

## Supporting information

### Preparation of aminated nanofibrillated cellulose (A-NFC)

#### 1. Experimental

##### 1.1. Materials

HNO<sub>3</sub> (65 %) was obtained from Fluka Chemicals and used as received. Propargyl amine (98 %), L-ascorbic acid (99 %), CuSO<sub>4</sub>·5H<sub>2</sub>O (99 %), epichlorohydrin (99 %), ninhydrin (95 %), diethylenetriamine (99 %), 2-propanol (99.8 %) and NaNO<sub>2</sub> (97 %) were purchased from Sigma-Aldrich and used as received. NaN<sub>3</sub> (99 %), acetic acid (100 %) and NaOH (99 %) were purchased from Merck and used as received.

Nanofibrillated cellulose was prepared at VTT Technical Research Centre of Finland by mechanical disintegration (Pääkkö et al., 2007). Bleached birch pulp was pre-treated with a Voith refiner and then fluidized by seven passes through an M7115 fluidizer from Microfluidics Corp (Newton, MA, USA). The solids content of the prepared water dispersion was 1.66 wt-%, with a xylan content of 25%.

##### 1.2. Preparation of 1-Azido-2,3-epoxypropane

The synthesis of 1-azido-2,3-epoxypropane was done starting from epichlorohydrin. The ring-opening reaction of the epoxide with azide-ion was done according to a slightly modified method (Fringuelli et al., 1999, Pahimanolis et al., 2010). Isopropanol (109.0 ml) and acetic acid (7.2 ml, 125.8 mmol) were mixed with a solution of NaN<sub>3</sub> (8.177 g, 125.8 mmol) in 74.0 ml of water. Epichlorohydrin (6.6 ml, 84.2 mmol) was then added under stirring and the reaction was continued at 30 °C for 21 h, until <sup>1</sup>H- and <sup>13</sup>C-NMR

analysis showed complete consumption of the epoxide. A water solution of  $\text{NaNO}_2$  (11.5 ml, 41.6 mmol) was then added, followed by the dropwise addition of  $\text{HNO}_3$  (5.76 ml, 83.8 mmol) to eliminate any excess azide-ions. The stirring was continued until the formation of nitrous oxides ceased. The obtained solution of 1-azido-3-chloropropanol (yield 100 % by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR analysis) was stored in dark at room temperature and used without further purification.

Warning! Low molecular weight organic azides are potentially explosive substances and handling concentrated solutions should be avoided.

$^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ , ppm):  $\delta = 3.41\text{-}3.50$  ( $\text{CH}_2\text{-Cl}$ ),  $3.58\text{-}3.69$  ( $\text{CH}_2\text{-N}_3$ ),  $4.02\text{-}4.07$  ( $\text{CH-OH}$ )

$^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}$ , ppm):  $\delta = 70.46$  ( $\text{C-OH}$ ),  $53.87$  ( $\text{C-N}_3$ ),  $46.64$  ( $\text{C-Cl}$ ).

The conversion of 1-azido-3-chloropropanol to 1-azido-2,3-epoxypropane was done just prior to use, by adding 26.3 ml of 5 M NaOH to the prepared 1-azido-3-chloropropanol-solution and stirring the mixture for 10 minutes. The obtained epoxide-solution (yield 100% by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR analysis) was immediately used for the azide-functionalization of NFC.

$^1\text{H}$ -NMR ( $\text{D}_2\text{O}$ ):  $\delta = 2.80\text{-}2.81$  and  $2.91\text{-}2.93$  ( $\text{CH}_2\text{O}$ ),  $3.25\text{-}3.35$  ( $\text{CH}_2\text{-N}_3$ ),  $3.70\text{-}3.73$  ( $\text{CHO}$ ).

$^{13}\text{C}$ -NMR ( $\text{D}_2\text{O}$ ):  $\delta = 52.38$  ( $\text{C-N}_3$ ),  $52.08$  ( $\text{CHO}$ ),  $46.12$  ( $\text{CH}_2\text{O}$ ).

### *1.3. Introducing azide-groups to the surface of NFC*

The azide-functionalization of NFC was done following a slightly modified method (Pahimanolis, et al. 2010): To a water suspension of NFC (1000 g, 16.6 g of solid content) 11.0 ml of 5M NaOH solution was added and the mixture was stirred for 60 minutes at 30 °C. The freshly prepared solution of 1-azido-2,3-epoxypropane (197 ml,

84.2 mmol) was then added and the reaction was continued for 24 h at 30 °C, pH=11.6, until <sup>1</sup>H-NMR analysis showed complete consumption of the epoxide. The suspension was then purified with deionized water by several centrifugation (20 000 g for 20 minutes) and redispersion steps until the pH of the suspension became neutral. The obtained azide functionalized NFC was stored in dark at room temperature for further use.

#### *1.4. Introducing primary amine groups to NFC Using CuAAC*

Propargyl amine (1.00 g, 18.2 mmol) was added to the suspension of azido-NFC (900 g, 1.66 % solids content). A freshly prepared solution of CuSO<sub>4</sub>·5H<sub>2</sub>O (0.203g, 0.81 mmol) and ascorbic acid (AAc) (0.288 g, 1.64 mmol) in 2ml of water was then added, yielding an immediate bright yellow color. The reaction was carried out for 3 hours at 30 °C, after which diethylenetriamine (0.300 g, 2.91 mmol) was added to the reaction mixture in order to complexate the copper ions. The suspension was stirred for another 30 minutes and by this time the color of the suspension turned from yellow to light blue. The suspension was then purified with deionized water by several centrifugation (20 000 g for 20 minutes) and redispersion steps, until the supernatant became neutral and no amines were detected with the ninhydrin test.

## **2. Characterization**

### *2.1. NMR*

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded on a Bruker Ultrashield Plus 400 MHz spectrometer in deuterium oxide (D<sub>2</sub>O). For quantitative <sup>13</sup>C-NMR, the decoupler was gated on only during acquisition, in order to suppress the nuclear Overhauser effect.

## 2.2. FT-IR

The infrared-spectra were obtained with Nicolet Magna IR750 from dried NFC-sheets.

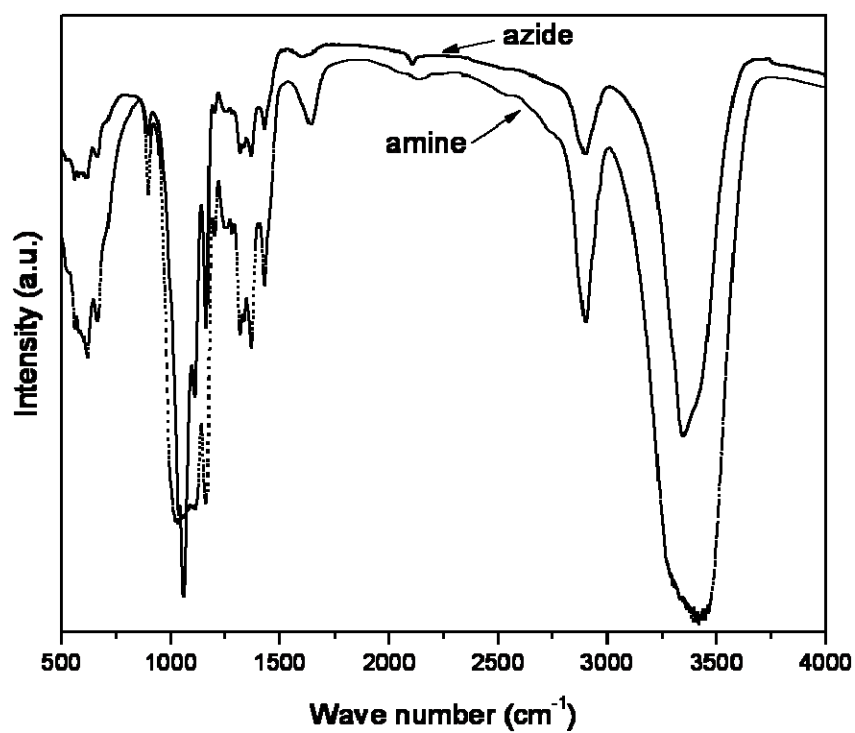
## 2-3. Elemental analysis

Elemental analysis was performed using a Perkin Elmer 2400 Series II CHNS equipment.

The EA results for the azidated NFC: (atom-%): C 27.42, H 47.22, N 0.20.

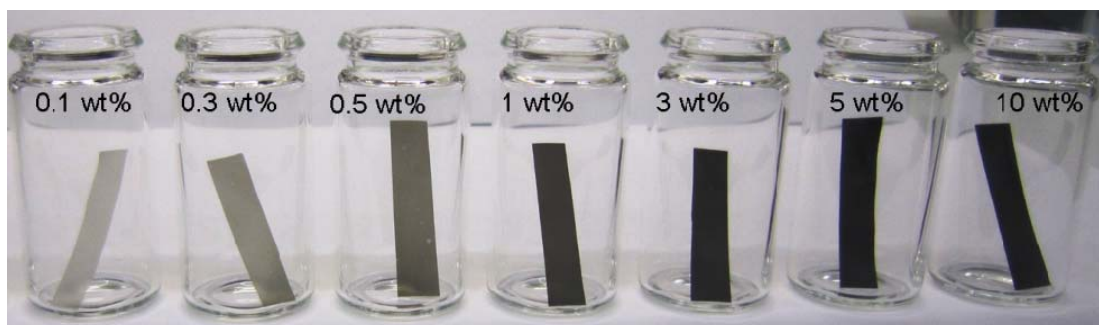
And for amino-functional NFC: (atom-%): C 27.76, H 46.75, N 0.26.

The increase in nitrogen is about 30%, as would be expected from the reaction of azide with propargyl amine.

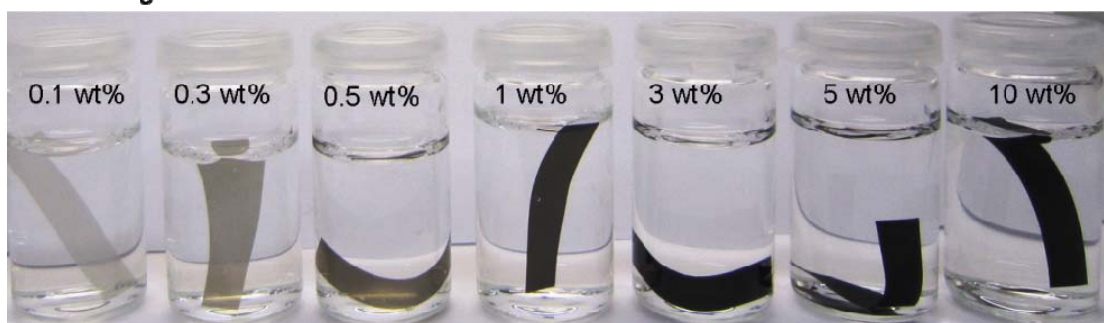


**Fig. S11.** FT-IR spectra of azide-functionalized NFC and amine-functionalized NFC.

**Before: dried state**



**after being immersed in water for 3 months**



**Fig. S12.** Photographs of RGO/A-NFC composite papers with different content of graphenes before and after being immersed in de-ionized water at ambient temperature for three months, showing the high stability of the papers in water environment.

## References

1. Fringuelli, F., Piermatti, O., Pizzo, F., Vaccaro, L. (1999). Ring opening of epoxides with sodium azide in water. A regioselective pH-controlled reaction. *Journal of Organic Chemistry*, 64, 6094-6096.
2. Pahimanolis, N., Vesterinen, A-H., Rich, J., Seppala, J. (2010). Modification of dextran using click-chemistry approach in aqueous media. *Carbohydrate Polymers*, 82, 78-82.
3. Pääkkö, M., Ankerfors, M., Kosonen, H., Nykanen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., Lindström, T. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*, 8, 1934-1941.