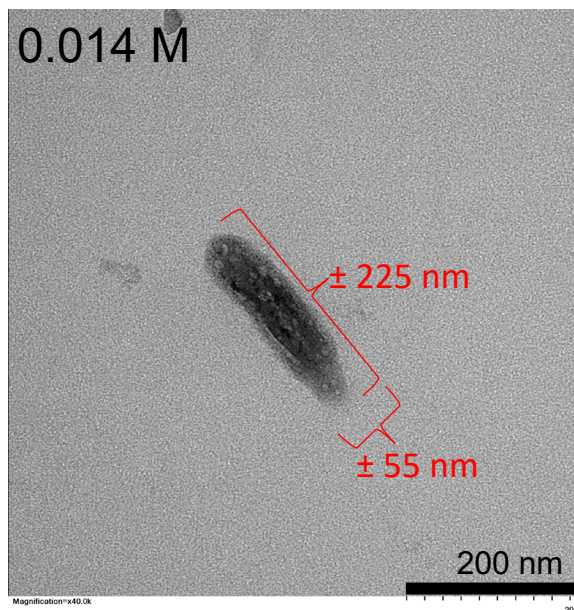
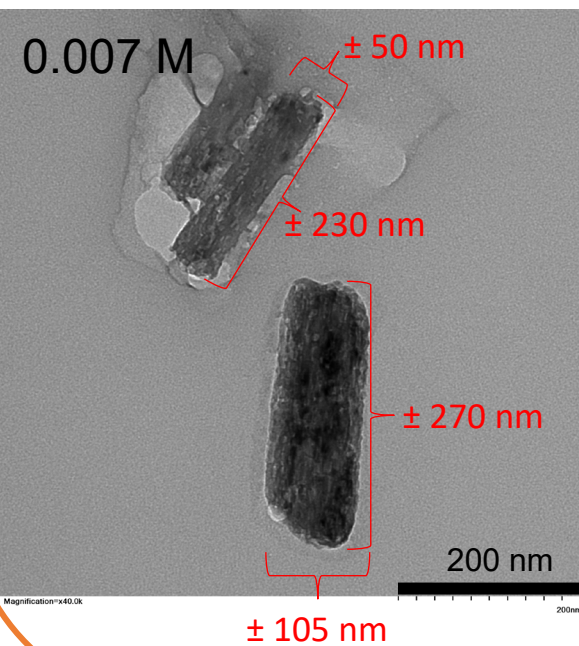
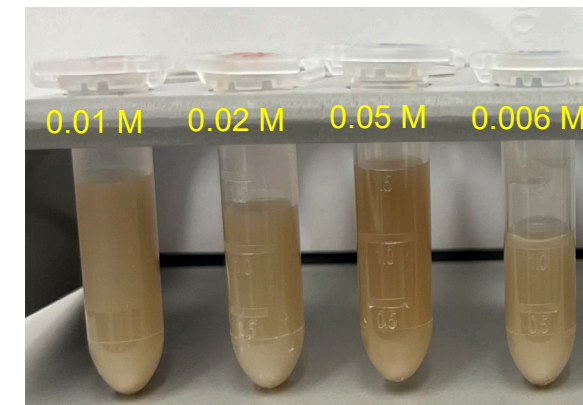
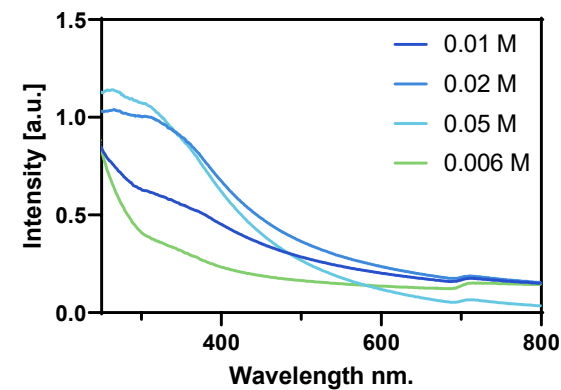
NaBH₄

0.1 wt.% CNC-PAA_{15k}

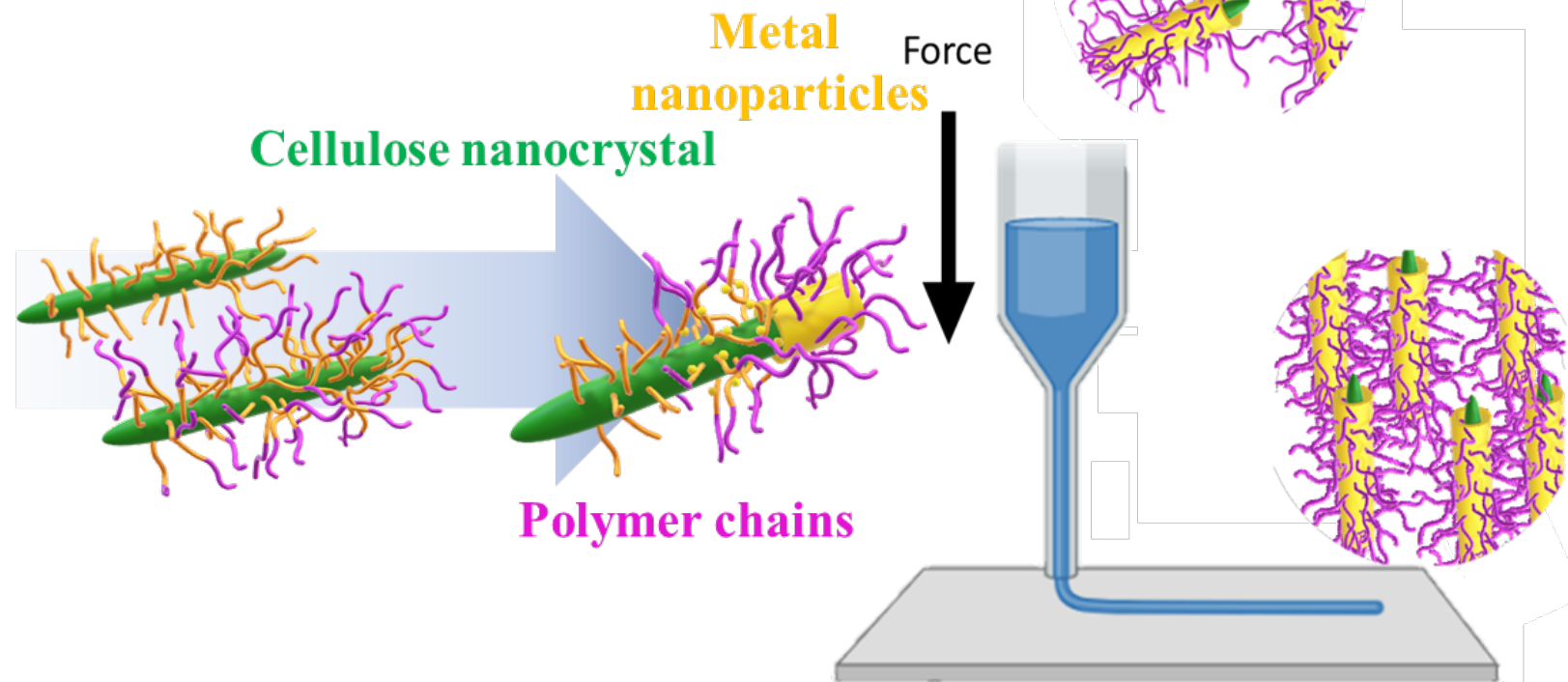


NaOH

0.1 wt.% CNC-PAA_{15k}



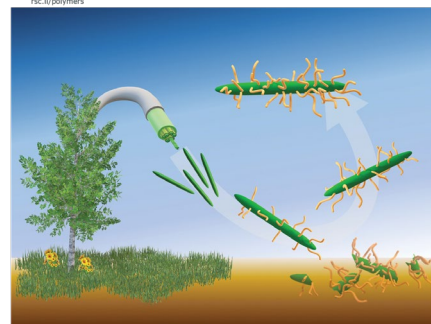
- Design various CNC-polymer brush systems tuning hydrophilic/hydrophobic nature
- Synthesize gold and silver NPs with controllable sizes on CNC and CNC-PAA, improving stability



Polymer
Chemistry

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rsc.li/polymers



ROYAL SOCIETY
OF CHEMISTRY

PAPER
Nitin Arora et al.
Activation of the cellulose nanocrystal surface chemistry for
guided formation of polymer brushes



Thank you

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Associate supervisor: Professor Alan Rowan



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Centre for Advanced Imaging
Centre for Microscopy and Microanalysis

UQ RTS scholarship