

Supporting Information

Fully-biobased zwitterionic membranes with superior antifouling and antibacterial properties prepared via surface-initiated free-radical polymerization of poly (cysteine methacrylate)

*Luis Valencia¹, Sugam Kumar¹, Blanca Jalvo¹, Andreas Mautner², German Salazar-Alvarez¹
and Aji P. Mathew^{1*}*

*¹Division of Materials and Environmental Chemistry, Stockholm University, Frescativägen 8,
10691, Stockholm, Sweden*

*²Polymer and Composite Engineering (PaCE) Group, Institute of Materials Chemistry and
Research, Faculty of Chemistry, University of Vienna, Währinger Str. 42, 1090 Wien, Austria*

±Author to whom correspond: aji.mathew@mmk.su.se

1.1. Extraction of Nanocellulose. Cellulose nanofibers (CNF) were prepared by means of mechanical fibrillation of cellulose fibers using an ultrafine friction grinder (Masuko Supermasscolloider, model MKZA 10-15J Corp., Japan) at 1500 rpm. The suspension (2wt%) with a batch size of 2 L was passed through the Masuko 7 times to obtain a thick gel of nanofibers, and the processing time was 40 min per batch. The uniformity and quality of cellulose nanofibers was examined by Atomic Force Microscopy (Nanoscope V, Veeco Instruments, Santa Barbara, CA, USA). Images are presented in Supporting Information (S3)

1.2. Synthesis of Cysteine Methacrylate (CysMA). The synthesis of monomer was carried out following a reported procedure¹⁶. In a 250 mL round-bottom flask, L-cysteine (15.13 g, 124.88 mmol) was dissolved in deionized water. 3-(acryloyloxy)-2-hydroxypropyl methacrylate (29.43 g) was added to the solution, followed by dimethylphenyl phosphine (147 μ mol) and let stirring for 2 h at 20 °C. The reaction was washed twice with ethyl acetate (50 mL) and dichloromethane. The monomer was isolated as a pure white solid (86% yield) and concentrated by freeze-drying.

Table S1. XPS data for the Unmodified and ZM-2 membranes

Line	Unmodified			ZM-2			Interpretation
	BE, eV	FWHM, eV	AC, at. %	BE, eV	FWHM, eV	AC, at. %	
C 1s	285,0	1,15	5,83	285,0	1,3	28,04	C-(C,H)
	286,8	1,05	43,17	286,4	1,2	25,15	C-OH, C-NH ³⁺ , C-COOH
	288,3	1,05	10,81	288,9	1,15	6,15	O-C-O, C=O
	289,6	1,35	1,08	289,9	1	3,71	COOH
				291	1	1,05	O=C-O
O 1s				534	1,3	3,0	C=O
	533,2	1,4	39,11	532,6	1,7	23,43	C-OH
N 1s				400,0	1,6	0,86	NH ₂
				402,0	1,35	0,31	NH ₃ ⁺
S 2p				163,5	1,05	0,23	
				164,5	1,2	0,11	
Si 2p				102,7	1,45	4,01	Si-O

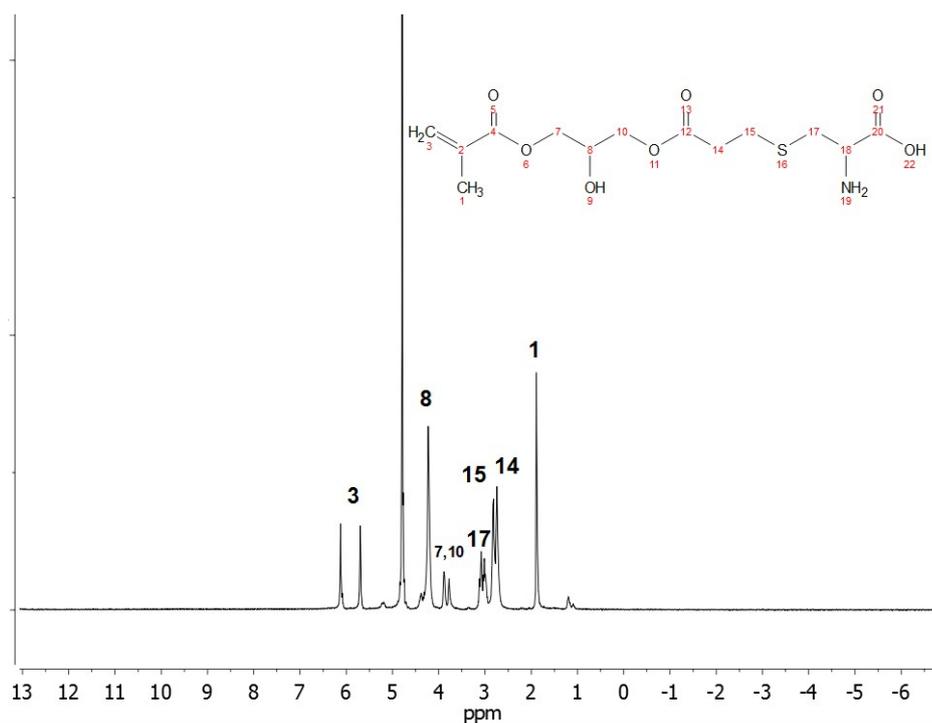


Figure S1. ¹H NMR of Cysteine methacrylate (CysMA)

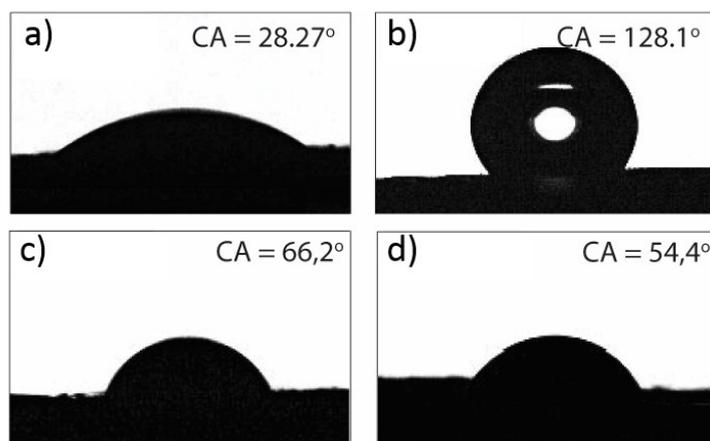


Figure S2. Contact angle measurements of nanocellulose membranes. (a) Unmodified membrane; (b) Membrane after immobilization of free radical initiator; (c) ZM-1; and (d) ZM-2

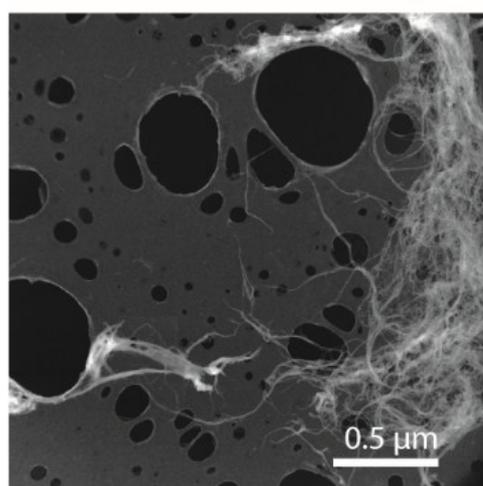


Figure S3. STEM image of the employed nanocellulose for fabrication of nanopapers. The average diameter is 3,95 nm

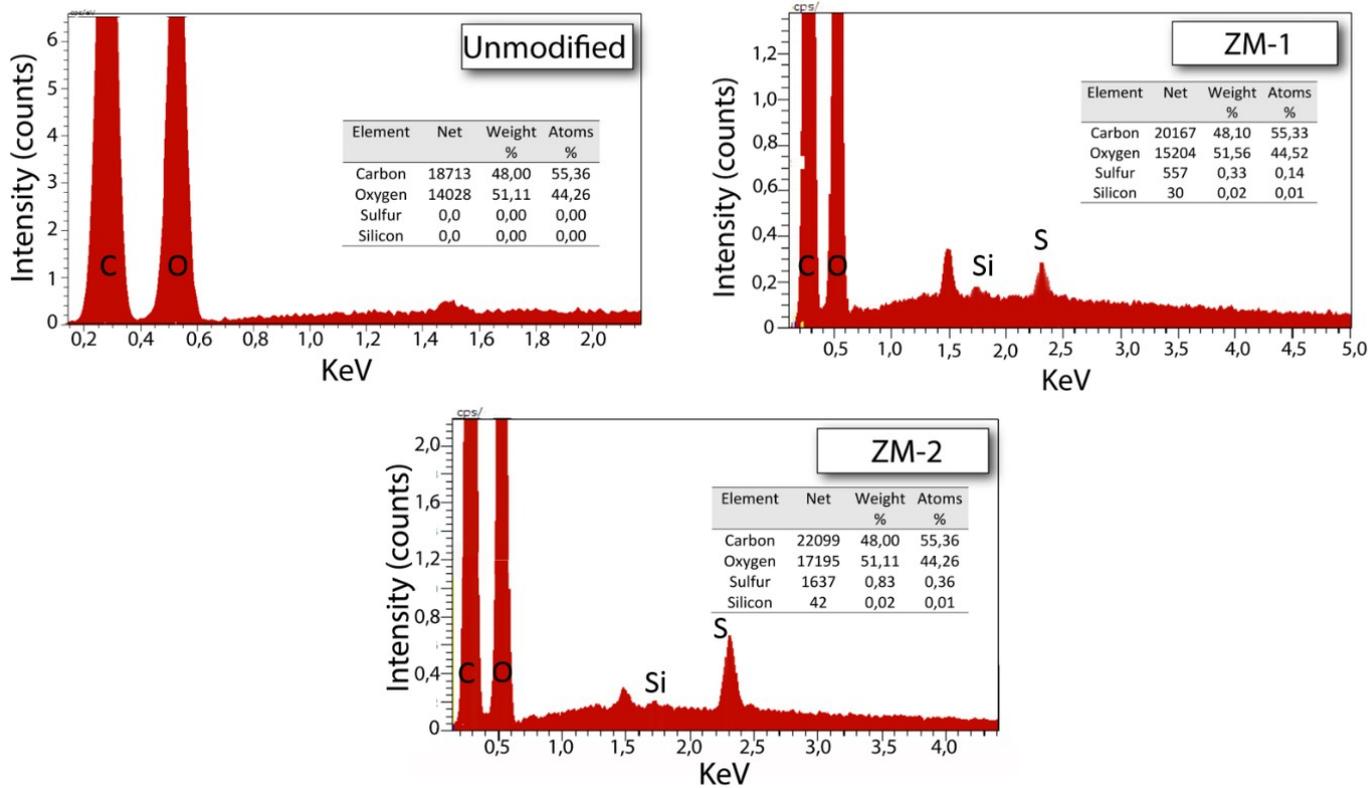


Figure S4. EDS Spectra of unmodified and Zwitterionic membranes

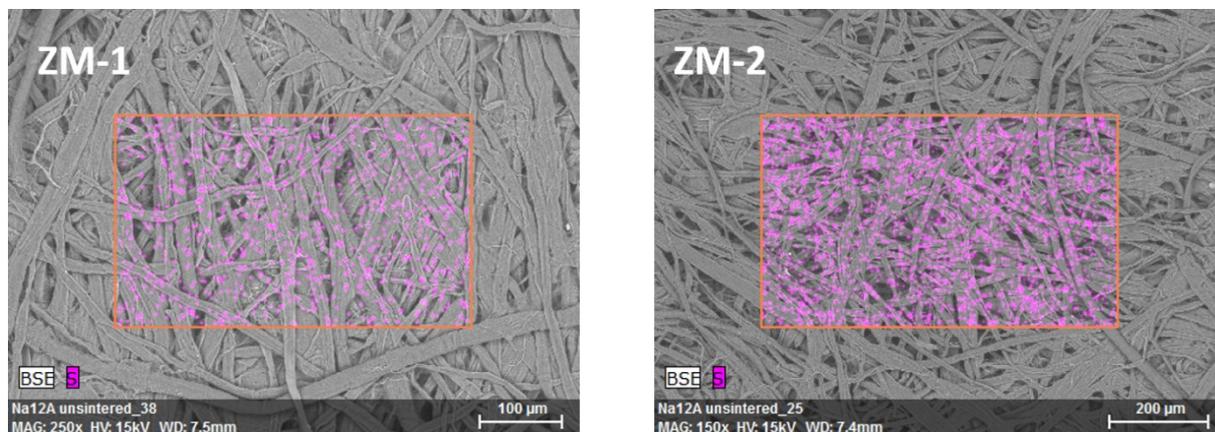


Figure S5. EDS elemental mapping from Sulfur of Zwitterionic membranes

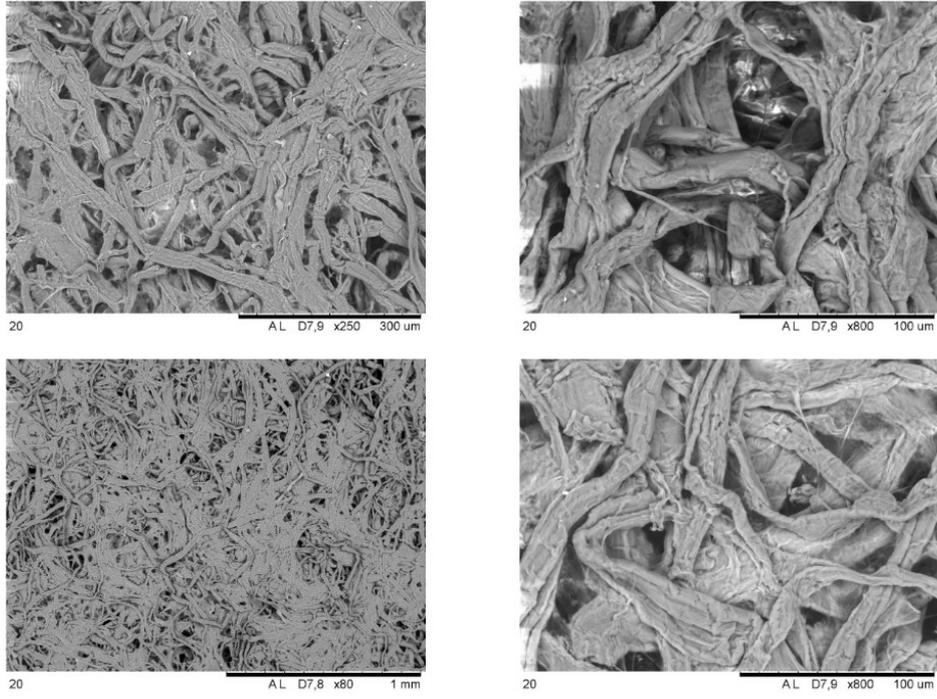


Figure S6. SEM micrograph of unmodified membrane

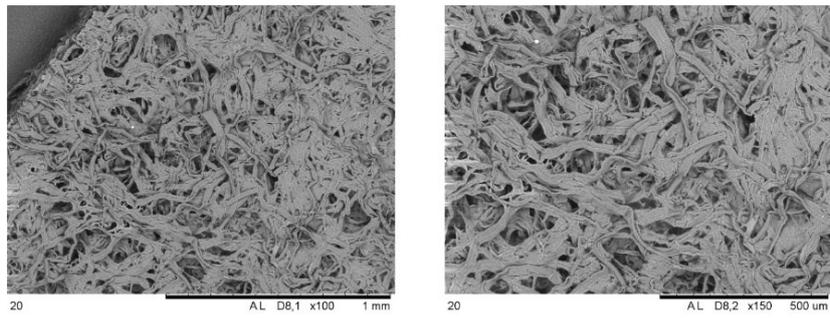


Figure S7. SEM micrograph of ZM-1

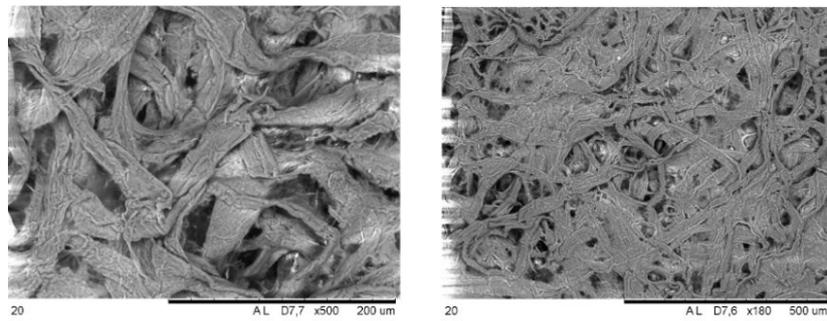


Figure S8. SEM micrograph of ZM-2

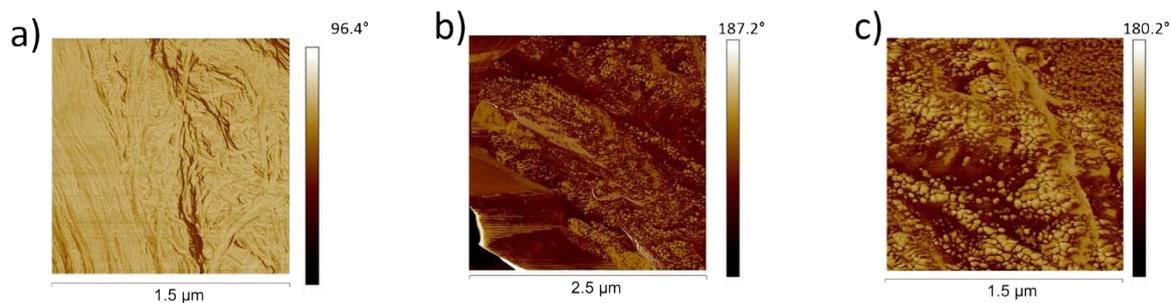


Figure S9. 2D AFM micrographs of Zwitterionic membranes: (a) Unmodified; (b) ZM-1, (c) ZM-2

Table S2. Relative quantification of *S. aureus* biofilm formation and BSA adsorption on the nanocellulose based materials.

Sample	FDA Relative biofilm formation (\pm SD)	Qubit Protein BSA adsorption (\pm SD)
Unmodified	1.00 \pm 0.12	70.27 \pm 3.25
ZM-1	0.38 \pm 0.14	59.71 \pm 2.26
ZM-2	0.13 \pm 0.09	11.17 \pm 2.11