Supporting Information

Acid- and Base-Resistant Antimicrobial Hydrogels based on Polyoxometalates and Chitosan

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Keywords: Polyoxometalate, chitosan, hydrogels, antimicrobial materials, acid-resistance, base-resistance

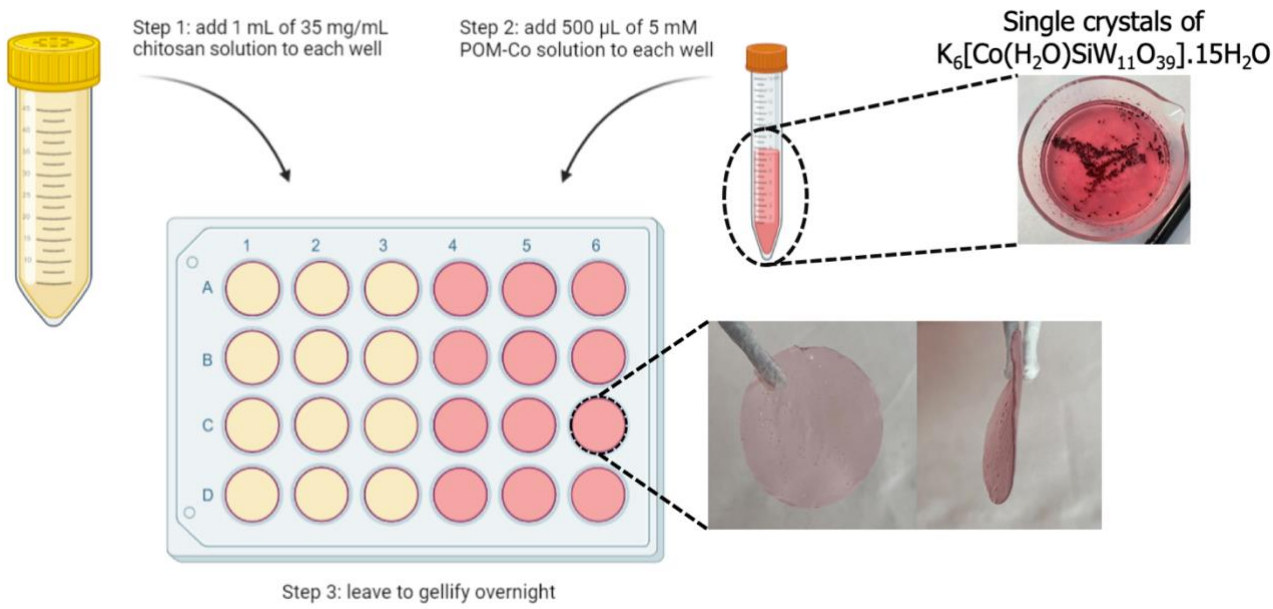

Figure S1. Schematic illustration of the synthesis of the $CoSiW_{11}$@CS hydrogel.

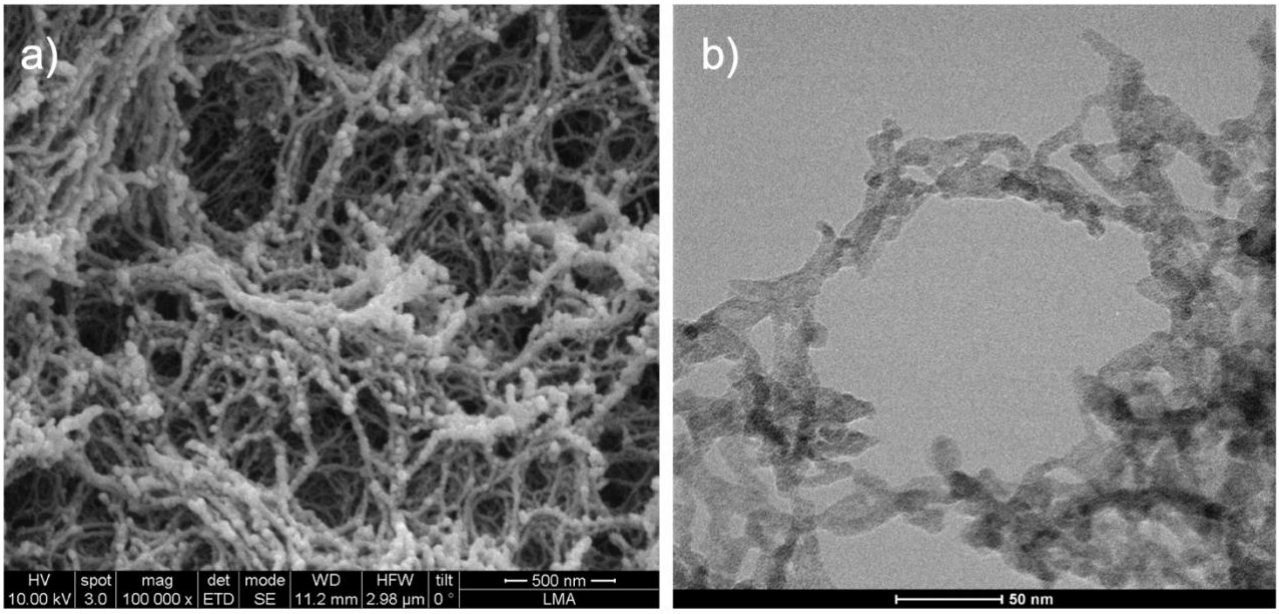

Figure S2. a) SEM and b) TEM images of $CoSiW_{11}$@CS after supercritical drying and coating with Au/Pd.

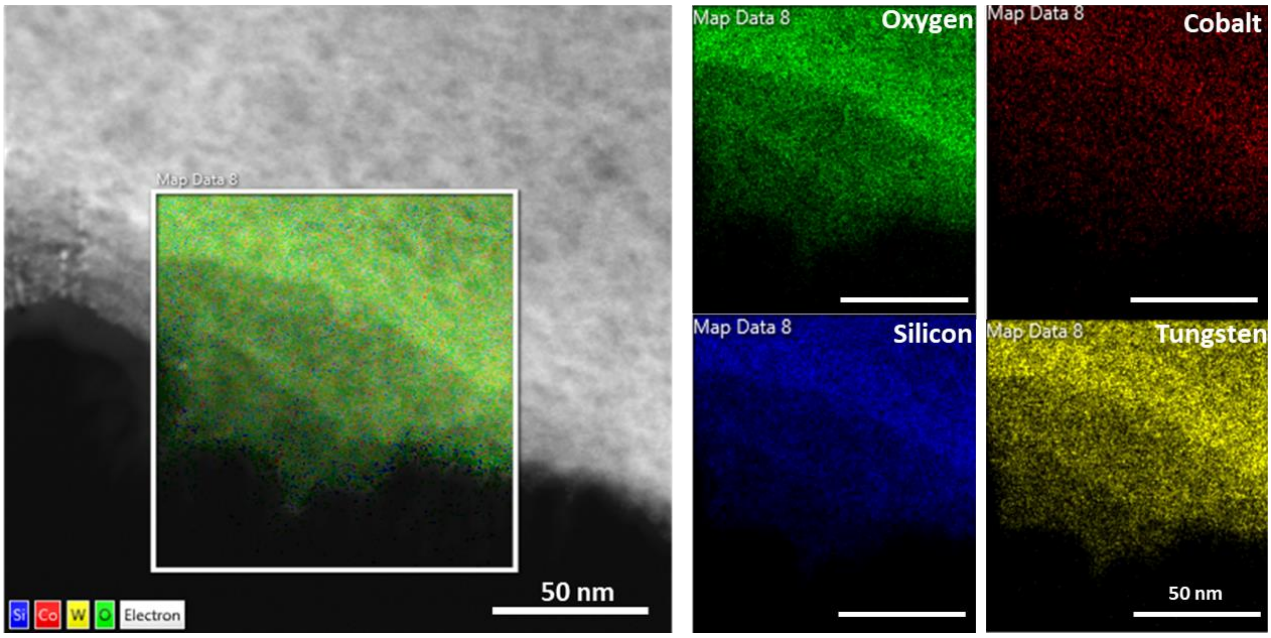

Figure S3. EDS imaging, via TEM, displaying the homogeneous dispersion of the elements of $K_6[Co(H_2O)SiW_{11}O_{39}]$ throughout the $CoSiW_{11}$@CS hydrogel.

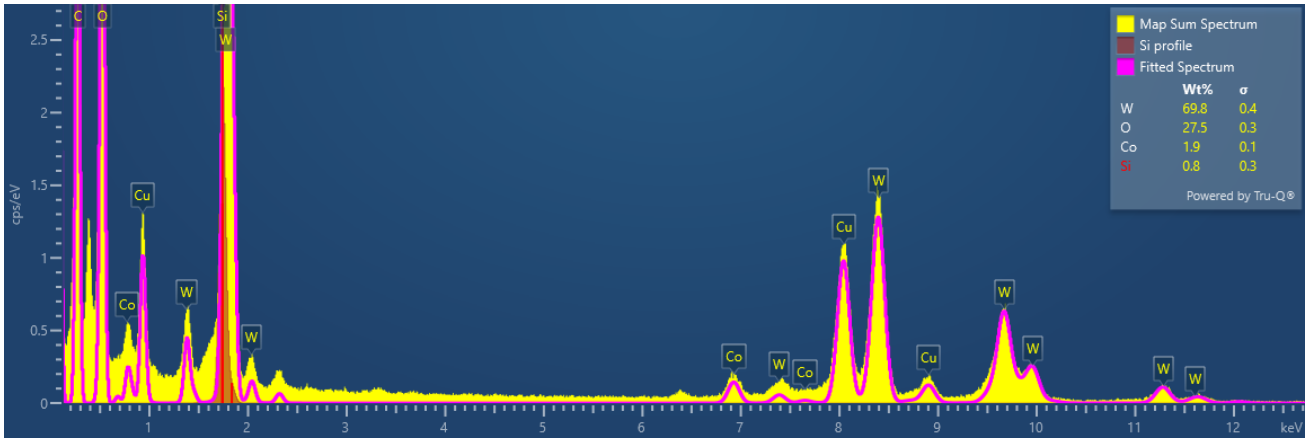

Figure S4. Corresponding EDS spectrum of $CoSiW_{11}$@CS. Note that the presence of Cu and C peaks corresponded to the copper TEM grid coated in carbon.

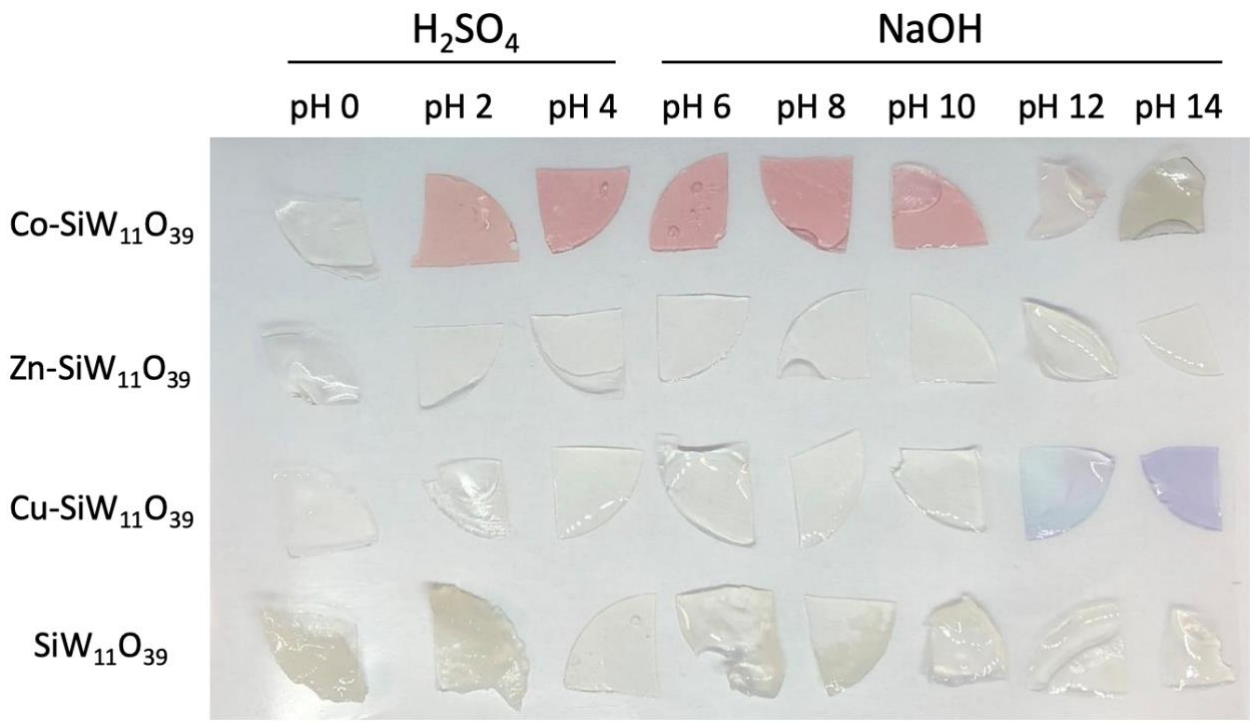

Figure S5. POM@CS hydrogels after 24 hours in solutions of different pH.

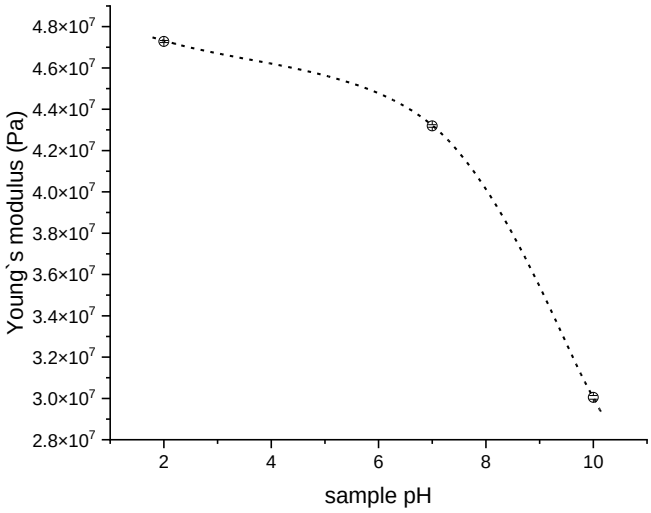

Figure S6. Young's modulus as a function of pH. The dotted line represents a guide for the general tendency of poorer stability and toughness at higher pH values.

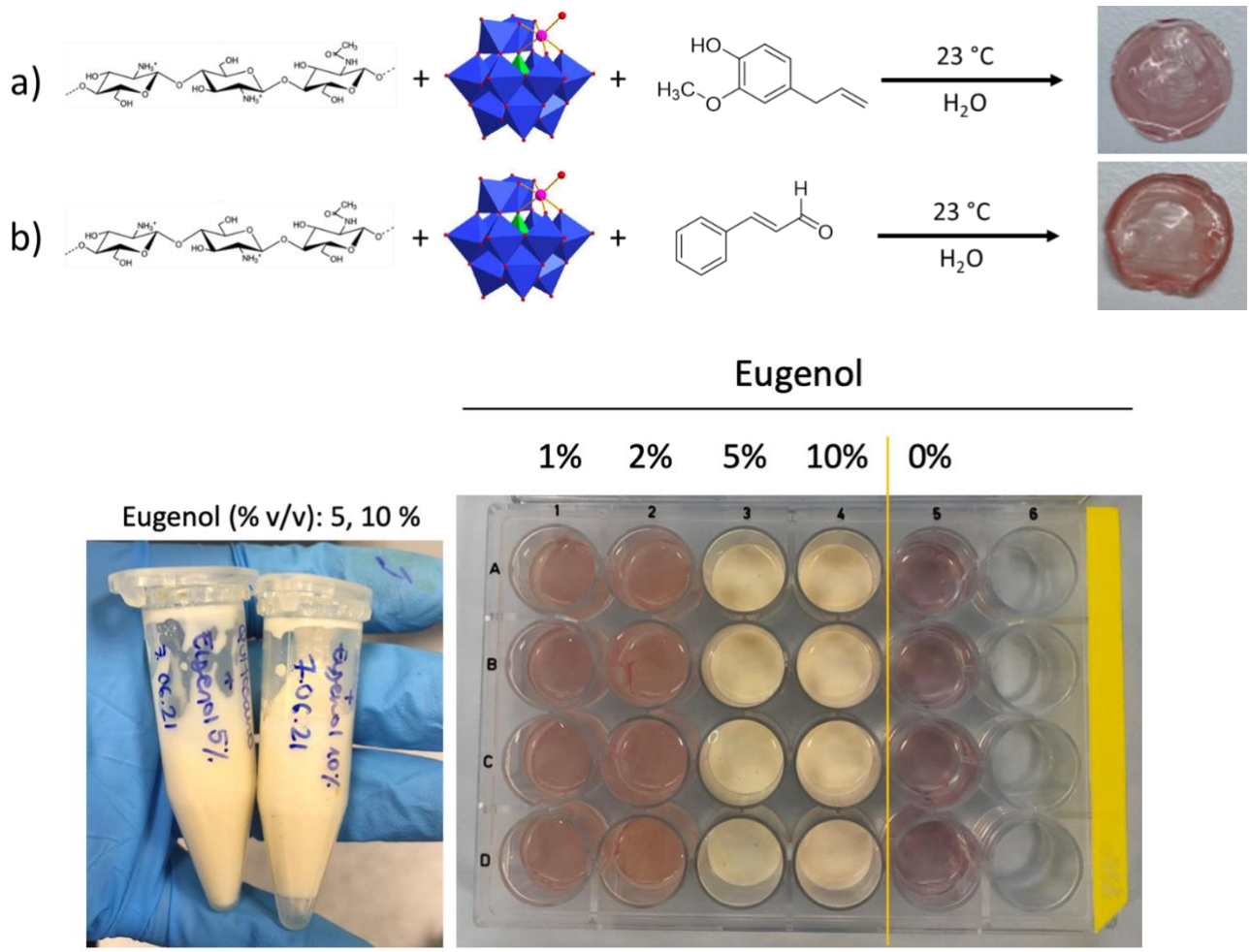

Figure S7. Synthesis of the $CoSiW_{11}$@CS@oil hydrogels with: a) eugenol, b) cinnamon oil. Below: chitosan solution and the corresponding essential oil were added to an Eppendorf vial and emulsified using a sonic tip and placed in well-plates for gelation.

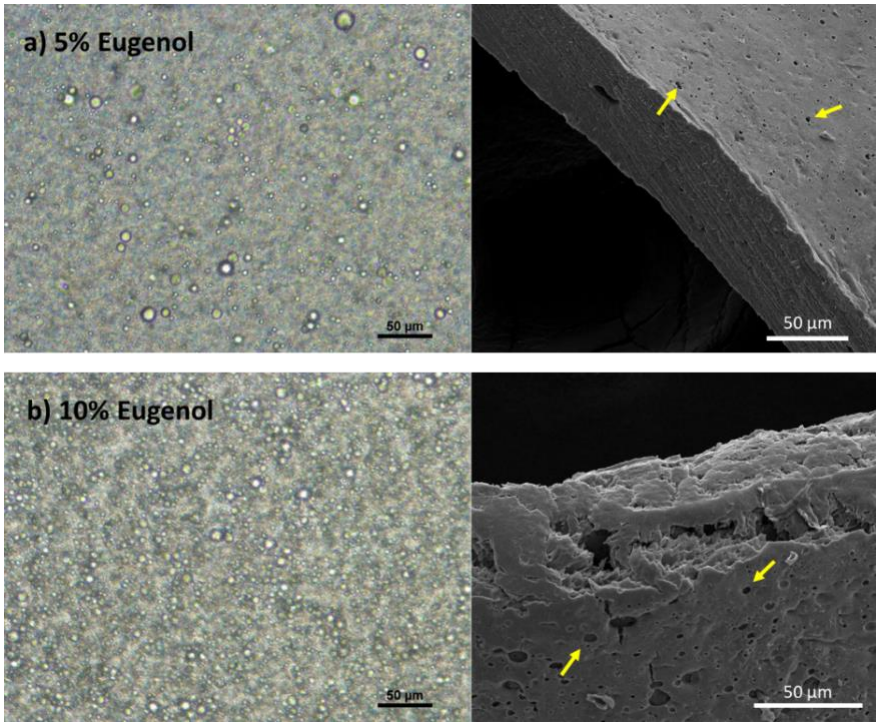

Figure S8. Optical microscopy imaging of 5 and 10% $CoSiW_{11}$@CS@oil hydrogels (doped with eugenol) with yellow arrows on the SEM images highlighting the oil droplets in the hydrogel.

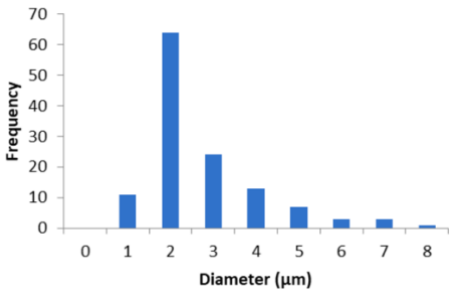

Figure S9. Size dispersion histogram of the oil droplets contained in $CoSiW_{11}$@CS@oil hydrogels. Data obtained from ImageJ measurements of the oil droplet diameters obtained from SEM images.

Table S1. Minimum Inhibitory Concentration (MIC) values: starting materials, eugenol, and cinnamaldehyde.

Compound	**MIC (mg/mL)**	
	E. coli	*B. subtilis*
$K_8[\alpha\text{-}SiW_{11}O_{39}]$	>12.68	12.68
Chitosan	0.25	0.15
Eugenol	0.50	0.50
Cinnamaldehyde	0.625	0.625

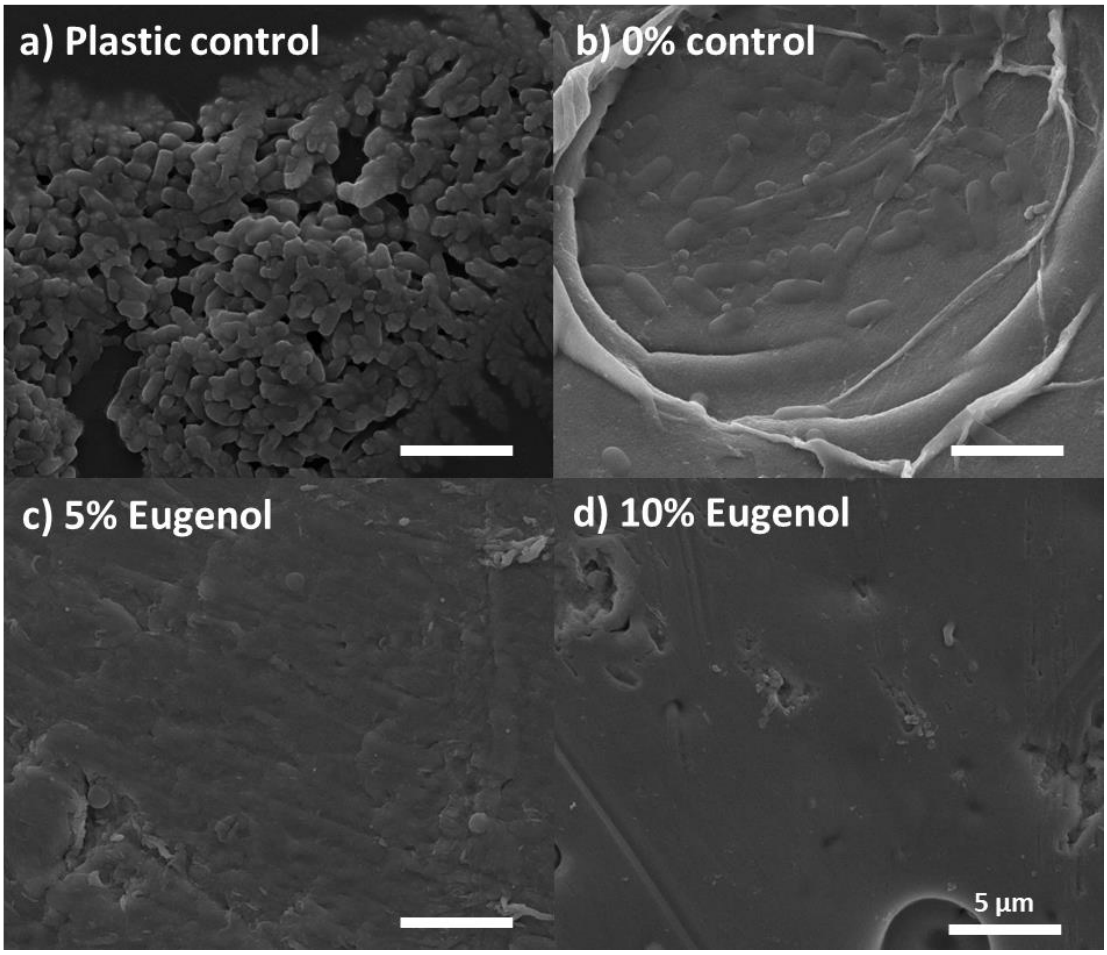

Figure S10. SEM imaging of washed samples; a) plastic control sample, b) $CoSiW_{11}$@CS hydrogel (0% oil content) and eugenol doped $CoSiW_{11}$@CS hydrogels; c) 5%, and d) 10%, after antibiofilm assay with *B. subtilis*.

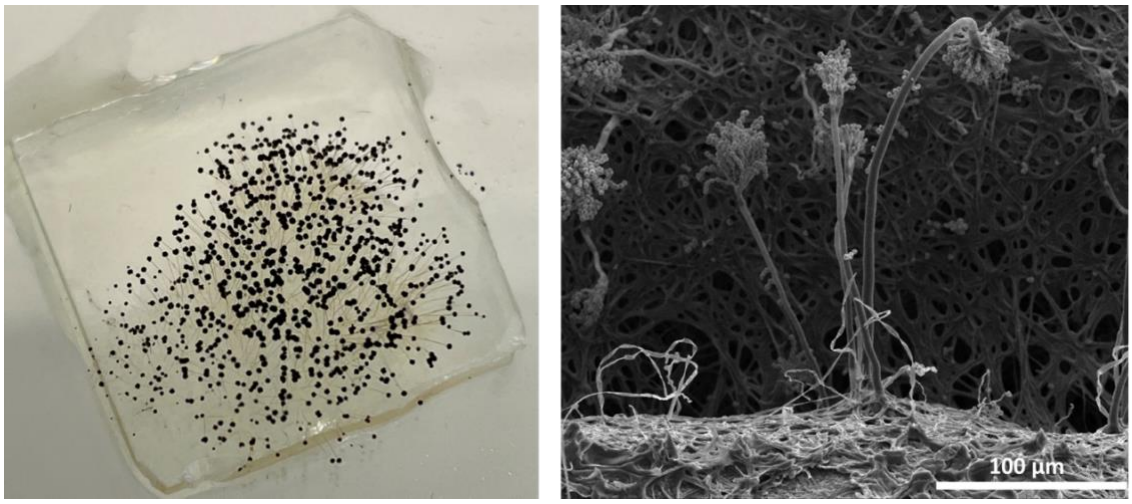

Figure S11. Conidiophores and conidia of *A. niger* visualised on the glass control sample (from the antifungal assay) and SEM imaging.

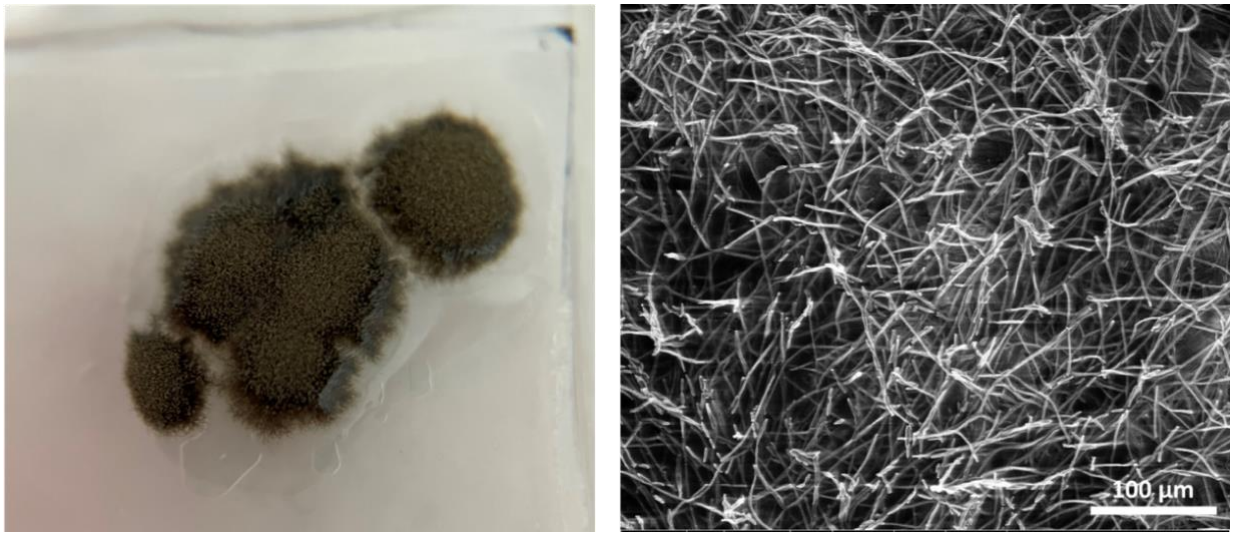

Figure S12. *C. cladosporioides* mould visualised on the glass control sample (from the antifungal assay) and SEM imaging.

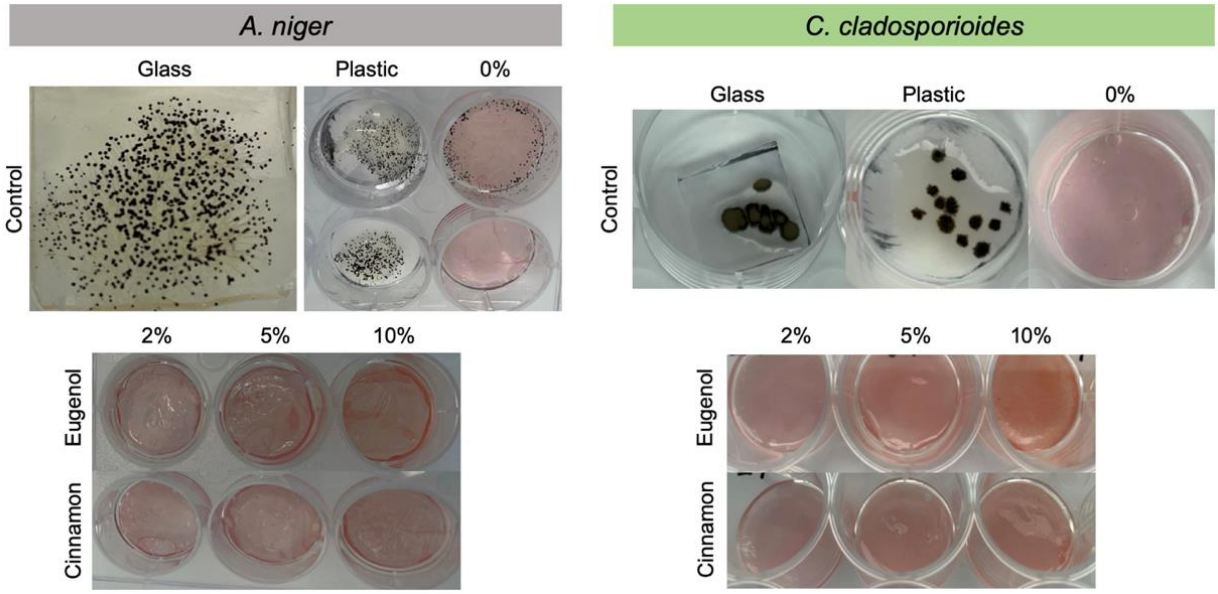

Figure S13. Performance of the $CoSiW_{11}$@CS and $CoSiW_{11}$@CS@oil hydrogels in antifungal assays against *A. niger* and *C. cladosporioides*, demonstrating the absence of fungal growth on $CoSiW_{11}$@CS and $CoSiW_{11}$@CS@oil hydrogels, compared with control growth on glass and on plastic.