Supporting Information: Surface sulfation of crab chitin for anisotropic swelling and nanodispersion

Xijun Wang,[†,‡] Pan Chen,[*,¶] Xiao Feng,[‡] Chao Dang,[‡] Baofeng Lin,[*,†] Yoshiharu Nishiyama,[*,§] and Haisong Qi[*,‡]

†*School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China*

‡*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China*

¶*Beijing Engineering Research Centre of Cellulose and Its Derivatives, School of Materials Science and Engineering, Beijing Institute of Technology, 100081, Beijing, P.R. China*

§*Univ. Grenoble Alpes, CNRS, CERMAV, 38000 Grenoble, France*

E-mail: panchen@bit.edu.cn; lbf@gxu.edu.cn; yoshi@cermav.cnrs.fr; qihs@scut.edu.cn

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1 Scheme of heterogeneous sulfation of chitin

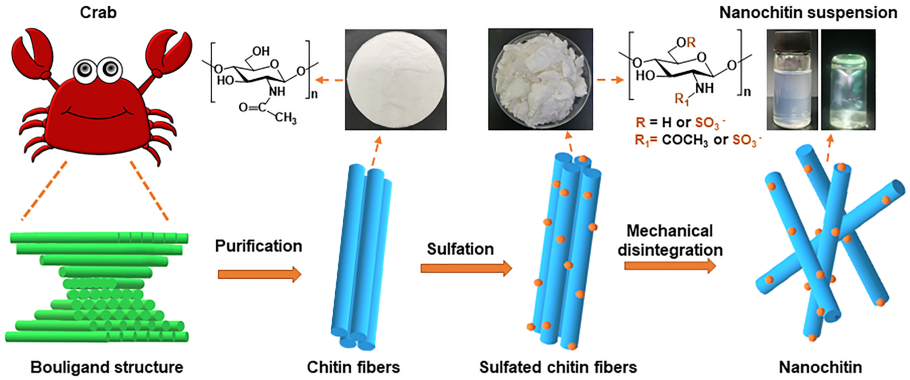

Figure S1: Schematic illustration of heterogeneous sulfation of chitin. Crab chitin containing Bouligand structures, are purified as white powder, heterogeneously sulfated to keep the macroscopic aspect, but can be dispersed in to nanochitin by mechanical disruption

2 Elemental analysis data used in the study

Table S1: Elemental analysis data and the corresponding degree of sulfation of samples used in the study

No	sulfation conditions			C	H	N	S	DS_1	DS_2	DS_3
	T(°C)	time (min)	C (g/L)							
0	-	-	-	43.41	6.515	6.31	0	–	–	–
1	60	5	50	44.07	6.77	6.58	0.07	0.00	0.00	0.00
2	70	5	50	43.3	6.69	6.41	1.02	0.07	0.07	0.07
3	80	5	50	38.45	6.33	6.12	3.3	0.26	0.24	0.24
4	90	5	50	36.29	6.57	6.46	4.34	0.36	0.33	0.29
5	100	50	5	33.09	6.57	6.56	4.41	0.40	0.36	0.29
6	80	5	10	44.26	6.56	6.38	0	0.00	0.00	0.00
7	80	5	30	44.15	6.46	6.86	1.98	0.13	0.13	0.13
8	80	5	70	39.58	6.29	6.43	4.73	0.36	0.33	0.32
9	80	5	100	36.22	6.23	6.96	4.99	0.41	0.37	0.31
10	80	15	50	35.85	6.12	6.67	4.81	0.40	0.37	0.31
11	80	30	50	35.43	6.21	6.99	5.13	0.43	0.39	0.32
12	80	60	50	36.21	6.28	6.89	5.19	0.43	0.39	0.33
13	80	120	50	37.04	6.18	6.77	5.52	0.45	0.40	0.36

3 Polarized optical micrographs

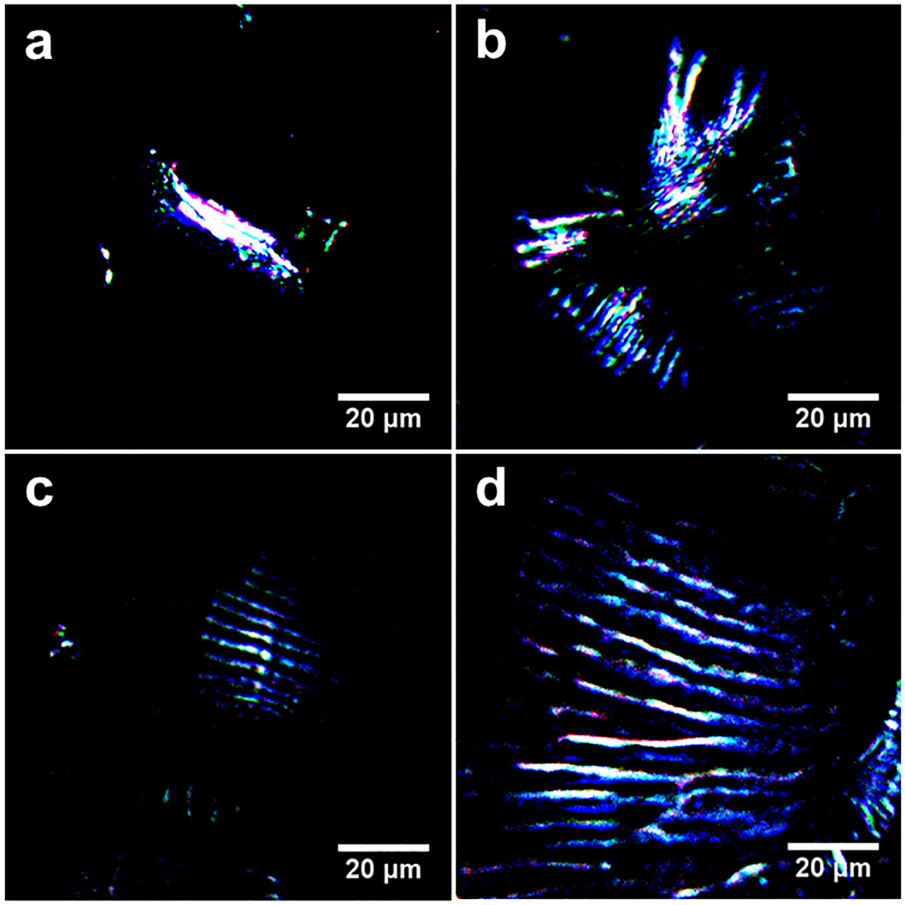

Figure S2: Polarized optical micrographs of chitin powder particles in water. a) before sulfationn b) after 5 min c) 15 min and d) 30 min of sulfation reaction using 50 gL^{-1} sulfamic acid at 80°C.

4 Fibril width from electron micrographs

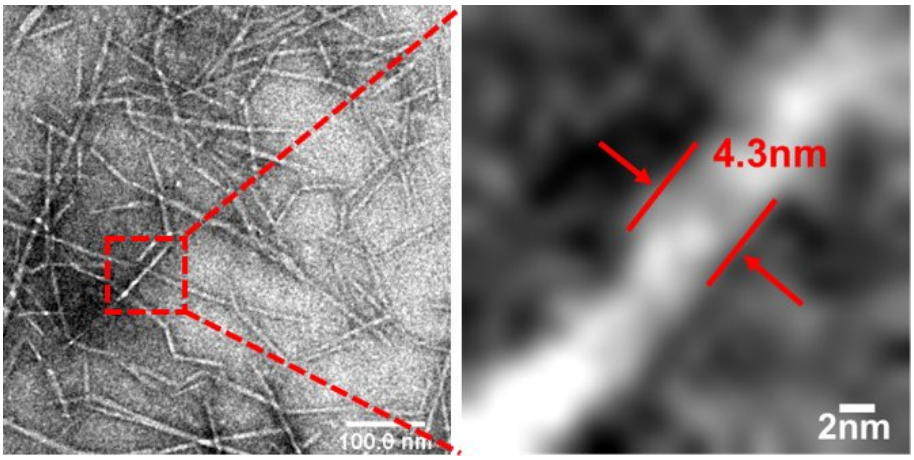

Figure S3: Example of negative stained electron micrographs and the width estimation of individual fibril taking the border of the negative stain

5 AFM images of chitin nanofibrils with longr treatment

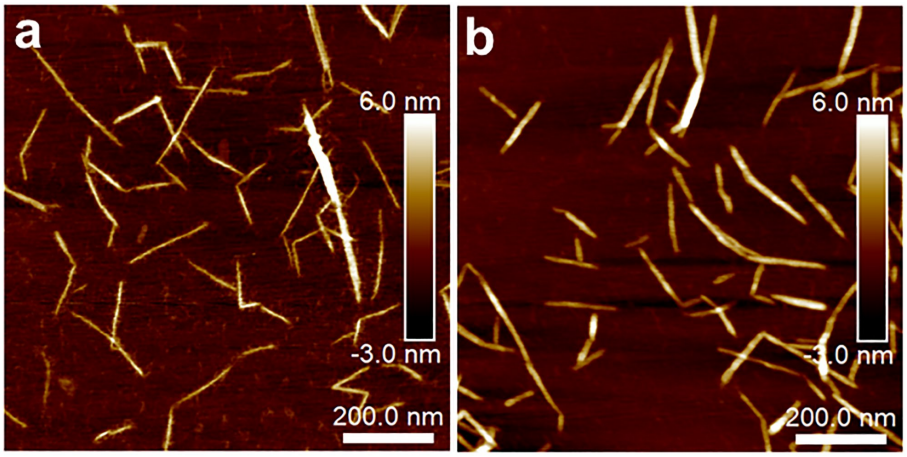

Figure S4: Atomic force micrographs (height images) of homogenized chitin after a) 15 min and b)30 min of sulfation reaction using 50 g/L sulfamic acid at 80°C.

6 Calculation of fibril cross-section from the turbidimetric data

The turbidity $\tau(\mathrm{cm}^{-1})$ is expressed[S1] as

$$\tau = \frac{88\pi^3 nc[\mathrm{g/cm^3}]}{15\lambda^3[10^{-21}\mathrm{cm^3}]N_A}\left(\frac{dn}{dc}\right)^2[\mathrm{cm^6/g^2}]\mu[\mathrm{dalton/cm}] \quad (1)$$

$$= \frac{88\pi^3 nc[\mathrm{g/cm^3}]}{15\lambda^3[10^{-21}\mathrm{cm^3}]}\left(\frac{dn}{dc}\right)^2[\mathrm{cm^6/g^2}]\mu'[\mathrm{g/cm}] \quad (2)$$

$$= \frac{88\pi^3 nc[\cancel{g/cm^3}]}{15\lambda^3[10^{-21}\cancel{cm^3}]}\left(\frac{dn}{dc}\right)^2[\cancel{cm^6/g^2}]\rho d^2[10^{-14}\cancel{g}/\mathrm{cm}] \quad (3)$$

$$= \frac{88\pi^3 nc}{15\lambda^3}\left(\frac{dn}{dc}\right)^2\rho d^2[10^7\mathrm{cm^{-1}}] \quad (4)$$

$$d = \frac{\sqrt{\tau\lambda^3 10^{-7}\frac{15}{88\pi^3 nc\rho}}}{\frac{dn}{dc}}[\mathrm{nm}] \quad (5)$$

where n is refractive index of water (1.33), c is concentration in g/cm^3, ρ is density in g/cm^3, refractive index increment in cm^3/g, wavelength λ in nm, turbidity τ in cm^{-1}

7 X-ray diffraction of chitin, sulfated chitin and nanochitin and corresponding Scherrer size

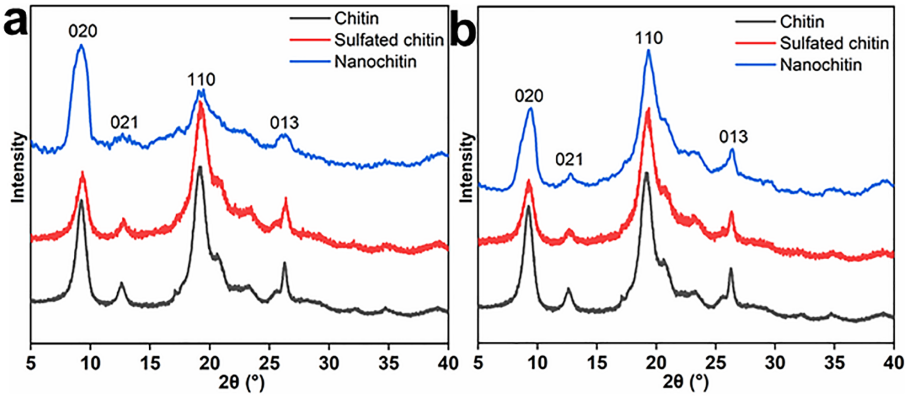

Figure S5: X-ray diffraction patterns of chitin powder, sulfated chitin powder and nanocellulose freeze-dried sample. Sulfation was carried at at 80°C using 0.5molL−3 sulfamic acid in DMF for **a** 15 min and **b** 30 min

Table S2: Scherrer sizes (nm) of chitin and modified chitin samples from 0 2 0 reflection line broadening

sulfation reaction time	5 min	15 min	30 min
sulfated chitin	6.5	7.2	7.3
nanochitin	5.5	5.2	5.5

References

(S1) Carr Jr., M. E.; Hermans, J. Size and Density of Fibrin Fibers from Turbidity. *Macromolecules* **1978**, *11*, 46–50.