Supplementary information (SI)

Nanocellulose-Zeolite Composite Films for Odor Elimination

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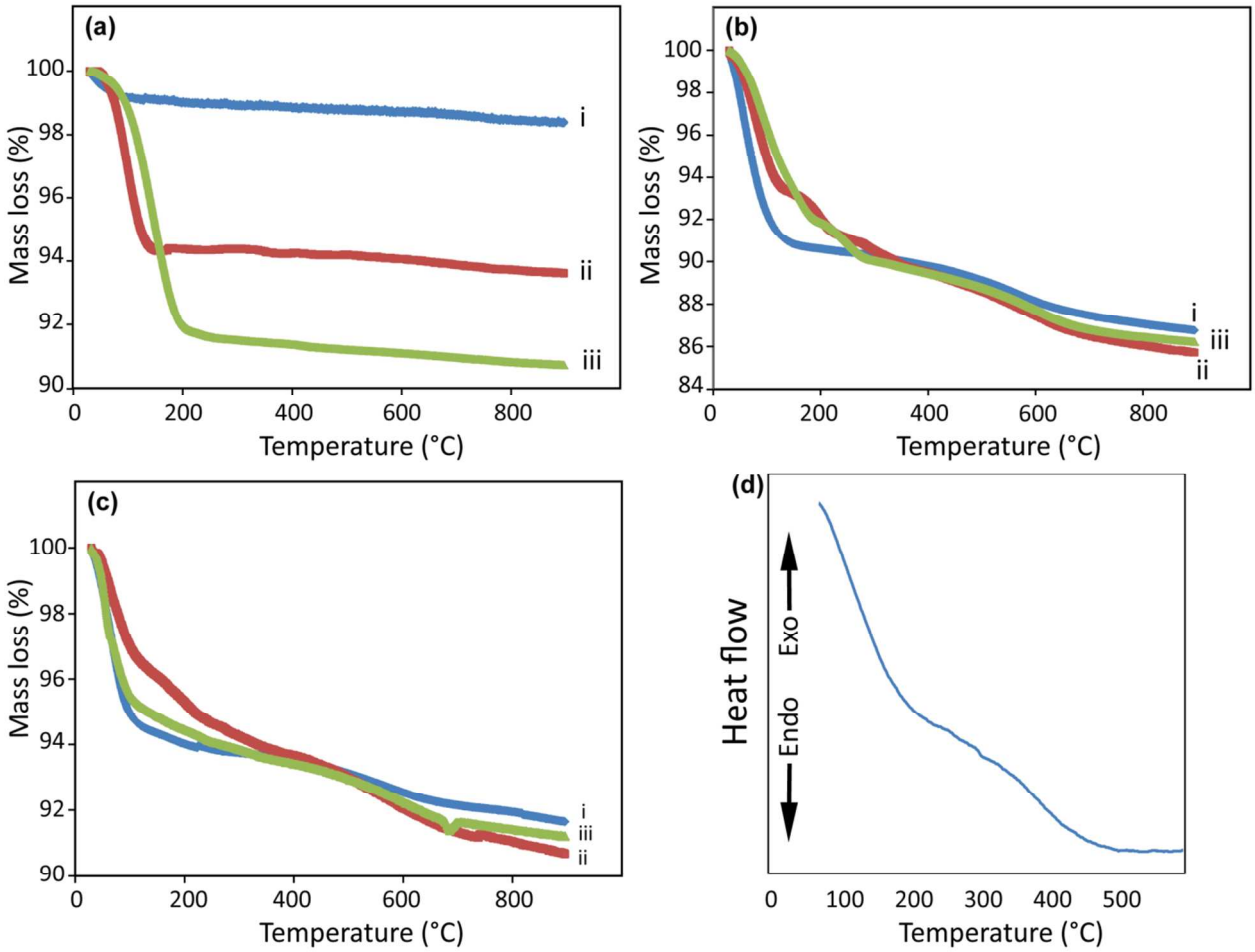

Fig S1. Uptake of thiols by zeolites; (a-c) Thermo gravimetric (TG) curves of (a) silicalite-1 powder,(b) zeolite Beta powder, (c) mordenite powder (i) as received; (ii) after exposure to ethanethiol for 1h; and (iii) after exposure to propanethiol for 1h.; and (d) The differential thermal analysis curve of ZSM-5 powder that was exposed to ethanethiol. The powders were not pre-treated (degassed) before exposure to thiols. Both water evaporation and ethanethiol desorption are represented by decreasing the heat flow.

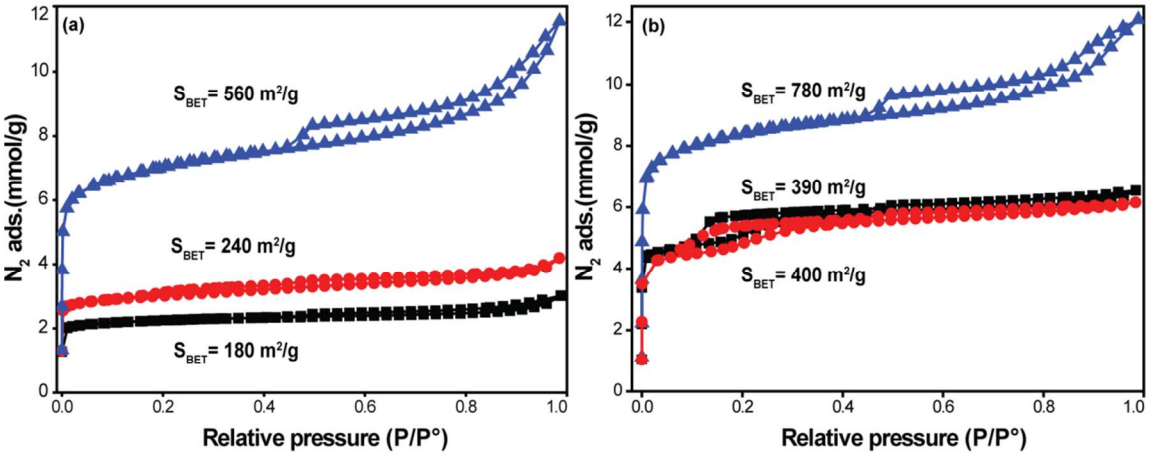

Fig S2. The nitrogen adsorption-desorption isotherms at 77K and BET surface area of (a) zeolite-CNF films; (b) zeolite powders. Zeolite Y-CNF film and zeolite Y powder (blue triangles); ZSM5-CNF film and ZSM5 powder (red circles); silicalite-CNF film and silicalite powder (black squars). The films were degased in vacuum at 80 °C for 5 h and zeolite powders were degased in vacuum at 300 °C for 10 h.

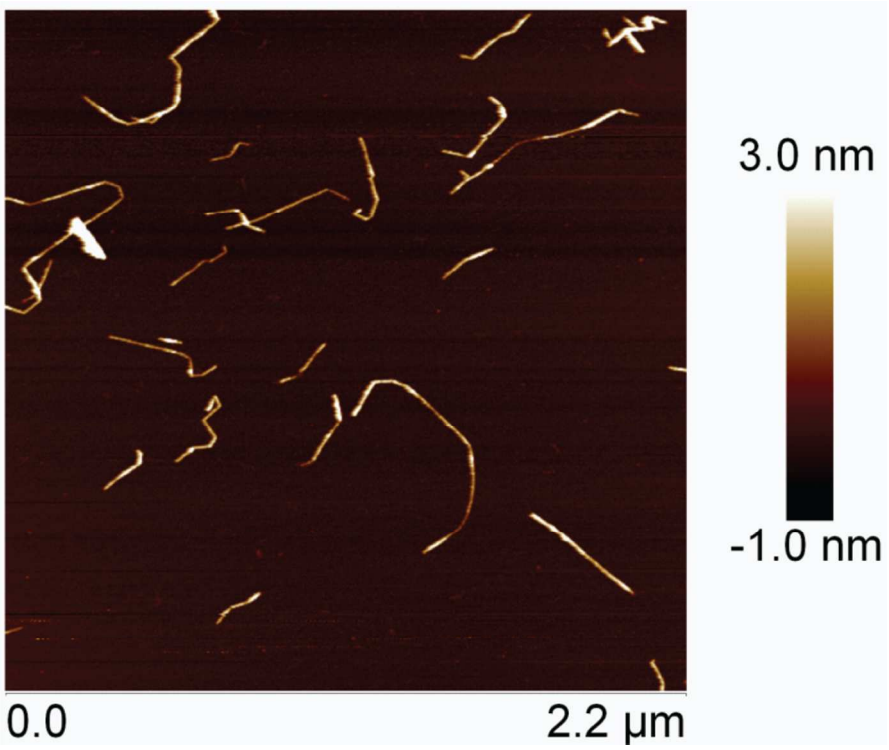

Fig S3. The picture of cellulose nanofibrils (CNF) captured by atomic force microscopy (AFM). The fibrils with a diameter in the range of 3 nm are presented by the bright contrast.

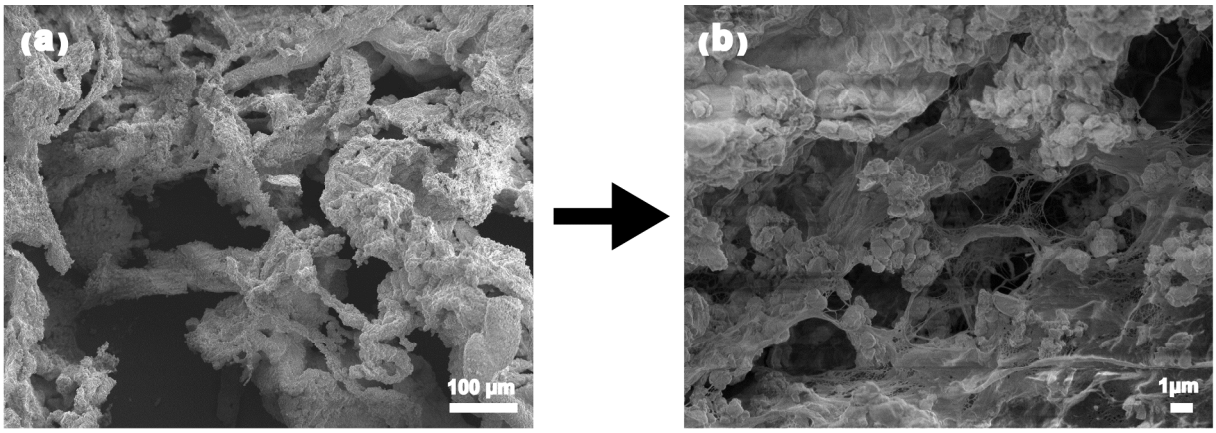

Fig S4. SEM micrograph of freeze-dried ZSM5-CNF dispersion; (a) Fluffy interconnected network of zeolite-CNF at low magnification; (b) ZSM5 particles wrapped within CNF network visible at higher magnification. Freezing was performed in liquid nitrogen followed by drying through sublimation of water at low pressures.

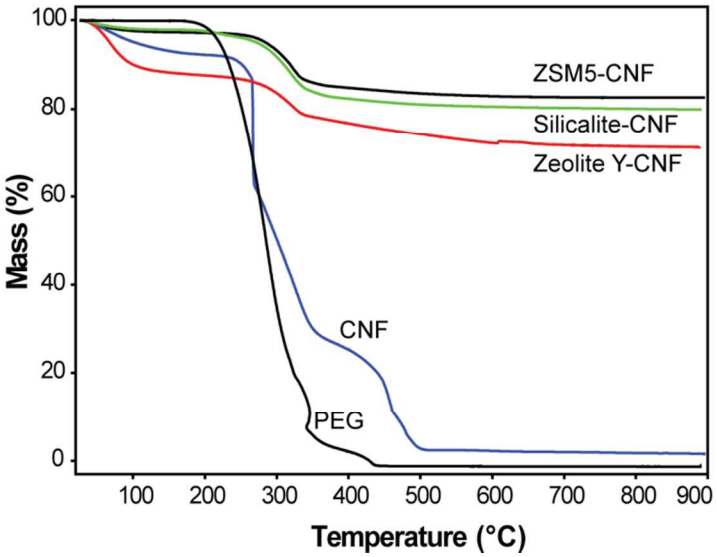

Fig S5. TGA curves of the three zeolite-cellulose nanofibrils films prepared with 10 vol% of CNF, cellulose nanofibrils (CNF) and Poly ethylene glycol.

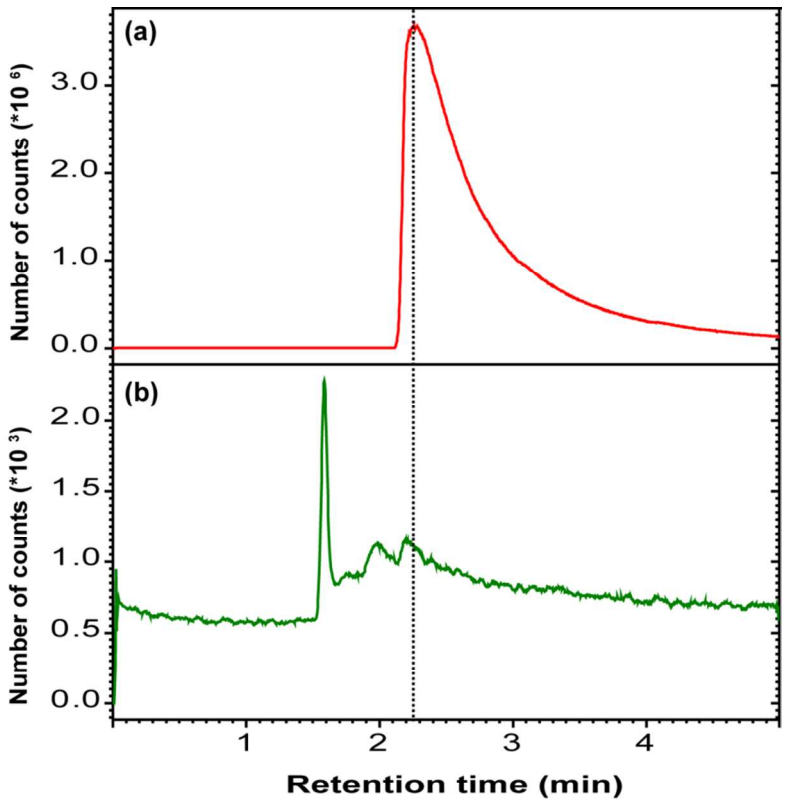

Fig S6. Headspace SPME/GC/MS analyses after 30-min sampling of (a) a reference 22ml vial containing 243 ppmv (0.02 µl) of proranethiol vapor representing full propanethiol release and (b) headspace of a sealed 22ml vial enclosing a 1.7 ml vial sealed with 10 layers of 1-mm zeolite-CNF film containing 2700 ppm_v propanethiol (0.02 µl) .

Table S1. Weight, volume (%) fractions of each component in ZSM5-CNF films containing varied amount of ZSM5 and calculated theoretical densities of the films. The zeolite density (ρ) is the skeletal density values.

Composite film	$W_{zeolite}$	W_{CNF}	W_{Ca}	W_{PEG}	$\rho_{zeolite}$ (gr/cm^3)	ρ_{CNF} (gr/cm^3)	ρ_{Ca} (gr/cm^3)	ρ_{PEG} (gr/cm^3)	ρ_{film} (gr/cm^3)	$V_{zeolite}$ (%)	V_{CNF} (%)	V_{Ca} (%)	V_{PEG} (%)
ZSM5-CNF	0.33	0.16	0.47	0.03	2.34	1.50	2.15	1.13	2.02	28.1	21.9	44.9	5.82
ZSM5-CNF	0.70	0.07	0.20	0.01	2.34	1.50	2.15	1.13	2.20	65.7	10.3	21.2	2.75
ZSM5-CNF	0.81	0.05	0.13	9×10^{-3}	2.34	1.50	2.15	1.13	2.22	77.2	6.68	13.7	1.77
ZSM5-CNF	0.90	0.02	0.06	4×10^{-3}	2.34	1.50	2.15	1.13	2.29	88.3	3.44	7.05	0.91

Table S2. Weight, volume (%) fractions of each components s in three different zeolite-CNF films and calculated densities of the films. The zeolite densities (ρ) are skeletal density values.

Composite film	$W_{zeolite}$	W_{CNF}	W_{Ca}	W_{PEG}	$\rho_{zeolite}$ (gr/cm^3)	ρ_{CNF} (gr/cm^3)	ρ_{Ca} (gr/cm^3)	ρ_{PEG} (gr/cm^3)	ρ_{film} (gr/cm^3)	$V_{zeolite}$ (%)	V_{CNF} (%)	V_{Ca} (%)	V_{PEG} (%)
ZSM5-CNF	0.70	0.07	0.20	0.01	2.34	1.50	2.15	1.13	2.20	65.9	10.3	21.1	2.37
Silicalite-CNF	0.70	0.07	0.20	0.01	2.36	1.50	2.15	1.13	2.20	65.7	10.3	21.2	2.75
Zeolite Y-CNF	0.70	0.07	0.20	0.01	2.27	1.50	2.15	1.13	2.10	66.6	10.1	20.7	2.68

Table S3. Physical properties of zeolite-CNF films prepared without addition of $CaCl_2$ and PEG. Theoretical porosities calculated according to appendix A, values of standard deviations are given in parenthesis.

Composite without Ca^{2+} and PEG	Porosity (vol%)	Youngs modulus (GPa)	Tensile strength (MPa)
ZSM5-CNF	60.0	0.99 (0.04)	10.0 (0.47)
Zeolite Y-CNF	72.0	0.65 (0.05)	6.00 (0.75)
Silicalite-CNF	54.0	0.78 (0.10)	7.35 (0.21)

Appendix A

Porosity calculation

The densities of zeolite-CNF films are determined by measuring the weight and volume of oven dried specimens. The volume is measured by knowing the thickness (Mitutoyo micrometer, accuracy of 0.001 mm) and area (Mitutoyo caliper, accuracy of 0.01 mm) of a square cut piece of the zeolite-CNF film.Theoretical density of the zeolite-CNF films thus can be calculated from equation 1.

$$\rho_{c,t} = \left(\frac{w_c}{\rho_c} + \frac{w_z}{\rho_z} + \frac{w_p}{\rho_p} + \frac{w_{Ca}}{\rho_{Ca}}\right)^{-1} \qquad \text{eq.1}$$

Finally the porosity of zeolite-CNF films are estimated based on the difference in experimental density and theoretical density, see equation 2.

$$Porosity = \frac{\rho_{c,t} - \rho_{c,m}}{\rho_{c,t}} * 100 \qquad \text{eq.2}$$

The signs in these two equations are as follow; $\rho_{c,m}$ is experimental density of composite, $\rho_{c,t}$ is theoretical density of composite, ρ_c is density of CNF (1.5 g/cc), ρ_z is density of zeolite particles, ρ_p is density of PEG (1.128 g/cc), ρ_{Ca} is density of $CaCl_2$ (2,15 g/cc), w_c is weight fraction of CNF, w_z is weight fraction of Zeolite particles, w_p is weight fraction of PEG and w_{Ca} is for weight fraction of $CaCl_2$.