Hybrid Materials of Nanocellulose and Graphene

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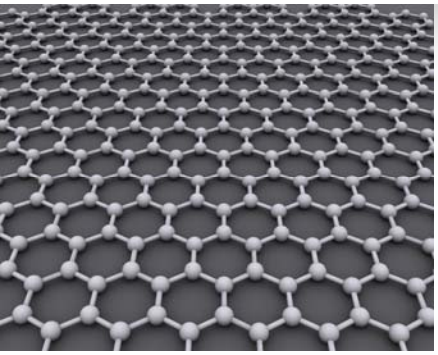


- 2D
- Transparent
- Flexible
- Super strong
- Conductive

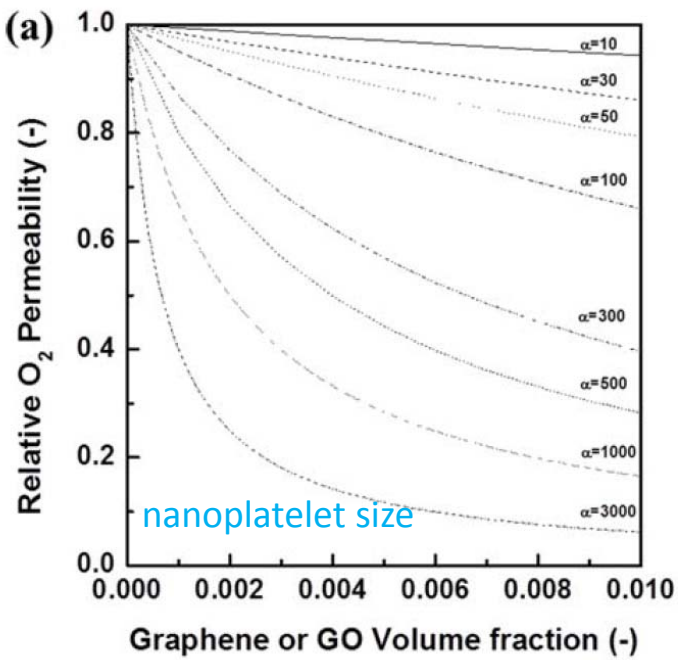
https://graphene-flagship.eu/what-is-graphene-(3)

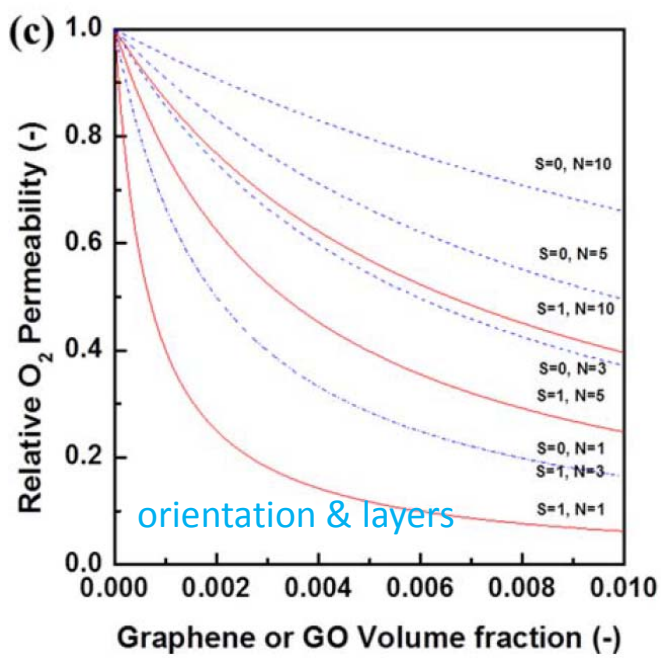
Why nanocellulose & graphene?

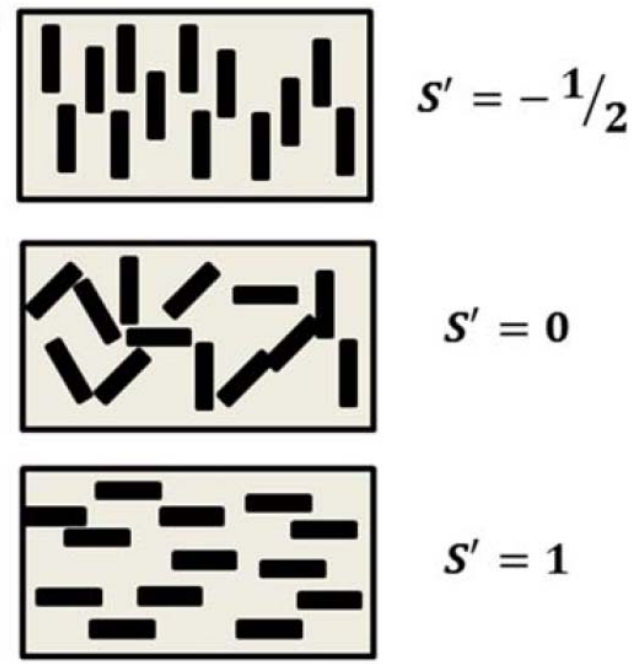
	NANOCELLULOSE	GRAPHENE
Water dispersibility	*Y*	*N*
Uniform material formation	*Y*	*N*
Industrially produced	*Y*	*Y**
Insensitive to moisture	*N*	*Y*
High strength	*Y*	*Y (1 TPa)*
Conductive (electric/thermal)	*N*	*Y*
Barrier properties	*Y**	*Y**

Can we use nanocellulose to *disperse* graphene in water and obtain *uniform materials* with barrier and conductive properties?

Barrier properties of graphene: Effect of size aspect ratio, exfoliation, & orientation

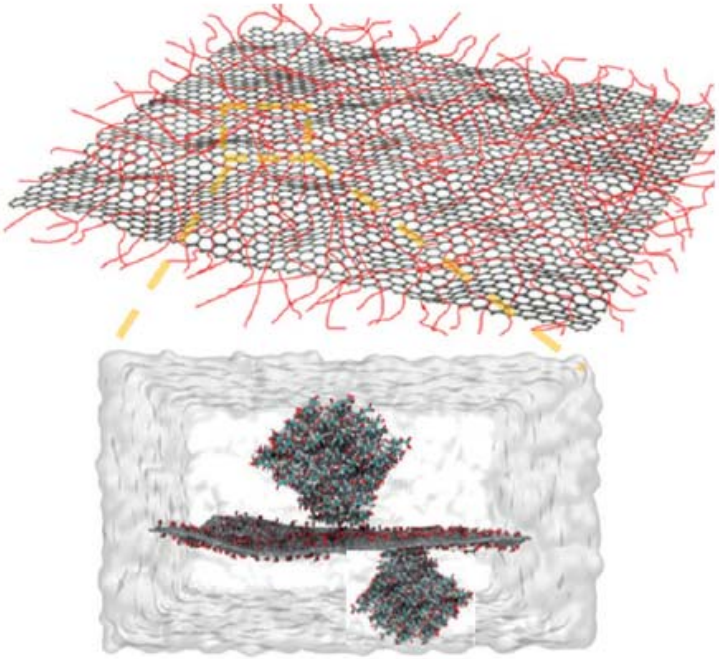




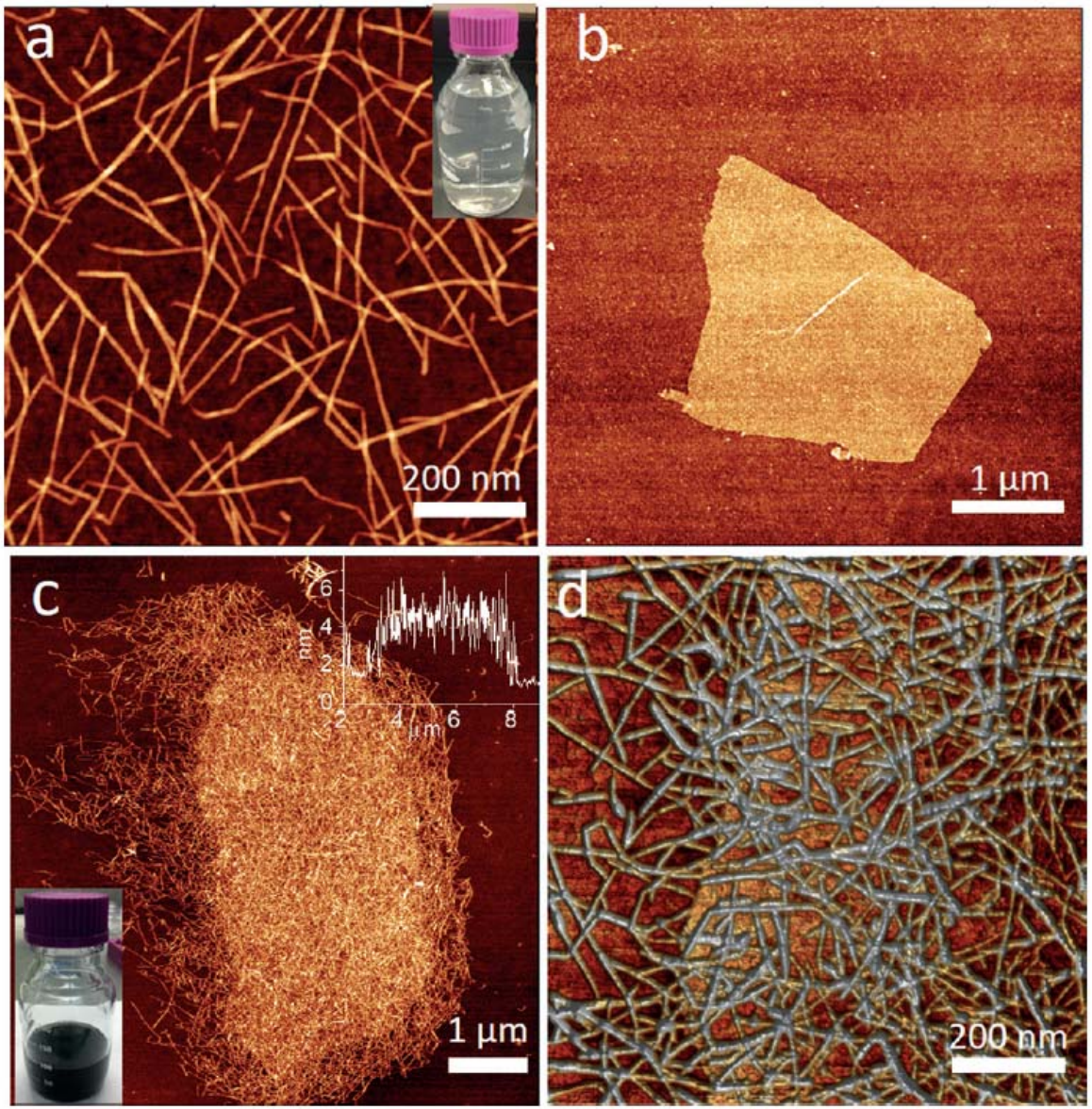


Yoo 2014, J. APPL. POLYM. SCI.

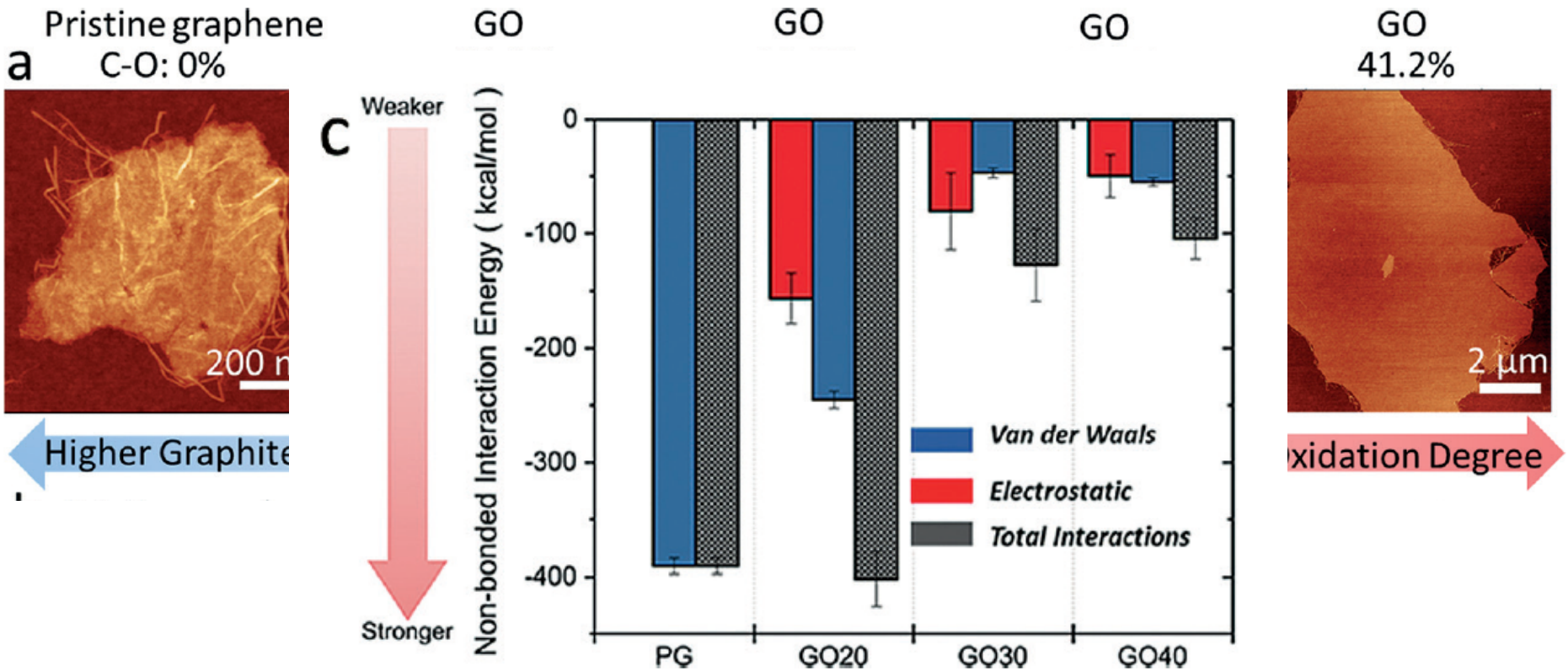
Interaction between nanocellulose and graphene



Xiong et al., Angew. Chem. 2018, 130, 8644 –8649



Interactions between NC and graphene



Xiong et al., Angew. Chem. 2018, 130, 8644 –8649

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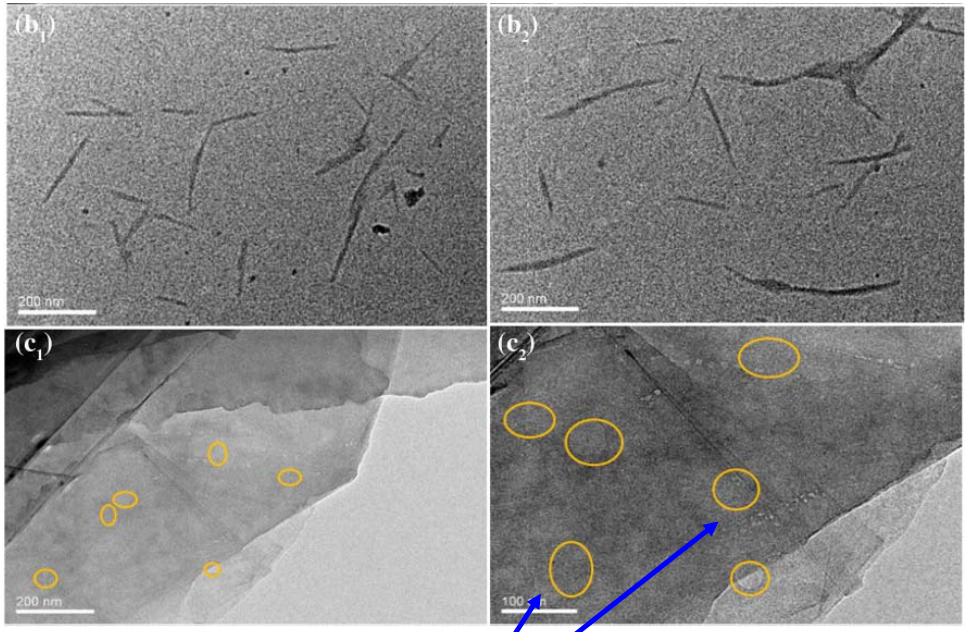
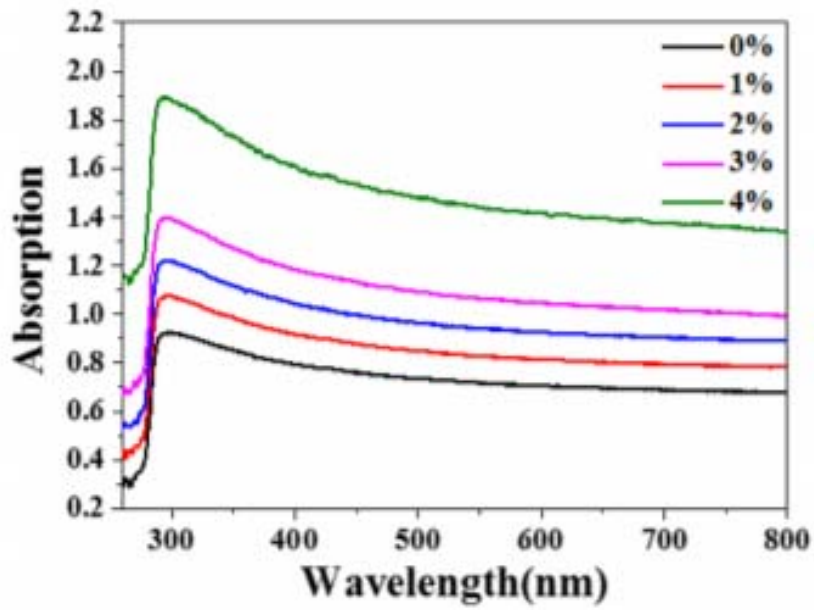
ORIGINAL PAPER

Dispersion and Rheological Properties of Aqueous Graphene Suspensions in Presence of Nanocrystalline Cellulose

Xinqi Zhang[1] · Yanjun Tang[1,2,3,4,5] · Xiaoyu Wang[1] · Junhua Zhang[1] · Daliang Guo[1] · Xueming Zhang[1,6]



CNC only on chemiccally exfoliated graphene surface?



(Zhang et al., *Journal of Polymers and the Environment.*, **2018**)

Stability of multilayer graphene/nanographite

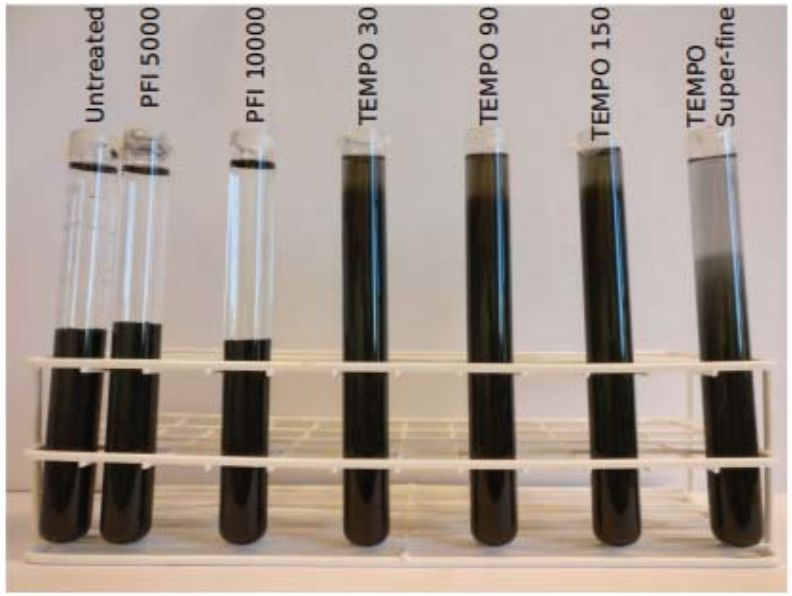
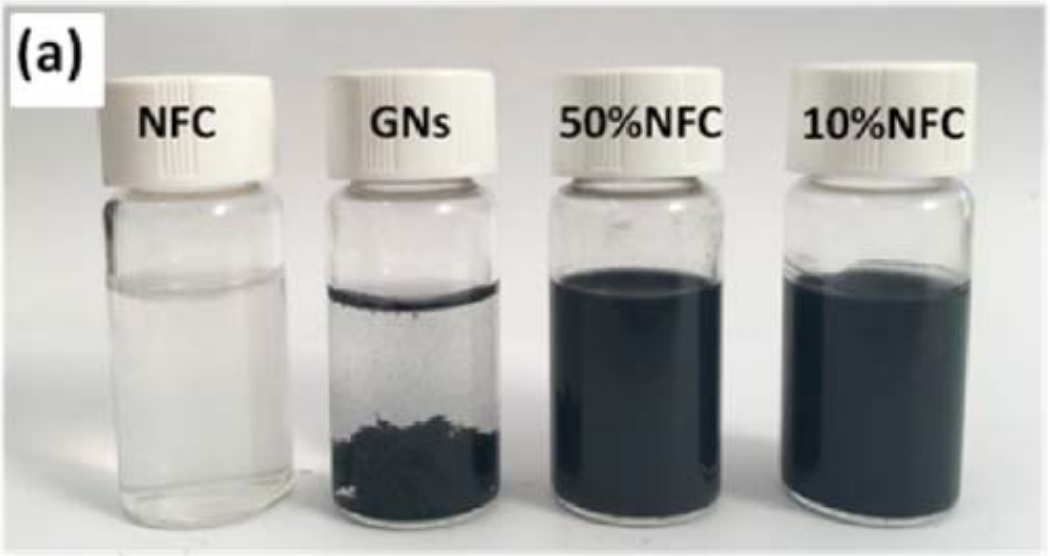


Fig. 2. Sedimentation samples containing cellulose with different qualities 31 days after preparation. The TEMPO-oxidized samples provided a significantly better stabilization of the graphite dispersions than the samples with coarser qualities.

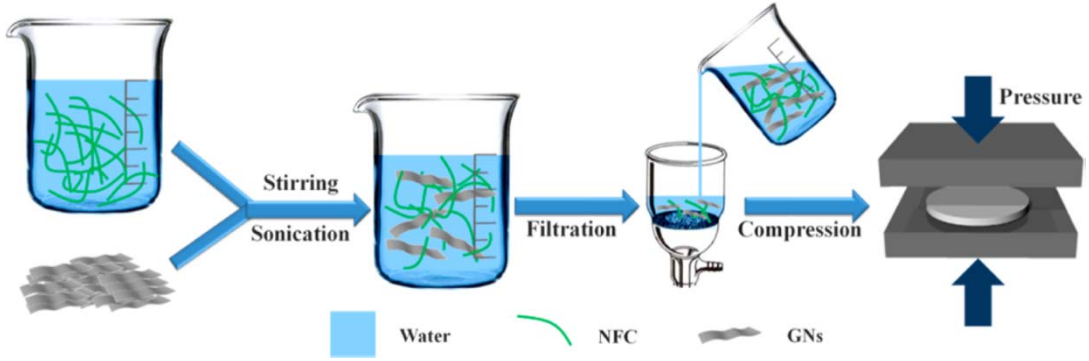
Andres et al., Materials and Design, 2018, 141, 342–349

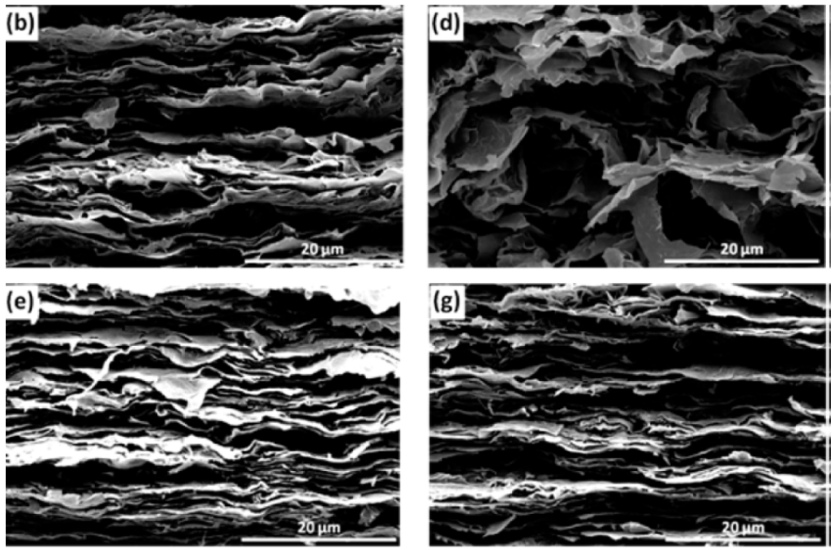


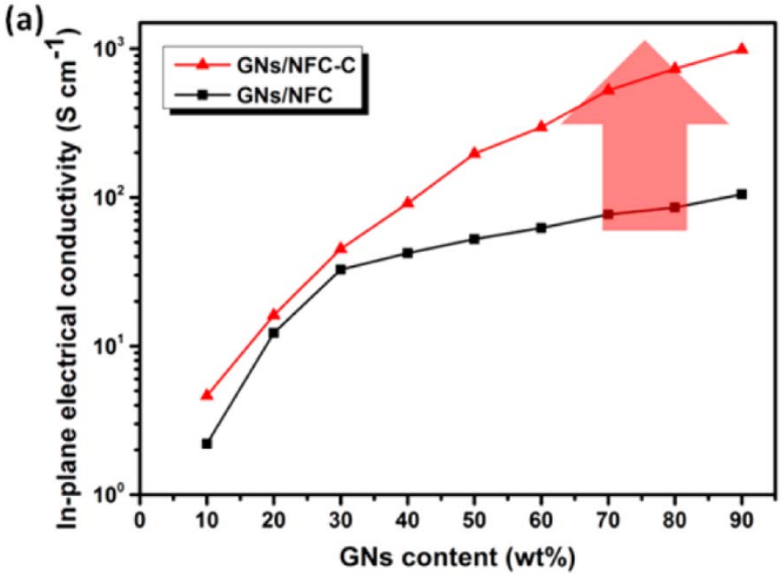
Yang et al, ACS Sustainable Chem. Eng. 2017, 5, 9102−9113

Yang et al, ACS Sustainable Chem. Eng. 2017, 5, 9102−9113

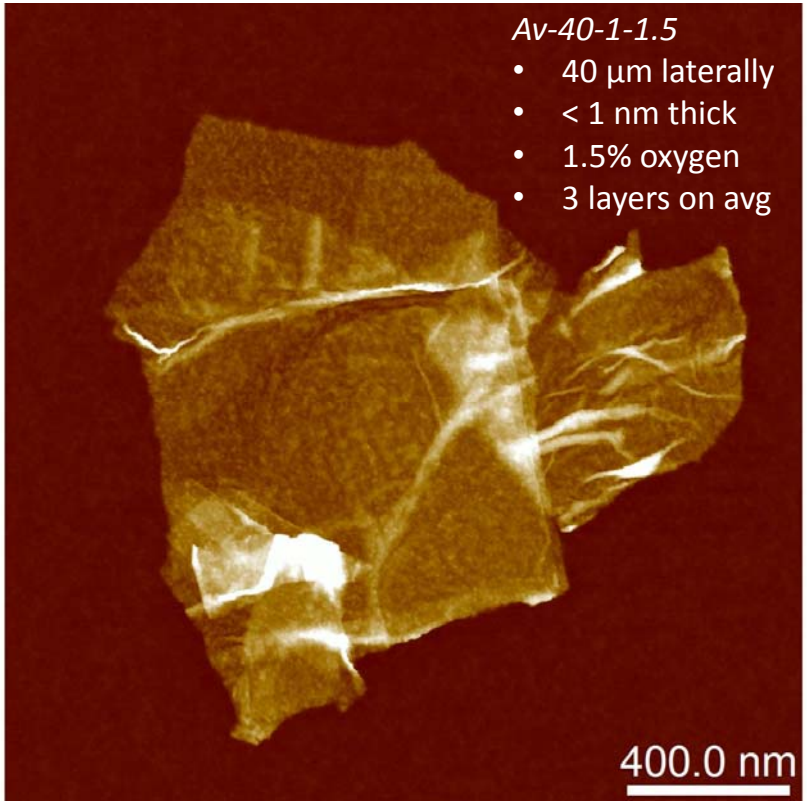
Films of nanocellulose and graphene



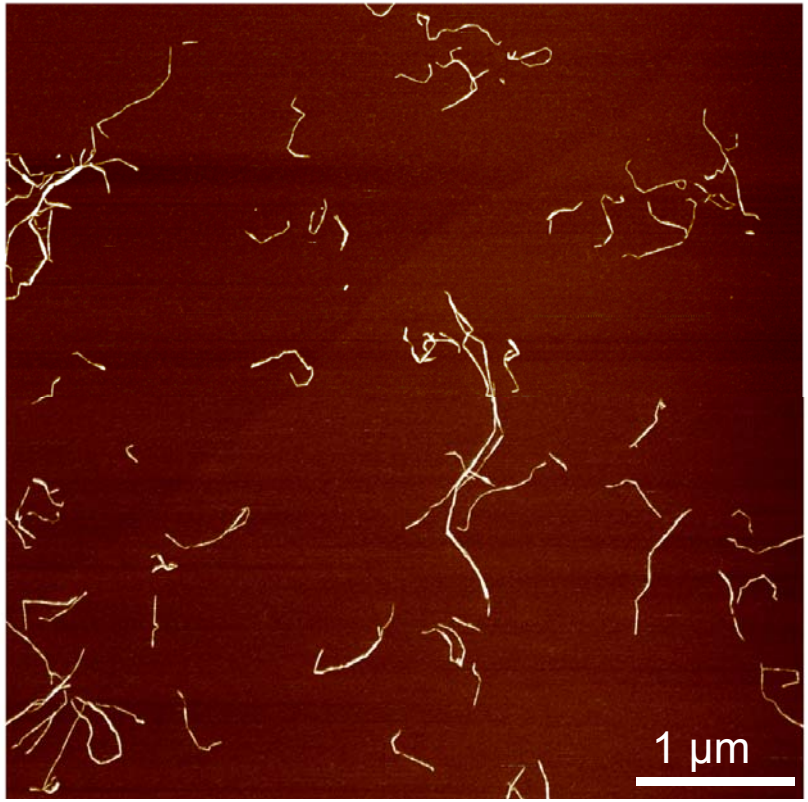




Materials in this study

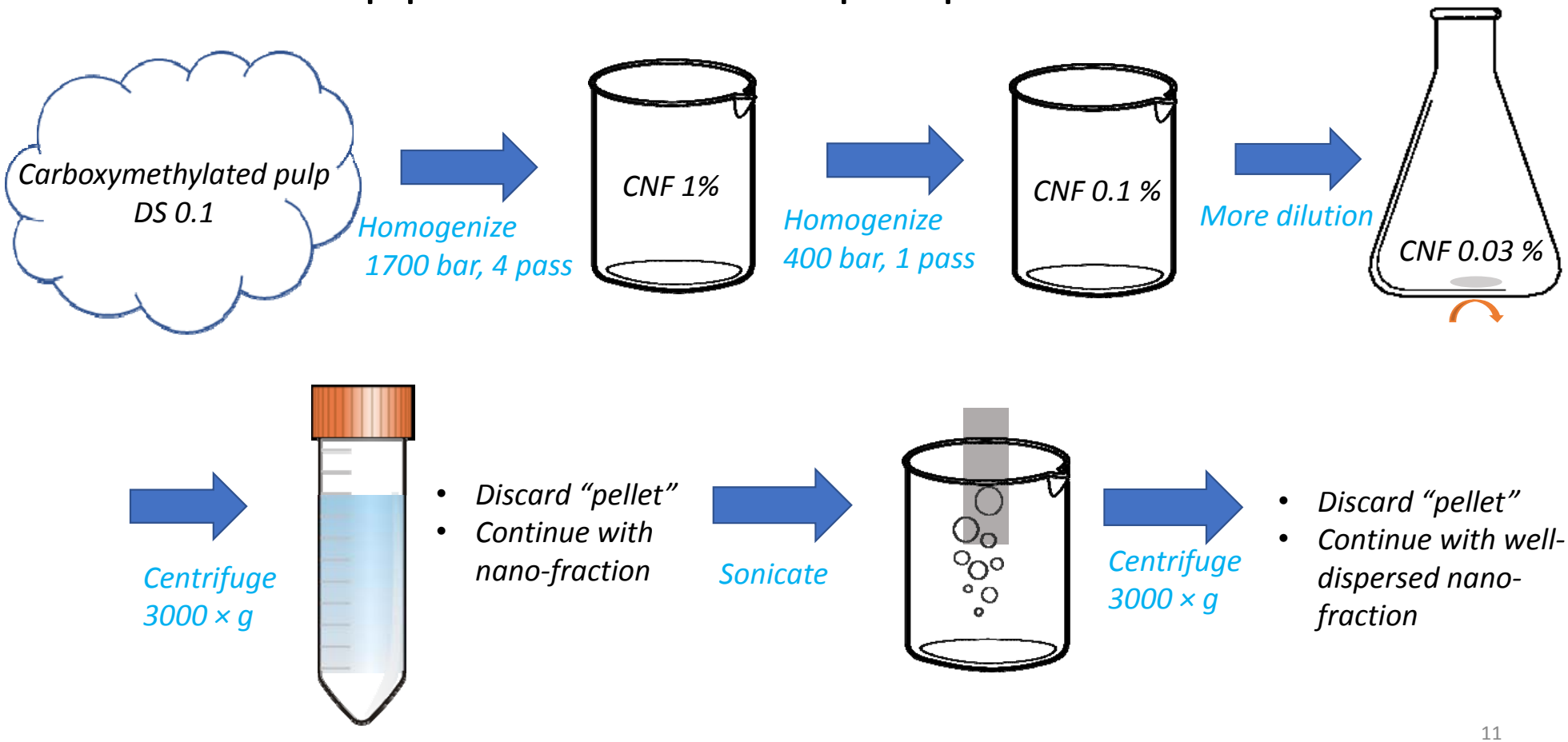


Avanzare graphene

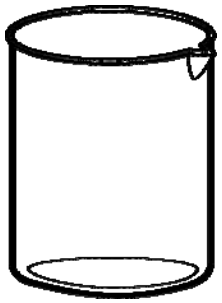


Carboxymethylated CNF, DS 0.1, 600 µeq/g

Current approach – CNF preparation



Current approach – CNF/graphene dispersion



Graphene + CNF
1:10 G:CNF

Sonication, 5 min

Characterize dispersions:

- Visually
- UV-Vis

Centrifuge 3000 × g, 20 min

Characterize supernatant:

- Visually
- UV-Vis
- DLS/Zeta Potential
- AFM
- TGA
- RAMAN
- Aging by centrifugation + UV-Vis
- Turbidity
- Films – barrier properties

Rationale!

- CNF @ high degree of fibrillation & fractionated
  - Only colloidally stable nanofraction used
- CNF @ concentrations below percolation
  - No network entrapment of graphene
- CNF in excess
  - From literature review – CNF adsorbs to graphene surface – enough to reach adsorption limit
- All CNF/graphene dispersions fractionated
  - Only “stable” dispersions characterized

Visual appearance of dispersions

CNF 0.03 %

1:10 G:CNF ~0.01%

- Highly transparent pure CNF dispersions were obtained
- CNF clearly stabilizes the graphene
  - Transparent, colored dispersions obtained

DLS/Zeta potential

CNF 0.03 %

1:10 G:CNF ~0.01%

DLS measurements (1 mM NaCL):

	Size (d(h), nm)	SD (nm)
DS 0.1 +S+C	270	24
DS 0.1 + G +S+C	1440	129

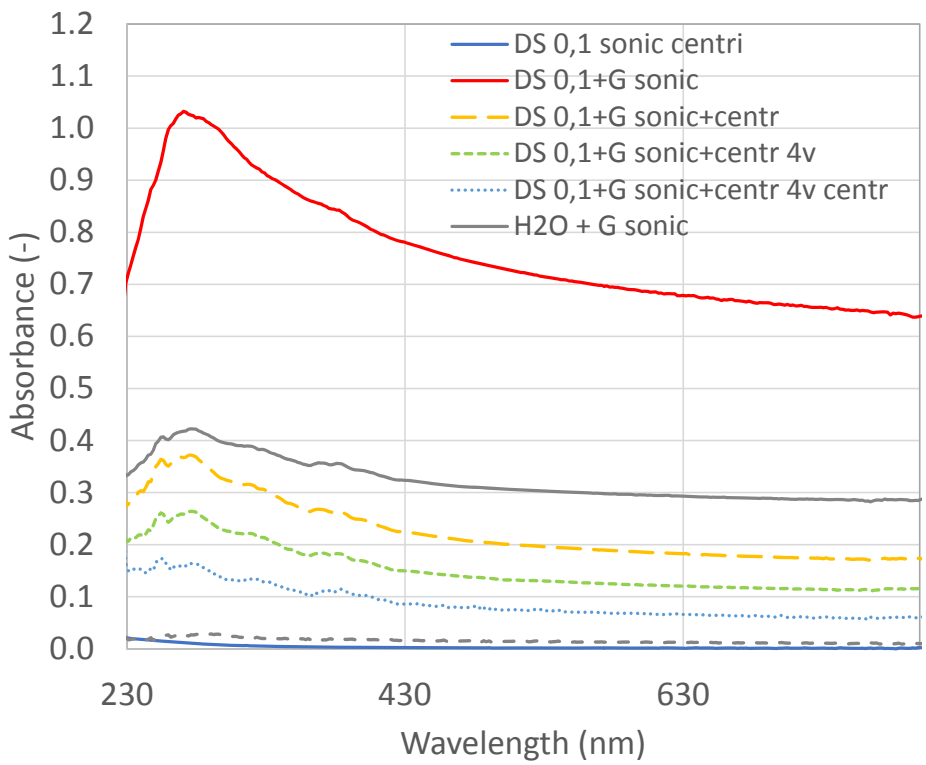
- Size of CNF as expected
- Size when G present smaller than expected -> large flakes removed during centrifugation? Speed too high?

Zeta-Potential measurements (1 mM NaCL):

	Charge (Z-pot, mV)	SD (mV)
DS 0.1 S+C	-24	2.12
DS 0.1 +G +S+C	-28	0.51

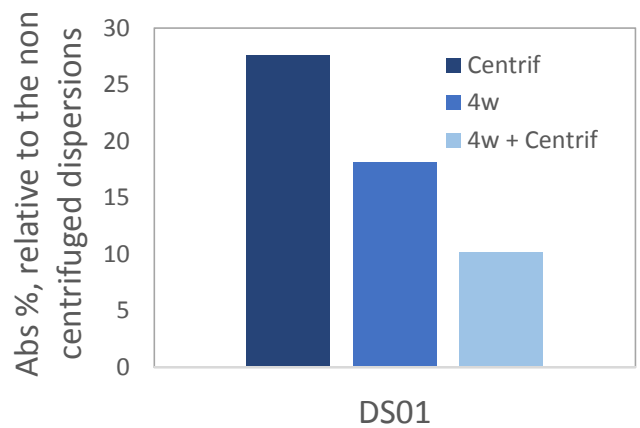
- Z-potential doesn't seems to change upon G addition.

Stability by UV-Vis



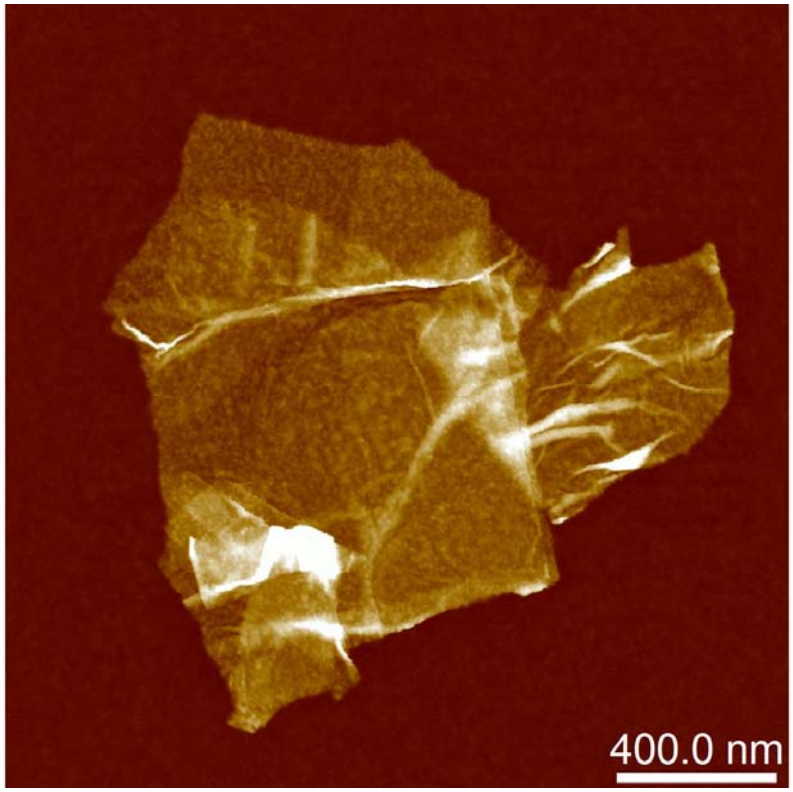
Higher the peak = more stabilized graphene

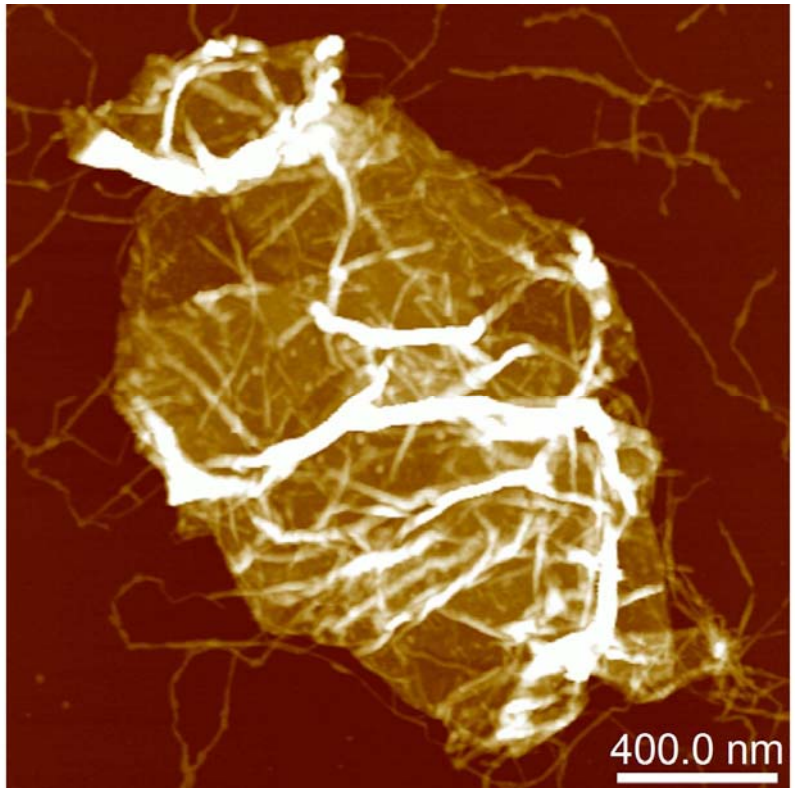
Absorption @ 500 nm



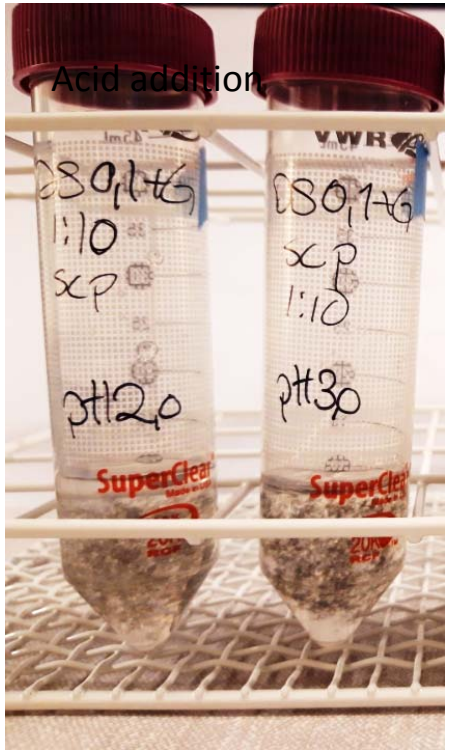
- Continual graphene sedimentation
- Difference between graphene content in dispersion before and after centrifugation decreases with time

Interaction by AFM





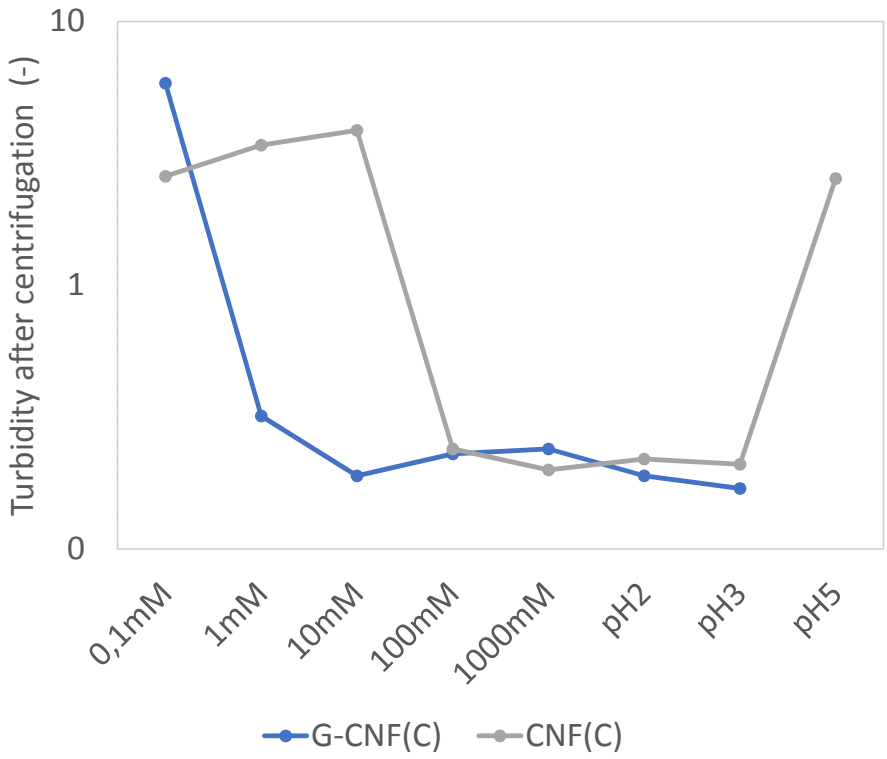
Colloidal stability: Samples equilibrated for 1 day after addition of acid or salt



pH

Increasing NaCl content from 0.1 mM to 1 M

Colloidal stability assessed by turbidity

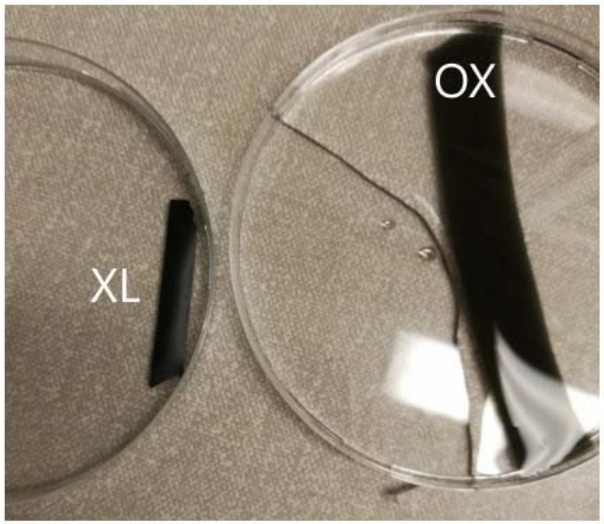


Take home message:

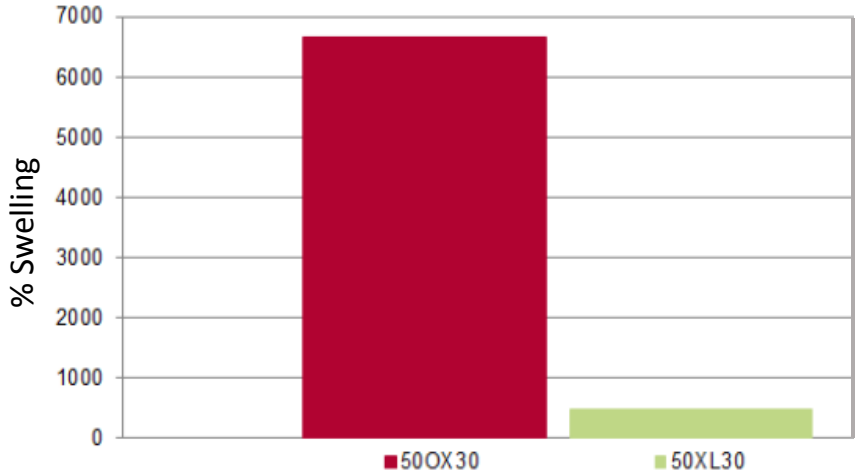
- Significant drop in turbidity indicates sedimentation upon centrifugation
- G-CNF unstable > 1 mM NaCl, whereas pure CNF is more resistant to salt
- G-CNF behaves like a hybrid particle (differs from pure CNF).

Barrier properties: Swelling

Material	O content	Bulk density	BET surface area	Sheet length	Layers
Graphenit-OX	2.28 wt%	0.2 g/ml	110 m^2/g	4 μm	<5
Graphenit-XL	1.05 wt%	0.04 g/ml	N/A	40 μm	5-10

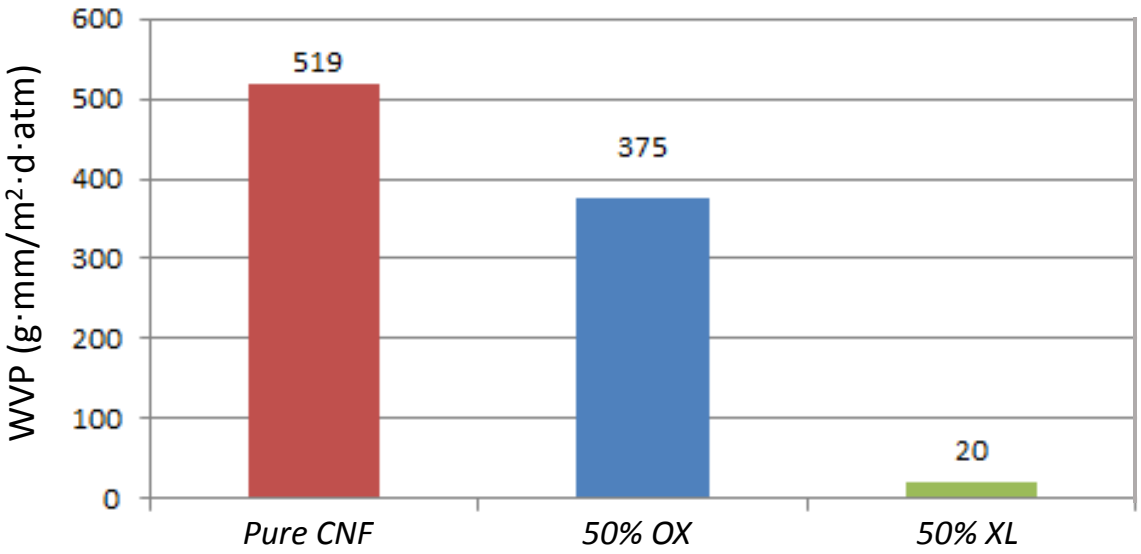


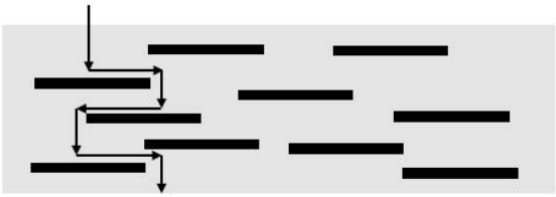
Depends on graphene quality



- XL swells less
- OX breaks down in hours

Barrier properties: WVP





- 25× decrease in WVP compared to pure CNF
- XL is 18× better than OX

Conclusions

- CNF indeed stabilizes aqueous dispersion of graphene via adsorption
- Stability changes with time
- Hybrid CNF/G particle is less able to withstand added electrolyte
- Films cast from CNF + G mixtures give films with improved barrier properties
- G is available in many variations = many aspects to test, such as platelet size & oxygen content
- Optimization required: G type, CNF type, G:CNF ratio, chemical environment, etc.,

Thank you

& THANKS to BK and the Nanocellulose Competence Platform @ RISE for support

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