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# Cellulose membranes for piezo- and triboelectric nanogenerators (P&TENG)

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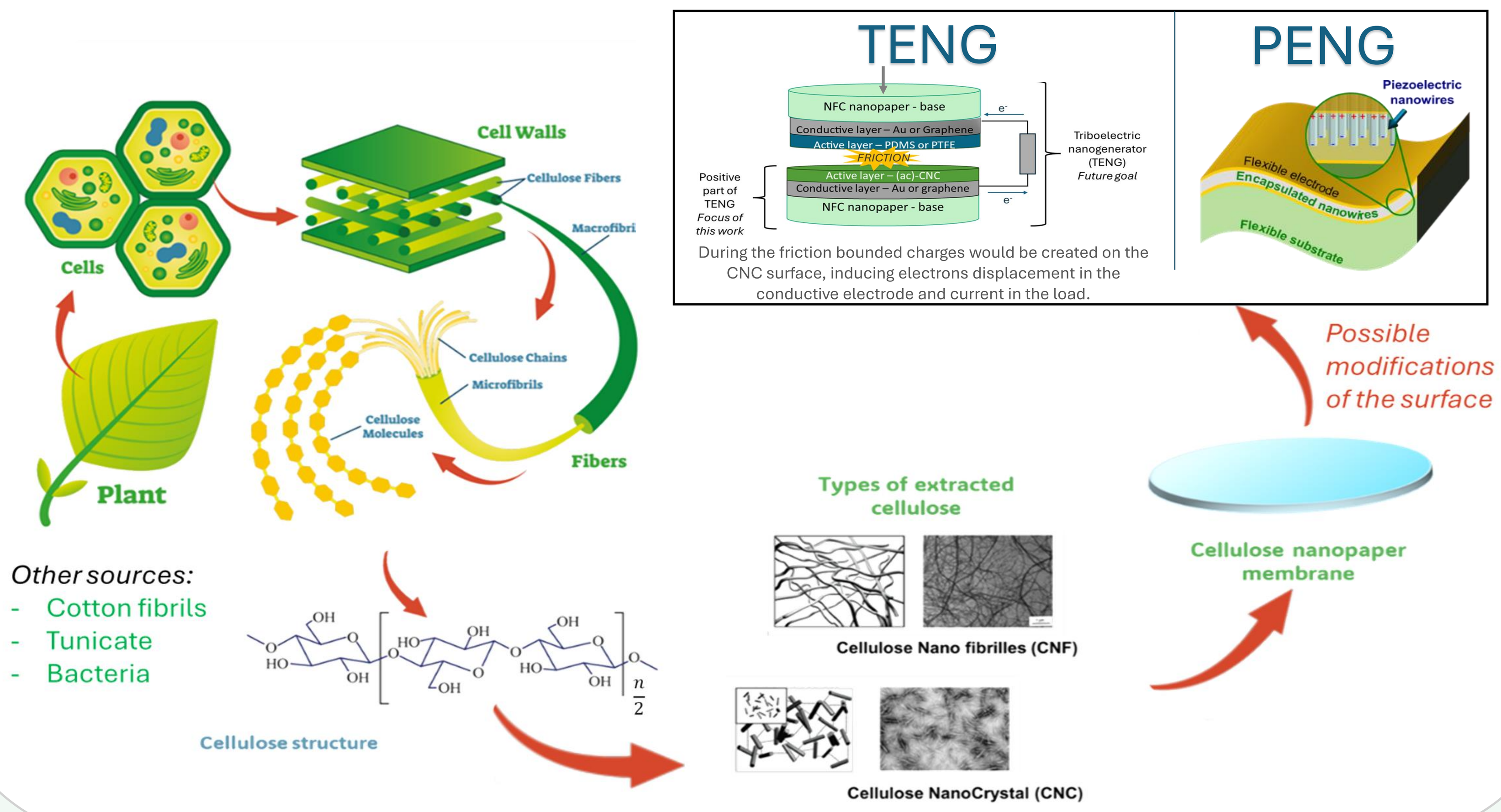
## Introduction

Thin, flexible, flat and hydrophobic nanopapers are being developed for piezoelectric (PENG) and triboelectric (TENG) nanogenerators, based on cellulose nanofibrils (NFC) and nanocrystals (CNC). Prepared by the air-casting method, the mechanical properties of these membranes were optimized for use as support layers. Different strategies were applied to improve surface smoothness and achieve high surface hydrophobicity through acetylation. This flat, water-resistant nanopaper can then be used to deposit a conductive layer of gold thin film or single large graphene sheet. On top of this electrode, an AlN nanowires piezoelectric film will be transferred for PENG applications, whereas a single layer of CNC acetate is added to form the triboelectric active layer of the TENG positive electrode. The study opens the door for further researches, leading to deep understanding of the factors influence triboelectric properties of the cellulose-based materials and their implementation for energy generation.




## Strategies for obtaining flat surface

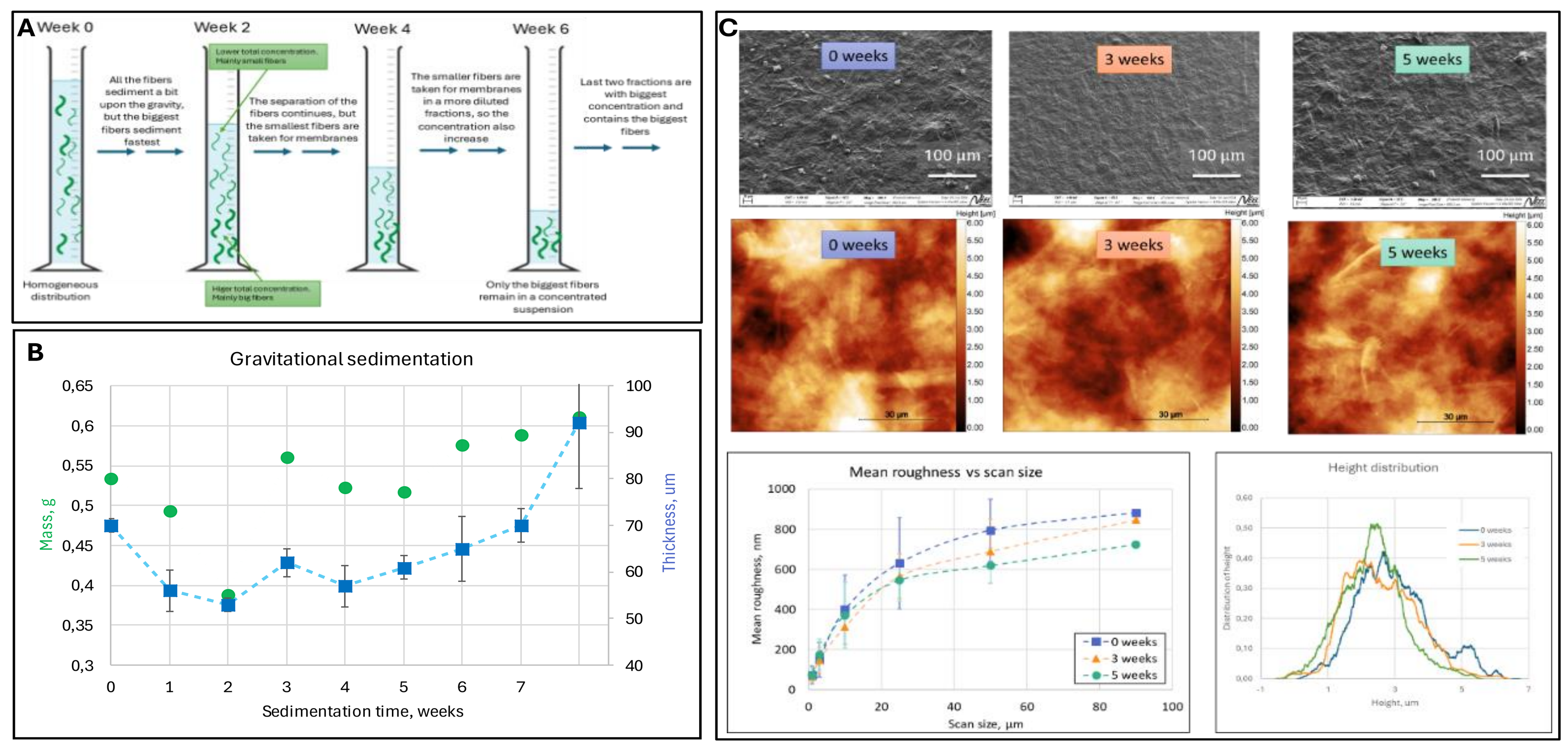



*Fig. 3:* ***Sedimentation process –*** *A. Summary of the principle. B. Mass and thickness of the casted membranes. C. SEM and SFM images, roughness extracted from the SFM images.*

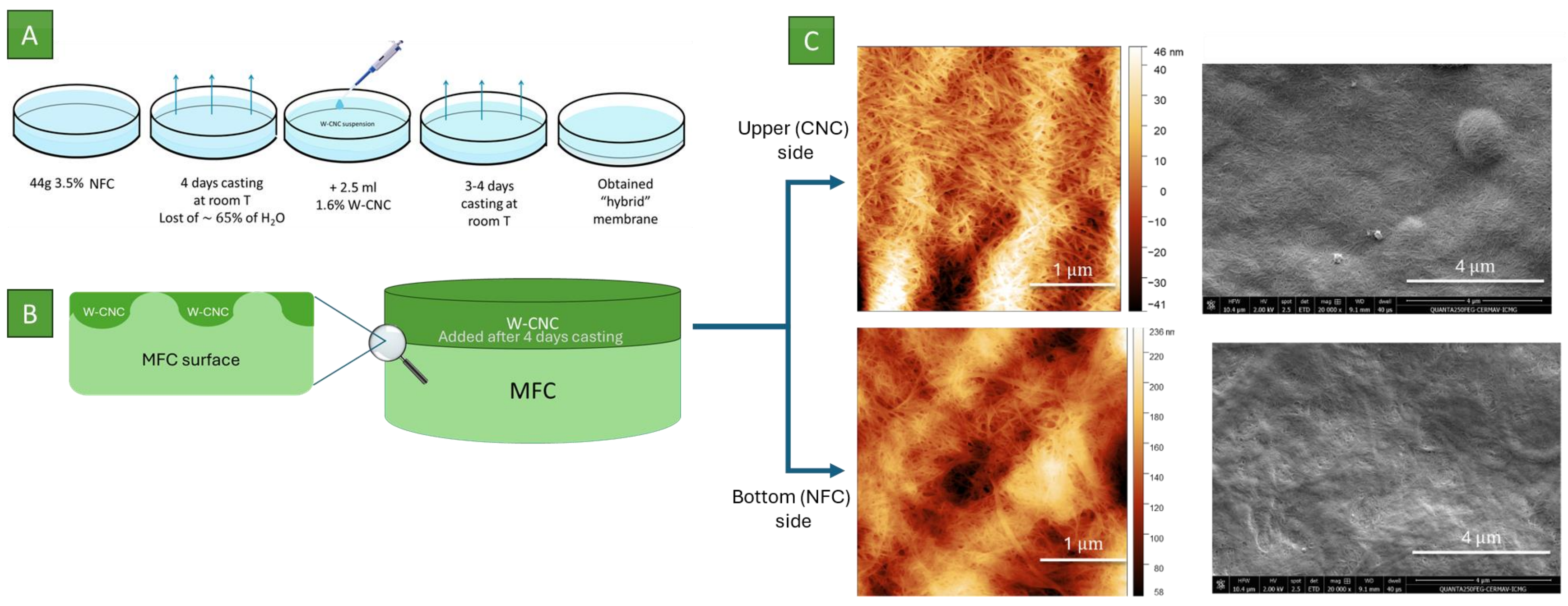
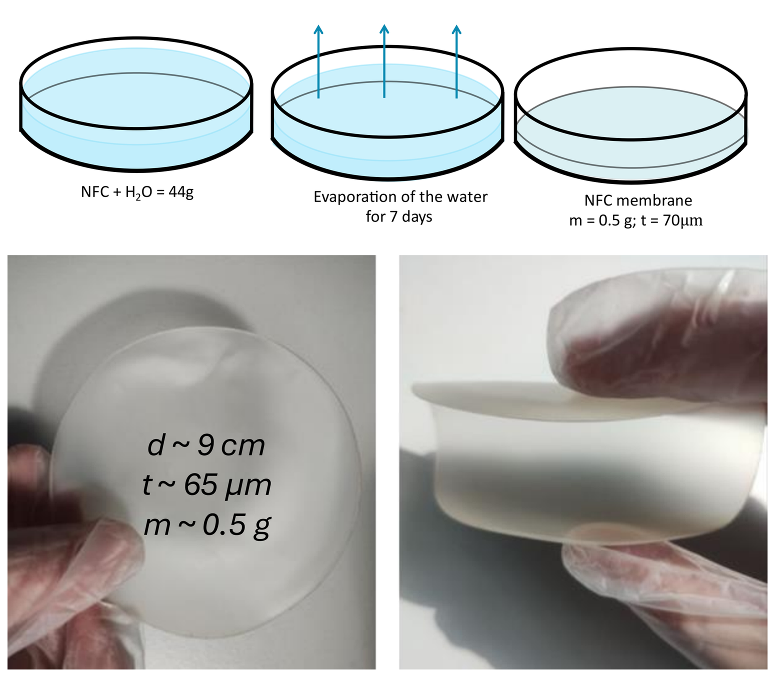
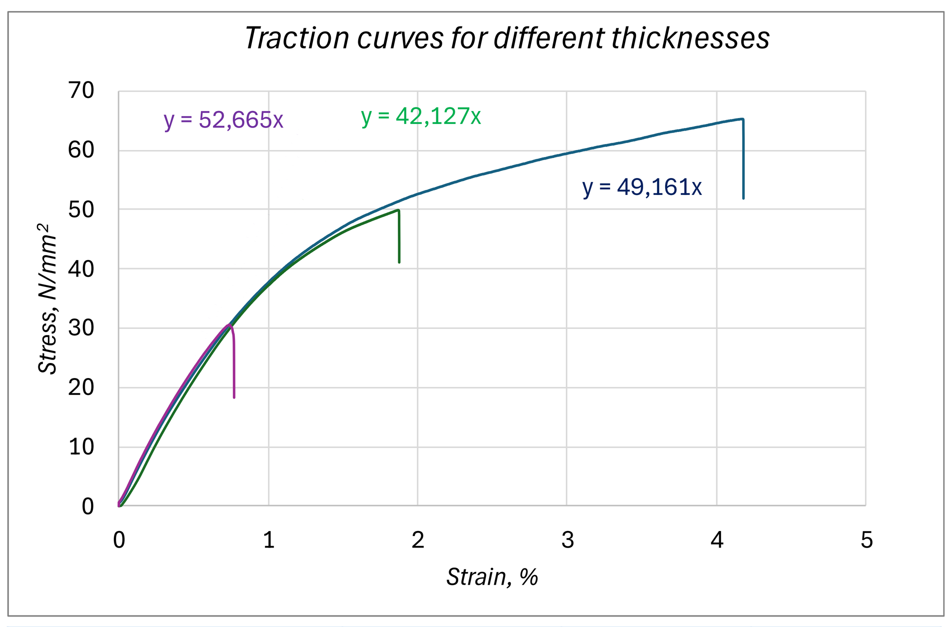



*Fig. 4: Schematic of A. hybrid casted membrane, i.e. NFC membrane with thin layer of W-CNC on the top. B. CNC effect on flatness. C. SFM and SEM of the both sides of the membrane.*

## NFC membrane as flexible support

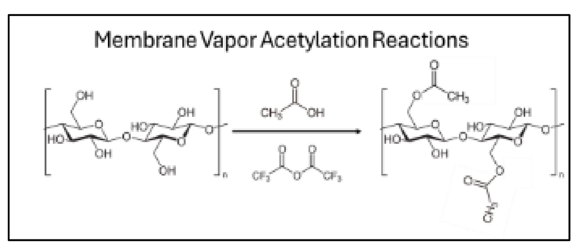



| | Young modulus | BP stress | BP strain |
|---|---|---|---|
| NFC membrane 65 µm | ~50 MPa | 65 N/mm² | 4% |
| Plain paper 110 µm | ~25 MPa | 40 N/mm² | 3% |

*Fig. 1: Air-casting method for preparing the NFC membrane (top left), flexibility and dimensions of the membrane (bottom left), tensile curve of NFC membrane with different thicknesses and comparison between nanopaper and plain paper (right)*

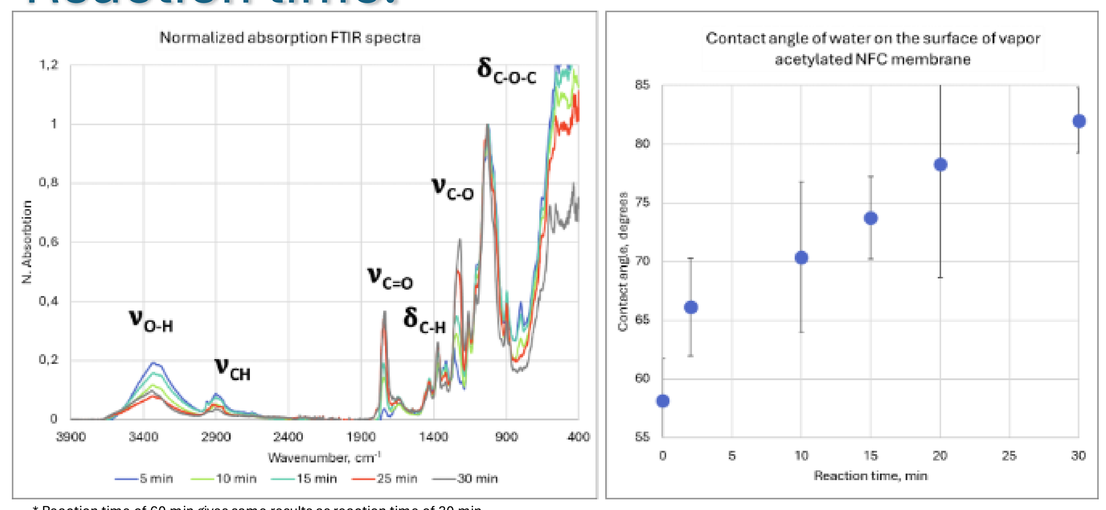
## Surface acetylation reaction



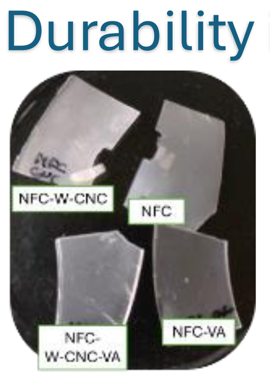

**Reaction Protocol:**

- NFC membrane: ~0.5 g, ~65µm, d = 8.5 cm, washed with EtOH
- Reaction mixture: 3 ml AcOH (0.05 mol) + 7 ml TFAA (0.05 mol)
- 1 min of pumping to obtain pressure < 100mBar, X min of acetylation at room T under saturation vapor
- 10 min of pumping, after ejection of the reaction mixture for the system – for removing absorbed gases from the membrane surface and washing for 2h with toluene

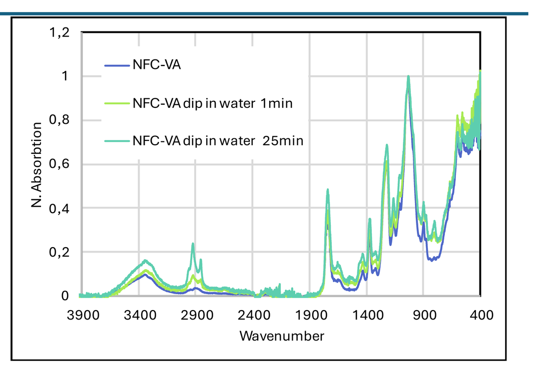
### Reaction time:




### Durability in water:



Acetylated membranes survive up to 15 min in water, while non-acetylated start swelling after less than 1 min.




**Conclusion:** No significant change in the chemical composition after contact with water.

*Fig. 2: Summary of the acetylation process for obtaining water-resistivity of the supporting membrane. The same reaction is used for acetylation of the triboactive CNC layer.*

## Conductive electrode and active layer

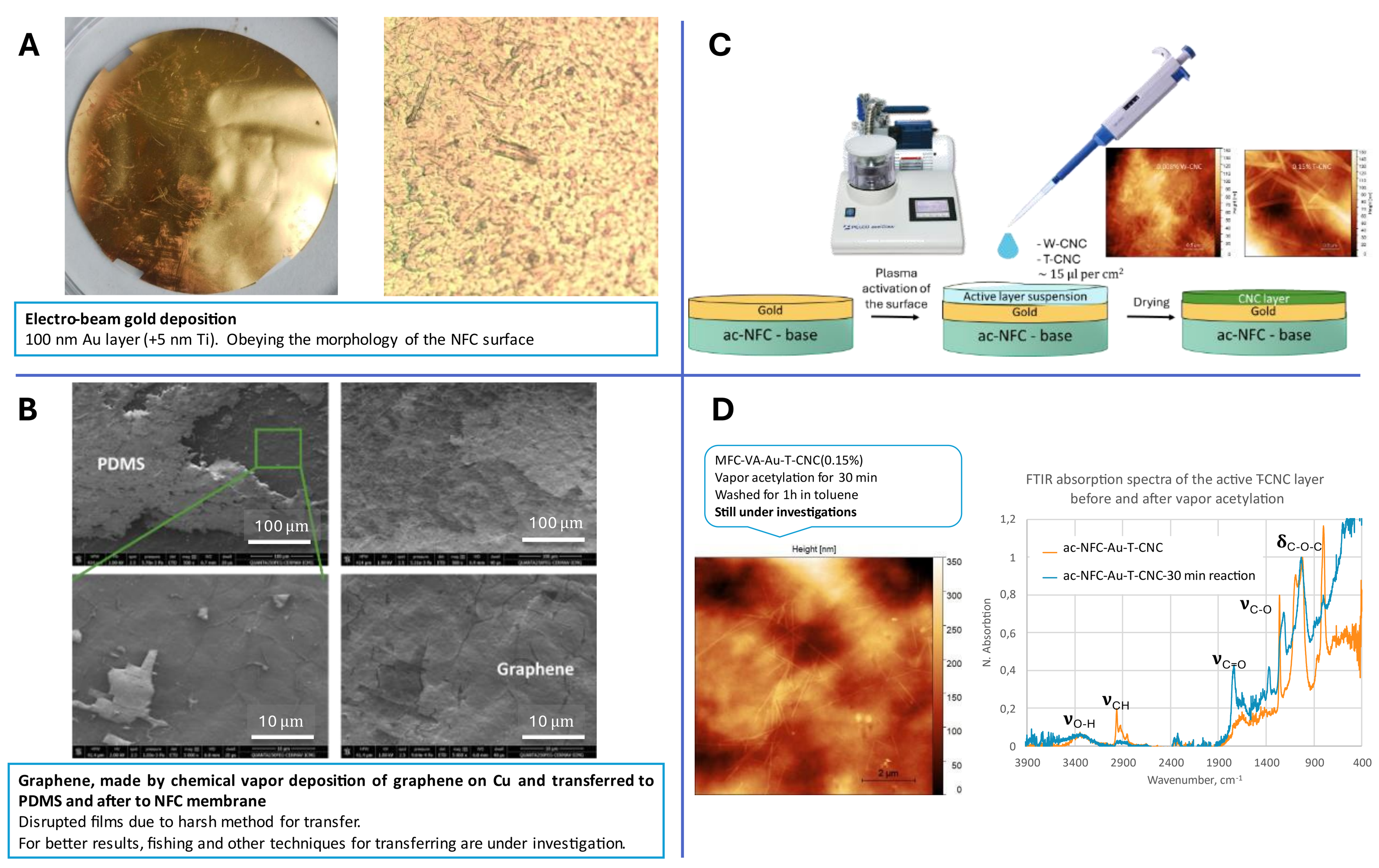



*Fig. 5: A. Gold layer obtained by electro-beam deposition: picture and optical microscope image. B. Graphene layer produced by CVD onto copper after transferring to PDMS to NFC membrane. C. Deposition of the triboelectric active layer based on W-CNC or T-CNC. D. SFM image and FTIR spectra after acetylation of the T-CNC layer.*

## Conclusion

The casting of flexible, waterproof NFC membranes with improved surface roughness was achieved by adding a thin layer of CNC to the NFC membranes and/or by removing large fibers from the initial NFC suspension through a sedimentation process. The water sustainability of the membranes was achieved by modifying the surface using vapor acetylation surface modification. On the resulting flexible nanopaper substrate, graphene or gold layer was successfully deposited as a conductive electrode. Multilayer graphene is being investigated as a means of improving conductance. A monolayer of CNC dispersed on the gold/nanopaper layer will serve as the proactive part in the final TENG device. The vapor acetylation of this top CNC is under investigation, but preliminary tirbocharging tests have been carried out.

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