Supplementary Information (SI) for Nanoscale.

Supporting Information

Cellulose nanopapers with polymeric nanoparticle additives – what is the role of nanoparticle surface functionality?

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1. Synthesis of macroCTAs

The water-soluble oligomeric block responsible for nanoparticle stabilization (macroCTA) is synthesized in solution polymerization. The polymers are purified through dialysis or precipitation before chain extended in emulsion polymerization.

1.1 Formulations macroCTA

Table S1. *MacroCTAs and their formulations.*

	CTPPA	monomer	initiator	solvent	monomer	monomer	rxn time	conversion
	mg, eq	ml, mg, eq	mg, eq	ml	vol %	[M]	hr	%
PMAA	832; 1	6.33; 6457; 25	84; 0.1	23.7	21	2.5	4	95
PGMA	334; 1	NA; 5304; 25	33.75; 0.12	18	8.6	1.3	4	98
POEGMA	111; 1	4.76; 5000; 25	11; 0.1	15.2	24	0.5	20	97

RAFT agent CTPPA, initiator ACVA, monomer conversion calculated by ^{1}H NMR.

1.2 Synthesis of macroCTA_A: (MAA)$_{25}$-CTPPA

In this section we detail the synthesis of the hydrophilic block used in PISA to make particles with anionic poly(methacrylic acid) shell surface.

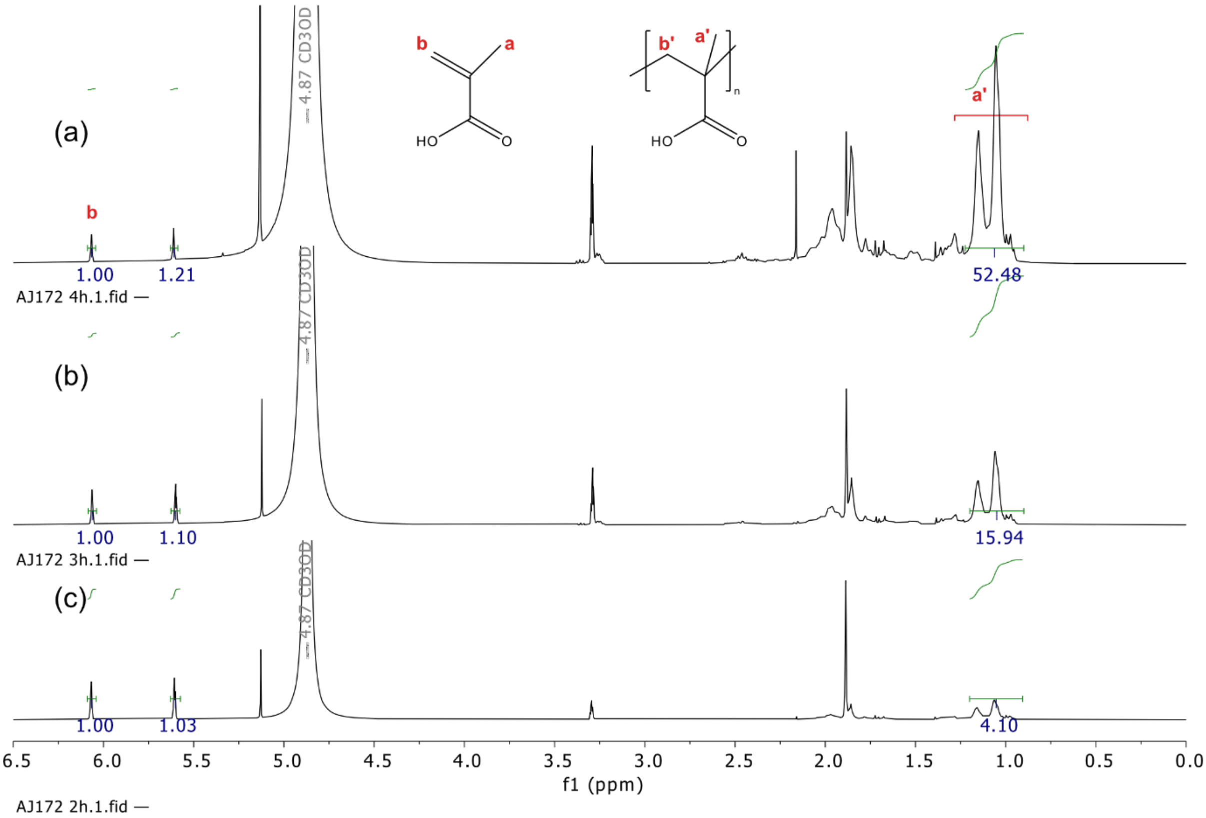


Figure S1. RAFT polymerization of methacrylic acid (MAA) in water for (a) 4, (b) 3 and (c) 2 hours. Spectra in deuterated methanol CD$_3$OD, with an aliquot of the crude reaction mixture at each time point.

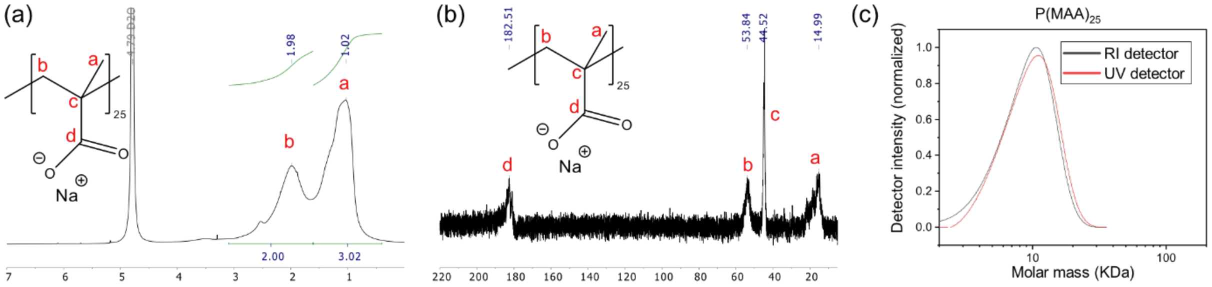


Figure S2. *Purified macroCTA poly(methacrylic acid)-CTPPA (PMAA). ^{1}H-NMR (a), ^{13}C-NMR in D_2O (b) and (c) size exclusion chromatography in DMSO, showing refractive index (RI) signal and UV signal (280 nm) confirming trithiocarbonate moiety on chains throughout distribution. The polymer end-groups are not visible in ^{1}H or ^{13}C NMR.*

Table S2. *DMSO-SEC values from methylated and non-methylated anionic macroCTA_A (mCTA).*

Target M.W.	mCTA_A (RI-DMSO)		mCTA_A (UV-DMSO)		mCTA_A-me (RI-DMSO)		mCTA_A-me (RI-DMF)	
	M_n	Đ	M_n	Đ	M_n	Đ	M_n	Đ
kDa	kDa	-	kDa		kDa	-	kDa	-
2.4	7.7	1.26	8.6	1.20	4.3	1.38	4.0	1.28

1.3 Synthesis of macroCTA_G: (GMA)$_{25}$-CTPPA

In this section we detail the synthesis of the hydrophilic block used in PISA to make particles with non-ionic poly(glycerol monomethacrylate) shell surface.

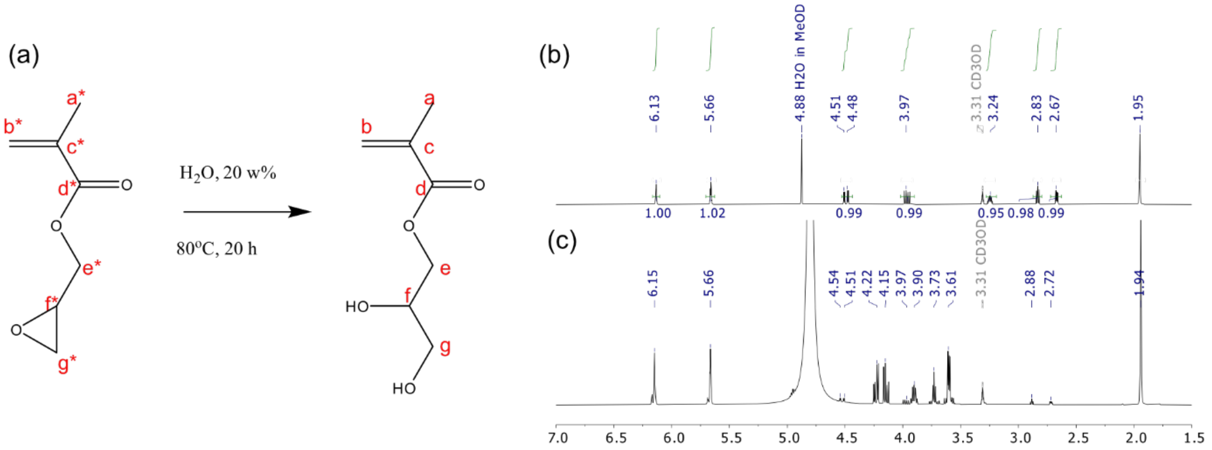


Figure S3. *(a) Synthesis of glycerol methacrylate (GMA) by hydrolysis of glycerol methacrylate (GlyMA). (b) Glycerol methacrylate starting material, and (c) hydrolysis product into GMA with conversion ~84%.*

Table S3. *Assignments and integrals of GlyMA and GMA.*

Peak	**GlyMA**		**GMA**	
ppm	**assign.**	**integral**	**assign.**	**integral**
6.13	**b***	**1**	**b**	1.24
5.66	**b***	1.02	**b**	1.35
4.51	**e***	0.99	-	-
4.48	**e***		-	-
4.21	-	-	**e**	1.06
4.15	-	-	**e**	1.04
3.97	**e***	0.99	-	0.19
3.90	-	-	**f**	**1**
3.73	-	-	-	0.85
3.61	-	-	**g**	2.03
3.24	**f***	0.95	-	-
2.83	**g***	0.98	-	0.13
2.67	**g***	0.99	-	0.13
1.95	**a***	3.05	**a**	3.68

Conversion ~84% calculated from signals e and f at 3.97 and 3.90 ppm.*

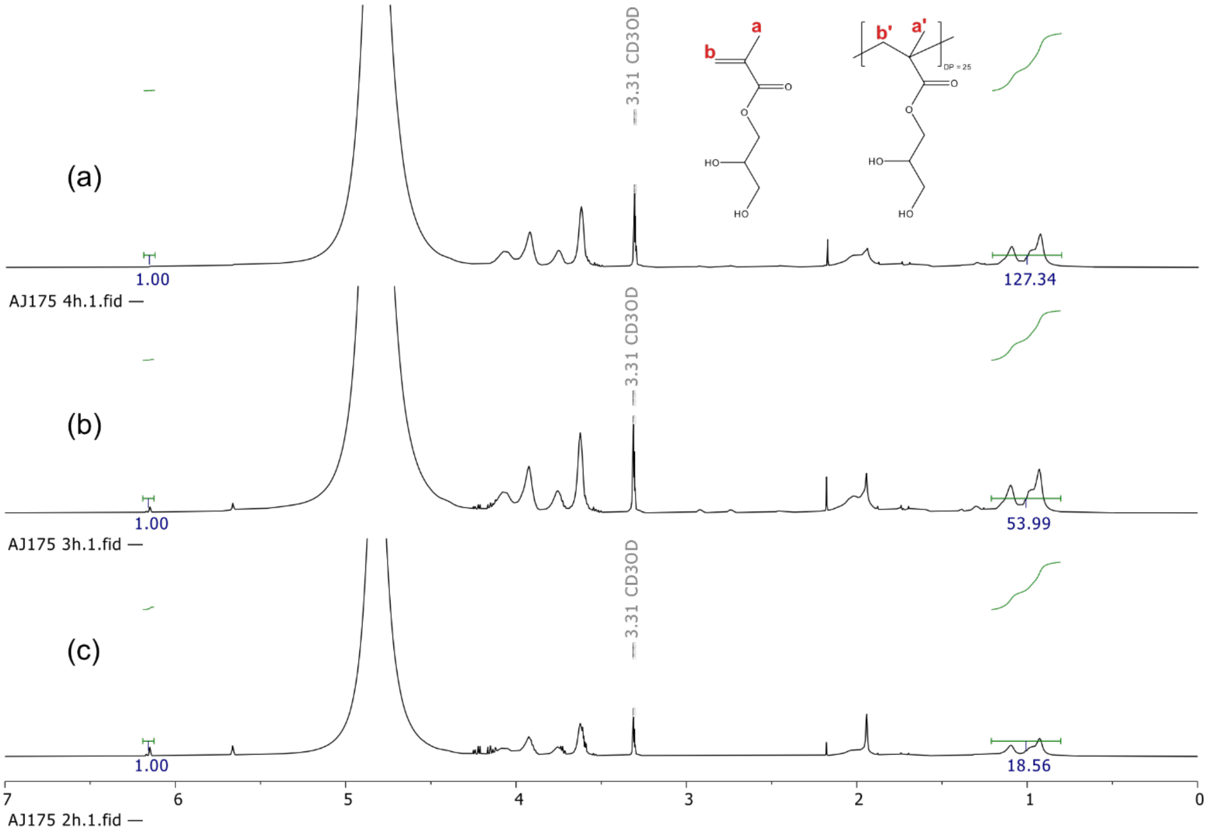


Figure S4. *RAFT polymerization of glycerol monomethacrylate (GMA) in water for (a) 4, (b) 3 and (c) 2 hours. Spectra in deuterated methanol CD_3OD.*

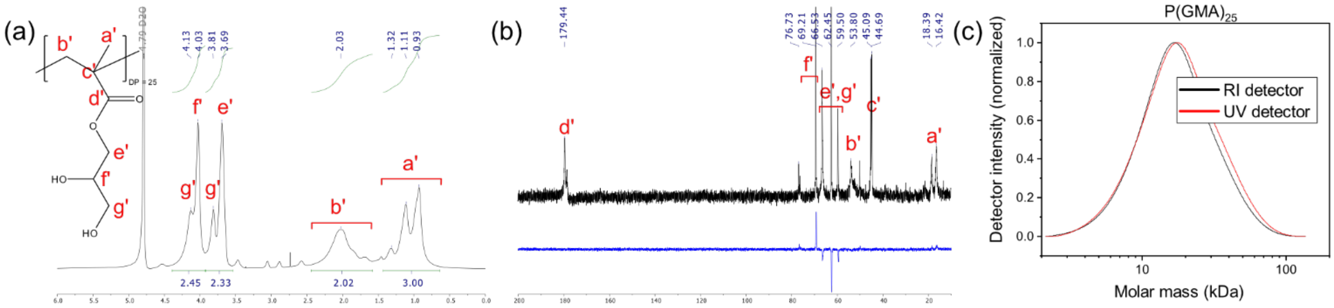


Figure S5. *Purified macroCTA poly(glycerol monomethacrylate)-CTPPA (PGMA).* ^{1}*H-NMR (a),* ^{13}*C-NMR in* D_2O *(b) and (c) size exclusion chromatography in DMSO, showing refractive index (RI) signal and UV signal (280 nm) confirming trithiocarbonate moiety on chains throughout distribution. The polymer end-groups are not visible in* ^{1}*H or* ^{13}*C NMR.*

1.4 Synthesis of macroCTA_O: (OEGMA$_{500}$)$_{25}$-CTPPA

In this section we detail the synthesis of the hydrophilic block used in PISA to make particles with polymeric/brush-type poly(ethylene glycol) shell surface.

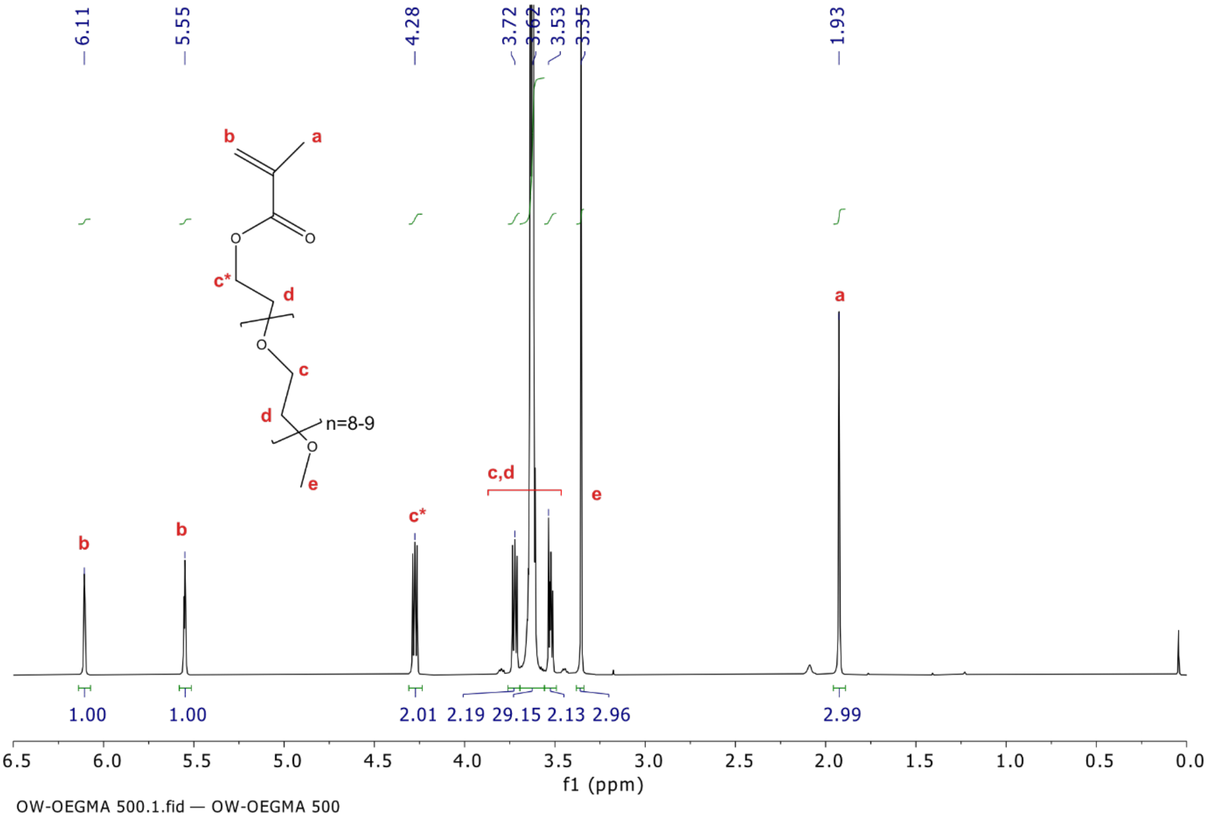


Figure S6. *Commercial monomer of oligoethylene glycol methacrylate (OEGMA) with reported average molecular weight 500 g mol*$^{-1}$*.* ^{1}*HNMR of monomer shows a degree of polymerization (DP) of 8.9, i.e.* M_n *of 465 g mol*$^{-1}$*.*

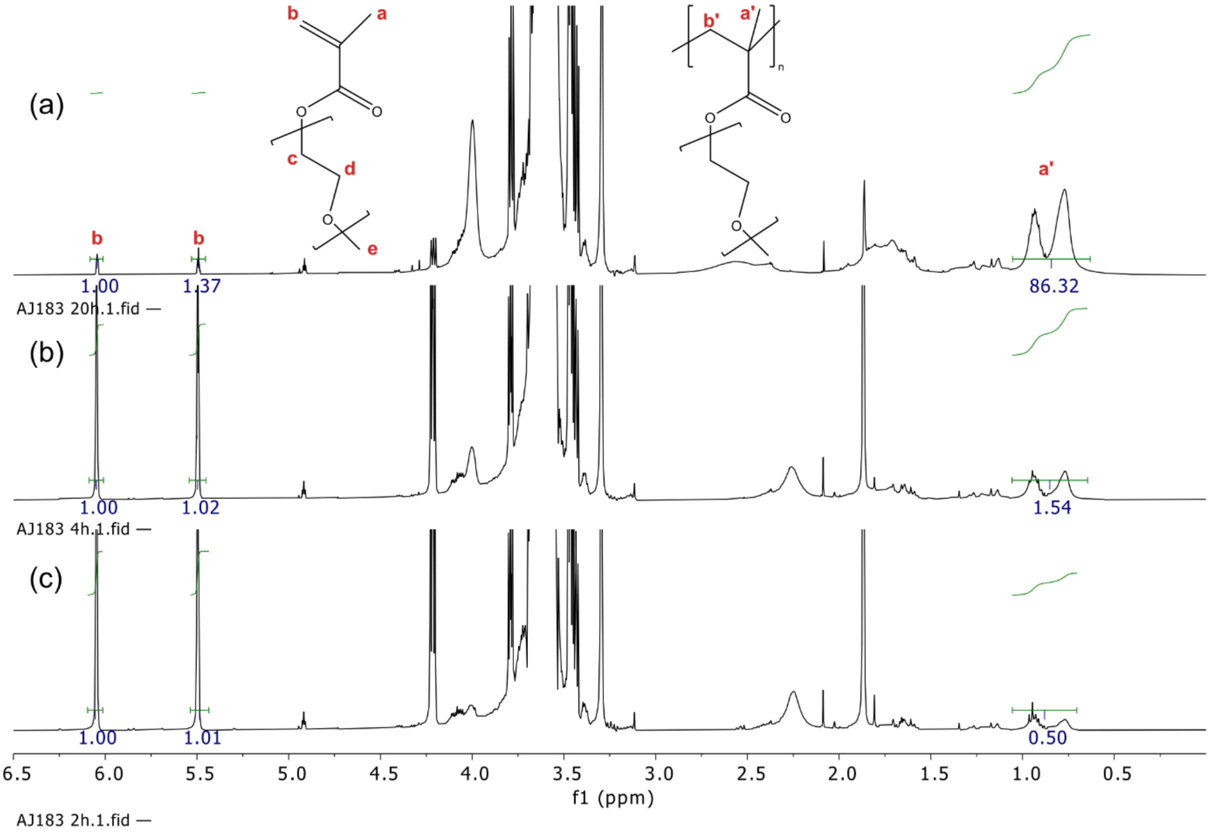


Figure S7. *RAFT polymerization of OEGMA500 in 1,4-dioxane for (a) 20, (b) 4 and (c) 2 hours. Spectra in $CDCl_3$.*

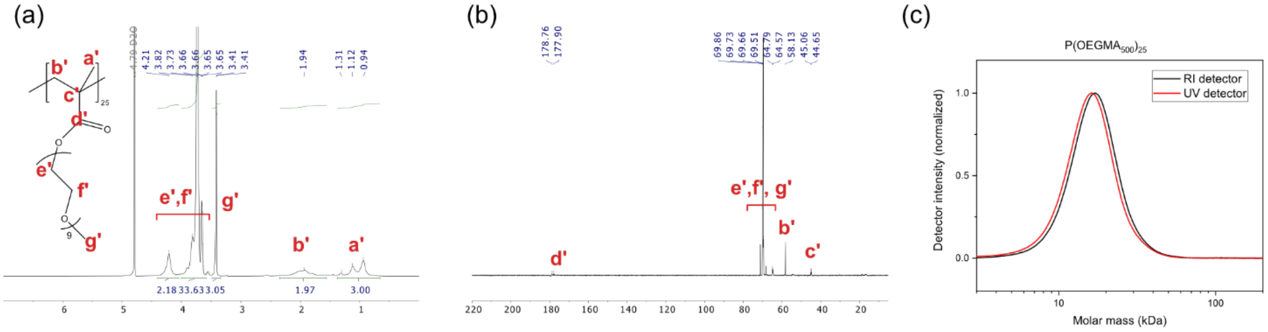


Figure S8. *Purified macroCTA poly(oligoethylene glycol)-CTPPA (POEGMA). ^{1}H-NMR (a), ^{13}C-NMR in D_2O (b) and (c) size exclusion chromatography in DMSO, showing refractive index (RI) signal and UV signal (280 nm) confirming trithiocarbonate moiety on chains throughout distribution. The polymer end-groups are not visible in ^{1}H or ^{13}C NMR.*

Table S4. *DMSO-SEC values from poly(glycerol monomethacrylate) macroCTA_A (mCTA).*

mCTA_O (RI-DMSO)		mCTA_O (UV-DMSO)		mCTA_O (RI-DMF)	
M_n	*Đ*	M_n	*Đ*	M_n	*Đ*
15.3	1.17	14.3	1.18	12.8	1.18

2. Polymerization-induced self-assembly (PISA)

2.1 Formulations PISA

Table S5. *Formulations of block copolymers made through polymerization-induced self-assembly (PISA).*

	macroCTA	MMA	initiator	solvent	dry content	monomer	rxn time	conversion
	mg, eq	ml, mg, eq	mg, eq	ml	wt%	[M]	hr	%
np_A	228, 1	2.0, 1880, 200	3.16, 0.12	19	10	0.54	5	93
np_G	659, 1	1.5, 1410, 100	4.74, 0.12	18.7	10	0.7	4	93
np_O	900, 1	1.5, 1410, 200	2.37, 0.12	20.8	10	0.63	4	>80

2.2 Polymerization-induced self-assembly (PISA) – polymer characterization

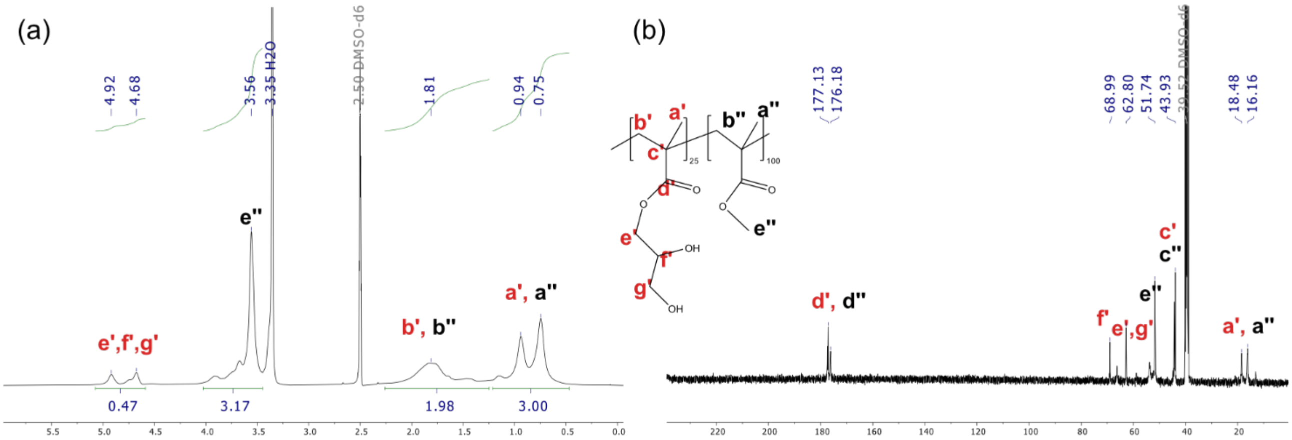


Figure S9. *(a) ^{1}H NMR of the P(GMA)-b-P(MMA) block copolymer made through RAFT-PISA.*

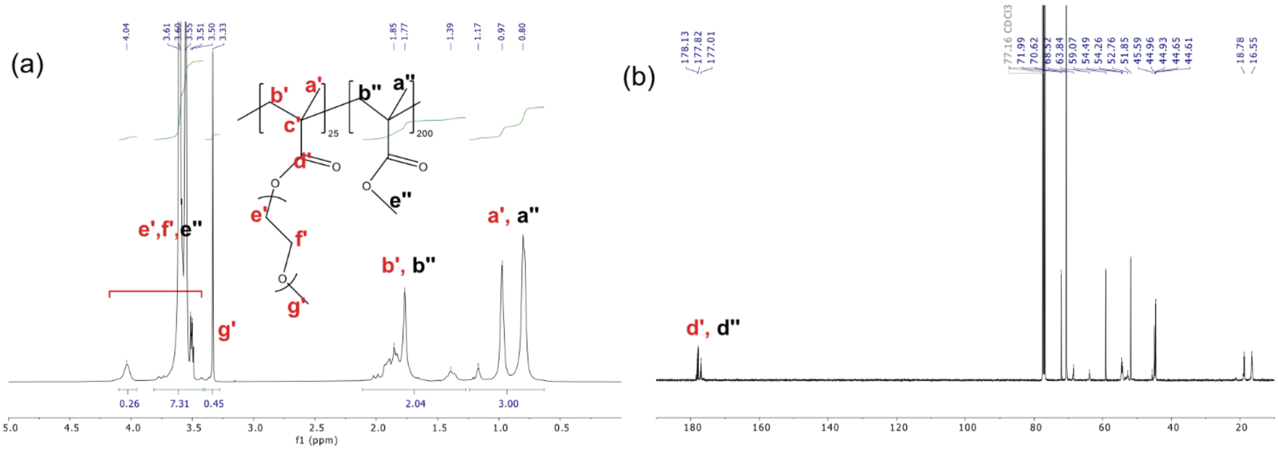


Figure S10. *(a) ^{1}H NMR of the P(OEGMA)-b-P(MMA) block copolymer made through RAFT-PISA. The ratio between OEGMA and MMA units is calculated from the methyl signals at 1.2-0.8 ppm vs. the methyl signal at 3.33 ppm belonging only to OEGMA. (b) ^{13}C NMR of the block copolymer.*

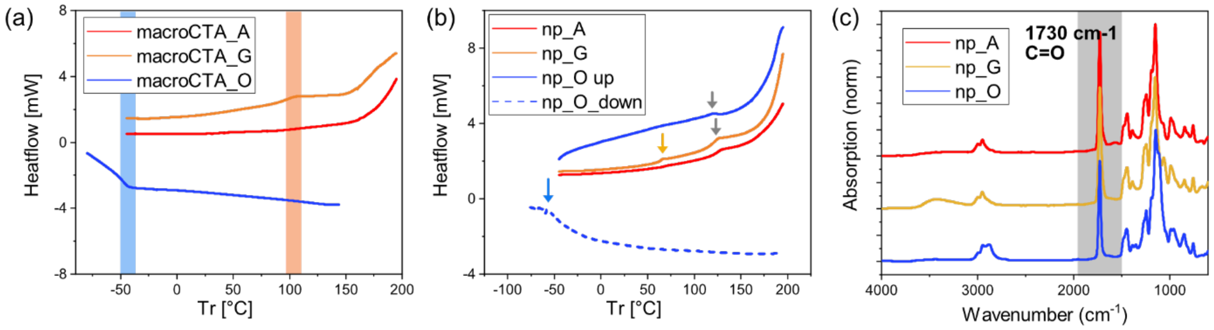


Figure S11. *(a) DSC curves of macroCTAs, (b) DSC curves of nanoparticles, and (c) ATR-FTIR of all nanoparticles made through RAFT-PISA.*

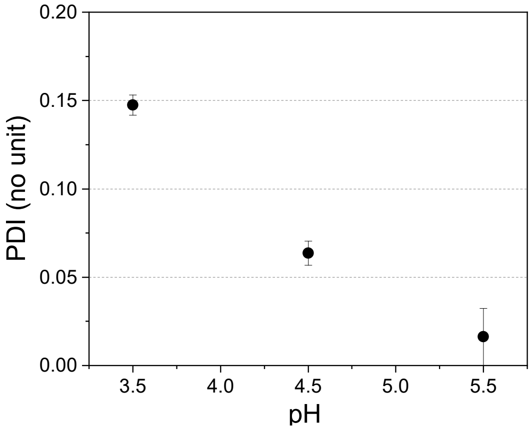


Figure S12. *Influence of pH on PISA of macroCTA_A shows the importance of pH and ionization to achieve low PDI (ie size dispersity).*

2.2 Polymerization-induced self-assembly (PISA) – colloidal characterization

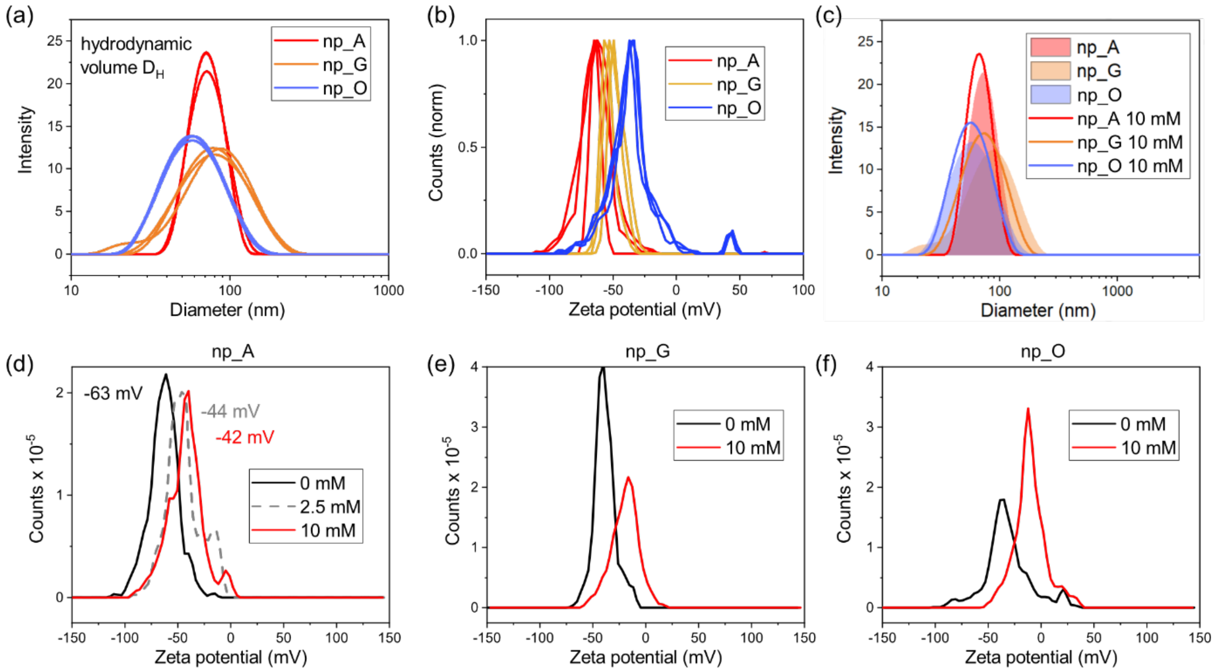


Figure S13. *DLS and zeta potential of colloidal nanoparticles. (a) hydrodynamic diameters and distributions from DLS, (b) zeta potential distributions, (c) influence of buffer (10 mM) on particle size, (d-f) influence of buffer (10 mM) on zeta potential.*

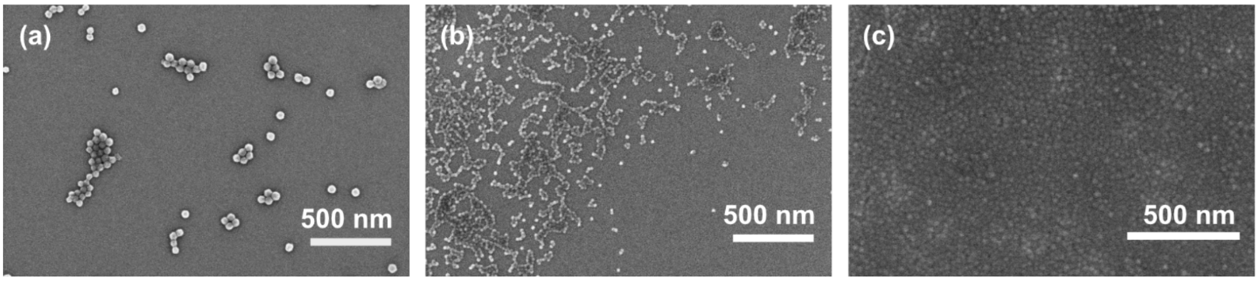


Figure S14. *FE-SEM of polymeric nanoparticles cast on silicon wafer. (a) anionic MAA particles, (b) glycerol-functional particles and (c) PEG/OEGMA functional particles. The sizes of nanoparticles are analyzed in ImageJ and reported as D_{SEM} in the main manuscript.*

3. Preparation of cellulose nanofibrils (CNFs)

3.1 Preparation of cellulose nanofibrils (CNFs)

Table S6. *Characterization of CNFs*

Surface charge (µmol g^{-1})
770 ± 10

4. Fabrication of nanopapers

4.1 Formulations nanopapers

Table S7. *Details of the hybrid nanopapers fabricated in this study.*

Sample name	Latex (wt%)	CNF disp. 2.77 g L^{-1} (ml)	Water (ml)	Latex disp. (ml)	Buffer molarity in latex (mM)	Buffer molarity total (mM)
CNF	0	88.19	33.95	0.00	-	0
CNF_A_0.5	0.5	87.75	33.78	0.61	10	0.1
CNF_A_25	25	66.14	25.46	30.54	10	2.5
CNF_O_0.5	0.5	87.75	33.78	0.61	10	0.1
CNF_O_25	25	66.14	25.46	30.54	10	2.5
CNF_G_0.5	0.5	87.75	33.78	0.61	10	0.1
CNF_G_25	25	66.14	25.46	30.54	10	2.5
CNF_A_25_B0	25	66.14	25.46	30.54	0	0
CNF_G_25_B0	25	66.14	25.46	30.54	0	0

Hybrid dispersions are made, keeping dry content 2 g L^{-1} constant and with varying ratios between CNF and latex. CNF dispersion with dry content 2.77 g L^{-1} is diluted with distilled water. The latex is diluted in phosphate buffer to 1 g L^{-1} before use, the total buffer content in hybrid dispersion is shown.

4.2 Characterization of nanopapers

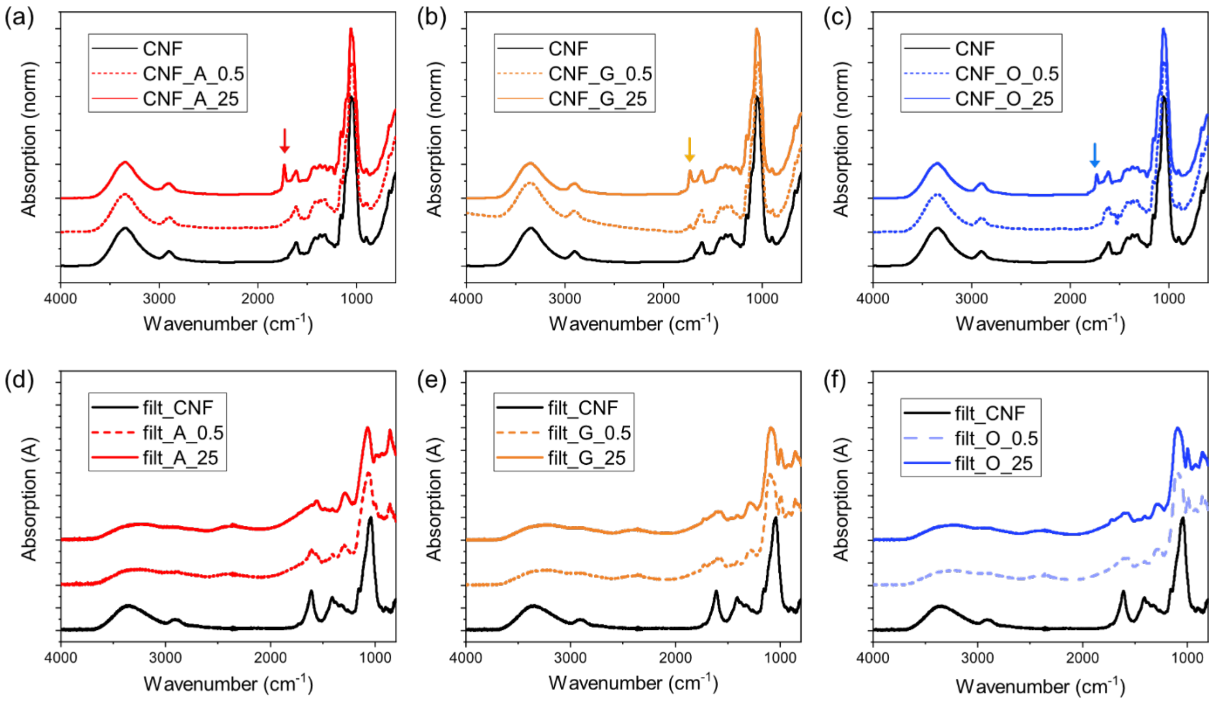


Figure S15. *FTIR of nanopapers and filtrate. (a-c) FTIR-ATR of CNF sheet surfaces, and (d-f) FTIR-ATR of freeze dried filtrate waters.*

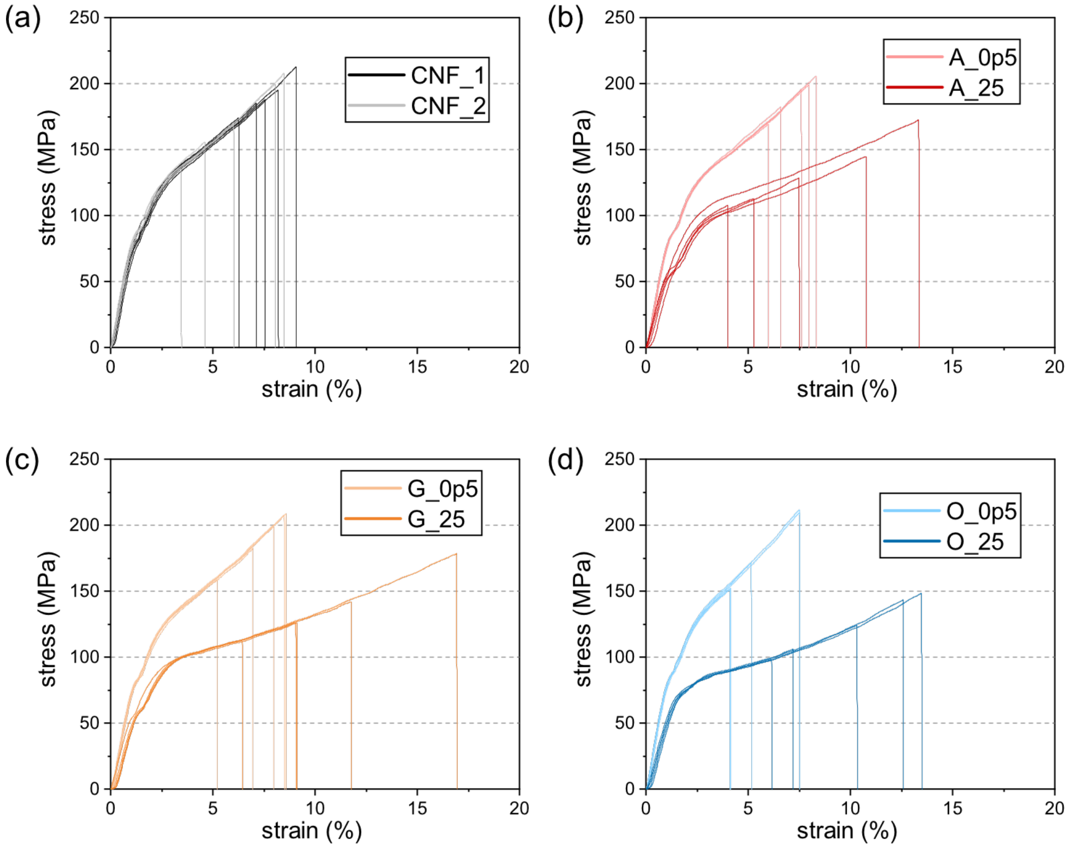


Figure S 16. *Stress-strain curves for nanopapers (a) CNF reference (CNF_1 and CNF_2 are two different nanopapers), (b) nanopapers made with np_A and buffer, (c) nanopapers made with np_G and buffer, and (d) nanopapers made with np_O and buffer.*

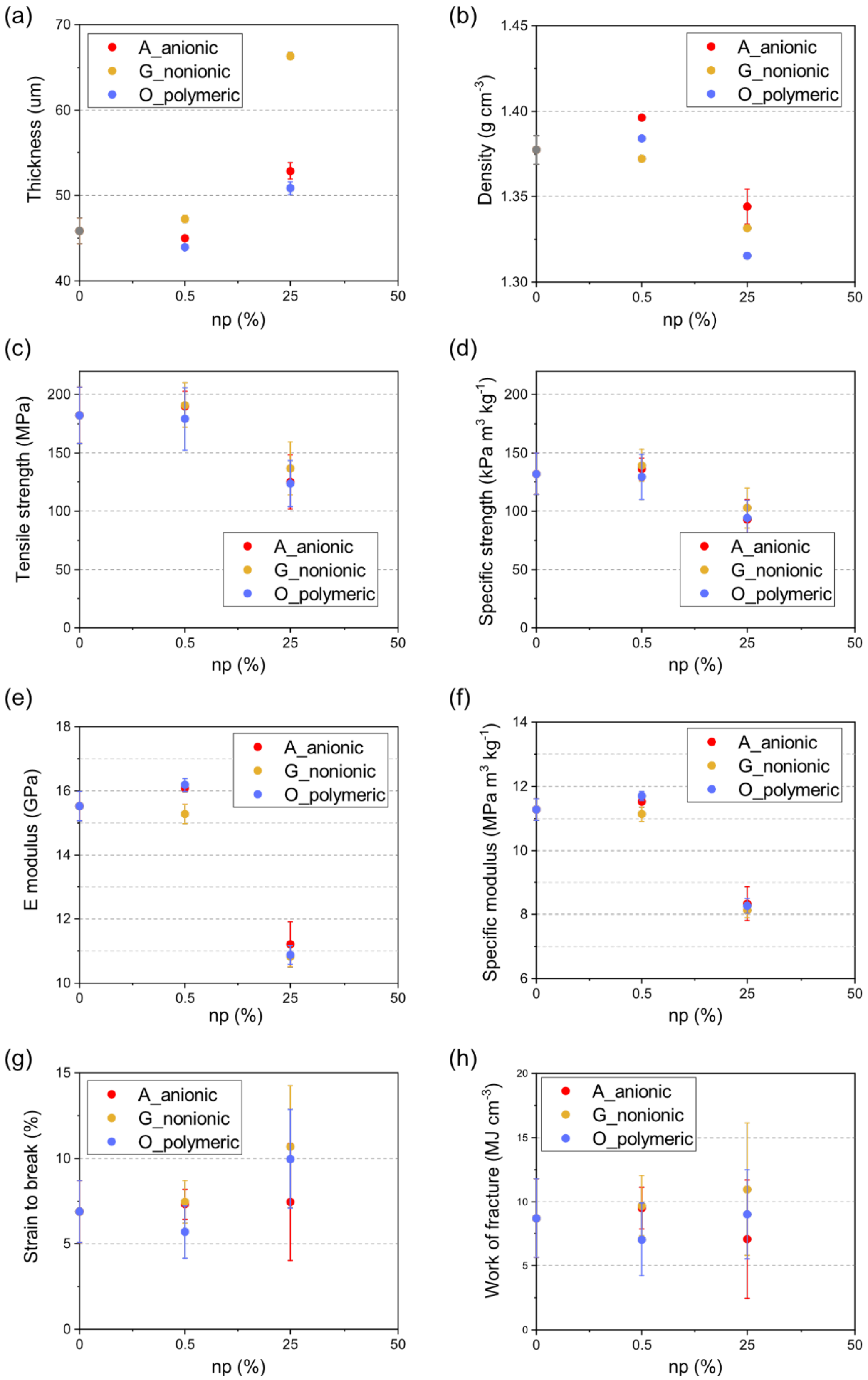
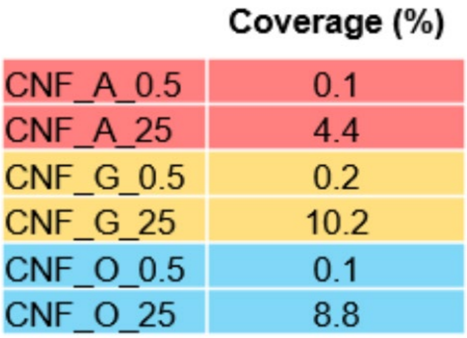


Figure S17. *Characterization of hybrid nanopapers. (a) thickness and (b) density. (c,d) Tensile strength and specific strength, (e,f) Young's modulus and specific modulus, (g) strain at break and (h) toughness / work of fracture.*



	Coverage (%)
CNF_A_0.5	0.1
CNF_A_25	4.4
CNF_G_0.5	0.2
CNF_G_25	10.2
CNF_O_0.5	0.1
CNF_O_25	8.8

Figure S18. *Theoretical surface coverage of CNFs by nanoparticle additives*